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Controllable Fabrication and Electrical Performance of Single Crystalline Cu_2O Nanowires with High Aspect Ratios

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ABSTRACT

We report a facile, solution-phase route to large-scale fabrication and characterization of single crystalline Cu_2O nanowires with controllable diameter, different morphologies, and high aspect ratios. The synthesis of Cu_2O nanowires is achieved by the reduction of cupric acetate with *o*-anisidine, pyrrole, or 2,5-dimethoxyaniline under hydrothermal conditions. The electrical properties of individual Cu_2O nanowires have been examined by *I*−*V* characteristics. The output properties of Cu_2O/poly(2,5-dimethoxyaniline) core/shell nanowires show n-type characteristics and improved conductivity, while those of Cu_2O nanowires are linear. The results from this study provide a low-cost, naturally abundant nanostructured material for use in electronic devices.

Cuprous oxide (Cu_2O) is a typical p-type direct band gap semiconductor with a band gap of 2.17 eV[1] and has potential applications in solar energy conversion,[2] electrode materials,[3] sensors,[4] and catalysis.[5,6] It has also been found that high-intensity photoexcitation can give rise to the coherent propagation of Cu_2O excitons through Cu_2O solid owing to the large exciton binding energy of 150 meV.[7] Single crystalline Cu_2O with nanoscale dimensions could be anticipated to have spatially confined excitons and thereby increase their concentration. The large excitonic binding energy offers the possibilities to observe excitonic features in the absorption and luminescence spectrum.[8,9] Such unique electronic structures of Cu_2O spur a growing amount of interest in its single crystalline nanostructures. Recently, different Cu_2O nanostructures including nanospheres,[9,10] naocubes,[11] and nanowires,[12,13] have been synthesized with a variety of techniques.

One-dimensional (1D) nanomaterials such as nanowires,[14] nanotubes,[15] and nanobelts[16] are highly attractive building blocks for devices because of the inherent anisotropies and efficient transport of electrons and excitons within the smallest dimension. Although the electronic features of Cu_2O determine that 1D Cu_2O nanostructures are most promising for their use as components in nanoscale electronic devices, not until recently have limited techniques that allow one to prepare Cu_2O nanowires been developed.[12,13] Cuprous oxide is isotropic with a primitive cubic crystal structure. Thus, there are great challenges to achieve anisotropic growth of Cu_2O molecules to form 1D single crystalline nanostructures in the absence of templates with 1D-confined structures. As a matter of fact, previous efforts on 1D Cu_2O nanostructures yield polycrystalline, bent, entangled nanowires with low aspect ratios. Yet, the yields are not high.

Herein, we have developed novel solution-based syntheses of bulk quantities of single crystalline Cu_2O nanowires with tunable diameter and morphology. We achieve uniform Cu_2O nanowires in diameter through the reduction of cupric acetate ($Cu(Ac)_2$) with *o*-anisidine, pyrrole, or 2,5-dimethoxyaniline as the reductant in dilute aqueous solutions under hydrothermal conditions. More importantly, the core/sheath structured Cu_2O/poly(2,5-dimethoxyaniline) nanowires can be available in large quantities. The corresponding oxidative polymerizations of these monomers dictate the well-defined 1D growth of Cu_2O single crystals. Consequently, no additional structure-directing reagents are required. In this work, we also demonstrate the electrical performances of individual Cu_2O nanowire devices at different temperatures. The *I*−*V* characteristics of the Cu_2O and Cu_2O/poly(2,5-dimethoxyaniline) core/sheath nanowire devices were compared. Despite the ohmic behavior of Cu_2O nanowires on gold contacts, the output properties of the single Cu_2O/poly(2,5-dimethoxyaniline) nanowire devices exhibit n-type characteristics and enhanced conductivity.

