

How Copper Nanowires Grow and How To Control Their Properties

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ABSTRACT: Scalable, solution-phase nanostructure synthesis has the promise to produce a wide variety of nanomaterials with novel properties at a cost that is low enough for these materials to be used to solve problems. For example, solution-synthesized metal nanowires are now being used to make low cost, flexible transparent electrodes in touch screens, organic light-emitting diodes (OLEDs), and solar cells. There has been a tremendous increase in the number of solution-phase syntheses that enable control over the assembly of atoms into nanowires in the last 15 years, but proposed mechanisms for nanowire formation are usually qualitative, and for many syntheses there is little consensus as to how nanowires form. It is often not clear what species is adding to a nanowire growing in solution or what mechanistic step limits its rate of growth. A deeper understanding of nanowire growth is important for efficiently directing the development of nanowire synthesis toward



producing a wide variety of nanostructure morphologies for structure-property studies or producing precisely defined nanostructures for a specific application.

This Account reviews our progress over the last five years toward understanding how copper nanowires form in solution, how to direct their growth into nanowires with dimensions ideally suited for use in transparent conducting films, and how to use copper nanowires as a template to grow core-shell nanowires. The key advance enabling a better understanding of copper nanowire growth is the first real-time visualization of nanowire growth in solution, enabling the acquisition of nanowire growth kinetics. By measuring the growth rate of individual nanowires as a function of concentration of the reactants and temperature, we show that a growing copper nanowire can be thought of as a microelectrode that is charged with electrons by hydrazine and grows through the diffusion-limited addition of $Cu(OH)_2^{-}$. This deeper mechanistic understanding, coupled to an understanding of the structure-property relationship of nanowires in transparent conducting films, enabled the production of copper nanowires that can be coated from solution to make films with properties that rival the dominant transparent conductor, indium tin oxide. Finally, we show how copper nanowires can be coated with Zn, Sn, In, Ni, Co, Ag, Au, and Pt to protect them from oxidation or enable their use as transparent electrocatalysts.

1. INTRODUCTION

Copper is only 6% less conductive than the most conductive element, silver, but it is 1000 times more abundant. These properties have made it the metal of choice for macroscale electrical wires. Since microprocessors with copper-based interconnects were first introduced in 1997, the high conductivity of copper and its resistance to electromigration have played a central role in enabling the scaling of device architectures to the nanoscale.^{1,2} The copper nanowires (CuNWs) in integrated circuits are made with the damascene process, which involves electrodeposition of copper into a dielectric mold made by photolithography.

In this Account, we describe our efforts to develop an alternative method of producing CuNWs that involves no photolithography. Instead, these CuNWs, with diameters <100 nm and aspect ratios >100, are grown in solution. Visualization of the growth of CuNWs in real-time has enabled the first direct measurement of the growth kinetics for individual nanowires in solution, which in turn has enabled an

unprecedented level of understanding of the mechanistic processes involved in solution-phase nanowire growth. Specifically, we now know the key intermediates involved in the growth of CuNWs, the activation energy of nanowire growth, as well as the rate limiting step for growth of CuNWs. We expect that the approach for understanding the mechanism of nanowire growth described here can be applied to a wide variety of nanowire syntheses.

Our efforts to better understand CuNW growth have been driven in part by a desire to control their structure, which in turn determines their properties. In addition to improving the fundamental understanding of the structure—property relationship of CuNWs, such an improved control can enable tuning the structure of CuNWs for a given application. We have focused on the properties of CuNW networks as transparent conducting films, which may serve as a low-cost alternative to

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Figure 1. (A) Blue $Cu(OH)_4^{2-}$ complex solution from mixing $Cu(NO_3)_2$, NaOH, and EDA, (B) clear $Cu(OH)_2^{-}$ solution formed after N_2H_4 addition, and (C) red solution of CuNWs. Dark field optical microscope (DFOM) images and corresponding SEM images (insets) of (D) Cu_2O particles, (E) Cu agglomerates, highlighted in circles, and (F) CuNWs.

