Synthesis of Ag/CuInS$_2$ Core-Shell Nanoparticles

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In this work, the facile synthesis of Ag/CuInS$_2$ composite nanoparticles (NPs) with a core-shell structure is demonstrated for the first time. In our procedure, the pre-formed Ag NPs were subsequently coated with a CuInS$_2$ shell through the thermal decomposition of the metal thiolate complex. The Ag/CuInS$_2$ composite NPs took Ag core-CuInS$_2$ shell structures (Ag@CuInS$_2$) when an oleic acid-oleylamine mixture was used as the co-surfactant. High-resolution transmission electron microscopy (TEM) indicated the epitaxial growth of the CuInS$_2$ shell on the Ag NPs. In the extinction spectrum of the Ag@CuInS$_2$ NPs, the localized surface plasmon resonance (LSPR) peak of the Ag core broadened and red-shifted to 2.21 eV, confirming that the LSPR can be tuned by the CuInS$_2$ shell. Finite-difference time-domain (FDTD) simulations indicated the enhancement of the electric field in the CuInS$_2$ shell region and the surface of the Ag@CuInS$_2$ NPs. This enhancement effect may improve the efficiency of incident light absorption in CuInS$_2$ quantum dot sensitized solar cells.

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1. Introduction

Combining noble metal and semiconductors onto a single nanoparticle (NP) can provide not only metal and semiconductor properties, but also novel synergistic functions$^{[1,2]}$. In the last decade, noble metal/chalcogenide composite NPs such as Au/CdSe$^{[3,4]}$, Au/CuS$^{[5]}$, Ag/Ag$_2$S$^{[6]}$, Au/Cu$_2$ZnSnS$_2$$^{[7]}$, Au/Ag$_2$S$^{[8]}$, and Au/Cds$^{[9]}$ with unique properties have been synthesized successfully. These composite NPs can be categorized by their morphology as open-type composite NPs, such as dumbbell$^{[3,4]}$ and Janus-like NPs$^{[6,7,9]}$, or closed-core-shell$^{[8,9]}$ type composite NPs. In an open-type composite NP, a metal or a chalcogenide phase is not perfectly surrounded by other phases. Because Au and Ag bulk phases are good conductors of electricity and heat, the metal part of the composite NP is considered to play an important role during the transfer of energy. In the case of Au/CdSe/Au dumbbell-like composite NPs, the metal part of the composite NP can serve as a charge separator$^{[3,5]}$, and enhance the charge transfer from the semiconductor phase to the outer side of NPs$^{[4]}$. Therefore, open-type noble metal/semiconductor composite NPs have been investigated for their application in solar cells and photocatalysts$^{[3,5,8]}$.

Noble metal NPs such as Au and Ag have unique optical properties that are attributed to a localized surface plasmon resonance (LSPR)$^{[10]}$. Various applications in the optical and biological fields have been proposed for Au or Ag/chalcogenide core-shell NPs. For example, Nan et al.$^{[8]}$ reported the synthesis and tunable optical properties of Ag$_2$S-coated Au nanorods (Au@Ag$_2$S nanorods), where the plasmon resonance and local field confinements could be controlled by the shell morphology. Consequently, the appropriate shell structure was able to enhance the nonlinear and saturable intensity of the Au-nanorods$^{[8]}$. Lin et al.$^{[9]}$ also observed that the confined surface plasmon of the Au core led to an increase in the photoluminescence (PL) intensity of CdS shells. Except for these confinement effects, the enhancement of the carrier photo-excitation efficiency in chalcogenide NPs can be expected because LSPR produces a markedly intensified electric field around the metal NPs, which may improve the quantum dot-sensitized solar cell energy conversion efficiency$^{[11]}$.

This study demonstrates the facile synthesis of Ag/CuInS$_2$ composite NPs with a closed core-shell structure. We used 1-dodecanethiol (1-DT; C$_{12}$H$_{25}$SH) as the chalcogen source, and employed hot injection for the NP synthesis. In this procedure, the pre-generated Ag NPs were subsequently coated with a CuInS$_2$ shell by the thermal decomposition of metal thiolate complexes. Using tri-n-octylamine (TOCA) and 1-DT prevented the formation of Ag$_2$S phase. Therefore, our synthesis system is considered to be suitable for Ag-metal/chalcogenide composite NPs. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopic (EDX) analyses revealed the formation of Ag core-CuInS$_2$ shell structures. In addition, the ultraviolet-visible (UV-Vis) spectra of the NPs, which could be correlated with the calculated results obtained by using the finite-difference time-domain method (FDTD), confirmed the enhancement effect of the electric field in the CuInS$_2$ shell region, which is attributed to LSPR of the Ag core.