The Synthesis of Single Crystalline Cu_2O Nanowires. The redox reaction between Cu^{2+} and the above-mentioned

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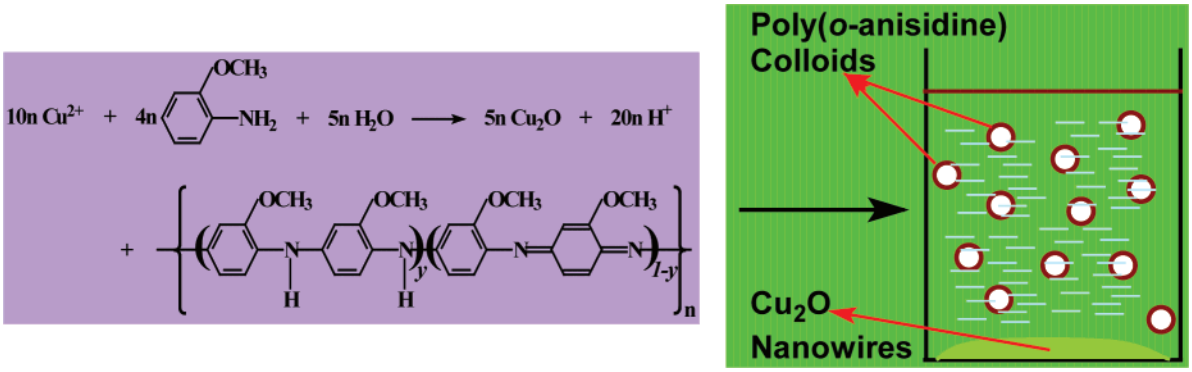

Figure 1. Schematic diagram depicting the formation process of Cu_2O nanowires synthesized with *o*-anisidine as the reductant in autoclave.

monomers does not occur in dilute solutions of the starting reactants even at 120 °C and under normal atmospheric pressure because the oxidizing ability of the Cu^{2+} ion is weak. To implement the redox reactions for the preparation of Cu_2O nanowires, the experiments should be carried out at temperatures above 110 °C under hydrothermal conditions. Typically, 0.10−0.30 g of $Cu(Ac)_2$ was dissolved in 40 mL of deionized water. Afterward, to this solution was added 10 mL of an aqueous solution of *o*-anisidine or pyrrole (0.10 M), which invokes the reaction mixture to become dark green or olive green owing to the coordination of Cu^{2+} and *o*-anisidine or pyrrole. The reaction mixture was transferred to a 50 mL autoclave. The autoclave was sealed and maintained at 140−180 °C for 10 h or at 250 °C for 5 h and subsequently cooled to ambient temperature naturally. In the case of the reductant 2,5-dimethoxyaniline, the synthetic procedure is similar to that described above. However, taking the low solubility of 2,5-dimethoxyaniline in water at ambient temperature into account, 2 mmol of 2,5-dimethoxyaniline was dissolved in 40 mL of heat-deionized water (60 °C), and then 10 mL of 0.05 M $Cu(Ac)_2$ was added. This reaction mixture was loaded in an autoclave and maintained at 180 °C for 10 h.

Interestingly, the oxidative polymerization initiated by Cu^{2+} results in poly(*o*-anisidine), poly(pyrrole), or poly(2,5-dimethoxyaniline) forming stable colloidal solution. The as-prepared Cu_2O nanowires are in the form of yellow green or brown (using *o*-anisidine (250 °C) or 2,5-dimethoxyaniline as the reductant) sediments at the bottom of autoclave. Particularly, when *o*-anisidine is used as the reductant, voided or solid spherical poly(*o*-anisidine) colloids are yielded.[17] Figure 1 depicts the chemical reaction equation and the distribution of the products in the reaction vessel. The sediments (Cu_2O nanowires) could be readily isolated by pouring off the supernatant colloidal polymer solution. The isolated sediments were washed with ethanol for many times and dried.

