Photoluminescence Films by Hybridization of CuInS$_2$ Nanocrystals and Polyacrylates

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In this report, we describe the facile fabrication procedure of a flexible photoluminescence (PL) film of CuInS$_2$ nanocrystals (CIS NCs) embedded in polyacrylates. The CIS NCs with the sizes of 2.2±0.5 nm were synthesized by simple pyrolysis of low-toxic Cu and In acetate precursors in 1-octadecene, and successively were dispersed in a mixture of acrylate monomers. Irradiation of the mixture with UV light brought about the formation of a clear PL film of polyacrylates hybridized with CIS NCs. Moreover, we found excellent mechanical flexibility of the hybrid film. The present report opens promising ways to impart unique photonic devices by combining the inorganic NCs and photopolymers.

Keywords: Semiconductor nanocrystals, Acrylate, Photopolymerization, Flexible film, Photoluminescence

1. Introduction

Polymers are widely used in versatile photonic devices of displays, recording media, and photovoltaics because of their intrinsic features of softness, large-size processability, and low-cost [1]. Recent trend in this research field has devoted to the hybridization of inorganic nanomaterials as guests in polymers as host matrices, i.e., so-called nanocomposites. They can have sophisticated optoelectronic functionalities, which are tunable by selecting the inorganic substances. Such hybridized nanocomposite polymers have been prepared by a wide variety of techniques. Among them, photopolymerization is one of the most popular and simple fabrication methodologies [2–4].

With regard to nanomaterials, colloidal nanocrystals (NCs) of inorganic semiconductors have attracted much attention from recent perspectives of nanoscience and nanotechnology. One of the majorly appealing features of semiconductor NCs is that the photoluminescence (PL) peak can be tuned by preparing nanometer-sized semiconductor NCs. Such phenomenon is nowadays well-known as the quantum size effect or quantum confinement effect [5,6]. For instance, the NCs of CdS, CdSe, PbS, and so on have been frequently investigated owing to their attractive optical properties including high PL quantum yield (PL-QY) values and the stability rather than those of organic dyes [7–12]. Therefore, the nanocomposite polymers with NCs have potentials for practical applications to active optical components such as lasers, sensors, optical switching, and other optoelectronic and photonic devices [2,3,13,14].

However, the traditional semiconductor NCs cannot be applied to the fabrication of optoelectronic devices in a straightforward way, because they contain high-toxic elements such as Cd, Se, and Pb. It is clear by the example that such elements have been strictly regulated by the Restriction of Hazardous Substances (RoHS) directive from a standpoint of current environmental issue. So, to adopt the NCs in devices, we should develop low-toxic NCs excluding Cd, Se, and Pb and so forth. Among all, CIS NCs are one of the most known example of I-III-VI semiconductor NCs which have been focused for over three decades [15–18].

In this report, we describe facile fabrication of a flexible PL film of CIS NCs embedded in
polyacrylates by photopolymerization [19, 20].

2. Experimental

2.1. Synthesis of CIS NCs

We synthesized CIS NCs according to a similar synthetic procedure of AgInS_{2} NCs reported in our recent study [21]. Briefly, copper(II) acetate [Cu(OAc)_{2}] (0.3 mmol), indium(III) acetate [In(OAc)_{3}] (1.8 mmol), oleic acid (3.6 mmol), tri-octylphosphine (1.8 mL, 4.0 mmol), and 1-dodecanethiol (21.6 mL, 90 mmol) mixed in 1-octadecene (72 mL). We carried out this synthesis under inert N\textsubscript{2} atmosphere. The mixture was stirred at 800 rpm and heated at 120 °C so as to become a transparent solution. Subsequently, the reaction temperature was increased to 230 °C and stirred for 30 min and gently cooled down to 75 °C. After washing with ethanol three times, the products were dispersed in spectrophotometrically graded toluene. Finally, this CIS NC solution was filtrated through polytetrafluoroethylene (PTFE) membrane filters with a pore size of 0.2 \( \mu \)m. Thus, we obtained clear solution of CIS NCs.

The resultant CIS NCs were analyzed by transmission electron microscopy (TEM) observations, powder X-ray diffraction (XRD) measurements, and optical measurements.

2.2. Fabrication of PL film by photopolymerization

Butyl acrylate (BA) at 93 wt%, 1,4-bis(acryloyloxy)butane (BAOB) at 5 wt%, and 1-hydroxycyclohexyl phenyl ketone (HCPK) at 2 wt% were homogeneously mixed to prepare a photocurable mixture of acrylates (BA_BAOB). BA and BAOB are used as a main solvent of liquid monoacrylate monomer and a crosslinking agent of diacrylate, respectively. We adopt herein HCPK as a photopolymerization initiator [22].

The CIS NCs, mentioned above, were collected by centrifugation, followed by drying at 60 °C for 1 hour. After that, the dried CIS NCs were re-dispersed in the BA_BAOB mixture to obtain a solution of CIS NCs (BA_BAOB_CIS).

