Electronic Supplementary Information (ESI)

CuO/ZnO Core/Shell Heterostructure Nanowire Arrays: Synthesis, Optical Property, and Energy Application

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1. NW synthesis

First, a 10 mm wide × 20 mm long × 0.5 mm high copper foil (99.9%), which had been used as a substrate, was cleaned in a diluted hydrochloric acid solution (1 mol/L) for 1–3 minutes, followed by rinsing with deionized water and dried in air for several minutes. Then the cleaned copper foil substrate was immediately placed on a quartz holder and heated to 500°C in air followed by fixing at 500°C for 4 hours. After that, the copper foil was quickly quenched to room temperature, and as a result the CuO NW arrays were prepared. Second, several droplets of saturated ethanol solution of zinc acetate were dropped onto the prepared CuO NW arrays and dried under ambient conditions of 25°C and relative humidity of 70%. This step was repeated 3–5 times. After that, the zinc acetate covered CuO NWs were baked at 350°C for 20 minutes in air and then cooled down to room temperature. Finally, the CuO-core/ZnO-shell heterostructure NW arrays were obtained. Detailed process is schematically shows in Fig. S1.

Fig. S1  Schematic process of fabrication of the CuO/ZnO core/shell heterostructure NW arrays.
2. Influence investigation of oxidation time and temperature on length, diameter, and density of the CuO NWs

To know the influence of oxidation time and temperature on the growth of the CuO NWs, including length, diameter, and density, an investigation has also been carried out. Fig. S2a–e show the top view SEM images of the CuO NWs taken at 500°C for oxidation times from 5 min to 10 min, 30 min, 1 hr, and 3 hr, respectively. The measured results (Table 1) indicate that, at an oxidation temperature of 500°C, with an increase of the oxidation time, the diameters of the CuO NWs increase from 95 nm (for 5 min) to 107 nm (for 3 hr), while the lengths of the NWs increase form 2.3 μm (5 min) to 12.7 μm (3 hr) and the density increase from 1.2×10⁶ wires/mm² (5 min) to 15.1×10⁶ wires/mm² (3 hr). Fig. S2f–i show cross section view SEM images of the CuO NWs taken at oxidation temperature from 400 to 450, 500, and 580°C, respectively, for 4 hr. The measured results (Table 2) indicate that the diameter of NWs increases from 79.9 nm at 400°C to 194.2 nm at 580°C while the length of NWs increases form 5.1 μm at 400°C to a maximum of 13.9 μm at 500°C and then decrease to 6.9 μm at 580°C. The density of NWs decreases from 17.2×10⁶ wires/mm² at 400°C to 14×10⁶ wires/mm² at 580°C. According to above investigation, an optimal NW growth condition of 500°C for 4 hr is decided. So the CuO NWs used in this study were synthesized at 500°C for 4 hr. From the above mentioned, the average density, length, and diameter of CuO nanowires that synthesized at 500°C for 4 hours is about 10⁷ wires/mm², 10 μm, and 130 nm, respectively. Therefore, the surface area of CuO NWs on per unit area is about 25 time of the substrate. So the main part of the sample surface is CuO-core/ZnO-shell NW arrays rather than CuO/ZnO films.

Table 1 Average diameter (d), length (L), and density of the CuO NWs at temperature (T) of 500°C for different oxidation times (t).

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>t [min]</th>
<th>d [nm]</th>
<th>L [μm]</th>
<th>Density [×10⁶ wires mm⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>5</td>
<td>95</td>
<td>2.3</td>
<td>1.2</td>
</tr>
<tr>
<td>500</td>
<td>10</td>
<td>98</td>
<td>5.1</td>
<td>4.6</td>
</tr>
<tr>
<td>500</td>
<td>30</td>
<td>112</td>
<td>8.5</td>
<td>6.4</td>
</tr>
<tr>
<td>500</td>
<td>60</td>
<td>115</td>
<td>10.8</td>
<td>8.2</td>
</tr>
<tr>
<td>500</td>
<td>180</td>
<td>107</td>
<td>12.7</td>
<td>15.1</td>
</tr>
</tbody>
</table>

Table 2 Average diameter (d), length (L), and density of the CuO NWs at different oxidation temperatures (T) for oxidation time (t) of 4 hr.

