Sensitized Photopolymerization of an Ionic Liquid-Based Monomer by Using CdTe Nanocrystals

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ABSTRACT: Semiconductor nanocrystal has been demonstrated as a photosensitizer for the photopolymerization of acrylic monomer in combination with an onium salt coinitiator. An acrylic monomer designed based on ionic liquid was able to dissolve both coinitiator and cationic CdTe nanocrystals and polymerized by visible irradiation. Since the onium salt has no sensitivity in the visible region, the polymerization occurred by the indirect activation of coinitiator. Emission quenching study of CdTe nanocrystals with the coinitiator and electrochemical studies on them revealed that the polymerization was initiated by the photoinduced electron transfer from the CdTe nanocrystal to the onium salt. The polymerization kinetics was compared with the organic dye sensitized photopolymerization system by monitoring the conversion of monomer with FT-IR. The large extinction coefficient and long excitation lifetime of CdTe nanocrystals were considered to be responsible for the efficient electron transfer with onium salt and the efficient and rapid photopolymerization.

Introduction

Low dimensional semiconductor nanomaterials, especially semiconductor nanocrystals (NCs), have attracted a great interest for the past few decades because of their unique properties, unlike the bulk materials due to the quantum size confinement effect.[1−4] The recent progress in the wet-chemical synthesis of highly luminescent semiconductor NCs[5−7] explores their extensive uses ranged from organic electronics to biotechnologies as an alternative to the conventional organic dye molecules. Compared to organic dyes, semiconductor NCs have several specific and advantageous properties as follows. They show the size-dependent absorption and emission spectra, giving the wide color tunability by using a single synthetic route. Besides their strong emission, semiconductor NCs indicate significant coloration ability derived from their large molar extinction coefficient.[8] Though the excitation lifetime of semiconductor NCs is also size-dependent, it is usually several times longer than those of conventional organic dyes. Considering these features described above, semiconductor NCs are promising candidates for the photosensitizer which has strong sensitivity in the visible region for several photochemical reactions induced by visible light irradiation. There have been lots of reports addressing the photocatalytic aspects of semiconductor NCs,[9−17] and the electron transfer on semiconductor NCs has been also extensively studied in connection with photoelectrochemistry.[18−20] Some examples have demonstrated the semiconductor NC-initiating photopolymerization,[21−24] whereas the polymerization rate and efficiency have been substantially low because they directly used the inherent free radicals on NC surface[25] generated by photoexcitation as the initiating species. In addition to the low reaction efficiency, they often employed near-UV-sensitive NCs such as ZnO and CdS. The possibility of semiconductor NCs as the donor−acceptor electron transfer initiators in combination with coinitiator of cationic or radical photopolymerization such as onium salts[26] has never been studied.

Sensitized photopolymerization is widely used in the field of imaging technologies, including photoresists, laser imaging, and holography.[27,28] The dye-sensitized photopolymerization is based on the generation of the initiating species such as radical or cation via either photoinduced reduction or oxidation of initiator with dye.[29−32] The efficient electron transfer between dye and initiator is required for the proceeding of sensitized photopolymerization. The tuning ability of the sensitivity of dyes for the monochromatic light or narrow band light sources such as lasers and LEDs is also important. Taking the long excitation lifetime, high molar extinction coefficient, and the easy tunability of colors into consideration, semiconductor NCs seem to be fairly advantageous as a sensitizer for donor−acceptor initiators of the visible light initiating polymerization system.

