Colloidal Syntheses, Characterizations and Applications of Inorganic Nanowires

By

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Abstract

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One-dimensional inorganic nanowires have many properties different from their bulk form. They have been demonstrated as crucial building blocks in various applications such as electronics, optics, catalysts, and sensors. Colloidal synthesis is a powerful method for the preparation of nanowires, not only because it is low-cost and scalable, but also due to its flexibility in achieving shape and composition control. To fully exploit nanowires’ unique traits in functional devices, the syntheses of materials should be tailored to the particular application. How to rationally design new chemistry to produce nanowires that suffice specific chemical and physical requirements is essential. This dissertation explores the cases where the unique geometry of nanowires is elegantly utilized, in transparent conductors and as catalyst. The efforts that have been made to design, and develop new materials towards better device performance are discussed. Advanced characterizations and carefully contemplated control experiments are also described in detail, aiming to provide new insights into reaction mechanism and structure-function correlation.

Metal (especially copper and silver) nanowire mesh is considered among the best candidates for replacing indium-tin-oxide as the next generation transparent electrode material. Compared to conventional oxide based conductors, nanowire mesh has the advantage of high mechanical flexibility, and low processing cost while maintaining good optical-electrical performance. However, the major challenges of nanowire electrodes are the strong light scattering and low air stability. Large aspect-ratio, small-diameter and surface stabilized metal nanowires are desired for achieving a high-performance transparent conducting film. A new, general synthesis approach which uses heat driven organic radicals as a mild reducing agent to make high-aspect ratio ultrathin copper nanowires (diameter ~ 17nm; length ~ 17 μm) has been developed. The reaction mechanism has been studied in detail using in-situ, temperature dependent electron paramagnetic resonance spectroscopy. These mild radicals slowly reduce copper ion into decahedral nanoseeds in presence of primary amine and then grow further into five-fold twinned nanowires. The transparent conducting films made from the ultrathin nanowires exhibit excellent transparency and conductivity (sheet resistance ~ 28 Ω/sq, transmittance ~ 90%, haze ~ 2%). Moreover, these films show significantly reduced haze factors in comparison with reports thus far, mainly due to the small diameter. Furthermore, to overcome the limitation of copper’s low stability towards oxidation, we developed a solution based approach to coat reduced graphene oxide nanosheets onto the nanowire surface. The core-shell structure greatly enhanced the air-stability of the
conducting films. The resulting nanowire electrodes maintained its original conductivity after being stored over 200 days in ambient air and up to 48 hours in high temperature high humidity environment. We also successfully grow a few atomic layers of gold atoms on to the copper surface. These epitaxial Cu@Au core shell nanowire films exhibit even greater stability which can hold up their original conductivity up to 700 hours in harsh environment.

Metal nanowires can also be used as catalyst. Copper is uniquely active for the electrocatalytic reduction of carbon dioxide (CO₂) to products beyond carbon monoxide, such as methane and ethylene. Therefore, understanding selectivity trends for CO₂ electrocatalysis on copper surfaces is critical for developing more efficient catalysts for CO₂ conversion to higher order products. We investigate the electrocatalytic activity of ultrathin (diameter ~20 nm) five-fold twinned copper nanowires for CO₂ reduction. These copper nanowire catalysts were found to exhibit high methane selectivity over other carbon products, reaching 55% Faradaic efficiency (F.E.) at -1.25 V vs. RHE while other products were produced with less than 5% F.E. This selectivity was found to be sensitive to morphological changes in the nanowire catalyst observed over the course of electrolysis. Wrapping the wires with graphene oxide was found to be a successful strategy for preserving both the morphology and selectivity of the Cu nanowires. These results suggest that product selectivity on Cu nanowires is highly dependent on morphological features, and that hydrocarbon selectivity can be manipulated by structural evolution.

Semiconductor nanowires are an important class of nanomaterials. Silicon is the most important semiconductor in microelectronics industry. Continuous device miniaturization has led to the emergence of the nanoelectronics industry, in which Si nanowires can play an essential role. Most of the bottom-up synthesis of silicon nanowires are via the vapor-liquid-solid method, which normally requires temperature above 400 °C. In this work, an approach of low-temperature synthesis of silicon nanowires is described. This method uses tris(trimethylsilyl)silane or trisilane as the Si precursor via a Ga-mediated solution-liquid-solid approach to cut down the growth temperature of silicon nanowire to below 200 °C. It is further demonstrated that this Si chemistry can be adopted to incorporate Si atoms into III-V semiconductor lattices, which holds promise to produce new Si-containing alloy semiconductor nanowire.
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To my mom, my dad and my fiancé.
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Chapter I

Introductions to Inorganic Nanowires

1.1 Introduction to One-Dimensional Nanomaterials

Nanomaterials describe a class of materials with at least one dimension in the range of one to several hundreds of nanometers. Due to the reduced size, they often exhibit exotic optical, electrical and mechanical properties and thus, have been demonstrated as interesting building blocks in various applications. Although nanotechnology is a fairly modern concept in scientific history, the use of nano-scaled materials can date back to several centuries, such as carbon-nanotube-containing wools steel developed in ancient India 6th centuries BC, and the use of metal particles as coloring reagents for pottery and glass in the Middle Ages. These embedded nanostructures bring out unusual, and often exceptional properties in the applied objects, though the correlation between the properties and material structures were not fully appreciated back then. Starting from 1980s, several breakthroughs in material sciences, particularly the maturity of electron microscopy, the discovery of nanocarbons, and the development of colloidal chemistry, have lead a bloom in the field of nanomaterials. Researchers not only acknowledge the existence and the size-dependent properties of nanoscaled materials, but also have the tools to purposely engineer their shape, composition, crystal structure and surface structure to tailor them toward various functions. Nowadays, nanomaterials are utilized in a variety of applications, including electronics, sensors, imaging, drug delivery and so on and so forth.

Depending on the number of dimensions which are measured within nanoscale, nanomaterials can be classified as 0 D- zero dimensional, e.g. metal nanoparticles, and quantum dots; 1 D, which is confined in one dimension, e.g. quantum wires, nanowires; 2 D systems, in which the confinement is within a plane, e.g. single layered materials, thin films; and 3 D materials, also called bulk nanomaterials, which are often referring to structures built of lower-dimensional nanomaterials as building blocks. This dissertation focuses on the inorganic one-dimensional nanomaterials (in greater details on metallic and semiconducting materials), or more commonly termed in the field as nanowires.

Nanowires are usually defined as elongated nanostructure with diameter constrained to less than 100 nm and with an unstrained length (or in practice, the aspect ratio greater than 500). When the diameter is small enough to the extent that quantum effects are significant, nanowires are referred to quantum wires instead. A variety of nanowires have been made including metallic (e.g. silver, copper, gold), semiconducting (e.g. silicon, III-V, II-VI), ceramic (e.g. SiN4, AlN, CeO2), and organic. Nanowires have been intensively researched and steadily commercialized in numerous applications, for not only the convenience of miniaturization, but also the many unique properties they have that are different from their bulk counter parts. They have been demonstrated as crucial building blocks in various applications such as electronics, optics, catalysts, energy conversion and sensors. For most applications, the quality of the nanowires synthesized is the
key factor in achieving high performance devices, for the reason that the unique properties caused by the physical geometry are strongly dependent on the materials’ morphology, size distribution, defect level, surface arrangement and crystalline structures.

1.2 Synthesis of Inorganic Nanowires

1.2.1 General Strategies for Achieving One-Dimensional Inorganic Nanowire Growth

One of the most critical aspects of nanowire synthesis is shape-controlling, to force the material forge into a one-dimension structure. Over the past few decades, a tremendous amount of efforts has been devoted to developing novel strategies for making high-quality and well-controlled nanowires.

There are two ways to make nanowires: top-down and bottom-up. A top-down approach starts with a piece of bulk material and uses patterning techniques to selectively etch away the unwanted portion of materials, leaving the desired nanostructure behind. In this sense, the materials are “engineered” rather than “synthesized”. The top-down method heavily relies on lithography. The initial development of procedure and equipment is usually costly, but for existed, repeating structure fabrication, this approach can be very efficient and scalable. The uniformity and crystallinity of the nanowires made from top-down approaches are often excellent since they are evolved from single-crystalline bulk.

In contrast, the bottom-up approach refers to the building of nanowires from the bottom, atom by atom. The growth of nanowires can take place either in vapor phase or liquid phase. Because the nanowires are form from attaching atoms to atoms, a greater variety of composition can be accessed through this approach than the top-down method. The nanowires’ diameter can yield below 20nm, even below 5 nm. Dimension this small is exceedingly challenging for top-down nanofabrication. Another appealing benefit of the bottom-up approach is that, if combined with colloidal chemistry, the cost of making large-scale materials can be remarkably cheap. In the following sections, several well-established methodologies of bottom-up growth of nanowires will be reviewed.

1.2.2 Vapor-Phase Growth

Semiconducting nanowires can be synthesized in gas phase using nano-sized particles/domains as shape confining catalyst. One of the most commonly used techniques is the vapor-liquid-solid method. In this approach, the underlying substrate (often the same material as the targeted nanowires) is decorated with nanoparticles (usually metals, e.g. Au is used in Si nanowire growth) as catalysts. At high enough temperature, where catalyst is melted to liquid form, gaseous precursor is (for example, SiCl4 as the precursor for silicon nanowire synthesis) introduced. These precursors preferentially absorb on and then dissolve in the catalyst forming a eutectic alloy. Further, the vapor continuously diffuse into the metal droplets until the superstation is reach and solid crystals nucleate at the liquid/solid interface. VLS method usually involves chemical vapor deposition system (CVD). CVD controls the flow rate of the precursors and regulates the temperature and pressure. These parameters are well tuned such that self-nucleation of crystals outside the catalysts is minimized. The diameter of the nanowires is defined by the properties of the liquid alloy. Incorporation of metal atoms into the semiconductor lattice during growth is
possible but usually undesired. Inert, noble metals are frequently used to avoid contamination. Below eutectic point of the catalyst, nanowire growth can still happen in certain systems, known as VSS-vapor-solid-solid approach. This allows the syntheses accessible at a lower temperature. VLS approach yields high-quality crystalline nanowires of many type of semiconductors, including Si, Ge, III-Vs and numerous heterostructures. Coupled with lithography patterning of catalysts, nanowires with specific geometric alignment, e.g. periodic arrays, can be synthesized. The constraints of this method are low yield, high cost and the demanding requirements in precise control of all experimental parameters. Further, the impurities introduced by metal catalysts is difficult to eliminate.

The vapor-phase growth of nanowires can also be achieved without catalyst via selective area epitaxy (SAE) method. This technique relies on patterned masks (through lithography) to selectively expose nanosized openings on a faceted crystalline substrate. Then metalorganic chemical vapor deposition (MOCVD) or molecular beam epitaxy (MBE) can be used to epitaxially deposit crystals in the exposed pitches. The nanowires grown in this manner are usually of a higher quality and better uniformity. However, it is not widely applied due to the high cost of equipment and low throughput.

1.2.3 Colloidal Chemistry

Colloidal synthesis has been proven a powerful method for the preparation of nanowires. It is based on wet chemistry process in which the precipitation of crystals is carefully controlled by the type of solute (often referred to as precursors, can be in molecular or ionic forms), solvents, coordinating ligands, temperature and pressure. Tremendous efforts have been devoted to developing novel syntheses that can better engineer the nanowires’ composition, size, and surface structures, and deciphering the mechanism underlying the growth of anisotropic nanostructures via many advanced characterizations.

Catalyst-assisted nanowire growth

Semiconductor nanowires can be grown in solution in a similar fashion as the VLS method: solution-liquid-solid method. This approach also uses a metal particle as the shape-defining catalyst, yet the melting temperature of this metal is low enough that it can sustain a liquid form in an organic solvent. For example, bismuth particles have been used as the catalyst to grow GaP nanowires. Like VLS, the precursors in solution, diffuse and dissolve in the metal catalyst. Further, supersaturation and nucleation occur at the interface between the metallic liquid and solution, initiating one-dimensional growth. The SLS method has several attractive advantages. The synthetic temperature is much lower than that used in VLS condition. And the colloidal synthesis can effortless enable large-scale production of nanowires than vapor-phase-based methods. The diameter of SLS nanowires can be routinely made to sub-ten nanometers which is difficult for gas-phase syntheses. The downside of the SLS approach is the easily induced defects, less controlled crystal growth direction, and the difficulty in directional assembly for device applications.

Seeded nanowire growth
Seeded nanowire growth describes a process in which the nanowire synthesis is initiated by the formation of small particles with specific composition, size, or exposed facets. These particles serve as the starting seeds for further crystal deposition. Seeded growth of both metal and semiconductor nanowires have been reported.

Colloidal syntheses of metal nanowires are commonly achieved this way. A typical recipe consists of certain types of metal precursors to be reduced, organic ligands as the coordinating ligands of the precursor and/or the surfactants of the formed crystals, solvents, and desired temperature, atmosphere and pressure. These conditions need to be well tuned to ensure the best environment for the formation of the seeds. Surfactants play a major part in shape controlling. They selectively protect or expose certain facets of the seeds, promoting anisotropic crystal growth. For example, in the synthesis of silver nanowires, $\text{AgNO}_3$ is dissolved in ethylene glycol and serves as the precursor. In the presence of polyvinylpyrrolidin (PVP), the added ligands, when Ag(I) is reduced to Ag(0), the Ag(0) preferentially form five-fold twined particles. On the surface of these particles, PVP binds strongly with Ag’s (100) while leaving (111) open for further silver metal deposition. Elongation happens, and the seeds grow into nanowires.

One can also synthesize semiconductor nanowires using this approach. For example, ZnO nanowire arrays have been grown in solution from ZnO nanoparticle seeds. The selectivity of crystal deposition is realized by modifying the charging effect on different facets via the pH tuning. The facet-dependent electrostatic interaction influences precursor absorption and facilitates one-dimensional growth.

**Oriented-Attachment Method**

In the oriented attachment method, nanowires are formed by fusing small particles together from one specific orientation. This assembly can be dominated by dipole-dipole interaction in the case of semiconductors. Certain faceted or sphere particles can be drawn to each other and form a linear configuration. Then, facets are fused together with enough thermal energy input. This approach has been applied to a number of semiconductor systems including PbSe, CdSe, and ZnO. Ultrathin gold nanowires with diameter around 2 nm have also been reported to form via this mechanism. The gold first grows into short nanorods and then forge a chain-like structure by fusion and eventually grow into nanowires.

**1.2.4 Other Notable Techniques**

**Electrochemical deposition**

Electrodeposition can also be used to produce nanowires. The morphology of the nanowires is defined by external template (e.g. pores anodic aluminum oxide). Various types of nanowires have been made through electrochemical synthesis, e.g. Co, ZnS, Bi$_2$Te$_3$. Unlike the generally high-temperature, organic-solvent-based colloidal approach, this technique can grow nanowires in ambient conditions. But the control over nanowires’ diameter and composition are not as easily achieved as the more popular colloidal or VLS methods.

**Electrospun nanowires/nanofibers**
Recently, electrospinning has been employed in synthesizing nanowires (mostly metals, or metal oxides). Electrospinning is a process that utilizes electric force to draw charged liquid polymer precursors (melts or solution) to fabricate thin polymer fibers. During this process, if metal salts were added in the starting liquids, the resulting fiber would be a composite consist of polymers and metal compounds. Then, the fibers go through calcination in air to form metal oxide/polymer. If metal nanowires are desired, a last step of reduction is performed. Notably, Cu$_{37}$ V$_2$O$_5$ nanowires have been made using this method.

1.3 Structural Characterizations of Nanowires

Structural characterizations are of great importance in materials science. The properties of materials are directly linked to its structure: morphology, crystallinity, composition, and surface environments. In nanoscience, the tools for material characterizations are often specialized to fit in the nanoscale domain. This section details a list tools commonly used in nanowire characterizations.

1.3.1 Electron Microscope Imaging

Electron microscope is probably the most fundamental and indispensable instrument for nanomaterial characterizations. The resolution of an optical microscope is restricted to the wavelength of incident probing photons, which is hundreds of nanometers. In contrast, accelerated electrons are used as the source of illumination in an electron microscope. The high-speed electrons have a wavelength as low as several pm ($10^{-12}$ meter) and for that, an electron microscope can reach a resolution suitable for nanomaterials. When the incident beam interacts with the sample, the electrons can be transmitted, diffracted, absorbed and scattered. These electrons contain information of the sample’s structure. With different techniques, we can extract part of the information and piece back the certain structural characters of the materials.

*Transmission electron microscopy (TEM)*

In the standard TEM operating mode, a beam of electrons is directed to a thin sample and the transmitted electrons are collected to form an image. The electron beam is produced by electron gun and then accelerated by voltage usually between 60 kV to 200 kV. For the electrons to transmit through the sample, the specimen must be less than 200 nm. Standard TEMs, or low-resolution TEMs are used primary as the microscope for morphology checking. The resolution can range from 0.1 to 5 nm depending on the models of TEMs.

*High-resolution transmission electron microscopy (HRTEM)*

HRTEM is an advanced mode of TEM that can probe the lattice and atomic structures of the sample. When electrons transmit through the specimen, the transmitted beam can further interact with the diffracted beam. Due to the beams’ phase difference, certain inference patterns can be observed. This phase contrast information is related to the atomic arrangement of the sample. With complex logarithm and well aligned microscope, the formed image from phase-contrast, can be used to interpret the crystal structure of the specimen.
Scanning electron microscope (SEM)\textsuperscript{40}

In a SEM, images of a sample are produced by scanning the surface with electron beam. Instead of analyzing the transmitted electrons in TEM, SEM collects the secondary electrons emitted by the sample when its surface atoms are excited by the incident beam. It is most commonly used to determine the topography of the specimen.

1.3.2 Diffraction\textsuperscript{41}

X-ray diffraction (XRD)

Although XRD does not count as a nano-specific characterization, it is a routine tool for determine the crystal structure of nanomaterials. This technique collects the scattered X-ray beam and plots out the function of scattered angel verse the incident angle. In nanoscience, it is a handy tool to quickly determine the phase of nanomaterials.

Electron diffraction

Transmission electron microscopes can also be used in electron diffraction mode. In selected area diffraction, the beam is localized to a known spot while the diffraction is taken. Thus, the crystal structure can be correlated to the appearance of the nanomaterials. One can also control the incident angle of beam with respect to the facets of nanomaterials.

1.3.3 Composition Characterizations

Making nanowire heterostructures has been a constant research interest. Many applications require more than one materials within the same nanowire structure, either an axial heterojunction or a core-shell geometry. So, it is vital to know the composition and the element distribution within the nanowires.

Energy dispersive X-ray spectroscopy (EDS)\textsuperscript{42}

EDS is an analytical technique used for elemental analysis. It uses a high energy source, for example, accelerated electrons, to excite inner-shell electrons of atoms to escape the orbital. Electrons from outer shells subsequently migrates to inner shell to fill the created vacancy, emitting photons in the process (usually in the X-ray region). The energy of emitted photons is characteristic of the atoms in play. EDS can be combined with TEM and SEM, which makes it a powerful tool for elemental mapping with resolution as low as several angstroms.

Inductively coupled plasma mass spectrometry (ICP-MS)\textsuperscript{43}

ICP is a type of mass spectrometry that detects and quantifies trace elements. During the measurement, the samples are ionized by inductively coupled plasma and the ions are then quantified by the attached mass spectrometer. ICP is commonly used in nanoscience to determine the elemental composition, and quantify the amount of materials.
1.3.4 Surface Characterization

A lot of applications of nanowires are sensitive to their surface structure. It is useful to understand the atomic arrangement and the chemical environment of nanowires.

