

The Self-Assembling Growth of Copper Nanowires for Transparent Electrodes

Wu Junqing,¹ Guo Le,¹ Wen Min,¹ Bu Tongle,¹ Zhou Peng,¹ Zhong Jie,¹ Huang Fuzhi,¹ and
Zhang Qi,^{1,2}

(1.School of Materials Science and Engineering, and State Key Laboratory of Advanced Technology for Materials Synthesis and
Processing, Wuhan University of Technology, Wuhan 430070, China;

(2.School of Aerospace, Transport and manufacturing, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK)

Abstract: Cu nanowires (CuNWs) have attracted great interest due to their growing application in transparent electrodes. In this work, we have prepared long (15 - 40 μm), thin (diameter of 20 ± 5 nm), well-dispersed CuNWs. The high-resolution TEM and selected area electron diffraction showed the CuNWs were single crystalline. To investigate the growth mechanism, we examined the microstructure of the samples at different reaction times. It was found that the CuNWs were actually formed by self-assembling of Cu nanoparticles along the [110] direction. The transparent electrodes fabricated using the CuNWs achieved a high transparency of 76 % at $31 \pm 5 \Omega/\square$.

Key words: Cu nanowires; growth mechanism; self-assembling; transparent electrodes

1. Introduction

Transparent electrodes (TEs) are widely used in various optoelectronic devices, including touch screens, light-emitting diodes, flat-panel displays, and photovoltaic cells.¹⁻³ Most of the TEs are made by indium tin oxide (ITO) due to its high transmittance and low resistivity. However, ITO actually is an expensive material as indium is a rare element. In addition, ITO thin film is brittle thus not suitable for flexible devices.^{4,5} The low-cost alternatives such as carbon nanotubes (CNTs),⁶ graphene,⁷ and metal nanowires⁸ have attracted considerable attention. Carbon nanotubes (CNTs) films have been extensively explored, but they have much poorer conductivity compared to ITO at the same transmittance.⁹ Although graphene holds great promise because of its exceptionally high charge mobility and excellent transparency, its sheet resistances (100-1000 Ω/\square at 80-90% transmittance) still could not compete with ITO.¹⁰ Comparatively, thin films of metal nanowires are the most promising alternative because of their high conductivity and optical transmittance. Thin films of silver nanowires (AgNWs) have a transmittance and sheet resistance similar to ITO,^{11,12} but silver is too expensive to be used in a large quantity.

Copper costs much less than silver or indium, and its electrical conductivity is close to silver.^{13,14} Copper nanowires films coated via a solution method have therefore emerged as a perfect alternative to AgNWs or ITO for fabricating low-cost transparent electrodes.¹⁵ Herein, we reported a facile synthesis of long single-crystalline Cu nanowires (CuNWs) with excellent dispersibility in ink. We also intuitively observed the self-assembling growth of Cu nanowires. This self-assembling growth mechanism is quite different with the common growth mechanism in literature where a seeding growth mechanism was normally proposed. It was normally found that the CuNWs were grown from spherical copper seeds,¹⁶ or tapered Cu nanocrystals.¹⁷ In addition, Hsing-Yu Tuan observed copper atoms deposition and crystallization on the Cu nanoparticles to form CuNWs.¹⁸ However, we observed the Cu nanocrystals

self-assembled to form the CuNWs, which is unique among previous observations.

2. Experimental

2.1 Chemicals

Copper (□) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, AR, Aladdin), Nickel(□) acetylacetonate ($\text{Ni}(\text{acac})_2$, 95%, Aladdin), Oleylamine (80-90%, Aladdin), ethanol (AR, SCR), and hexane (AR, SCR) were all used as received.