<table>
<thead>
<tr>
<th>t [hr]</th>
<th>T [°C]</th>
<th>d [nm]</th>
<th>L [μm]</th>
<th>Density [×10⁶ wires mm⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>400</td>
<td>79.9</td>
<td>5.1</td>
<td>17.2</td>
</tr>
<tr>
<td>4</td>
<td>450</td>
<td>92.6</td>
<td>6.8</td>
<td>15.9</td>
</tr>
<tr>
<td>4</td>
<td>500</td>
<td>155.3</td>
<td>13.9</td>
<td>15.7</td>
</tr>
<tr>
<td>4</td>
<td>580</td>
<td>194.2</td>
<td>6.9</td>
<td>14</td>
</tr>
</tbody>
</table>
Fig. S2  SEM images of the CuO NWs oxidized at (a) 500°C for 5 min (top view), (b) 500°C for 10 min (top view), (c) 500°C for 30 min (top view), (d) 500°C for 1 hr (top view), (e) 500°C for 3 hr (top view), (f) 400°C for 4 hr (cross section view), (g) 450°C for 4 hr (cross section view), (h) 500°C for 4 hr (cross section view), and (i) 580°C for 4 hr (cross section view).

3. **Photoelectrochemical setup**

In the setup, the CuO-core/ZnO-shell NW arrays on the copper substrate are used as photoelectrode (working electrode), a platinum (Pt) foil as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. The three electrodes were immersed in a NaOH electrolyte (0.1 mol/L) that is contained in a two-compartment commercial poly(methyl methacrylate) (PMMA) cell, the PMMA cell had a flat quartz window for incoming radiation as show in Fig. S3. Before measurement, the dissolved oxygen in the aqueous electrolyte was removed by N₂ gas. For easy measurement, the copper substrate of the core/shell NWs was connected with a copper wire through high-purity silver conducting paint. To prevent photocurrent leakage, the copper wire and the copper substrate of the core/shell NWs were sealed by a non-conducting and non-transparent epoxy resin, excluding an area of 0.25 cm² at the centre of the substrate surface for absorbing the light. Linear sweep voltammagrams were performed at a scan rate of 10mV/s at applied potentials from -0.2 V to 1.0 V. The Photoelectrochemical performances were tested on Preston 2273 and CHI842 electrochemical station.
4. Schematic energy band diagram

Fig. S4 shows a schematic energy band diagram of the CuO-ZnO p-n heterojunctions at thermal equilibrium condition. In Fig. S5, \( E_F \) is the Fermi level at equilibrium condition, \( E_{g1} \) is the bandgap of CuO, and \( E_{g2} \) is the bandgap of ZnO. \( E_{c1} \) and \( E_{v1} \) is the energy levels of the bottom of the conduction band and the top of the valence band of the CuO core, while \( E_{c2} \) and \( E_{v2} \) is the energy levels of bottom of the conduction band and the top of the valence band of the ZnO shell. Under white light illuminates, photons with energy large than the energy of bandgap will be absorbed, electrons in the valence band of both the CuO core and ZnO shell will be excited to the conduction band, meanwhile, holes are generated in the valence band.
5. Short circuit current density and open circuit voltage

Fig. S5 is a magnified view for the acquisition of open circuit voltage and short circuit current under white light illumination. From it we obtained that the open circuit voltage is \(-8\, \text{mV}\) and the short circuit current density is \(1.5\, \mu\text{A/cm}^2\) under white light illumination of 100 mW/cm². The very low open circuit voltage and very small short circuit current owe to the Fermi level and band energy of the ZnO move upward while the Fermi level and band energy of the CuO move downward due to the band bending under white light illumination. The band bending causes photo-generated potential in the p-CuO/n-ZnO core/shell heterostructures in the opposite direction to the interface of the ZnO and the electrolyte (Fig. S4).

