ABSTRACT: Among the issues that restrict the power conversion efficiency (PCE) of quantum-dot-sensitized solar cells (QDSSCs), insufficient catalytic activity and stability of counter electrodes (CEs) are critical but challenging ones. The state-of-the-art Cu/Cu2S CEs still suffer from mechanical instability and uncertainty due to the reaction of copper and electrolyte. Herein, ITO@Cu2S core–shell nanowire arrays were developed to fabricate CEs for QDSSCs, which have no such issues in Cu/Cu2S CEs. These nanowire arrays exhibited small charge transfer resistance and sheet resistance, and provided more active catalytic sites and easy accessibility for electrolyte due to the three-dimensional structure upon use as CEs. More interestingly, it was found that the interface of ITO/Cu2S significantly affected the performance of ITO@Cu2S nanowire array CEs. By varying synthetic methods, a series of ITO@Cu2S nanowire arrays were prepared to investigate the influence of ITO/Cu2S interface on their performance. The results showed that ITO@Cu2S nanowire array CEs with a continuous Cu2S nanocrystal shell fabricated via an improved cation exchange route exhibited excellent and thickness-dependent performance. The PCE of corresponding QDSSCs increased by 11.6 and 16.5% compared to that with the discrete Cu2S nanocrystal and the classic Cu/Cu2S CE, respectively, indicating its promising potential as a new type of CE for QDSSCs.

KEYWORDS: nanowires, quantum dots, solar cells, interface, counter electrodes
sional nanowire array provides more active catalytic sites and easy accessibility for electrolyte.\textsuperscript{35–38} Given that the catalytic activity of CE should be proportional to the number of catalytic sites and the interface between ITO and Cu\textsubscript{2}S could affect the charge transport and chemical stability of Cu\textsubscript{2}S shell on ITO core in electrolyte, several types of ITO@Cu\textsubscript{2}S core–shell nanowire arrays with different morphologies, coverage of Cu\textsubscript{2}S and interfaces of ITO/Cu\textsubscript{2}S were herein fabricated by different methods to investigate these effects. It was found that the successive ionic layer adsorption and reaction (SILAR) method produced a full coverage of Cu\textsubscript{2}S nanocrystals on ITO nanowire cores as well as separate Cu\textsubscript{2}S nanocrystal aggregates of micrometer size on top of nanowire arrays. Physical vapor deposition via the magnetron sputtering (PVD) method deposited a homogeneous Cu\textsubscript{2}S shell with a smooth surface on ITO nanowire cores, but the resulted Cu\textsubscript{2}S shell had very poor chemical stability in electrolyte, probably due to inferior interface with ITO. The improved cation exchange method could easily grow a uniform Cu\textsubscript{2}S nanocrystal shell on ITO with a good interface, leading to fast charge transport and a higher short-circuit current density as well as high chemical stability. After the optimization of the thickness of the Cu\textsubscript{2}S shell, the power conversion efficiency of QDSSCs with the ITO@Cu\textsubscript{2}S CE fabricated by this method increased by 16.5% compared to that with the classic Cu/Cu\textsubscript{2}S CE, indicating its promising potential as its substitute for QDSSCs.