2. Experimental Procedure

All reagents were used as received. To synthesize the Ag/CuInS$_2$ composite NPs, we employed the metal – thiol single precursor$^{[12,13]}$ and improved the detailed procedure. Typically, 0.4 mmol of anhydrous copper acetate, 0.4 mmol of non-hydrous silver acetate, 0.4 mmol (116.8 mg) of anhydrous indium acetate, 4.8 mmol of oleylamine (OLA; C$_{16}$H$_{33}$NH$_2$) and 4.8 mmol of oleic acid (OA; C$_{17}$H$_{33}$COOH) were mixed with 20 mL of TOCA ((C$_{17}$H$_{37}$)$_2$N) in a round-bottom flask, which was then degassed by a vacuum pump for 3.6 ks at 423 K. After degassing, 10 mmol of 1-DT were injected into the above-mentioned solution, which was then annealed for 7.2 ks at 483 K in an Ar atmosphere. After the hydrophilic solvent was mixed with the solution at 298 K, a dark purple precipitate was obtained. The precipitate was separated by the centrifugation method to remove excess reagents, and re-dispersed in hexane. The precipitation/re-dis-
To estimate the enhancement of an electric field in the CuInS$_2$ composite NP-hexane dispersion was placed on a carbon-coated microgrid and observed in a field emission scanning TEM (STEM, JEOL, JEM - 2100F) at 200 kV with a point-to-point resolution of 0.23 nm. The NP-hexane dispersion was injected into quartz cuvettes (optical length = 10 nm), which were used to obtain extinction spectra in a UV-Vis-near-infrared (NIR) spectrophotometer (JASCO V-570, equipped with a PbS detector) with a scan range of 200–2200 nm.

In order to estimate the enhancement of an electric field in the CuInS$_2$ shell and on the surface of the Ag NPs, the FDTD method was employed. The FDTD simulation was conducted using the FDTD solutions software Ver. 8.15 (Lumerical software. Co. Ltd). We selected a total field scatter field (TFSF) light source (Source field dimension: 40 nm × 40 nm × 40 nm) and used perfectly matched layer as boundary conditions. The time step, dimensions of mesh, and simulation area were 0.00019 fs, 0.1 nm × 0.1 nm × 0.1 nm, and 100 nm × 100 nm × 100 nm, respectively. The refractive index of hexane was taken to be 1.375$^1$ and the dielectric functions of CuInS$_2$ and Ag NP were taken from the literature$^{[15,16]}$.

### Results and Discussion

During the degassing process, the solution color was turned into transparent reddish brown. This color change indicated the formation of the seed Ag NPs, which were capped with OA and OLA, by using TOCA as a reducing agent. Then, the addition of 1-DT, which is a soft base, to the reaction solution containing the seed Ag NPs led to the formation of Cu$_2$(C$_{12}$H$_{25}$S$_3$)$^+$(OA$^-$) and In$_3$(C$_{12}$H$_{25}$S$_3$)$_3$ via a ligand exchange reaction. When the solution temperature exceeded 473 K, the CuInS$_2$ phase was deposited on the seed Ag NPs via the thermolysis of the Cu$_2$(C$_{12}$H$_{25}$S$_3$) and In$_3$(C$_{12}$H$_{25}$S$_3$)$_3$ mixture$^{[11,12]}$. The different Ag/CuInS$_2$ composite NPs were examined by TEM/STEM–EDX imaging. The morphology of the CuInS$_2$ composite NPs was examined under various experimental conditions, as summarized in Table 1. The In:Cu ratios of the shell region were measured, along with the charge ratio, co-surfactants, and other experimental conditions in a single NP taken along the marked line on Fig. 1(e), where the Ag peak was located at the center of the Ag@CuInS$_2$ NPs, whereas the shell region was abundant in copper, indium, and sulfur. However, further details on the nanostructure of the Ag@CuInS$_2$ NPs could not be obtained from the TEM images because of the low point-to-point resolution and large probe diameter (1 nm) of the apparatus.