indium tin oxide (ITO) in thin-film solar cells, touch screens, and OLEDs. 3

A well-known disadvantage of copper is its tendency to oxidize. We describe how to deposit shells of Zn, Sn, In, Ni, Co, Ag, Au, and Pt on CuNWs in order to protect them from oxidation. In addition, we show that the growth of such shells onto CuNWs can alter their chemical properties and allow them to serve as transparent electrocatalysts for the oxidation or reduction of water. This example highlights the potential of CuNWs to serve as a low-cost, highly conductive support for electrocatalysis.

2. THE GROWTH MECHANISM OF CuNWs

2.1. The Stages of CuNW Growth

We have focused on the ethylenediamine (EDA)-mediated synthesis of CuNWs to better understand the mechanism of nanowire growth. An EDA-mediated synthesis of CuNWs involves heating an aqueous alkaline mixture of copper salt precursor, a reducing agent, and a capping agent between 50 and 90 °C to generate CuNWs.⁴⁻⁶ Typically, Cu(NO₃)₂, hydrazine (N_2H_4) , and EDA serve as the metal precursor, reducing agent, and capping agent, respectively. The stages of an EDA-mediated CuNW synthesis are shown in Figure 1.7 The initial mixing of $Cu(NO_3)_2$, NaOH, and EDA results in a blue complex, $Cu(OH)_4^{2-}$ (Figure 1A). After the addition of N_2H_4 , the blue solution turns colorless (Figure 1B), and is comprised mainly of $Cu(OH)_2^-$ with a small amount of Cu_2O nanoparticles \sim 70 nm in diameter (Figure 1D). These Cu₂O nanoparticles are further reduced to metallic Cu aggregates (Figure 1E), which serve as seeds that sprout CuNWs via continuous reduction of $Cu(OH)_2^-$ (Figure 1C,F).

One role that EDA plays in the synthesis of CuNWs is that it prevents $Cu(OH)_2^-$ from completely precipitating out of solution in the form of Cu₂O nanoparticles. In the absence of EDA, a high yield of Cu₂O octahedra with edge lengths >230 nm form seconds after addition of N₂H₄, and the blue solution turns into a cloudy orange color (Figure 2A).⁷ In the presence of EDA, the reaction solution turns colorless after addition of N₂H₄, accompanied by the disappearance of a broad absorbance peak at 650 nm, suggesting that the blue Cu(OH)₄²⁻ complex has been reduced to a water-soluble

colorless Cu(I) complex (Figure 2B).⁸ The calculated Pourbaix diagram at 25 °C of the Cu–EDA–H₂O system indicates this Cu(I) species is Cu(OH)₂⁻ at pH \approx 15 (Figure 2C).

To provide further insight into the thermodynamic driving forces involved in the reaction, we measured the open circuit potential (OCP) in the growth solution with a CuNW network on a glass substrate as the working electrode. An OCP of -0.30V was measured in a solution of Cu(II)/EDA/NaOH, a potential at the edge of thermodynamic stability for Cu(II) (Figure 2C). Addition of N_2H_4 lowered the OCP to -0.62 V, a potential sufficient to reduce Cu(II) to Cu(I) but insufficient to further reduce Cu(I) to Cu(0) at room temperature. This accounts for why the clear reaction solution containing $Cu(OH)_2^{-}$ is stable at room temperature. Elevating the solution temperature in the electrochemical cell to 70 °C decreased the OCP to -0.70 V, indicating an increased potential for N₂H₄ to give up its electrons to Cu(I) at this higher temperature. The increase in temperature also changed the onset potential of reduction of Cu(I) to Cu(0) from -0.75to -0.68 V, thereby enabling the reduction of Cu(OH)₂⁻ to metallic copper at this elevated temperature.

