Synthesis of Chalcopyrite Nanoparticles via Thermal Decomposition of Metal-Thiolate

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CuInS₂ nanoparticles (NPs) have been synthesized via thermal decomposition of metal-thiolate in high boiling temperature solvent. This method does not require toxic, unstable and expensive raw materials. Nearly monodispersed NPs with average diameter ranging from 1.8 to 2.8 nm are obtained. The NPs are found to be compositionally copper rich, Cu : In : S = 1.6 : 1.0 : 1.3. They exhibit size-dependent optical properties such as photoluminescence (PL) and optical absorption, indicating quantum confinement effects. In PL spectra, the Stokes-shifts (~300 meV) from the absorption band edge and their broad PL spectra indicate that PL is ascribed to a donor-acceptor transition. These results demonstrate that chalcopyrite NPs are promising candidates for luminous and solar cell materials. [doi:10.2320/matertrans.MBW200724]

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1. Introduction

Nano-sized materials reveal anomalous optical and catalytic properties for various applications. Semiconductor nano-particles (NPs) are model systems of zero-dimensional quantum confinement and in the last decade novel methods have been proposed to synthesize monodispersed II-VI semiconductor NPs with high quantum yield.^{1,2)} Indeed, II-VI semiconductors such as CdS, CdSe and CdTe are useful for fluorescent probes of bio-medical makers.³⁾ They are also expected to be tunable absorbers and emitters in nanoscale electronics, quantum dot lasers, optical devices and new type solar cells.⁴⁾ However, the use of toxic heavy metals such as Cd, Hg and Pb must be inhibited.

In this context, ternary chalcopyrites, CuMX₂ (M = Al, Ga, In; X = S, Se) are alternative materials of II-VI semiconductors, because they are direct-band gap semiconductors. Their optimum band gaps (CuInS₂: ~1.5 eV, CuInSe₂: ~1.1 eV), large absorption coefficients (10⁵ cm⁻¹) and large tolerance for cosmic rays are prominent for absorber layers of hetero-junction solar cells.⁵⁻⁷⁾ Actually a CuInS₂ thin-film cell has a quantum efficiency of 12.5%⁸⁾ and tunable PL is observed in ZnS-CuInS₂ mixed crystal NPs.⁹⁾ Moreover, it has been reported that a CuInS₂ quantum dot solar cell has an overall energy conversion efficiency 4%.¹⁰⁾ These results encourage us to fabricate chalcopyrite NPs.

In solution phase synthesis, chalcopyrite NPs have been prepared by a TOP/aliphatic amine-S system⁹⁾ or a thermolysis of single-source precursor such as copper-indium thiolate,¹¹⁾ (PPh₃)₂AgIn(SeC{O}Ph)₄,¹²⁾ (TOP)₂CuIn(S-n-Pr)₄¹³⁾ and (PPh₃)₂CuIn(SET)₄.¹⁴⁾ In particular, chalcopyrite NPs with the quantum yield of about 5% were successfully synthesized via the thermal decomposition of single source precursors.^{13,14)} However, this method has several disadvantages: it is sensitive to atmospheric conditions, needs expensive starting reagents and the methodology becomes

cumbersome. In this paper, we present a moderate and facile synthesis route of CuInS₂ NPs via thermal decomposition of Cu-In-thiolate at 473 K without using toxic raw materials.¹⁵⁾ UV-vis and photoluminescence (PL) studies on nearly monodispersed NPs with average diameter ranging from 1.8 to 2.8 nm evidently indicate quantum confinement effects.

2. Experimental Procedures

The following is a typical experimental procedure for synthesis of CuInS₂ NPs. All reagents were used as received. 0.4 mmol of copper (II) acetate (Cu(ace)₂) and 0.4 mmol indium (III) acetate (In(ace)₃) were mixed with 2.46 ml of 1-dodecanethiol (DT) in tri-n-octylamine (TOCA). After being degassed by Ar gas flushing for 7.2 ks, the mixture solution was heated up to 503 K. Then, it was cooled down to room temperature and 30 ml of ethanol was mixed. The precipitates were separated by centrifuging the colloidal solution to remove excess reaction agents and then redispersed in hexane. This precipitate — redispersion procedure was repeated several times to purify the precipitates. For transmission electron microscope (TEM) observation, a drop of CuInS₂ colloidal solution was placed on a carbon-coated TEM grid and examined with Hitachi HF-2000 field emission TEM operating at 200 kV. The crystal structures of CuInS₂ NPs were identified by X-ray diffraction (XRD, Mac Science, M18XCE) on sol samples dried onto a glass plates. Chemical composition of prepared NPs were estimated by an EDX analyzer installed in a scanning electron microscope (Hitachi, S-4700 FE-SEM). UV-vis absorption spectra were observed between 200 and 2200 nm using JASCO V-570 equipped with a PbS detector and PL spectra were recorded on Otsuka Electronics PTI5100S PL-spectrometer at ambient temperature.

