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Communication

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Alkylthiol-Enabled Se Powder Dissolution in Oleylamine at Room Temperature for the Phosphine-Free Synthesis of Copper-Based Quaternary Selenide Nanocrystals

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Supporting Information

ABSTRACT: Enhancement of Se solubility in organic solvents without the use of alkylphosphine ligands is the key for phosphine-free synthesis of selenide semiconductor nanocrystals (NCs). In this communication, we demonstrate the dissolution of elemental Se in oleylamine by alkylthiol reduction at room temperature, which generates soluble alkylammonium selenide. This Se precursor is highly reactive for hot-injection synthesis of selenide semiconductor NCs, such as $Cu_2ZnSnSe_4$, $Cu(InGa)Se_2$, and CdSe. In the case of $Cu_2ZnSnSe_4$, for example, the as-synthesized NCs possessed small size, high size monodispersity, strong absorbance in the visible region, and in particular a promising increase in photocurrent under AM1.5 illumination. The current preparation of the Se precursor is simple and convenient, which will promote the synthesis and practical applications of selenide NCs.

Exploring novel approaches to produce low-cost, high-efficiency photovoltaic cells has attracted great interest because of the urgent need for clean and renewable energy sources.[1,2] Recent advances in the colloidal synthesis of semiconductor nanocrystals (NCs) have opened the door to address this challenge.[3−5] Various II−VI and I−III−VI_2 semiconductors such as CdSe, CdTe, $CuInS_2$, $CuInSe_2$, and $Cu(InGa)Se_2$ have been studied intensively.[6−12] However, despite their appealing photovoltaic performance, the intrinsic toxicity of cadmium and the limited supply and increasing price of indium and gallium shed doubt on the future applicability of these NCs.[13−19] Therefore, alternative materials with high abundance and low cost and toxicity must be found. Most recently, Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ NCs have been explored and are regarded as potential candidates because of the suitable band gap (1.0−1.5 eV), high absorption coefficient (up to 105 cm^{-1}), good photostability, low toxicity, high photovoltaic efficiency, and relative abundance of the component elements.[20,21] However, to the best of our knowledge, only a few reports have been devoted to the synthesis of $Cu_2ZnSnSe_4$ NCs by wet chemical methods.[22,23]

The conventional synthesis of selenide NCs usually involves the preparation of soluble Se precursors using alkylphosphines, such as trioctylphosphine (TOP) and tributylphosphine (TBP),[6,7] but TOP and TBP are hazardous and unstable, requiring the use of a glovebox. The current trend in synthesizing selenide NCs involves phosphine-free routes, which have been implemented by directly dissolving Se powder or other Se precursors in high-boiling-point solvents such as octadecene, oleylamine (OLA), olive oil, and paraffin.[24−31] Such a strategy is also applicable for synthesizing copper-based ternary and quaternary selenide NCs.[26−31] However, the reactivity of Se precursors in this approach is difficult to control. It has recently been reported that Se powder can be reduced by sodium borohydride ($NaBH_4$) in the presence of OLA.[32−34] However, $NaBH_4$ is easily oxidized in the open air, and the reduction reaction between $NaBH_4$ and Se powder must be assisted with ultrasonication. These facts inspired us to exploit low-toxicity, safe, and cheap Se precursors for the synthesis of high-quality selenide NCs.

Herein we present an additional phosphine-free route for synthesizing high-quality $Cu_2ZnSnSe_4$ NCs in organic solvents. Se powder is foremost reduced by dodecanethiol (DT) in the presence of OLA to generate a soluble alkylammonium selenide at room temperature. This Se precursor is highly reactive and suitable for the synthesis of $Cu_2ZnSnSe_4$ NCs. In a typical synthesis, stoichiometric amounts of $CuCl_2$, $SnCl_4$, and $ZnCl_2$ were placed in a four-neck flask contained OLA and DT at room temperature and cycled between vacuum and nitrogen three times. Afterward, the mixture was kept at 60 °C under vacuum for 30 min and then heated to 180 °C. At this temperature, the Se precursor prepared by dissolving Se powder in the mixture of OLA and DT was injected. The reaction mixture was maintained at 180 °C for 30 min to allow NCs to grow. After that, the flask was rapidly cooled to room temperature, and the as-synthesized NCs were washed three times by precipitation with ethanol and redispersed in toluene or chloroform.

