# A Redox Reaction To Synthesize Nanocrystalline $Cu_{2-x}Se$ in Aqueous Solution

**Weixin Zhang, Xiaoming Zhang, Lei Zhang, Jianxin Wu, Zehua Hui, Youwei Cheng, Juewen Liu, Yi Xie, and Yitai Qian***

Department of Chemistry and Structure Research Laboratory, University of Science and Technology of China,
Hefei, Anhui 230026, P. R. China

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Nanostructured materials are currently the focus of considerable interest because of their unconventional physical and chemical properties. Few reports of the preparation of nanocrystalline copper selenide could be found generally; however, the microstructure of copper selenide in a powder form or thin film has induced great interest in its impact on material and device performance.[1−4] Nanocrystalline copper selenide will have potential application in the preparation of selenide photoabsorber layers in solar cells.

Traditionally, bulk copper selenide can be synthesized by solid-state reaction between elements at 400−470 °C in flowing Ar.[5] The obvious drawback is the requirement of high temperature. High-energy ball milling made the elemental reaction take place at room temperature; however, the product quality was difficult to control.[6]

Usually, a solution-phase synthesis is a low-energy approach. In *n*-butylamine solvent, the elemental reaction produced crystalline $Cu_{2-x}Se$ at room temperature, but the product was not nanosized and the reaction time was as long as 4 h.[7] In ethylenediamine solvent, nanocrystalline $Cu_{2-x}Se$ was obtained through a solvothermal method at 90 °C for 4 h.[8]

Herein we report a redox reaction between an alkaline selenium solution and an aqueous solution of a cupric complex to synthesize nanocrystalline $Cu_{2-x}Se$ at room temperature under atmospheric pressure. Compared with other reported methods, the synthesis method established in aqueous solution is rather simple and safe.

All reagents were of 99.9% purity from Shanghai Chemistry Co. and were used without further purification. Manipulations and reactions were carried out in air. The alkaline selenium aqueous solution was prepared as follows: 0.45 mol of NaOH and 0.002 mol of elemental Se were added to 40 mL of distilled water. The mixture reached about 80 °C in a few minutes because the dissolution of NaOH in water was an exothermic process and the produced heat can guarantee the dissolution of elemental Se.

$CuCl_2 \cdot 2H_2O$ (0.0026 mol) was added to 15 mL of an EDTA aqueous solution (0.2 M), and then the mixture was combined with the alkaline selenium aqueous solution through rapid stirring. A great amount of black precipitate occurred. After being filtered and washed with dilute HCl solution (0.1 M) and distilled water, the precipitate was dried in a vacuum at 50 °C for 4 h. The final product was collected for characterization.

The X-ray powder diffraction (XRD) pattern of the product was recorded on a Rigaku D/max-rA rotation anode X-ray diffractometer with Ni-filtered Cu Kα radiation. All diffraction peaks could be indexed to cubic $Cu_{2-x}Se$ with a cell constant $a = 0.573$ nm, which was close to the reported value (JCPDS, File No. 6-0680). The peaks were broad, which might result from fine particle size and lattice strain.[9] The diffraction width of the peak was corrected by subtracting the diffractometer width obtained from the diffractometer width working curve. Then, according to the Debye−Scherrer formula, the particle size determined at the 022 diffraction peak was 15.8 nm. The result was obtained through correction; therefore it should be proved by the TEM image of the same sample.

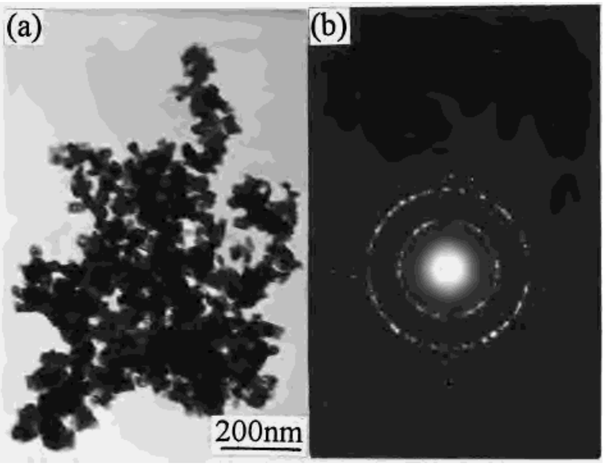

**Figure 1.** Transmission electron microscopy (TEM) image (a) and electron diffraction (ED) pattern (b) of the sample $Cu_{2-x}Se$.

