Ambient synthesis of one-/two-dimensional CuAgSe ternary nanotubes as counter electrodes of quantum-dot-sensitized solar cells

Xin Qi Chen
University of Wollongong

Yang Bai
University of Queensland

Zhen Li
University of Wollongong, zhenl@uow.edu.au

Lian Zhou Wang
University of Queensland

S X. Dou
University of Wollongong, shi@uow.edu.au

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Abstract
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ambient, cells, solar, sensitized, dot, quantum, electrodes, counter, nanotubes, ternary, cuagse, dimensional, two, one, synthesis

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Ambient Synthesis of One-/Two-Dimensional CuAgSe Ternary Nanotubes as Counter Electrodes of Quantum-Dot-Sensitized Solar Cells

Xin Qi Chen,[a, d] Yang Bai,[c] Zhen Li,*[a, b] Lian Zhou Wang,[c] and Shi Xue Dou[a]

One-/two-dimensional ternary CuAgSe nanotubes (NTs) were successfully prepared from copper selenide (Cu$_2$Se) NTs at room temperature within a short reaction time by the facile cation-exchange approach. Cation exchange leads to the transformation of the crystal structure from cubic into orthorhombic and/or tetragonal with good retention of morphology. The exchange reactions are spontaneous owing to large negative changes of the Gibbs free energy. The effects of parameters such as reaction time, precursor source, and precursor ratio on the exchange reaction were investigated. The resultant CuAgSe NTs were explored as counter electrodes (CEs) of quantum-dot-sensitized solar cells (QDSSCs) and achieved higher conversion efficiency ($\eta = 5.61\%$) than those of QDSSCs with the gold as the CE (3.32%).

Introduction

One-/two-dimensional (1D/2D) ternary semiconductor nanotubes (NTs) have been the subject of extensive studies not only because their electronic structures and properties can be engineered over a broad range for diverse applications such as photodetectors,[1, 2] photovoltaics,[3] and electronics,[4] but also because their unique morphology consists of internal tubes and external nanosheets to form a large surface area, which enables them to be good electron transporters and show better performance than that of solid analogues.[5] For example, ternary CuAgSe has high mobility from both Cu$^{+}$ and Ag$^+$.

[a] X. Q. Chen, Prof. Z. Li, Prof. S. X. Dou
Institute for Superconducting and Electronic Materials, Squires Way Innovation Campus of the University of Wollongong Wollongong, 2500, New South Wales (Australia)
Fax: (+61)-2-42215731
E-mail: zhenli@suda.edu.cn

[b] Prof. Z. Li
School of Radiation Medicine and Radiation Protection
Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions Soochow University, 199 Ren Ai Road, Suzhou Industrial Park Suzhou 215123 (P.R. China)

[c] Dr. Y. Bai, Prof. L. Z. Wang
Nanomaterials Centre, School of Chemical Engineering and Australian Institute for Bioengineering and Nanotechnology (AIBN)
University of Queensland, QLD 4072 (Australia)

[d] X. Q. Chen
Institute of Nanoscience and Nanotechnology
Department of Physics, Central China Normal University Wuhan, 430079 (P.R. China)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cplu.201500466. It contains low-magnification SEM image and EDX pattern of CuAgSe NTs, XRD patterns of CuSe and Ag$_2$Se, XRD patterns of the products prepared from different molar ratios of Cu$_2$Se to Ag$_2$NO$_3$, XRD patterns and SEM images of CuAgSe NTs, and XPS spectra of Ag 3d in the samples prepared from silver acetate and collected after different reaction times.
to the single-atom level. Hollow and cave-shaped nanoparticles of Cu$_2$S$_x$Se$_{1-y}$ were prepared from core–shell Cu$_2$Se/Cu$_2$S nanocrystals by the diffusion of Cu$^+$ from the Cu$_2$Se core into the Cu$_2$S shell. Recently, phase-selective cation exchange enabled the successful transition of CdS nanowires into Cu$_2$S nanowires with tunable crystal structures. Owing to complications of partial or complete cation exchange between binary compounds, very few reports are available on the preparation of hierarchical 1D/2D ternary CuAgSe NTs.

In this study, we synthesized 1D/2D ternary CuAgSe NTs from Cu$_2$Se NTs through the facile cation-exchange method at room temperature with a short reaction time. The resultant CuAgSe NTs were employed as the counter electrodes (CEs) of quantum-dot-sensitized solar cells (QDSSCs) to generate a conversion efficiency ($\eta$) of 5.61%. To the best of our knowledge, this is the first report on 1D/2D ternary CuAgSe NTs and their application in QDSSCs.