Figure 2 shows the powder X-ray diffraction (XRD) pattern of the sediments obtained with *o*-anisidine as the reductant, in which a set of Bragg peaks can be perfectly indexed as the pure cubic cuprite structure ($Pn\bar{3}m$, JCPDF no. 78−2076) with lattice constant $a = 4.267$ Å. Scanning electron microscopy (SEM) overviews reveal that the Cu_2O sediments are long, straight nanowires (Figure 3a). The length

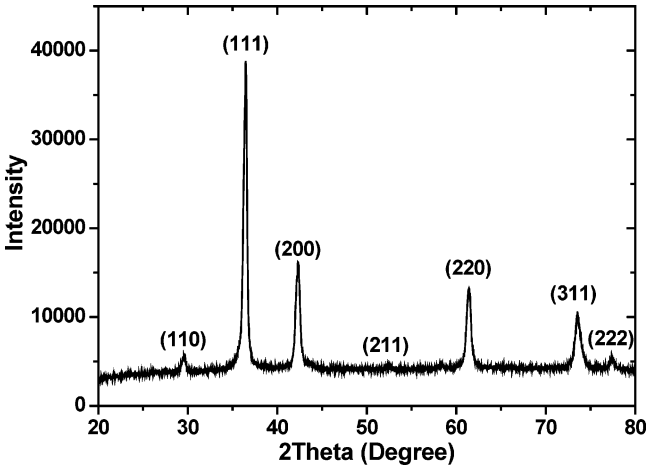

Figure 2. Powder X-ray diffraction pattern of the as-prepared Cu_2O nanowires.

of the Cu_2O nanowires ranges from tens of micrometers to more than a hundred micrometer. The corresponding transmission electron microscopy (TEM) image in Figure 3c displays that the diameters of the Cu_2O nanowires are typically 40−70 nm and uniform along their length. In addition, small burrs grow on the surfaces of Cu_2O nanowires. Such branched nanowires are highly desirable for the improvement of the performance of nanowire-based sensors[18] and photovoltaic devices[19] owing to an increase in the wire surface area. The nanowires' length and diameter are independent of hydrothermal reaction time and temperature. The yield of the reaction at 140−180 °C is ca. 85% based on the weight of the isolated nanowires, and the reaction can be easily scaled up to gram scale as 1.0 g of nanowires can be obtained from a 500 mL synthesis by the reduction of 0.038 M $Cu(Ac)_2$ with 0.02 M *o*-anisidine. Surveys of numerous samples synthesized at different temperatures using selected area electron diffraction (SAED) and high-resolution TEM (HRTEM) indicate that the Cu_2O nanowires are consistently single crystal. HRTEM images reveal most nanowires with well-resolved (111) and (110) lattice planes (Figure 3d,e). The insets in Figure 3d,e illustrate the corresponding SAED patterns. HRTEM and the assignments of SAED consistently indicate that the preferential growth direction for Cu_2O nanowires is [110].

In contrast, the morphology of Cu_2O nanowires changes as increasing the reaction temperature to 250 °C, while the