CuNWs synthesized through the EDA-mediated approach grow along the [110] direction with a pentagonal cross-section and a twin boundary extending along the nanowire length (Figure 3).^{4,7,9} This growth direction and crystal structure is similar to silver nanowires (AgNWs) grown with a polyol synthesis using polyvinylpyrrolidone (PVP) as a capping agent,¹⁰ as well as CuNWs grown with an alkylamine-mediated synthesis.¹¹ Unlike the case of AgNWs, the CuNWs in the EDA-mediated reaction do not grow from individually dispersed, pentagonally twinned decahedra but instead grow from irregularly shaped, polycrystalline copper seeds 200-500 nm in diameter.⁷ It may be that defects on the surface of these polycrystalline seeds serve as sites for growth of pentagonally twinned CuNWs. Indeed, a copper nanorod with a clear twin boundary extending along its length and into a secondary particle on a copper seed can be observed by TEM imaging of a sample from a reaction at t = 40 min (Figure 3 D,E). Such twin boundaries have previously been indicative of a pentagonally twinned crystal structure.¹⁰

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Figure 2. (A) SEM image of Cu₂O octahedra formed in the absence of EDA. The inset shows the orange solution of Cu₂O octahedra. (B) UV-vis absorbance spectra of (i) 14.3 M NaOH + 4.7 mM Cu(NO₃)₂, (ii) solution i + 110 mM EDA, and (iii) solution ii + 25 mM N₂H₄. (C) Pourbaix diagram of Cu–EDA–H₂O system at 25 °C.

2.2. Kinetics of CuNW Growth

Observing the stages of nanostructure growth has been the dominant method by which researchers have sought to gain some insight into their growth mechanisms. However, the identification of possible mechanisms for a reaction can be greatly facilitated by measuring the kinetics for that reaction and experimentally determining the rate law. To obtain the growth kinetics for individual nanowires, we have visualized the growth of CuNWs in real time with DFOM (Figure 4A).⁸ The CuNWs are grown in a reaction cell consisting of two microscope coverslips stuck together with a double sided tape. The temperature of this reaction cell is regulated with a transparent ITO heater. The growth rate of individual nanowires can be determined by measuring the change in the length of each nanowire over a series of time-lapse images (Figure 4B–E).



Figure 3. (A) Selected area electron diffraction pattern from the nanowire shown in panel B indicates that the nanowire grew along the [110] direction. (C) The cross section of the CuNW shows a pentagonally twined crystal structure. (D) TEM image of a Cu seed with sprouted nanowires. (E) A magnified view of the region highlighted in panel D shows a clear twin boundary extending along its length.

To construct a simple model for nanowire growth, we examined the dependence of the growth rate of the nanowires on the initial concentration of the copper precursor, [Cu(II)], hydrazine, $[N_2H_4]$, and the reaction temperature. As shown in Figure 5A, the growth rate (dL/dt, where *L* is the nanowire length and *t* is the growth time) increased linearly from 17 to 103 nm s⁻¹ with a slope of 24 nm s⁻¹ mM⁻¹ when [Cu(II)] was increased from 1.9 to 5.6 mM with $[N_2H_4] = 25$ mM at 70 °C. In contrast, the growth rate is independent of $[N_2H_4]$ between 19.8 and 62.6 mM with [Cu(II)] = 4.7 mM at 70 °C (Figure 5B), indicating that the reduction of the ionic copper precursor is not the rate-limiting step responsible for nanowire growth. A fit to the temperature dependent growth rate of CuNWs (Figure 5C) gives the low activation energy of 11.5 kJ mol⁻¹ also suggesting that the growth of CuNWs is diffusion-limited.