**Results and Discussion**

The 1D/2D ternary CuAgSe NTs were fabricated by cation exchange from freshly prepared Cu$_2$Se NTs reacted with a solution of AgNO$_3$ in ethanol. Typical field-emission (FE) SEM and TEM images of the initial Cu$_2$Se NTs show their 1D/2D morphology with an inner diameter of 300 nm and an outer diameter of 600 nm, on average (Figure 1 a, b). After partial exchange of copper ions with silver ions, the nanosheets on the surfaces of the resultant CuAgSe NTs become smaller (Figure 1 d, e) and the 1D/2D tubular structure is retained (Figure S1 in the Supporting Information). The HRTEM images clearly display continuous lattice fringes with spacings of 0.33 and 0.2 nm (Figure 1 c, f), which match well with those of the (111) planes of Cu$_2$Se and the (152) planes of CuAgSe, respectively. The FFT patterns also support the transition of the crystal structure after cation exchange. A STEM image and the corresponding EDX elemental mapping images of a single CuAgSe NT are shown in Figure 1 g; these results reveal the homogeneous distribution of Cu, Ag, and Se throughout the whole NT. The EDX spectrum of an individual CuAgSe NT (Figure S2 in the Supporting Information) further confirms the presence of these elements with a ratio of 1.46/1.1/1, which is consistent with that (1.22/1/1.04) determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The transformation of Cu$_2$Se NTs into CuAgSe NTs is also proved by the XRD patterns (Figure 2). The diffraction peaks in the orange pattern in Figure 2 match well with orthorhombic CuAgSe (JCPDS 10-0451) and tetragonal CuAgSe (JCPDS 25-1180), which are different from those of the cubic structure of Cu$_2$Se (JCPDS 88-2043; Figure 3). It should be noted that there is no big difference between these two structures, except that the orthorhombic structure features a sequence that repeats itself periodically every five tetragonal cells in the b direction. They have similar layered structures with alternating stacking of the Ag and CuSe layers, in which Ag atoms almost lie in the same plane and are bonded closely to Se atoms, which allows high mobility of Ag atoms and the formation of Ag–Ag metallic bonds. Selenium atoms form a squashed tetrahedron, in which each corner is shared with an adjacent tetrahedron, and copper atoms are offset from the center within the tetrahedron.

![Figure 1](image1.png)

**Figure 1.** FESEM images of the Cu$_2$Se NTs (a) and resultant CuAgSe NTs (d). TEM images of Cu$_2$Se NT (b) and CuAgSe NT (e). c,f High-resolution (HR) TEM images of the selected areas in (b) and (e), respectively. The insets contain fast Fourier transform (FFT) patterns of the HRTEM images. g) Scanning transmission electron microscopy (STEM) image and energy-dispersive X-ray spectroscopy (EDX) elemental mapping of Cu, Ag, and Se for a typical CuAgSe NT.

![Figure 2](image2.png)

**Figure 2.** XRD patterns of a) Cu$_2$Se NTs and b) CuAgSe NTs with standard XRD peaks.

![Figure 3](image3.png)

**Figure 3.** Structure diagrams of cubic Cu$_2$Se, and tetragonal and orthorhombic CuAgSe unit cells.
Because stoichiometric Cu$_2$Se is easily oxidized into nonstoichiometric Cu$_{2-x}$Se,$^{[30]}$ X-ray photoelectron spectroscopy (XPS) was used to determine the valence states of elements in both Cu$_{2-x}$Se and CuAgSe NTs (Figure 4). The spectra of Cu 2p confirm the presence of both Cu$^+$ and Cu$^{2+}$ (with a calculated ratio of 3.16) in Cu$_{2-x}$Se NTs, from which the Cu$^{2+}$ ions were completely transformed into Cu$^+$ in CuAgSe NTs after cation exchange, as evidenced by the disappearance of the characteristic peak of Cu$^{2+}$ at around 942 eV. Two peaks at 373.2 and 367.6 eV of Ag 3d in the product indicate the absence of other Ag species. The binding energy of Se 3d$_{3/2}$ at 53.7 eV corresponds to Se$^2-$ in both Cu$_{2-x}$Se and CuAgSe NTs, and the small peak at 58.2 eV in the Cu$_{2-x}$Se sample is attributed to surface-adsorbed Se (the ratio of Se$^2-$ to Se$^0$ in Cu$_{2-x}$Se was calculated to be 3.33).$^{[14,31–33]}$