We describe herein a novel photopolymerization system that consists of CdTe NCs as the photosensitizer and diphenyliodonium salt[26] as a coinitiator. Diaryliodonium salts explored by Crivello[26] are efficient cationic polymerization initiators which show photolysis by UV irradiation with high quantum yield. While they have been extensively studied as the electron-accepting initiators reduced with photoexcited polynuclear aromatic compounds such as thioxanthones,[33,34] pyrene,[35] anthracene,[36,37] acridine derivative,[38] squaraine dyes,[39] methylene blue,[40] and carbazole-pendant polymer,[41] the combination with semiconductor nanomaterials has been unexplored yet. However, the solubility of such nanomaterials may often limit their use as an alternative to organic dyes. Recently, we have succeeded in the efficient phase transfer of cationic CdTe NCs into hydrophobic ionic liquids, in which CdTe NCs are stably dispersed and show remarkable enhancement in their optical properties.[42] This technique was also applicable to a polymerizable ionic liquid containing an acrylate group,[43] giving the highly luminescent polymer composites by the extraction followed by polymerization of ionic liquid.[44] In this study, therefore, an ionic liquid-based acrylate derivative, which is capable of dissolving CdTe NCs stably, is employed as a monomer. The reaction kinetics of NC-sensitized photopolymerization was compared with the conventional sensitized-polymerization system which employs an organic dye as a sensitizer. The rapid photopolymerization triggered by the efficient photoinduced electron transfer between the NC and a diphenyliodonium has been demonstrated for the first time.

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Experimental Section

General. Water-soluble thiocholine bromide (TCB)-capped cationic CdTe NCs were synthesized by following the previous reports.[42,44,45] 1-(3-Acryloyloxypropyl)-3-methylimidazoliumbis-(trifluoromethanesulfonyl)imide (apmimTFSI), an ionic liquid-based monomer, was employed as a monomer and synthesized according to the previous reports.[43,44] The monomer was purified carefully according to the literature,[46] and its purity was confirmed by ^{1}H NMR. 1-Butyl-3-methylimidazolium TFSI (bmimTFSI), which was purchased from Kanto Chemical Co. Inc., was employed as solvent for the spectroscopic measurements and the electrochemical study. The commercial diphenyliodonium hexafluorophosphate (DPI) was employed as a coinitiator. The organic dye, acridine orange, was used as a conventional photosensitizer.

IR spectra were recorded on a JASCO FT/IR-4200 infrared spectrometer. Absorption and emission spectra were measured using a JASCO V-550 spectrophotometer and a JASCO FP-6500 spectrofluorometer, respectively. The photoluminescence lifetime measurement of CdTe NC was conducted by using a picosecond fluorescence lifetime measurement system (Hamamatsu Photonics, C4780) with integrated streak scope system (Hamamatsu Photonics, C4334). The second harmonic generation (400 nm) from a mode-locked Ti:sapphire laser (Coherent, Mira model 900-F) was used as an excitation light source (repetition rate, 78 MHz; fwhm, 80 fs). Reduction potentials of DPI and CdTe−NCs were measured by cyclic voltammetry on a μAutolab III potentiostat/galvanostat (ECO CHEMIE, Inc.) in a standard three-electrode cell. A grassy carbon (GC) disk electrode was used as the working electrode. An Ag/Ag$^+$ electrode and a Pt wire were used as the reference and counter electrodes, respectively. All measurements were carried out with a scan rate of 20 mV/s in bmimTFSI without any additional electrolyte.

Photopolymerization. TCB-capped CdTe NCs could be stably dispersed in apmimTFSI by the simple biphasic liquid−liquid extraction process from water to the ionic liquid without any degradation and flocculation.[42,44] Bulk monomer containing given amounts of DPI and TCB-capped CdTe NCs was placed in Pyrex tubes and flushed with dry nitrogen. Photopolymerization was carried out by the irradiation with an Hg−Xe lamp, MUV-202U (Moritex, Inc.), through a $\lambda > 440$ nm cutoff filter and a cold filter. The cutoff filter and cold filter were used to prevent direct excitation of DPI and thermal polymerization, respectively. The intensity of incident light after passing filters was found to be 13 mW cm^{-2} at 500 nm.

Photopolymerization Kinetics Using Real-Time FT-IR Study. Photopolymerization of monomers was monitored by real-time Fourier transform infrared (RT FT-IR) spectroscopy.[47] Sample solutions were prepared by mixing apmimTFSI (1.0 g) containing TCB-capped CdTe NCs (3.9×10^{-5} M) or acridine orange (6.3×10^{-5} M) and DPI (2.0×10^{-5} mol, 1.0 mol %). Films were made by squeezing a drop of monomer mixture between KBr plates divided with 2 μm of polystyrene beads (Polybead Microspheres Polysciences, Inc.) as a spacer. All samples were prepared inside an Ar-filled drybox, and polymerization and measurements were carried out under ambient conditions. The plates were set into an IR spectrometer, and IR spectra were recorded at the rate of 1 spectrum/s using ITM-4000, interval acquisition software obtained from JASCO Corp. While IR spectra were measured, the visible light in the same condition described above was irradiated at an incident angle of 45° onto the sample window. During irradiation, the progress of polymerization was monitored by following the decrease in the intensity at 1410 cm^{-1} (part of the bending vibrations of the acrylic CH group) and the shift in the peak of C═O stretching vibration (acrylic ester).