To explain the observed nanowire growth kinetics, we considered the CuNW as an ultramicroelectrode (Figure 5D). In this model, we assume that N_2H_4 is oxidized on the surface of the CuNW¹² and provides an electrochemical potential for reduction of Cu(I) to Cu(0) at the end of the nanowire. Since the rate of CuNW growth is independent of $[N_2H_4]$, we assume that the reduction of Cu(I) to Cu(0) is fast relative to the diffusion and adsorption of Cu(I) to the end of the CuNW. Starting from the diffusion-limited steady state current at an ultramicroelectrode and taking into account the pentagonal geometry at the end of the nanowire, one can derive the diffusion limited growth rate of a nanowire to be

$$\frac{\mathrm{d}L}{\mathrm{d}t} = 1.23 \left(\frac{M}{\rho r}\right) DC \tag{1}$$

where *M* is the molar mass of copper, ρ is the density of copper, *r* is the average nanowire radius, and *D* and *C* are the diffusion coefficient and concentration for Cu(OH)₂⁻, respectively.⁸ With this formula and the requisite variable values, we calculated the expected diffusion-limited nanowire growth rate to be 25.9 ± 5.3 nm s⁻¹ mM⁻¹ at 70 °C. This agrees very well



Figure 4. (A) Camera image and cross-sectional view of the reaction cell with DFOM. Real-time growth of CuNWs recorded at (B) 0, (C) 32, (D) 65, and (E) 108 s.



Figure 5. Dependence of the growth rate on (A) [Cu(II)], (B) $[N_2H_4]$, and (C) temperature. (D) A schematic illustration of growth model of CuNWs.

with the independent, experimentally measured value of 23.8 \pm 1.7 nm s⁻¹ mM⁻¹ and provides strong support for the model of a growing CuNW as a microelectrode that is charged with electrons by N₂H₄ and grows through the diffusion-limited addition of Cu(OH)₂⁻.

3. STRUCTURE-PROPERTY RELATIONSHIPS FOR CuNW NETWORKS

The potential for utilizing CuNWs as a replacement for ITO in thin-film solar cells, OLEDs, and large-area touch screens provides an exciting opportunity to specifically synthesize CuNWs with dimensions that optimize their properties for a given application. Here we briefly summarize how the dimensions of nanowires influence the transparency and conductivity of a nanowire network.

The transmittance of a nanowire network can be described with eq 2,

$$T = e^{-AF \times Q_{ext}}$$
(2)

where AF is the area fraction of the nanowires on a substrate, and Q_{ext} is the extinction efficiency of the nanowires in the film.^{3,13} Since Q_{ext} increases with increasing nanowire diameter, the transmittance of a nanowire film at a given area coverage increases with decreasing nanowire diameter (Figure 6).¹⁴

It has been shown with numerical calculations and experimentally that, if the resistance in a nanowire network is dominated by the contact resistance between nanowires, the sheet resistance of a nanowire network at any area fraction can be decreased by increasing the aspect ratio (L/D) of nanowires in a film.¹⁵ Such behavior can be intuitively understood by the fact that increasing L/D puts more of the cross-sectional area of a nanowire in the length rather than the width. At low area fractions, increasing L/D results in more nanowires touching, resulting in percolation and conductivity that would not occur with lower L/D nanowires (Figure 7A). At higher area fractions, at which point all the nanowires in a network are in



Figure 6. Optical transmittance (% T) versus area fraction (AF) of CuNWs with 75, 52, and 35 nm diameters.

contact, higher L/D results in higher film conductivity because it reduces the number of nanowire–nanowire contacts in the film. Figure 7B joins the calculations of transmittance with the sheet resistance calculations to illustrate the expected effect of L/D on the transmittance and sheet resistance of a nanowire film.

Motivated by these calculated predictions of the structureproperty relationship of nanowires, we have directed synthetic development to produce CuNWs with higher L/D and smaller diameters. Figure 8A shows the original CuNWs synthesized by stirring the reaction at a constant temperature of 80 °C.⁴ These nanowires have a length = 10 μ m and a diameter = 90 nm, giving them an L/D of 110. Further experimentation revealed that eliminating stirring and lowering the reaction temperature during nucleation and growth of the CuNWs resulted in longer (28 μ m), thinner (75 nm) nanowires with an L/D of 330 (Figure 8B).⁵ A detailed study of the stages of CuNW growth revealed that nanowires in the early stages of a reaction have a diameter of 35 nm and length of 63 μ m, giving them an L/D of 1860 (Figure 8C).⁶ As the reaction proceeds, copper plates onto the sides of the nanowires, increasing their diameter to 150 nm, and decreasing their L/D to 360. By reducing the concentration of N2H4, this diameter growth could be eliminated, allowing for the consistent production of CuNWs with L/D > 1800.

