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## ARTICLE

# New Insights into the Phosphine-Free Synthesis of Ultrasmall $\text{Cu}_{2-x}\text{Se}$ Nanocrystals at the Liquid-Liquid Interface

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In this work, we first demonstrate a liquid-liquid interfacial strategy to prepare ultra small-size colloidal  $\text{Cu}_{2-x}\text{Se}$  NCs with blue-fluorescence (<5 nm) under moderate conditions. Specifically, preparation of  $\text{Cu}_{2-x}\text{Se}$  NCs proceeds via reaction of copper (II) stearate  $[\text{Cu}(\text{SA})_2]$  with  $\text{NaHSe}$  in the presence of phosphine-free oleic acid (OA) or oleylamine (OAm) as capping ligands under 95 °C at the toluene/water interface. The as-prepared NCs display a narrow size distribution compared with traditional high-temperature organic methods. Furthermore, a noncaustic and environmentally friendly ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ) as useful agents was introduced to replace the long-chain organic ligands for fabrication of NC-sensitized solar cells. The results indicate that the  $\text{Cu}_{2-x}\text{Se}$  NCs have potential applications in future optoelectronic devices.

## 1. Introduction

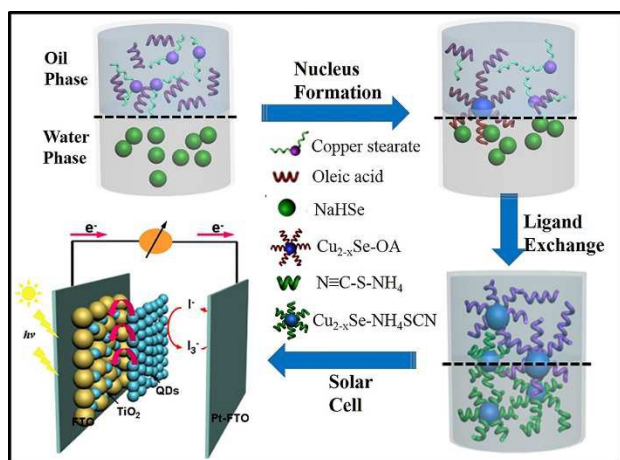
Colloidal semiconductor nanocrystals (NCs) with unique optical and electronic properties are receiving intensive attention in the fields of both fundamental science and technological application.<sup>1-3</sup> As a kind of binary compound, copper selenide can form in a wide range of stoichiometric compositions ( $\text{CuSe}$ ,  $\text{Cu}_2\text{Se}$ ,  $\text{CuSe}_2$ ,  $\text{Cu}_3\text{Se}_2$ ,  $\text{Cu}_5\text{Se}_4$ ,  $\text{Cu}_7\text{Se}_4$ , etc.) and non-stoichiometric compositions ( $\text{Cu}_{2-x}\text{Se}$ ), and can be constructed into several crystallographic forms (monoclinic, cubic, tetragonal, hexagonal, etc.).<sup>4,5</sup> Among them,  $\text{Cu}_{2-x}\text{Se}$ , with a direct band gap of 2.2 eV and indirect band gap of 1.4 eV at room temperature, is an attractive semiconductor for optoelectronic and biomedical applications, such as photovoltaics, optical filters, dry galvanic cells, gas sensors and cancer therapy.<sup>6-10</sup> Specifically,  $\text{Cu}_{2-x}\text{Se}$  is a desirable photovoltaic material due to avoiding the use of toxic heavy-metal ions, compared to other semiconductors including cadmium chalcogenides and lead chalcogenides. To date, various typical methods for fabricating  $\text{Cu}_{2-x}\text{Se}$  NCs have been widely investigated, such as hot-injection, template-assisted, sonochemical, solvothermal and microwave-assisted heating approaches.<sup>7,10-16</sup> Most recently, Deka et al. reported the synthesis of colloidal  $\text{Cu}_{2-x}\text{Se}$  NCs in hot coordinating solvents, using noncoordinating 1-octadecene (ODE) as solvent and oleylamine as both the reductant and the ligand.<sup>11</sup> Hessel et al. successfully fabricated the amphiphilic polymer-coated  $\text{Cu}_{2-x}\text{Se}$  NCs (~16 nm) by a colloidal hot injection method.<sup>8</sup>

Nonetheless, these techniques failed to obtain ultra small-size  $\text{Cu}_{2-x}\text{Se}$  NCs (<5 nm) exhibiting quantum confinement effects and photoluminescence (PL).