### Experimental conditions.

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>OA (10$^{-3}$ mol)</th>
<th>OLA (10$^{-3}$ mol)</th>
<th>1-DT (10$^{-3}$ mol)</th>
<th>TOCA (ml)</th>
<th>Temperature (K)</th>
<th>Degassing/Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. #1</td>
<td>4.8</td>
<td>4.8</td>
<td>10</td>
<td>20</td>
<td>423/483</td>
<td>Degassing/Annealing</td>
</tr>
<tr>
<td>Exp. #2</td>
<td>4.8</td>
<td>4.8</td>
<td>20</td>
<td>20</td>
<td>423/483</td>
<td></td>
</tr>
<tr>
<td>Exp. #3</td>
<td>4.8</td>
<td>4.8</td>
<td>10</td>
<td>20</td>
<td>423 ⇒ RT*</td>
<td></td>
</tr>
<tr>
<td>Exp. #4</td>
<td>4.8</td>
<td>4.8</td>
<td>20</td>
<td>423 ⇒ RT*/503</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exp. #5</td>
<td>4.8</td>
<td>4.8</td>
<td>10</td>
<td>20</td>
<td>423 ⇒ RT*/503</td>
<td></td>
</tr>
</tbody>
</table>

$^*\Rightarrow$ RT” represents ’quenched to 298 K’.

The band structure, electrical conductivity, and dielectric constant of the shell region affect the energy transfer phenomena and optical properties of the NPs. These properties are typically varied by the chemical composition of the NPs. This system, the chemical composition was tuned by the charge ratio, co-surfactants, and other experimental conditions. The EDX analysis results of the shell regions are summarized in Table 2. The In/Cu ratios of the shell region were estimated to be lower than the charge ratios under all experimental conditions. Moreover, the In/Cu ratio considerably depended on the OA concentration. When the OA content was 10$^{-3}$ mol, the In/Cu molar ratio of the chalcogenide shell was reduced to 0.06.

The reaction scheme is summarized in Fig. 3, where it can be observed that the ligand mixture of OA and OLA reacts with the metal cation to form metal–OA complexes. These complexes are considered to be solvated by several OLA mol-
The Ag\(^{+}\)(C\(_{17}\)H\(_{33}\)COO\(^{-}\)) complex was decomposed into the seed Ag NPs at temperatures higher than 333 K. When 1-DT was injected into the solution containing seed Ag NPs and \(M^{m+}(C\(_{17}\)H\(_{33}\)COO\(^{-}\))\(_{m}\) complexes (\(M = Cu^{+}, In^{3+}\)), the C\(_{17}\)H\(_{33}\)COO\(^{-}\) ion of the \(M^{m+}(C\(_{17}\)H\(_{33}\)COO\(^{-}\))\(_{m}\) complex was exchanged by the C\(_{12}\)H\(_{25}\)S\(^{-}\) ion to form \(M^{m+}(C\(_{12}\)H\(_{25}\)S\(^{-}\))\(_{m}\). At temperatures higher than 473 K, the thermolysis of the Cu\(^{+}\)(C\(_{12}\)H\(_{25}\)S\(^{-}\)) and In\(^{3+}\)(C\(_{12}\)H\(_{25}\)S\(^{-}\))\(_{3}\) complex mixture provided the CuInS\(_{2}\) shell. The Hard and Soft Acids and Bases (HSAB) theory predicts that the In\(^{3+}\)(C\(_{17}\)H\(_{33}\)COO\(^{-}\))\(_{3}\) complex (hard acid–hard base pair) is more stable than the In\(^{3+}\)(C\(_{12}\)H\(_{25}\)S\(^{-}\))\(_{3}\) complex\(^{18}\). Therefore, the lower indium composition may be attributed to the masking effect of OA for In\(^{3+}\). Furthermore, an increase in the concentration of OA prevented the formation of In\(^{3+}\)(C\(_{12}\)H\(_{25}\)S\(^{-}\))\(_{3}\). Subsequently, a Cu\(_{2}\)S shell with a hexagonal structure was deposited on the Ag NPs. Some of the Cu\(^{+}\) ion on the surface of Cu\(_{2}\)S was exchanged by the In\(^{3+}\) ion in In\(^{3+}\)(C\(_{17}\)H\(_{33}\)COO\(^{-}\))\(_{3}\). The In\(^{3+}\) and Cu\(^{+}\) ions easily diffuse through the sulfur sub lattice (Cation exchange)\(^{18,19}\). Cation exchange reaction represents as the following equation;

\[
3Cu^{+} \text{ in lattice} + In^{3+}(C_{12}H_{25}S^{-})_{3} \rightarrow In^{3+} \text{ in lattice} + 3Cu^{+}(C_{12}H_{25}S^{-})
\]