Figure 8D shows the properties of the CuNW films as a function of L/D. These nanowires all have different diameters, so the plot does not look exactly like the calculated %*T* vs R_s plot in which the diameter is held constant, but the

experimental results clearly support the trend of increasing performance with increasing L/D.

4. COPPER-BASED CORE-SHELL NANOWIRES

The relative abundance of copper, coupled with the level of control that has been achieved over the dimensions of CuNWs produced in a given synthesis, make CuNWs an attractive core for growing shells of other materials. Such an approach can result in nanowires with not only controlled dimensions but also a wide range of shell-dependent optical, electrical, magnetic, and chemical properties. To date we have focused on two approaches to growing shells on copper, electroplating and electroless plating.

4.1. Electroplating

The electroplating process starts with the production of CuNW films to serve as working electrodes.^{16–18} The basic plating process involves depositing the desired metal ions onto the CuNW surface by holding the CuNW film electrode at a negative potential. For example, nickel can be continuously deposited onto CuNWs by applying a potential of -0.75 V vs NHE for various times.¹⁶ As shown in Figure 9A and 9B, the color of light scattered from the nanowires changes from reddish-orange to neutral gray upon coating with 33 wt % nickel for 30 min. The SEM images in Figure 9C and 9D show that the surface roughness of the nanowires increased after Ni coating and the diameter of the nanowires increased from 70 ± 25 nm to 95 ± 30 nm. The TEM images in Figure 9E and 9F show a clear core—shell structure in the Cu–Ni NWs after Ni coating on CuNWs.

Zn, like Ni, can be easily plated onto CuNWs to create a shell 15 nm thick after electroplating at -1.15 V (vs NHE) for 10 min (Figure 10A).¹⁷ However, holding the bias at a constant potential does not produce uniform shells for other metals, such as Sn. For Sn, the constant-potential electroplating at -0.65 V resulted in uneven coatings consisting of nanoparticles with diameters in the tens to hundreds of nanometers. To overcome this problem, the electroplating of Sn(II) to Sn(0)was carried out by alternating the reduction and oxidation of Sn at -0.70 and -0.20 V, respectively, with successive cyclic voltammetry scans.¹⁷ As a result, a smooth Sn shell with an average thickness of 3-5 nm was achieved after 250 cycles of successive CV scans (Figure 10B). For metals more noble than Cu, such as Pt, care must be taken to prevent galvanic etching of the Cu metal by Pt, or the film will become nonconductive. Galvanic etching by Pt can be prevented by holding the film at



Figure 7. (A) Example images of nanowire networks for two different L/D and two different AF. (B) Plot of transmittance versus sheet resistance for networks consisting of nanowires with different L/D.

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Figure 8. SEM images of CuNWs with controlled L/D of (A) 110, (B) 370, and (C) 1860. (D) Experimental transmittance versus sheet resistance of films of these CuNWs.



Figure 9. (A, B) DFOM, (C, D) SEM, and (E, F) TEM images of CuNWs (A, C, E) and Cu-Ni NWs (B, D, F) formed by electroplating.

-0.30 V prior to the addition of K₂PtCl₆ to the plating solution.¹⁸ With a preapplied negative potential, CuNWs with a uniform 7 nm Pt shell were formed within 10 min (Figure 10C).