Organic Surfactants

As above mentioned, colloidal syntheses make up a large portion of nanowire production. Often, organic ligands are used to promote the anisotropic growth. The type and density of surfactants covering the nanowires sometimes need to be carefully monitored. Fourier-transform infrared spectroscopy (FTIR) is a commonly used technique for organic ligand characterization in nanoscience. It probes the vibration energy of certain function groups and is used to identify and semi-quantify organic molecules in the presence. Similarly, Raman spectroscopy can also be used to pin down certain molecules.

Surface atomic structure

In some cases, where the nanowires’ functions are sensitive to surface atomic structure or composition, characterization need to be limited to the first few atomic layers. X-ray photoelectron spectroscopy (XPS) is an ideal technique for this purpose. During measurements, X-rays are directed to a sample and these high-energy photons excite the electrons within an atom to escape the orbitals. The emitted electrons are then measured in numbers and energy. The photoelectrons need to travel out of the material to be collected (during which electrons can quickly relaxes interacting with atoms), only the materials near the surface could contribute to the signals. XPS can offer information of the type, oxidation states, local bonding and electron states of surface atoms. HRTEM also have the capability to probe the atoms close to the surface, as discussed in the last section.

1.4 Dissertation Outline

As an important class of nanomaterials, nanowires have attracted extensive research attention, much of which aim to develop new syntheses to produce nanowires for specific applications. The following chapters details a list of applications that elegantly utilized the unique geometry of nanowires, and the rational design of new chemistry that tailor the materials towards a better performance. Advanced characterizations and carefully contemplated control experiments are also discussed, aiming to provide new insights into reaction mechanism and structure-function correlation.

Chapter II describes the synthesis of ultrathin copper nanowires using heat-driven tristrimethylsilylsilane radical as reducing agent. A study of the growth mechanism using high-resolution transmission electron microscopy reveals that the copper nanowires adopt a five-fold structure and evolve from decahedral nano-seeds. We further expand the radical chemistry to carbon based radicals, e.g. benzoin. In-situ temperature dependent electron paramagnetic resonance (EPR) spectroscopic studies prevail that the active reducing agent is the free radicals produced by benzoin under elevated temperature. Furthermore, the reducing power of benzoin
can be readily tuned by symmetrically decorating functional groups on the two benzene rings. When the aromatic rings are modified with electron donating (withdrawing) groups, the reducing power is promoted (suppressed). Fabricated transparent conducting films exhibit excellent transparency and conductivity. An additional advantage of our nanowire transparent conductors is highlighted through reduced optical haze factors (forward light scattering) of the conducting films due to the small nanowire dimensions.

In chapter III, we aim to tackle the copper nanowires’ low-stability issue with core-shell structures. Two types of core-shell structures were developed: Cu@rGO (reduced graphene oxide) shell and Cu@Au shell. Cu@rGO core-shell synthesis is guided with copper nanowire and graphene oxide self-assembly. The electrode made from Cu@rGO exhibit excellent optical and electric performance with further reduction of haze factor. It also enables the production of highly stable conducting films (over 200 days stored in air). Cu@Au core-shell nanowires are synthesized using trioctylphosphine as a strong binding ligand to prevent galvanic replacement reactions. The epitaxial overgrowth of a gold shell with a few atomic layers on the surface of copper nanowires can greatly enhance their resistance to heat (80 °C), humidity (80%) and air for at least 700 hours, while their optical and electrical performance remained similar to the original high-performance copper (e.g. sheet resistance 35 Ω sq⁻¹ at transmittance of ~89% with a haze factor < 3%).

Chapter IV explored the role of copper nanowires as a catalyst in the CO₂ electrochemical reduction reaction. Copper is uniquely active for the electrocatalytic reduction of carbon dioxide (CO₂) to products beyond carbon monoxide, such as methane and ethylene. Therefore, understanding selectivity trends for CO₂ electrocatalysis on copper surfaces is critical for developing more efficient catalysts for CO₂ conversion to higher order products. We investigate the electrocatalytic activity of ultrathin (diameter ~20 nm) five-fold twinned copper nanowires for CO₂ reduction. These nanowire catalysts were found to exhibit high methane selectivity over other carbon products, reaching 55% Faradaic efficiency (F.E.) at -1.25 V vs. RHE while other products were produced with less than 5% F.E. This selectivity was found to be sensitive to morphological changes in the nanowire catalyst observed over the course of electrolysis. Wrapping the wires with graphene oxide was found to be a successful strategy for preserving both the morphology and selectivity of the copper nanowires. These results suggest that product selectivity on copper nanowires is highly dependent on morphological features, and that hydrocarbon selectivity can be manipulated by structural evolution.

In the last Chapter, an approach of low-temperature synthesis of silicon nanowires is described. This method uses tris(trimethylsilyl)silane or trisilane as the Si precursor via a Ga-mediated solution-liquid-solid (SLS) approach to cut down the growth temperature of silicon nanowire to below 200 °C. It is further demonstrated that this Si chemistry can be adopted to incorporate Si atoms into III-V semiconductor lattices, which holds promise to produce new Si-containing alloy semiconductor nanowire.

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Chapter II

Synthesis of Ultrathin Copper Nanowires Using Heat-Driven Free Radicals and Their Applications in Transparent Conductors


2.1 Introduction to Nanowire Transparent Conductors

Transparent conductors are indispensable in consumer electronics, such as touch panels, displays, photovoltaic devices, and electro chromic windows.\textsuperscript{1-4} The majority of current technologies rely on indium-tin-oxide (ITO)-based thin films, which have high optical transparency and low electrical resistivity.\textsuperscript{5} However, ITO suffers from several drawbacks, including the high cost of sputtering manufacturing techniques,\textsuperscript{6} low flexibility,\textsuperscript{7} the scarcity of indium, and strong optical absorption in the near infrared (NIR) wavelength window. A wide variety of materials, such as conducting polymers,\textsuperscript{8} graphene,\textsuperscript{9} carbon nanotubes (CNTs),\textsuperscript{10} patterned metal gratings\textsuperscript{11} and metallic nanowire meshes,\textsuperscript{12} have been explored in an attempt to replace ITO as a transparent conductor. Among these alternative materials, metal nanowire network is currently among the most promising avenue to replace ITO and has received growing attention over the years.\textsuperscript{13-17}

Copper is a promising candidate for nanowire-based electrodes as it has high intrinsic conductivity (only second to silver), and it is very abundant (1000 times more abundant than silver).\textsuperscript{6} It has been well established through theoretical simulations and experiments that the transparency/conductivity performance of a metal nanowire mesh film is largely determined by the aspect ratio of nanowires (over 400 is desired).\textsuperscript{18} To achieve high transparency and good conductivity, many works have been devoted towards synthesizing long copper nanowires with small diameter. One approach to making copper nanowires is via electrospinning/metal evaporation.\textsuperscript{19} Copper nanowires can also be obtained via colloidal chemistry by reducing Cu ion/ion complex in presence of capping ligands. Notably, large aspect ratio copper nanowires (with diameter ranging from 15 to 100 nm) were successfully synthesized using reducing agents such as glucose,\textsuperscript{20, 21} ascorbic acid,\textsuperscript{22, 23} hydrazine,\textsuperscript{24-26} and even primary amines with assist of high pressure (hydrothermal),\textsuperscript{27} catalysts (Pt\textsuperscript{28}, Ni\textsuperscript{29}) or choice of more active Cu precursor.\textsuperscript{30} Using these Cu nanowires, thin films with good optical transmittance and electric conductivity have been achieved. Another important, yet often overlooked parameter of transparent conductor is haze: a measure of the scattering of light by a material that is responsible for the reduction in contrast and
sharpness of objects viewed through it. The large amount of forward scattering due to dense microstructures limits the commercial appeal of metal nanowire conducting films. According to simulations, with the same area coverage, the haze factor of a nanowire mesh film is approximately linear to nanowire diameter (for nanowire with diameter smaller than 100nm). Hence, the metal nanowires’ diameter should be small (e.g. <20 nm) to keep light scattering (haze) at a minimum and to afford a good transparency/conductance trade-off, while at the same time not too thin to introduce stability issues during film fabrications.

2.2 Synthesis of Ultrathin Copper Nanowires Using Tris(Trimethylsilyl)Silane as Reducing Agent

We have developed a synthetic approach that uses tris(trimethylsilyl)silane (TTMSS) as a mild reducing agent to grow ultra-thin high-quality copper nanowires with average diameter less than 20 nm. In a typical reaction, 85 mg of CuCl₂·2H₂O (0.5 mmol) and 5 g of oleylamine were mixed in a reaction vessel and then sonicated at room temperature to fully dissolve copper precursor. 0.5 g of tris(trimethylsilyl)silane (2 mmol) was added in to the solution as reducing regent. The resulting clear blue mixture was heated up to 120 °C until the solution turned into light yellow. Afterwards, the reaction temperature was slowly turned up to and kept at 165 °C for 10 h while stirring. The product was harvested by centrifugation and then washed with toluene.
Figure 2.1 Synthesis of ultra-thin copper nanowires. a, Copper nanowire synthetic reaction and optical images of reactants (left inset) and products (right inset); b, X-ray diffraction pattern of copper nanowires. Inset, SEM (left) and TEM (right) images of as-grown copper nanowires. c, Proposed mechanism of tris(trimethylsilyl)silane radical reduction.

Figure 2.1a presents the chemical reaction and optical photos before and after the synthesis. In our synthesis, oleylamine (OLA) is used as a coordinating ligand for the CuCl₂ precursor. During the reaction, the mixture forms Cu(II)-OLA complexes, which result in a clear blue solution. When the solution was placed under elevated temperature, Cu(II) species is gradually reduced to Cu(I) species at around 100 °C, which is indicated by a blue-to-light yellow color transition. With further increase of temperature to about 165 °C, the clear yellow solution slowly turns reddish which marks the formation of copper nanoparticles. Apart from being a coordinating solvent to copper precursors, OLA also serves as a capping ligand on the copper nanowire surface. Tris(trimethylsilyl)silane (TTMSS), which is widely used in organic synthesis, is introduced here as a mild reductant for the copper reduction, and it is found to play a key role for achieving high quality copper nanowires. Oleic acid serves as a supplementary ligand, to help enhance the copper nanowire dispersion and to prevent the wires from collapsing and aggregating at elevated temperatures. Small amount of oleic acid in the reaction system can greatly improve copper nanowires’ dispersion. Copper nanowire synthesized with oleylamine as the sole ligands show severe aggregation which is not suitable for the formation of loose nanowire network.

Figure 2.1b inset (left) shows the scanning electron microscopy (SEM) image of the ensemble copper product. The predominant products are nanowires (with less than 10% of nanoparticles by counts) with an average length measured to be 17 μm. The right inset is the transmission electron microscopy (TEM) image of the as-grown nanowires. The nanowires have a mean diameter of 17.5 nm with a standard deviation of ~3 nm, which was calculated from 300 randomly selected images from different batches of the reaction. The x-ray diffraction (XRD) spectrum shown indicates that copper nanowires have a face-centered cubic (FCC) structure. The 2 theta peaks at 43.3°, 50.5°, 74.1°, 89.9°, and 95.1° correspond to the {111}, {200}, {220}, {311}, and {222} planes of the FCC copper.

A proposed reaction mechanism is shown in Figure 2.1 c. Because no free radical initiator exists in the reaction mixture, silane free radicals are generated by thermal cleavage of the Si-H bond at over 150 °C. Oleylamine serves as a weak free radical quencher, catches the hydrogen free radicals immediately. Slightly bubbling of the solution was observed at this stage due to the production of hydrogen molecules. The oleylamine free radicals can generate more silane free radicals by taking the hydrogen atoms away from the TTMSS molecules or form other types of byproducts. The thermally generated TTMSS free radicals are relatively stable in the solution and react with Cu(I) complex (produced at ~100 °C without the help of silane, light yellow colored) to give Cu(0) species.
To prove that copper ions are indeed reduced by the TTMSS free radicals, we used azobisisobutyronitrile (AIBN) as a free radical initiator and carried out the reaction at ~80 °C (TTMSS doesn’t thermally decompose at this temperature). As shown in Figure 2.2, the reaction mixture turned from pale yellow to dark red within 1 hour after injection of AIBN, and large amount of Cu nanoparticles can be obtained with a diameter of 4~8 nm. Note that toluene was used as the solvent instead of oleylamine for the reduction at 80 °C, because oleylamine quenches the 2-methylpropionitrile free radicals (generated by AIBN) and the TTMSS free radicals cannot be initiated. It is also worth to mention that tris(trimethylsilyl)silane plays a key role in forming this ultra-thin dimension. It acts as a mild reducing regent to slowly reduce the metal source and allows time for the nucleation of the five-twined seeds.
Figure 2.3 Atomic structure and growth mechanism of copper nanowires. (a) HRTEM images and (b) SAED pattern when one of the side surface is perpendicular to the electron beam as demonstrated in (a) inset. (c) HRTEM images and (d) SAED pattern when one of the side surface is parallel to the electron beam as demonstrated in c inset. (e) TEM images of Cu products when the reaction was carried out for two hours. (f) HRTEM images and (g) fast Fourier Transformation (FFT) pattern of five twinned decahedral nanoparticles. (h) Statistic and distribution of decahedral seeds diameter and final nanowire diameter. (i) Schematics of copper source reduction, five twinned seeds nucleation and nanowire evolution.

The detailed structure of the copper nanowires was analyzed using HRTEM and SAED as shown in Figure 2.3 a-d. Copper nanowires were shown to have five-fold twinned pentagonal structure, which is commonly adopted by metal nanowires/nanorods materials. The five-fold symmetry of the as-grown copper nanowires can be visualized as consisting of five single-crystalline units (T1-T5) with a FCC structure, as illustrated in the insets of Figure 2.3 a and 2c. Figure 2.3 a and 2.3 b show HRTEM images and SAED patterns with the electron beam perpendicular to one of the side facets (indicated by red dot line). In Figure 2.3 b, two sets of FCC pattern are observed: one along the zone axis [001] generated from the subunit T1 and the other in [1-10] direction generated from T3 and T4. The Moiré pattern in Figure 2.3 a is generated from the overlap copper FCC unit cell {111} and {220} planes. When the electron beam is directed parallel to the side facets, as shown in Figure 2.3 c and 2.3 d, the diffraction pattern corresponds to the overlap of two FCC patterns with [1-10] and [-111] zone axes. A comprehensive analysis of the diffraction patterns and HRTEM images suggests that the nanowires have a five-fold symmetry with {100} facets as side surfaces and {111} planes bound at the ends. The growth direction is determined to proceed along [110] direction.
In an effort to better understand the one-dimensional growth mechanism, we investigated the product at the nucleation stage of the reaction. Figure 2.3 e shows the reaction products after 2 hours. The primary products are nanoparticles with a small number of elongated rods observed in the solution. A closer examination revealed that some of the nanoparticles are pentagonally shaped. The crystal structures of these nanoparticles were subsequently analyzed using HRTEM. Figure 2.3 f shows the HRTEM image of one of the pentagonal dots, which exhibits a five-fold twinned structure. To further demonstrate the atomic details of the five twining and their twinning boundaries, a focal series of HRTEM images was utilized to reconstruct the exit-plane wave function in the middle area of the twin structure with optimized phase contrast. The result is shown with false color in the inset of Figure 2.3 f, where perfect five sub-crystal lattices together with sharp twin boundaries can be observed. Moreover, the five-fold twin structure was confirmed by the FFT pattern of Figure 2.3 f. The pattern (Figure 2.3 g) gives an unambiguous representation of its five-fold symmetry. To further confirm this hypothesis, a comparison between the diameters of the nanowires and the irregular dots was made (Figure 2.3 h). The average diameter of the particles was measured to be 16.1 ± 1.2 nm based on 300 randomly selected dots in the TEM images. The diameter of the seeds has a strong correlation with that of the nanowires.

Figure 2.3 i summarizes the proposed mechanism. A Cu (II) complex is initially converted to a Cu (I) species at 100°C, then reduced further to Cu (0) at 150°C via TTMSS. It is believed that TTMSS decomposes at over 150°C with thermal cleavage of the Si-H bond. The silicon fragment can act as electron donor. It is relatively stable in the solution due to the protection of its bulky ligands and slowly reacts with the Cu (I) complex to produce Cu (0). Aside from acting solely as a reducing agent TTMSS plays a key role in forming ultra-thin nanowires: the mild reducing power of TTMSS affords sufficiently slow reduction kinetics to allow time for the nucleation of the nano-seeds and subsequent nanowire growth.
The nucleation favors multiply twinned decahedral seeds bounded by the more closely packed \{111\} planes. Twinning is often observed among FCC structured materials (particularly noble metal elements), with low twin boundary energy and surface energy difference.\textsuperscript{37} The anisotropic elongation is modulated by OLA and a high concentration of amine is favorable to asymmetric growth. The role of oleylamine in shape controlling of copper nanowires is shown in Figure 2.4. With presence of non-coordinate solvent only, the reduction of copper ion to copper metal particles is also possible which proves that tristimethysilylsilane acts as the effective reducing regent in this system. With the increasing amount of oleylamine concentration, the shape of copper products becomes better defined. An increasing tendency of anisotropic growth can also be seen correlated with the increasing amount of oleylamine. This can be explained by the fact that OLA preferentially binds with \{100\} over \{111\} planes.\textsuperscript{38} Loosely packed \{100\} planes tend to offer more space for the attachment of bulky surfactants and copper complex. Moreover, the more closely packed \{111\} facets serve as low-surface energy sites for the deposition of Cu (0) species.

As shown in Figure 2.5, the size of nanowires can be modified by changing reducing reagent amount and copper precursor concentration. For example, nanowire diameter can be tuned from 15.5 nm to 22.5 nm when the molar ratio of TTMSS/CuCl\textsubscript{2} decreases from 8 to 2. During the nucleation, the more reducing regent, the more nuclei it will generate, the smaller the seeds.
Table 2.1 lists the copper product within several control experiments when the reaction conditions are changing. When no TTMSS in the reaction system, copper chloride cannot be reduced to copper metal. When small amount of TTMSS (10 % of CuCl₂) is added, copper cubic nanoparticles are observed in the product. However, the yield of Cu (0) is very low. These imply that TTMSS does act as the effective reducing reagent of copper precursor, and insufficient loading of silane cannot fully reduce CuCl₂. The nanowire diameter can be tuned by controlling the molar ratio of TTMSS/CuCl₂. With set amount of CuCl₂, the nanowire diameter decreases as TTMSS increases. The size of the nanowire is also sensitive about reactant concentration. Smaller concentration results in thicker nanowires. The red highlighted condition is chosen as the optimized condition for typical nanowire growth in this work for the reason that it gives less particle byproducts.

### 2.3 Synthesis of Cu Nanowires Using Heat Driven Benzoin Radicals

In copper nanowire synthesis, to gain better control over the morphology of the synthesized NWs, a critical factor is to precisely control the nucleation rate. And thus, the choice of reducing agent should be taken into great consideration. In the last section, we’ve discussed that TTMSS can be used as a mild reducing agent to synthesize ultrathin copper nanowires. Yet, silicon based reducing agent has a lot of limits in real applications. For one thing, TTMSS is a quite expensive and air sensitive; for another, the structure of silane is very rigid, leaving little room to tune its activity. Carbon based free radical have the advantages of low-cost, and flexibility in structure tuning. Here, we demonstrated that benzoin can also generates free radicals and act as a great reducing agent for copper nanowire synthesis.
Figure 2.6. (a) Overall reaction scheme of Cu NW synthesis using benzoin as reducing agents. (b) Heat induced radical generation from benzoin. (c) Proposed mechanism of Cu complex reduction via benzoin radicals and one-dimensional NW growth.