\section*{RESULT AND DISCUSSION}

Four types of ITO@Cu\textsubscript{2}S core–shell nanowire arrays were fabricated by different methods, including the successive ionic layer adsorption and reaction method (SILAR), physical vapor deposition (PVD), the traditional cation exchange method (EX1), and the improved cation exchange method (EX2). Details for the fabrication are presented in the Experimental Section. Figure 1a–e shows typical high-magnification scanning electron microscopy (SEM) images of pure ITO and ITO@Cu\textsubscript{2}S nanowire arrays prepared with these different methods. Pure ITO nanowires display the smooth side surfaces and faceted shape with a diameter in a range of around 100–120 nm (Figure 1a). In the case of the ITO@Cu\textsubscript{2}S nanowires synthesized via the EX1 method (Figure 1b), Cu\textsubscript{2}S nanocrystals in a diameter of about 20 nm distributed discretely on the ITO nanowire, leaving an appreciable amount of ITO surface uncovered. The SILAR method is frequently used to load quantum dots on mesoporous titania in the fabrication of photoanodes for QDSSCs. As seen in Figure 1c, by using the SILAR route to grow Cu\textsubscript{2}S, the ITO nanowire could be effectively covered by Cu\textsubscript{2}S nanocrystals with almost no ITO nanowire surface exposed. However, it can also be seen that the growth of Cu\textsubscript{2}S was not in a well-defined way. The growth rate varied largely in different positions. Irregular Cu\textsubscript{2}S nanocrystals grew on the surface of ITO nanowires or in their interspace. Large aggregates in micrometers could be easily found on the top of ITO@Cu\textsubscript{2}S nanowire arrays (see low-magnification SEM image, Figure S1 in the Supporting Information). PVD via magnetron sputtering is a method widely used to form a conformal coating on a variety of materials. In this study, the morphology of ITO@Cu\textsubscript{2}S prepared through the PVD route showed a replica of the ITO nanowire core with a very compact and smooth coating (Figure 1d) except that the color of the film turned into dark brown from light blue, which indicated the successful coating of the Cu\textsubscript{2}S layer. Lastly, an improved cation exchange method (EX2) was also employed in an attempt to grow a continuous and compact Cu\textsubscript{2}S nanocrystal layer coating on the surface of the ITO nanowire cores. The method is referenced to that widely used in thin film solar cells to grow the CdS layer and form a high quality P–N junction with the absorption layer, followed by a cation exchange process to convert CdS into a Cu\textsubscript{2}S shell. As shown in Figure 1e, a well-defined ITO@Cu\textsubscript{2}S nanowire array with a continuous Cu\textsubscript{2}S nanocrystal shell was prepared with the EX2 method. The diameter of the nanowires clearly increased from around 100–120 nm for ITO nanowires to around 250–300 nm for core–shell nanowires. Unlike ITO@Cu\textsubscript{2}S prepared via the EX1 method, the entire surface of ITO nanowires was covered with polycrystalline nanocrystals. Figure 1f presents a typical transmission electron microscopy (TEM) image of this type of ITO@Cu\textsubscript{2}S nanowire. The clear contrast difference indicates that the nanowire has a core–shell structure. The shell thickness in this case is around 80 nm. It can be also seen that the shell is composed of a continuous layer of polycrystalline nanocrystals with rough surface rather than smooth compact layer like PVD sample, which will provide a larger surface area and thus more catalytic sites when it was used as a CE for QDSSCs.

To confirm the successful growth of Cu\textsubscript{2}S and reveal its crystalline structure, X-ray diffraction (XRD) experiments were carried out on all four samples. Figure 2 shows the typical XRD patterns of the ITO nanowire (black line) and four types of ITO@Cu\textsubscript{2}S nanowires prepared with different methods. The diffraction peaks of ITO nanowire arrays can be well indexed to cubic In\textsubscript{2}O\textsubscript{3} (JCPDS Card No. 06-0416), except for three peaks marked as stars at 26.6°, 51.8°, and 65.9°, which can be
attributed to the diffraction on the (110), (211), and (301) crystallographic planes of SnO$_2$ (JCPDS Card No. 41-1445). After the fabrication of Cu$_2$S through different methods, three more peaks (marked as hollow inverted triangles) at 27.6°, 38.5°, and 44.8° appear, which can be ascribed to the diffraction from the (122), (240) and (204) crystallographic planes of low-chalcocite Cu$_2$S. A small difference can be found in XRD patterns of different types of ITO@Cu$_2$S nanowires. Relatively strong diffraction peaks from the (240) and (204) crystallographic planes of Cu$_2$S emerged in ITO@Cu$_2$S prepared by the EX1 method, whereas diffraction from (122) planes for the SILAR sample, and (240) planes for the PVD sample were enhanced. All these three diffraction peaks can be distinguished in the EX2 sample. These results confirm that the low-chalcocite Cu$_2$S formed in all four samples but the crystallographic orientation of Cu$_2$S nanocrystals might be different in each sample.