4.2. Electroless Plating

While electroplating is quite versatile and easy to use, it is difficult to apply uniformly over a large area of film due to the resistance of the nanowires, and it obviously cannot be applied to nanowires before their incorporation into a film. Thus, we have in parallel developed electroless plating processes that can be applied to a large quantity of nanowires in a scalable, solution-phase process. Unlike electroplating, which uses electrical current as a source of electrons to reduce metal ions onto the CuNWs, electroless plating involves the use of a chemical reducing agent as a source of electrons. For example, cupronickel nanowires were synthesized by adding CuNWs to a solution containing PVP (dispersing agent), ethylene glycol (solvent), Ni(NO₃)₂ (metal precursor), and N_2H_4 (reducing agent) at 120 °C.9 As the Ni was reduced onto the CuNWs, they became darker in color. Figure 10D shows an EDS image of a CuNW coated with 54 mol % Ni (roughly 1:1 Cu/Ni). The shell thickness was controlled by the initial molar ratio of Cu to Ni ions. Since Cu and Ni are completely miscible in all proportions, these two elements interdiffused after the Ni coating to form a nanowire consisting of a cupronickel shell. Electroless plating of Ni onto CuNWs can also be realized at a lower temperature with the assistance of a catalyst.¹⁹ Following acetic acid treatment, the surface of the CuNW films was activated by dipping them into a solution containing Pd²⁺. The Pd-activated CuNWs were then transferred to an aqueous Ni plating solution containing Ni(NO₃)₂ and N₂H₄ at 75 $^{\circ}$ C. The color of the nanowires changed from reddish to gray upon Ni



Figure 10. EDS mapping images of (A) Cu–Zn, (B) Cu–Sn, (C) Cu–Pt, (D) Cu–Ni, (E) Cu–Ag, and (F) Cu–Au core–shell nanowires by (A–C) electroplating and (D–F) electroless plating.



Figure 11. (A) Sheet resistance versus time for films of Ag, Cu, and Cu–Ni NWs stored in a dry oven at 85 °C. (B) Sheet resistance versus time for Cu, Ag, and Cu–Ag NWs at 160 °C. (C) Sheet resistance and %T change as a result of electroplating of Zn onto CuNW films and subsequent oxidation of Cu–Zn NWs in H₂O₂. (D) Sheet resistance and %T of Cu, Cu–Zn, Cu–Sn, and Cu–In NW films versus time at 85 °C/85% RH.

coating. The amount of Ni deposited on the CuNWs correlates linearly to the time spent in the nickel solution.

To plate metals with higher reduction potentials than Cu, it is necessary to prevent galvanic replacement. For example, Ag^+ , Au^{3+} , and Pt^{4+} will oxidize the CuNWs, leading to broken or etched nanowires and the formation of hollow structures. This problem can be avoided by adding ascorbic acid to the electroless plating solution.²⁰ The reduction potential of ascorbic acid (-0.35 V) is such that it can remove the copper oxide on the nanowire surface and prevent the oxidation of CuNWs but not so high that it reduces the noble metal ions in solution and produces nanoparticles. Instead, Ag, Au, and Pt were uniformly deposited on the CuNWs in the presence of 0.58 M ascorbic acid. The shell thickness could be controlled by changing the molar ratio of the metal ions to Cu. The EDS mapping images in Figure 10E,F show continuous, smooth layers of Ag (5 nm) and Au (7 nm) on the CuNWs.

4.3. Oxidation Resistance of Cu-Based Nanowires

Coating with a different metal shell such as Ni, Co, Pt, Ag, or Au enables the CuNWs to become highly resistant to oxidation.^{9,16,19} The sheet resistance of the bare CuNW films typically begins to increase after 1 day in a dry oven at 85 °C, and increases by an order of magnitude after 5 days (Figure



Figure 12. (A) %T of Cu–Ni NW networks versus catalytic current density of water oxidation. (B) %T versus wavelength for a Cu–Ni NW film after sustained water oxidation and a NiO_xH_y cluster film on ITO. (C) Catalytic current density (-0.65 V) and Pt-mass normalized catalytic current density versus Pt content for HER. (D) Catalytic current density (-0.65 V) and %T of CuNW network versus CuNW loading.