The synthesis of Cu NWs is summarized in Fig. 2.6 a. Copper chloride, which is dissolved in oleylamine, can be slowly reduced under heating condition in presence of benzoin, and eventually form one-dimensional NWs. Oleylamine here acts as the sole solvent as well as surface ligands. In this reaction, we believe that benzoin acts as the key reducing agent, which reduces Cu (II) species to Cu (I) and then to Cu metal. Commonly used as a photoinitiator in polymerization, benzoin’s application in colloidal nanomaterial synthesis is rarely documented, even more rare so under heating conditions. It is well known that, under UV illumination, benzoin produces two radicals via $\alpha$-cleavage, in which the carbon-carbon sigma bond undergoes homolytic bond cleavage upon absorption of light. We hypothesize here that under heating condition, benzoin behaves in a similar manner. At elevated temperature, it yields radicals in an inert environment and the resulting radicals can act as efficient electron donors. The detailed proposed reaction mechanism is shown Fig. 2.6 b and 2.6 c. When benzoin is heated up, it decomposes into two radical segments, benzoyl radical and $\alpha$-hydroxybenzyl radical. In an air-free atmosphere, the radicals are relatively stable due to the conjugation of benzene ring, and thus have a long enough lifetime to reduce metal complex in solution. The reduction of copper complex takes place in two steps: at lower temperature Cu (II) species are first reduced to Cu (I) which is indicated by the disappearing the fingerprint blue color; then at higher temperature, Cu (I) complexes are further reduced to Cu (0). With oleylamine as the coordinating surfactants, the copper nucleation is known to favor five-fold-twinned structure. With (100) facets selective protected by amine groups, newly formed copper metal preferentially deposits on to (111) surfaces, promoting one-dimensional growth.
Figure 2.7. (a) SEM and (b) TEM and (c) HRTEM images of as synthesized Cu NW at 190 °C. (d) XRD pattern of as made Cu NWs, inset is a schematic representation of the NW’s micro structure. Pink lines are the standard XRD pattern of FCC copper. (e) Diameter distribution of Cu NWs synthesized at 190 °C (red), 180 °C (blue), and 160 °C (orange).

The morphologies of the product are examined by scanning electron microscope (SEM) and transmission electron microscope (TEM) as shown in Fig. 2.7 a, b. The majority of the products are uniform NWs with minimum portion of nanoparticles. Such NWs have length of up to 20 μm, and diameter of 18.5 ±3.5 nm. The detailed structure of the Cu NWs is studied using high resolution (HR) TEM and X-ray diffraction (XRD). The NW has the five-fold twinned structure, which consists of five face centered cubic (FCC) single crystalline units. Fig. 2c shows the HRTEM image taken when the incident electron beam is perpendicular to one of the side facets. Clear Moiré pattern is observed in the center of the NW, which correspond to the overlap between the upper single unit and the underlying two units as drawn in the inset. Fig. 2.7 d shows the XRD pattern of the as-made Cu NWs. The wires adopt the common FCC pattern. The clean pattern indicates that the products are pure from copper oxides. The inset demonstrates the overall microstructure of the five-fold twinned Cu NW, with {100} facets as side surfaces and [110] being the growth direction. This structure has been well documented within oleylamine modulated Cu NW syntheses.
Figure 2.8. TEM images of copper nanowire synthesized using benzoin at (a) 190 °C; (b) 180 °C; and (c) 160 °C. Scale bar is 100 nm.

The diameter of the as-grown Cu NWs can be readily tuned by changing reaction temperatures. We observed that with higher reaction temperature, the NWs synthesized are of a smaller diameter as shown in Fig. 2.8. Fig. 2.7 e summarizes the diameter distribution of Cu NWs grown under different temperatures. The averaged NW diameter is increased from 18.5 nm with the reaction temperature of 190 °C, to 23.0 nm with 180 °C and to 36.2 nm with 165 °C. The logic behind the diameter control can be explained by close examination of the nucleation stage. At a higher temperature, the reduction of Cu complex is faster, leading to a faster nucleation and thus more nucleation sites at the same time frame. Considering that the precursor concentration is kept the same for all experiments, more nucleation sites imply smaller volume for each nucleates, which later will grow into thinner NWs.

Table 2.2 Summary of reducing power of benzoin and similar structures toward Cu (II) reduction

<table>
<thead>
<tr>
<th>Reducing agent used</th>
<th>Reactivity toward Cu(II)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Reductant 1" /></td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Reductant 2" /></td>
<td>No</td>
<td></td>
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<tr>
<td><img src="image" alt="Reductant 3" /></td>
<td>No</td>
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<tr>
<td><img src="image" alt="Reductant 4" /></td>
<td>No</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Reductant 5" /></td>
<td>No</td>
<td>R = CH₃, CH₃CH₂-</td>
</tr>
<tr>
<td><img src="image" alt="Reductant 6" /></td>
<td>Yes</td>
<td>X = CH₂OH, CH₂-, Cl, F-, F- can slightly react above 200 °C</td>
</tr>
</tbody>
</table>
To investigate benzoin’s role as a reducing agent, we carried out a series of control experiments with benzoin-like chemicals and the results are summarized in Table 1. Benzaldehyde, which is the main byproduct of benzoin’s decomposition,\(^{40}\) shows no activity towards reduction of copper salt at the condition of interest. Benzoin esters are also tested under the similar condition. Despite the fact that benzoin esters exhibit similar behavior and activity when used as photoinitiator,\(^{39}\) no reactivity towards copper reduction is observed here. This suggests that the actual reductants are probably the \(\alpha\)-hydroxybenzyl radicals, rather than its benzoyl counterpart. Another interesting observation is that, when we attach one Cl atom to the aromeric ring (4-chlorobenzoin), again no reduction of copper happens. This is probably because that the asymmetrical structure makes homolytic bond cleavage no longer favorable, and thus radicals are not among the major products. This further implies the radical-involving nature of this reaction.

To further understand the proposed radical-involving mechanism, in-situ temperature dependent electron paramagnetic resonance (EPR) spectroscopy is used to track the reduction progress. EPR is a spectroscopic technique that detects species with unpaired electrons, and is informative towards reactions involving free radicals and/or active metal complexes. In our study, we simulate the typical reaction in a vacuum sealed quartz tube and follow the evolution of the reactants’ EPR signals during. Similar to the Schlenk tube reaction, the reactants were first mixed and then left at room temperature (RT) for two hours before slowing heated up to 170 °C, and then left to react for another three hours. Simultaneously, EPR responses of the solution were acquired at different time/temperature intervals.
Figure 2.9. (a) In-situ EPR response of the reactants at RT. From the top, it shows the reactant’ EPR signals upon mixing (blue), after 30 mins at RT (green) and 2 hours after RT (grey). (b) EPR signals of the reaction during heating. From the top, it shows EPR spectra of the reaction before heating (grey, the enlarged purple area in Fig. 3a), at 70 °C (yellow), at 120 °C (orange), at 170 °C (red), and 3 hours at 170 °C (wine).

The results of the EPR measurements are shown in Fig. 2.9. The first spectrum (blue) in Fig. 2.9 a is taken immediately after the reactants are mixed at RT. Broad EPR signal centering at 3165 G (g-factor, or g = 2.09559) is observed. This strong and broad feature can be assigned to Cu (II) species which originated from Cu losing two electrons, and taking 3d⁹ electron configuration, rendering one unpaired electron.⁴² The absence of subtle features is due to line broadening caused by strong dipolar interaction.⁴³, ⁴⁴ This broadening is commonly observed in concentrated solution.³⁹ After 30 mins at RT the broad feature (green), preserves its general centering position but with intensity visibly reduced. In addition, subtle patterns are resolved due to lowered concentration.

Figure 2.10. Optical pictures of reactants (CuCl₂, oleylamine, and benzoin) in EPR quartz tube (a), immediately after preparation; (b), after 2 hours at room temperature; and (c), at end of reaction.

After 2 hours, the Cu (II) pattern is undetectable (grey). Coupled with the disappearance of the signature blue color, we believe that Cu (II) is completely reduced to Cu (I) species at this stage as shown in Fig. 2.10 a, b. A control experiment without benzoin, shown in Fig. 2.11, indicates no change in the spectra at RT, indicating that benzoin, rather than oleylamine reduces Cu (II) to Cu (I).
Figure 2.11. EPR spectra of oleylamine and Cu(II) only at different temperature.

Fig. 2.9 b keeps track of the EPR response during the heating of the reaction solution. Sharp features with g factor calculated as 2.00331 are observed. EPR lines with g-value close to 2, correspond to a free radical signal,\(^4\), which we believe is produced by the thermal decomposition of benzoin. In the first spectrum (enlarged purple area of Fig 2.9 a), taken at RT, a sharp radical-like feature is already resolved. This echoes with the observation of room-temperature reduction of Cu (II) complex. It indicates that, without heating, benzoin is already slowly decomposing and producing radicals. This decomposition, even though slow, can already build up a steady-state concentration which can be detected by EPR spectroscopy. The radicals produced have efficient reducing power to reduce Cu (II) to Cu (I) but no further, likely due to the low concentration.

As the temperature reaches 70 °C, the radical signal becomes stronger (yellow). Evidently as temperature is increased, the decomposition of benzoin become faster, and the concentration of radicals also increases. As the reaction temperature goes up to 120 °C, reddish copper product starts to precipitate out in the EPR tubes. The EPR signal (orange) becomes stronger. The asymmetric shape of the EPR spectrum infers that there are multiple radical species present in the sample, causing superposition of lines with different g-values.\(^4\)
Figure 2.12. EPR spectra of oleylamine and benzoin at different temperatures. Inset shows the possible resonance scheme and possible structure of the detected radical.

The spectrum of the primary radicals in the system has six well resolved hyperfine lines. The missing of one intense central line suggests that there exist an odd number of equivalent hydrogens contributing in hyperfine coupling.\textsuperscript{45} The spectrum obtained here does not match with previously reported data for low temperature (< 100 K) benzoyl (three lines with one strong center)\textsuperscript{46}, nor α-hydroxylbenzyl radical (evenly distributed 21 lines)\textsuperscript{47}. Due to the high-temperature enhanced line shift/broadening effect,\textsuperscript{44} a full interpretation of this spectrum is not straightforward. One possible explanation is shown in Fig. 2.12, that at high temperature, benzoyl radicals (α-radical) resonance into its β-isomer.\textsuperscript{48} The energy barrier of this transformation is easily overcome by thermal input and thus comparable amount of both species exist under the reaction condition.\textsuperscript{49} Further studies are need to elucidate the exact reaction mechanism.

As the temperature continues to increase, more copper product emerges from the tube. Meanwhile, the radical signal (red) decreases due to the consumption of the material. Then, the solution was left to react at 170 °C for 3. The radical signals keep declining as the reaction goes on. It is worth to note that the radicals are not instantly consumed even at this high temperature. Rather, the radical signals are still strong after 30 min’s reaction, and well resolved even after 1.5 hours of heating. This indicates that the radicals have a long enough lifetime to build up a detectable concentration at high temperature for several hours. And the long-lasting radicals serves as the active reducing agent throughout the entire reaction. However, the long maintained radical signal level does not necessarily point to ultra-stable radical species. This equilibrium concentration is
balanced by benzoin’s decomposition and radical consumption. In the final spectrum (wine), the radical signal is barely resolved. Copper metal can be observed within the EPR tube (Fig. 2.10 c).

Figure 2.13. Pictures of different stages of Cu NWs synthesis using (a), 4,4-dimethoxybenzoin, (b), 4,4-dimethylbenzoin, (c), benzoin, (d), 4,4-dichlorobenzoin and (e), 4,4-difluorobenzoin as reducing agents. The upper and middle panel show the pictures of reactions run for 1 hour and 2 hours respectively; the lower panel shows the chemical structures used in corresponding reactions. The reactions were all carried out at 180 °C.

The reactivity of benzoin can be tuned by introducing electron-donating/electron-withdrawing groups on the benzoin molecule. We find that, with electron-donating group as substitution, the reducing power is largely promoted; while electron-withdrawing substitution diminishes benzoin’s reduction reactivity. Fig. 2.13 shows the series of control experiments carried out to test the reactivity of different benzoin derivatives. When heated at 180 °C for 1 hour, large amount of copper is already reduced out using dimethoxybenzoin as reducing agent, comparing to the smaller amount in the case of dimethylbenzoin, and no visible copper species in the case of benzoin, dichlorobenzoin and difluorobenzoin. Two hours into the reaction, the production of copper follows the same trend, with electron donating modification promotes the reaction while the electron withdrawing case suppress the reduction. The yield of copper product after three hours’ reaction time are measured to be 94.0%, 65.3%, 31.3%, 2.5% and 0% for reactions with 4,4’-dimethoxybenzoin, 4,4’-dimethylbenzoin, benzoin, 4,4’-dichlorobenzoin and 4,4’-difluorobenzoin, respectively. The TEM images of the products are shown in Fig 2.14. The substitutes may either modify the carbon-carbon bond cleavage energy or the redox potential of the resulting free radicals, and these modifications eventually change the reactivity of the radicals.
Figure 2.14. TEM images of copper nanowire synthesized using (a), 4,4-dimethoxybenzoin, (b), 4,4-dimethylbenzoin, (c), 4,4-dichlorobenzoin as reducing agents.

Figure 2.15. TEM images of as-grown (a), silver and (b) gold NWs using benzoin as reducing agent.

Additionally, benzoin is compatible with both hydrophilic and hydrophobic solvent systems. This gives it great potential as a generalized reducing agents in the broader nanomaterial syntheses. For example, colloidal synthesis of silver NWs is only possible when (polyvinylpyrrolidon) PVP, a hydrophilic surfactant, is used as shaping ligands. Benzoin can be readily used as a reducing agent for silver NW syntheses as well. Silver nitrate can be reduced to silver metal by benzoin at 130 °C. The NW formation undertakes the similar mechanism as copper. Ag (0) tend to nucleate to five-fold-twinned seeds in presence of PVP and then grow to one-dimensional NWs. A control experiment without addition of benzoin shows no silver ion reduction at the same temperature, giving evidence to the benzoin’s role of reducing agent. The resulted silver NWs have the mean diameter of 50 nm as shown in Fig. 2.15a. Ultrathin gold NWs, shown in Fig. 2.15a, can also be synthesized using benzoin as reducing agent in presence of oleylamine. The averaged diameter of as grown gold NW is around 3 nm.

3.4 Fabrication of Transparent Conductors Using Ultrathin Copper Nanowires

Following synthesis, we next fabricated high-performance copper nanowire electrodes on glass using a filtration method. A dilute copper nanowire suspension was filtered through a
nitrocellulose membrane through vacuum filtration, and the resulting film was subsequently transferred onto a glass substrate by pressing it against nitrocellulose membrane. Then, the electrode was annealed under forming gas (10% hydrogen in argon) at around 200℃ to remove surface organic ligands and native oxides, and more importantly, to partially sinter the wires together to create intimate contact junctions.

Figure 2.16. AFM images of copper nanowire film (a), before annealing and (b), after annealing.

AFM images of copper nanowire film before annealing and after annealing were taken (Figure 2.16). Before annealing, the two measure nanowires have diameter of 16.66 nm and 16.98 nm. The measured junction height is 33.74 nm which is almost the same with the summation of two individual nanowire diameters (33.64 nm). In the case annealed nanowire film, the measured diameters of the two individual wires are 14.50 nm and 15.00 nm which add up to 29.50 nm. The annealed junction has the height of 24.46 nm which is 5 nm short of the summation. This shows that the thermal annealing can partially wield nanowire together which can enhance the junction contact.
Figure 2.17. Dependency between film sheet resistance and annealing temperature.

The heat treatment is found to have a considerable impact on the film properties. As shown in Fig. 2.17, films’ sheet resistance is highly dependent on the annealing temperature. 200°C is the optimized annealing temperature. If the temperature is lower, it cannot effectively melt the nanowire to form intimate contact at the wire-wire junction. An increase in sheet resistance is observed. When the annealing temperature is lower than 150 °C, the nanowire film is almost insolated due to the presence of oxides on the surface of the nanowire. The temperature cannot be too high either. Overheating will severely melt nanowire and damage the nanowire percolation, which will result in degrading in film conductivity.

Figure 2.18. SEM images of nanowire conducting film when annealed at (a) 200 °C when most nanowires are intact; (b) 230 °C, when some of the nanowires are visibly melted; and (c) 260 °C, when most of the nanowires are deformed.

As shown in Figure 2.18, overheating easily breaks the copper nanowires due to their ultra-thin diameters and consequently depressed melting points, while under-heating does not provide enough thermal energy to weld the individual nanowires together.
Figure 2.19. Ultra-thin copper nanowire transparent conductor and its optical and electrical performance. (a) Optical images of transparent electrodes with increasing copper nanowire loading amounts (from left to right). (b) Wavelength dependent transmittance, sheet resistance and corresponding SEM images of transparent conductors. Substrate contribution is excluded. (c) Plot of transmittance versus conducting film sheet resistance. Characteristic transmittance data are acquired at 550 nm of wavelength.

Fig. 2.19 a shows the optical images of the copper nanowire transparent conductor with different loading amounts. Figure 2.19 b shows their corresponding SEM images, transmittance spectra and measured sheet resistances. The films show great transparency from ultraviolet-visible range to infrared (350-1700 nm), rendering them suitable materials not only for displays in consumer electronics but also for photovoltaic cells or thermal applications, where transmission in the near-infrared region is also important. Moreover, the conducting films exhibit outstanding performance in the trade-off between transparency and resistance as plotted in Fig. 2.19 c. For a film with transmittance of 77%, the sheet resistance is as low as 5.32 ohms/sq. As the transmittance increases to 86%, the sheet resistance increases slightly to 15.0 ohms/sq. Another sample shows 90% in transmittance and 34.8 ohms/sq in sheet resistance. This performance clearly stands out in comparison with other reports on solution-based copper nanowire/nanofiber transparent conductors that demonstrate 50 ohms/sq at 90%, 19 75 ohms/sq at 88%,22(b) 35 ohms/sq at 85%,24(a) and 23.3 ohms/sq at 78%.24(b)
Figure 2.20. Conductivity performance of ITO and Cu nanowire conductor upon mechanical bending. Inset, flexible copper nanowire conducting film fabricated on polyethylene terephthalate (PET). Transparent PET (175 micron) substrates (MELINEX® ST506) were purchased from TEKRA. ITO (sheet resistance at the range of 80–90 ohms/sq) on PET (175 micron) was purchased from Sigma-Aldrich. Bending angle is around 90 degree.

Copper nanowire conducting films can also be fabricated on plastic substrates via a modified processing approach. Fig. 2.20 compares the conductivity performance of ITO and Cu nanowire conductor upon mechanical bending. The nanowire film on PET shows great flexibility and the sheet resistance is maintained at its original level after 1000 times bending cycles (around 90 degree of bending angle). In contrast, ITO on PET shows severe degradation in conductivity when it is applied with mechanical bending. The sheet resistance increased almost 100 times when the sheet was bended 500 cycles.

The excellent performance of our copper nanowire electrodes can be attributed to several factors. First, the thin diameter of the nanowires would, in principle, boost light transmission while maintaining high conductance. In addition, the well-controlled synthesis in this report results in high-quality, mono-dispersed copper nanowires. Oversized cluster byproducts, which greatly reduce transparency while contributing little to conductance, are minimized. Finally, the film fabrication process is carefully optimized to provide the best quality. Undesirable byproducts of the synthesis are mostly nanoparticles with the diameters between 30-100 nm. The 220 nm pore size nitrocellulose membrane used in the process enables the byproduct nanoparticles to be effectively washed through rather than be incorporated into the film. Diluting the nanowire suspension as well as multiple rinses before and after the filtration also helps get rid of the undesired nanoparticles.
Figure 2.21. Stability test of copper nanowire transparent conductors. Each color represents a different loading amount. It is also worth to note that the Cu NW film cannot keep the high conductivity permanently. After several months’ exposure in ambient air, the conductivity of the copper film degrades significantly.