Recently, a liquid-liquid interface method has been illustrated as a beneficial alternative route to traditional homogeneous synthesis. As early as 1994, Brust et al. first developed the liquid-liquid interface approach to synthesize gold nanoparticles in an open system below 100 °C.<sup>17</sup> A modified liquid-liquid interface thermal approach (i.e., a liquid-liquid interface reaction in an autoclave, generally with the temperature above 100 °C) was further extended to synthesize II-VI semiconductor NCs ( $\text{CdS}$ ,  $\text{CdSe}$ ,  $\text{ZnS}$ ,  $\text{CdSe/CdS}$ , etc.) and some metal oxide NCs ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4$ , etc.) by An and colleagues.<sup>18-23</sup> Moreover, the liquid-liquid interfacial platform can be utilized to fabricate ordered architecture towards multifunctional performance. Russell and co-workers explored ultrathin membranes and capsules of NCs stabilized by cross-linked polymers at the toluene/water interface.<sup>24,25</sup> Taking advantage of the interface-directed synthetic pathway, our group developed one-dimensional ordered fluorescent microfibers<sup>26</sup> and multiple structures, such as belt-like, sheet-like, petal-like microstructures and etc.<sup>27-29</sup> Most recently, we first reported a toluene/water interfacial synthesis of single-crystalline  $\text{ZnTe}$  nanorods with high blue fluorescence for applications in LEDs.<sup>30</sup> Compared with traditional hot-injection methods, the creative interfacial method features obvious advantages: (1) the whole processes can be achieved under a moderate temperature of ~90 °C in most cases; (2) the limited

reaction area enables a slow nucleation and growth period resulting in smaller particle sizes; (3) the liquid-liquid interface method provides a favorable opportunity to construct multifunctional ordered architectures.

Herein, we demonstrate the first phosphine-free synthesis of  $\text{Cu}_{2-x}\text{Se}$  NCs with blue PL emission via a liquid-liquid interfacial strategy though there have been reports of the phosphine-free synthesis of copper-based selenide nanocrystals.<sup>31-34</sup> This work devotes an available low-temperature synthetic approach to achieving high-quality  $\text{Cu}_{2-x}\text{Se}$  NCs with quantum confinement effects. Preparation of  $\text{Cu}_{2-x}\text{Se}$  NCs proceeds via reaction of copper (II) stearate [ $\text{Cu}(\text{SA})_2$ ] with NaHSe in the presence of oleic acid (OA) or oleylamine (OAm) as capping ligands under 95 °C at the toluene/water interface. OA was added dropwise into toluene containing  $\text{Cu}(\text{SA})_2$  dissolved in toluene under vigorously stirring, followed by the addition of isometric water to form liquid-liquid biphasic system degassed with  $\text{N}_2$ . Afterwards, aqueous solution of fresh NaHSe was injected dropwise into the above  $\text{N}_2$ -saturated biphasic solution, and the reaction occurred at toluene/water interface. It turned out that the as-prepared  $\text{Cu}_{2-x}\text{Se}$  NCs can be grown into relatively monodispersed system by controlling variations in the reaction conditions and the size of which is very small with ~4 nm in diameter. We further attempted to investigate the potential photovoltaic properties of the original  $\text{Cu}_{2-x}\text{Se}$  NCs by fabricating NC-sensitized  $\text{TiO}_2$  solar cells, which showed a high fill factor indicating their potential application in photovoltaic devices.



**Scheme 1** Schematic representation of the synthesis of  $\text{Cu}_{2-x}\text{Se}$  NCs at the toluene/water interface and their application in sensitized  $\text{TiO}_2$  solar cells.

## 2. Experiment

### 2.1 Materials

Copper (II) stearate ( $\text{Cu}(\text{SA})_2$ , 99%), elemental selenium (Se, 99.99%), sodium borohydride ( $\text{NaBH}_4$ ), oleylamine (OAm, 90%), oleic acid (OA, 99%), 1-octadecene (ODE, 90%) and ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ , 99.99%) were purchased from Aldrich and used as received. Reagent-grade toluene,

methanol, and acetone were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as purchased without further purification. High-purity water with the resistivity of greater than  $18 \text{ M}\Omega\cdot\text{cm}^{-1}$  was used in the experiments.

### 2.2 Preparation of fresh oxygen-free NaHSe solution

In a typical procedure, 1.2 mmol (0.0454 g)  $\text{NaBH}_4$  was transferred to a small flask, and then 1.5 mL of ultrapure water was added. After 0.5 mmol (0.0395 g) of selenium powder was added, the reaction flask was cooled by ice. During the reaction, a small outlet connected to the flask was kept open to discharge the pressure from the resulting hydrogen. After several hours, the black selenium powder disappeared and white sodium tetraborate precipitate appeared on the bottom of the flask instead.

### 2.3 Synthesis of colloidal $\text{Cu}_{2-x}\text{Se}$ NCs capped with OA or OAm ligands

Typically,  $\text{Cu}(\text{SA})_2$  (0.6300 g, 1.0 mmol) and 2.0 mL OA (1.7870 g, 6.0 mmol) or 2.0 mL OAm (1.4830 g, 5.0 mmol) were first dissolved in toluene (50 mL), then 50 mL deionized water was added closely followed by the vigorously stirring for 1 h, and such mixed solution was degassed with  $\text{N}_2$  for 30 min. After that, the fresh oxygen-free NaHSe was added dropwise into the above  $\text{N}_2$ -saturated solution under stirring. Finally, the mixture was heated at 95 °C for 4 h to obtain  $\text{Cu}_{2-x}\text{Se}$  NCs. After cooling to a room temperature, the NCs were achieved by adding an excess amount of the absolute ethanol into the reacted solution. The as-formed NCs were easily dissolved in various apolar organic solvents (e.g. cyclohexane).

