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Formation of hybrid structures: copper oxide nanocrystals templated on ultralong copper nanowires for open network sensing at room temperature

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Abstract

A facile large-scale synthesis approach for producing intrinsically p-type nanowires with uniform coverage of nanocrystals to form a highly interconnected porous nanowire network is of great demand for p-type sensing. Here, we have demonstrated synthesis of a very high aspect ratio (10^2-10^5) open network of interconnected hybrid nanocrystals–nanowire copper and copper oxide nanomaterials. The copper nanowire scaffold is employed to realize a porous and highly interconnected network of hybrid metal–metal oxide nanocrystal–nanowire structures. The structural and composition tunability of the hybrid nanomaterials is demonstrated. The hybrid copper–copper oxide nanowires exhibit enhanced gas/light sensing properties without any operating temperature. This may be attributed to enhanced medium diffusion due to the porous network of highly interconnected nanocrystal–nanowire structures.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Oxides of Cu predominantly exist in two forms. Both Cu₂O $(E_g = 2.14 \text{ eV}, \text{ direct})$ and CuO $(E_g = 1.2 \text{ eV}, \text{ indirect})$ are intrinsic p-type semiconductors which can be synthesized from the oxidation of Cu metal. This can be achieved by thermal oxidation or treatment in an oxygenated environment or by exposing Cu to specific chemical environments [1-4]. Both copper oxides are known for being useful in transistors, electrochemical cells, photovoltaic, sensors, field emission and other devices [5–12]. Among the studies done on metal oxides for gas sensor applications, understanding and improvement of gas sensing performance of n-type semiconductors has been the focus of research. On the other hand, there is a lack of fundamental research and understanding on p-type semiconductor sensing due to the difficulty in producing p-type semiconductors. One of the most common ways to produce p-type semiconductor nanowire is to dope with acceptor impurities. However, p-doped semiconductor nanowires achieved via this method may not have uniform doping and are generally poor in reproducibility and stability. Therefore, it is highly desirable to fabricate and study intrinsic p-type metal oxide nanowires for various sensing applications.

In addition, the synthesis of hybrid structure often requires multistep procedures like synthesis of nanostructures followed by physical deposition (sputtering, evaporation, etc) or impregnation of another type of nanostructure [13, 14]. Often, in the case of sputtering the coverage is not uniform due to directional impingement of atoms or line-of-sight deposition, which is expected to deposit more at the top than the bottom/shadowed areas. Moreover, good control of synthesis outcomes in terms of one-dimensional ultrahigh aspect ratio structure, good uniformity, tight size distribution as well as high yield of monodisperse copper/copper oxide nanowires often requires the additional use of physical or chemical templates. Physical templates such as anodic aluminum oxide (AAO) and ion etched polymer membrane have been used to grow copper oxide nanowires, while capping agents selectively adhering to crystalline facets such as surfactants and/or organic polymers have also been employed [15–17]. However, such methods have some disadvantages; for instance, there can be difficulty in controlling the structure and composition of the nanowires and/or a limitation in mass production. Therefore, a



Figure 1. SEM images of ultralong Cu nanowires at ((a) and (b)) low and ((c) and (d)) high resolutions. The nanowires are monodispersed and have diameters of \sim 50–200 nm.

facile synthesis approach for producing a high yield of uniform diameter, intrinsically p-type nanowires with good nanocrystal coverage is in great demand.

In this work, we report for the first time the synthesis of a very high aspect ratio $(10^2 - 10^5)$ open network of interconnected hybrid nanocrystals-nanowire copper and copper oxide nanomaterials. This process is scalable since it is based on facile and inexpensive hydrothermal synthesis. The tunability of the structure and composition of the hybrid nanomaterials can be demonstrated. In regard to the synthesis, most synthetic difficulties such as low aspect ratio structure, polydispersivity, poor crystallinity, low yield and process complexity are eliminated. The uniform coverage of hybrid copper-copper oxide nanocrystals-nanowires exhibits good gas/light sensing properties without any operating temperature. This translates to long term stability since operating sensors at high temperature (200-750 °C) results in subsequent structural instability [18, 19]. Furthermore, high temperature operation of sensors is not favorable in many cases, particularly in explosive environments [18, 19].