The copper films have decent stability in air over time. As shown in Fig. 2.21, typically, after the first 24 hours of exposure in air, the conductivity shows a sharp decrease of about 30% and then stabilizes for up to three weeks tested. The degradation in conductivity likely plateaued because of self-passivation: the formation of a thin layer of oxides on the mesh surface effectively prevents further oxidation and preserves electrical contact between individual nanowires.

Besides the merits of sheet resistance and transmission, optical haze is also an important factor in characterizing the quality of a transparent electrode. Haze is especially important in display applications where scattering will reduce the sharpness of an image. Haze is numerically defined as the percentage of transmitted light that is scattered more than a certain angle off the principal axis of the incident beam. In our case, the measurement follows the D1003-13 standard (See SI for detailed method). Large value in haze is an ongoing challenge for nanowire-based transparent electrodes because the nanowires are strong scattering centers. For example, Hu et al. reported a silver nanowire mesh with a scattering of 13% at 79% total transmittance, which means roughly 16.4% of transmitted light is scattered away off its original direction. In another example, the forward light scattering of a copper fiber-based electrode contributed 10% of its 92% of total transmittance. Even though some films show great conductivity with high transparency, a large portion of the transmitted light diverges from its original path which makes them unsuitable in display applications.
Figure 2.22. Light pathway through the copper film and haze factors. (a) Percentages of light absorbed, reflected, scattered (diffusive transmittance) and directly transmitted by a copper nanowire film. (b) Plot of the haze factors of copper nanowire conductors versus their total transmittance values. All characteristic optical property data are discussed at wavelength of 550nm.

The haze factor of a transparent conducting film heavily depends on nanowire diameter, with lower diameter nanowires featuring less haze. We examined the haze of the thin films fabricated using our ultra-thin copper nanowires. Figure 2.22 a shows specular transmittance, diffuse transmittance, reflectance, and absorbance of a typical copper nanowire film with sheet resistance of 35 ohms/sq. When the light is directed at the copper film, 1.1% is reflected; 88.7% is transmitted and 10.2% is absorbed. Of the total transmitted light, 86.1% is specular transmittance (direct transmission) and 2.6 percent is scattered away. Figure 2.22 b lists several haze values at different total transmittance values. The haze value decreases almost linearly with the increase of total transmittance. When the total transmittance is 90%, the haze factor is only about 2–3%. The haze factor increases to 4% when the total transmittance is 81%. These results demonstrate that the ultrathin copper nanowire-based films show significantly lower scattering effect than that of similar nanowire transparent conductors reported in literatures.

2.5 Conclusions

In conclusions, a synthetic approach that using TTMSS as a mild reducing reagent to achieve ultra-thin, uniform, and high-quality copper nanowires was described in this chapter. This solution-based method is easily scalable and produces five-fold copper nanowires with 17.5 ± 3 nm in
diameter. Detailed mechanism analysis of the growth is carried out to suggest that five-twelved pentagonal nanoparticles are ascertained to serve as seeds for the nanowire growth.

Furthermore, we demonstrated that benzoin can also be used as a carbon sourced reducing grow high quality Cu NWs. The active species during the reduction are attributed to the free radicals produced via thermal decomposition of benzoinos. The reaction mechanism was studied using in-situ temperature-dependent EPR spectroscopy. Reduction of copper is observed in line with evolution of free radicals. Benzoin is shown to have a wide tunability of reducing powers by changing its substitution derivatives. These unique features make benzoin and its derivatives useful in metal nanowire growth and also open up new opportunities for the broader nanomaterial synthesis.

High performance transparent conducting films were fabricated and exhibit high transparency with low sheet resistance. Moreover, the resulting thin films show a dramatically reduced haze factor due to the ultra-thin diameter, making them suitable for display applications. This work also demonstrates that TTMSS is a unique reducing reagent for metal nanomaterial synthesis, and our approach advances research into the commercialization of copper nanowire mesh electrodes.

2.6 References

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Chapter III

Copper Based Core-Shell Nanowires for Highly-Stable Transparent Conductors


3.1 Core-Shell Structure Design for A More Stable Copper Nanowire Electrode

Copper nanowire (Cu NW) based transparent conductors are promising candidates to replace ITO (indium-tin-oxide) owing to the high electrical conductivity and low-cost of copper. However, thin Cu NWs are intrinsically unstable under ambient conditions. Rapid surface oxidation of the Cu NWs reduces the conductivity dramatically, preventing the practical application of such transparent electrodes. To improve the stability of the Cu NWs films, several approaches have been examined. For example, over-growth of a layer of Ni on Cu NWs, 1 or coating the Cu NWs with a very thin layer of Al₂O₃ by atomic layer deposition, 2 etc. Although the stability indeed improved, either the total transparency or the overall conductivity of the films decreased significantly. Another approach is to construct hybrid films consist of large graphene/graphene oxide sheets and metal NWs.3-6 Ideally, to maintain high optical transparency and good electrical conductivity, coating or wrapping a very thin conformal layer of conductive and chemically stable material on the surface of the Cu NWs is desired. Recently, wrapping graphene on Cu NWs has been proposed to address this issue. By studying individual core-shell nanowires, it was found that the graphene coating could improve not only the stability, but also the electric and thermal conductivity of the Cu NWs.7 To synthesize these structures, plasma enhanced chemical vapor deposition method (at 500 ~ 700 °C) was used to grow the thin layer of graphene on the metal NWs.8-9 This procedure however is not compatible with the low-cost high-throughput production required for practical applications.

To improve the stability of the Cu NWs films, we developed a solution-based method to produce high quality ultrathin copper-reduced graphene oxide core-shell nanowires. By controlling the surface chemistry, graphene oxide (GO) nanosheets are wrapped onto the Cu NWs surface to form a uniform coating with thickness of around 3 to 5 nm.10 We fabricated transparent conducting films using the core-shell nanowire colloidal suspensions and show that excellent conductivity (sheet resistance = 28 Ohms/sq; transparency = 89% at 550 nm) and significantly improved stability under air exposure. Moreover, the core-shell nanowire based films show even lower haze values compared to the naked Cu wire, making it particularly interesting to display panels.
In another approach of solving the copper nanowire stability issue, we aim to synthesize core-shell or alloyed copper nanowires in which another metal material shall be more oxidation-resistive precious metals (e.g. platinum, silver, gold etc.). The goal is to incorporate a small amount of precious metal within the copper lattice (either at the exterior, thus core-shell structure, or form a stable alloy phase with copper material) to enhance the stability of the copper nanowire film. Other advantages of this approach also include possibility of tuning film optical transmission property and heat response behavior (by changing metal melting points). In part two, we document the initial trails for Cu-Pt, and Cu-Ag core-shell nanowire synthesis. In part three, the most successful system, Cu-Au core-shell nanowires are discussed in detail.

3.2 Cu-Reduced Graphene Oxide Core-Shell Nanowires Based Transparent Conductors.

Figure 3.1 An illustration of the graphene oxide wrapping, film deposition, and reduction process to fabricate the transparent conducting films.

Figure 3.1 shows an illustration of the overall strategy of GO wrapping and film fabrication. The Cu NWs with an average diameter of \(~17\ \text{nm}\) were synthesized using our recently developed silane based chemistry. To achieve uniform surface wrapping, GO nanosheets with an average diameter of \(~10\ \text{nm}\) were synthesized. The as-synthesized Cu NWs are covered by oleylamine as the surface ligands and can be dispersed in non-polar solvent such as toluene. However, GO is not soluble in such solvent and the mixture of Cu NWs and GO nanosheets can only be achieved in an “intermediate” solvent. We found that the mixing and wrapping processes occur effectively in methanol with mild ultra-sonication and the resulting Cu GO core-shell NWs can be well dispersed in polar solvents such as methanol, ethanol, and isopropanol (IPA). The thin native oxide layer (1~3 nm) on Cu surface may have strong interactions with the functional groups on GO and thus provide driving forces for the replacement of oleylamine ligands to GO.
Figure 3.2 Structural characterization of the copper-graphene oxide core-shell nanowires. a, Images showing the nanowire suspension stability. Left: Cu NWs in toluene; Middle: Cu NWs in IPA; Right: Cu GO core-shell NWs in IPA. b, After 20 min. c, After 24 hours. d, A TEM image the Cu GO core-shell nanowire. Scale bar: 50 nm. e, A high-resolution TEM image the Cu GO core-shell nanowire. Scale bar: 5 nm. f, FTIR spectra of the Cu nanowires before and after GO wrapping. g-k, EDS analysis of a core-shell nanowire showing the elemental distribution of copper, carbon, oxygen, and the combination of the three elements. Scale bars: 40 nm.

Figure 3.2 shows the structural characterization of the copper-graphene oxide core-shell nanowires by a variety of techniques. Interestingly, after wrapping, the core-shell NWs form a very stable colloidal suspension in IPA for several days, whereas the as-synthesized Cu NWs aggregate after a few minutes in either toluene or IPA (Figure 3.2 a-c). These results provide an indirect evidence of successful GO wrapping. The well-dispersed NWs are important to film fabrication because strong aggregation can lead to larger effective diameter of the wires, stronger light absorption and scattering; therefore, reduce the performance. Figure 3.2d shows the transmission electron microscopy (TEM) images of a GO wrapped Cu NW. It can be seen that a thin layer of GO with thickness of around 1 to 5 nm have been coated uniformly along the Cu NW. A higher resolution image (Figure 3.2e) indicates a clear interface between the crystalline Cu and amorphous GO. Figure 2f shows the fourier transform infrared (FTIR) spectroscopy of the Cu NWs before and after GO wrapping. The signature of oleylamine at 2800 ~ 3000 cm⁻¹ becomes negligible, while features of hydroxyl groups (3000 ~ 3500 cm⁻¹) and carbon-carbon double bonds of GO (~ 1600 cm⁻¹) show up for the GO wrapped Cu NWs. Furthermore, the energy-dispersive X-ray spectroscopy mapping on a single wire confirms the proposed core-shell architecture. As shown in Figure 3.2g-k, Cu element exists only in the core of the wire, while carbon and oxygen elements form a uniform thicker shell around the Cu wire. All these results indicate that the GO nanosheets can be effectively wrapped onto the surface of the ultrathin Cu NWs, without changing the morphology of the Cu NWs.
Figure 3.3. Optical and electrical performance of the nanowire-based transparent conducting films. a, Transmittance spectra of the films from UV to near-IR and corresponding optical images (inset). b, Transmittance versus the sheet resistance of different type of films.

We fabricate the core-shell nanowire conducting films on glass using a filtration method. Dilute nanowire suspension in IPA was filtered onto a filter membrane by vacuum and then the resulting film was transferred to a glass substrate by pressing the open side of the membrane. The films were then annealed under argon with 10% hydrogen (at 180 or 260 °C) to reduce GO and any residual native copper oxides, and create an intimate contact junction between wires. Figure 3a shows the optical images of the core-shell nanowire transparent films with different loading amount and the corresponding transmittance spectra from UV to near-IR. The films show great transparency from UV-Visible range all the way to infrared, which make them suitable materials for not only display but also for multijunction photovoltaic cell or thermal applications. Figure 3.3 b summarizes the transmittance versus the sheet resistance of different type of films. The black and blue curves indicate the performance of the Cu NW films and Cu GO core-shell NW films annealed at 180 °C; respectively.
Figure 3.4 The sheet resistance of the core-shell NW film at different annealing temperature. All the films have a similar transparency of ~ 85% (at 500 nm).

The core-shell NW films show significantly lower performance, because GO cannot be thermally reduced at 180 °C and such insulating layer prevent efficient charge transfer between individual Cu wires. It is known that GO can be effectively reduced under heating at over 250 °C and the reduced GO (r-GO) shows good electric conductivity. To improve the performance of our Cu GO core-shell NW transparent conductors by thermally reducing the GO layer, we annealed the films at higher temperature (from 200 to 350 °C). As shown in Figure 3.4, the sheet resistance of the core-shell NW film decreases as the annealing temperature increases to around 260 °C, and at higher temperature the sheet resistance increases dramatically due to the damage of the Cu NWs.

Figure 3.5. Scanning electron microscopy of the films annealed at different temperature. (a) 200 °C; (b) 260 °C; (c) 300 °C; (d) 350 °C.
Figure 3.5 shows the scanning electron microscopy of the films annealed at different temperature. The nanowire morphology are well preserved at 200 and 260 °C. At 300 °C, some very thin wires start to melt, and thick bundles of wires (~100 nm) form. And all the wires melt under 350 °C heating. Note that the Cu NWs without GO coating start to melt at lower temperature (~230 °C), indicating that the GO wrapped wires have slightly higher melting points and better thermal stability. The optimized condition for the Cu GO core-shell NW films is 260 °C, which is higher than the Cu NWs without GO coating. Under this condition, the GO nanosheets can be thermally reduced to form r-GO, as indicated by the color of the power, the FTIR spectra, X-ray diffraction, and X-ray photoelectron spectroscopy studies as shown in Figure 3.6. Upon effective annealing, the yellowish graphene oxide powder turned to black in; while in the meantime, C=O group can be seen significantly reduced both in FTIR and XPS spectra (Figure 3.6b, d)

![Figure 3.5](image1.png)

**Figure 3.6.** GO thermal reduction. (a) Optical images, (b) FTIR spectra, (c) X-ray diffraction, and (d) X-ray photoelectron spectroscopy studies showing the GO before and after annealing at 260 °C.

The pink curve in Figure 3.3b shows the performance of the high temperature annealed films. Interestingly, they show greatly enhance performance compared to the 180 °C annealed core-shell NW films, and their performance is even slightly better than the naked Cu NW films. For example, sheet resistances of 14.8 Ohms/sq at transparence of 86.5% (wavelength = 550 nm), 28.2 Ohms/sq at transparence of 89.3%, and 75.0 Ohms/sq at transparence of 93.9% have been achieved, which are close to the commercial ITO or silver NW transparent electrodes (red and green circles in Figure 3.3b).

The improvement can be attributed to the following: First, higher temperature annealing can effectively reduce GO and improve the connection and charge transfer between wires. Additionally, the r-GO layer facilitates electric conduction from wire to wire, because the thickness of the r-GO layer is very small and the work functions of r-GO and Cu are similar, resulting in an Ohmic
Second, the core-shell NWs form a better colloidal suspension, indicating less wire–wire interaction and aggregation. Therefore, during the filtration process, fewer large bundles form compared to the Cu NWs without GO coating. Third, similar to the case for graphene wrapped Cu NWs, the r-GO coating may also improve the electric and thermal conductivity of the individual Cu NW itself.

The stability of the transparent films in air was studied to demonstrate the advantages of the GO wrapping approach. Three types of conducting film were recorded: Cu NWs (180 °C annealed), Cu GO core-shell NWs (180 °C annealed), and Cu r-GO core-shell NWs (260 °C annealed). The sheet resistance of 5 films for each type at both room temperature and 80 °C (humidity = 40 ± 10 %) were recorded and the average values are summarized in Figure 3.7. The Cu NW films show poor stability and degraded in a few days at room temperature and in a few hours at 80 °C. When wrapped with GO and annealed at 180 °C, the stability improved significantly. The sheet resistance of the Cu GO core-shell NW films doubled after two weeks at room temperature and 2 days at 80 °C. The Cu r-GO core-shell NW films show even better stability and no obvious degradation was observed, indicating the r-GO wrapping can effectively prevent Cu NW oxidation. The slight improvement after the thermal reduction is probably due to the enhanced packing of r-GO nanosheets, which limits the diffusion of oxygen molecules through the protecting layer.
3.7c shows the long-term stability of the Cu r-GO core-shell NW films stored in air for 160 days. These results indicate that the Cu r-GO core-shell NW based transparent conductors are highly stable.

Haze is another important parameter that defines the quality of a transparent electrode. It is defined as the percentage of transmitted light that is scattered through a larger angle than a specified reference angle (e.g. 2.5°) with respect to the direction of the incident beam. It is particularly important for display applications, in which light scattering will greatly reduce the sharpness of the image and result in a blurred image. The haze of the nanowire mesh conducting film highly depends on the diameter of the nanowire and a previous study showed that our ultrathin Cu NWs can be used to produce conducting thin films with very small haze. Here we find that the Cu r-GO core-shell NW films show even lower haze values compared to the Cu NW films. Figure 3.8a shows the haze values of Cu and Cu r-GO NW films at different total transmittance at a wavelength of 550 nm. Clearly, the haze values of the core-shell NW films are 0.5 ~ 1% lower than the Cu NW films in a large range of total transmittance, indicating the Cu r-GO core-shell NWs have less light scattering effects. This improvement may be the result of two different phenomena. First, wire-wire aggregation in the well-dispersed GO coated nanowires during the filtration process is largely reduced. Figure 3.8b shows that the average size of the wire bundles reduced from 29.7 to 23.0 nm in diameter (from SEM images of the annealed samples with similar total transmittance, wires are coated with ~3 nm gold). The thinner wire bundles should reduce the light scattering effect. Second, the r-GO coating introduces a gradual change in refractive index from copper to...
air, leading to a smaller light scattering cross section for the ultrathin NWs. Figure 8c shows the optical simulation results of a 17 nm thick Cu NW coated with a thin graphene layer which indicate that the light scattering cross section in the visible region is reduced. This is because the carbon has an intermediate refractive index \( n = 2.3 \) at 550 nm) between air \( (n = 1.0 \) at 550 nm) and copper \( (n = 3.3 \) at 550 nm) and such refractive index gradient decreases the portion of scattered light at higher angles.

We further developed a method to model the transmission, haze, and sheet resistance of the core-shell nanowire meshes using Mie theory.\(^{12-14}\) The calculated haze versus transmission for Cu and Cu r-GO nanowires with different thicknesses of r-GO is shown in Figure 3.8d. This calculation shows that graphene coating decreases haze of the conducting films relative to Cu. The reduction in haze is consistent with the experimental data. The results imply that the average thickness of r-GO around Cu NW is probably less than 1 nm. The details about the simulation can be found in Appendix B. The model for Cu rGO core-shell nanowires presented here can predict the experimental results well, and it can also be extended to other core shell nanowire systems. The simulation results also indicate the r-GO wrapping approach is a feasible way to improve the stability and conductivity of Cu NWs.

<table>
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<th>Time (min)</th>
<th>( H_2 )(sccm)</th>
<th>Covered</th>
<th>Uncovered (ohms/sq)</th>
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<tr>
<td>1</td>
<td>100</td>
<td>Not conductive</td>
<td>1425</td>
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<tr>
<td>1</td>
<td>50</td>
<td>Not conductive</td>
<td>896</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>Not conductive</td>
<td>167</td>
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GO-Cu nanowire film can also be reduced to conductive by hydrogen plasma etching instead of high temperature annealing. This opens the opportunity for patterning. One demonstration is made and the results are shown in Table 3.1. In the experiment, we take one as-made GO-Cu nanowire film and cover half of the film with a simple glass cover slip. Then, we take this film and do plasma etching on the whole ensemble. As shown in the Table 1, the parts of the films that are covered are not conductive at all in all the plasma condition we tried. The exposed films are reduced to be conductive. The conductivity of the films depends on the conditions we use during the etching.

