

Surface State Analysis of Photobrightening in CdSe Nanocrystal Thin Films

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Received: May 28, 2003; In Final Form: August 26, 2003

We report the changes in surface state of tri-*n*-octylphosphine oxide (TOPO) capped CdSe nanocrystals by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). In the photobrightening state, where photoluminescence (PL) intensity increased during the illumination, surface ligand rearrangement such as the TOPO–Se complex and TOPO dimers are formed, which might be deeply correlated with the PL enhancement. It was also observed that surface oxidation and decomposition of TOPO, which is followed by the desorption, occurred in photodarkening state.

Chemically synthesized semiconductor nanocrystals (NCs), or colloidal quantum dots, are small molecular clusters whose size is ca. 1–10 nm in diameter and exhibit unique optical properties arising from 3-dimensional quantum confinement of carriers, which are different from bulk crystals.¹ Quantum confinement leads to formation of discrete and blue-shifted absorption bands and increase of oscillator strength due to electron–hole overlap, giving enhanced emission efficiency and optical nonlinearity, and the emission wavelengths can be changed by simply controlling the nanocrystal size. The optical properties of CdSe NCs are being extensively investigated.^{2,3} It has been reported that a single CdSe NCs shows intermittent emission or blinking, which is not observed in ensemble of CdSe NCs.⁴ In the ensembles of CdSe NCs, several groups recently reported that CdSe NC thin films show photobrightening, where photoluminescence (PL) intensity of CdSe thin films increase with the duration of illumination with a UV light source, and which is followed by photodarkening or photobleaching, where the PL intensity gradually decreases.^{5–7} The PL efficiency is deeply correlated with the surface state of NCs such as the degree of surface passivation and adsorption state of organic ligand. Cordero et al. showed that PL could be strongly influenced by light-induced changes in the surface states following adsorption of water. Hess et al. claimed that photodarkening is attributed to surface defects due to a transformation of the surface by heating. In this paper, we investigate a change in surface states of CdSe NCs before and after the irradiation of blue light. To investigate the surface states, X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements were performed.

Tri-*n*-octylphosphine oxide (TOPO) capped CdSe nanocrystals used in the present study were prepared by the colloidal chemical method.⁸ A mixture of dimethylcadmium and selenium, dissolved in tributylphosphine (TBP), was rapidly

injected into TOPO, which was heated to 300–350 °C. The precipitation and the removal of excess TOPO adding methanol was carried out. The diameter of CdSe NCs used in this study is about 3.5 nm. The NCs were dissolved in CHCl₃ and the NC solutions were spun coat onto a Si wafer rotating at 1000 rpm for 1 min and dried in a vacuum at room temperature. A fluorescence microscope equipped with an optical multichannel analyzer was used to measure the PL intensity change of the CdSe NC thin film with He–Cd laser (442 nm) cw excitation, whose power density was about 1 W/cm². CdSe NC films were irradiated by He–Cd laser power of 30 mW/cm² for about 30 min to prepare the photobrightening (PB) state and by the power of 200 mW/cm² for about 30 min to prepare the photodarkening (PD) state, respectively. To investigate the surface state change among initial (INI), PB, and PD, XPS (PHI, Quantum 2000) and ToF-SIMS (ION-TOF, TOF-SIMS IV) measurements were performed. All measurements were performed at room temperature.

Figure 1 shows PL spectra and the intensity change of the CdSe NC thin film as a function of illumination time in air. Figure 1a shows PL spectra at different illumination times: (1) 0 min, (2) 1 min, and (3) 30 min. In Figure 1b, the solid line shows PL intensity change and the dotted line shows peak position change. PL intensity increased during the first 1 min and then gradually decreased, which indicates that photobrightening and photodarkening occurred with this excitation energy. The peak position shifted to a shorter wavelength by 12 nm during the illumination. A gradual blue shift of CdSe NCs illuminated in air has been previously observed in room-temperature luminescence from single NC and NC monolayer films, and no blue shift was observed in the nitrogen atmosphere, which is attributed to a shrinkage of the CdSe core by photooxidation.^{4,6}

To investigate surface state change of CdSe NCs during the illumination, XPS measurements were performed in the initial state (INI), the photobrightening state (PB), and the photodarkening state (PD). Figure 2 shows XPS narrow spectra of Cd 3d, Se 3d, and P 2s. There was no significant change in Cd spectra during the illumination. Though the intensity of the Se 2s peak around 54 eV decreased during the illumination, the