Therefore, the difference of the lattice energies of Cu\(_{2}\)S and In\(_{2}\)S\(_{3}\) and the stabilities of In\(^{3+}\)(C\(_{17}\)H\(_{33}\)COO\(^{-}\))\(_{3}\) and Cu\(^{+}\)(C\(_{17}\)H\(_{33}\)COO\(^{-}\)) gave the driving energy to the cation exchange reaction\(^{19}\). From this process it is gathered that the

Fig. 1 (a) TEM image of the Ag NPs. (b) Electron diffraction patterns of the Ag NPs (left) and Ag@CuInS\(_{2}\) NPs (Exp. #1) (right). (c) TEM, (d) HR-TEM, and (d) EDS analysis of the Ag@CuInS\(_{2}\) NPs (Exp. #1). The inset in Fig. 1(c) shows the size distribution of the Ag@CuInS\(_{2}\) NPs.
The hexagonal sulfur sub-lattice of high chalcocite Cu$_{2-x}$S resembles that of WZ-CuInS$_2$, and the nature of super ionic conductors. These facts indicate that a cation exchange reaction between Cu$_{2-x}$S and In$_3^+(C_{17}H_{33}COO^-)_3$, which followed the thermolysis of Cu$^+(C_{17}H_{33}COO^-)$, is an alternative path to form WZ-CuInS$_2$ shells.

According to the In$_2$S$_3$-Cu$_2$S phase diagram$^{20}$, the CuInS$_2$ single phase can be obtained with a slightly In$_2$S$_3$ rich composition. However, there is no ring pattern that corresponds to Cu$_2$S in the electron diffraction pattern of the In-poor CuInS$_2$ shells obtained in Exp. #1, #2, #4 and #5. Usually, CuInS$_2$ NPs derived from Cu-In thiolate are capped by thiol molecules and found to be Cu-rich. Due to the affinity of thiol to Cu, CuInS$_2$ NPs with Cu-rich surfaces are considered energetically favored$^{12}$. Chen et al.$^{21}$ reported that Cu$_3$In$_3S_3$ nanocrystals, which contain 3 times as many Cu atoms as In atoms, could take a chalcopyrite structure.

The extinction spectra of the Ag and Ag@CuInS$_2$ NPs, in conjunction with that of CuInS$_2$ NPs for reference, are shown in Fig. 4. The extinction spectrum of the seed Ag NPs shows a relatively sharp absorption band at around 2.7 eV attributed to the LSPR. In the extinction spectrum of Ag@CuInS$_2$ NPs (Exp. #1) and (Exp. #3), the LSPR absorption bands broadened and red-shifted to 2.21 eV (Exp. #1) and about 2.1 eV (Exp. #3), respectively.

The absorption ($C_{Abs}$) and scattering ($C_{Scatt}$) cross sections of Ag and a single Ag@CuInS$_2$ NP were calculated using FDTD simulations. The cross section, $C$, was derived using the power, $P(W)$, absorbed or scattered by a single NP, and the source intensity $I_0 (W/m^2)$, using the following equation:

$$P = C I_0$$

The power ($P$) absorbed or scattered by a single NP was defined as the net power flow through a cubical volume surrounded by a single Ag@CuInS$_2$ NP. The dimensions of the $C_{Scatt}$ and $C_{Abs}$ cubical volumes were 50 × 50 × 50 (nm) and 15 × 15 × 15 (nm), respectively. The extinction cross-section ($C_{Ext} = C_{Abs} + C_{Scatt}$) shown in Fig. 4(b) indicates that the Ag NP has the characteristic LSPR absorption band centered at 3.0 eV (in hexane). The FWHM of the extinction cross-section peaks of the Ag NP was estimated to be less than the experimental result shown in Fig. 4. Usually, Ag NPs are coated by capping agents and/or an oxide layer, whose dielectric constant (refractive index) is considered to be larger than that of hexane. However, in our calculation model, these
surface structures were ignored. The existence of these surface structures leads to the red-shift and broadening of the LSPR peak.