3.3 Ultrathin Epitaxial Cu@Au Core-Shell Nanowires for Stable Transparent Conductors

So far, we have demonstrated that reduced graphene oxide can enhance copper’s resistance towards oxidation while keeping or even slightly promoting nanowires’ electrical contacts. However, the protection is impaired under harsh environments was not great due to the difficulty of achieving a complete and well-defined coverage. The high conductivity of graphene can even promotes the electrochemical reaction at the interface and catalyze the corrosion of copper over long time scales.\(^{15}\) Coating of metals generally provides a good solution with both oxidation protection and electrical contacts. In particular, a study by Stewart et al. coated Cu nanowires with Ag, Au and Pt shells.\(^{16}\) The Cu@Ag nanowires with a shell thickness of ~5 nm exhibit comparable performance to pure silver or copper nanowires, while the protection of the copper core under humid conditions is not sufficient unless the shell thickness is increased to 15 nm. The enhanced
stability endowed by the thick shell is at the expense of optical performance, especially the haze factor which is proportional to nanowire diameter.\textsuperscript{17,18} Although the underlying reason for the insufficient protection using thin shells is largely unclear, the imperfect coverage of inert shell on copper surface and the indefinite interface between shell material and copper may play critical roles. We envision that this issue can be addressed through the epitaxial growth of a conformal and uniform shell of noble metal with a few atomic layers on copper nanowires.

The epitaxial overgrowth of a noble metal onto the surface of a less noble metal represents a synthetic challenge. Galvanic replacement usually dominates the growth process and results in hollow nanostructures.\textsuperscript{19} Yang et al. revealed that galvanic reaction between Ag and H\textsubscript{Au}Cl\textsubscript{4} could be blocked in the presence of strong reducing agents.\textsuperscript{20} Another synthetic strategy demonstrated by Gao et al. suggested that the galvanic replacement-free overgrowth can be achieved by simultaneously decreasing the reduction potential of gold salts and providing sufficient protection on the metallic Ag surface.\textsuperscript{21} In the following section, I will show a successful case of epitaxial deposition of a conformal, ultrathin (1–2 nm) gold shell on the surface of copper nanowires by modifying the ligand environment of the gold precursor solution.

Figure 3.9. Schematic illustration of the reduction of H\textsubscript{Au}Cl\textsubscript{4} in the presence of Cu nanowire seed under different ligand environments and injection rates. With weakly bound ligand, such as oleylamine (OAm), fast injection induced homogeneous-nucleation of Au(0) species, while slow injection resulted in galvanic replacement between gold cations and Cu nanowires. With strongly bound ligand, such as trioctylphosphine (TOP), epitaxial growth was favored, independent of the injection rates.
Our attempts to synthesize Cu@Au core-shell nanowires started by sequential reduction of the two metals in a fashion of seeded growth (Fig. 3.9, route 1). The ultrathin copper nanowires were first prepared in oleylamine (OAm) using tris(trimethylsilyl)silane as a reducing reagent, and served as seed for gold deposition. After the depletion of most of the copper precursor, HAuCl₄ dispersed in oleylamine was quickly injected into the growth solution. The products turned out to be a mixture of small nanoparticles and nanowires as shown in Fig. 3.10 a. Energy dispersive spectroscopy (EDS) mapping in Fig. 3.10 b shows that the small nanoparticles are pure gold, while the nanowires are composed of copper and gold, although the atomic ratio of gold is as low as 1% according to EDS quantitative analysis. The small nanoparticles could be separated via differential-speed centrifuging (Fig. 3.10c). The characteristic d-band transition peak observed at 525 nm in the ultraviolet-visible (UV-Vis) spectrum (Fig. 3.10d), along with the powder X-ray diffraction (XRD) patterns (Fig. 3.10e), further confirms the fact that they are gold nanoparticles. We rationalized this observation to be a consequence of homogeneous-nucleation at the initial stage of gold reduction. As HAuCl₄ was rapidly introduced into the growth solution, instantaneous reduction of the gold precursor led to a rapid increase of the concentration of gold atoms, initiating the nucleation and crystal growth on their own.
Figure 3.11. TEM image of the nanowires obtained via a slow injection of the oleylamine dispersion of gold(III) chloride trihydrate (Scheme 1, route 2).

We therefore modified the synthesis and slowly fed HAuCl₄ into the growth solution via syringe pump (Fig. 3.9, route 2). In this way, the concentration of newly formed gold atoms could be maintained at a relatively low level. As shown in Fig. 3.11 The absence of small gold nanoparticles in the products indicates the homogeneous-nucleation was indeed suppressed using slow injection. However, pores and voids are prevalent in the obtained nanowires, implying that oxidation of the copper nanowire with HAuCl₄.

The occurrence of galvanic replacement is not unexpected due to the more noble nature of gold compared to copper. One possible solution is to reduce the reduction potential of Au³⁺ by lowering its activity on the basis of the Nernst equation (Eq. 1):

\[
E_{\text{red}} = E_{\text{red}}^\ominus + \frac{RT}{zF} \ln \left( \frac{a_{\text{Au}^{3+}}}{a_{\text{Au}}} \right) 
\]  

(1)

where \(E\) stands for the electrode potential, \(R\) for the gas constant, \(T\) for the absolute temperature, \(z\) for the charge exchanged per particle during the course of the reduction, \(F\) for the Faraday’s constant, and \(a_{\text{Au}^{3+}}\) and \(a_{\text{Au}}\) for the activities of the oxidized Au³⁺ and reduced gold species. Given that the activity of pure substances in condensed phases is usually taken as unity (\(a_{\text{Au}} = 1\)), the reduction potential therefore depends solely on the activity of Au³⁺ at a given temperature. The activity of Au³⁺ can be tuned through the process of complexation with a ligand (\(L\)) with a Lewis base functional group (Eq. 2):

\[
\text{Au}^{3+} + nL \overset{k}{\leftrightarrow} \text{AuL}_n^{3+}
\]  

(2)

A high stability constant of the complex (\(k\)) and a high concentration of the Lewis base (\(a_L\)) will effectively decrease the activity of Au³⁺ (\(a_{\text{Au}^{3+}}\)), and thus its reduction potential. The stability of metal complexes can be qualitatively predicted and explained by hard and soft acids and bases.
Specific to our synthesis, the gold cation acts as a soft Lewis acid, but the co-existing Lewis bases like chloride (Cl\(^-\), from HAuCl\(_4\)) and OAm (C\(_{18}\)H\(_{35}\)NH\(_2\)) are both hard. We therefore reasoned that the introduction of a soft Lewis base such as phosphine would strongly bind to the gold cation and keep its activity and thus the reduction potential low.

![Figure 3.12](image)

**Figure 3.12.** Reduction kinetics studies of gold(III) chloride trihydrate at 140 °C under different ligand environments. UV-Vis absorption spectra and corresponding photographs of reaction solutions recorded at different reaction times (second) after injecting the gold(III) chloride trihydrate pre-dispersed in 1 mL of OAm (a) and TOP (b) into 5 mL of pre-heated OAm.

Given this, we optimized our synthesis using trioctylphosphine (TOP), a common phosphine ligand in colloidal synthesis,\(^{25}\) to replace OAm in dissolving the gold precursor (Fig. 3.9, route 3). It should be mentioned that the injection speed does not matter too much under this condition as revealed by reduction kinetics studies using UV-Vis spectroscopy. When HAuCl\(_4\) was dispersed in OAm, a strong LSPR band emerged within 3 minutes after a quick injection at 140 °C (Fig. 3.12a), reflecting the instant reduction of HAuCl\(_4\) to gold nanoparticles. As a sharp comparison, the adsorption spectrum showed little change even 30 minutes after the one-shot injection of HAuCl\(_4\)/TOP at the same temperature (Fig. 3.12b), and the reaction solution remained colorless. This suggests the reduction kinetics of Au\(^{3+}\) are quite sluggish in the presence of TOP. Since the concentration of newly-reduced gold atoms always stays low due to the retarded reduction rate, it is not necessary to use the time-consuming slow-injection strategy. The UV-Vis spectroscopic study indicates that TOP is capable of changing the reduction kinetics of the Au precursor,
although it was initially intended to modify the reaction thermodynamics by way of reducing the reduction potential of Au\textsuperscript{3+}.

**Figure 3.13.** TEM images with different magnifications (a, b), SEM image (c), HAADF-STEM image (d), and the corresponding EDS mapping images (e–f) of Cu@Au core-shell nanowires. In the EDS maps, red colour represents Au and green colour represents Cu.

Fig. 3.13a depicts the transmission electron microscopy (TEM) image of the products obtained from the optimized synthetic protocol. Nanowires are in high purity with an average diameter of 21 ± 4 nm. In the enlarged TEM image (Fig. 3.13b), the nanowires can be observed intact without any surface pores or voids. We also noticed that Moiré patterns spread over these nanowires, which is an indicator of the superimposition of two different phases with different lattice constants.\textsuperscript{26} The lengths of the nanowires are in the range of 10 to 20 micrometers as shown in the scanning electron microscope (SEM) image (Fig. 3.13c). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) shows a brighter contrast on the edges of the nanowires.
(Fig. 3.13d), suggesting a local enrichment of the heavier gold atoms. The core-shell structural feature is confirmed by EDS mapping (Fig. 3.13e). Whereas copper (green color) is distributed in the central zone of the nanowires, gold (red color) is mainly located in the outer region. The gold shell thickness is measured to be about 2 nm in average.

![Image of nanowires with copper and gold distribution](image)

**Figure 3.14.** The compositional line profiles of Cu and Au across three aligned nanowires.

The compositional line profiles of copper and gold across three aligned nanowires present an alternating pattern (Fig. 3.14), also suggesting the core-shell distribution of the two elements. The bulk composition of the core-shell nanowires is determined to be Cu$_{86}$Au$_{14}$ via quantitative analysis of the EDS spectra. The gold content in the products is slightly lower than the feeding ratio of the metal precursors (Cu:Au = 5:1). This could be attributed to the incomplete consumption of Au precursor due to its sluggish reduction rate in the presence of TOP.
Figure 3.15. TEM images at different magnifications of the nanotubes produced by acid corrosion of Cu@Au core-shell nanowires.

To demonstrate the global uniformity of the gold shell on copper, we selectively removed the copper phase in the core-shell nanowires by acetic acid corrosion. Fig. 3.15 shows TEM images of the corroded Cu@Au. High-quality nanotubes were generated after acid treatment. The uninterrupted shell of the nanotubes suggests the conformal, uniform, and complete coating of gold on the surface of copper nanowires. The successful preparation of Cu@Au core-shell nanowires demonstrates the aforementioned reasoning: the employment of soft Lewis base in the synthesis does redirect the growth pathway from galvanic replacement to surface deposition.
Figure 3.16. HAADF-STEM images of Cu@Au core-shell nanowires synthesized with Cu: Au feedings of 5:1 (a), 10:1 (b), 20:1 (c). Corresponding atomic resolution STEM images (d–f). Whereas the lattice distance in the core area is measured to be 0.21 nm, it is 0.23 nm in the shell area, agreeing well with the Cu(111) and Au(111) lattice spacings, respectively.

The thickness of the gold shell can be regulated with atomic precision by controlling the amount of gold precursor added into the reaction solution. As shown in Fig. 3.16a–c, the shell thickness could be changed from ~2 nm to ~1.5 nm and ~1 nm by altering the Cu: Au feeding ratio from 5:1 to 10:1 and 20:1, respectively. The core-shell nanowires are accordingly termed as Cu@Au (2 nm Au), Cu@Au (1.5 nm), and Cu@Au (1 nm Au). Atomic resolution HAADF-STEM images (Fig. 3.16 d–f) reveal the shells containing different numbers of gold atomic layers, approximately corresponding to 11, 7, and 4 layers, respectively. From the high-resolution STEM images, we also notice that the surface of the nanowires is quite smooth without the presence of cuprous oxide layers which are regularly observed in pure copper nanostructures. The uninterrupted lattice fringes from the core to the shell manifest the epitaxial growth of gold on copper. This is critical for the electrical properties and the stability of the nanowires because the number of interface defects are minimized in this manner. The distances between the adjacent lattice fringes in the
cores are measured to be 0.21 nm for all the three samples, in good agreement with the lattice spacing of the Cu(111) plane, while the distances in the shell areas expand to 0.23 nm.

Figure 3.17. SEM images of transparent conducting films that are made on thin glass slides with different nanowire loadings.

![SEM images of transparent conducting films](image)

Figure 3.18. Transmittance spectra of transparent conducting films made from Cu@Au core-shell nanowires.

3.4 Optical and Electrical Performance of the Cu@Au Core-Shell Nanowire Electrodes

Transparent conducting films were made on thin glass slides using vacuum filtration method. As shown in Figure 3.17, the nanowires are evenly distributed throughout the film with no obvious aggregation. The UV-Vis absorption spectra of the core-shell nanowire mesh made from Cu@Au (1 nm Au) and Cu@Au (2 nm Au) are given in Figure 3.18. Overall, the films are highly transparent in a large wavelength window, from 350 nm to 1700 nm. Both cases of the core-shell films have the copper signature d-band transition dip at around 550 nm.\(^\text{16}\) However, a notable
flattening of the copper feature was observed for the thicker shell conductors due to the increased content of gold.

Figure 3.19. Plots of (a) transmittance vs sheet resistance and (b) haze factor vs total transmittance of transparent conductors made from bare copper nanowires, Cu@Au (1 nm Au) and Cu@Au (2 nm Au). Background substrate transmittance has been subtracted from all the data. Characteristic transmittance and haze factors are acquired at 550 nm of wavelength. Inset in (a) shows the optical image of Cu@Au (2 nm) nanowire film.

Figure 3.19 summarizes the optical and electrical performance of the Cu@Au core-shell nanowire electrodes, which exhibit excellent figures of merit in transparency, conductivity and haze. Figure 3.19a plots the transmittance versus sheet resistance relationship of three types of nanowire mesh films: bare Cu, Cu@Au (1 nm Au) and Cu@Au (2 nm Au). Even though the electrical conductivity of bulk gold is 30% lower than that of copper, the Cu@Au core-shell nanowires exhibit almost identical transparency-resistivity performance to bare Cu nanowires. No obvious degradation of electrical conductivity was observed after gold overgrowth due to the ultrathin nature of the shell
layer. However, we do see a slight decrease in the conductivity in denser films. This is because when more material is applied, the contribution of bulk metal’s intrinsic conductivity cannot be ignored. The inset of Figure 3a is the optical image of the Cu@Au nanowire film. The background pattern is seen in excellent clarity.

Figure 3.20. Simulated transmittance versus the sheet resistance (a) and simulated haze versus transmittance (b) of simplified nanowire structures: Cu (d = 17 nm), Cu@Au (d= 19 nm with 1 nm Au shell), and Cu@Au (d = 21 nm with 2 nm Au shell).

We also calculated the electrical and optical properties of the Cu@Au nanowires using the semi-empirical models (see Appendix B) developed previously for Ag and Cu@r-GO core-shell nanowires. The calculated transmission versus sheet resistance is shown in Figure 3.20a. This simulation agrees well with experimental data. The decrease in conductivity is most likely introduced by the more resistive gold shell and its contact.

Another important figure of merit of transparent conductors is their light-scattering effect, which is quantified in haze factor. Figure 3.19b presents the haze factor of the three types of films as a function of their total transmittance. In general, the haze factors of all three conductors decrease linearly with total transmittance. The small values of haze factors of the core-shell nanowire electrodes indicate that the light-scattering is minimized by their ultrathin dimension. When the total transmittance is at 91.5% for the 2 nm gold shell nanowire mesh, the haze factor is only 1.85%; this value is even smaller for the 1 nm gold shell nanowire mesh, which is 1.56% at the
same total transmittance. Interestingly, the core-shell nanowire network exhibits the same level of, or even slightly lower, haze values compared to the bare copper electrodes. This result is counter intuitive because larger haze factor is expected with the increase in the mean diameter.\textsuperscript{27} The reduced haze and scattering could result from the differences in the optical properties of the two metals, as suggested by finite-difference time-domain (FDTD) simulations.\textsuperscript{28} Our semi-empirical simulations show very close haze values between the Cu and the Cu@Au core-shell nanowires (Figure 3.20b), supporting that the ultrathin gold shells (< 2 nm) hardly sacrifice the optical properties of the parental Cu nanowires.

**Figure 3.21.** (a) Stability of Cu@Au (2 nm Au) core-shell nanowire mesh films in high humidity and high temperature environment (temperature = 80 °C, humidity = 80 ± 5 %). Different colored labels represent films with different wire loading amounts. (b) Stability comparison of nanowire transparent electrodes made from bare Cu, Cu@Ag (with a composition of Cu\textsubscript{90}Ag\textsubscript{10}), Cu@r-GO, Cu@Au (1 nm Au), and Cu@Au (2 nm Au).

Finally, we tested the core-shell nanowire conductors’ ability to sustain their original conductivity and showed that the electrodes exhibit spectacular resistance towards degradation. The standard harsh condition (80 °C, 80 ± 5% humidity in air atmosphere) was used to evaluate the nanowires’
stability towards oxygen, moisture and heat. The results are shown in Figure 3.21a. Seven individual Cu@Au (2 nm Au) films with different wire loadings were placed under heated, high-humidity environment and their conductivity was traced with time. Impressively, throughout the 712 hours of testing, the films maintained almost the same level of conductivity independent of the initial loading amount.

Figure 3.22. EDS mapping of Cu@Ag nanowires. Scale bar: 40 nm.

Figure 3.21b compares the harsh-environment aging behavior of the conducting films made from nanowires with different composition. Not surprisingly, the unprotected copper nanowire has the worst stability. After one hour of exposure, the sheet resistance increased more than four-fold. After three hours, no conductivity could be measured in the copper nanowire mesh. Cu@Ag core-shell nanowires (Figure 3.22) appear to be more durable than bare copper, but still show considerable decay in conductivity. After 48 hours of exposure to the harsh environment, the resistivity increased almost six times. Our previously reported Cu@r-GO nanowire electrodes exhibit significant enhancement in stability. After degradation treatment for 48 hours, the sheet resistance only increased by 40 percent. The Cu@Au nanowires reported here are undoubtedly the most stable. After being exposed to high temperature and high humidity environment for 48 hours, when most copper-based nanowire electrodes lose conductivity, gold-protected nanowires show no sign of degradation. The thicker the gold shell is, the more enduring the film can be. In the case of Cu@Au nanowire with 2 nm of Au shell, the sheet resistance increased by 24 percent throughout the 712 hours of testing. The remarkable stability of Cu@Au core-shell nanowires can be mainly accredited to the epitaxial growth of gold shell. This synthesis provides a route to uniform and complete coverage of gold on the copper surface. Moreover, the epitaxial nucleation affords a thin, single-crystalline gold shell, which leaves few sites for oxygen or water to oxidize the interior copper atoms.
To investigate the aging mechanism of Au@Cu core-shell nanowires under harsh conditions, ambient pressure X-ray photoelectron spectroscopy (AP-XPS) experiments were performed at Beamline 9.3.2 of the Advanced Light Source by introducing 185 mTorr H$_2$O and 65 mTorr O$_2$ into the UHV chamber. The ratio was chosen to reflect a similar ratio of water to oxygen as is present in 80% humidity, the condition of the harsh stability test applied to these nanowires. The temperature of the sample was first raised to 80 °C, followed by heating to 100 and 120 °C. At each temperature, the sample was allowed to equilibrate until consecutive spectra looked identical. For Cu@Au (1 nm Au) nanowires, an increase in Cu:Au ratio at their surface was observed after increasing the temperature to 80 °C in the humidified oxygen atmosphere of the chamber (Figure 3.23a). Increasing the temperature to 100 or 120 °C brought about a slight further increase in the amount of copper at the surface of the Cu@Au (1 nm Au) sample. The increase in copper concentration at the surface of this sample is attributed to the more oxophilic nature of copper than gold. The thin layer of gold does not shield the copper atoms well enough from the O$_2$ and H$_2$O molecules, and the increased thermal energy allows for the highly mobile Cu atoms to diffuse to the nanowire surface. An identical experiment was performed on the Cu@Au (2 nm Au) nanowires (Figure 3.23b). Up to 120 °C in the H$_2$O/O$_2$ atmosphere, no increase in copper concentration at the nanowire surface was observed indicating the improved stability of the Cu@Au (2 nm Au) core-shell nanowire due to a slightly thicker gold shell protecting the copper from oxidizing molecules on the surface.