![Fig. S5 A magnified view of Current density vs.bias potential curves for observation of short circuit current density and open circuit voltage.](image)

6. XRD analysis and high resolution TEM characterization

From the XRD spectrum of the CuO NWs (Fig. S6a), the main peaks can be readily indexed to the monoclinic symmetry of the CuO (space group \(\text{C}_{2h}^6\), \(a = 4.684\, \text{Å}, \ b = 3.425\, \text{Å}, \ c = 5.129\, \text{Å}, \ \beta = 99.47^\circ; \ \text{PDF file No. 05-0661}\)). In the XRD spectrum (Fig. S6a), Cu₂O peaks are also appeared. This is because during the sample preparation, the copper was oxidized in air, so a Cu₂O thin-film precursor was formed firstly before the growing of the CuO NWs. Fig. S6b shows the XRD spectrum of the CuO-core/ZnO-shell heterostructure NWs. Comparing the spectra of Fig. S6b with S6a, two additional diffraction peaks of ZnO are appeared. The two diffraction peaks are assigned to (100) and (101) surface of ZnO. It should be mentioned that the diffraction peak of Cu appeared in Fig. S6b is from the Cu substrate.

Fig. S7a shows the TEM image of a CuO/ZnO NW. It can be seen that the ZnO shell covered the whole surface of the CuO NW. Figure S7b shows the magnified view image of the CuO/ZnO NW from the selected area of Fig. S7a (green dashed frame). It can be seen that the CuO/ZnO NW is core-shell structure and the interface of CuO core and ZnO shell is clear. Fig S7c is a magnified view image from the selected area of Fig. S7a (green cross). Fig. 7d is the HRTEM image of the ZnO shell taken from the selected area of Fig. S7c (yellow dashed frame). The measured distance between lattice fringes is 0.28 nm for \((10\overline{1}0)\) plane. It confirmed that the composition of the shell is ZnO.

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Fig. S6  XRD curve of the CuO NWs and CuO/ZnO NWs on copper substrate.

Fig. S7  (a) TEM images of a CuO/ZnO NW placed on TEM grid by ultrasonic wave. (b) Magnified view image of the CuO/ZnO NW taken from the selected area of Fig. S7a (green dashed frame). (c) Magnified view image of the CuO/ZnO NW taken from the selected area of Fig. S7a (green cross). (d) High resolution TEM image of the ZnO shell taken from the selected area of Fig. S7c (yellow dashed frame).

7. Calculation of photon-to-hydrogen generation efficiency

The photon-to-hydrogen generation efficiency versus bias potential was calculated according to $\eta = I(1.23 - V_{\text{bias}})/J_{\text{light}}$,\textsuperscript{1,2,3} where $I$ is the photo-generated current density (ie.
Influence of nanostructural parameters on the photovoltaic performance

For the CuO/ZnO core/shell nanostructures, the length of the CuO core influences optical absorption, the diameter of the CuO core influences separation and the collection of carriers, and the thickness of the ZnO shell influences carrier collection. With an increase of the nanowire length, more illuminated light can be absorbed for carrier generation. But more carrier traps and scattering centers will also be induced. These traps and centers will cause carrier recombination. The optimal nanowire length should be 10–30 μm. Similarly, with a decrease of the NW diameter, carrier diffusion length will be decreased, this will benefit to carrier collection. But the surface state density will also be increased. This increase is not good for carrier collection. The optimal diameter of the nanowires is ~200 nm. To improve the efficiency of separation and collection of the carriers, the thickness of the ZnO shell should be as close as possible to the width of space charge region (tens to hundred nanometers).

References