As indicated in Figure 1a, Se powder cannot be dissolved in DT or OLA alone but does dissolve in their mixture. In the proposed reduction reaction between Se powder and DT (Figure 1b), Se powder is reduced by DT, whereas DT is oxidized to disulfides. The formation of disulfides was verified both by NMR spectroscopy and mass spectrometry (Figures S1

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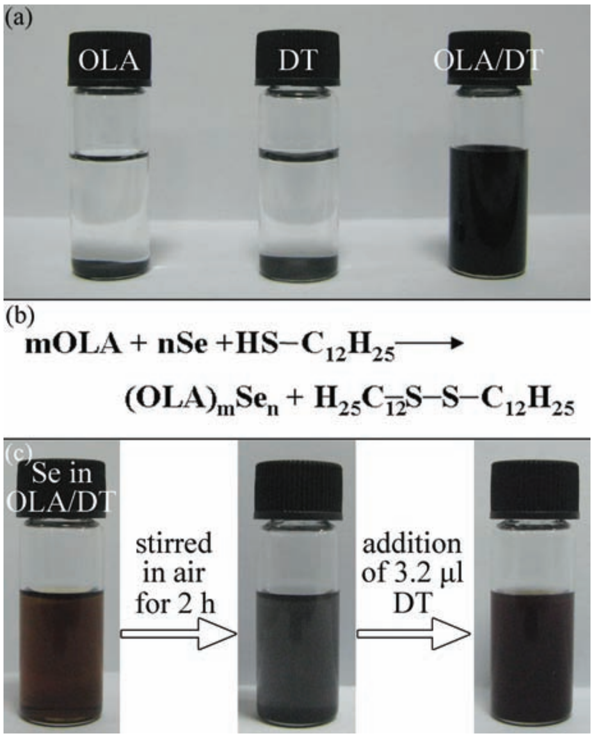

Figure 1. (a) Photograph of vials containing 1.5 mmol of Se powder in 1.5 mL of OLA, 1.5 mL of DT, and a mixture of 0.75 mL each of OLA and DT. (b) Equation for the reaction between Se powder and DT in the presence of OLA. (c) Entire redox cycle of the OLA/DT/Se system. The initial solution contained 0.0125 mmol of Se, 1.5 mL of OLA, and 3.2 μL of DT).

and S2 in the Supporting Information). Although the exact valence state of the reduced Se was difficult to determine, the Se should exist in the form of OLA−Se complexes.[32−34] As mentioned above, Se powder can be reduced with $NaBH_4$ to give Se^{2-}, which further associates with OLA to form OLA_2Se, thus making elemental the Se soluble.[32−34] In our system, the Se powder completely dissolved as the DT/Se molar ratio reached 1/1, indicating that the OLA−Se complexes should be in the form OLA_mSe_n ($m \leq n$) rather than OLA_2Se. Besides DT, other alkylthiols, such as hexadecanethiol (HT) could also dissolve Se. A photograph of Se powder dissolved in the mixture of OLA and HT is shown in Figure S3.

The resultant Se solution was very stable and difficult to oxidize because of the strong antioxidant ability of DT. In comparison, the Se precursor prepared by $NaBH_4$ reduction was easy to oxidize. Figure 1c shows a redox cycle of the OLA/DT/Se system with decreased amounts of Se powder and DT to investigate the reduction reaction. After addition of DT to Se-containing OLA with a DT/Se molar ratio of 1/1, the Se powder completely dissolved and formed a clear solution in the color of bright wine, indicating that the Se powder was reduced by DT. The solution was then stirred in the open air to oxidize the Se solution. After the solution was stirred for 2 h, the bright color faded and the mixture became gray with visible suspended black grains, representing oxidation of the Se solution. At this time, adding to the solution the same amount of DT as was used to make Se powder dissolve caused the black suspension to return to the bright wine color, indicating the reduction of Se. The aforementioned redox cycle firmly supported the reaction between Se and DT and meanwhile exhibited the high antioxidant ability of the OLA/DT/Se system as a Se precursor for synthesizing selenide NCs such as $Cu_2ZnSnSe_4$.

Figure 2a shows a transmission electron microscopy (TEM) image of the as-synthesized $Cu_2ZnSnSe_4$ NCs. The NCs are fairly monodisperse and appear to be spherical with an average diameter of 3.4 nm. The high-resolution TEM (HRTEM) image shown in Figure 2b indicates that the NCs are well-formed single crystals with the interplanar distances of 0.33 nm, consistent with the (112) crystallographic facet of tetragonal $Cu_2ZnSnSe_4$.[22,23] The Fourier transform (FT) and X-ray diffraction (XRD) patterns (Figure 2d,e) firmly support that these NCs possess a tetragonal structure. The diffraction peaks in the XRD pattern appear at 27.2, 45.2, 53.3, 65.9, and 72.7°, consistent with the (112), (220/204), (312), (400/008), and (316) planes, respectively, of tetragonal-phase $Cu_2ZnSnSe_4$.[22,23] Notably, this is the first synthesis of $Cu_2ZnSnSe_4$ NCs with such a small size. This resulted from the existence of DT in the system, which suppressed the growth of bigger NCs by forming strong metal−S bonding on the NC surface.