2. Experimental procedure

0.53 g of octadecylamine (ODA) and 0.13 g of anhydrous copper (II) chloride were added to 80 ml of deionized water and stirred for 5 min. The mixture was then repeatedly sonicated using an ultrasonic probe and stirred until a smooth, light blue emulsion was formed. The emulsion was then transferred to a teflon-lined autoclave and heated at 160 °C for 48 h. The supernatant could be easily separated from the Cu nanowires

as it was found that the latter formed into thick sheets which eventually settled at the bottom. The Cu nanowire sheets were then picked out using tweezers, and centrifuged twice in deionized water, hexane and ethanol. The Cu nanowire sheets were then suspended in ethanol. Following this the suspension was sonicated using an ultrasonic probe (130 W at 30% power) for 1 min to allow homogeneous dispersion of the nanowires. Oxidation of the Cu nanowires was carried out by heating them from room temperature to the desired temperature at a rate of $2 \,^{\circ}$ C min⁻¹ in a muffled furnace under atmospheric conditions, and subsequently leaving them to dwell for 6 h before removing them for further characterization. The temperatures used in this study range from 70 to 400 °C.

Scanning electron microscopy (SEM) observations were carried out on a FESEM JSM-6700F operating at 15 kV. Transmission electron microscopy (TEM) characterizations were conducted using a JEOL-2100 TEM with an accelerating voltage of 200 kV. X-ray diffraction (XRD) experiments were performed on a Bruker GADDS XRD using monochromatized Cu K α ($\lambda = 0.154$ nm) radiation under 40 kV and 40 mA. Raman spectra were acquired using a Renishaw 2000 Raman Spectrometer and a 50× objective with a 514 nm argon ion laser as the excitation source.

3. Results and discussion

Figure 1 shows the SEM images of the copper nanowires that were produced. A high yield of reddish sheet-like structures with the characteristic color of metallic copper were observed after the growth. It is important to note that the synthesis methodology allowed large-scale production and easy collection of nanowires since they settled to the bottom of the autoclave vessel due to their large quantity (weight). From low resolution SEM images (figures 1(a) and (b)), the nanowires are observed to be exceptionally long (hundreds of micrometers in length). The aspect ratio can be as high as 10^2-10^5 . High magnification SEM images reveal that the nanowires are smooth, monodispersed and rather uniform in diameter (50–200 nm) (figures 1(c) and (d)). The structural and chemical compositions detected using XRD, EDX and TEM clearly indicate the face-centered cubic phase of the copper nanowires. Evidently, the copper (II) chloride has been completely reduced by the octadecylamine into copper metal.

In order to optimize the calcination temperature to obtain the desired highly interconnected network of hybrid structure and composition nanomaterial useful for gas sensing applications, we have systematically studied the surface morphology transformation of Cu nanowire annealed at different temperatures. The copper nanowire used as the scaffold for the formation of hybrid structure and composition nanomaterial was a thicket bundle of nanowires which was highly intertwined. The SEM images of figure 2 show the copper nanowires subjected to various annealing temperatures of 200-450 °C in air. At relatively low annealing temperature of 200-300 °C, the structural integrity of the copper nanowires was intact since the nanowires were observed to remain onedimensional in structure (figures 2(a)-(d)). However, the initial relatively smooth surfaces of the copper nanowires had transformed to a rough texture. During the oxidation process, the copper nanowires react with oxygen to form nanocrystallites of 5-30 nm in diameter on the surfaces of the nanowires. The formation of nanocrystallites on the surface of the nanowires leads to rough texture and an increase in diameter. Further increase in annealing temperature to 400 and 450 °C, transformed the nanowire into a different morphology where the nanocrystallites were the dominant structures (figures 2(e)-(h)). Evidently, a higher annealing temperature promotes nanocrystallite growth. In addition, it is observed that the annealing temperature is sufficiently high to partially vaporize the core of the copper nanowires which then results in intermittent breakages of the ultralong nanowires (as indicated by the arrows in figure 2(f)). The end product exhibits highly agglomerated nanocrystallites with a porous nanowire core. It is also believed that the oxidation of the copper oxide nanowires induces strain on the whole structure which then causes breakages of the nanowires. However at 450 °C, severe sintering and necking processes set in and at the same time hollowing of the nanowire core leads to the collapse of the one-dimensional structure (figures 2(g)) and (h)). The sintered nanocrystallites form spherical and faceted nanocrystals which no longer conform to the onedimensional nanowire scaffold.