High-resolution transmission electron microscopy (HRTEM) was further used to reveal the crystallographic orientation of Cu$_2$S nanocrystals and investigate the interfaces between ITO and Cu$_2$S in each case. As shown in Figure 3, clear crystal lattice fringes in the whole imaging region demonstrate that ITO@Cu$_2$S nanowires prepared by all four synthetic methods were well crystallized. The lattice fringe distance of 0.33 nm in shell parts of ITO@Cu$_2$S prepared by the EX1 method, whereas diffraction from (122) planes for the SILAR sample, and (240) planes for the PVD sample were enhanced. All these three diffraction peaks can be distinguished in the EX2 sample. These results confirm that the low-chalcocite Cu$_2$S formed in all four samples but the crystallographic orientation of Cu$_2$S nanocrystals might be different in each sample.

In the PVD case, long continuous lattice fringes with few defects can be observed in the shell part, suggesting the single-crystalline-like Cu$_2$S shell can be deposited via the PVD route. However, a disordered layer between lattice fringes of ITO and Cu$_2$S was always found in this case (marked with two red dashed lines in Figure 3c), which means that a defect layer existed between the ITO core and the Cu$_2$S shell. The existence of this defect layer would be responsible for the chemical instability of this type of ITO@Cu$_2$S in the electrolyte as mentioned hereinafter. Moreover, continuous lattice fringes of a large size were found in the shell part of the SILAR sample (Figure 3b). No clear interface could be resolved between ITO and Cu$_2$S along the whole nanowire. This could be probably due to the formation of a thick shell and larger crystal grains. The interplanar spacing of 0.41 nm corresponds to the (211) crystallographic planes of Cu$_2$S.

Furthermore, the elemental mapping is a powerful technique to characterize the morphology and composition of nanowires with a core–shell structure. Figure 4 shows, as an example, typical results of elemental mapping for a single ITO@Cu$_2$S nanowire prepared with the improved cation exchange method. Referenced to the morphology shown in low-magnification TEM image (Figure 4a), it can be clearly seen that the elements In (blue) and Sn (yellow) were detected only in the core part, whereas a large amount of Cu (red) was distributed in the whole region of the nanowire. The intensity of the Cu signal in the outer layer was slightly stronger than that in the central part. These results unambiguously corroborated the fact that the Cu$_2$S layer coaxially grew on the ITO nanowire core. It should be noted that a nickel grid instead of a copper grid was used for sample preparation, to preclude the signal from the TEM grid and get an accurate result in the elemental mapping experiment.

To evaluate the role of the interface engineering of ITO@Cu$_2$S nanowire array CEs in enhancing the performance of
QDSSCs, we first investigated the influence of annealing on the interface of ITO and Cu₂S and the device performance. Figure S2 (Supporting Information) shows typical TEM images of ITO@Cu₂S nanowire arrays prepared without or with the annealing process at 300 °C after the formation of the Cu₂S shell, with the EX1 method as an example. It is clearly seen that the lattice fringes of Cu₂S nanocrystals before annealing are more disordered than those after annealing. Many more defects were found in the former, while the clearer and more continuous lattice fringes emerged in Cu₂S nanocrystals after annealing, and the interface of ITO and Cu₂S had much less defects in the latter. These results indicate that the crystallinity of Cu₂S nanocrystals and the interface quality of ITO and Cu₂S were much improved by the annealing process. The QDSSCs were further fabricated by using ITO@Cu₂S nanowire arrays without or with the annealing process as CEs. As shown in Figure S3 (Supporting Information), PV−IV measurement revealed that both voltage of open circuit (V_{oc}) and short circuit current density (J_{sc}) of QDSSCs were enhanced by using the annealed CE and thus the device PCE was increased by 21.0% (Table S1, Supporting Information). Therefore, the above-mentioned four types of ITO@Cu₂S nanowire arrays prepared with the EX1, SILAR, PVD, and EX2 methods were annealed before TEM characterization and use as counter electrodes to fabricate QDSSCs. Moreover, the widely used brass based Cu/Cu₂S CE was also compared as a control CE to evaluate the performance of the ITO@Cu₂S nanowire arrays reported here.