The exchange reaction was investigated by analyzing the intermediate products collected after different reaction times. Figure 5 a shows the XRD patterns of samples collected at 1, 2, 10, and 20 min during the exchange reaction. When a solution of Cu$_{2-x}$Se in ethanol was reacted with a solution of AgNO$_3$ in ethanol for 1 min, the product obtained was a mixture of CuAgSe, Ag$_2$Se, and a small amount of Ag. This result demonstrates the fast exchange reaction between copper and silver ions, which is attributed to their strong mobility and capability for diffusion into/out of the lattice.$^{[7]}$ After reaction for 2 min, the product was still composed of these three compounds, but the amount of Ag$_2$Se and Ag decreased, as indicated by the lower intensity of the peaks in the XRD patterns. The intermediate sample collected at 10 min was a mixture of CuAgSe and Ag$_2$Se, and the peak corresponding to Ag disappeared or was not detectable. The final product collected at 20 min was pure CuAgSe, which demonstrated the complete transformation of Cu$_{2-x}$Se NTs into CuAgSe NTs. The transformation was also supported by XPS spectra of Ag$^+$ and Ag$^0$ in all samples collected at different reaction times (Figure 5 b). Within the initial 2 min, Ag 3d$_{5/2}$ peaks in the collected samples can be fitted into two peaks at 368.7 (Ag$^0$) and 367.3 eV (Ag$^+$). The Ag$^0$/Ag$^+$ ratios in the samples collected at 1 and 2 min decreased from 12.83 to 10.48, which meant that there was conversion of Ag$^0$ into Ag$^+$ as the reaction time was extended. When the mixture was reacted for 10 min, the absence of any Ag$^0$ peak suggested that all Ag formed was completely converted. The evolution of the morphology during cation exchange was monitored by SEM (Figure 5 c–f). There is no big difference in the morphologies, except that the surface nanosheets became thicker and rougher with increasing reaction time.

From the perspective of the molecular formula, Cu$_{2-x}$Se ($0 \leq x \leq 1$) could be considered as a mixture of CuSe and Cu$_2$Se, and the transformation of Cu$_{2-x}$Se into CuAgSe could be treated as their reactions with AgNO$_3$ [Eqs. (1) and (2)]. Cu$_2$Se could react with AgNO$_3$ to form CuAgSe, Ag, and Cu(NO$_3$)$_2$ through the redox reactions between Cu$^+$, Ag$^+$, and NO$_3^-$, as evidenced by the XRD and XPS results. CuSe reacted with AgNO$_3$ to form Ag$_2$Se owing to its greater solubility ($K_{sp}$ (CuSe) = 7.94 × 10$^{-48}$) than that of Ag$_2$Se ($K_{sp}$ (Ag$_2$Se) = 2.0 × 10$^{-48}$), which was proved by mixing a solution of pure CuSe in ethanol with a solution of AgNO$_3$ in ethanol at room temperature to form Ag$_2$Se (Figure S3 in the Supporting Information). The characteristic blue solution suggests the formation of Cu(NO$_3$)$_2$ during exchange reactions. Thus-formed Ag reacted with residual Se (adsorbed by Cu$_{2-x}$Se NTs) to form Ag$_2$Se [Eq. (3)], which further reacted with Cu$_2$Se to form CuAgSe [Eq. (4)].$^{[14]}$ To demonstrate these reactions, the effects of the molar ratio of Cu$_{2-x}$Se NTs to AgNO$_3$ in the product were investigated. In the cases of more Cu$_{2-x}$Se NTs (i.e., Cu$_{2-x}$Se/AgNO$_3$ = 2.5/1 or 1.5/1), there is insufficient AgNO$_3$ for the reactions and the main product is Cu$_{2-x}$Se, which is labeled with * in Figure S4 in the Supporting Information. In the opposite
cases (i.e., Cu₂Se/AgNO₃ = 1/2 or 1/3), excess AgNO₃ leads to the formation of Ag (marked with △ in Figure S4 in the Supporting Information). Therefore, it is crucial to control the molar ratio of Cu₂Se/AgNO₃; the optimal ratio is 1/1.