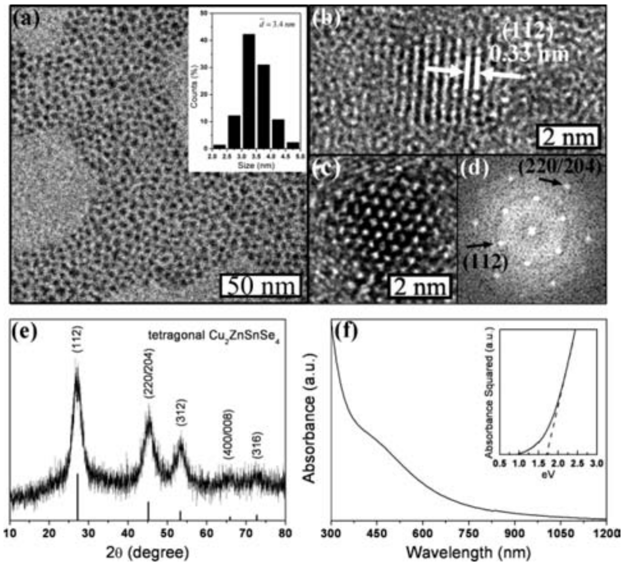

Figure 2. (a) TEM and (b, c) HRTEM images of $Cu_2ZnSnSe_4$ NCs. (d) FT pattern of the selected area of the same particle showed in (c). (e) XRD pattern and (f) UV−vis absorption spectrum of the $Cu_2ZnSnSe_4$ NCs. Insets: (a) size distribution of the NCs; (f) plot of the squared absorbance vs photon energy.

The UV−vis absorption spectrum of the $Cu_2ZnSnSe_4$ NCs (Figure 2f) shows that the NCs have strong absorbance in the visible region. The band gap of the NCs was estimated to be 1.7 eV by extrapolating the linear region of a plot of the squared absorbance versus the photon energy (Figure 2f inset). In previous reports, the band gap of $Cu_2ZnSnSe_4$ NCs was 1.0−1.5 eV.[22,23] The difference is mainly attributed to the small size of $Cu_2ZnSnSe_4$.[35] With decreasing NC size, an obvious increase in the band gap is revealed (Figure S4).

The composition of the as-synthesized $Cu_2ZnSnSe_4$ NCs was characterized by energy-dispersive X-ray spectroscopy (EDX) (Figure S5), which showed a Cu/Zn/Sn/Se/S atomic ratio of 2.02/0.37/1.00/3.43/0.59. This ratio is not consistent with the amount of the coprecursors used. We ascribe this discrepancy to the different reactivities of the cationic precursors, especially at low reaction temperature. In our method, the synthesis temperature is only 180 °C. The copper and tin had higher reactivity than zinc in the reaction with selenium. Thus, Cu_2Se nucleated first, while tin and subsequently zinc gradually entered into the structure of the NCs in the crystal growth stage.[36] This led to a decrease in the zinc content in the as-synthesized NCs. Doubling the amount of zinc precursor only slightly increased the zinc content in the as-synthesized NCs (Figures S6 and S7), clearly showing the low reactivity of zinc. The low synthesis temperature also lowered the homogeneity in single NC composition, which has been systematically revealed by previous works.[23,36] Moreover, the high sulfur content revealed the presence of alkylthiol on the NC surface, which might influence the optoelectronic applications of the as-synthesized NCs. In this scenario, the alkylthiol is replaceable with proper molecular metal chalcogenide complexes.[37] Figure S8 shows the Raman spectrum of the $Cu_2ZnSnSe_4$ NCs. Because of their small size, the NCs exhibited a broad peak rather than the sharp peaks of bulk $Cu_2ZnSnSe_4$ crystals.[38,39] The peak-fit processing confirmed that the NCs are mainly quaternary $Cu_2ZnSnSe_4$, though the significant presence of Cu_2SnSe_3 cannot be arbitrarily ruled out.