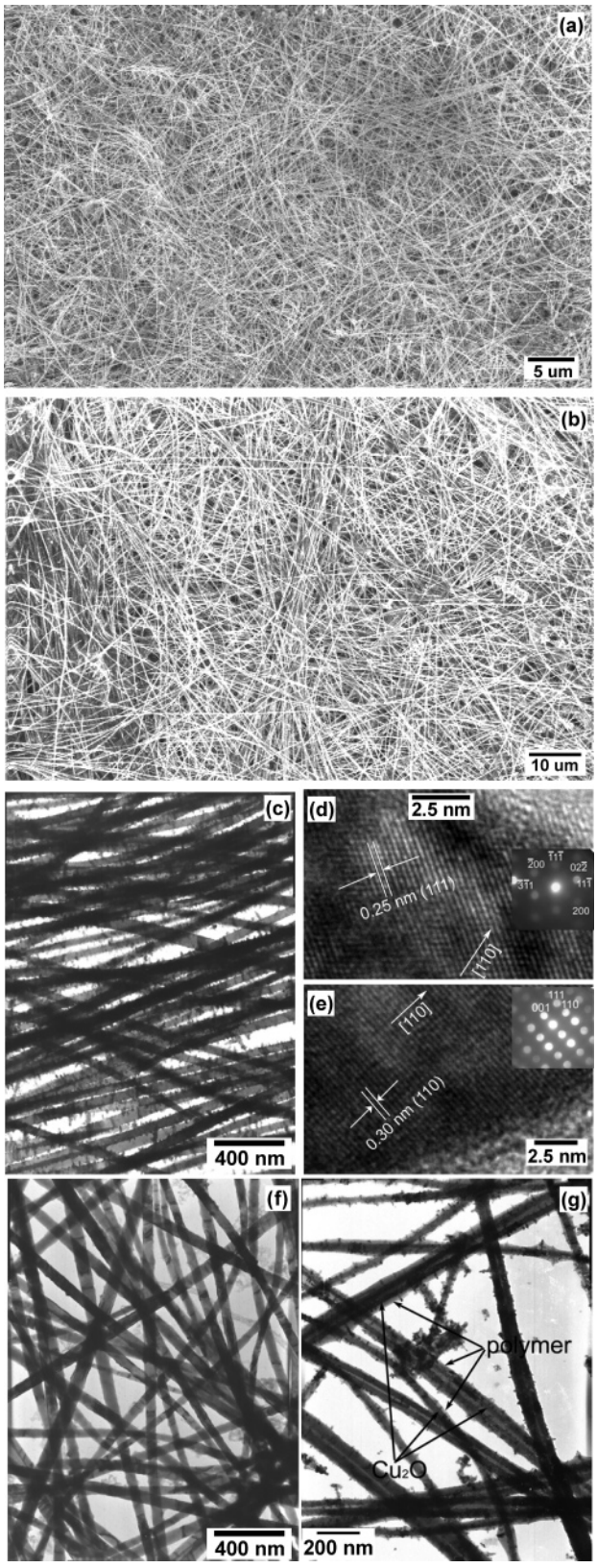

Figure 3. SEM images of Cu_2O nanowires synthesized at 180 °C with (a) *o*-anisidine and (b) pyrrole as the reductant. (c) TEM and (d,e) HRTEM images of the Cu_2O nanowires from the sample in panel a. The insets show the corresponding SAED patterns. (f) TEM image of Cu_2O nanowires synthesized at 250 °C with *o*-anisidine as the reductant. (g) TEM image of Cu_2O/poly(2,5-dimethoxyaniline) core/sheath nanowires synthesized at 180 °C with 2,5-dimethoxyaniline as the reductant.

length and diameter of the nanowires remain unchanged. The surface of the Cu_2O nanowires becomes smooth because no burrs grow on the nanowires (Figure 3f). The goal of this synthesis is that straight nanowires with minimal surface roughness may be useful as high-performance FETs for the high carrier mobilities.[20] Likewise, XRD measurements, TEM observations, and ED patterns confirm that single crystalline Cu_2O nanowires are also available in bulk quantities with pyrrole or 2,5-dimethoxyaniline as the reducing reagent. If pyrrole is utilized as the reductant, the diameter of the Cu_2O nanowires increases to 130−170 nm (Figure 3b). It can also be seen that the length of most Cu_2O nanowires exceeds one hundred micrometers. In particular, use of the reductant 2,5-dimethoxyaniline allows us to synthesize Cu_2O/poly(2,5-dimethoxyaniline) core/sheath nanowires (Figure 3g). The core/sheath nanowires are tens of micrometers in length with a 20−50 nm diameter core of Cu_2O and a 2−25 nm thick outer sheath of polymer. The Cu_2O core can be etched out with 1.0 M hydrochloric acid over 9 h, leading to yielding poly(2,5-dimethoxyaniline) nanotubes in the form of precipitates. The TEM image in Figure 4a clearly demonstrates the tubular morphology of poly(2,5-dimethoxyaniline). The outer diameter and wall thickness are 30−70 and 5−15 nm, respectively, in good agreement with the corresponding values obtained from Figure 3g. The Fourier transform infrared (FT-IR) spectrum confirms that this tubular polymer is in the form of emeraldine base, as shown in Figure 4b.[21]