### 2.4 Fabrication of solar cell devices

A sandwich solar cell was fabricated from the as-prepared  $\text{Cu}_{2-x}\text{Se}$  NCs with a Pt-FTO electrode (Rainbow Solar Technology) as the counter electrode. Firstly, the  $\text{TiO}_2$ -FTO electrodes (Rainbow Solar Technology) were immersed in the concentrated toluene solution of  $\text{Cu}_{2-x}\text{Se}$  colloidal NCs for 48 h in the dark and then dried under vacuum. To remove the long capping group, the NCs film was then exchanged for ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ) by immersing the substrate in 130 mM (1% weight/volume) ammonium thiocyanate in acetone for 30 sec., followed by immersing in pure acetone for two minutes, and drying, all under nitrogen. The electrodes were sealed with a polymer gasket (Surlyn) and several drops of electrolyte (acetonitrile solution containing  $\text{I}^-/\text{I}_3^-$  redox couple, Rainbow Solar Technology) were infiltrated to the sealed electrodes through the hole on the work electrode. All the tests of the devices were processed in the glove box.

### 2.5 Material characterization

#### 2.5.1 Spectroscopy analysis

To further investigate the optical properties and ligand chemical structure of the as-prepared  $\text{Cu}_{2-x}\text{Se}$  NCs, Fourier-transform infrared (FT-IR) analysis was performed using a Nicolet-6700

spectrometer from Thermo Electron at room temperature. Ultraviolet-visible (UV-vis) absorption spectra were taken with a Perkin-Elmer Lambda 900 UV-vis spectrometer with the scan range 290-1000 nm. Photoluminescence (PL) spectra were measured on a Cary Eclipse fluorescence spectrophotometer at room temperature operating with a 350 nm laser beam as a light source and Xe lamp as excited source; the excitation and emission slits were 5 nm.

### 2.5.2 Transmission Electron Microscopy (TEM)

Low-resolution Transmission Electron Microscopy (TEM) images were recorded on a JEOL JEM 1011 microscope operating at 100 kV. The high-resolution transmission electron microscopy (HRTEM) observations and the selected area electron diffraction (SAED) were performed on a JEOL JEM-2010UHR instrument at an acceleration voltage of 200 kV. The samples for TEM analysis were prepared in a glove box by depositing a few drops of a dilute solution of nanocrystals onto carbon-coated Cu grids. The latter were then transferred immediately into the microscope. The particle diameter was estimated by using ImageJ software analysis of the TEM micrographs.

### 2.5.3 Powder X-ray Diffraction (XRD)

XRD was performed on a ARL X'TRA powder X-ray diffractometer with Cu K $\alpha$  radiation source ( $\lambda = 0.15406$  nm) at a scanning speed of 5°/min with  $2\theta$  range from 20° to 80°.

### 2.5.4 X-ray photoelectron spectroscopy (XPS)

To investigate the valence state of copper in the as-prepared Cu<sub>2-x</sub>Se NCs, X-ray photoelectron spectroscopy measurements were carried out on a Thermo Scientific Escalab 250Xi spectrometer (USA). A thick film of nanocrystals was prepared on a Si-substrate by dropcasting.

### 2.5.5 Photovoltaic measurement

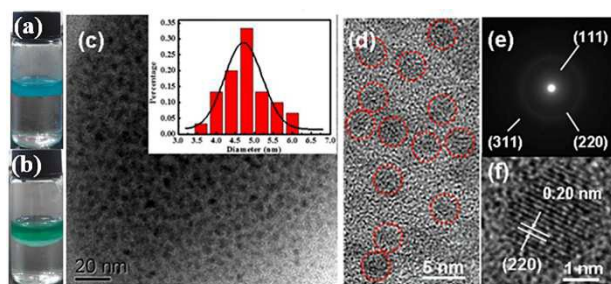
Photocurrent-voltage measurements were performed using a Keithley 2420 source meter (Keithley, USA). A 450 W Xenon lamp (Oriel, USA) was used as the light source and the light intensity was AM 1.5G one sun (100 mW cm<sup>-2</sup>) calibrated with a standard Si solar cell. The active area of the tested solar cells was 0.36 cm<sup>2</sup>.

## 3. Results and discussion

### 3.1 Characterization of Cu<sub>2-x</sub>Se NCs capped with OA or OAm

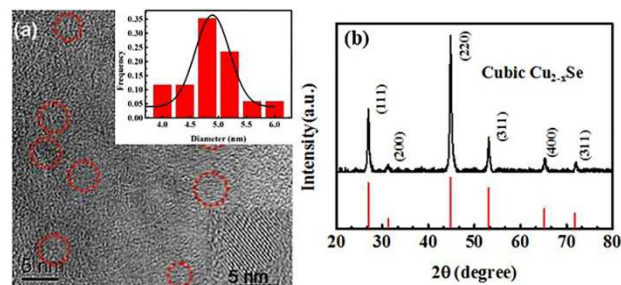
The liquid-liquid interfacial synthetic strategy permits the fabrication of high-quality blue fluorescent Cu<sub>2-x</sub>Se NCs. Fig. 1a-b show photographs of the toluene/water interface before and after the generation of the Cu<sub>2-x</sub>Se NCs capped with OA, respectively. TEM images of the as-synthesized Cu<sub>2-x</sub>Se NCs using OA as the stabilizing ligands are shown in Fig. 1c-d. The NCs are nearly monodisperse and spherical, and the histogram of the size distribution shown in the inset of Fig. 1c