Photomicrographs were taken with a Hitachi H-800 transmission electron microscope (TEM). Figure 1 shows that the particles are spherical and slightly agglomerated. The average particle size is about 16.6 nm, which is consistent with the XRD analysis. The electron diffraction (ED) pattern furthermore identifies that $Cu_{2-x}Se$ has a good crystallinity.

Figure 2 showed the X-ray photoelectron spectra (XPS) of the product recorded on an ESCALab MKII instrument with Mg Kα radiation as the excitation source. There is a little oxygen and carbon contamination and no charging effect. The C1s line of carbon contamination appears at 284.9 eV. The binding energy of the Cu $2p_{3/2}$ peak is 932.3 eV. The kinetic energy of the Cu $L_3VV$ peak is 917.8 eV. Therefore the value of the "modified Auger parameter" ($\alpha'$) is 1850.1 eV, which can be used to differentiate it from Cu, $Cu_2O$, and CuO.[10−12] The binding energy of Se 3d is 54.1 eV. The photoelectron emission arising from

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* Corresponding author.

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elemental selenium or selenium oxides is not obvious. The main O 1s peak is located at 532.45 eV. Since the binding energies of O 1s for $Cu_2O$ and CuO are 530.4 and 529.6 eV, respectively,[10] the little oxygen contamination is likely water vapor absorbed on the surface of the product and oxygen as oxide or mixed oxide is absent. No obvious peaks for Na 1s and N 1s are observed, which confirms that no Na and EDTA exist in the product. XPS analysis demonstrates that the purity of the product $Cu_{2-x}Se$ is quite high. The contents of Cu and Se are quantified by Cu $2p_{3/2}$ and Se 3d peak areas, and an average composition of $Cu_{1.86}Se$ is given.

In our route, the reactions may take place as follows.

dissolution reaction of selenium

$$3Se + 6NaOH \rightarrow 2Na_2Se + Na_2SeO_3 + 3H_2O \qquad (1)$$

$$Na_2Se + (x-1)Se \rightarrow Na_2Se_x \qquad (2)$$

complex reaction

$$Cu^{2+} + (edta)^{4-} \leftrightarrow [Cu(edta)]^{2-} \qquad (3)$$

precipitation reaction

$$(2-x)Na_2Se_x + (2-x)Cu^{2+} \rightarrow -(x-1)^2Se + (4-2x)Na^+ + Cu_{2-x}Se\downarrow \qquad (4)$$

$$(2-x)Na_2Se + (2-x)Cu^{2+} \rightarrow (1-x)Se + (4-2x)Na^+ + Cu_{2-x}Se\downarrow \qquad (5)$$

The selenium source is a deep red aqueous solution containing $Se^{2-}$, $[SeO_3]^{2-}$ and $Se_x^{2-}$ ions. The solution is only stable with excessive $OH^-$ ($[OH^-] > 10$ M) at room temperature. If it is diluted with much water, Se will precipitate. Therefore the volume of cupric complex solution is smaller than that of the alkaline selenium solution in order to avoid much dilution of the selenium source.

The precipitation reactions are redox reactions. The calculated emf ($E° = 0.933$ V) is positive by using half-cell potentials ($E°(Cu^{2+}/Cu^+) = +0.153$ V, $E°(Se/Se^{2-}) = -0.78$ V).[13] Therefore the precipitation of black $Cu_{2-x}Se$ occurs spontaneously. The freshly produced selenium is active and can dissolve in the excessive alkaline solution at once.