Concerning the anisotropic growth mechanism for the formation of single crystalline Cu_2O nanowires, we suggest that the polymers formed in situ selectively adsorb onto the crystallographic planes of Cu_2O. We speculate that the adsorption of the polymers on Cu_2O crystallites is based on the chemical interaction between the given Cu_2O facets and the ligand amine group (−NH−). However, our studies reveal that not all derives of *o*-anisidine are effective in producing Cu_2O nanowires. Instead, when aniline, 2-methylaniline, or 2,6-dimethylaniline is used as the reductant under otherwise conditions identical with those for synthesizing Cu_2O nanowires, spherical Cu_2O nanoparticles with diameters of 3−20 nm are obtained. Therefore, the key to controlling 1D growth of the Cu_2O nanocrystals is the type/site of ortho-group in the reductants. The size and/or position of ortho-group related to the ligand amine group can determine the selectivity of the polymer adsorption due to the steric effects. Note that the diameter of the Cu_2O nanowires decreases with the increase of the number of methoxy group in the reductant molecules (i.e., the $-OCH_3$ number ratio of pyrrole/*o*-anisidine/2,5-dimethoxyaniline is 0:1:2). This result indicates that increasing the number of methoxy group makes the steric effects more intensive, being responsible for the higher adsorption selectivity. Accordingly, the growth of the given Cu_2O facets is effectively suppressed. On the other hand, this means the stronger chemical adsorption of the amine group on the Cu_2O facets due to the donating electron effect of the methoxy group thus further suppressing the transverse growth of the Cu_2O nanowires. It is the reason why the Cu_2O/poly(2,5-dimethoxyaniline)

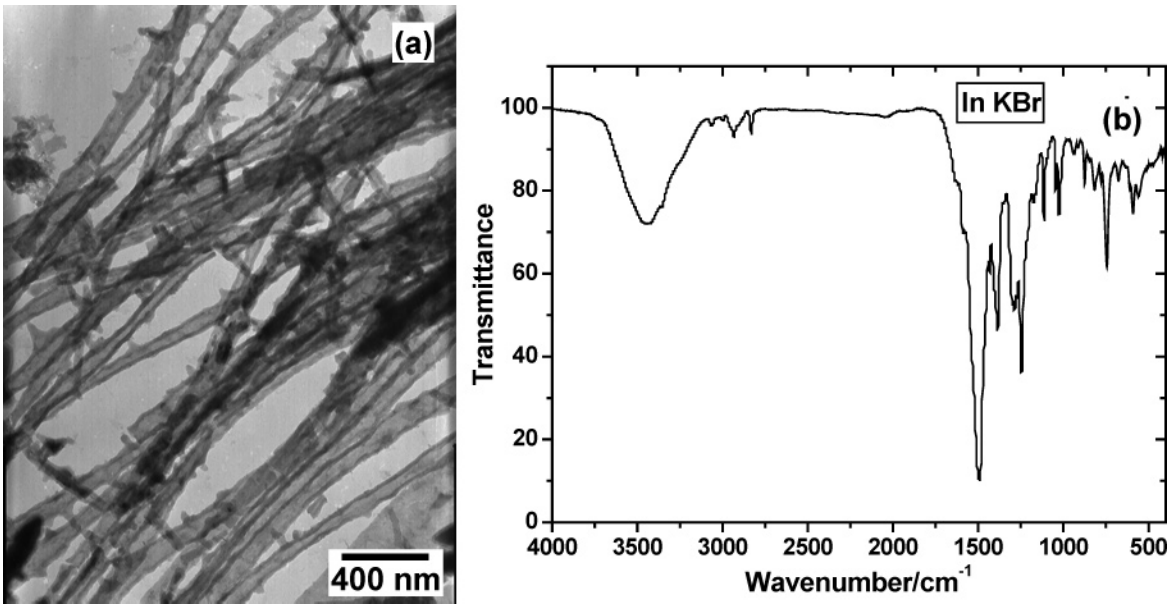

Figure 4. (a) TEM image of poly(2,5-dimethoxyaniline) nanotubes obtained after etching out the Cu_2O nanowire cores. (b) FT-IR spectrum of poly(2,5-dimethoxylaniline) nanotubes.

core/sheath nanowires are formed after 2,5-dimethoxyaniline is polymerized to give two *ortho*-methoxy groups on each segment of a pair of amine-linked benzene rings.