3.5 Summary

In summary, to enhance the stability of the copper nanowire electrodes, we have developed two solution-based methods to grow a thin layer of protective shell outside of copper nanowires.

In the first case, we have demonstrated a solution-based approach to wrap GO nanosheets on the surface of ultrathin copper nanowires. By mild thermal annealing, GO can be reduced and high
quality Cu r-GO core-shell NWs can be obtained. High performance transparent conducting films were fabricated with these ultrathin core-shell nanowires; excellent optical and electric performance was achieved. The core-shell NW enables highly stable conducting films, which have comparable performance to ITO and silver NW thin films. This work demonstrates a new approach to improve and stabilize ultrathin metal nanowires, and takes one step further towards the commercialization of copper nanowires as a low cost transparent conductor for optoelectronic devices.

In the second case, in order to achieve super durable Cu-based transparent conductors resistant to a harsh environment, ultrathin Cu@Au core-shell nanowires have been prepared through seeded overgrowth. The introduction of a phosphine ligand is believed to reduce both the reduction potential and the reduction rate of the gold precursor, shifting the growth mechanism into a galvanic-replacement-free pathway that is compatible with rapid injection. This versatile synthesis is capable of producing core-shell nanowires with tunable shell thickness to atomic precision, complete and conformal coverage, and nearly perfect interface rendered by the epitaxial growth of the single-crystalline gold shell. These features have produced enormous benefits to the optical and electrical properties as well as the stability of transparent conductive films. Compared to the original high-performance ultrathin Cu nanowires, transparent films fabricated from Cu@Au core-shell nanowires show comparable figures of merit in transparency, conductivity and haze. Furthermore, these thin films exhibited unprecedented stability under long-term exposure to heat, humidity and air, far surpassing other Cu-based core-shell nanowires. Our results highlight the significance of precise structure control over the protective shell materials in promoting the applications of Cu nanowires in transparent conductors, particularly under harsh conditions.

### 3.6 References

Chapter IV

Ultrathin Five-twinned Copper Nanowires for CO₂ Electrochemical Reduction

Much of the content of this chapter was originally written by the author for the following publications (* denotes equal contributions): Li, Y. F. *; Cui, F. *; Ross, M. B.; Kim, D.; Sun, Y.; Yang, P. D. “Structure-Sensitive CO₂ Electrocatalysis to Hydrocarbons on Ultrathin 5-Fold Twinned Copper Nanowires”, Nano Lett. 2017, 17, 1312. Reprinted and adapted from the above publications with permission. Copyright 2014, American Chemical Society.

4.1 Introduction to Copper-Catalysed CO₂ Electrochemical Reduction

Electrocatalytic CO₂ conversion to value-added products is an attractive means for mitigating the unsustainable rise in anthropogenic CO₂ emissions. Coupled with renewably-generated electricity, a CO₂ electrolyzer provides simultaneous carbon fixation and renewable energy storage.¹⁻³ Many catalytic studies in recent years have refined the electrocatalytic conversion of CO₂ to CO, increasing its commercial viability by reducing overpotential and increasing current density.⁴⁻⁹ However, an efficient electrocatalyst for the conversion of CO₂ to higher order products beyond CO has yet to be developed. Though several metals and metal alloys are known to produce small quantities of higher order products at high overpotentials,¹⁰ only copper has been shown to do so with appreciable activity.¹¹ Controlling product selectivity, meanwhile, remains a challenge using a copper foil catalyst.¹² Comparisons between the same copper foil under various chemical treatments, creating different nanostructures, resulted in remarkable differences in product selectivity.¹³ Therefore, understanding how to manipulate selectivity on the copper surface via surface structure is critical for the development of new selective catalysts.

Nanoscale catalysts present considerable advantages compared to their bulk counterparts, including higher surface areas and a high density of low-coordination, high-activity catalytic sites. Indeed, nanostructuring has been shown to improve activity for a variety of catalytic materials, primarily by improving turnover (i.e. partial current density towards products) and/or selectivity at lower overpotentials.⁵,⁶,⁸,¹⁴ Typically, nanostructured catalyst films are produced through chemical and electrochemical treatments of copper foil, resulting in drastically improved selectivity and activity for high-value products like ethylene.¹⁵⁻¹⁹ However, the mechanism and origin for the improved activity is poorly understood, requiring a platform with precise control over size, shape, and composition. Colloidal nanomaterial synthesis provides a means to synthesize such well-defined electrocatalysts, but has only recently been explored for studying CO₂ electrocatalysis. For example, several recent works have conducted investigations into electrocatalytic CO₂ reduction on various colloidal Cu nanomaterials.²⁰⁻²⁴

One-dimensional nanowires (NWs) are an especially intriguing class of nanostructure for CO₂ electrocatalysis. Previous work on CO₂ reduction on Cu NWs have shown improved performance on wires with diameters ranging from 100 nm to several microns.²⁵⁻²⁷ However, the catalytic activity of ultrathin Cu NWs, with well-defined twin boundary edges, has yet to be investigated.
The presence of low-coordination edge sites on an ultrathin nanowire presents a catalytic surface with potential for high activity and unique selectivity, due to the difference in intermediate binding on low-coordination sites. Zhu et al have previously shown markedly higher CO selectivity on ultrathin Au NWs, which they attribute by DFT calculations to enhanced intermediate binding on edge sites. In addition, the presence of grain boundaries in copper nanoparticles have been shown to directly promote CO electroreduction to multi-carbon products. Thus, studying the catalytic influence of the ultrathin NW morphology using ultrathin Cu NWs is highly relevant to CO₂ electroreduction.

Another point of interest for the nanowire geometry is its ability to be modified by graphene oxide wrapping. Previous work on copper nanoparticles has shown a tendency for particles to sinter at high bias, potentially as a result of electrochemical migration or copper dissolution and redeposition. We have recently demonstrated that ultrathin Cu NWs can be wrapped with a thin reduced graphene oxide (rGO) shell to enhance their structural stability. The wrapped Cu NW system provides an intriguing platform for studying the catalytic effects of morphological change and its prevention. Therefore, we set out to investigate how well-faceted Cu NW surfaces change over electrolysis and whether the electrocatalytic activity changes in conjunction. Subsequently, we wished to study whether rGO-wrapping could preserve the Cu NW morphology under electrolytic conditions, and whether such a strategy simultaneously preserves electrocatalytic properties hypothesized to be morphology-dependent.
4.2 Five-Twinned Copper Nanowires for CO₂ Electrochemical Reduction

Figure 4.1 Synthesis of five-fold twinned copper nanowires. (a) TEM image of bare wires, around 20 nm in diameter, before loading. Inset: illustration of the five-fold twinned structure, showing a high proportion of low-coordination edge sites (dark red) brought about by five-fold twin boundaries. (b) TEM micrograph of Cu NWs loaded on carbon black with 20 wt% loading. (c) SEM micrograph of the CuNW/CB catalyst dispersed on a glassy carbon surface, used as the electrode for electrochemical experiments.

Figure 4.1a shows a transmission electron microscope (TEM) micrograph of the as-synthesized bare Cu NWs, which have a diameter of approximately 20 nm. The five-fold-twinned structure of the NWs with well-defined edges is illustrated in the inset. To test their catalytic behavior toward CO₂ reduction, freshly made Cu NWs were loaded onto carbon black (CB) to make a 20 wt% CuNW/CB catalyst suspension in hexanes, as confirmed by TEM (Fig. 4.1b). This suspension was pasted onto glassy carbon plates to make a working electrode, which scanning electron microscopy (SEM) revealed to be a conductive mesh of Cu wires and carbon black (Fig. 4.1c).
Figure 4.2 Comparison of Cu NW catalysts directly dropcast on a glassy carbon electrode before and after 1 C electrolysis at -1.2 V vs. RHE. In addition to a visible loss of catalyst material after electrolysis, the direct loading of Cu NWs results in significant bundling of wires.
Figure 4.3 Comparison of Cu NW catalysts with carbon black loading on a glassy carbon electrode before and after 1 C electrolysis at -1.2 V vs. RHE. Dispersion with carbon black is observed to improve both catalyst adhesion and wire separation.

Direct loading of the Cu NW catalyst onto the glassy carbon substrate was also explored. It was found that while the catalytic activities between the CuNW/GC and CuNW/CB/GC electrodes were comparable, the latter formulation was more mechanically stable. Without carbon black, the Cu NWs visibly disappear from the electrode after 1 C of electrolysis (Fig. 4.2, 4.3).

Thereafter, the CuNW/CB catalyst was tested over a range of potentials for catalytic activity, which showed a marked selectivity for methane at potentials more negative than -1.1 V vs. RHE (Fig. 4.4a). Faradaic efficiencies (F.E.s) for methane at the potentials tested reached a maximum of 55% at -1.25 V vs. RHE. Notably, while polycrystalline copper has frequently been reported to produce a spread of C1 and C2 products at potentials below -1 V vs. RHE, the CuNW catalyst produces nearly exclusively methane among the carbon-derived products. In fact, in the potential region tested spanning 600 mV, neither carbon monoxide (CO) nor ethylene (C2H4) exceed 5% of all products, while formate is only substantially produced at potentials more positive than -1 V vs. RHE. Total F.E.s consistently reached 90-100% at potentials where methane was produced selectively (Fig. 4.4b), suggesting the successful detection of all major products at methane-selective potentials.

Figure 4.4 Cu NW initial electrocatalytic activity and selectivity. (a) Products of CO2 reduction, showing the prevalence of CH4 at high bias over other products (CO, C2H4, formate, and ethanol). Acetate, methanol, and n-propanol were detected in trace. (b) Total F.E. of CO2RR and the competing reaction, hydrogen
evolution (HER). (c) Partial current density towards methane of the Cu NW catalyst compared with a cleaned polycrystalline copper foil, showing the increased activity at more negative potential. (d) Total geometric current density over the range of potentials, compared to background current from the glassy carbon substrate with bare carbon black loaded. Initial activity electrocatalytic tests were conducted over the potential range of -0.85 to -1.35 V vs. RHE in 0.1 M KHCO₃ over 1 C of passed charge.

To more aptly gauge the activity of the catalyst towards methane, the partial current density towards methane ($j_{CH4}$) was also calculated and compared with a reference polycrystalline Cu foil. The corresponding measured $j_{CH4}$ values for the Cu foil are within range of previous results.²⁰,³¹ Although $j_{CH4}$ for the two catalysts is comparable at lower overpotentials, the CuNW-loaded electrode achieves partial current to methane double that of Cu foil past -1.2 V vs. RHE (Fig. 4.4c). The background current contributed by the same mass of carbon black on glassy carbon was minimal even at the most negative potentials applied (Fig. 4.4d), confirming that the measured $j_{CH4}$ is due to the Cu NW catalyst.

4.3 Cu@GO Core-Shell Structure as a Durable Catalyst

![Figure 4.5.](image)

**Figure 4.5.** Electrocatalytic and morphological evolution of the Cu NW catalyst. (a) Rapid onset of C₂H₄ formation with a concurrent decrease in CH₄ activity after the first Coulomb of electrolysis. (b) Representative Cu NWs imaged under TEM after a given amount of charge passed, showing visible fracturing and the formation of small Cu NPs. (c), (d) Analogous electrocatalytic and morphological characterization for the rGO-Cu NW catalyst, showing preservation of selectivity as well as morphology.
Electrocatalytic activity was also measured with varying amounts of passed charge before product measurement. Strikingly, the selectivity of the catalyst was observed to change with increasing charge passed at -1.25 V vs. RHE (Fig. 4.5a). Coulomb-by-Coulomb analysis of the activity evolution shows that the hydrocarbon selectivity shifts from almost entirely CH4 to higher production of C2H4 over the course of 5 C passed. Other products (such as CO, H2, and liquid products) were not observed to change substantially over this period. The shift in selectivity appears shortly after the first Coulomb passed. This change in activity suggests that the catalyst is rapidly evolving at potentials relevant to hydrocarbon formation. TEM confirms that the morphological of the catalyst changes as a function of charge passed during electrolysis. For example, figure 3b shows that after 1 C, the wire morphology begins to degrade, resulting in particle formation, wire bundling, disintegration, and fracturing.

To investigate whether the structure of a wire could be preserved, thereby also preserving the CO2 electrocatalytic selectivity for methane, we studied the electrocatalytic properties of rGO-wrapped copper nanowires. Wrapped Cu NWs were loaded on carbon black and glassy carbon under identical loading conditions to the bare Cu NWs and tested for CO2 electrocatalytic activity. Figure 4.5 c shows analogous electrocatalytic and TEM results to Figure 3a-b using the rGO-wrapped CuNWs/CB catalyst. In contrast with the bare wires, rGO-wrapped wires preserve their selectivity for methane over ethylene for up to 5 C passed. Simultaneously, the wires show no morphological evolution under TEM. Typical single wires were selected for Figure 3b and 3d to highlight the morphological difference between rGO-CuNWs and bare CuNWs under bias.
**Figure 4.6.** Evidence for the protective role of reduced graphene oxide. (a) From bottom to top, Raman spectra of bare CuNWs, GO-wrapped CuNWs before electrolysis, and rGO-wrapped CuNWs after electrolysis. The D and G peaks attributable to graphene oxide are indicated, showing its presence and retention after 5 C electrolysis. (b) CH$_4$ and C$_2$H$_4$ selectivity at 5 C on Cu NWs wrapped with varying amounts of GO used in preparation, showing preservation of CH$_4$ selectivity with increasing rGO wrapping. (c) EDS mapping showing the increasing presence of carbon species attributed to graphene oxide surrounding the wires as the amount of GO used in preparation of the catalyst is increased. (d) Scheme for the correlation between morphology and selectivity observed in this study. C$_2$H$_4$ onset is thought to be due to the transformation of NW edge sites to small NPs deposited on the surface (left), which rGO wrapping prevents (right).

To verify the presence of rGO on the surface of the catalyst, we conducted Raman spectroscopy on the rGO-CuNW catalyst pre- and post-electrolysis. Both before and after 5 C of electrolysis, Raman spectra of the rGO-CuNW exhibit the characteristic D and G bands of GO or rGO (Fig. 4.6a). For comparison, a Raman spectrum of the unwrapped wires is shown, which exhibits no peaks attributed to rGO. Wrapped Cu NWs with varying amounts of rGO were then used as electrodes for CO$_2$ electroreduction to probe whether increasing rGO wrapping better preserves electrocatalytic selectivity. Figure 4.6b shows that increasing the amount of rGO wrapping on the wires increasingly preserves high methane selectivity over ethylene over 5 C of electrolysis. Energy dispersive X-ray spectroscopic (EDS) mapping of carbon further verifies the presence of rGO on the surface of the Cu NWs, and that increasing the mass ratio of GO to copper used in the preparation qualitatively increases the amount of rGO wrapping in the final catalyst (Fig 4.6b).

Taken together, these data suggest that nanowire-specific structural features, such as edge sites, are responsible for stabilizing intermediates that lead to improved methane selectivity in CO$_2$ electroreduction. The five twin boundaries on the ultrathin Cu NW present a unique active site for stabilizing CO$_2$ intermediates, which previous DFT studies have suggested enhance methane formation. As the wires evolve under bias, the well-defined twin boundaries degrade, while Cu nanoparticles simultaneously nucleate on the NW surface and create a variety of ill-defined active sites. The shift in selectivity from methane to ethylene shown here is approximately 10% F.E., such that the final ethylene selectivity at -1.25 V vs. RHE is comparable to previous reports of ethylene selectivity for polycrystalline copper foil. However, it is difficult to identify the active site of the evolved catalyst, as it consists of a diverse array of roughened wires, small particles, and likely some remaining twin boundaries, all of which exhibiting distinct catalytic selectivity. The tunability of electrocatalytic selectivity with amount of rGO directly supports the role of rGO in preserving structure and selectivity. Figure 4.6d summarizes the effects of changing and preserving morphology on electrocatalytic selectivity: copper nanoparticle formation and edge loss shifts the morphology from high-density methane-selective sites to a mix of methane-selective and mixed-selectivity sites. Introducing rGO as a wrapping layer impedes nanoscale structural change and prevents the loss of methane-selective sites.

### 4.4 Conclusions

In this chapter, we have shown that one-dimensional ultrathin five-fold twinned copper nanowires exhibit high methane selectivity for CO$_2$ electrocatalysis relative to other carbon products. The origin of the methane selectivity is likely due to the presence of a high density of edge sites owing to the twin boundaries. Furthermore, the morphology of these wires and their electrocatalytic
selectivity evolve, losing methane selectivity in favor of ethylene formation. We posit that the change in electrocatalytic selectivity is due to the change in morphology, a claim directly supported by the observation that rGO wrapping simultaneously preserves morphology and methane selectivity over the same electrocatalytic conditions. This study highlights the importance of manipulating nanostructural transformations of copper electrocatalysts under conditions relevant to CO₂ electroreduction, a topic that merits in-depth future study. Moreover, it demonstrates the employment of rGO wrapping as a strategy for electrocatalyst stabilization, a method that may be explored for other catalysts in which morphological change is evident.

4.5 References

Chapter V

Low-temperature Synthesis of Si and III-V Nanowires in Solution via Solid-Liquid-Solid Method


5.1 Introduction to Si Nanowire Synthesis

Silicon (Si) is the most important semiconductor in microelectronics industry. Continuous device miniaturization has led to the emergence of the nanoelectronics industry, in which Si nanowires (NWs) can play an essential role. For example, proof-of-principle Si-NW based electronic nanodevices have been demonstrated. The photovoltaics industry, crystalline Si modules are the most frequently used and heavily studied material. Device physics modeling has suggested that radial p-n junction NW photovoltaic devices can potentially achieve higher efficiency relative to the conventional planar devices because the unique one-dimensional structure allows both good light absorption and efficient charge carrier collection. This device concept has been demonstrated at both a single NW level and oriented NW array level. In addition, Si NW array-based energy conversion devices such as solar water splitting cells and lithium ion batteries have also been reported recently.

To date, the Si NW-based devices have been predominantly fabricated by either top-down methods using single-crystalline Si wafers or bottom-up methods using metal nanoparticles (NPs) and molecular Si precursors via a vapor-liquid-solid (VLS) mechanism. Compared to the top-down methods, the bottom-up methods offer greater flexibility in controlling NW properties, but generally require high growth temperatures even for the metals that can form eutectic phase at low temperature with Si. To achieve low-temperature (< 400 °C) VLS growth of Si NWs, the Si precursors must be activated (or dissociated) first. This can be achieved by means of in situ H2 plasma treatment, which has resulted in the growth of Si NWs at temperatures as low as 240 °C. Semiconductor NWs growth can also be achieved in solution via a solution-liquid-solid (SLS) mechanism using metal NPs with low melting point. Compared to the VLS method, the SLS method has the advantage of surface passivation, ease of implementation, and large-scale production. As such, the SLS approach is potentially promising for cost-effective solution-processable fabrication of NW-based devices. Recently, metal NP-mediated SLS growth of Si NWs or nanorods has been reported. However, the growth temperatures remained to be higher than 410 °C because the precursor activation method employed in the VLS growth cannot be directly adopted in the solution-phase synthesis. Very recently, it was reported that short Si nanorods (<50 nm in length) could be grown by a Sn-seeded SLS method using cyclohexasilane...
as the Si precursor at temperatures as low as 200 °C. In general, it remains a big challenge in the SLS chemistry to achieve Si NW growth at low temperatures.