Photocurrent−voltage (J−V) curves of all QDSSCs are presented in Figure 5a, and the corresponding data are listed in Table 1. The statistical analysis based on the data measured on five cells for each type of counter electrodes is shown in Figure S4 (Supporting Information). the PVD-ITO@Cu₂S device

![Figure 4. Morphology and of elemental mapping images of EX2-ITO@Cu₂S nanowire: (a) morphology, (b) In, (c) Sn, and (d) Cu.](image-url)

![Figure 5. a) Photocurrent−voltage (J−V) curves of QDSSCs with different ITO@Cu₂S CEs. (b) J−V curves and (c) IPCE spectra of QDSSCs fabricated by EX2-ITO@Cu₂S CEs with different Cu₂S shell thicknesses. (d) Nyquist plots from EIS measurements on EX2-ITO@Cu₂S CEs with three thickness of Cu₂S. The dots and the lines are the experimental data and the fitted curves, respectively.](image-url)
showed the worst performance with the lowest fill factor (FF) of only 31.67% and the lowest $J_{sc}$ which could be ascribed to the worst interface of ITO and Cu$_2$S (Figure 3c) and the relatively small surface area of Cu$_2$S catalysts in view of the morphology with smooth surfaces (Figure 1d). Actually, it should be noted that the dark brown color of the PVD-ITO@Cu$_2$S CE usually changed to light blue after measurement, implying that the Cu$_2$S layer partially peeled off from the ITO nanowire during the testing process. This phenomenon could be occasionally observed for the brass-Cu$_2$S CE, which was due to that Cu$_2$S on brass lacks chemical stability in a multisulfide electrolyte upon work.

The SILAR-ITO@Cu$_2$S device showed improved performance better than the PVD-ITO@Cu$_2$S device but still inferior to the brass-Cu$_2$S device. The possible reasons are that the SILAR-ITO@Cu$_2$S had a better interface of ITO and Cu$_2$S and larger surface area of Cu$_2$S compared to PVD-ITO@Cu$_2$S, but the nonuniform growth and inevitable agglomeration of Cu$_2$S nanocrystals might be unfavorable for the charge transfer from the electrolyte to conductive transparent oxide (CTO) and thus degraded the device performance. On the other hand, ITO@Cu$_2$S CEs prepared via two kinds of cation exchange methods demonstrated better performance compared to the classic brass-Cu$_2$S CE. Specifically, device PCE with the EX1-ITO@Cu$_2$S CE and the EX2-ITO@Cu$_2$S CE increased by 4.4% and 16.5%, respectively, compared to that with brass-Cu$_2$S CE. Especially, $V_{oc}$ and $J_{sc}$ of EX2-ITO@Cu$_2$S device enhanced to 0.560 V and 15.55 mA cm$^{-2}$ from 0.513 V and 13.54 mA cm$^{-2}$ for the brass-Cu$_2$S device, respectively. This improvement could be attributed to the high-quality interface between ITO and Cu$_2$S favorable for electron transfer, as well as the three-dimensional structure of nanowire arrays ~10 μm long, which benefits mass transfer and more efficient light scattering in the former. In a comparison of the two cation exchange methods, the EX2-ITO@Cu$_2$S CE achieved an apparent enhanced performance (11.6% increase in PCE). This could be ascribed to much higher coverage of Cu$_2$S nanocrystals on ITO, which provided more active catalytic sites. It should be noted that the fill factor of the device with the EX2-ITO@Cu$_2$S CE was not enhanced compared to that with the EX1-ITO@Cu$_2$S CE. The reason is that the fill factor is usually related to the series resistance and shunt resistance of a quantum-dot-sensitized solar cell. The series resistance is composed of sheet resistance and charge transfer resistance. Although the EX2-ITO@Cu$_2$S CE exhibited a smaller charge transfer resistance (1.72 vs 2.64 Ω cm$^{-2}$) thanks to the more active catalytic sites, it had larger sheet resistance (6.32 vs 4.66 Ω) because it had a thicker Cu$_2$S shell and the electron conductivity of Cu$_2$S is smaller than that of ITO (the data can be found in Table 2 and ref 29). Taking into account these two factors together, it is reasonable that the device with the EX2-ITO@Cu$_2$S CE exhibited a fill factor close to that with the EX1-ITO@Cu$_2$S CE.