X-ray photoelectron spectroscopy (XPS) was also performed to investigate the valence states of the four constituent elements in the as-synthesized $Cu_2ZnSnSe_4$ NCs (Figure S9). The copper spectrum shows two narrow and symmetric peaks at 931.8 and 951.5 eV, indicative of Cu(I), which has a peak splitting of 19.7 eV. The zinc 2p peaks at 1021.7 and 1044.8 eV show a peak separation of 23.1 eV, consistent with the standard splitting of 22.97 eV for Zn(II). The tin 3d peaks at 485.9 and 494.3 eV with a peak splitting of 8.4 eV indicate Sn(IV). The asymmetric peak at 54.2 eV is representative of the Se 3d binding energy for lattice Se^{2-}.[21,29] It is interesting to mention that the sulfur spectrum of the NCs shows two sulfur $2p_{3/2}$ peaks at 160.1 and 165.7 eV, indicating that the sulfur has two valence states. The peak at 160.1 eV corresponds to the DT, whereas the peak at 165.7 eV is assigned to the disulfides. This result is consistent with the fact that Se powder was reduced while some DT was oxidized to disulfides.

This Se precursor could also be used for the synthesis of $Cu(InGa)Se_2$ NCs. As shown in Figure S10a, the as-synthesized NCs are slightly polydispersed and appear to be highly faceted with polyhedral geometries. The average diameter of the NCs is 6 nm. The XRD pattern (Figure S10b) firmly supports that these NCs possess tetragonal structures.[15] Figure S10c shows the UV–vis absorption spectrum of the NCs, which have strong absorbance in the visible region. Moreover, quantitative analysis of the EDX data revealed the average Cu/In/Ga/Se ratio to be ca. 2/1/1/4, which corresponds well with the elemental ratio of $Cu(InGa)Se_2$ (Figure S11). In addition, other selenide NCs (i.e., CdSe) were also synthesized using this Se precursor (Figure S12). The size and size distribution of CdSe NCs were comparable to those reported for the previous methods.

A photoresponse device with a metal/semiconductor/metal structure was fabricated to validate the optoelectronic properties of the as-synthesized $Cu_2ZnSnSe_4$ NCs. As shown in the bottom-right inset of Figure 3, the film was fabricated on a quartz substrate via spin-casting using a toluene solution of $Cu_2ZnSnSe_4$ NCs. The gold electrode was then patterned. The top-left inset of Figure 3 shows the mask template of the electrode. The current–voltage ($I-V$) curves of the device measured for a 2 V bias range under AM1.5 illumination and in the dark are compared in Figure 3. The device showed a promising increase in current by ca. 3 times under AM1.5 illumination relative to the dark state. Moreover, a Schottky contact of Au/$Cu_2ZnSnSe_4$ NCs was confirmed from the nonlinear $I-V$ curves. This obvious photoresponsive behavior suggests that the as-synthesized $Cu_2ZnSnSe_4$ NCs would be a potential candidate in the fabrication of photovoltaic devices.

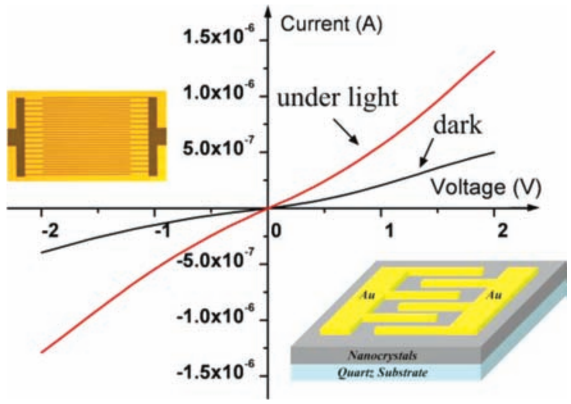

Figure 3. $I-V$ curves of $Cu_2ZnSnSe_4$ NCs thin films in the dark state (black) and under AM1.5 illumination (red). Insets: (top left) mask template of the electrode; (bottom right) experimental setup for measuring the photoresponsive properties of the NCs.

In summary, we have demonstrated a new Se precursor for phosphine-free synthesis of high-quality selenide semiconductor NCs. This method employs alkylthiol to reduce Se powder and subsequently dissolve Se in OLA at room temperature, thus bypassing the conventional requirement of extended heating. This Se precursor has been successfully applied to synthesize $Cu_2ZnSnSe_4$, $Cu(InGa)Se_2$, and CdSe NCs. Typically, The as-synthesized $Cu_2ZnSnSe_4$ NCs possessed small size, size monodispersity, strong absorbance in the visible region, and promising photoresponsive properties. Because the current phosphine-free synthesis is simple and convenient, we believe that it can be extended to the synthesis of other selenide NCs, thus facilitating the development of synthesis techniques and practical applications of NC-based photovoltaic devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures; additional NMR and mass spectra and EDX, Raman, and XPS analyses of $Cu_2ZnSnSe_4$ NCs; and characterization of $Cu(InGa)Se_2$ and CdSe NCs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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