

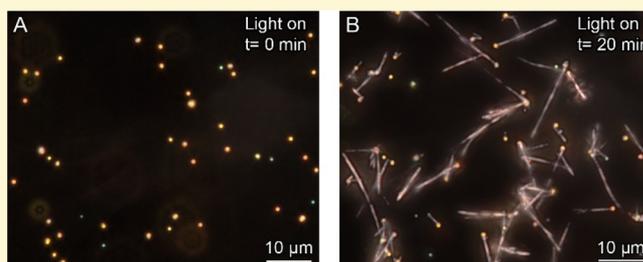
Photocatalytic Growth of Copper Nanowires from Cu₂O Seeds

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S Supporting Information

ABSTRACT: This article describes the photocatalytic growth of copper nanowires from Cu₂O octahedra. When exposed to visible light with an energy greater than the band gap of Cu₂O, electrons excited from the valence band to the conduction band within Cu₂O octahedra reduce Cu(OH)₂⁻ onto the octahedra to form copper nanowires. This phenomenon was used to turn nanowire growth on and off with visible light, as well as pattern the growth of nanowires on a substrate.



■ INTRODUCTION

The fabrication of devices from nanowires often requires that the nanowires are located on a particular area of a substrate. One approach is to blanket a substrate with nanowires and then remove them with chemical etchants^{1–3} or a laser.⁴ A second approach is to print the nanowires to desired locations on a substrate. Printing can be attractive because it can involve fewer manufacturing steps than subtractive (deposit-pattern-etch) processes and produce less waste. However, printing of nanowires onto a substrate requires transfer of the nanostructures from their reaction solution to an ink with properties suitable for printing.^{5–7} The formulation of inks capable of not only printing nanowires at high speed and micron-scale fidelity but also storing nanowires for long periods of time is challenging. Once an ink is obtained, there are several printing techniques that enable printing of features with dimensions on the order of microns,^{8–12} but obtaining such resolution can require a great deal of skill and/or the purchase of expensive automated printing equipment.

A third approach to patterning nanowires is to pattern a catalyst for nanowire growth on a substrate and grow the nanowires from this patterned catalyst.^{13,14} One benefit of this approach is that it can produce vertically oriented nanowires. However, because patterning the catalyst requires either a subtractive deposit and etch process or an additive printing process, this approach provides little benefit if the goal is to obtain laterally oriented nanowires.

A fourth and infrequently studied approach is to pattern the growth of nanowires from a substrate with light. For example, semiconductor nanowires and carbon nanotubes were grown from specific locations on a substrate coated with nanoparticle catalysts using laser-assisted chemical vapor deposition.^{15,16} The semiconductor nanowires were thought to grow from the nanoparticles during laser heating via a vapor–liquid–solid mechanism. At present, this is the only approach that has been reported for patterning the growth of nanowires with light.

Here we report an entirely new approach to controlling the growth of nanowires with light that enables their patterning on

specific areas of a substrate. In the presence of an appropriate reaction solution, copper nanowires (CuNWs) grow from Cu₂O octahedra only when exposed to visible light with an energy greater than the band gap of Cu₂O. The results presented here suggest that the Cu₂O seeds serve as a photocatalyst for the growth of CuNWs, with hydrazine serving as the source of electrons.

■ EXPERIMENTAL SECTION

Light-Induced Synthesis of CuNWs. Figure S1 in the Supporting Information outlines the steps required to prepare a reaction solution for the photocatalytic growth of CuNWs. A growth solution was prepared by mixing 20 mL of an aqueous solution containing 15 M NaOH (Acros Organics) with 1 mL of an aqueous solution containing 0.1 M Cu(NO₃)₂ (Sigma-Aldrich) in a 50 mL round-bottomed flask. Next, 150.4 μL of ethylenediamine (Sigma-Aldrich) was added, and the solution was stirred at 700 rpm for 5 min in a 50 °C water bath. While still being heated in the water bath, 6.26 μL of an aqueous solution containing 35 wt % hydrazine (Sigma-Aldrich) was added to the growth solution. The addition of hydrazine caused the appearance of the solution to change from blue and transparent to white and translucent after 1 min. The solution then turned colorless and transparent after 3 min.