2.2 Synthesis of Cu nanowires

CuNWs were synthesized by reducing $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with oleylamine and $\text{Ni}(\text{acac})_2$ as catalyzer, following the approach developed by Guo et al. with some modification.¹⁹ In brief, 200 mg $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 200 mg $\text{Ni}(\text{acac})_2$ were mixed with different volumes (10, 20, and 30 mL) of oleylamine in a 50 mL three-necked flask and kept under a flow of common purity Nitrogen at 80 °C for 40 min with strong magnetic stirring. After fully dissolution, turn off the magnetic stirring. Then, the solution was heated up to 160 °C and kept at this temperature for 4 h, and then cooled to room temperature. The prepared Cu nanowires were washed by adding hexane and acetone (1:3 in volume) in the reaction mixture with sonication for 2 min, followed by centrifugation at 7000 rpm for 5 min. The washing process was repeated three times. Finally, the Cu nanowires were kept in hexane.

2.3 Fabrication of transparent conductive films

Thin films were prepared by spin-coating method. The glass were degreased with detergent, rinsed with deionized water and ultrasonically cleaned in ethanol for 20min. Typically, Cu nanowires were dispersed in hexane by bath sonication for 10 min, and then the CuNWs ink was spin-coated on the cleaned glass at 2000rpm for 20s, which repeated five times, and then the films was dried at room temperature after 10 min.

2.4 Characterization

The Cu nanowires and electrodes were characterized by X-ray diffraction measurements (Panalytical X'Pert Pro X-ray power diffractometer using Cu-K α radiation), scanning electron microscope (JSM-5610LV), transmission electron microscope (JEM-2100F STEM/EDS) and optical microscope (OLYMPUS). The transmittance was test on a PerkinElmer UV/VIS/NIR Spectrometer. The sheet resistance was measured using a four-point probe resistivity meter (SDY-6).

3. Results and discussion

Our synthesis strategy relies on self-catalytic growth of Cu nanowires in Oleylamine solution. Upon addition of the precursor, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, long nanowires were prepared through a $\text{Ni}(\text{acac})_2$ catalytic process. Fig. 1a shows the scanning electron microscopy (SEM) images of the Cu nanowires made by 20 mL oleylamine. No large bundles were observed, and the nanowires were well dispersed. It can be seen that these CuNWs length is up to 25 μm . Fig. 1b shows the high magnification SEM image of the CuNWs. The average diameter of the nanowires was ~ 50 nm. The nanowires were found to be single-crystalline and the growth direction of these wires is along [110] as shown in the selected area electron diffraction (SAED) pattern (Fig. 1c). The X-ray diffraction (XRD) pattern in Fig. 1d shows three peaks at $2\theta=43.5$, 50.7 , and 74.4° , which correspond to the (111), (200) and (220) planes of a FCC Cu (JCPDS #03-1018) respectively. No other peaks were observed, confirming the pure copper nanowires were formed.

Fig.1 (a) and (b) SEM images of Cu nanowires. (c) SAED pattern of the Cu nanowires shown in the inset. (d) XRD pattern of Cu nanowires.

The structure of the nanowires was further studied by the high-resolution TEM. On the basis of SAED and XRD analysis, these nanowires were single-crystalline and grew along the [110] direction. Such, the side faces of nanowires should be the (200), (111) planes which was confirmed by the corresponding high-resolution TEM images (Figure. 2a,c) taken from the middle and end portions of two different Cu nanowires. The Figure. (2b.c) clearly showed fringes corresponding to the (111), (200) planes along the axis of the nanowires.

Fig.2 (a,c) TEM images taken from two different Cu nanowires; (b,d) HRTEM images of the boxed areas in (a) and (c), respectively.