indicates an average particle diameter of 4.6 nm with a relatively narrow size distribution. Fig. 1f illustrates the HRTEM image of an individual NC with clearly visible atomic lattice fringes, which demonstrate the highly crystalline nature of the Cu<sub>2-x</sub>Se NCs. The lattice fringes are separated by distances of 0.20 nm, which matches well with the expected lattice spacing of the (220) cubic Cu<sub>2-x</sub>Se crystal. The clear diffuse rings in the selected area electron diffraction (SAED) pattern also manifest excellent monodispersity and finely preserved crystalline structure of NCs in nature (Fig. 1e). The SAED data correspond to the cubic structure of Cu<sub>2-x</sub>Se NCs. The X-ray diffraction (XRD) analysis further verifies the cubic structure of Cu<sub>2-x</sub>Se (JCPDS card no. 06-0680). As revealed from the Fig. 2b, the four diffraction peaks can be indexed to the (111), (220), (311), and (400) diffraction of facecentered cubic (fcc) Cu<sub>2-x</sub>Se (JCPDS Card File, 6-680).



**Fig. 1** Photographs of the toluene/water interface (a) before and (b) after the generation of the Cu<sub>2-x</sub>Se NCs capped with OA, respectively. (c) TEM image of OA capped Cu<sub>2-x</sub>Se NCs with an average diameter of 4.6 nm. Upper inset shows size distribution of Cu<sub>2-x</sub>Se-OA NCs. (d) HRTEM image of Cu<sub>2-x</sub>Se NCs. (e) SAED pattern of Cu<sub>2-x</sub>Se NCs. (f) HRTEM image of a single NC.

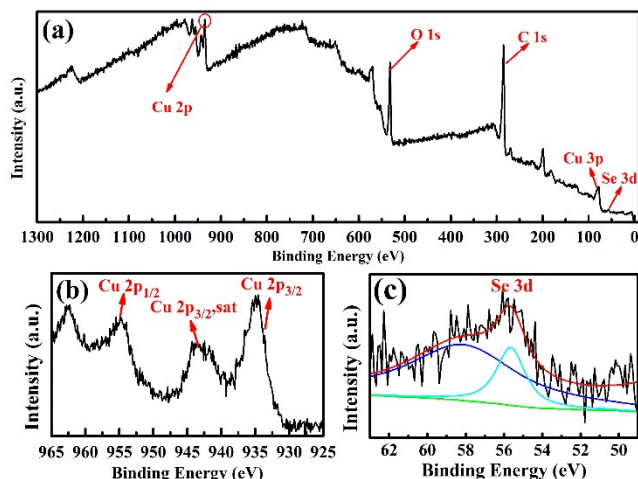
Moreover, in order to investigate the influence of ligand type (fatty amines) on the morphology of the NCs, OAm capped Cu<sub>2-x</sub>Se NCs was also studied. As shown in Fig. 2a, the as-synthesized Cu<sub>2-x</sub>Se NCs capped with OAm have also a narrow size distribution with an average size of 4.7 nm (Fig. 2a), and the resulting NCs modified with OAm ligands are approximately spherical in shape.



**Fig. 2** (a) TEM image of OAm capped Cu<sub>2-x</sub>Se NCs. The upper inset in (a) is the size distribution of Cu<sub>2-x</sub>Se-OAM and the under inset in (a) is HRTEM image of a single NC. (b) XRD pattern of Cu<sub>2-x</sub>Se NCs capped with OAm.

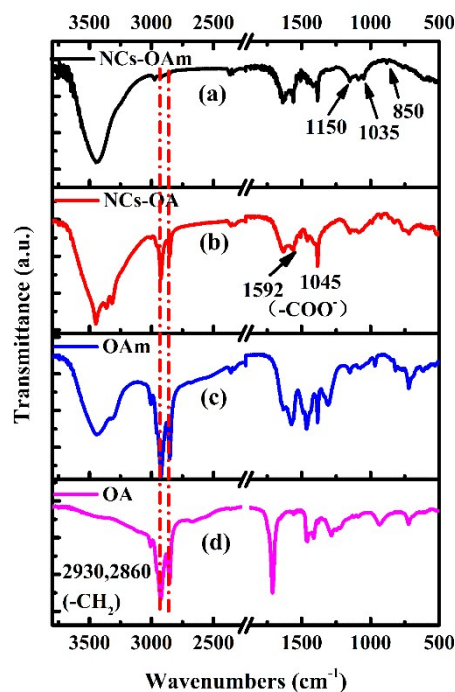
### 3.2 XPS and FT-IR representation of $\text{Cu}_{2-x}\text{Se}$ NCs

