Research Article

Facile Synthesis of Colloidal CuO Nanocrystals for Light-Harvesting Applications

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CuO is an earth-abundant, nontoxic, and low band-gap material; hence it is an attractive candidate for application in solar cells. In this paper, a synthesis of CuO nanocrystals by a facile alcoholothermal route is reported. The nanocrystals are dispersible in a solvent mixture of methanol and chloroform, thus enabling the processing of CuO by solution. A bilayer solar cell comprising of CuO nanocrystals and phenyl-C61-butyric acid methyl ester (PCBM) achieved a power conversion efficiency of 0.04%, indicating the potential of this material for light-harvesting applications.

1. Introduction

Solution-processable solar cell technologies can enable the realization of low-cost and high-throughput photovoltaic production [1]. While much work has previously focused on organic semiconductors [1], colloidal inorganic semiconductor nanocrystals (NCs) are starting to attract attention for photovoltaic applications [2]. NCs have the advantages of being solution-processable, capable of absorbing a large fraction of the solar spectrum, and tunable band-gap due to quantum-confinement effects [2]. While early NC solar cell work was based on CdSe [3] and CdTe [4], impressive results have been achieved with CuInSe₂ [5], PbSe [6–10], and PbS [11–15] NCs in recent years. In particular, Sargent and coworkers have reported a PbS NC/TiO₂ bi-layer solar cell with a power conversion efficiency (PCE) as high as 5.1% [15].

The above-mentioned materials may be good test-beds for studies of NCs as photovoltaic materials but may not be feasible candidates for wide-spread deployment due to toxicity and availability—Cd and Pb are toxic heavy metals, while In and Te are among the least abundant elements in the Earth's crust [16]. It is thus desirable to explore other alternative solar cell materials. Copper- and iron-based semiconductors have emerged as attractive materials from an analysis by Wadia et al. based on abundance and cost [17].

For instance, Wu et al. [18] recently reported a Cu₂S NC-based solar cell with a promising PCE of 1.6%. Copper (I) oxide (Cu₂O) and copper (II) oxide (CuO) are also attractive candidates for light-harvesting applications due to their band gap energies of 1.4 eV (indirect) for CuO [19] and 2.0 eV (direct) for Cu₂O [20] that are quite close to the ideal band-gap for a single junction photovoltaic cell estimated from detailed balance [21]. Cu₂O has been investigated as a solar cell material for several decades [22], with recent reports of PCE up to 2.0% [23–25]. CuO has been employed in photo-electrochemical cells [26, 27] and as a cathode for dye-sensitized solar cells [28]. The use of CuO as the active layer in solid state solar cells has, to the best of our knowledge, not yet been investigated, and is the focus of this work. From a detailed balance analysis, CuO with a band gap of 1.4 eV can reach an ultimate solar cell efficiency of almost 30%, significantly higher than the 20% limit for Cu₂O (2.0 eV band gap) [21].

Copper oxide NC syntheses via various routes have been reported in the literature [29–44]. Relatively few of these reports, however, discuss the dispersibility of copper oxide NCs in common solvents [41–44], which is critical for solution-based processing of NC thin film absorber layers. In particular, Yuhas and Yang [43] and Hung et al. [44] reported solar cells based on films spin-coated from Cu₂O NC solutions, with PCE from 0.05% to 0.14%. In this

paper, the synthesis of colloidal CuO NCs by a facile alcohothermal method is reported. The NCs are characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and UV-visible absorption spectroscopy. Finally, as a proof of concept, a bilayer solar cell-based on CuO and phenyl-C₆₁-butyric acid methyl ester (PCBM) is demonstrated.

2. Experimental

2.1. Synthesis of CuO NCs. 0.29 g of copper (II) acetate (Sigma Aldrich) was added to 30 mL of reagent alcohol (Sigma Aldrich) under vigorous stirring. 1 mL of deionized (DI) water was added, and the mixture was heated to 75°C. In a separate container, 1.3 mL of 25% tetramethylammonium hydroxide (TMAH) in methanol (Sigma Aldrich) was added to 10 mL of reagent alcohol. After 15 minutes of stirring, when the copper acetate has fully dissolved, the TMAH solution was gradually added over 5 minutes in regular intervals. The reaction was allowed to proceed at 75°C for 60 minutes, and the resultant product was collected by precipitation with hexane and then centrifuging at 3750 rpm for 5 minutes.

2.2. NC Characterization. TEM samples were prepared by drop-casting very dilute NC suspensions in methanol onto carbon grids (Electron Microscopy Sciences), and images were taken using an FEI T12 Spirit TEM. X-ray diffraction was performed on a Bruker General Area Detector Diffraction System (GADDS). A Thermo Scientific Nicolet iS10 FT-IR spectrometer was used to perform FTIR spectroscopy on NC samples drop-casted from methanol. These NCs have been washed and centrifuged three times with reagent alcohol to get rid of unreacted precursors. UV-visible absorption spectroscopy was performed using a Shimadzu UV-3101PC UV/Vis/Near-IR Spectrophotometer. All film thickness measurements were done using a Tencor P10 Profilometer.