\[
\begin{align*}
\text{Cu}_2\text{Se} + 2 \text{AgNO}_3 & \rightarrow \text{CuAgSe} + \text{Ag} + \text{Cu(NO)}_3_2 \quad \text{(1)} \\
\text{CuSe} + 2 \text{AgNO}_3 & \rightarrow \text{Ag}_2\text{Se} + \text{Cu(NO)}_3_2 \quad \text{(2)} \\
2 \text{Ag} + \text{Se} & \rightarrow \text{Ag}_2\text{Se} \quad \text{(3)} \\
\text{Cu}_2\text{Se} + \text{Ag}_2\text{Se} & \rightarrow 2 \text{CuAgSe} \quad \text{(4)}
\end{align*}
\]

These exchange reactions took place spontaneously as a result of three factors. First, the high mobility of Cu²⁺, Cu⁺, and Ag⁺ ions and their strong capability for diffusion into/out of the lattice ensure fast reactions. The presence of copper vacancies also significantly accelerates the cation-exchange process at room temperature.\[34\] Second, the changes of Gibbs free energy (ΔG) for the reactions in Equations (1)–(4) are calculated to be −85.7, −55.8, −43.5, and −84.4 kJ mol⁻¹ based on the assumption that the reaction temperature is constant at 298 K and no entropy changes occur during the reaction. The standard ΔH° values at 298 K for CuSe, CuSe, Ag₂Se, AgNO₃, Cu(NO₃)₂, and CuAgSe are −65.3, −41.8, −43.5, −124.4, −302.9, and −96.9 kJ mol⁻¹, respectively.\[6,7,35,36\] Third, similar crystal structures of intermediate Ag₂Se and the CuAgSe product minimize the distortion of the crystal structure.

To better control the exchange process, we selected silver acetate to repeat the experiments and collected the intermediate products after different exchange times (i.e., 1, 2, 10, 20, and 60 min; Figures S5 and S6 in the Supporting Information). The results show that the complete transformation of Cu₂Se NTs into CuAgSe NTs took 60 min, owing to the lower dissociation capability of silver acetate in ethanol relative to that of AgNO₃. The same intermediate products (Ag₂Se and Ag) formed at an early stage (i.e., 1 and 2 min) and confirmed the same exchange process discussed above. Similar to the product prepared from AgNO₃, the morphology of CuAgSe NTs obtained from silver acetate is retained (Figure S7 in the Supporting Information).

As mentioned above, ternary CuAgSe might exhibit better electrochemical performance than that of its binary counterparts.\[37\] To evaluate the electrocatalytic activity, the resulting 1D/2D CuAgSe NTs were fabricated into CEs and then assembled with CdS/CdSe quantum dot (QD)-sensitized photoanodes to construct QDSSCs devices containing polysulfide electrolyte. The electrocatalytic activities were compared with those of CEs fabricated from Cu₂Se NTs and Au under the same conditions.\[38,39\] The average photovoltaic performance parameters are provided in Table 1. Compared with the Cu₂Se NT and Au CEs, QDSSCs incorporating CuAgSe NT CEs delivered a larger \(J_{SC}\) value of 17.57 mA cm⁻² (Figure 6a), which indicated the fast reduction of \(S_2^-\) to \(S^-\). In addition, the remarkable enhancement of the \(V_{OC}\) value of 581 mV, FF of 55.0%, can be ascribed to better electrical conductivity, and thus, suppressed charge recombination. Figure 6b shows the IPCE spectra of typical QDSSCs based on three different CEs. Compared with both Au and Cu₂Se NT CEs, the IPCE profile of QDSSCs employing the CuAgSe NT CE is higher over the entire wavelength region. This is consistent with the achieved \(J_{SC}\) value. The significant increase in IPCE further verified that CuAgSe NTs possessed both superior catalytic activity and high electrical conductivity. To understand the improved QDSSC performance, EIS and Tafel polarization measurements were performed on dummy cells assembled with two identical electrodes. Figure 6c shows the Nyquist plots of the dummy cells fabricated with three CEs; the inset shows the equivalent circuit. D) Tafel polarization of different dummy cells that were the same as those used for electrochemical impedance spectroscopy (EIS) measurements.