In order to study the growth mechanism, we stopped the CuNWs reaction at different times and examined the product with electron microscopy. At the initial stage ($t=30$ min), the SEM image (Fig. 3a) showed the Cu nanoparticles whose diameter gradually changed from 40 nm to 180 nm were formed, which exhibited the development of nanowire embryos from the nanoparticles. After the reaction had proceeded to $t=1$ h (Fig. 3b, 3c), we observed that the nanoparticles (diameter of 100 nm) began to self-assemble into a line. As the reaction was continued to 2h (Fig. 3d), the assembled Cu nanoparticles grew into nanowires. Then after 2.5 h of reaction (Fig. 3e), it was found that the surface of Cu nanowires became smooth although the Cu nanowires were incomplete fusion. These results indicate that the Cu nanowires were originated from nanocrystals, through a one to one self-assembling between the initial seeds. This self-assembling growth mechanism is unique among the preciously observed seeds-growth mechanism where Cu nanoparticles were formed and acted as seeds that started to grow into nanowires along a specific crystal orientation.^{22,23}

Fig.3 (a-d) SEM images of Cu nanowires synthesized ed at reaction times of (a) 0.5, (b,c) 1, (d) 2, (e) 2.5 h.

Why the nanocrystals would like to self-assemble to form nanowires? When the reaction is under thermodynamic control, Cu nanocrystals attempt to minimize the total surface energy.²⁴ For an FCC structure, the energetic sequence of $\gamma(111) < \gamma(100) < \gamma(110)$. This implies that Cu nanocrystals should maximize the exposed (111) facets. The oleylamine is an effective capping agent for Cu, with a good selectivity toward the (200) facets. Besides, The Cl^- ions forming CuCl_2 precursor is attached onto the (200) facets and leads to a strongly anisotropic growth.²⁵ Therefore, the Cu nanocrystals would be inclined to be connected by the active (110) facets, leading to preferential growth of the nanowires along the [110] direction. This is well consistent with the SAED and TEM results.

It is important to mention that with the absence of $\text{Ni}(\text{acac})_2$, we did not observe any particles or nanowires even after 10 h reaction. Because Cu^{2+} ions were strongly coordinated by Cl^- , which prevents Cu^{2+} from being reduced. This suggests the catalytic role of Ni^{2+} ions during the Cu nanowires formation. The Ni^{2+} ions were reduced by oleylamine to form $\text{Ni}(0)$, then the oxidation of $\text{Ni}(0)$ back to Ni^{2+} ions during the galvanic replacement reaction with Cu^{2+} ions.

On the basis of the above observations and analysis, the formation mechanism can be proposed (Fig. 4). Firstly, Ni^{2+} ions were reduced to $\text{Ni}(0)$ atoms in oleylamine solution. Secondly, Upon the addition of $\text{Cu}(\text{Cl})_2$, the precursor rapidly involves into the galvanic replacement reaction with $\text{Ni}(0)$. Then, the Cu nanocrystalline seeds start to form. Subsequently, the nanoparticles began to assemble into a line and

connect to form nanowires by Ostwald ripening along the [110] direction, as their side (200) facets were stabilized by oleylamine and Cl^- . Thus a long Cu nanowire is formed.

Fig.4 Schematic of the formation mechanism of CuNWs.

Surfactants typically play a crucial role in controlling the size and shape of chemically synthesized nanoparticles. So we can control the diameter of CuNWs by adjusting oleylamine volume. Fig. 5a-f shows the SEM images of the CuNWs in various volumes of oleylamine (10, 20, 30 mL, respectively). At low oleylamine concentration, the average diameter of CuNWs (Fig. 5a, b) is 20 nm and the length is 15 - 40 μm . By increasing the oleylamine volume to 20 mL, the average diameter of CuNWs (Fig. 5c, d) increases to 50 nm, and the length is 15 - 25 μm . Further increasing the oleylamine volume to 30 mL, the CuNWs (Fig. 5e,f) are wide (120 nm), and short (4 - 16 μm). It can be concluded that the aspect ratio of the CuNWs decreases with the increase in the concentration of oleylamine. It is believed that the decrease in the oleylamine amount resulted in the formation of small size of the assembled Cu nanoparticles.²⁶ Therefore, with the decrease in oleylamine amount, thinner and longer Cu nanowires were formed by the self-assembling of smaller nanoparticles (Fig. S1†). The study concludes that the diameter of Cu nanoparticles formed at the initial stage restricts the final diameter and length of CuNWs.