On the contrary, thermal annealing in vacuum at 300 (figures 3(a) and (b)) and $400 \,^{\circ}C$ (figures 3(c) and (d)) does not result in the formation of hybrid nanocrystals-nanowire structure, as seen in the SEM images. This suggests that the formation of nanocrystals on the nanowire scaffold is due to oxidation of the copper nanowires in air and the size

of the nanocrystals is observed to increase with annealing temperature. Thus, an annealing temperature up to 400 °C results in oxidation of the copper nanowire scaffold, which increases the structural porosity without completely collapsing the framework of one-dimensional highly intertwined hybrid nanostructures. The copper oxide nanocrystals at lower annealing temperature are conformed to the one-dimensional structure of the copper nanowire bundles to form hybrid copper oxide nanocrystallites on the copper metal nanowire. The hybrid structure (nanocrystals-nanowire) as well as the hybrid composition (copper oxide and copper core) based on the scaffold assisted thermal oxidation can produce a novel heterogeneous composition, increased porosity and a highly interconnected network. This is an advantageous structure for sensing applications for enhanced gas diffusion with high response and possibly room temperature operation. It is noted that the copper nanowire scaffold is necessary to realize the porous and highly interconnected network of hybrid metalmetal oxide nanowire-nanocrystal structures. Otherwise, a continuous and dense copper oxide thin film would be formed if a compact film and a non-one-dimensional structure were used as the scaffold.

TEM examination of as-grown Cu nanowires shows that there is the presence of a thin layer \sim 5–10 nm oxide sheath (figure 4(a)). This is in agreement with the XRD results (to be discussed later). At high resolution (figure 4(b)), the core of the nanowire is observed to be made up of a single crystal with an interplanar spacing of d = 2.08 Å, which is the Cu(111), while the sheath has d = 2.13 Å, Cu₂O(200). At oxidation temperature up to 200 °C, the thickness of the thin oxide sheath has increased tremendously such that it has transformed to core-shell structures (figure 4(c)). Similarly, only the presence of Cu (core) and Cu₂O (shell) is detected (figure 4(d)). The inset to figure 4(d) shows a high resolution image of the Cu₂O shell. However, at a higher oxidation temperature of above 400 °C, the core-shell structures collapsed to form irregularly shaped spherical and elongated nanocrystals (figure 4(e)). The formation of these highly crystalline nanocrystals is due to sintering and necking of the highly agglomerated nanocrystallites (figure 4(e) inset). The nanocrystals are observed to have a wide range of diameters consisting of numerous agglomerated nanocrystallites. The high resolution image of figure 4(f) shows that the nanocrystals are made up of Cu_2O and CuO(002) (d = 2.52 Å) matrix.