After the addition of hydrazine to the growth solution, a seed solution was made by combining 20 mL of an aqueous solution containing 15 M NaOH with 1 mL of an aqueous solution containing 0.1 M Cu(NO₃)₂ in a 50 mL round-bottomed flask. The seed solution was stirred at 700 rpm for 5 min while being heated in a water bath set to 50 °C. After the addition of 25 μL of a 35 wt % aqueous solution of hydrazine to the seed solution, the color changed from blue to orange after 1 min. Between 1 and 5 mL of the seed solution was then added to the growth solution, and this mixture was stirred for 1 min before adding 4 μL of the mixture to a reaction cell. The reaction cell was made by punching a 7-mm-diameter hole through 90-μm-thick double-sided tape (FindTape.com) and placing the tape on a glass slide. After the reaction mixture was pipetted into the reaction cell, it was sealed with a glass coverslip.

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CuNWs were grown from the Cu_2O seeds in the reaction mixture with the halogen light source of a dark-field optical microscope (100 W, Olympus BX51 fitted with a SC30 CMOS camera). Cu_2O seeds were also exposed to light from LEDs (1 W, from PlasmaLed) with wavelengths of 464, 519, and 629 nm. The wavelengths of the LEDs were measured with a Labsphere Cd 2100 spectrometer.

Larger-Scale Photocatalytic CuNW Growth for Characterization by Scanning Electron Microscopy (SEM). Larger amounts of CuNWs were grown for characterization by SEM by pipetting 15 mL of a reaction mixture containing 20 mL of a growth solution and 5 mL of a seed solution into a polystyrene Petri dish. The reaction mixture was irradiated for 10 min with a blue LED UFO Grow Booster from HTC Supply ($\lambda = 430$ and 460 nm, 135 W) placed ~ 12 cm above the Petri dish. The reaction mixture was then transferred into a separatory funnel along with ~ 30 mL of a solution containing 1 wt % poly(vinylpyrrolidone) (PVP; Sigma-Aldrich, MW = 10K) and 3 wt % diethylhydroxylamine (DEHA; Acros Organics). This mixture was swirled until the CuNWs floated to the top. The white cloudy layer was then drained away, and another ~ 30 mL of the PVP/DEHA blend was added. The solution was centrifuged at 7000 rpm for 10 min and decanted. Then ~ 10 – 25 mL of a 3 wt % aqueous solution of DEHA was added, and the suspension was vortexed. This process of centrifugation, decantation, addition of DEHA, and vortexing was repeated six more times. Approximately 15 μL of the suspension was pipetted onto a silicon wafer and dried in a nitrogen box for 3 h. The CuNWs were characterized using SEM (FEI XL30 SEM-FEG).

Photolithographic Patterning of CuNW Growth. A chrome-on-glass photomask with diamond-shaped areas of chrome 150 μm in edge length and 75 μm apart was ordered from Photoplotstore.com. Approximately 0.5 mL of a reaction mixture containing 20 mL of a growth solution and 13 mL of a seed solution was pipetted onto the mask and left to sit for 1 h before irradiating it with the 135 W blue LED light positioned ~ 12 cm below the mask. The CuNWs were then viewed using a MT8530F metallurgical microscope.

RESULTS AND DISCUSSION

Figure 1A shows a camera image of the dark-field optical microscope and reaction cell used to visualize the photocatalytic growth of CuNWs from Cu_2O seeds. A diagram of the reaction cell and its constituents is shown in Figure 1B. When the reaction mixture was left in the cell without exposure to light, no CuNWs grew from the seeds after a period of 20 min (Figure 1C,D). Even after a period of 3 h, no CuNWs grew from the seeds without exposure to light. In contrast, when the Cu_2O seeds in the reaction solution were exposed to light from the halogen lamp, CuNWs of 15–20 μm in length grew from the seeds over the course of 20 min (Figure 1E,F).

Previous CuNW syntheses without Cu_2O seeds^{17–20} used a higher concentration of hydrazine, 20–70 mM, than the reaction mixture used for photocatalytic growth (5.3 mM). The relatively high concentration of hydrazine used previously reduced the Cu_2O nanoparticles into Cu aggregates. CuNWs grew from these Cu aggregates through the diffusion-controlled reduction of $\text{Cu}(\text{OH})_2^-$ at temperatures greater than 50 $^\circ\text{C}$.^{20,21} Given the elevated temperature and higher concentration of hydrazine, no light was needed for CuNW growth. In contrast, the lower temperature and lower concentration of hydrazine used in the reaction mixture for photocatalytic growth were not sufficient to reduce Cu_2O or $\text{Cu}(\text{OH})_2^-$ into metallic Cu.

