Ligand Control of Semiconductor Nanocrystals for Efficient Carrier Injection

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ABSTRACT

Inorganic/organic hybrid material of CdSe/ZnS core/shell nanocrystals (NCs) covered with organic ligands was prepared with ligand exchange reaction in order to facilitate carrier injection into NCs through the organic ligands. The organic ligands used in this study, 2-naphtalenethiol and bathophenanthroline, were selected as model compounds according to adjustment of highest occupied molecular orbital and lowest unoccupied molecular orbital of the ligand to valence band maximum and conduction band minimum of the CdSe NCs, respectively. The prepared hybrid NCs easily disperse in polar organic solvents such as $CHCl_3$ and show photoluminescence only from the CdSe/ZnS core/shell NCs. Current-voltage characteristics of the ligand exchanged NCs thin films sandwiched between electrodes were investigated. It was shown that conductivity of the film was improved by the introduction of carrier injecting ligands in comparison to the ligand unexchanged trioctylphosphine oxide-capped CdSe/ZnS NC thin film.

INTRODUCTION

Recently, much attention has been paid to colloidal semiconductor nanocrystals (NCs) covered with organic ligands as a building block for electronic devices such as light emitting diodes (LEDs) [1-3] and photovoltaic cells [4,5]. For such integrated device applications, electron and hole transfer into/from the NCs is one of key issues. Trioctylphosphine oxide (TOPO)-capped NCs are considered to be unsuitable for the purpose because TOPO is insulating molecule and tremendously reduces electron transfer efficiency. Therefore, electronic interaction between NCs and other organic ligands has been extensively investigated [6-8].

For LED application, the ligands require several functions: 1) prevention of NC aggregation, 2) inhibition of NC fluorescence quenching, 3) lack of fluorescence from the ligands themselves, and 4) carrier transport that allows efficient charge injection into the NCs. In the present work, we study CdSe/ZnS core/shell NCs covered with two types of organic ligands in order to realize the functions above. One is for dispersibility, and the other is for carrier injection. In the latter, the ligand itself should not show any fluorescence, and its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are adjusted to match valence band maximum (VBM) and conduction band minimum (CBM) of the NCs for the purpose of efficient carrier injection through the ligands to the NCs.

Following this strategy, we select tetradecaphosphonic acid as dispersing ligand, and 2-naphtalenethiol (2NT) or bathophenanthroline (Bphen) as carrier injecting ligands which do not luminesce. We study electronic interaction between CdSe/ZnS core/shell NCs and 2NT or Bphen before and after the introduction of the ligands to the NCs surface. In addition, we investigate current-voltage (I-V) characteristics of thin films of the prepared NCs.

EXPERIMENTAL DETAILS

CdSe NCs used in this study were synthesized as reported previously [9,10]. ZnS Shell of the CdSe NCs was prepared according to literature [11] with excess TOPO and tetradecaphosphonic acid (TDPA), giving TOPO-capped CdSe/ZnS NCs. Commercially available 2NTs and Bphens were used without further purification. Ligand exchange reaction from TOPO to 2NT or Bphen was carried out in solution under N_2 at room temperature. The TOPO-capped CdSe/ZnS core/shell NCs and 2NT or Bphen were co-dispersed in toluene and stirred for several hours. The product was precipitated with methanol to remove TOPO and excess 2NT or Bphen, and then redispersed in $CHCl_3$. The 2NT- and Bphen-capped CdSe/ZnS NCs were abbreviated as CdSe/ZnS-2NT and CdSe/ZnS-Bphen, respectively, and the TOPO-capped as CdSe/ZnS-TOPO. UV-vis absorption and photoluminescence (PL) spectra of the NCs were measured by HP UV8453 and HITACHI F-2500 spectrometers, respectively.

I-V characteristics of thin films of the NCs were measured according to the reported device structure [12]. Indium-tin oxide (ITO) coated glass substrates were washed with 2-propanol and dried under N_2. Thin films of the NCs were prepared by spin coating of the $CHCl_3$ solution (*ca.* 50mg/mL) onto the ITO substrate at speed of 1000 rpm. Thickness of the film was measured with Seiko SPA300/SPI3700 atomic force microscope. Al contacts were deposited on top of the NCs thin films by thermal evaporation under vacuum. Dimension of the Al electrode was 3 mm x 3 mm. I-V curves were measured with a Keithley 2400 source meter unit at room temperature at an ambient condition.