The Electrical Transport Properties. Typically, the electrical transport properties of the single crystalline Cu_2O nanowires prepared with *o*-anisidine as the reductant at 180 °C were studied on devices consisting of individual nanowires. A standard electron-beam lithography technique was used to design pairs of metal electrodes on a silicon substrate capped with a 50 nm silicon dioxide layer (the SiO_2/Si substrate), followed by metal deposition of Ti/Au (10 nm/100 nm) by electron beam evaporation to complete the device structure. The Cu_2O nanowires were transferred onto the prefabricated electrodes by touching the nanowire sample with the electrodes, by which only a single Cu_2O nanowire lying across two electrodes can be easily made. The electrical properties of individual nanowires in more than 20 devices were investigated in vacuum (1.0×10^{-3} Pa) at room temperature and high temperatures. A linear current (I_{ds}) versus voltage (V_{ds}) curve was observed in all devices measured, indicating the ohmic nature of the contact with Au electrode. For a p-type Cu_2O semiconductor, the ohmic contact is due to the work function of the contact metal (Au), which is larger than that of Cu_2O.[22] Figure 5a illustrates the $I_{ds}-V_{ds}$ curves from a randomly selected sample at different temperatures. The inset of Figure 5a shows a SEM image of a bottom-contact Cu_2O nanowire device in which a Cu_2O nanowire spans the source-drain gold electrodes. By means of the measured resistance value of the device, the cross-section size (73 nm), and the length (1.3 μm) of the Cu_2O nanowire (measured by SEM imaging), we can calculate the resistivity to be 4.7×10^4, 1.8×10^4, and 0.8×10^4 Ω·cm at 298, 373, and 450 K, respectively. It can be seen that the resistivity of Cu_2O nanowires decreases with increasing temperature. This variance trend of resistivity with temperature is observed in all Cu_2O nanowire devices. This behavior is consistent with the expected resistivity−temperature relationship for semiconductors.

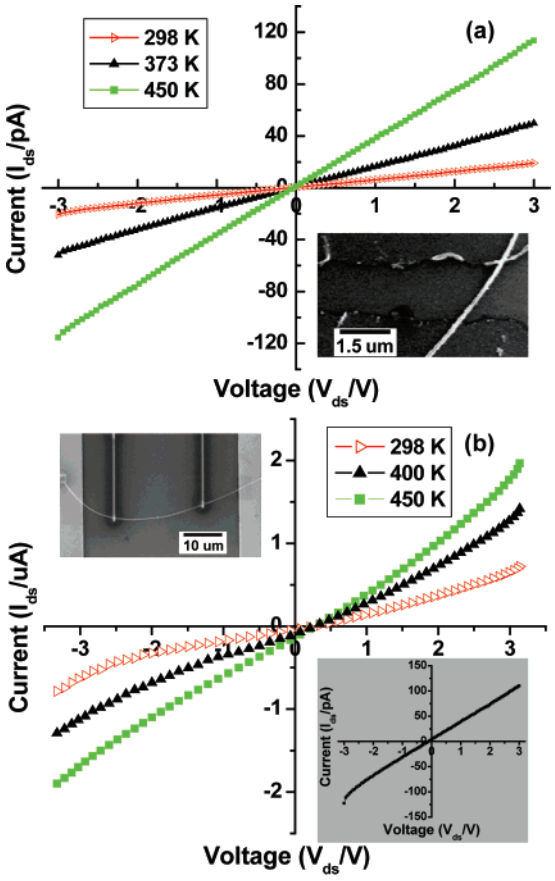

Figure 5. $I_{ds}-V_{ds}$ characteristics of (a) an individual single crystalline Cu_2O nanowire and (b) an individual Cu_2O/poly(2,5-dimethoxyaniline) core/sheath nanowire device measured at different temperatures. Insets in panels a and b are the SEM images of a Cu_2O nanowire and a Cu_2O/poly(2,5-dimethoxyaniline) core/sheath nanowire device and the room-temperature $I_{ds}-V_{ds}$ curve of poly(2,5-dimethoxyaniline) nanotubes, respectively.