11A).⁹ In contrast, the sheet resistance of AgNW films increases by an order of magnitude after 13 days. However, with as little as 10% nickel relative to copper (9:1 Cu:Ni), the sheet resistance of the cupronickel nanowire film remained remarkably stable over a period of 30 days, increasing by only 10 Ω sq⁻¹ (from 30 to 40 Ω sq⁻¹). With Ni contents of 34% or greater, the change in the sheet resistance over 30 days is within the error of the measurement. Based on the temperature-dependent oxidation kinetics, the times for the sheet resistance of the nanowire films to double ($\Delta R/R_0 = 1$) at 25 °C are estimated to be 0.2, 3, 400, and 1000 years for networks of Cu, Ag, 20% Ni, and 54% Ni NWs, respectively.^{3,9} Upon exposure in a dry oven at 160 °C, the CuNWs quickly become insulating due to thermal oxidation, but the sheet resistance of a Cu–Ag NW film is stable over 24 h (Figure 11B).

Films of Cu-Ni NWs were 1000 times more resistant to oxidation than films of CuNWs, but their transmittance was up to 10% lower than films of CuNWs at a sheet resistance of 60 Ω sq⁻¹. This decrease in transmittance was principally because the Ni coating increased the nanowire diameter, which in turn increased the amount of light blocked by the nanowires at a given area coverage. Recently, we demonstrated that coating CuNWs with a transparent metal oxide shell could protect CuNWs from oxidation without degrading the transmittance and conductivity of the CuNW networks.¹⁷ The initial 39 mol % Zn coating on the CuNWs resulted in a decrease in transmittance from 85% to 76% at $\lambda = 550$ nm (Figure 11C). However, the decrease in the transmittance upon coating of Zn can be recovered by transformation of Zn into transparent ZnO. When the Cu–Zn NW film was dipped in H_2O_2 (2 wt %), its transmittance gradually increased to 84.3% after 15 min, a value close to that of the CuNWs prior to Zn coating (85%),

while its sheet resistance remained nearly unchanged (Figure 11C). Unlike films of CuNWs, the sheet resistance of films of Cu-Zn NWs remains low after extended exposure to conditions designed to accelerate the oxidation of Cu. In an environmental chamber at 85 °C and 85% relative humidity (RH), the sheet resistance of CuNWs increased rapidly, becoming insulating in less than 30 min (Figure 11D). The increase in sheet resistance is much slower for Cu-Zn NWs; the sheet resistance increased from 25 to ~300 Ω sq⁻¹ in 24 h. The transmittance of the Cu-Zn NWs increased by 7% over the test period, and this change is accompanied by a color change from gray to reddish-orange, indicating the oxidation of Zn. Similarly, the sheet resistances of Cu-Sn and Cu-In NW films increased by only ~4 times after exposure at 85 $^{\circ}C/85\%$ RH for 24 h, while the transmittances of both films nearly recovered their original values prior to coating due to conversion of the metal shells to their transparent oxides (Figure 11D).

4.4. Catalytic Properties of Cu-Based Nanowires

Solar-driven water splitting with photoelectrochemical cells (PECs) is an attractive means to convert intermittent solar radiation into H₂ for use as a storable, nonpolluting fuel. An important consideration in the design of PECs is that the water splitting catalysts do not obstruct the transmission of light to the dye or photovoltaic component, but the design of highly active transparent catalysts for PECs has received relatively little attention.^{21,22} Currently, most PEC designs rely on ITO as the transparent electrode substrate. It has previously been estimated that the cost of a PEC must reach ~\$30 m⁻² to be competitive with fossil fuels,²³ but the cost of ITO film by itself exceeds \$30 m⁻². In addition to the high cost of ITO, the water splitting catalyst deposited on ITO can obstruct the transparent that the cost of the structure of the transparent that the cost of the transparent splitting catalyst deposited on ITO can obstruct the transparent that the cost of the transparent provide the transparent that the cost of a PEC must reach ~\$30 m⁻² to be competitive with fossil fuels,²³ but the cost of ITO film by itself exceeds \$30 m⁻². In addition to the high cost of ITO, the water splitting catalyst deposited on ITO can obstruct the transparent that the cost of ITO, the water the transparent the trans