### Table 1. Photovoltaic parameters of QDSSCs with different CEs.\[\text{[4]}\]

<table>
<thead>
<tr>
<th>CEs</th>
<th>(V_{OC}) [mV]</th>
<th>(J_{SC}) [mA cm⁻²]</th>
<th>FF [%]</th>
<th>(\eta) [%]</th>
<th>(R_s) [Ω]</th>
<th>(R_w) [Ω]</th>
<th>(Z_w) [Ω]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAgSe NT</td>
<td>581</td>
<td>17.57</td>
<td>55.0</td>
<td>5.61</td>
<td>10.8</td>
<td>0.67</td>
<td>4.17</td>
</tr>
<tr>
<td>Cu₂Se NT</td>
<td>559</td>
<td>17.13</td>
<td>54.2</td>
<td>5.19</td>
<td>12.9</td>
<td>0.81</td>
<td>4.81</td>
</tr>
<tr>
<td>Au</td>
<td>507</td>
<td>13.34</td>
<td>49.1</td>
<td>3.32</td>
<td>16.0</td>
<td>42.43</td>
<td>72.13</td>
</tr>
</tbody>
</table>

[a] \(V_{OC}\) = open-circuit voltage, \(J_{SC}\) = short-circuit density, FF = fill factor, \(\eta\) = conversion efficiency, \(R_s\) = series resistance, \(R_w\) = charge-transfer resistance, \(Z_w\) = Warburg diffusion impedance.

\[\text{Figure 6. a) The photocurrent density-voltage (J-V) curves and b) incident photon-to-electron conversion efficiency (IPCE) spectra of QDSSCs with different CEs. c) Nyquist plots of the symmetrical dummy cells fabricated with three CEs; the inset shows the equivalent circuit. d) Tafel polarization of different dummy cells that were the same as those used for electrochemical impedance spectroscopy (EIS) measurements.}\]
the polysulfide electrolyte. The highest FF value for the QDSSCs with the CuAgSe CE can be attributed to the smallest $Z_{\text{v}}$ and $R_\text{sh}$ values. Figure 6d shows the logarithmic current density (logJ) as a function of the voltage (V) for the oxidation/reduction of polysulfide to form sulfide. The slopes for the anodic and cathodic branches are in the order of CuAgSe NTs > Cu$_2$Se NTs > Au. The larger slope for the CuAgSe NT indicates a larger exchange current density, which is consistent with the EIS results. Better electrochemical performance of the CuAgSe CE compared with that of the Cu$_2$Se CE is due to the higher mobility of both Cu$^+$ and Ag$^+$ ions in the CuAgSe NTs. The electrical conductivity of a single NT, to provide direct evidence for comparison of the electrical performances of these two NTs, will be measured and reported in our next study. The higher conversion efficiency of QDSSCs from ternary and binary NT-based CEs is attributed to the higher stability of metal selenides in polysulfide electrolyte than that of the Au CE because good conductivity is retained by avoiding corrosion and passivation.

The superior electrical conductivity and electrocatalytic activity of CuAgSe NTs relative to Cu$_2$Se NTs led to an enhancement in power conversion efficiency of QDSSCs made with CuAgSe CE ($\eta$ = 5.61%) in comparison with that made with Cu$_2$Se CE ($\eta$ = 5.19%), although this is not the highest record for QDSSCs.\textsuperscript{[44–46]} It should be noted that these values are lower than those in our previous reports because the photovoltaic devices used herein are made from commercial TiO$_2$ nanoparticles rather than porous TiO$_2$ nanosheets, which could effectively scatter the incident light and improve the conversion efficiency.\textsuperscript{[47]} The use of commercial TiO$_2$ nanoparticles would be important for evaluating the practical application of our 1D/2D CuAgSe NTs.

Conclusion

One-/two-dimensional pure ternary CuAgSe NTs were successfully prepared from Cu$_2$Se NTs by cation exchange with silver nitrate (or silver acetate) at room temperature within a short time. Fast cation exchange is due to the ionic characteristics of copper/silver chalcogenides, and the strong capability of copper and silver ions to diffuse into/out of the lattice. The CuAgSe NTs with a designed architecture were used to fabricate CEs for QDSSCs that showed better electrochemical performance and higher conversion efficiency ($\eta$ = 5.61%) than those of the original Cu$_2$Se NT CE ($\eta$ = 5.19%) and Au CE ($\eta$ = 3.32%). Our research not only opens up a new way to design more effective CE catalysts for highly efficient QDSSCs, but also provides a facile method to fabricate nanostructures of ternary selenides with specifically designed architectures for diverse applications.

Experimental Section

Chemicals

NaOH (97.0%, Alfa Aesar), Cu(NO$_3$)$_2$·3H$_2$O (99.5%, Aldrich), ethylenediamine (99.0%, Alfa Aesar), hydrazine (35 wt% in H$_2$O, Aldrich), 2-mercaptoethanol (> 99.0%, Aldrich), selenium powder (~325 mesh, 99.5%, Alfa Aesar), silver nitrate (> 99.0%, Sigma–Aldrich), silver acetate (> 99.9%, Sigma–Aldrich), anhydrous ethanol (> 99.5%, Sigma–Aldrich), acetone (> 99.9%, Sigma–Aldrich), and Milli-Q water (18.2 MΩ·cm) were used as received.