To investigate the valence state of copper in the as-prepared  $\text{Cu}_{2-x}\text{Se}$  NCs, X-ray photoelectron spectroscopy (XPS) was further presented (Fig. 3a-c). As shown in Fig. 3a, there existed C, O, Cu and Se peaks observed showing samples with high purity. Fig. 3b manifested that the Cu  $2p_{3/2}$  peak at 935.6 eV and the Cu  $2p_{1/2}$  peak at 955.2 eV implied that the oxidation state of the copper species corresponded to Cu (I). In addition, the Cu  $2p_{3/2, \text{sat}}$  peak, a satellite line of Cu 2p at 940-945 eV, indicated the presence of Cu (II) in  $\text{Cu}_{2-x}\text{Se}$ . A small peak at 58-60 eV in Fig. 3c showed a high oxidation state of Se,<sup>11</sup> which may be originated from the contamination before XPS test.



**Fig. 3** (a) XPS survey spectrum of  $\text{Cu}_{2-x}\text{Se}$  NCs. (b) XPS core-level spectra of  $\text{Cu}_{2-x}\text{Se}$  from Cu  $2p^3$  and (c) Se 3d.

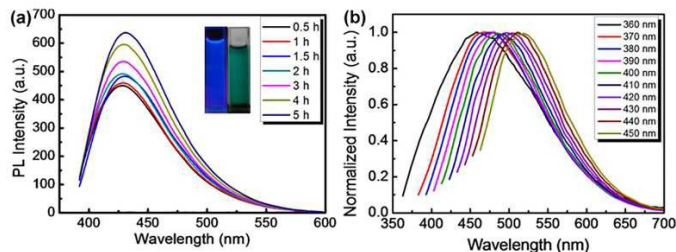
The FT-IR spectrum of  $\text{Cu}_{2-x}\text{Se}$  NCs stabilized with OA and OAm are presented in Fig. 4. In detail, the presence of strong stretching at 2930 and 2860  $\text{cm}^{-1}$  in both samples was respectively assigned to the asymmetric and symmetric stretching vibrations of methylene ( $-\text{CH}_2$ ) in the long alkyl chain. Broad peaks at 1592  $\text{cm}^{-1}$  and 1405  $\text{cm}^{-1}$  revealed the existence of the alkaline carboxyl groups on the surfaces of  $\text{Cu}_{2-x}\text{Se}$  NCs. Additionally, the three sharp peaks at 1150, 1035 and 850  $\text{cm}^{-1}$  in the IR spectrum of  $\text{Cu}_{2-x}\text{Se}$ -OAm NCs were indexed to C-N stretch of OAm. Based on the FT-IR analysis of  $\text{Cu}_{2-x}\text{Se}$  NCs, it is confirmed that these as-obtained  $\text{Cu}_{2-x}\text{Se}$  NCs are possibly coated by octadecylamine and oleic acid, respectively.



**Fig. 4** FT-IR spectra of (a) as-prepared  $\text{Cu}_{2-x}\text{Se}$  NCs capped with oleylamine, (b) as-prepared  $\text{Cu}_{2-x}\text{Se}$  NCs capped with oleic acid, (c) oleylamine and (d) oleic acid.

### 3.3 Effect of the reaction time on the formation and the PL properties of $\text{Cu}_{2-x}\text{Se}$ NCs

To acquire insight into the synthesis of NCs at the liquid-liquid interface, the influence of the reaction parameters on the formation and the PL properties of  $\text{Cu}_{2-x}\text{Se}$  NCs were systematically investigated. In order to avoid the oxidation of  $\text{Cu}_{2-x}\text{Se}$  into the Se phase when injecting NaHSe solution at 95  $^{\circ}\text{C}$ . In this case, we alternatively injected the fresh oxygen-free NaHSe solution into the precursor solution at room temperature, and the mixture was then heated at 95  $^{\circ}\text{C}$ . Fig. 5a shows the PL spectra of  $\text{Cu}_{2-x}\text{Se}$ -OA NCs taken at different injecting timing intervals during a reaction at 95  $^{\circ}\text{C}$ . It indicated that PL properties was obviously improved with the extended reaction time.



**Fig. 5** (a) Temporal evolution of PL emission spectra of the  $\text{Cu}_{2-x}\text{Se}$  NCs. Upper inset shows photographs of the NCs under (right) the room light and (left) a UV lamp (b) Normalized PL spectra of  $\text{Cu}_{2-x}\text{Se}$  NCs at different excitation wavelength (in 10 nm increment starting from 360 nm to 450 nm).