5.2 Low-Temperature Synthesis of Si Nanowires

In this section, I will show that both tris(trimethylsilyl)silane [(TMS)₃SiH], which is widely used as a radical-based reducing agent in organic synthesis, and trisilane can be used as the Si precursor for Ga-catalyzed SLS growth of colloidal Si NWs at temperatures of about 200 °C, which is more than 200 °C lower than the previously reported SLS growth temperatures and also lower than that achieved in the VLS growth. Ga was chosen as our SLS catalyst for two reasons. First, the Ga-Si system has a very low eutectic temperature of 30 °C, which is ideal for low-temperature growth of Si NWs. Second, Ga NPs are readily accessible through thermal decomposition of organometallic Ga precursors. Our synthesis was conducted in a non-coordinating saturated hydrocarbon solvent such as hexadecane and squalane. No surfactants were added. In a typical synthesis, a mixed precursor solution containing 0.15 mmol of triethylgallium (TEG) and 1 mmol of (TMS)₃SiH in 2 g of hexadecane was quickly injected into a preheated hexadecane (15 g) under vigorous magnetic stirring at a certain temperature in the range of 200-300 °C. The reaction mixture remained clear for a short period of time and then turned to yellowish, indicting formation of Ga NPs. After this, the solution gradually changed to dark brown, indicating NW growth.

Figure 5.1. (a) TEM image of an as-grown sample synthesized using triethylgallium and tris(trimethylsilyl)silane precursors in hexadecane at 274 °C, showing nanowires with attached nanoparticles at one end. (b) EDS spectra collected from the nanoparticle (top panel, in blue) and the
nanowire (bottom panel, in red). The Cu and C signals are from the Cu TEM grids with C support. The Al signals are from the Al sample holder. (c) HRTEM image of a single nanowire.

Transmission electron microscopy (TEM) image of an as-grown sample prepared at 274 °C shows NWs with attached NPs at one end (Fig. 5.1a). We note that some NPs are detached from the wires, which is likely due to the ultrasonication step in the NW purification process for preparing TEM samples. Energy-dispersive X-ray spectra (EDS) collected from the NP and the NW show Ga and Si signals, respectively, confirming the Ga-catalyzed SLS growth of Si NWs (Fig. 5.1b). No Si was detected in the NP, which is consistent with the very low solubility of Si in Ga. The weak oxygen peaks in the EDS spectra suggest that both the Ga NPs and the Si NWs are surface oxidized. The expected diamond cubic crystal structure of the Si NWs was confirmed by powder X-ray diffraction. High-resolution TEM (HRTEM) image of a single NW (Fig. 5.1c) shows the single-crystalline nature of the wires. The spacing of the well-resolved lattice fringes perpendicular to the NW growth direction was measured to be 0.315 nm, which is consistent with the \( d \) spacing of the (111) planes in cubic Si and indicates the \(<111>\) wire growth direction. The amorphous layer on the nanowire surface is composed of oxidized silicon and surface adsorbed organic molecules.

![TEM image of Ga-catalyzed Si nanowires synthesized using triethylgallium and tris(trimethylsilyl)silane precursors in hexadecane at 210 °C.](image)

**Figure 5.2.** TEM image of Ga-catalyzed Si nanowires synthesized using triethylgallium and tris(trimethylsilyl)silane precursors in hexadecane at 210 °C.

To find out the lower limit for the NW growth, we further decreased the reaction temperature. Interestingly, we observed NW growth at a temperature as low as 210 °C. Figure 5.2 shows the Si products grown at 210 °C. Nanowires can still be synthesized at this low temperature, but with a much lower yield.
Figure 5.3. Proposed free-radical involved solution-liquid-solid (SLS) growth of colloidal Si nanowires using triethylgallium and tris(trimethylsilyl)silane as the precursors at low temperatures.

To understand the dramatic growth temperature decrease of Ga-catalyzed Si NWs, a control experiment was conducted in the absence of TEG but showed no silicon nanowire growth, indicating that TEG plays a critical role in catalyzing the reaction. The role of TEG in this can be twofold. Firstly, thermal decomposition of TEG produces nano-scale gallium metal particles in the solution, which were observed in the TEM study. As proposed in many SLS mechanism studies\(^{10,15}\), melted metal droplets can provide ideal surfaces, lowering the energy barrier for precursor absorption and decomposition. This could be the main reason that accounts for the sharply decreased reaction temperature. Secondly, it’s well known that thermal decomposition of TEG not only produces Ga metal but also releases ethyl radicals.\(^{17}\) The active radical species could help break Si-Si or Si-H bond in the precursor as analogous to Si precursor activation pathway using H\(_2\) plasma treatment for the low-temperature gas-phase Si NWs growth. Particularly in the case of using (TMS)\(_3\)SiH as the Si source, alkyl radical can react with (TMS)\(_3\)SiH to generate (TMS)\(_3\)Si radicals. We believe that (TMS)\(_3\)Si radicals serve as the active species for silicon growth and ethyl free radical accelerated the production of silyl radicals.\(^{18,19}\) The scheme of the reaction is proposed in Fig. 5.3. Other control experiments in replacement of (TMS)\(_3\)SiH with organosilanes that have similar molecular structures but are more difficult to form free radicals, including [(TMS)\(_3\)SiCl] and tetrakis(trimethylsilyl)silane [(TMS)\(_4\)Si] failed to grow Si NWs, which further supports our proposed reaction pathway.

5.3 Synthesis and Band Gap Measurements of Si\(_x\)(Gap)\(_y\) Alloyed Nanowires

Recently, Si-containing IV-III-V semiconductor films have been synthesized at high temperatures (~500 °C) by a gas-phase molecular beam epitaxy (MBE) method.\(^{20-22}\) Another work demonstrated that Si can be used as dopants in III-V materials.\(^{23}\) Theoretical calculations have shown that these materials would be promising for solar energy conversion due to significantly enhanced visible-light absorption relative to Si.\(^{24}\) Because of our success in the Si NW growth discussed above, we next investigated the possibility of using (TMS)\(_3\)SiH to incorporate Si atoms into other semiconductor lattices to produce new silicon-containing alloy NWs in a solution phase synthesis at low temperatures. Owing to our previous success in self-seeded SLS growth of GaP NWs,\(^{16}\) we naturally combined the Si and GaP syntheses at the same growth conditions.
Figure 5.4. (a) and (b) Low- and high-magnification TEM images of Ga-removed GaP nanowires synthesized using TEG and (TMS)$_3$P precursors in hexadecane at 278 °C. (c) and (d) Low- and high-magnification TEM images of Ga-removed Si-GaP mixture nanowires synthesized using TEG, (TMS)$_3$P, and (TMS)$_3$SiH precursors in hexadecane at 277 °C. The initial Si:GaP ratio was 1:1. (e) High angle annular dark field (HAADF) image of a single Si-GaP mixture nanowire. The red arrow shows an EELS line scan pathway. (f) The intensity of HAADF, Ga, and Si signals vs. distance along the line scan pathway shown in (e).

Fig 5.4a and b show the low- and high-magnification bright-field TEM images of Ga-removed GaP NWs synthesized using TEG and tris(trimethylsilyl)phosphine [(TMS)$_3$P] precursors in hexadecane at 278 °C. The wires are typically longer than 1 µm and have relatively uniform diameter along the length of the wire. When we introduced increasing amount of (TMS)$_3$SiH into the GaP growth solution, the obtained wires became shorter and more tapered and frequently exhibited diameter expansion at the larger-diameter end (Fig 5.4c and d), indicating that the growth behavior of the new wires is quite different from that of GaP. A high angle annular dark field (HAADF) image of a single wire (Fig 5.4e) exhibits substantial Z-contrast along the growth
direction because of the largely different atomic numbers of Si ($Z = 14$) and Ga ($Z = 31$).\textsuperscript{25} Electron energy loss spectra (EELS) were collected along the wire length from a point near the small-diameter end (corresponding to the initial growth) all the way to the large-diameter end (corresponding to the final growth). They reveal the presence of four distinct growth stages (Fig. 5.4f). During the initial wire growth for ~150 nm, GaP dominated. Then, an increasing amount of Si was incorporated into the wire for a distance of ~200 nm, forming a Si$_x$(GaP)$_y$ region. Si dominated at the third stage. Finally, GaP dominated again, which is likely due to the complete consumption of the in situ generated (TMS)$_3$Si- radicals or the further GaP growth during the cooling process. This inhomogeneous distribution of elements along the length of the nanowire suggested unbalanced reactivities of the molecular precursors during the nanowire growth. Although further efforts are needed to fully understand this complex NW growth behavior, our results have already demonstrated the possibility of incorporating Si into other semiconductor lattices at low temperatures.
An interesting question regarding the Si<sub>x</sub>(GaP)<sub>y</sub> region in the NW is whether the element distributions are atomically homogeneous or not. To address this question, we next used TEAM 0.5 microscope, which is a double-aberration-corrected transmission electron microscope capable of producing images with 50 pm resolution, to acquire an atomically resolved Z-contrast image of the Si<sub>x</sub>(GaP)<sub>y</sub> region in the <110> projection (Fig. 5.5a). This allowed us to identify composition fluctuations locally by detecting the asymmetrical GaP dumbbells and the symmetrical Si dumbbells (Fig 5.5b-d). The image shows that GaP- and Si-rich nanometer-sized domains exist, indicating compositional inhomogeneity in the Si<sub>x</sub>(GaP)<sub>y</sub> region while the crystal structure of each component is maintained. This implies that lattice mismatched growth occurred since the lattice parameters of Si (a = 0.543 nm) differs from the one of GaP (a = 0.545 nm). Interestingly, we frequently observed the transition from the Ga-P dumbbells to the P-Ga dumbbells separated by Si-Si dumbbells, indicating the polarity reversal of GaP across the Si-rich region (Fig. 5.5b), which can significantly alter the properties of the materials.

**Figure 5.5.** (a) Atomically resolved Z-contrast image acquired from the Si<sub>x</sub>(GaP)<sub>y</sub> region in the <110> projection. The asymmetrical GaP and symmetrical Si dumbbells can be seen in this projection. The white box highlights a transition from the Ga-P dumbbell to the P-Ga dumbbell separated by Si-Si dumbbells. (b) Structural model of the polarity reversal of the GaP lattice induced by non-polar Si lattice.

![Figure 5.5](image)

**Figure 5.6.** Bandgap values vs. distance along the line scan through single NW. Inset is the corresponding HAADF image. Scale bar, 100nm.

Based on the clear evidence of nanoscale mixing of GaP and Si, an intriguing tunable property one may expect is the tunable bandgap. Using 80kV monochromated valence EELS (VEELS) measurements by the TEAM 1 microscope, we successfully measured the bandgap change along single NW (Fig 5.6).
Figure 5.7. (a) Zero-loss peak (ZLP) of a monochromated electron beam in TEAM 1 with Schottky field-emission source. The energy spread of a monochromated ZLP was ~100 meV in full-width at half-maximum (FWHM). The energy dispersion was 0.01 eV/\text{ch}. The camera length was 29.5 mm and the entrance aperture of the GIF system was 2.5 mm in diameter. The convergence and collection angles are 26 mrad and 39 mrad, respectively. Low voltage (80 kV) VEELS was applied aiming at improving the energy resolution and decreasing the delocalization of the energy loss, while minimizing the relativistic effects. (b) Demonstration of the ZLP background removal using a power-law subtraction. (c) Bandgap value was obtained by fitting the intensity onset with (E-E_g)^{3/2} type function.

Monochromated VEELS, as shown in Fig. 5.7 provides high spatial resolution while maintaining good energy resolution (~100 meV), offering the opportunity of detecting bandgap changes on tens of nanometer level. For the bandgap measurement, the influence of zero-loss peak was removed using a power-law subtraction\textsuperscript{31,32} and the bandgap values were obtained by fitting the intensity onset with (E-E_g)^{3/2} type function as both GaP and Si are indirect bandgaps.\textsuperscript{29,33,34} As shown in Figure 4, the bandgap values approach to the theoretical 2.3 eV of GaP at the two ends of GaP dominated regions, whereas in the mixture region, the bandgaps tend to decrease to the level of Si (1.1 eV). The probable reason that the edge bandgap only approaches but not equal to 2.3 eV is that the GaP dominated region at the end of the wire is not purely GaP. They still have sparse silicon atoms distributed within the lattice. The fluctuation of some data points may be attributed to the random distribution of GaP- and Si-rich domains in the mixture region, which also confirms our previous conclusion of the compositional inhomogeneity.
To further balance the precursor reactivities in order to achieve homogenous growth of Si-containing alloy nanowires, we replaced (TMS)$_3$SiH with trisilane (Si$_3$H$_8$), which is a highly pyrophoric Si precursor with higher reactivity. Different from the relatively short tapered wires, less-tapered long wires were obtained by using TEG, (TMS)$_3$P, and Si$_3$H$_8$ precursors at a lower temperature of 180 °C (Fig. 5.8). EDS analysis along the length of individual nanowires showed much more homogeneous Si distribution (Fig. 5.9), indicating that the reactivities of the three precursors were better balanced. However, HRTEM images still showed GaP- and Si-rich nanometer-sized domains. Further efforts such as using single-source precursors are necessary to achieve growth of new Si-containing alloy nanowires with atomically homogeneous composition.
5.4 Conclusions

In summary, we have shown that both (TMS)$_3$SiH, a free radical-based reducing agent in organic synthesis, and Si$_3$H$_8$ are sufficiently reactive Si precursors for the Ga-catalyzed SLS growth of colloidal Si NWs at record low temperatures. Unlike Au, which is the most widely used catalyst material for the growth of Si NWs but is known to be deleterious to the electronic properties of Si, Ga is a shallow p-type acceptor and won’t introduce trap sites that serve as the undesired electron-hole recombination centers. Therefore, our low-temperature Ga-catalyzed synthesis holds great promise for cost-effective solution-processable fabrication of Si NW-based devices that would find applications in broad fields such as electronics and energy conversions. In addition, we also demonstrated the possibility of incorporating Si atoms into III-V semiconductor NWs at low temperatures, which could open new avenues for growing novel alloy semiconductor NWs with tunable properties.

5.5 References


Appendix A

Supporting Information for Synthesis of Ultrathin Copper Nanowires Using Heat-Driven Free Radicals and Their Applications in Transparent Conductors

Regents:

Tris(trimethylsilyl)silane (TTMSS, 97%), copper (II) chloride dihydrate (CuCl₂·2H₂O, 99.999%), oleylamine (70%), oleic acid (90%), benzoin (98%), benzaldehyde (99.5%), benzophenone (99%), benzoil (98%), benzoin methyl ether (96%), tetrahydrofuran (THF, anhydrous, ≥99.9%), 1,8-diazabicycloundec-7-ene (DBU, 98%), 4-fluorobenzaldehyde (98%), 4-chlorobenzoin (97%), 4-chlorobenzaldehyde (98%), 4,4’-dimethoxybenzoin (95%), 1,3-Dimethyl-1H-benzimidazolium iodide and nitrocellulose filter membranes (25 mm diameter, 220 nm pore size), were purchased from Sigma-Aldrich and used as received. Unless otherwise stated, all of other chemicals were purchased from Sigma-Aldrich and used as received. 4,4’-dimethylbenzoin (98%) was bought from TCI America and used as received.

Material preparations

Synthesis of copper NWs using TTMSS: In a typical reaction, 85 mg of CuCl₂·2H₂O (0.5 mmol) and 5 g of oleylamine were mixed in a reaction vessel and then sonicated at room temperature to fully dissolve copper precursor. 0.5 g of tris(trimethylsilyl)silane (2 mmol) was added into the solution as reducing regent. The resulting clear blue mixture was heated up to 120 °C until the solution turned into light yellow. Afterwards, the reaction temperature was slowly turned up to and kept at 165 °C for 10 h while stirring. The color of the solution turned reddish brown, indicating formation of copper nanowires. The product was harvested by centrifugation at 6000 rpm for 5 mins. Then, the nanowires were washed repeatedly with toluene using centrifugation-redispersion cycles to remove excess oleylamine. Finally, the product was dispersed in toluene for further characterization and film fabrication.

Synthesis of copper NWs using benzoin: In a typical reaction, 85 mg of CuCl₂·2H₂O (0.5mmol), and 5g of oleylamine were mixed in a reaction vessel. The mixture was sonicated at room temperature until it became a clear blue solution. Then, 0.424g of benzoin was added in the solution. The mixture was then degassed and purged with nitrogen at 70 °C for 30 minutes. And next, the reaction temperature was raised to 120 °C under N₂ atmosphere and kept for around 20 min until the color of the solution reached clear yellow. Next, the temperature was raised to 185 °C and allowed to stay for 3 hours until the reaction is complete. The product was harvested by centrifugation at 8000rpm for 5mins. Then, the NWs were washed with toluene, and then toluene/isopropanol (1:1) three times to remove excess oleylamine and benzoin for further characterizations.
Synthesis of Ag and gold NWs using benzoin: To synthesize silver NWs, 0.15M polyvinylpyrrolidone (PVP, Mw ~ 55,000) and 0.1M AgNO₃ solution in ethylene glycol were prepared in advance. 2mmol of benzoin was dissolved in ethylene glycol and the solution was purged with N₂ to remove oxygen. Then, the benzoin solution was slowly heated up to 130 °C under argon protection. 3 ml of PVP solution and 3 ml of AgNO₃ solution was simultaneously injected in a dropwise fashion. Next, the reactants were left to react for 10 min before ramped up to 140 °C and stayed for an extra hour. The product was harvest by centrifuging and washed 3 times with isopropanol. To synthesize gold NWs, 0.3 mg oleylamine, 22 mg HAuCl₄ and 8.77 mg benzoin were dissolved in 13 g of hexanes under vigorous stirring. After the solution was clear, the mixture was left at room temperature undisturbed for 5 hours. The product was collected by centrifuging and washed 3 times with toluene.

Preparation of benzoin derivatives: 4,4’-Dichlorobenzoin and 4,4’-difluorobenzoin are synthesized using a documented approach. 20mmol 4-chlorobenzaldehyde (or 4-fluorobenzaldehyde), 1 mmol 1,3-dimethylbenzimidazolium and 1 ml of 1,8-diazabicycloundec-7-ene were dispersed in 50 ml of tetrahydrofuran. The mixture was heated up to 66 °C and gently refluxed under N₂ environment for 12 hours. Then the solution was cooled down to room temperature and was concentrated by evaporation of solvent under reduced pressure using rotovap. The residue was purified using column chromatography (chloroform and hexanes as eluent) to remove unreacted precursors and side products. The final product benzoins were extracted from evaporation of solvents and dried in vacuum oven overnight before usage.

Benzoin reactivity tuning: Five types of benzoins were set to compare their reducing power in the copper NW synthesis reaction. These five benzoins list as 4,4’-dimethoxybenzoin, 4,4’-dimethylbenzoin, benzoin, 4,4’-dichlorobenzoin and 4,4’-difluorobenzoin. In each of the five reactions, 0.5 mmol CuCl₂·H₂O (0.5mmol), 2mmol benzoin of one type and 5g of oleylamine were mixed in a reactor. Then the mixture went through the same heating steps as described before and then kept at 175 °C for the same amount of time. Pictures of reaction progress were taken at 1 hour and 2 hours in to the reaction. All reactions were stopped at 3 hours. The products were harvested through centrifuge. No extra washing steps were carried out to preserve the products as much as possible. Then, the collected materials were dispersed in toluene and vacuum filtered on to a nitrocellulose membrane. The copper products on filter membrane were dried in vacuum oven and weighed for yield calculation.