Synthesis of CuAgSe NTs

Cu$_2$Se NTs were prepared as described elsewhere.\textsuperscript{[46]} In a typical synthesis, as-prepared Cu$_2$Se NTs (0.15 mmol) were dispersed in anhydrous ethanol (0.5 mL), followed by the addition of solutions (2.5 mL) of silver nitrate or silver acetate (0.15 mmol) in ethanol under gentle stirring for 20–40 min. The black precipitates were purified by rinsing with distilled water and ethanol several times, followed by drying at room temperature.

Evolution of CuAgSe NTs

The evolution of NTs was investigated by characterizing samples collected at different reaction times. Two groups of experiments were performed. The first group of experiments were performed by using silver nitrate for the cation-exchange reaction, and the samples were collected at 1, 2, 10, and 20 min. The second group of experiments were conducted by using silver acetate for cation exchange, and the samples were collected at 1, 2, 10, 20, and 60 min.

Characterization of nanostructures

Powder XRD patterns for all samples were collected by using Cu K$_\alpha$ radiation ($\lambda$ = 1.5406 Å) at 40 kV and 25 mA with a position-sensitive detector. EDX, XPS, and ICP-AES measurements were used to characterize the chemical composition and crystal structure of the samples. The FE-SEM images of all the samples were collected by using a JEOL JMS 7500-FA microscope with an accelerating voltage of 5 kV and a secondary electron detector. The TEM images were collected on a JEOL ARM200F microscope operated at 200 kV.

Preparation of photoelectrodes

CdS- and CdSe-sensitized TiO$_2$ working electrodes were prepared by successively casting the commercial TiO$_2$ pastes on fluorine-doped tin oxide (FTO) substrates by using the doctor blade technique. The TiO$_2$ film was composed of a 13.7 µm transparent layer (18NR-T paste, Dysol) with a thickness of approximately 50 nm (obtained from the calibration curve of the sputtering).

Preparation of CEs

The CuAgSe and Cu$_2$Se electrodes were prepared on FTO substrates by using the doctor blade technique with CuAgSe and Cu$_2$Se pastes, respectively. The pastes were prepared from CuAgSe and Cu$_2$Se powders according to a previous study with some modifications.\textsuperscript{[20]} The newly formed films were annealed at 350°C for 30 min in an argon atmosphere to remove the binder and enhance the contact between the film and substrate. For comparison, gold electrodes were prepared by sputtering to yield a thickness of approximately 50 nm (obtained from the calibration curve of the sputtering).
Assembly and measurements of QDSSCs

The solar cells were fabricated by assembling the CE (CuAgSe, Cu$_2$Se, and Au) and QD-sensitized TiO$_2$ film electrode with a binder clip separated by a 60 μm thick spacer. A mask with a window area of 0.16 cm$^2$ was clipped onto the TiO$_2$ side to define the active area of the cell during testing. The polysulfide electrolyte was composed of 2 M Na$_2$S, 2 M S, and 0.2 M KCl in Milli-Q water. For QDSSCs assembled under each set of conditions, at least eight cells were prepared and tested in parallel, and the one with the medium value was chosen for the final data. For EIS and Tafel polarization measurements, symmetric dummy cells were assembled from two identical CEs with the same polysulfide electrolyte. The active area of the dummy cells was 0.64 cm$^2$. The J–V tests on the QDSSCs were performed under one sun conditions by using an air mass (AM) 1.5 solar simulator (Newport 1200-MS). The light intensity was fully calibrated with certified silicon solar cells. The light intensity from the solar simulator was controlled by using an air mass (AM) 1.5 solar simulator (Newport 1200-MS). The light intensity was set at 0 V and 10 mV, and the frequency ranged from 10$^6$ to 10$^{-2}$ Hz. Then, the Tafel polarization measurements were performed in the dark at a scan rate of 20 mV s$^{-1}$ on an electrochemical workstation (CHI660d).

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Metal exchange: One-/two-dimensional CuAgSe nanotubes are prepared from Cu$_2$Se nanotubes by a cation-exchange approach and explored as counter electrodes in quantum-dot-sensitized solar cells to achieve high conversion efficiency (see figure).