2.3. Solar Cell Fabrication and Testing. Solar cells were fabricated on prepatterned indium tin oxide (ITO) coated glass substrates (Kintec, Hong Kong), which were cleaned by sonication in a mild detergent, rinsed in deionized water, dried in a nitrogen stream, and treated with a 10-minute UV-ozone exposure. CuO NCs were dispersed in a solvent mixture of 2:1 chloroform and methanol at a concentration of $\sim 10 \text{ mg mL}^{-1}$, and then spin-coated on top of the ITO at 2000 rpm to give a film $\sim 40 \text{ nm}$ thick. A cell with a thicker CuO layer ($\sim 70 \text{ nm}$) was also fabricated by performing the spin-coating step 3 times. This is possible because the underlying layer is not completely dissolved during the spin-coating of subsequent layers. PCBM solution (20 mg mL^{-1} in chloroform) was then spin-coated on top of the CuO at 2000 rpm to give a film $\sim 120 \text{ nm}$ thick. Finally, $4 \text{ \AA}$ of CsF and $400 \text{ \AA}$ of Al were thermally evaporated under high vacuum ($\sim 10^{-6} \text{ Torr}$) to form the cathode for the devices. A shadow mask was used in the evaporation to define a device-active area of 3 mm^2 . Control PCBM-only solar cells (without CuO) were also fabricated.

Device current-voltage curves were obtained with a Keithley 236 source-measurement-unit (SMU) in the dark and as well as under AM 1.5 100 mW cm^{-2} illumination from a Solar Light 16S-002 solar simulator. Light output power was calibrated using a Newport 818P-010-12 thermopile high power detector, which has a flat response over a broad spectral range. EQE measurements were performed using a Newport 1000 W xenon lamp coupled to an Oriel Cornerstone 260 1/4 m monochromator as the light source, a Keithley 236 SMU to measure short circuit current, and a Newport 918D-UV3-OD3 low power detector to monitor the light intensity.

3. Results and Discussion

The CuO NC synthesis is modified from a previously reported method for the synthesis of soluble zinc oxide NCs [9, 45]. Copper (II) acetate, $\text{Cu}(\text{OAc})_2$, was dissolved in reagent alcohol and then reacted with tetramethylammonium hydroxide (TMAH) to form copper (II) hydroxide. CuO was then formed through heating:

Figure 1(a) shows TEM image of CuO NCs, in which it can be seen that they have a rather large size distribution of around 4–5 nm. The relatively broad size distribution of the CuO NCs is likely the result of the nucleation and growth dynamics of the reaction. Unlike the “hot-injection” synthesis [46], the simplified alcohothermal method lacks a single well-defined nucleation event leading to broader NC diameter distributions. X-ray diffractograms (Figure 1(b)) of the NCs are consistent with the literature values for CuO (JPCD no. 05-0661). It was observed that the addition of a small amount of deionized (DI) water (3% by volume) during the CuO synthesis produced NCs with more well-defined and narrower XRD peaks as compared to NCs synthesized without water. In previously reported syntheses of ZnO nanoparticles with zinc acetate in alcohol [47, 48], it was observed that the role of water was to increase the concentration of Zn^{2+} ions in the solution, since zinc acetate is more soluble in water than alcohol [47, 48]. Thus, it seems reasonable to arrive at a similar conclusion for the CuO synthesis, that the role of water is to promote the forward reaction due to a higher concentration of Cu^{2+} ions in the solution. Fits of the XRD peaks to the Scherrer equation for the NCs synthesized with water gave a CuO NC size of $(5.1 \pm 0.8) \text{ nm}$, which is consistent with the average NC size discerned from the TEM image.

Importantly, the CuO NCs can be dispersed in a 2:1 solvent mixture of chloroform and methanol (see inset in Figure 1(a)). To understand the dispersion behavior, the NC surface chemistry and surface bound species were investigated using infrared spectroscopy. Figure 2 shows an FTIR spectrum of drop-casted CuO NCs. The peak at 1560 cm^{-1} is rather difficult to assign since both the water H-O-H scissoring vibration and the carboxylate anion asymmetrical stretching fall within this range [49], but both should be

FIGURE 1: (a) TEM image of CuO NCs, (b) X-ray diffractograms of CuO NCs, with comparison between 2 syntheses: one with water added and the other without any water. The black lines represent literature values for CuO (JPCD# 05-0661). Inset shows a dispersion of CuO NCs in a solvent mixture of methanol and chloroform.

FIGURE 2: FTIR spectrum of CuO NCs.

represented since they are both present in the reaction. The data thus suggests that acetate (accounting for both the carboxylate and CH peaks), hydroxide, and water molecules from the synthesis are adsorbed onto the NC surfaces. The presence of both polar and organic groups explains why the CuO NCs can be readily dispersed in the chloroform and methanol mixture.