To fabricate polymer with UV-irradiation, the mixture of BA_BAOB_CIS was sandwiched between a pair of glass substrates. The film thickness was controlled to be 300 \( \mu \)m by PTFE spacer films. At this state, the PL spectrum of BA_BAOB_CIS was taken by optical excitation with 375 nm light. To generate the photopolymerization of BA_BAOB mixture, we irradiated with UV light at 365 nm with the intensity of 9.6 mW/cm\textsuperscript{2} for 20 minutes. Subsequently, we measured the PL spectrum of BA_BAOB_CIS again [19, 20, 23].

3. Results and discussion

3.1. Structure analysis and optical measurement of CIS NCs

TEM observation confirmed that the average particle size of CIS NCs is 2.2±0.5 nm with the dispersion of 1.5–3.5 nm, as shown in Fig. 1 (a). From this TEM image, it turned out that the CIS NCs adopt relatively spherical shape. Subsequently, we measured the XRD profile of CIS NCs to characterize the lattice structure. Figure 1 (b) shows the XRD patterns with three broad peaks around 2\( \theta \) of 28°, 46°, and 55°. They correspond to each of (112), (024/220), and (132) planes of a tetragonal structure of CuInS\textsubscript{2} bulk state, respectively [24]. Such a broad profile of XRD pattern attributed to small particle sizes of CIS NCs. The previous reports suggested us similar appearance of broad XRD patterns of NCs, and Scherrer formula also implies that the NC size is distinctly related to the full width at half-maximum of XRD peak in line with the precedents [10, 17, 25, 26].

The solution of CIS NCs in toluene exhibited a broad absorption band, however, there was no sharp exciton peak typically observed for chalcogenide-type semiconductor NCs such as CdS and CdSe [21].

![Fig. 1. (a) TEM image of CIS NCs with size of 1.5-3.5 nm. (b) XRD patterns of CIS NCs synthesized in this study (lower) and bulk material of tetragonal CuInS\textsubscript{2} (upper; PDF# 00-047-1372) for comparison.](image-url)
When the PL spectrum was measured by optical excitation with 375 nm light, we observed a broad band with the maximum PL wavelength of 650 nm. In addition, the PL-QY was found to be an adequately high value of 34.0%.

3.2. Fabrication and properties of films of CIS NCs in polyacrylates by photopolymerization

Figure 2 shows the PL spectra of CIS NCs dissolved in a BA_BAOB mixture before and after photopolymerization. At the initial state, we found that the maximum PL peak appear at 670 nm, which is red-shifted about 20 nm rather than that of the solution of CIS NCs in toluene. This happened probably from the difference in molecular interaction of CIS NCs with BA_BAOB mixture or toluene.

After irradiation with UV light, we confirmed that the fluidity of BA_BAOB_CIS mixture thoroughly vanishes. This result provides a clear evidence that radical polymerization of acryloyl groups takes place owing to free radicals of HCPK cleaved by UV-irradiation [19,20,23]. At this stage, we found not only an intense PL peak at 670 nm, but also weak PL peak at 500 nm, as shown in Fig. 2. The latter derives from polymerized BA_BAOB mixture, not from CIS NCs. Because the BA_BAOB without CIS NCs also showed a weak PL peak at 500 nm after UV-irradiation.

Moreover, the PL intensity of CIS NCs also maintained after photopolymerization with UV light. Additionally, it was found that the PL intensity is not dependent on the location, suggesting that the CIS NCs are uniformly dispersed in the whole polymerized area. Considering the experimental facts, polymerization enables the prevention of aggregation of CIS NCs [4]. Therefore, we could observe the clear PL from CIS NCs even in polymerized BA_BAOB.

As the most essential finding of this study, we could obtain the flexible film by peeling it from the glass substrates. Figures 3 (a) and 3 (b) show photographs of the flexible film of CIS NCs embedded in polymerized BA_BAOB under UV light and room light, respectively. As is clear from images, this film showed mechanical flexibility.

It is plausible that the functionalities of acrylate monomers affect not only the reaction rate, but also the hardness of solid-state polymerized film. The multifunctional monomer of BAOB would polymerize rapidly as compared with the monofunctional monomer of BA, resulting in the formation of high-density polymer network. This suggests that the BAOB diacrylate has influence on the formation of robust films, and the mechanical flexibility of polymerized film can be tuned by controlling the mix ratio of BA and BAOB [23].

Further studies would lead to the development of novel photonic devices by means of hybridization of inorganic semiconductor NCs and photopolymers [4,20,27].

4. Conclusion

In this study, we synthesized the CIS NCs by the pyrolysis of low-toxic precursors of Cu and In acetates in one-pot way. Subsequently, the solid-state film of CIS NCs embedded in polyacrylates was prepared by a simple procedure of photopolymerization. After photopolymerization with UV light, the PL feature of CIS NCs was maintained even in the solid-state film. Such a hybrid film exhibited clear PL and mechanical flexibility. As compared to dispersions of NCs, the solid-state films are practical advantageous due to their easy handling [2]. The present film of CIS NCs in polyacrylates is not optimal. Further improvement of PL and mechanical properties of the film could be achieved by tailoring the materials.
and mixing conditions, thereby leading to the fabrication of next-generation light-emitting devices.

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