### 3.4 A proposed mechanism for a formation of $\text{Cu}_{2-x}\text{Se}$ NCs at a toluene/water interface

Notably, to the best of our knowledge, this is the first synthesis of fluorescent  $\text{Cu}_{2-x}\text{Se}$  NCs with such a small size. The as-prepared  $\text{Cu}_{2-x}\text{Se}$  NCs could be stably dispersed in organic solvents (toluene, n-hexane or hexamethylene) for a few months without any precipitation. Fig. 6 illustrates a proposed mechanism for formation of  $\text{Cu}_{2-x}\text{Se}$  NCs at a toluene/water interface by using  $\text{Cu}(\text{SA})_2$  as copper precursor and water soluble  $\text{NaHSe}$  as selenium precursor, respectively. In order to further slow the reaction rate, the biphase interfacial method involves reaction of two kinds of molecular precursors spatially separated in the toluene and aqueous phases, and the nucleation and growth of NCs only occur at the liquid-liquid interface, which experiences a much longer nucleation stage overlapped with the growth stage comparing with the one-phase system, and the formed NCs show extremely narrow size distributions. The size distribution can be focused during the diffusion-controlled growth process. The diffusion-controlled growth rate ( $dr/dt$ ) of particles is dependent on particle size according to Reiss' theoretical calculation.<sup>35</sup>

$$dr/dt = DV_m(C_b - C_r)/r \quad (1)$$

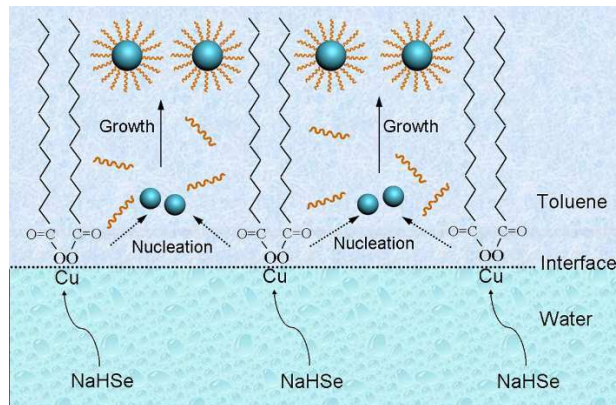
Where  $D$  is the diffusion coefficient,  $r$  is the particle radius,  $V_m$  is the molar volume of the materials,  $C_r$  and  $C_b$  are the solubility of the NCs and corresponding bulk solid, which could be concluded from the Gibbs-Thomson equation.<sup>36</sup>

$$C_r = C_b \exp(2\sigma V_m/rRT) \quad (2)$$

Where  $\sigma$  is the specific surface energy,  $R$  is the gas constant, and  $T$  is the temperature. Therefore, the growth rate  $dr/dt$  can also be deduced from Eq. (1) and Eq. (2) as:

$$dr/dt = DV_m C_b [1 - \exp(2\sigma V_m/rRT)]/r \quad (3)$$

This equation means that the growth rate  $dr/dt$  is lowered with increasing particle radius  $r$ . In other words, the smaller particles have a faster growth rate than the larger ones, so the smaller particles can always catch up with the larger ones with increasing reaction time and their size distribution can narrow with the growth of nanocrystals. Therefore, a lengthy growth process is very important to the size distribution of NCs. In this toluene/water interface system, when the nuclei and NCs form, they will go into toluene, and then go back to the toluene/water interface to continue growth, which can further slow the rate of growth of  $\text{Cu}_{2-x}\text{Se}$  NCs, favouring the formation of monodisperse and ultrasmall NCs. The formed nuclei and NCs, capped by long-chain ligands (OA or OAm), can be well dispersed in toluene.  $\text{Cu}_{2-x}\text{Se}$  NCs have a long nucleation and growth period compared with those made by the hot-injection approach (15 minutes), but the final NCs still exhibit an extremely narrow size distribution.

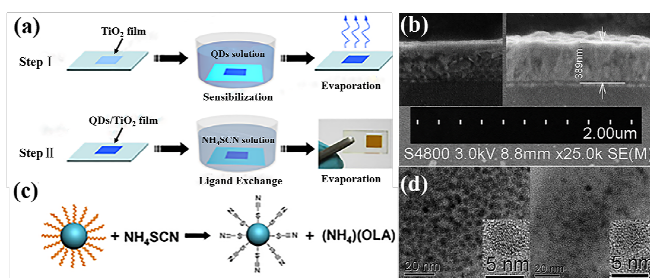


**Fig. 6** A proposed mechanism for a formation of oil-soluble  $\text{Cu}_{2-x}\text{Se}$  NCs at a toluene/water interface by using water-soluble  $\text{NaHSe}$  as selenium precursor.