Results and Discussion

Figure 1 shows the absorption spectra of coinitiator, DPI, and TCB-capped CdTe NC in bmimTFSI. The TCB-capped CdTe NCs were stably dispersed in bmimTFSI with the simple biphasic technique from the aqueous solution. BmimTFSI could also dissolve DPI stably without any surfactants. In bmimTFSI, DPI exhibits a strong absorption below 300 nm region with a weak tail extending to 350 nm. Although the absorption maximum cannot be obtained because of the strong absorption by bmimTFSI itself, there is no doubt that DPI has almost no sensitivity in the visible region. On the other hand, CdTe NC has an absorption band at around 500 nm due to the first exciton absorption of nanocrystals, which is identical to that in water.[42,44] The photoirradiation, therefore, was carried out with a light longer than 440 nm by using a long pass filter in order to avoid the direct excitation of DPI.

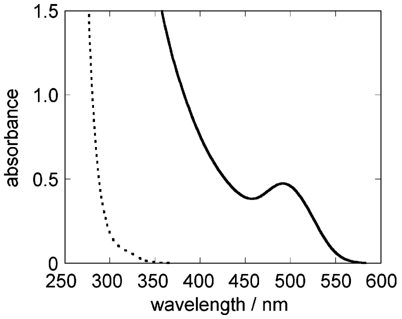


Figure 1. Absorption spectra of DPI (dotted line) and TCB-capped CdTe NCs (solid line) in bmimTFSI. The concentration of DPI and CdTe NCs were 1.0×10^{-3} and 6.0×10^{-6} M, respectively.

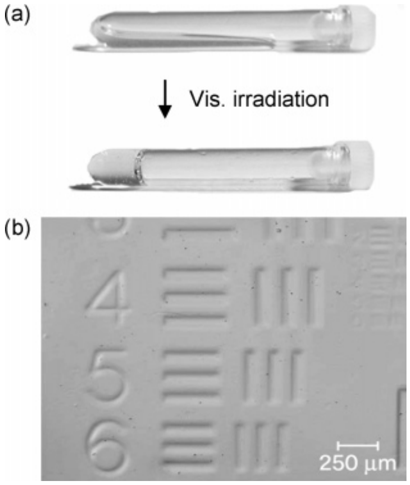
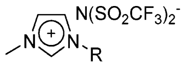
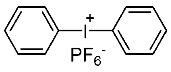


Figure 2. (a) Photograph of the mixture of monomer, CdTe NC sensitizer, and DPI coinitiator before and after the visible irradiation. (b) Optical microscope photograph of a pattern obtained by the irradiation of the present photopolymer system through a mask pattern. The concentrations of CdTe NC and DPI were 6.0×10^{-6} and 0.050 M, respectively.



bmimTFSI: R = $(CH_2)_3CH_3$
apmimTFSI: R = $(CH_2)_3OCOCH{=}CH_2$



DPI

The solubility of DPI in the monomer, apmimTFSI, was substantially the same as that in bmimTFSI, giving the clear solution below ca. 10 wt %. ApmimTFSI could also stably dissolve the cationic TCB-capped CdTe NCs. As shown in Figure 2a, upon visible irradiation for a couple of minutes the mixture of monomer, DPI, and CdTe NCs was solidified by the polymerization of the ionic liquid-based monomer in bulk. For this sample, CdTe NC and DPI were dissolved in neat apmimTFSI with the concentration of 6.0×10^{-6} and 0.050 M, respectively. Because this type of polymer formed a certain