3. Results

Initial mixture solution turned to be transparent-yellowish

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Fig. 1 TEM image of CuInS₂ NPs synthesized at 503 K.

Fig. 2 XRD patterns of CuInS₂ NPs synthesized at (a) 473 K, (b) 503 K and (c) 533 K.

solution at about 353 K. It immediately changed to orange and finally dark red above 473 K. NPs were easily precipitated by polar solvent (ethanol) and redispersed in non-polar solvent such as hexane, benzene and toluene, indicating an NP-surfactant (DT) core-shell structure. TEM image of NPs prepared at 503 K is shown in Fig. 1. The formation of very fine NPs can be detected.

Figure 2 shows XRD patterns of the NPs obtained at various reaction temperatures, (a) 473, (b) 503 and (c) 533 K. The thermal decomposition of Cu-In-thiolate leads to the

Fig. 3 Chemical composition of CuInS₂ NPs synthesized at (a) 473 K, (b) 503 K and (c) 533 K.

formation of CuInS₂ NPs with the chalcopyrite structure. The average sizes of NPs estimated by the Scherrer equation are (a) 1.8, (b) 2.0 and (c) 2.8 nm, being consistent with the TEM image in Fig. 1.

Since optical properties of semiconductor compounds usually depend on the chemical composition, the chemical compositions of synthesized NPs were determined to be Cu : In : S = (a) 1.68 : 1 : 3.03, (b) 1.52 : 1 : 2.96 and (c) 1.47 : 1 : 2.74 (see Fig. 3). For surfactant-capped CuInS₂ NPs, Cu-rich layers are presumably deposited on NPs surfaces because of the affinity of capping agent for Cu atom.¹³ Therefore, the Cu to In ratio increases with the increase in the surface to volume ratio, that is, the decrease in NP's size. This is consistent with our experimental results. Comparing with aliphatic phosphine,¹³ DT is a suitable capping agent for CuInS₂ NPs because the Cu to In ratio of CuInS₂ NPs derived from Cu-In thiolate is closer to the stoichiometry.

Figure 4 shows UV-vis and PL spectra of CuInS₂ NCs obtained at various preparation temperatures, (a) 473, (b) 503 and (c) 533 K. In Fig. 4(a), the UV-vis spectra of CuInS₂ NCs exhibit absorption shoulders at around (a) 2.45, (b) 2.25 and (c) 2.04 eV, which were determined from the extremums of the second derivative of absorption spectra. They are attributed to the HOMO-LUMO transition beyond the band gap, where the long absorption tail is also observed at the lower energy side.

In Fig. 4 the PL spectra of CuInS₂ NCs obtained at 473, 503 and 533 K reveal the maxima at (a) 2.00, (b) 1.88 and (c) 1.70 eV. The Stokes-shifts in the PL spectrum from the band gap ((a) 2.45, (b) 2.25 and (c) 2.04 eV) are about 0.3 eV. Such Stokes shift and its wide full width at half maximums (FWHM) of PL resemble the reported results,^{13,14} indicating that ambient temperature PL is not attributed to the exciton recombination.

Fig. 4 UV-vis, and PL spectra of CuInS₂ NPs synthesized at various reaction temperature. Inset values represent transition energies for UV-vis and PL peak position for PL.

4. Discussion

4.1 Formation processed of CuInS₂ NPs

Our previous results indicated that Cu-thiolate was decomposed into copper sulfide and organic byproducts.¹⁶⁾ Since the decomposition of In-thiolate requires higher reaction temperature, possible reaction paths for CuInS₂ NPs formation are summarized as follows (Fig. 5).

I: Metal ions, Cu²⁺ and In³⁺, react with DT to form bridged complexes (-Cu-SR-In-SR-)_n, where Cu²⁺ is reduced to a monovalent ion. Then, thermal decomposition of (-Cu-SR-In-SR-)_n leads to formation of CuInS₂ monomers and their polymerization (crystal growth).

II: Cu-SR complexes are decomposed into Cu₂S monomers. Then, Cu₂S monomers react with In-SR complexes to form CuInS₂ monomers.