### 3.5 Preparation and characterization of solar cells based on the as-synthesized $\text{Cu}_{2-x}\text{Se}$ NCs

To make the best use of these  $\text{Cu}_{2-x}\text{Se}$  NCs with high-quality and low toxicity, we fabricated solar cells with a sandwiched structure based on the as-synthesized  $\text{Cu}_{2-x}\text{Se}$  NCs. As shown in Fig. 7a, the photoelectrode was firstly fabricated by direct absorption of  $\text{Cu}_{2-x}\text{Se}$  NCs onto a  $\text{TiO}_2$  film residing on a FTO transparent substrate. Fig. 7b showed the SEM images of  $\text{TiO}_2$  film (Left) and QDs/ $\text{TiO}_2$  film (Right). Generally, the efficiency of moving charges in and out of NCs strongly depends on the NC environment.<sup>37,38</sup> However, the presence of large, bulky ligands on the surface of as-prepared  $\text{Cu}_{2-x}\text{Se}$  NCs creates an insulating barrier around each NC and suppresses interparticle charge transport, a limitation for device integration. To address these problems, several approaches including thermal decomposition of the original ligand, or ligand-exchange process have been explored. 1, 2-ethanedithiol and hydrazine have been used to exchange the longer ligands used in NC synthesis and assembly to increase film conductivity and fabricate solar cells<sup>39</sup> and QD FETs.<sup>37,40</sup> Recently, the development of novel and short inorganic ligands serving as useful agents for ligand-exchange has become a hot research topic.<sup>41,42</sup> Murray and co-workers employed nitrosonium tetrafluoroborate ( $\text{NOBF}_4$ ) as a new inorganic ligand to replace the long-chain original ligands of various NCs (metal oxides, metals, semiconductors, and dielectrics) of different sizes and shapes.<sup>43</sup> More interestingly, the hydrophilic NCs acquired by  $\text{NOBF}_4$  treatment can readily experience further surface modification, because there exist the weak binding affinity between  $\text{BF}_4^-$  anions and the NC surface. Talapin et al. used highly nucleophilic metal chalcogenide complexes (MCCs), such as  $\text{Sn}_2\text{S}_6^{4-}$  and  $\text{In}_2\text{Se}_4^{2-}$  for ligand exchange, allowing phase transfer of NCs from a hydrophobic solvent to various hydrophilic media.<sup>44,45</sup> The reduced interparticle spacing that results from the exchange of long hydrocarbon molecules with the much smaller MCC clusters enables strong electronic coupling between neighboring NCs, yielding highly conductive NC films. However, the expensive  $\text{NOBF}_4$ , the high reactivity

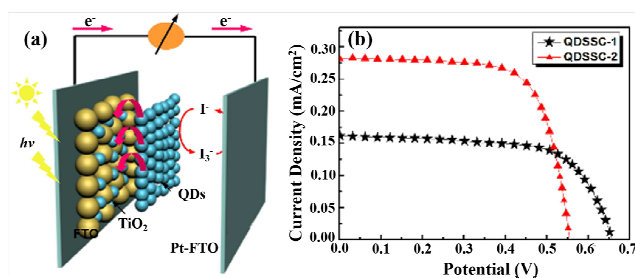
of hydrazine and the high toxic MCCs, such that the ligand-exchange reactions must be performed with great caution under inert environment, limited the further wide application of these approaches. In addition, they most recently explored the simplest and cheapest metal-free inorganic ligands, such as  $S^{2-}$ ,  $HS^-$ ,  $Se^{2-}$ ,  $HSe^-$ ,  $Te^{2-}$ ,  $HTe^-$ ,  $TeS_3^{2-}$ ,  $OH^-$  and  $NH_2^-$  to obtain all-inorganic colloidal NCs towards FETs.<sup>46</sup> Herein, we first introduced a noncaustic and environmentally friendly  $NH_4SCN$ , which present attractive applications in nanodevices,<sup>47,48</sup> to replace the long, insulating ligands for fabrication of NC solar cells. Typically, the  $TiO_2$ -FTO photoanode (Rainbow Solar Technology) was immersed in  $Cu_{2-x}Se$  colloidal solutions for 48 h in the dark and then dried under vacuum. Then the NCs sensitized  $TiO_2$  photoanode was dipped into a 130 mM (1% weight/volume)  $NH_4SCN$  in acetone for 30 sec, followed by washing in pure acetone for 30 sec, to remove any  $NH_4SCN$  and the replaced organic ligand residues. The detailed preparation of the NC sensitized  $TiO_2$  photoanode and the mechanism of ligand-exchange are presented in fig. 7a-c. Fig. 7d showed the TEM images of  $Cu_{2-x}Se$  capped with OA (Left) and  $Cu_{2-x}Se$  capped with  $SCN^-$  (Right). Afterwards, a platinum-coated FTO substrate (Rainbow Solar Technology) was used as the counter electrode. The electrodes were sealed with a polymer gasket (Surlyn) and several drops of electrolyte (acetonitrile solution containing  $I^-/I_3^-$  redox couple, Rainbow Solar Technology) were infiltrated to the sealed electrodes through the hole on the work electrode. Finally a sandwich solar cell was successfully fabricated as shown in Fig. 8a.



**Fig. 7** (a) Schematic presentation of the  $Cu_{2-x}Se$ -Based NCSSC. (b) SEM images of  $TiO_2$  film (Left) and QDs/ $TiO_2$  film (Right) (c) Schematic of NCs surfactant ligand removal using  $NH_4SCN$ . (d) TEM images of  $Cu_{2-x}Se$  capped with OA (Left) and  $Cu_{2-x}Se$  capped with  $SCN^-$  (Right).