Equations 4 and 5 also indicate that cupric ion $Cu^{2+}$ is the direct oxidizing agent for preparing $Cu_{2-x}Se$. In fact at the beginning of the synthesis, only a very small amount of $Cu^{2+}$ exists in the cupric complex solution. With the precipitation of $Cu_{2-x}Se$, the equilibrium state of the complex is destroyed and free $Cu^{2+}$ ion continuously dissociated from the complex reacts with $[Se_x]^{2-}$ or $Se^{2-}$. The reason for using cupric complex instead of $Cu^{2+}$ as a reagent is that cupric complex is much more stable than $Cu^{2+}$ in alkaline solution and will decrease the byproduct, such as hydroxide or oxide of copper. In our experiments, with an appropriate excess (less than 30%) of cupric complex, the impurities in the product were not detected by XRD. However there was still a little oxides in the product and pure $Cu_{2-x}Se$ was obtained only after acid washing, which was confirmed by XPS. At the end of the reactions, excessive cupric complex can be easily removed with water. If reagent elemental Se is excessive, it will precipitate in the product in posttreatment of washing and be difficult to remove.

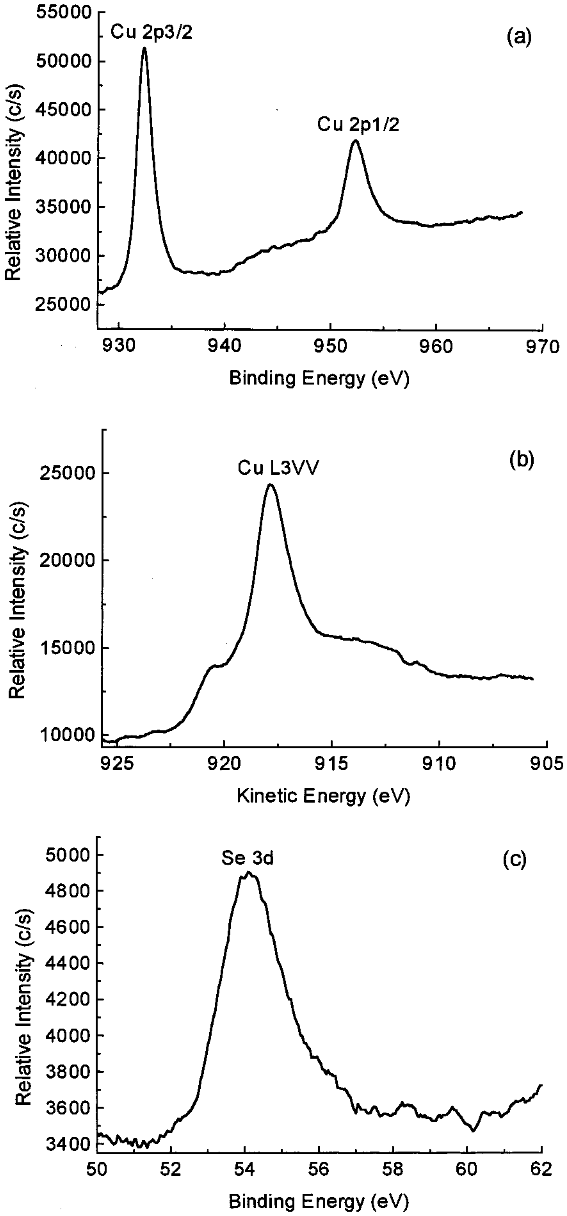

**Figure 2.** X-ray photoelectron spectra (XPS) analysis of the sample $Cu_{2-x}Se$: (a) Cu $2p_{3/2}$, Cu $2p_{1/2}$; (b) Cu $L_3VV$; (c) Se 3d.

In summary, we have succeeded in synthesizing nanocrystalline $Cu_{2-x}Se$ with an average particle size of 16.6 nm through a redox reaction. The alkaline selenium solution as a selenium source makes the final product crystallize well in aqueous solution at room temperature under atmospheric pressure. The cupric complex instead of cupric ion as a reagent reduces the byproduct greatly. This technique established in aqueous solution makes the synthesis of nanocrystalline $Cu_{2-x}Se$ convenient and safe.

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**Supporting Information Available:** Three figures depicting the XRD pattern, the XPS survey spectrum, and the particle size dispersion of the product $Cu_{2-x}Se$. This material is available free of charge via the Internet at http://pubs.acs.org.

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