The extinction cross-section of Ag@CuInS2 NPs with core diameters of 5.4 nm and shell thicknesses of 1.05 nm (Exp. #1) is shown in Fig. 4(c). The red-shift and broadening of the LSPR absorption peak that occurs when these NPs are overcoated with CuInS2 could be represented by the Ag-core/ CuInS2-shell model. The calculated LSPR wavelength of Ag@CuInS2 is about 2.4 eV, which is somewhat larger than that of the experimental results.

The XY cross-section of near electric field distributions around the Ag, Ag@CuInS2 (Exp.#1), and 7.5 nm-CuInS2 NPs are shown in Figs. 5(a), (b) and (c), respectively. The electromagnetic wave, whose electric field was polarized along the x-axis, was injected along the z-axis. The color variation in the images denotes the relative intensities of the electric field ($|E|/|E_0|$), where $E$ is the amplitude of the electric field, and $E_0$ is the amplitude of the electric field of the incident source) evaluated at wavelengths that correspond to the LSPR of the Ag and Ag@CuInS2 NPs. The enhancement of the near electric field on the surface of the seed Ag NPs could be confirmed by the calculated results (Fig. 5(a)). The relative intensity ($|E|/|E_0|$) near the surface of the Ag NP increased to about 12. The maximum $|E|/|E_0|$ in the CuInS2 shell and near the surface of the Ag@CuInS2 NP reached about 2 and 4, respectively. The large light absorption coefficient of the CuInS2 shell reduced the enhancement effect induced by LSPR. Therefore, a thinner CuInS2 shell was required for LSPR to have an effect on the Ag core. Compared with the 7.5 nm CuInS2 NPs (Fig. 5(c)), the Ag core apparently enhanced the $|E|/|E_0|$ value in the CuInS2 shell region, and especially on the surface of the Ag@CuInS2 NP. Ag core condenses the incident light to the CuInS2 shell and its surface. This condensing effect indicates that Ag@CuInS2 NPs are strong candidate for the light absorption material of quantum dot sensitized solar cells (QDSSC).

Although the CuInS2 NPs obtained by the thermolysis of Cu-In thiolate exhibited a strong photoluminescence (PL), PL could not be detected in the Ag@CuInS2 NPs (Exp. #1). The work function of the Ag bulk metal was reported to range from $-4.64$ to $-4.35$ eV\textsuperscript{22}) which is a range smaller than the energy level of the conduction band of CuInS2 ($-3.70$ eV)\textsuperscript{23}). Therefore, an excited electron is considered to transfer from the CuInS2 shell to the Ag core by exchanging its energy for a phonon (quenching). This process may prevent the recombination of the excited electron and hole in the CuInS2 shell region. The enhancement of the electric field in the CuInS2 shell region is believed to lead to an increase in the absorption coefficient of CuInS2. However, this core-shell structure makes it difficult to extract an excited electron from the CuInS2 shell to the outer phase. An insulator, such as an oxide or Ag$_2X$ (X = Cl or Br), has to be introduced between the Ag core and CuInS2 shell.

4. Conclusions

In this work, Ag-core CuInS2-shell NPs were successfully synthesized by 1-DT injection using the mixture of OA and OLA as the co-surfactant. The HR-TEM images indicated
that every third [112] atomic chalcopyrite plane was aligned with every fourth [111] atomic Ag plane. The UV-Vis absorption band of the Ag@CuInS2 NPs was broadened and red-shifted to 2.21 eV by the Ag LSPR effects. The FDTD simulation confirmed the enhancement of the relative electric field intensity (|E|/|E0|) in the CuInS2 shell region and near the Ag@CuInS2 surface. The core-shell structure prevented the recombination of an excited electron and hole in the CuInS2 shell region. The introduction of an insulator layer such as an oxide or Ag2X (X = Cl or Br) between the Ag core and CuInS2 shell prevents the quenching of an excited electron and enables us to fabricate the high efficiency LSPR effect quantum dot sensitized solar cells.

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REFERENCES


Fig. 5 XY-Cross sections of local field distributions for a 5.4 nm seed Ag NP (a), Ag@CuInS2 NP (Exp. #1) (b) and 7.5 nm CuInS2 NP (c) at around their LSPR peaks.