For comparison, another  $TiO_2$  photoanode without  $NH_4SCN$  treatment was also made under the same sensitization time of about 48 h and its photovoltaic properties were also tested in parallel. The measurement was performed in a standard AM1.5 G irradiation and the J-V characteristics of as-prepared  $Cu_{2-x}Se$ -OA NCSSC is shown in Fig. 8b. The detailed data of the short-circuit current density ( $J_{sc}$ ), open circuit voltage ( $V_{oc}$ ), fill factor (FF) and power conversion efficiency (PCE) are listed in the table 1. Interestingly, it could be seen that cell with  $NH_4SCN$  treatment exhibits higher  $\eta$  and FF compared with the cell without  $NH_4SCN$  treatment. Though the PCE is relatively low compared with other NCs sensitized solar cells such as PbS and CdS, the high FF offers promising opportunities for

further development of  $Cu_{2-x}Se$  NCs. In addition, further study of photoresponse characteristics of the device shown in Fig. 9 reveals that the device can follow the fast-varying optical signal with good stability and reproducibility.



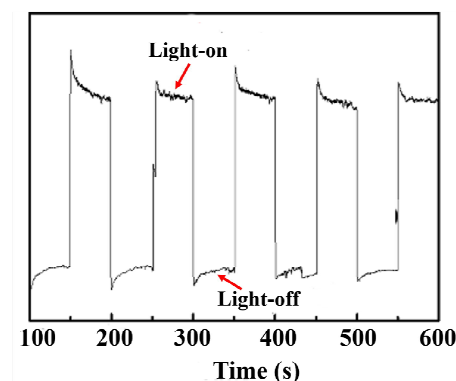
**Fig. 8** (a) A sandwich solar cell (b) Characteristic J-V curves for NCSSC-1 (without  $NH_4SCN$  treatment) and NCSSC-2 (with  $NH_4SCN$  treatment) measured under one-sun illumination (AM 1.5 G,  $100 \text{ mW}\cdot\text{cm}^{-2}$ ). The active areas of the photoelectrodes were all  $0.36 \text{ cm}^2$  for the both NCSSCs.

**Table 1.** Results obtained from the photocurrent-voltage (J-V) measurements of two QDSSCs.

Sample	$J_{sc}^a$ ( $\text{mA}/\text{cm}^2$ )	$V_{oc}^b$ (V)	FF <sup>c</sup> (%)	Eff <sup>d</sup> (%)	Cell area ( $\text{cm}^2$ )
QDSSC-1	0.162	0.657	62.7	0.071	0.36
QDSSC-2	0.289	0.552	56.0	0.111	0.36

<sup>a</sup> Short-circuit current density. <sup>b</sup> Open circuit voltage. <sup>c</sup> Fill factor.

<sup>d</sup> Light-electron conversion efficiency.



**Fig. 9** On-off curves of photocurrent versus time show the reproducibility of time resolved photocurrent.

## 4. Conclusions

In summary, we first present a liquid-liquid interfacial strategy to prepare monodispersed colloidal  $Cu_{2-x}Se$  NCs (<5 nm) under mild conditions. Encouragingly, this approach shows the unique advance in that the as-prepared NCs have a narrow size distribution compared with traditional high-temperature organic methods. The obtained  $Cu_{2-x}Se$  NCs exhibit bright blue fluorescence due to the quantum confinement. In order to develop it in the photovoltaic application, we introduced a noncaustic and environmentally friendly  $NH_4SCN$  as useful agents to replace the long-chain organic ligands for fabrication

of NCSSC. We further attempted to investigate the photovoltaic properties of the original  $\text{Cu}_{2-x}\text{Se}$  NC-based solar cells, which showed a high fill factor indicating their potential application in photovoltaic devices.

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### Notes and references

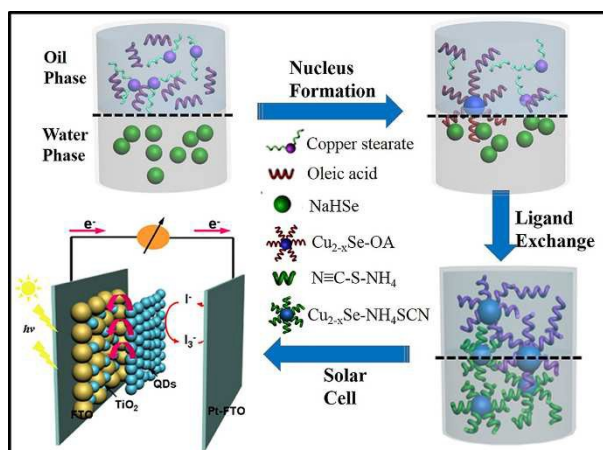
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## Phosphine-Free Synthesis of Ultrasmall $\text{Cu}_{2-x}\text{Se}$ Nanocrystals at the Liquid-Liquid Interface

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We first demonstrate a liquid-liquid interfacial strategy to prepare ultra small-size ( $<5$  nm) colloidal  $\text{Cu}_{2-x}\text{Se}$  NCs with blue-fluorescence under moderate conditions, using a noncaustic and environmentally friendly ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ) as useful agents to replace the long-chain organic ligands for fabrication of NC-sensitized solar cells.