RESULTS AND DISCUSSION

Figure 1 is an energy level diagram for CdSe/ZnS NCs, TOPO, 2NT, and Bphen. For CdSe NCs and Bphen, the energy levels are taken from literatures [13,14], whereas for 2NT, the energy levels of HOMO are taken from literature [15] and bandgaps between HOMO and LUMO were determined using its UV-vis absorption spectra. Energy level of HOMO of TOPO was calculated with MOPAC. As described in the introduction, 2NT and Bphen were selected as model compounds. In both cases, energy differences between the HOMOs and VBM and between the LUMOs and CBM of the ligands and CdSe NCs are smaller than that in the case of TOPO.

Ligand exchange was carried out in solution, resulting in NCs dispersed in polar organic solvent such as $CHCl_3$. Figure 2 is UV-vis absorption spectra of CdSe/ZnS-2NT and CdSe/ZnS-Bphen taken in $CHCl_3$ before and after ligand exchange. No additional peak was found after the exchange reaction in both cases, suggesting that the quantized electronic states of the NCs are basically stable. It should be noted that the resulting NCs after ligand exchange reaction was not dispersible in organic solvent unless TDPA was used during shell formation. This suggests that TDPA molecules still exist at the NC surface after ligand exchange and contribute to the dispersibility of the NCs in solution.
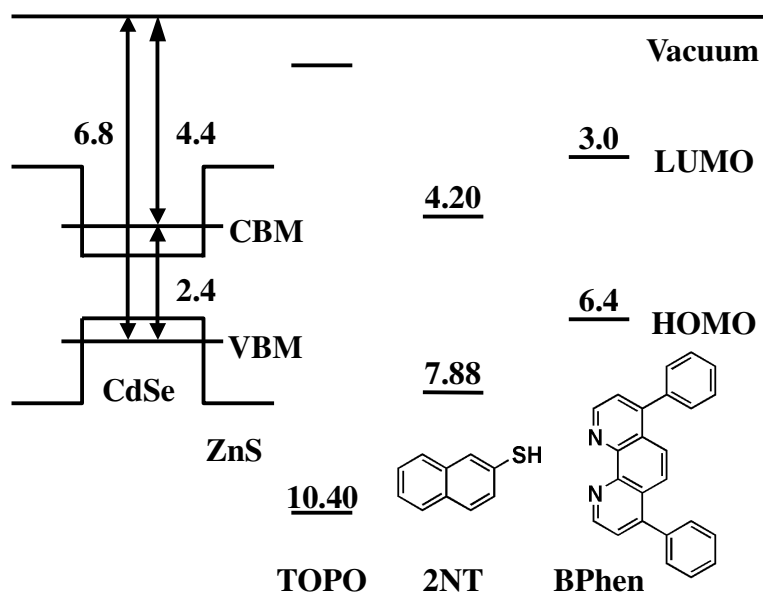
Figure 1. Schematic illustration of energy level diagram for CdSe/ZnS nanocrystal, TOPO, 2NT, and Bphen. The numbers in the figure represent energy levels (eV).
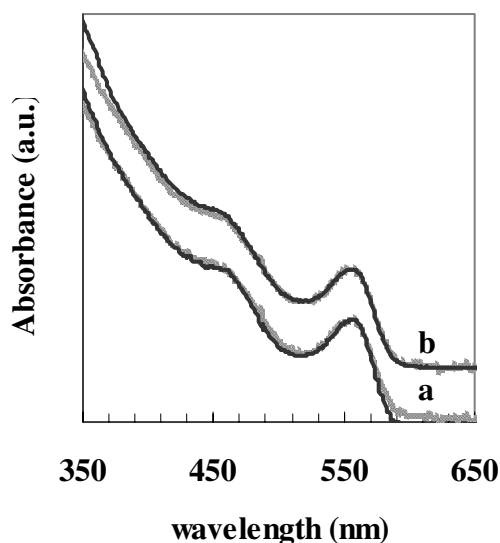

Figure 2. UV-vis absorption spectra of (a) CdSe/ZnS-2NT and (b) CdSe/ZnS-Bphen before (gray lines) and after (black lines) ligand exchange reaction.
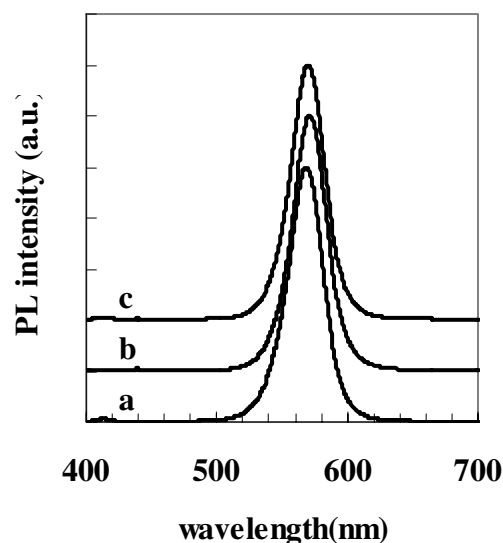
Figure 3. Photoluminescence (PL) spectra of (a) CdSe/ZnS-TOPO, (b) CdSe/ZnS-2NT, and (c) CdSe/ZnS-Bphen.