Characterizations and Measurements

Characterizations of NWs: The morphologies of the as-grown copper nanowires were examined using a transmission electron microscope (TEM, Hitachi H7650) and scanning electron microscope (SEM, JOEL JSM - 6340F). The structure of copper nanowires was analyzed using high resolution transmission electron microscopy (HRTEM, FEI Tecnai G20), selected area electron diffraction (SAED) and X-ray diffraction pattern analysis (Bruker D8 Advance). Exit-wave reconstruction was performed using MacTempas software. Sheet resistance of nanowire thin film was measured using a four-point probe method (CDE-RESMAP-270). The transmittance and haze measurement was carried out on an ultraviolet-visible near-infrared spectrophotometer with
an integrating sphere (Shimadzu UV-2550). AFM images of the copper nanowires and their junction were taken using an Asylum MFP 3D in tapping mode. The as-made Cu nanowire film on glass without heat treatment and the one with 30 minutes forming gas annealing were used for the measurements.

**In-situ electron paramagnetic resonance (EPR) measurement:** EPR sample was prepared in air-tight EPR tubes (4 mm LPV 250mm EPR sample tube) purchased from Wilmad LabGlass. All sample tubes were cleaned with acetone and isopropanol under ultrasonication and then dried in heated oven before use.

Before loading sample in EPR tubes, benzoin and CuCl₂ solution was prepared freshly right before the measurement. Benzoin were dispersed in oleylamine under vigorous stirring with concentration of 0.8mmol/g. CuCl₂ oleylamine solution with concentration of 0.02mmol/g was prepared. In a standard reaction sample preparation, 75μL 0.8mmol/g benzoin oleylamine mixture was added to the EPR tube with gentle shaking. Then 75μL of CuCl₂ solution was added on top of the mixture in the tube. The tube was shaken back and forth until the solution was well mixed and settled to the bottom. The loaded EPR tube was connected to a Schlenk line then degassed and purged with Argon for 5 cycles and finally, sealed with slight vacuum before going through the measurement.

The EPR measurement was conducted on a Bruker EMXplus EPR Spectrometer. The microwave frequency was set at 9.286 GHz with power of 20 mW. For the measurement of Cu(II) complex signals, the center field was kept at 3200G, with sweep width of 1000G. In the measurement targeting radical signals, the field was centered at 3300G with sweep width being 300G. Each spectrum was integrated from 60 or 15 scans. The freshly made sample tube was inserted in the measurement chamber and then put through different temperature that mimic the Schlenk tube reaction condition. Spectra were collected at appropriate temperatures and time intervals: ~1 min at room temperature (RT), 30min at RT, 2 hours at RT, 30 min at 70 °C, 30 min at 120 °C, 30 min at 170 °C, and finally, 3 hours at 170 °C. All spectra were collected from one sample, and the EPR tube was kept sealed under vacuum throughout the measurement.

**Fabrication of copper nanowire transparent conductor:** To make a conductive thin film, copper nanowires were diluted using toluene and sonicated for 15 min to form a homogenous suspension. The thin film was constructed by filtering down the nanowires from the dispersion onto a nitrocellose porous membrane (pore size 220 nm) via vacuum filtration. The nanowire network was transferred to a transparent substrate (glass or PET) by applying pressure to the back side of the membrane and forcing an intimate contact with the substrate. The copper nanowire thin film was then annealed under forming gas (10% H₂ and 90% Ar) at 200 °C for 30 min to improve junction contact.

**Haze measurement:** The haze measurement is carried out by D1003-13 standard. Shimadzu UV-2550 ultraviolet-visible near-infrared spectrophotometer with an integrating sphere was used for haze measurement. Four transmittance scans of a sample with different configurations were acquired for its haze calculations: T₁, incident light; T₂, total light transmitted by the specimen; T₃, light scattered by the instrument and T₄, light scattered by the instrument and specimen. The haze
factor of one specimen can be calculated by the equation: 

$$\text{Haze, } \% = \left[ (T_4/T_2) - (T_3/T_1) \right].$$

Unless specified, all haze factors in discussion is the value measured at 550 nm of wavelength. The contribution of glass substrate is already excluded.

**Reference**

Appendix B

Supporting Information for Copper Based Core-Shell Nanowires for Highly-Stable Transparent Conductors

Regents:

Tris(trimethylsilyl)silane (TTMSS, 97%), copper (II) chloride dihydrate (CuCl₂·2H₂O, 99.999%), oleylamine (70%), trioctylphosphine (90%), gold(III) chloride trihydrate (HAuCl₄·3H₂O, ≥49.0%) and nitrocellulose filter membranes (25 mm diameter, 220 nm pore size) were purchased from Sigma-Aldrich. Toluene (≥99.9%) was purchased from Fisher Scientific. All chemicals were used as received without further purification.

Material preparations:

**Cu GO core-shell nanowire preparation:** Graphene oxides nanosheets aqueous solution (1 mg/mL, 0.5 mL) was diluted in 20 mL methanol. To this diluted GO solution, Cu NW toluene suspension (2 mg/mL, 2.5 mL) was added with stir. The mixture was ultrasonicated for 3 min to form the Cu GO core-shell NWs. The NWs was separated by centrifugation at 10000 rmp for 10 mins. Then, the nanowires were washed twice with isopropanol by going through centrifugation-redispersion cycles to remove excess GO and impurities. The product was dispersed in 3 mL isopropanol for storage. The ratio of Cu NW and GO can be modified to tune the coverage and shell thickness of the resulting core-shell NWs.

**Synthesis of Cu@Au nanowires:** In a typical synthesis, CuCl₂·2H₂O (85 mg, 0.5 mmol) and oleylamine (0.5 g) were charged in a Schlenk flask. The mixture was stirred at 70 °C until the dissolution of the copper precursor. Tris(trimethylsilyl)silane (0.5 g, 2 mmol) was added into the solution under inert gas atmosphere. The resulting clear blue solution was slowly heated up from 70 °C to 120 °C in an oil bath. When the reaction solution turned into clear yellow at 120 °C, the reaction temperature was further raised to and kept at 165 °C for 18 hours under stirring. Afterwards, a TOP solution of HAuCl₄·3H₂O (0.1–0.025 M, 1 mL) was injected by syringe at 140 °C. The reddish reaction solution became crimson after the introduction of gold precursor, and was cooled down to room temperature one hour later. The product was collected by centrifugation (6000 r.p.m., 5 min) and washed repeatedly with toluene using redispersion-centrifugation cycles to remove excess oleylamine. The product was dispersed in toluene for further characterization and film fabrication.

**Conducting film fabrication:**
In the case of Cu@rGO nanowires, Cu nanowires were diluted using isopropanol by 100 times and ultrasonicated for 5 min to form a homogenous suspension. The thin film was constructed by filtering down the nanowires from the dispersion onto a polytetrafluoroethylene porous membrane (Sartorius Stedim Biotech, pore size 450 nm) via vacuum filtration. The nanowire network was
transferred on to a piece of glass by applying pressure to the backside of the membrane and forcing an intimate contact with the substrate. Then, the copper nanowire thin film was annealed under forming gas at different temperature for 30 min to improve junction contact.

In the case of Cu@Au nanowires, a dilute suspension of nanowires in toluene was made via sonication. The thin film was fabricated by filtering down the nanowire suspensions onto a nitrocellose porous membrane (pore size 220 nm) under vacuum. The nanowire network was transferred to a transparent substrate (glass or PET) by applying pressure to the back side of the membrane and forcing an intimate contact with the substrate. The thin film was then annealed under forming gas (10% H₂ and 90% Ar) at 200 °C for 30 min to improve junction contact before measurements.

Characterizations and measurements

**Characterizations:** Transmission electron microscopy (TEM) was performed with a Hitachi H-7650. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), energy dispersive spectroscopy (EDS) mapping, and quantitative EDS were carried out with an FEI TitanX 60-300. Aberration-corrected high-resolution scanning transmission electron microscopy (AC-HRSTEM) was performed on a double aberration-corrected TEAM 0.5 microscope at 300 kV using a high-angle annular detector resulting in ‘Z-contrast’ images. Experimental AC-HR STEM images were deconvoluted using the maximum entropy method. Scanning electron microscope (SEM) images were obtained on a JOEL JSM-6340F field emission scanning microscope. X-ray diffraction (XRD) was acquired using a Bruker D-8 General Area Detector Diffraction System (GADDS) with HI-STAR area charge-coupled device (CCD) detector, equipped with a Co-Kα source (λ = 1.789 Å). Sheet resistance of nanowire thin films was measured using a CDE-RESMAP-270 four-point probe resistivity mapper. The transmittance and haze measurement was carried out on a Shimadzu UV-2550 UV-Vis-NIR spectrophotometer with an integrating sphere. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) was performed at the Scienta R4000 HiPP endstation at the Lawrence Berkeley National Laboratory Advanced Light Source (ALS) Beamline 9.3.2. Samples were prepared on silicon substrates and mounted on a ceramic button heater sample holder in order to heat the sample up to 120 °C during experiments. The atmosphere was controlled at UHV (~ 10⁻⁹ Torr) or by introducing H₂O and O₂ gases into the chamber through different molecular leak valves. XPS spectra were collected using an incident X-ray energy of 390, 490, or 750 eV. The binding energy for XPS spectra was calibrated to the valence band spectra of the metallic nanowires. The XPS spectra were quantitatively analyzed by subtracting a Shirley background.

**Haze measurement:** The haze measurement is carried out with the same procedure as in Chapter II.

**Stability test under harsh environment:** Freshly-made nanowire films were placed in air with temperature of 80 °C and water humidity of 80 ± 5 %. The sheet resistance of films was tested with respect of time.

**Optical simulation:** Simulations discussed in Figure 3.8 were conducted using the Lumeral FDTD Solutions 8.12 software package applied to the simplified Cu graphene core-shell structure. Simulations were
performed with both p- and s-polarized light at 550 nm and the total electric fields averaged to provide the equivalent of unpolarized incident light.

All other simulations were conducted using the semi empirical models developed previously for Ag\(^1\). Briefly, the transmission (T) and haze (H) were calculated using the Mie formalism for core shell rods.\(^2-4\) The optical constants of Cu and Ag, and the diameters of core D\(_2\) and shell D\(_1\) were used as input into the Mie equation to calculate T and H as a function of surface areal coverage \(\alpha_s\) using equation A9 and A10 in ref. 1. The calculation also requires an “effective refractive index” for the Fresnel transmission factor for the Cu@Au film on glass. It was found that \(n_{eff} \sim 1.1\) gave the best fit to the H vs T data, which was reasonable considering that Cu has real index between 0.2 and 1 in the visible wavelength range,\(^5\) no binder was used (i.e the Cu@Au films were in air) and the surface coverage was \(\alpha_s \sim 0.2-0.4\). The sheet resistance \(R_s\) of the core-shell nanowire film was calculated using the same approach as for Ag nanowires (equation 18 in ref. 1) but modified to account for the core-shell geometry as two resistors in parallel with resistivities \(\rho_1\) (inner core) and \(\rho_2\) (outer shell), respectively. After some manipulation the sheet resistance equation becomes:

\[
R_s = \frac{C}{(\frac{\rho_2}{\rho_1} \frac{1-r}{1})} \left( \frac{8}{\pi d_1} \right) (\phi_s - \phi_c)^t
\]  

(1)

Where \(r = \left( \frac{d_2}{d_1} \right)^2\), \(\phi_s\) is the surface areal fraction covered by nanowires, \(\phi_c\) is the critical percolation areal fraction \(\phi_c = \frac{18 <d_1><L>}{<L^2>}\), L is the length of the nanowires, t is the critical exponent for electrical percolation in 2D networks (t \(\sim 1.3\)), and C is a parameter to account for contact resistance \(R_j\) between nanowires . When C\(\sim 1\) then \(R_j \sim 0\).

References

Appendix C

Supporting Information for Ultrathin Five-twinned Copper Nanowires as CO₂ Electrochemical Reduction Catalyst

Electrode preparations

Synthesis of Cu NWs: In a typical synthesis, 85 mg of CuCl₂•2H₂O, 0.5 g of tris(trimethylsilyl)silane were dissolved in 5 g of oleylamine in inert environment. The mixture was then slowly heated up to 110°C and kept at this temperature until the color of the solution turned light yellow. Then, the temperature of the reactants was slowly increased to 160°C. The reaction was left to continue for 12 hours. The copper nanowires were collected through centrifugation and further washed with toluene twice to remove ligands and unreacted reagents. The nanowires were finally dispersed in toluene and stored in a dry nitrogen box before use.

Preparation and characterization of copper-graphene oxide (GO) core-shell nanowires: Sub-ten nanometer graphene oxide nanosheets were synthesized using a previously reported approach. To make copper-GO core-shell nanowires, a dilute solution of graphene oxide nanosheets in methanol was prepared with a concentration of 0.05 mg/ml. 2.5 ml of 2 mg/ml copper nanowire toluene solution was added in 20 ml of GO solution in a dropwise fashion, upon vigorous stirring. Then, the mixture was ultrasonicated for 3 min. The core-shell nanowires were collected by centrifugation at 10000 rpm for 10 min. Then, the sample was further washed twice with isopropyl alcohol (IPA) to remove excess graphene oxide. The final products were dispersed in IPA and stored in a dry N₂ box. To change the thickness of the GO shell, we reduced the concentration of GO solution and follow the same procedure described above. The GO was then electrochemically reduced in situ to reduced graphene oxide (rGO). Energy dispersive spectroscopy (EDS) mapping was carried out with an FEI TitanX 60-300.

Preparation and characterization of CuNW/CB/GC electrodes: The washed CuNWs were first loaded onto carbon black (Ketjen) at loading ratio of 20% w/w and sonicated in hexanes for 30 minutes, creating a CuNW/CB stock solution. This solution was then spread on 1 cm² glassy carbon plates (Goodfellow) by micropipette and dried under nitrogen such that a total mass of 20 micrograms CuNW/CB was loaded per electrode.

Each individual electrode was only used for one electrolysis. After electrolysis, electrodes were immediately imaged using SEM (JEOL FE-SEM). The CuNW/CB catalyst was then recovered by sonication in solvents such as hexanes or 2-propanol and imaged under TEM (Hitachi H-7650). Between electrolyses, glassy carbon plates were wiped clear before being immersed in 0.5 M nitric acid overnight and rinsed copiously with nanopure water (EMD Milli-Q, 18.2 MΩ, <5 ppb TOC).

Electrodes for Raman spectroscopy were prepared by dropcasting bare and wrapped Cu NWs onto a piece of titanium foil to prevent any carbon signal arising from the substrate, at a geometric surface area coverage equivalent to that on glassy carbon. For the post-electrolysis sample,
Electrolysis was conducted in CO2-saturated 0.1 M KHCO3 at -1.25 V vs. RHE. The foil was then rinsed lightly with nanopure water before characterization. Raman spectroscopy was performed using a Horiba confocal Raman microscope with a 20x objective at 633 nm. Raman spectra were normalized by laser power (typically ~10 mW) and collection time (30-120s) and then corrected to a linear baseline.

**Electrocatalytic measurements**

**Electrocatalytic testing for CO2 reduction activity:** Electrocatalytic tests were conducted with a potentiostat (Bio-Logic) in a custom-built three-electrode cell. For both catholyte and anolyte, 0.05 M potassium carbonate solution was prepared by dissolving potassium carbonate (99.997% puratronic, Alfa Aesar) in nanopure water. Before electrolysis, the electrolyte was purged through in a sealed cell with ultrahigh purity CO2 (99.999%, Praxair) for at least twenty minutes to make a CO2-saturated 0.1 M KHCO3 solution. A composite platinum wire and gauze (Alfa Aesar) was used as a counter electrode in an anodic compartment separated from the rest of the cell using a Nafion cation exchange membrane to prevent product re-oxidation. All experiments were conducted using a Ag/AgCl (1 M KCl) reference electrode (CHI Instruments). For polycrystalline copper foil experiments, a 0.6 cm² rectangle of high-purity Cu foil (Alfa Aesar, 99.999%) was rinsed in 85% phosphoric acid for 30 seconds, then copiously rinsed with nanopure water before use as working electrode.

In a typical experiment, 10 mL of electrolyte was magnetically stirred in the cathodic compartment, resulting in a headspace of 41 mL. The electrode was held at constant bias using chronoamperometry for either a set time or a set amount of charge, after which a 1mL gas sample was taken by syringe from the headspace. The gas was injected into a gas chromatograph (SRI) equipped with a molecular sieve 13X column, HayeSep D porous polymer column, thermal conductivity detector, and flame ionization detector. Ultra high purity Ar (99.999%, Praxair) was used as carrier gas. The concentration of product gases was determined using calibration curves from standard gases (Matheson TriGas). Liquid sample was taken at the end of electrolysis and mixed with D2O at a 9:1 ratio for product analysis. Quantitative NMR was conducted on a Bruker AV-500 instrument with dimethyl sulfoxide as internal standard. Further details regarding calculations for gas and liquid products can be found in the appropriate sections below.

**iR compensation and current-time behavior:** The solution resistance was determined and compensated for using the in-built ZIR function of the potentiostat, compensating for 85% of the resistance. At all potentials tested, the potential was manually corrected for the remaining 15% using Ohm's law:

\[
\Delta E = i \times 0.15 \times R
\]

where \( R \) represents the calculated solution resistance, \( i \) the measured current, and \( \Delta E \) the additional uncompensated potential shift felt by the working electrode.

**GC quantification of gas products:** Because all experiments were conducted under a batch setup, the calculation of Faradaic efficiencies and partial current densities for gas products could be calculated simply using the charge passed and a measured headspace according to the following relation:
\[ F.E. = \frac{(ppm)(PV)(nF)}{Q(RT)} \]

where the \( ppm \) represents the measured concentration (by volume) of the analyte in the 1 mL sample, \( V \) represents the total headspace volume (typically 41 mL), \( P \) and \( T \) set by standard conditions (1 atm and 273.15 K), \( n \) the mole ratio of electrons to product formation from CO\(_2\) (e.g. 8 for CH\(_4\)), \( Q \) the total charge in C passed, and \( F \) the Faraday constant. The partial current density could then be calculated by multiplying the \( F.E. \) for a given product by the total current density, or equivalently through the following relation:

\[ j = \frac{(ppm)(PV)(nF)}{t(RT)} \]

where \( t \) represents the total time of electrolysis.

**NMR quantification of liquid products:** Liquid products were analyzed using quantitative nuclear magnetic resonance (qNMR) with a Bruker Avance 500 MHz instrument in a 9:1 mixture of sample to deuterium oxide with DMSO as an internal standard. Excitation sculpting\(^2\) was used to suppress the water signal, and each experiment consisted of 8 loops of 8 scans each with a delay time of 42 seconds to account for the long relaxation time of formate.

Because of the long delay time for each scan, the area ratio between an analyte peak and the DMSO peak should correspond well to the ratio of protons from the analyte and from DMSO, which in turn derives the concentration ratio of the analyte to the known concentration of DMSO. In addition, a calibration curve for formate, methanol, ethanol, and acetate was constructed by using the area ratio of known concentrations of analyte to the DMSO internal standard. Quantification of liquid products, especially formate, did not differ by more than 5% F.E. between these two methods. Finally, Faradaic efficiencies could be calculated as follows:

\[ F.E. = \frac{[A](V)(nF)}{Q} \]

where \([A]\) represents the concentration of analyte as determined by quantitative NMR and \( V \) the total volume of solution (typically 10 mL).

NMR samples from the anodic compartment were also taken, but no products, including formate or acetate, were observed. It is likely that Nafion, as a cation exchange membrane, restricts formate and acetate diffusion across compartments as may be observed for an anion exchange membrane.