Raman spectroscopy and x-ray diffraction were used to determine the phases present at various annealing temperatures. Figure 5(a) shows the corresponding XRD spectra for different annealing temperatures. The diffraction peaks for Cu, Cu₂O, and CuO were referenced with JCPDS file Nos 04-0836, 78-2076 and 70-6827 respectively. Both the Cu(111) and Cu₂O(111) phases are found to be present on the as-synthesized copper nanowires. This agrees with the TEM observation of the presence of a thin sheath of Cu₂O on the Cu nanowires. However, at higher temperatures, both the Cu and Cu₂O(111) peaks decrease in intensity, and at 400 °C, the peaks are no longer discernible. At 300 °C, it can be observed that the Cu₂O(111) phase is still present and it constitutes the hump in the main peak of CuO(002), as indicated by an



Figure 2. SEM images of Cu nanowire annealed at ((a) and (b)) 200, ((c) and (d)) 300, ((e) and (f)) 400 and ((g) and (h)) 450 °C in air.

arrow. The intensity of the Cu diffraction peak decreases and eventually disappears at an annealing temperature of 400 °C. This observation complements the SEM observation of hollowing of the Cu nanowire core and the eventual collapse of the nanowire scaffold. On the other hand, the CuO phase is not formed until the oxidation temperature reaches 150 °C and its intensity increases with annealing temperature. From the XRD spectra, it is clear that CuO starts to form at temperatures as low as 150 °C, while Cu₂O is present even at room temperature. The occurrence of these oxides is at much lower temperature than the bulk Cu, where Cu₂O and CuO are formed at 200 and 300 °C respectively. The increased solubility of oxygen in one-dimensional Cu nanowires (high surface to volume ratio) has a critical role to play in the higher Cu oxidation kinetics as compared with the bulk counterpart [20]. The observed oxidation is due to an effective diffusion of O₂, which explains why formation of both Cu₂O and CuO occurs at lower temperatures as compared to bulk samples.



Figure 3. SEM images of Cu nanowire annealed at ((a) and (b)) 300 and ((c) and (d)) 400 °C in vacuum.

Figure 5(b) shows the Raman spectra obtained from the samples at different oxidation temperatures. The Raman broad peak centered at 590 cm⁻¹ has been attributed to various peaks at 516, 570 and 627 cm⁻¹. These peaks (except for 627 cm⁻¹) together with the 215 cm^{-1} peak constitute contributions from Cu_2O [21]. On the other hand at temperatures of 200 °C and above, three peaks at around 293, 340 and 627 cm^{-1} , all of which belong to the A_g , $B_g^{(1)}$ and $B_g^{(2)}$ optical phonon modes of CuO, are observed. The wavenumbers are lower than those reported for the bulk (298, 345, and 632 cm⁻¹, respectively) due to the size effects. A broad peak at 1100 cm^{-1} has been found to be present in bulk CuO crystals, as well as in metallic Cu treated at temperatures as high as 800 °C, as reported in [22]. Hence, given the prevailing conditions used in these works, we attribute the broad 1100 cm^{-1} peak to CuO. Quantum confinement effects such as the gradual downshift and broadening of the peaks were not observed, possibly due to the relatively large diameter of the nanowires.

The structural transformation from nanowire to coreshell and composition transformation from Cu to CuO were investigated by SEM, TEM, Raman and XRD, as depicted by the schematic diagram of figure 6. Our observations suggest that the core-shell copper nanowires with nanocrystallite shell structures are formed by solid-gas reactions involving diffusion of reactants at the elevated oxidation temperature. At room temperature and the low temperature annealing temperature of 100 °C, it appears that oxygen in the air reacts with the outer surfaces of the copper nanowires to produce a Cu₂O thin sheath (figure 6(a)). In this low temperature regime, the formation of Cu₂O occurs predominantly via short-circuit diffusion of Cu through the grain boundaries and defects [23]. The reaction appears to proceed via the diffusion of both copper and oxygen. Subsequently, oxidation takes place at the Cu_2O/O_2 interface between the oxygen in the air and the copper ions of the copper nanowire. Cu ions migrate from the copper through the Cu_2O (thin sheath) to the Cu_2O/O_2 interface. In essence, the oxygen diffuses from the outside to the inside while the copper moves in the opposite direction, according to Fick's first law. By considering the nanowire diameters before and after annealing, it is also plausible that the oxide grows both inwards and outwards from the original Cu nanowire surface, causing the overall nanowire diameters and the Cu core diameters to increase and decrease, respectively (figure 6(b)). At even higher temperature, CuO will form via the reactions [24]

$$2Cu + 1/2O_2 \rightarrow Cu_2O$$
$$3Cu_2O + 1/2O_2 \rightarrow 2Cu_3O_2$$
$$Cu_3O_2 + 1/2O_2 \rightarrow 3CuO.$$

Over time, this Kirkendall effect may presumably cause the copper vapors to effectively diffuse toward the surface to react with oxygen to form the core–shell or porous structure (figure 6(c)). At a higher temperature of 450 °C, sintering and necking of the nanocrystallite set in and cause the collapse of the core–shell structure (figure 6(d)).