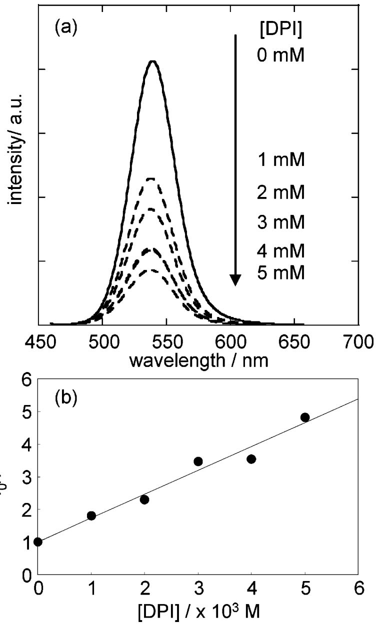


Figure 3. (a) Spectral change in the emission of CdTe NCs in bmimTFSI with the addition of DPI. [CdTe NC] = 2.8×10^{-6} M. (b) Stern−Volmer plot of CdTe NC emission quenching.

kind of ionomer in which the polymer chains possessing cationic moieties were cross-linked each other by the electrostatic interaction via the anionic species, the polymer obtained was hardly dissolved into any solvents.[43,44] The formation of polymer was also confirmed by the single-pass attenuated total reflection Fourier transformation infrared spectroscopy (ATR FT-IR). Both the shift of the peak of acrylic C═O stretching band at 1720 cm^{-1} to 1727 cm^{-1} and the decrease in the peak at 1410 cm^{-1} corresponding to acrylic C−H bending represented the conversion of monomer. Since the coinitiator DPI is insensitive to visible light,[26] the polymerization should occur by the sensitized activation of DPI with the CdTe NC. The control samples which lack both or either of DPI and CdTe NCs were not solidified with the few minutes of visible irradiation, also supporting the NC-sensitization mechanism. While the initiation mechanism of the polymerization of present monomer has not been defined yet, Crivello et al.[35] proposed the mechanism for the generation of several initiation-active species for such a donor−acceptor electron transfer initiation system involving a diaryliodonium. Figure 2b shows the pattern obtained by the visible light exposure of the present photopolymerization system through a photomask followed by washing with chloroform to remove the unreacted monomer. The resolution of the pattern is not so high because the present system has not been optimized. However, it clearly demonstrates that the photopolymerization progressed only in the visible light exposed area.

We then investigated the photoluminescence quenching of the CdTe NCs with the addition of DPI as a quencher in bmimTFSI. The degree of interaction between the CdTe NC and DPI can be evaluated from emission quenching experiments.[48] Figure 3a shows the spectral change in the emission of CdTe NCs ($\lambda_{ex} = 450$ nm) with variable concentration of DPI. As the concentration of DPI increased, the intensity of the band-edge emission of CdTe NCs at 540 nm was progressively decreased. The quenching should be attributed to the photoinduced electron transfer rather than energy transfer between the CdTe NC and DPI molecule since the singlet excitation energy of DPI is substantially higher energy than that of the CdTe NC. As shown in Figure 3b, the emission quenching of CdTe NCs by DPI in bmimTFSI gives almost a linear Stern−Volmer relationship (eqs 1 and 2)

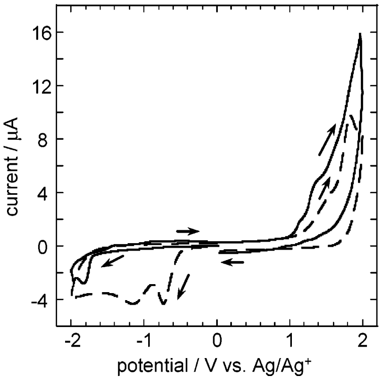


Figure 4. Cyclic voltammograms of CdTe NC (solid line) and DPI (broken line) dissolved in bmimTFSI. The concentration of CdTe NC and DPI were 1.8×10^{-5} and 1.0×10^{-2} M, respectively. The potential sweep rate was 20 mV s^{-1}.

$$I_0/I = 1 + K_{SV}[\mathrm{DPI}] \quad (1)$$

$$K_{SV} = k_q \tau_0 \quad (2)$$

where I_0 and I are the emission intensities in the absence and presence, respectively, of DPI, K_{SV} is the Stern−Volmer constant, [DPI] is the concentration of DPI, and τ_0 is the emission lifetime of CdTe NC in the absence of DPI in bmimTFSI. The quenching rate constant, k_q, obtained from the slope of the plot, K_{SV}, and the emission lifetime, τ_0, was estimated to be 4.5×10^{10} M^{-1} s^{-1}. Whereas the detailed quenching kinetics in the ionic liquid would be discussed elsewhere, the observation strongly suggests the electron transfer between the CdTe NC and DPI.