When the same bias was applied to a Cu_2O/poly(2,5-dimethoxyaniline) core/sheath nanowire device at different temperatures, nonlinear n-type $I_{ds}-V_{ds}$ characteristics and increased electric conductivity were observed, as shown in Figure 5b.[23] To reduce the contact resistance, individual Cu_2O/poly(2,5-dimethoxyaniline) nanowires were contacted with four platinum pad electrodes (0.8 μm thick) that were fabricated on a SiO_2 (500 nm)/Si substrate by using focused ion-beam-induced platinum deposition (Figure 5b, upper left inset). The observed conductivity of the Cu_2O/poly(2,5-dimethoxyaniline) nanowire increases with temperature and is several orders higher than that of the Cu_2O nanowires. Compared to the single Cu_2O nanowire device, these changes were detected in 80% of over 20 measured Cu_2O/poly(2,5-dimethoxyaniline) nanowire devices. To understand the changes, we also examine the $I_{ds}-V_{ds}$ characteristics of the poly(2,5-dimethoxyaniline) nanotubes prepared by etching out Cu_2O nanowires. The curve illustrates that the electrical behavior of the poly(2,5-dimethoxyaniline) nanotubes treated by HCl is similar to that of single crystalline Cu_2O nanowires (Figure 5b, lower right inset). Therefore, the enhanced conductivity and the change of output properties of the Cu_2O/poly(2,5-dimethoxyaniline) nanowires compared to pure Cu_2O nanowires may not result from the poly(2,5-dimethoxyaniline) shell itself.

The improved electrical properties of the Cu_2O/poly(2,5-dimethoxyaniline) nanowires may be attributed to the covalent bonding between the active amine group of poly(2,5-dimethoxyaniline) and Cu_2O as well as the conjugated segments comprised of continuous overlapping orbits (N═Q═N, Q = quinoid ring) in the polymer backbone, which act as the electron donors. As a result, poly(2,5-dimethoxyaniline) can provide electrons to the inner Cu_2O nanowires to produce an abundance of mobile or "carrier" electrons in the material. At this point, electrons are the majority carriers. Consequently, the Cu_2O/poly(2,5-dimethoxyaniline) nanowires exhibit the electrical properties of an n-type semiconductor. Actually, the increased conductivity may be also associated with the coating of the polymer. In a recent report by Wong and Wang et al.,[24] the increased conductivity of the organic molecules modified ZnO nanobelts was demonstrated. They proposed that the enhancement in conductivity of the ZnO nanobelts treated with small organic molecules is due to the decreases of both Schottky barrier height and the contact resistance on the basis of the formation of dipole. In our experiments, a dipole may likewise form at the interface of Cu_2O/polymer as a consequence of the covalent bonding between them.[25] Such a dipole layer can reduce Schottky barrier height and mediate the transport of electrons from the metal contact to semiconductor, leading to a remarkable decrease in the contact resistance. On the other hand, the presence of electron donors, that is, amine groups and the extended delocalized bonds in poly(2,5-dimethoxyaniline) chains, increases the carrier density, thereby inducing a further increase in conductance.

In conclusion, we have described solution-phase syntheses of single crystalline Cu_2O nanowires under hydrothermal conditions, which have the merits of low-cost, large-scale production, and facile manipulation. The diameter and morphology of Cu_2O nanowires can be easily tuned by the choice of reductant type and synthetic temperature. Moreover, the unique Cu_2O/poly(2,5-dimethoxyaniline) core/sheath nanowires are fabricated. The electrical transport properties of the as-synthesized single crystalline Cu_2O and Cu_2O/poly(2,5-dimethoxyaniline) core/sheath nanowires present ohmic and n-type characteristics, respectively. The conductivity of the Cu_2O/poly(2,5-dimethoxyaniline) nanowires is dramatically enhanced in comparison to that of single crystalline Cu_2O nanowires. The coating of poly(2,5-dimethoxyaniline) sheath plays an important role in varying electrical output properties of the Cu_2O nanowires. Such single crystalline Cu_2O nanowires are very desirable in field-effect transistor applications.

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