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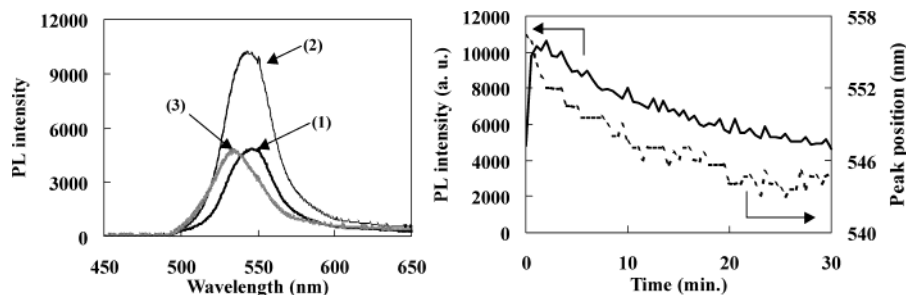


Figure 1. (a) PL spectra of CdSe NC thin film at different illumination times: (1) 0 min, (2) 2 min, (3) 30 min. The sample was excited at 442 nm, and the excitation energy was about 1 W/cm². (b) PL intensity (solid line) and peak position change (dotted line) as a function of illumination time.

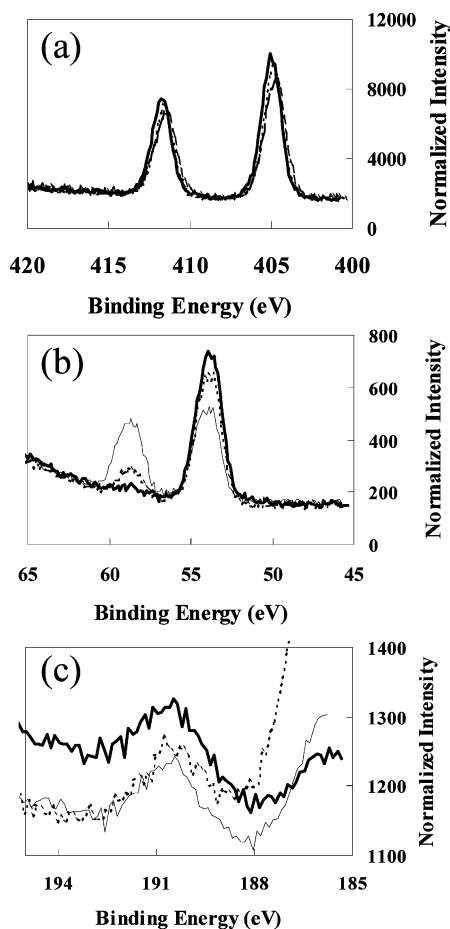


Figure 2. XPS narrow-scan spectra of (a) Cd 3d, (b) Se 3d, and (c) P 2s in (1) initial state (bold solid line), (2) photobrightening state (dotted line), and (3) photodarkening state (narrow solid line).

TABLE 1: Surface Atomic Composition of CdSe NCs in the Initial, Photobrightening, and Photodarkening States

| | C 1s | O 1s | P 2s | Se 3d (oxide) | Se 3d (CdSe) | Cd 3d5 | Cd/Se ratio | total (%) |
|-----------|------|------|------|------------------|-----------------|--------|----------------|--------------|
| INI state | 61.4 | 16.2 | 3.7 | 0.3 | 6.4 | 12.1 | 1.8 | 100.0 |
| PB state | 58.4 | 19.6 | 2.8 | 0.9 | 5.5 | 12.7 | 1.9 | 100.0 |
| PD state | 53.8 | 25.0 | 2.0 | 2.7 | 3.7 | 12.8 | 2.0 | 100.0 |

Se oxide peak appeared around 59 eV and the intensity increased, which indicates that Se oxidation occurred on the NC surface. Regarding phosphorus spectra, the decrease of the peak intensity was observed without any spectral change. Table 1 summarizes surface element ratio of CdSe NCs in INI, PB, and PD states. The Cd/Se ratio on the NC surface is approximately 1.8 in the initial state, which indicates that surface of NCs is Cd-rich. During the illumination, the Cd/Se ratio slightly increased, which means that the NC surface became

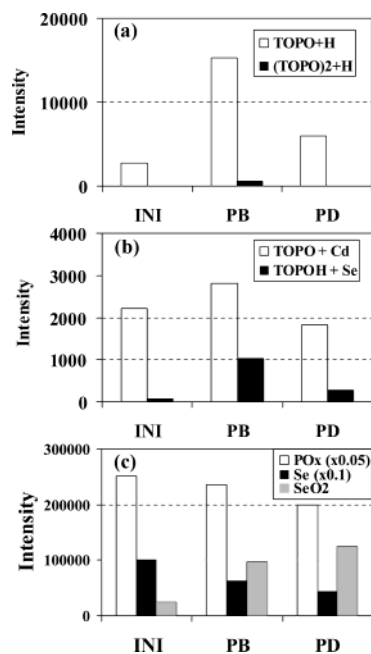


Figure 3. Intensity change of typical positive ((a) and (b)) and negative (c) fragment ions in initial, photobrightening, and photodarkening states.