The reduction potentials (vs Ag/Ag$^+$) of DPI and CdTe NC in bmimTFSI were evaluated from cyclic voltammetry shown in Figure 4 to be about −0.72 V (vs Ag/Ag$^+$) and −1.80 V (vs Ag/Ag$^+$), respectively. These voltammograms were obtained in the initial scans that were started with the scan direction of negative potential from 0 V (vs Ag/Ag$^+$). The oxidation potential of the CdTe NC was difficult to be estimated due to the oxidation of coexisting surface capping thiol molecules above 1.0 V (vs Ag/Ag$^+$) (see Supporting Information). In general, the thermodynamic feasibility for photoinduced electron transfer is verified with the free energy change given by the Rehm−Weller equation,[49] whereas it was hardly obtained because the oxidation potential of the CdTe NC was required for the estimation. However, it should be concluded that the CdTe NC and DPI serve as a donor and an acceptor, respectively, from the findings described above. The electron transfer also produces a hole in a CdTe NC. Although the present system did not include any hole scavengers such as amines or alcohols particularly, the water molecules slightly contained in the solution may act as a hole scavenger. It is also convincing that the hole oxidizes the surface thiole molecule to produce disulfide derivative since the onset of the oxidation curve of TCB overlaps with the oxidation peak of CdTe NC (see Supporting Information). While the production of disulfide derivatives may adversely affect the stability of NCs, the extent of damage was almost negligible.

We proved the efficiency of the CdTe NC-sensitized photopolymerization system by monitoring the change of FT-IR spectra during the polymerization. The change in the absorption peak at 1410 cm^{-1} (Figure 5a) was used for the calculations of the acrylic double-bond conversion, γ

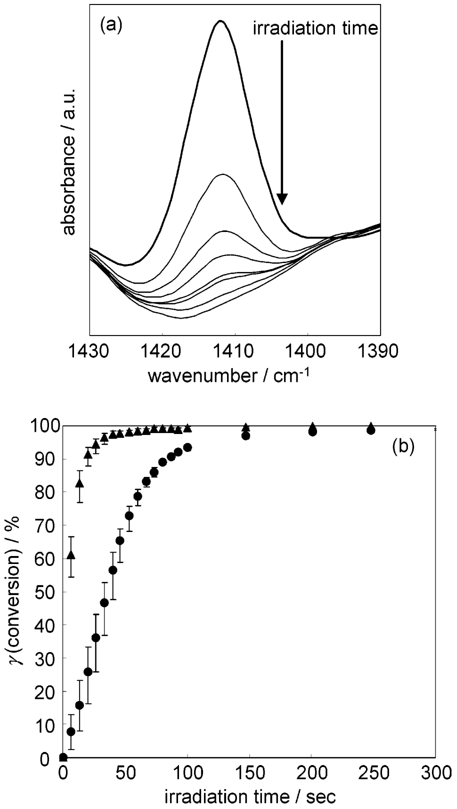


Figure 5. (a) Spectral change in FT-IR by the CdTe NC sensitized polymerization of monomer. The peak of acrylic C−H bending at around 1410 cm^{-1} is extracted. (b) Conversion profiles of the monomer by sensitized photopolymerization with CdTe NC(▲) and AO(●).