In further experiments, it was interestingly found that the thickness of the Cu$_2$S shell in EX2-ITO@Cu$_2$S can be well controlled by tuning the deposition time of the CdS precursor shell, followed by a solution cation exchange. Three thicknesses of around 30, 55, and 80 nm were chosen in this study. TEM observation displayed that all EX2-ITO@Cu$_2$S nanowires exhibited very similar core–shell nanowire morphologies with a continuous and compact Cu$_2$S shell but in different thicknesses. The performance of QDSSCs with these three types EX2-ITO@Cu$_2$S nanowire array as CEs was measured, and the corresponding data are listed in Table 2. The statistical data are shown in Figure S5 (Supporting Information). As shown in the $J$–$V$ curves (Figure Sb), $V_{oc}$ and $F_{sc}$ of the device increased first as the thickness of the Cu$_2$S shell in the CEs increased from 30 to 55 nm, but decreased when the thickness further increased to 80 nm. As a result, the device with a 55 nm thick Cu$_2$S shell reached the highest PCE. This is consistent with the results of incident photon-to-electron conversion efficiency (IPCE) measurements (Figure Sc). The IPCE spectra of devices with 30 and 55 nm thick Cu$_2$S had nearly the same curve shape, whereas those of the device with 80 nm Cu$_2$S apparently decreased in the whole wavelength range, resulting in a lower $J_{sc}$. The highest IPCE of 76.2% was achieved at the wavelength of 560 nm for the device with 55 nm thick Cu$_2$S.

An electrochemical impedance spectroscopy (EIS) experiment was carried out by using symmetrical dummy cells (two each) of CEs to analyze the sheet resistant and charge transfer resistant in the above-mentioned systems. The measurement was operated at zero potential bias with an AC amplitude of 10 mV and a frequency range between 100 mHz and 100 kHz. The corresponding equivalent circuit is shown in Figure S6 (Supporting Information). The constant-phase element (CPE) was used in the equivalent circuit, and the fitting parameters are listed in Table S2 (Supporting Information). As shown in Figure Sd and Table 2, EIS results indicated that no obvious charge transfer resistances at the solid/solid interface ($R_{ct1}$) were detected in all CEs, suggesting the high-quality interfaces were achieved between ITO and Cu$_2$S in all cases so that electrons could be efficiently injected from ITO to Cu$_2$S. All EX2-ITO@Cu$_2$S CEs with different thicknesses of Cu$_2$S shells exhibited a relatively small sheet resistance ($R_s$) and charge transfer resistance at the solid/liquid interface ($R_{ct2}$) in several ohms. The undetectable $R_{ct1}$ and small $R_s$ could be attributed to the formation of a high-quality tunnel junction between ITO and Cu$_2$S because both of them are degenerate semiconductors with a high electron conductivity. $R_s$ increased gradually from 5.71 to 7.08 Ω with the increase of Cu$_2$S thickness from 30 to 80 nm. The thicker the Cu$_2$S layer, the longer the electron transfer pathway, which results in the slight increase of $R_s$. The $R_{ct2}$ between Cu$_2$S and electrolyte decreased first from 3.38 to 2.00 Ω cm$^2$ when the thickness of the Cu$_2$S shell increased from 30 to 55 nm, indicating more efficient electron transfer in the latter, probably due to the increase of the amount of Cu$_2$S.