These paths, I and II, are influenced by their coordinating solvent and/or capping agent (co-ligand). In highly coordi-

nating solvent (such as tri-n-octylphosphine and di-octylamine) systems, relatively large NPs with a wurtzite structure (hexagonal), have been obtained.¹⁷⁾ A masking effect by highly coordinating solvent prevents the formation of (-Cu-SR-In-SR-)_n complexes (in path I) and/or the reaction between Cu₂S monomers and In-SR complexes (in path II). In order to clarify the real reaction path, we need further detailed investigation of NPs growth kinetics using mass and in-situ UV-vis spectroscopy.

4.2 Optical properties of CuInS₂ NPs

UV-vis spectra show typical curves for semiconductor materials, where the band gap energy larger than 1.53 eV has been reported for CuInS₂ bulk materials.¹⁸⁾ Based on the conventional quantum confinement theory, the following equation has been used to calculate the gap energy of CuInS₂ NPs,

$$\Delta E_g = \frac{h^2\pi^2}{2\mu R} - \frac{1.786e^2}{\epsilon_1 R} - \frac{0.124 \times 2\mu}{m_0\epsilon_1^2} \times 13.6058, \quad (1)$$

where R is the radius of NPs, $\mu = 1/m_e^* + 1/m_h^*$ (m_e^* , m_h^* = effective masses of electron and hole) and ϵ_1 is the dielectric constant of NP. Adopting $\mu = 0.14m_0$ (m_0 = free electron mass) and $\epsilon_1 = 8.5$, $E_{g,cal}$ are estimated to be (a) 4.5, (b) 3.9 and (c) 2.7 eV for CuInS₂ NPs.¹⁸⁾ These values are inconsistent with the experimental results because the formula does not take into account of surface effects of NPs'. Monodispersed semiconductor NPs usually exhibit a sharp UV-vis absorption feature, while the present CuInS₂ NCs have an indistinct absorption peak and a long absorption tail on the lower energy side. Though these results suggest the poor size uniformities of CuInS₂ NCs, the broad absorption peak is also observed even in monodispersed CuInS₂ NPs whose standard deviation is ~11%. The excitonic spectra of these monodispersed NPs indicate the presence of several intraband.^{14,17)}

The PL effect has been detected in CuInS₂ NPs at room temperature and easily confirmed with the naked eye. Moreover, PL spectra exhibit a marked Stokes-shift, where the energy difference between the absorption and emission peaks are larger than a binding energy of an exciton pair (~0.02 eV). In CuInS₂ crystals which contain various sorts of defects, vacancies, substitutional and interstitial sites, there are intraband states such as donor and acceptor levels. It has

Fig. 5 Reaction scheme for the synthesis process.

been proposed that CuInS₂ crystals have two donor and two acceptor states;¹⁴⁾ a sulfur vacancy level (D1), an In interstitial (or Cu-In substitution) level (D2), acceptor levels for Cu-rich (A1) and for In-rich (A2). The transition energies from these donor states to acceptor states are estimated by the following equation:¹⁴⁾

$$h\nu = E_g - E_A - E_D + e^2/4\pi\epsilon r, \quad (2)$$

where E_A , E_D (A1:0.15, A2:0.1 eV, D1:0.035, D2:0.07) and r are the activation energies of acceptor, donor and the distance between the acceptor and donor sites, respectively. Assuming that PL is originated from the donor-acceptor pair recombination, the stokes-shift in the emission wavelength is 0.14~0.22 eV, being smaller than the experimental results of about 0.3 eV. Moreover, the PL intensity is very sensitive to surface because the surfactants on CuInS₂ NPs eliminate surface-dangling bonds. When capping agents such as DT, fatty acid and aliphatic amine etc are added to the CuInS₂ colloidal solution, the PL intensity is enhanced, while it is suppressed by addition of excessive capping agents. Therefore, the large stokes-shift is ascribed to the unique surface structure of Cu-rich layers of NPs, where the donor-acceptor recombination originates from intrinsic defects and surface dangling bonds cause radiationless transitions.

5. Summary

We have developed the facile synthesis route of CuInS₂ NPs via thermal decomposition in low-coordinating solvent. Very fine CuInS₂ NPs with a chalcopyrite structure can be obtained. They exhibit a marked PL effect at room temperature and its wavelength varies within 1.7~2.0 eV. These stokes shifts and broad FWHM suggest that the observed PL is attributed to the donor-acceptor recombination in the Cu-rich surface layer.

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