Various sensors, namely gas, light and pH sensors, are fabricated using the copper nanowires oxidized at 400 °C. The device fabrication procedures are as shown in figure 7(a). The nanowires were processed into nanowire solution and then



Figure 4. TEM images of as-grown Cu nanowires ((a) and (b)) with the presence of a thin oxide sheath. Cu nanowires annealed at ((c) and (d)) 200 and ((e) and (f)) 450 °C to form core–shell and agglomerated nanocrystals respectively. The inset to (d) shows the high resolution image of a Cu₂O shell and the inset to (e) shows the necking of the nanocrystals.

aligned on a SiO₂ substrate via microfluidic assisted assembly. This method of alignment involves flowing the nanowire suspension through the 30 μ m wide microfluidic channel formed between a polydimethylsiloxane (PDMS) mold and a SiO₂ substrate (figure 7(a) (i)). The PDMS was then peeled back to reveal the aligned nanowires along the fluid flow direction (figure 7(a) (ii)). Platinum (Pt) contacts (100 nm thick) were then sputtered across the nanowire to fabricate the devices for gas and light sensing (figure 7(a) (iii)). On the other hand, fabrication of a pH sensor requires an additional processing step of a capping/passivation layer. A SiO₂ capping layer was used to passivate the metal electrodes, thus exposing only the nanowires to the pH solution (figure 7(a) (iv)). This prevents the pH solution from short-circuiting the device. Figures 7(b) and (c) show the low and high resolution

SEM images of the channels on a SiO_2 substrate where the nanowires have been aligned via PDMS microfluidic flow of the nanowire solution. The PDMS has clearly confined the flow of the nanowires such that the nanowires are aligned parallel to the channels. Figure 7(d) shows the typical SEM image of the Pt contact which has been sputtered on the nanowires for the subsequent electrical and sensing measurements.

I-V measurement was carried out on the fabricated twoterminal devices. The result of a voltage sweep on the device showed a linear behavior indicating good Ohmic contact at the junction (figure 8(a)). Both CuO and Cu₂O are ptype semiconductors with a work function of 4.8–5.2 eV, whereas platinum metal has a work function of 5.6 eV. Since the work function of platinum is larger than that of CuO, which is a p-type semiconductor, it is expected that the



Figure 5. (a) XRD and (b) Raman spectra of nanowires annealed in air at various temperatures.



Figure 6. Schematic diagram of the structural transformation. (a) Formation of the thin Cu_2O sheath. (b) Inward and outward Cu_2O growth, resulting in the overall nanowire and Cu core increasing and decreasing, respectively. (c) Kirkendall effect to form the core–shell structure. (d) Sintering and necking to form agglomerated nanocrystals.



Figure 7. (a) Fabrication process of microfluidic assisted assembly of nanowires. (b) Low and (c) high magnification of the nanowires aligned on a SiO_2 substrate. (d) A typical single nanowire device with Pt contacts.



Figure 8. (a) I-V measurement of the two-terminal device. (b) H_2 , (c) light and (d) pH sensing of a single nanowire device.

contact should display Ohmic behavior. The hydrogen gas sensing performance of the CuO nanowire was tested at room temperature by applying a voltage bias of 2 V and measuring the change in resistance of the nanowire when it was exposed to hydrogen gas. The device was first exposed to clean dry air (CDA) for 300 s before exposing it to hydrogen gas of three concentrations, namely 100, 500 and 2500 ppm for the next 600 s (figure 8(b)). This injection of hydrogen caused the resistance of the device to increase and the change in resistance was greater at higher concentrations of hydrogen gas. This increase in resistance in hydrogen gas ambient revealed the p-type semiconductor property of the copper oxide nanowires.