Table 2. Photovoltaic Parameters of QDSSCs and Resistances of Dummy Cells Fabricated by EX2-ITO@Cu$_2$S CEs with Different Cu$_2$S Thicknesses

<table>
<thead>
<tr>
<th>thickness of Cu$_2$S (nm)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct2}$ (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.534</td>
<td>15.76</td>
<td>49.64</td>
<td>4.18</td>
<td>5.71</td>
<td>3.38</td>
</tr>
<tr>
<td>55</td>
<td>0.560</td>
<td>15.55</td>
<td>52.02</td>
<td>4.53</td>
<td>6.32</td>
<td>1.72</td>
</tr>
<tr>
<td>80</td>
<td>0.514</td>
<td>14.28</td>
<td>53.64</td>
<td>3.94</td>
<td>7.08</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Table 1. Photovoltaic Parameters of QDSSCs with Different CEs

<table>
<thead>
<tr>
<th>counter electrodes</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EX1-ITO@Cu$_2$S</td>
<td>0.540</td>
<td>14.31</td>
<td>52.48</td>
<td>4.06</td>
</tr>
<tr>
<td>brass-Cu$_2$S</td>
<td>0.513</td>
<td>13.54</td>
<td>57.37</td>
<td>3.89</td>
</tr>
<tr>
<td>SILAR</td>
<td>0.506</td>
<td>13.34</td>
<td>48.05</td>
<td>3.24</td>
</tr>
<tr>
<td>PVD</td>
<td>0.535</td>
<td>12.59</td>
<td>31.67</td>
<td>2.14</td>
</tr>
<tr>
<td>EX2-ITO@Cu$_2$S</td>
<td>0.560</td>
<td>15.55</td>
<td>52.02</td>
<td>4.53</td>
</tr>
</tbody>
</table>
catalytic sites. In general, the performance of a CE is closely related to its series resistance, which consists of $R_h$, $R_{ct1}$, and $R_{ct2}$. It should consider the balance of three components in optimizing a CE. In the above-mentioned three EX2-ITO@Cu2S CEs, the CE with the 55 nm thick Cu2S exhibited the best performance as a result of balancing $R_h$ and $R_{ct2}$.

The stability is considered to be one of the most critical issues that restricts the application of QDSSCs. The widely used brass/Cu2S counter electrode usually suffered from the issues of copper dissolution and Cu2S peel off. To demonstrate the stability of the developed EX2-ITO@Cu2S CEs, the same CE was used to fabricate three QDSSCs with three photoanodes sequentially. After each time, the cell was measured for more than five times to get the average of the parameters. The CE was disassembled, washed with deionized (DI) water to remove any electrolyte residue, and then used to assemble the next cell. The photovoltaic parameters are listed in Table 3. It was interestingly found that three cells exhibited almost the same performance with very similar photovoltaic parameters. SEM observation was further carried out to investigate the morphology change of the CE before and after three times of measurement. The low-magnification SEM images in Figure 6 clearly revealed that the morphology was nearly unchanged after the whole process. These results demonstrated that EX2-ITO@Cu2S nanowires were quite stable in the multisulfide electrolyte in the system and could be used as stable CEs for long-life QDSSCs.

### CONCLUSION

In summary, four types of ITO@Cu2S core–shell nanowire arrays have been fabricated via four synthetic methods, including SILAR, PVD, and two different cation exchange methods, to investigate the influence of morphology, structure, and core–shell interface of ITO@Cu2S nanowire arrays on their performance as CEs in QDSSCs. It was found that the synthetic methods significantly affected the morphology of Cu2S shells and the interface between Cu2S shell and ITO nanowire core. A uniform and continuous Cu2S nanocrystal shell with a good interface with the ITO core was successfully fabricated on whole surfaces of the ITO nanowire via the improved cation exchange route. With the benefit from the high-quality Cu2S/ITO interface and three-dimensional core–shell structure of nanowire arrays with a conductive core for facilitating charge transport and a high surface area Cu2S nanocrystal shell as catalysts, this ITO@Cu2S nanowire array exhibited impressively small $R_h$ and $R_{ct2}$ as well as undetectable $R_{ct1}$ and thus excellent performance when used as CEs for QDSSCs. By optimizing the thickness of Cu2S shell, the device PCE with the developed ITO@Cu2S CE increased by 16.5% compared to that with the classic Cu/Cu2S CE. In view of no issues of mechanical instability and chemical instability in electrolyte, which Cu/Cu2S CE usually suffered from, the reported ITO@Cu2S nanowire array has demonstrated its promising potential as a high-performance CE for QDSSCs.