Figure 5. SEM image of Cu nanowires prepared with different volumes of oleylamine: (a, b) 10 ml; (c, d) 20 ml; (e, f) 30ml.

Two types of the prepared CuNWs, long (15 - 25 μm), thin (<60 nm) CuNWs and the longer (15 - 40 μm), thinner (20 nm) CuNWs were made into well-dispersed CuNWs ink separately and then coated as transparent electrodes on glass. The UV-Vis spectra (Fig. 6a) show that the transmittance of the two films made by the different CuNWs is similar ($T=76\%$). However, the longer and thinner CuNWs exhibited a lower sheet resistance of $31 \pm 5 \Omega/\square$ compared to the other one ($43 \pm 4 \Omega/\square$), which is comparable to the CuNWs TEs obtained by Wiley and co-workers with a sheet resistance $61 \Omega/\square$ at 67% transmittance.¹⁴ This difference in conductivity is accounted for the difference in nanowire length and diameter. The CuNWs films with low aspect ratio leave more open space than films of the CuNWs with high aspect ratio (Fig. 6b, c). Therefore, films of the CuNWs with high aspect ratio exhibited a lower sheet resistance at the same transmittance.

Fig. 6 (a) UV-Vis transmittance spectra for two different Cu nanowires electrodes, and the optical microscope images of (b) higher aspect ratio Cu nanowires ($T = 76\%$, $R_s = 31 \pm 5 \Omega/\square$) and (c) lower aspect ratio Cu nanowires ($T = 76\%$, $R_s = 43 \pm 4 \Omega/\square$).

4. Conclusions

In conclusion, we have shown that self-catalytic and self-assembling growth mechanism of the CuNWs, with the active Ni^{2+} , Cl^- ions and oleylamine as a critical role in synthesis of stable CuNWs. 15-40 μm long single crystalline CuNWs were synthesized and made into ink for preparation of transparent electrodes, achieving $31 \pm 5 \Omega/\square$ at 76% transparency. With the superior properties and low cost, CuNWs are believed to be the most promising alternative of ITO.

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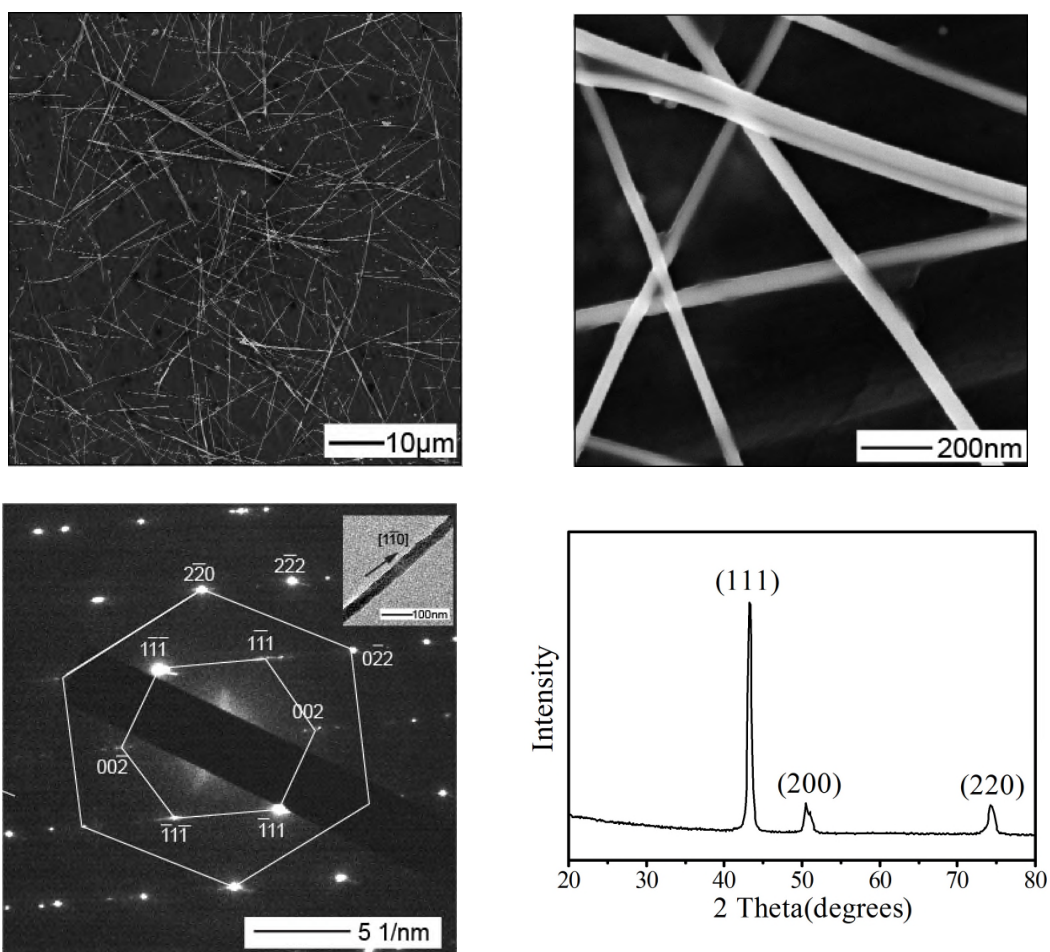