Cd-rich compared to the INI state. The surface element ratio of C and P, which derives from surface ligand TOPO, decreased respectively without the change in binding state. This result indicates that the decrease of C and P might be attributed to decomposition of TOPO, which is followed by the desorption of TOPO from the NC surface during the illumination.

To confirm the change in the state of surface ligands, ToF-SIMS measurements were performed. Figure 3 shows the intensity change of typical positive and negative fragment ions in INI, PB, and PD states. In the PB state, TOPO fragment ions were dramatically increased, which indicates that TOPO possesses slightly positive charge and the ionization probability of TOPO increased. Also, TOPO dimer fragment ions were observed only in the PB state. These results indicate that TOPO is activated in this state. Regarding TOPO-metal complex fragment ions, TOPO-Cd fragments were also increased in the photobrightening state. In addition, an interesting feature is that the increase of TOPO-Se fragment ions was observed in the PB state although TOPO-Se fragment ions were not almost observed in the initial state. In the PD state, TOPO-Se fragment ions were decreased again. This result might indicate that a part of TOPO on the NC surface migrated from Cd to Se atoms during the illumination. Regarding TBP-metal complex fragment ions such as TBP-Se, there were no such fragment ions observed in INI, PB, and PD states. Figure 3c showed that phosphate POx fragment ions were decreased and Se oxide

fragment ions were increased, which results are consistent with the XPS results.

We have shown that photobrightening and photodarkening occurred in CdSe thin films during the illumination. In general, luminescence quantum efficiency of NCs is deeply correlated with surface state, e.g., adsorption state of organic ligands and surface defects. It is qualitatively explained that the degree of passivation of surface traps was increased in the PB state. Cordero et al. suggested that light-induced passivation of the surface trap states following adsorption of water resulted in increased luminescence.⁶ It was claimed that a light-induced surface state change such as photooxidation, surface passivation due to water molecule, or surface oxidation is responsible for photobrightening and photodarkening. In addition to the above discussion, it is also considered that the adsorption state of TOPO on the NC surface has an important role in PB and PD. Therefore, we note a change in the adsorption state of TOPO during the illumination.

In general, it is reported that Cd atoms are bonded to TOPO, to the extent that such bonding is sterically allowed and most of the Se atoms on the surface are unbonded.⁹ ToF-SIMS measurements showed that TOPO binds to Cd atoms in the INI state because TOPO is electron-donating molecules (Lewis bases). However, it was observed that a part of TOPO formed TOPO–Se complexes in the PB state, which is almost not observed in the INI state. One possible explanation for the formation of a TOPO–Se complex in the PB state is that TOPO was activated and positively charged due to the laser excitation and a part of activated TOPO migrates on the NC surface, resulting in the change in the adsorption state of TOPO. It might be considered that the passivation of unbonded Se by TOPO contributes to the enhancement of luminescence.

It is reported that the PB state is thermally quasi-reversible.⁷ If the TOPO–Se complex formation is responsible for the photobrightening, the PB state might be reversible. ToF-SIMS and XPS measurements showed that Se oxidation slightly occurred even in the PB state. If the oxidation of Se mainly contributes to the enhancement of luminescence, the PB state might be irreversible. Therefore, the formation of TOPO–Se complex might be one of the factors that contributes to the photobrightening of CdSe NCs.

Upon further illumination, in the PD state, TOPO–Se complex ions were decreased, which also supports that TOPO–Se formation is responsible for the photobrightening. In the PD state, Se oxidation was increased although most Cd atoms were not oxidized. ToF-SIMS measurements showed that SeO_x desorbed from the NC surface and some TOPO decomposed and detached from the surface, where the PL intensity was decreased. The irreversible change in the surface state of NCs such as the desorption of SeO_x and decomposition of TOPO might be responsible for the decrease of PL intensity, which also means that the PD state is irreversible.

In summary, we have investigated the change in surface state of CdSe NCs before and after the irradiation of blue light by XPS and ToF-SIMS. The change in adsorption state of TOPO such as the TOPO–Se complex and TOPO dimers during the illumination is deeply correlated with photobrightening. In photodarkening state, SeO_x and decomposition of TOPO occurred and desorbed from the NC surface, which means that this state is irreversible. Surface rearrangement by photoexcitation has an important role in luminescent properties of CdSe NCs.

Acknowledgment. We thank H. Okuhira of Hitachi Science Systems, Ltd. for expertly operating the ToF-SIMS system. We also thank H. Yamauchi of CACs, Inc. for XPS measurements.

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