### EXPERIMENTAL SECTION

#### Synthesis of ITO Nanowire Arrays

FTO glass (14 Ω/cm, Nippon Sheet Glass) was used as substrate for ITO nanowire array growth. Before use, it was cleaned by sonication in water, ethanol, and acetone sequentially, followed by O3 plasma treatment. A sputtering coater (JFC-1600 Auto Fine Coater, JEOL) was used to sputter Au nanoparticles as catalysts for chemical vapor deposition (CVD) growth. High-purity (99.999%) metallic indium and tin powders were used as sources, in a weight ratio of 10:1, to grow ITO nanowire arrays under an air flow of about 1.5 sccm. The source temperature was 800 °C. Chamber pressure was 30 Pa. After growth, the transparent FTO substrate turned a white-gray color. During the growth, it was found that the average length of the ITO nanowires could be controlled by varying the distance from substrate to the source as well as the growth time. ITO nanowires prepared under exactly the same conditions were used for all the following experiments in this study. The average length was around 10 μm according to SEM observations.

#### Synthesis of ITO@Cu2S Nanowire Arrays with SILAR Method

CuCl and Na2S were used as the Cu+ and S2− sources for the SILAR process. Typically, ITO nanowire arrays on FTO substrate were successively immersed into 0.1 M CuCl(aq) and 0.1 M Na2S(aq) for 1 min. Following each immersion, the film was rinsed with DI water for 1 min to remove any excess precursor. This process was repeated for 10 times to achieve a certain amount of Cu2S loading.

#### Synthesis of ITO@Cu2S Nanowire Arrays with the PVD Method

The PVD deposition of Cu2S on ITO nanowire arrays was conducted on a magnetron sputtering system (PVD75, Kurt J. Lesker, USA) by using a RF power supply of 150 W for 1000 s. A Cu2S target was used as sources, in a weight ratio of 10:1, to grow ITO nanowire arrays under a nitrogen flow of about 1.5 sccm. The source temperature was maintained at 25 °C. The light yellow color of the substrate immediately changed to dark brown from light blue after sputtering.

#### Synthesis of ITO@Cu2S Nanowire Arrays with Cation Exchange Method EX1

In this procedure, a coaxial CdS shell was first fabricated by chemical bath deposition (CBD). A cation exchange process was then carried out to completely convert the CdS shell to a Cu2S shell. Typically, ITO nanowire arrays were placed into a solution containing 20 mM CdCl2, 66 mM NH4Cl, and 140 mM thiourea. The solution temperature was maintained at 25 °C by using a water circulator. After 2 h, the substrate with a yellowish product was washed thoroughly with DI water. A solution cation exchange process was then carried out by immersing the substrate into 0.5 M CuCl2(aq) at 50 °C. The light yellow color of the substrate immediately changed to dark brown. Five minutes later, the product was thoroughly washed with DI water, and then dried.