Figure 1. (a) and (b) SEM images of Cu nanowires. (c) SAED pattern of the Cu nanowires shown in the inset. (d) XRD pattern of Cu nanowires.

Figure 2. (a,c) TEM images taken from two different Cu nanowires; (b,d) HRTEM images of the boxed areas in (a) and (c), respectively.

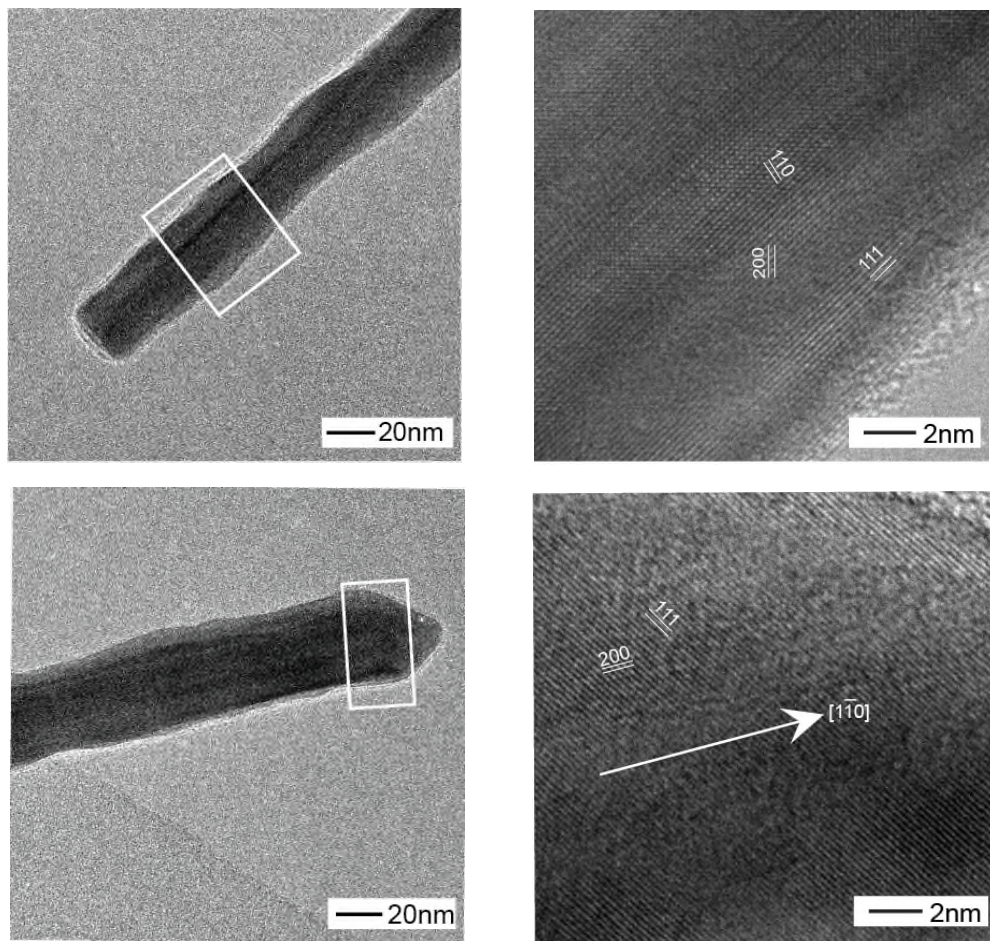


Figure 3. (a-d) SEM images of Cu nanowires synthesized at reaction times of (a) 0.5, (b,c) 1, (d) 2, (e) 2.5

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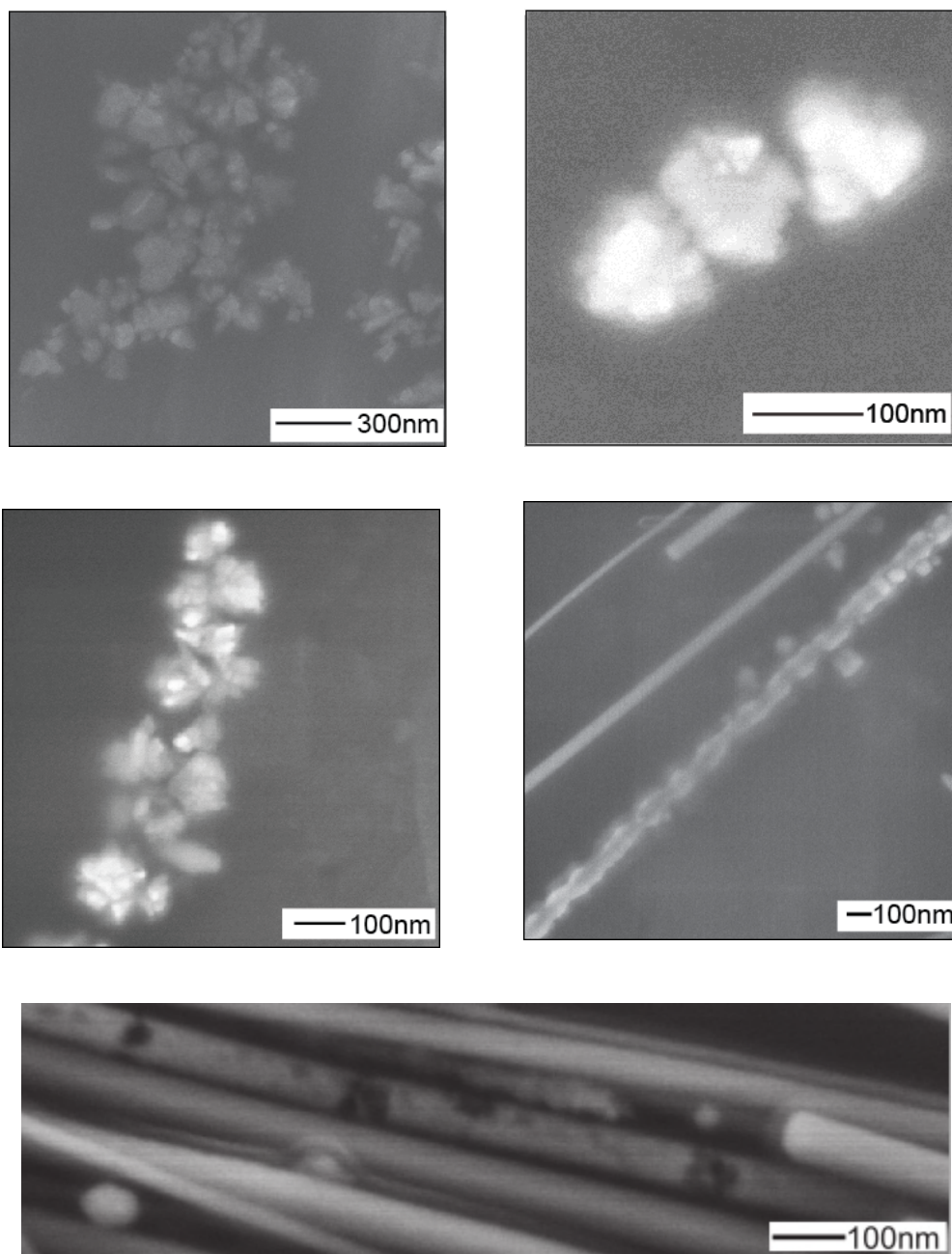