To further understand the role of light in the growth of CuNWs from Cu_2O seeds, the light from the microscope was turned on and off during the growth of CuNWs (Figure 2). After 5 min of exposure to light, CuNWs grew from the Cu_2O seeds to a length of 4.5–6.5 μm (Figure 2B). As soon as the halogen lamp was turned off, the growth of CuNWs halted

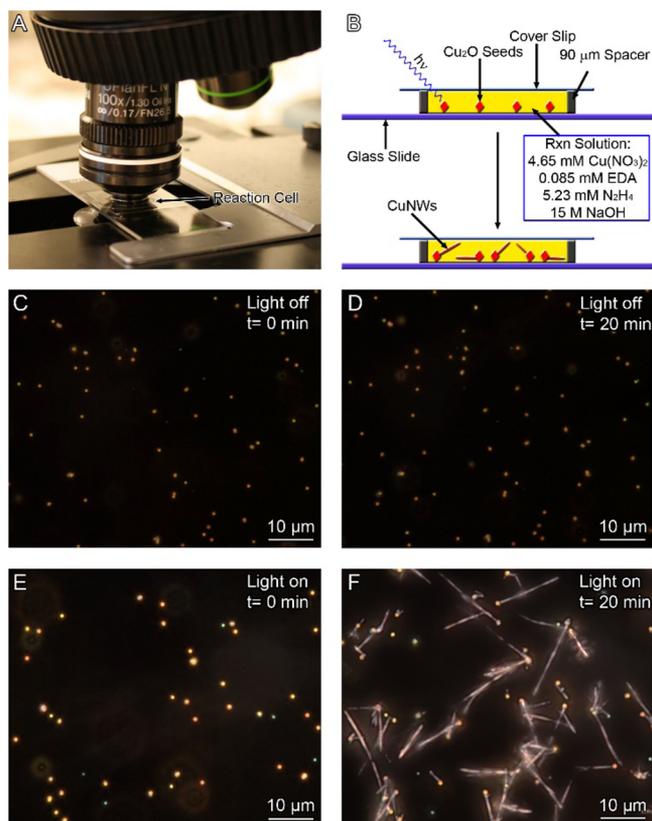


Figure 1. (A) Camera image of the dark-field optical microscope and reaction cell. (B) Illustration of reaction cell and its constituents. (C and D) CuNWs do not grow from Cu_2O seeds after 20 min in the dark. (E and F) CuNWs grow from Cu_2O seeds after 20 min when the halogen lamp in the microscope is turned on.

(Figure 2C), indicating that the continuous presence of light was necessary for the growth of CuNWs in this reaction solution. When the light was turned back on, new wires grew primarily from the Cu_2O seeds, while the CuNWs that formed during the first growth period no longer grew (Figure 2D). The length of the CuNWs was measured periodically during both growth stages and was plotted in Figure 2E to further illustrate that the nanowires that grew during the first growth stage did not resume their growth during the second growth stage. The nanowires grew from the Cu_2O seeds at roughly the same rate during both stages, suggesting that the growth mechanism of the CuNWs remained the same. In rare instances when the light was turned back on, a new CuNW grew from an existing wire but at a different angle (Figure 2D).

The fact that CuNWs grew from the Cu_2O seeds only when the light was on, and preferred to grow from the seed rather than the surface of a nanowire, suggests that the Cu_2O seeds were serving as a photocatalyst for the growth of CuNWs. Cu_2O is a p-type semiconductor with a band-gap energy of 2.0–2.2 eV that allows it to serve as a photocatalyst while being irradiated with visible light with a wavelength ≤ 619 nm.^{22–24} Thus, we used different light sources with wavelengths that were above and below the band gap of Cu_2O to determine whether it was serving as a photocatalyst for the growth of CuNWs. Figure 3 shows that LEDs with wavelengths shorter than the band gap (Figure 3A,B) produced CuNWs, while light with wavelengths longer than the band gap did not induce nanowire growth. We also grew the CuNWs photocatalytically