#### Synthesis of ITO@Cu2S Nanowire Arrays with Improved Cation Exchange Method EX2

To fabricate ITO@Cu2S nanowire arrays with a continuous and compact Cu2S shell, a modified CBD process was used to grow a CdS shell on ITO nanowires. In a typical procedure, ITO nanowire arrays on FTO substrate were put into a flask containing 22 mL of 15 mM CdSO4, 7.5 mL NH4OH(aq) (28 mL NH4OH in 150 mL of DI water) was then added into the flask. While the solution temperature was maintained at 65 °C, 22 mL of 0.75 M...
thiourea was added. After a certain time for designed thickness of CdS, the product was taken out and washed with DI water. A clear color change from white-gray to bright yellow was observed. A solution based cation exchange reaction was subsequently carried out to convert CdS into Cu$_2$S. In a typical process, the product was immersed into 0.5 M CuCl at 50 °C for 30 min for complete conversion, followed by washing with DI water and drying. The thickness of the Cu$_2$S shell was controlled by tuning the thickness of the CdS shell, which can be easily adjusted by changing the CBD time. Specifically, 8, 11, and 14 min of CBD can achieve a 30, 55, and 80 nm thick Cu$_2$S shell, respectively.

**Characterization.** Field emission scanning electron microscopy (JSM 6701, JEOL, Japan) and transmission electron microscopy (JSM 2100F, JEOL, Japan) were used to characterize the morphologies and compositions of all nanowire arrays. A Rigaku D/max-2500 diffractometer was used to carry out XRD experiments. Electrochemical impedance spectroscopy was carried out and analyzed on a potentiostat (PARSTAT 2273A, Princeton Applied Research).

**Preparation of Photoanodes.** Photoanodes were prepared by cosensitizing dyssol TiO$_2$ paste (18NR-T) with CdS/CdSe quantum dots according to literature. In brief, a 9 μm transparent TiO$_2$ film was coated on FTO substrate, followed by coating a 4 μm TiO$_2$ scattering layer (200 nm) via a screen printing method. The substrate with the TiO$_2$ film was treated with TiCl$_4$ and then calcined. After that, the film was cosensitized with CdS and CdSe quantum dots, and then passivated with ZnS as photoanodes.

**Preparation of Counter Electrodes.** To improve the interface between the ITO nanowire core and Cu$_2$S shell, all above-mentioned ITO/Cu$_2$S nanowire arrays on FTO substrates prepared by different methods were annealed at 300 °C for 30 min within Ar atmosphere, and then directly used as counter electrodes. Brass based Cu$_2$S counter electrodes were fabricated according to literature.

**Preparation of QDSSCs.** A series of QDSSCs were fabricated by using the same photoanodes and all above-mentioned ITO/Cu$_2$S nanowire counter electrodes as well as brass based Cu$_2$S counter electrodes. The polysulfide electrolyte was prepared by dissolving 1 M S$_2$, 1 M Na$_2$S, and 0.2 M KCl in water/methanol (S:S:v:v). A 3M adhesive tape with a thickness of about 50 μm was used as a spacer to encapsulate electrolyte between the photoanode and counter electrodes.

**Photovoltaic Measurements.** A solar simulator (450W Model 91150, Newport) with an AM 1.5 spectrum distribution was used as the irradiation source and calibrated against a NREL reference cell to accurately simulate one full-sun intensity (100 mW/cm$^2$). An IQE-200 spectrometer was used to carry out XRD experiments. Electrochemical impedance spectroscopy was carried out and analyzed on a potentiostat (PARSTAT 2273A, Princeton Applied Research).

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**ASSOCIATED CONTENT**

**Notes**

The authors declare no competing financial interest.

**REFERENCES**

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**Supporting Information**

Low-magnification SEM image of SILAR-ITO@Cu$_2$S nanowire CE, high-resolution TEM images of EX1-ITO@Cu$_2$S before and after calcination as well as the photocurrent—voltage curves of QDSSCs with the corresponding EX1-ITO@Cu$_2$S as CEs, statistical analysis on the power conversion efficiencies of QDSSCs with different CEs, statistical analysis on the power conversion efficiencies of QDSSCs with EX2-ITO@Cu$_2$S CEs in different Cu$_2$S shell thickness, and equivalent circuits for fitting EIS of CEs. This material is available free of charge via the Internet at http://pubs.acs.org.

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**S Supporting Information**

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