Figure 4. Schematic of the formation mechanism of CuNWs.

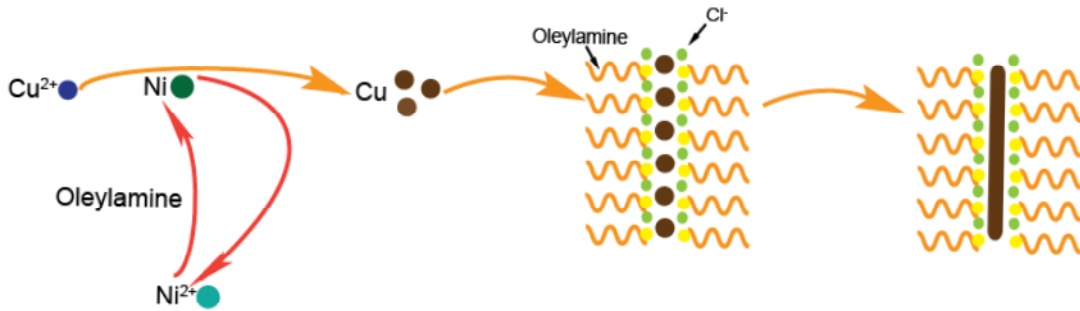
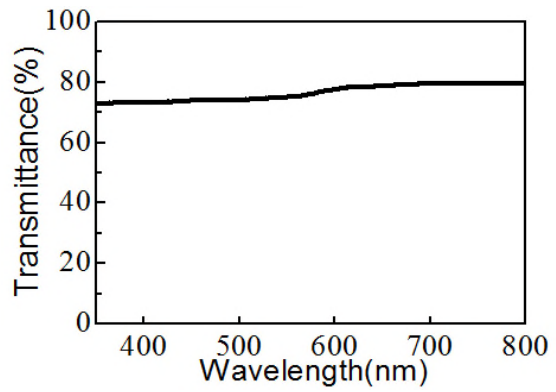
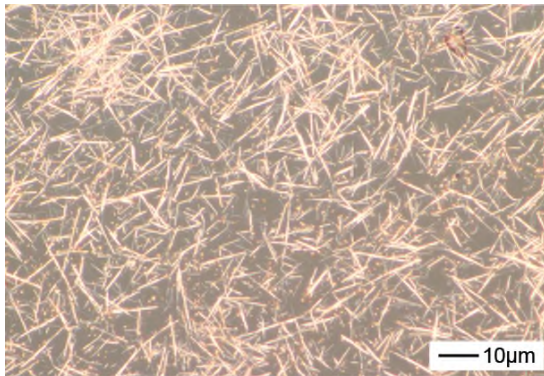


Figure 5. (a) the optical microscope image of Cu nanowires electrodes with 76.43% transmittance. (b) UV-Vis-NIR wavelength transmission spectra for Cu nanowire electrode (sheet resistance $\sim 43.28 \Omega/\square$).



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Wu, Junqing

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