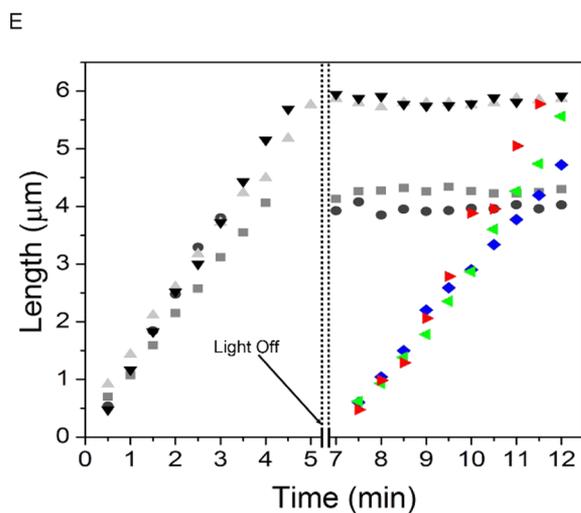
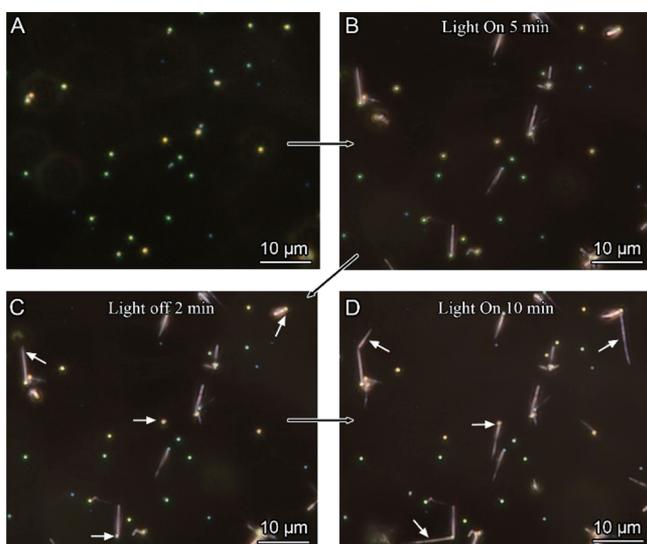


Figure 2. (A and B) CuNWs grow from Cu_2O seeds when illuminated with light. (C) CuNW growth stopped when the light was turned off. (D) New CuNWs grew when the light was turned back on but the CuNWs grown in the first 5 min did not continue to grow. (E) Graph of the growth of CuNWs over time.

at a larger scale so as to characterize them by SEM. Figure 3D shows that the CuNWs grew from the face of the octahedra Cu_2O and had an average diameter of 64.2 ± 11.6 nm.

Figure 4 illustrates the proposed mechanism responsible for the growth of CuNWs from Cu_2O seeds. Light with sufficient energy excites an electron from the valence band to the conduction band. This electron then travels to the surface and reduces $\text{Cu}(\text{OH})_2^-$ to Cu, which deposits onto the seed. Additional electrons then travel through the Cu and reduce more $\text{Cu}(\text{OH})_2^-$ into Cu at the tip of the nanowire. Hydrazine acts as a hole scavenger and source of electrons. CuNW growth was not observed in the absence of hydrazine.

To measure the effect of light intensity on the growth rate of CuNWs, the CuNWs were grown under dark-field optical microscopy with a filter with a transmittance of 6% and 25% T. As seen in Figure S2 in the Supporting Information, changing the intensity of the light did not appreciably affect the rate of CuNW growth. These results confirm the conclusions of previous work, which shows that the rate of CuNW growth is

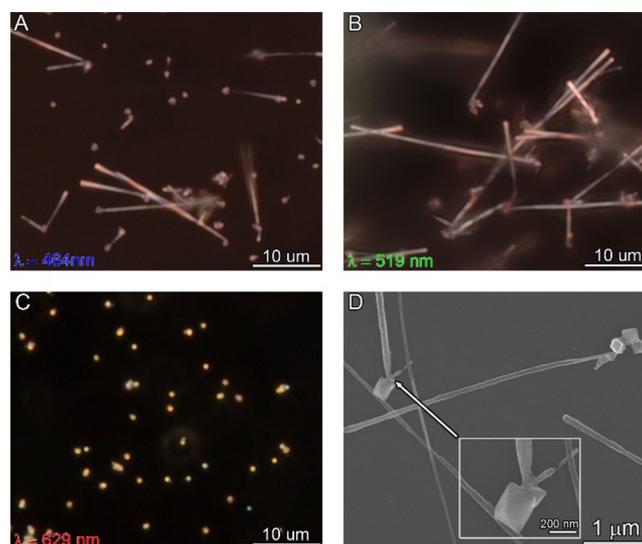


Figure 3. (A and B) CuNWs grew from Cu_2O when exposed to light with an energy greater than the band gap of Cu_2O (>2 eV or $\lambda < 619$ nm). (C) No CuNWs grew when Cu_2O was illuminated with light with a wavelength of 629 nm. (D) SEM image of CuNWs growing from Cu_2O octahedra.