Figure 3(a) shows the absorption spectra of CuO (80 nm) and PCBM (120 nm) films spin-casted from dispersions in their respective solvents. The CuO film absorption data was used to generate Tauc plots to determine the energy gap of the NCs (Figures 3(b) and 3(c)), which indicate a direct energy-gap at 3.07 eV and an indirect energy-gap at 1.40 eV. The latter value is similar to the value for the indirect bulk band-gap reported in the literature [19]. While there have been reports of quantum confinement observed in CuO nanostructures [33, 35], the authors did not perform an indirect energy-gap fit to their data; hence it is difficult to make meaningful comparisons.

As a proof of concept of the potential applications of the CuO NCs, a bilayer solar cell comprising of CuO and a fullerene derivative, phenyl- C_{61} -butyric acid methyl ester (PCBM), was fabricated. A single layer of CuO is unsuitable as the active layer, since the NC film contains cracks and pinholes and will result in a short-circuited device. This is similar to what has been reported about PbSe NC films, which require multiple sequential depositions of NCs and cross-linking to fill up the cracks [6]. PCBM is chosen since it is the acceptor of choice in solution-processable polymer solar cells [50], and its good film forming property allows it to cover up cracks in the CuO film. The literature value energy levels of the conduction and valence bands of CuO [19] and the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of PCBM [51] are such that CuO and PCBM form a type II semiconductor heterojunction; hence they are suitable as a donor and acceptor pair. Figure 4(a) shows a schematic of the device stack with indium tin oxide (ITO) forming the anode and CsF/Al as the cathode, as well as the literature values for the semiconductor energy levels [19, 51, 52]. Assignment of bulk CuO energy levels is supported by the small difference in NC optical band-gap relative to the literature (bulk) values [19].

Figure 4(b) shows the device current density voltage (J - V) curves both in the dark and light (under AM 1.5 100 mW cm⁻² illumination) of a bi-layer cell with a ~ 40 nm thick CuO layer. The device is characterized by a V_{OC} of 0.44 V, J_{SC} of 0.24 mA cm⁻², fill factor (FF) of 0.38, and a power conversion efficiency (PCE) of 0.040%. As a control, a PCBM-only cell (without CuO) was fabricated and tested (also shown in Figure 4(b)). It shows a much lower J_{SC} of 0.03 mA cm⁻² and PCE of 0.011%, although it gave a higher V_{OC} of 0.78 V and slightly higher FF of 0.41. Meanwhile, a bi-layer cell with a thicker CuO (~ 70 nm) layer is characterized by poorer J_{SC} (0.15 mA cm⁻²), FF (0.35), and PCE (0.024%) compared to the cell with thinner CuO (refer to Table 1 for a summary of device results). These results lead to the conclusion that efficient charge collection is only taking place in the thin CuO layer near the interface, and additional CuO layer thickness does not contribute to the photocurrent while possibly adding to series resistance and recombination as indicated by the poorer FF. Improvements in the charge collection from CuO NC absorber layers will therefore require better charge transport characteristics within the NC layer. One possible route to improving the charge collection is to use semiconductor nanowires (such

FIGURE 3: Optical properties of CuO NCs: (a) UV-Visible absorption spectra for spin-casted CuO and PCBM films (b) Tauc plot for the direct CuO band-gap fit (c) Indirect band-gap Tauc plot fit.

as n-type ZnO or TiO₂) as the acceptor material, and the CuO NCs are then infiltrated into the gaps of the nanowires. Such device architectures have the advantage of separating

FIGURE 4: Performance of a CuO/PCBM bilayer solar cell: (a) Device stack and energy level diagram, (b) J - V curves in the dark and light (AM 1.5 100 mW cm⁻²), (c) EQE comparison between the bilayer cell and a PCBM only cell.

the light absorption and charge collection pathways so that both processes can be efficient [8].

External quantum efficiency (EQE) spectra of the devices are shown in Figure 4(c). The bi-layer cell shows a superior EQE to the PCBM-only cell, and the improved EQE at higher wavelengths beyond 550 nm can be attributed to the contribution from the CuO by taking into account the

TABLE 1: Summary of solar cell device results.

Active layer	V_{OC} (V)	J_{SC} (mA/cm ²)	Fill Factor	PCE (%)
CuO (40 nm)/PCBM	0.44	0.24	0.38	0.040
CuO (70 nm)/PCBM	0.46	0.15	0.35	0.024
PCBM only	0.78	0.03	0.41	0.011

absorption spectra of both materials (Figure 3(a)). Since J_{SC} is the integration of the EQE across the solar spectrum, the higher J_{SC} observed in the bi-layer cell is clearly due to its superior EQE.

4. Conclusions

A synthesis of CuONCs by a facile alcohothermal route has been presented. The CuO NCs are soluble in a chloroform/methanol mixture, thus enabling the processing of these materials by solution. A bi-layer CuO and PCBM solar cell achieved a power conversion efficiency of 0.04%, which is 4 times higher than the control PCBM-only cell, indicating the potential of these CuONCs for light-harvesting applications.

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