$$\gamma = (A_0 - A_t)/A_0 \tag{3}$$

where A_0 and A_t are the integrated peak areas at around 1410 cm^{-1} before and after the irradiation for a period of time t, respectively. The γ values were plotted as a function of time. In this experiment, a polynuclear aromatic heterocycle, acridine orange (AO), was employed as a typical organic photosensitizer because of its good solubility to apmimTFSI. To compare the efficiency of sensitization, the concentrations of sensitizers were adjusted so that the integrated absorption peak areas above 440 nm for CdTe NC and AO were equal to each other. Consequently, the concentrations of sensitizer were prepared to be 3.9×10^{-5} M for CdTe NC and 6.3×10^{-5} M for AO, indicating the larger molar extinction coefficient of CdTe NC than that of AO. The coinitiator DPI was also dissolved into the monomer with the concentration of 1.0 mol %. Under this condition, 95% of CdTe NCs were quenched by DPI, indicating the electron transfer occurred efficiently. The time dependence of γ in the presence of CdTe NC and AO is shown in Figure 5b. These plots clearly indicate that the efficiency of the CdTe NC as a sensitizer is much higher than that of AO. The kinetic parameter determined from the slopes of the initial portion of the conversion vs time curve for CdTe NCs is 8 times larger than that of AO. The time required for the consumption of half of the monomer is within 6 s for CdTe NC-sensitized system, whereas that of AO-sensitized system was 38 s. Since the numbers of photons absorbed are almost the same in both samples, the numbers of excited sensitizers per second are also identical. The difference in the rate of photopolymerization, therefore, should be attributed to the difference in the efficiency of photoinduced electron transfer to the coinitiator. In these experiments, the sensitizers and coinitiator were not connected directly with chemical modifications or specific interactions and the photoactivation kinetics seems to follow diffusion-controlled bimolecular reaction constant, k_{diff}. The k_{diff} can be estimated from eq 4

$$k_{\mathrm{diff}} = \frac{2RT(R_{\mathrm{d}} + R_{\mathrm{a}})(R_{\mathrm{d}}^{-1} + R_{\mathrm{a}}^{-1})}{3000\eta} \tag{4}$$

where R_{a}, R_{d}, and η are diameters of donor and acceptor and viscosity of the medium, respectively. The difference of R_{a} and R_{d} in the CdTe NC/DPI system is significantly larger than that in the AO/DPI system, and therefore a larger k_{diff} can be expected for former case on the basis of eq 4. On the other hand, the long excitation lifetime of CdTe NC also remarkably contributes to the effective electron transfer with DPI. The emission lifetime of CdTe NCs is measured to be 16 ns, whereas that of AO was to be 3.2 ns in bmimTFSI. This difference is also observed for the Stern−Volmer constants K_{SV} estimated from the emission quenching measurements (see Supporting Infromation). The longer lifetime of excited state should enhance the probability of contact followed by the electron transfer between the excited CdTe NC and an acceptor, DPI.

Conclusions

In this paper, we demonstrated the use of semiconductor nanocrystals as a visible-sensitive sensitizer for photopolymerization in combination with diphenyliodonium salt as a coinitiator. The ionic liquid-based monomer easily polymerized upon the visible irradiation in the presence of the CdTe NC and DPI. The emission quenching experiment and electrochemical studies in an ionic liquid revealed that the coinitiator was activated via the photoinduced electron transfer from the excited CdTe NC to DPI. Kinetic studies by monitoring the conversion of monomer with FT-IR spectra during photoirradiation showed that the CdTe NC was a good sensitizer for the activation of DPI compared with a polynuclear heterocycle, acridine orange. The effects were explained by the large molar extinction coefficient and the long excitation lifetime of CdTe NC. It should be noted that the present combination of semiconductor NC with onium salt photoinitiator would be also applicable to other photopolymerization system by controlling the solubility of semiconductor nanocrystals to other monomers. Furthermore, the huge nonlinear optical properties of semiconductor nanocrystals[50,51,52] will afford us to develop efficient two-photon initiators for the three-dimensional microfabrication system.[53] These attempts are in under way in our laboratory.

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Supporting Information Available: Electrochemical studies of TCB, CdTe NC, and DPI in bmimTFSI, quenching experiment of AO with DPI, the data of FT-IR spectral change on photopolymerizaion, and the concentration effect of sensitizer CdTe NC on the conversion kinetics. This material is available free of charge via the Internet at http://pubs.acs.org.

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