The hydrogen gas sensing mechanism of the p-type oxide nanowires is explained as follows: upon exposure to reduction, the negatively charged oxygen molecules which were preadsorbed on the surface of the nanowires will react with the incoming hydrogen molecules. This reaction generates free electrons which will neutralize the hole states near the surface of the p-type nanowires. As a result, the total carrier density was reduced leading to an increase in the resistance of the copper oxide nanowires.

The sensitivity of the device was calculated by taking the percentage of the change in resistance over the steady state resistance in the clean dry air environment. At a hydrogen gas concentration of 100 ppm, the device displayed a sensitivity of 2.5%, which was increased to 14.7% at a concentration of 500 ppm. The sensitivity was further increased to 29.7% when the concentration was 2500 ppm. This value is quite impressive considering that the number of copper oxide nanowires being tested was very small. Apart from that, it should be noted that these experiments were conducted at room temperature, making them suitable for gas detection in ambient environments.

Light detection or photon detection is another area with a wide range of applications. For instance, it can be used in flame detection, military applications and space communication. The light detection ability of CuO nanowires was tested with a white LED. The device was subjected to a voltage bias of 3 V and the resistance of the device was measured in both dark and illuminated conditions, alternating every 400 s. The device exhibited high resistance in the dark and the resistance dropped greatly when exposed to white LED light, as shown in figure 8(c). This reduction in resistance is due to the generation of excess electron-hole pairs upon absorption of the photons. The sensitivity of the photodetection was 79% and it can be clearly seen from the sharp transition of the resistance from dark to illuminated environment that the CuO nanowire has a very fast response towards photons. The response was repeatable, as shown in the graph, where the same pattern was observed for another cycle. The time-dependent photoresponse of the CuO nanowires was investigated with a digital oscilloscope. The nanowire was biased at 2 V and illumination was provided using a white LED in conjunction with a function generator. When subjected to illumination using a 230 Hz square waveform, the photoresponse showed first-order exponential growth with an estimated time constant of $\tau_g = 0.35$ ms and a first-order exponential decay with time constant of $\tau_d = 0.92$ ms. The device has an estimated response time of 1.1 ms.

Finally, the pH sensor device was tested with pH solutions of pH 2, 7 and 10 to study its electrical response towards pH changes at room temperature. From figure 8(d), it can be clearly seen that the resistance of the CuO nanowires changed significantly in solutions of different pH. The nanowires showed the lowest resistance at pH 2 and the highest resistance at pH 10. This shows that CuO can exhibit different levels of resistance for different pH values, and its possibility to function as a pH sensor for biomedical applications. When the device is immersed in the solution, the protons in the solution attach to the surface of the CuO nanowires. A proton is an electron acceptor, hence the protons on the surface will induce generation of positive holes in CuO, reducing the resistance of the nanowires. Therefore, a lower pH value would increase the generation of electron-hole pairs in p-type CuO, exhibiting a lower resistance, while a higher pH value results in a higher resistance. However, detailed elucidation of the principle of pH sensing using the device remains as a subject for future study.

4. Summary

Ultralong copper nanowire with copper oxide nanocrystals core-shell structures were successfully synthesized and characterized. An annealing temperature up to 400 °C results in the formation of copper oxide nanocrystals on a onedimensional copper nanowire scaffold. The hybrid structure (nanocrystals-nanowire) as well as the hybrid composition (copper oxide and copper core) based on the scaffold assisted thermal oxidation has produced a novel heterogeneous composition with a highly interconnected network for sensing applications. Various sensors, namely gas, light and pH sensors, were fabricated which showed good response at room temperature sensing. This may be attributed to the enhanced gas/liquid diffusion due to the increased open network access of highly interconnected nanowires.

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