mission of light to the dye or photovoltaic component. To address these limitations, Cu-Ni or Cu-Co core-shell nanowire films can be used as optically transparent electrocatalysts for water oxidation.¹⁶ In this case, the shells both protect the Cu core from oxidation and serve as catalysts. These core-shell nanowire networks exhibited sustained electrocatalytic water oxidation with activities comparable to the benchmark cluster film of NiO, H, electrodeposited on ITO at the same geometric current density. As shown in Figure 12A, a catalytic current density of 1.40 mA cm⁻² could be achieved at a CuNW density of 100 mg m⁻², with an activity of 1 mA cm⁻² at an overpotential of about 440 mV. This is comparable to an activity of 1 mA cm⁻² at an overpotential of about 425 mV for an electrodeposited cluster film on ITO under the same pH. The trend in Figure 12A suggests that an even higher catalytic current density can be attained at the expense of film transmittance. The transmittance of Cu-Ni NW films is approximately 6.7 times more transparent (74% at λ = 550 nm) than the NiO_xH_y cluster film (11%) of the same activity. Averaging over the wavelengths of 300-1800 nm, the transmittance of the Cu-Ni NW film is 80.2% vs 39.3% for the NiO_xH_v cluster film on ITO (Figure 12B).

The stability of ITO becomes an issue at the potentials used for hydrogen evolution reactions (HERs) due to the reduction of In(III) oxide, which results in loss of its transmittance. To address this issue, we studied the use of Cu–Pt core–shell nanowires as an optically transparent and robust electrocatalyst for hydrogen evolution.¹⁸ The Cu–Pt NW films exhibited the highest mass activities (current density per microgram of platinum) at 2.5 mol % Pt, about 8 times higher than carbon supported Pt nanoparticles (Pt/C, Figure 12C), and can achieve current densities equivalent to or higher than those from a polycrystalline Pt foil under the same experimental conditions (Figure 12D). In contrast to ITO, the Cu–Pt NW network films retained their excellent optical and electrical performance during electrochemical reduction, making them a robust, high-performance alternative to ITO for use in PECs, dye-sensitized solar cells, and spectroelectrochemical studies.

5. CONCLUSION AND OUTLOOK

We have shown how real-time visualization can be used to obtain the kinetics of nanowire growth, which in turn can be used to reveal what species is adding to a nanowire, the activation energy of nanowire growth, the rate limiting step for nanowire growth, how a capping agent influences the growth rate of individual nanowires, and how the growth rate of a nanowire affects its morphology. CuNWs are currently the only solution-phase nanowire synthesis for which the growth kinetics are known, but this hopefully will not be the case for very long. There are a large number of nanowire syntheses for which the nanowire growth kinetics can likely be obtained with DFOM, and we expect the kinetic data obtained from visualization will have a tremendous impact on the understanding of nanowire formation processes in solution.

Such mechanistic information is important, because it will enable better control over the morphology and yields of nanowires produced in solution, as well as the development of lower-cost, more easily scaled syntheses. As an example, we have outlined how we used control over the morphology of nanowires to elucidate the structure—property relationship of nanowire-based transparent electrodes, which in turn was used to synthesize nanowires that could be used to produce transparent electrodes with properties that rival those of ITO. This iterative process continues, and we expect to have nanowire films with properties that exceed those of ITO in the near future. At the same time we are expanding the potential uses of CuNWs into other applications by coating them with shells of other materials. These coatings can not only prevent the oxidation of CuNWs so that they can be used in solar cells but also enable them to serve as transparent electrocatalysts for water splitting. Given the abundance and low-cost of copper, we are excited about the potential for CuNWs to serve as a versatile template for growing cores of a wide variety of materials, thus expanding their potential impact across additional applications.

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