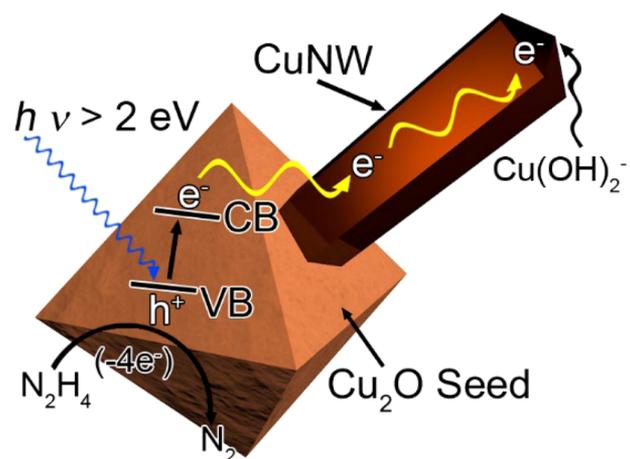


Figure 4. Illustration of the proposed mechanism for the growth of CuNWs from Cu_2O octahedra.

limited by the diffusion of $\text{Cu}(\text{OH})_2^-$ to the end of the nanowire.²⁰

Given that CuNWs only grew from the Cu_2O seeds exposed to light, we experimented with the possibility of using this phenomenon to pattern the growth of CuNWs in selected areas. We replaced the glass slide substrate with a chrome-on-glass photomask and exposed the Cu_2O seeds and reaction solution to light from an LED through the photomask (Figure 5A). A picture of the photomask showing the areas that allowed for transmittance of light is shown in Figure 5B. Figure 5C shows that nanowires only grew in open areas where light was transmitted. A few CuNWs extend from seeds in the transparent areas into the opaque regions. The resolution of the patterning is therefore roughly equivalent to the lengths of the CuNWs. The white spheres in the image are nitrogen bubbles that formed as a result of decomposition of hydrazine.

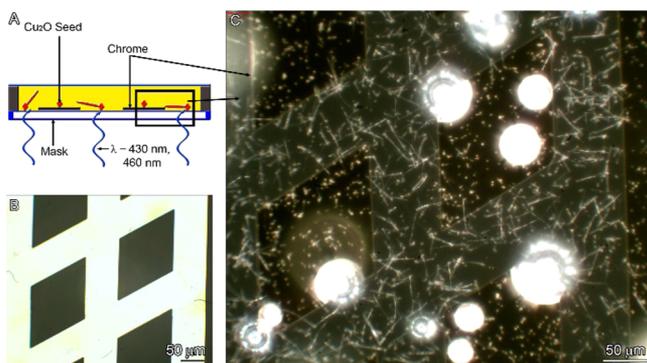


Figure 5. (A) Schematic of the setup used for patterning growth of CuNWs with light. (B) The pattern of the photomask showing the opaque and transparent areas (seen in white). (C) A dark-field optical microscope images demonstrating the patterned growth of CuNWs.

CONCLUSION

We have shown that, by using Cu_2O octahedra as photocatalysts, the growth of CuNWs can be turned on and off with a light switch. Cu_2O octahedra absorb light with a wavelength of less than 619 nm, exciting electrons that then reduce $\text{Cu}(\text{OH})_2^-$ onto the seed to form a CuNW. Hydrazine acts as a hole scavenger and source of electrons during this process. We used this phenomenon to pattern the growth of CuNWs in specific areas of a substrate with a photomask. The use of a photomask can likely be eliminated by using a focused laser as the source of photons, thereby enabling the writing of arbitrary patterns of nanowires onto a substrate. Future work may explore whether this process can be generalized to other photocatalytic materials and other metals besides Cu.

ASSOCIATED CONTENT

Supporting Information

Detailed description of experimental methods and additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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