Figure 3 shows PL spectra of CdSe/ZnS-TOPO, CdSe/ZnS-2NT, and CdSe/ZnS-Bphen. CdSe/ZnS-2NT and CdSe/ZnS-Bphen show fluorescence only from the CdSe/ZnS NCs with

slight peak shift from that of CdSe/ZnS-TOPO. It is possible that the PL peak shift is induced by the existence of the organic ligands at the surface (ligand effect). The PL intensity was decreased to some extent after ligand exchange. Interestingly, these results are different from that reported in refs. 6 and 7 where fluorescence from organic ligands are mainly observed from NC-ligand complexes. It is considered that ZnS shell may prevent energy transfer from photoexcited NCs to organic ligands. It should be stressed that the organic ligands chosen in this work show no fluorescence.
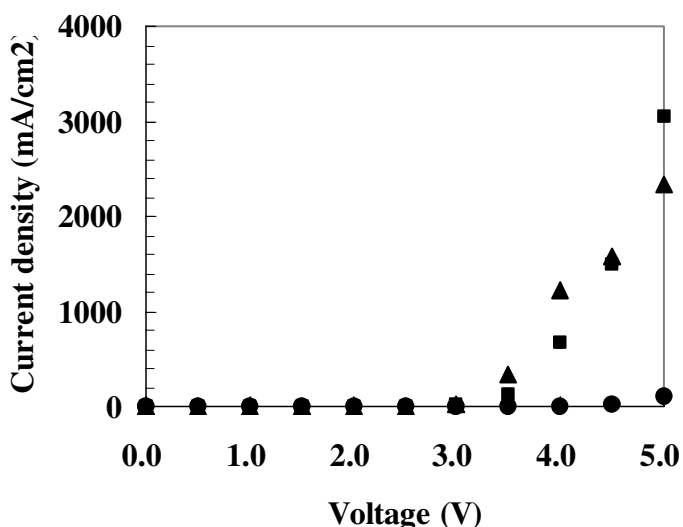

Figure 4. I-V curves for ITO/NCs /Al devices: (●) CdSe/ZnS-TOPO, (▲) CdSe/ZnS-2NT, and (■) CdSe/ZnS-Bphen.

As described earlier, I-V characteristics of thin films of CdSe/ZnS-TOPO, CdSe/ZnS-2NT, and CdSe/ZnS-Bphen were investigated. Thin films of NCs were sandwiched between ITO and Al electrodes without using any matrix. The film thickness was measured to be *ca.* 20 nm for these devices.

The I-V curves taken at room temperature are shown in figure 4. The film composed of CdSe/ZnS-2NT or CdSe/ZnS-Bphen exhibit higher current density than that composed of CdSe/ZnS-TOPO at 3.5 V or higher. This facile carrier injection of these film can be attributed to the smaller difference in energy levels between CdSe/ZnS NCs and 2NT or Bphen.

2NT and Bphen are model compounds, and the strategy demonstrated in this study can be easily extended to any other NC-ligand complexes. This strategy is useful to improve nanocrystal-based device performance.

CONCLUSIONS

CdSe/ZnS core/shell nanocrystals covered with both TDPA and 2NT or Bphen have been prepared by ligand exchange in solution.   The energy level of HOMO and LUMO of the 2NT and Bphen is close to that of VBM and CBM of CdSe nanocrystal respectively. The 2NT-capped

and Bphen-capped CdSe/ZnS nanocrystals partially covered with TDPA successfully disperse in common organic solvent such as $CHCl_3$, and their photoluminescence spectra show fluorescence only from the CdSe/ZnS nanocrystals. The conductivity of thin film of both 2NT-capped and Bphen-capped CdSe/ZnS nanocrystals is extremely improved in comparison with that of TOPO-capped CdSe/ZnS nanocrystals. The difference in the I-V behavior can be attributed to the alignment of the energy levels of the organic ligand molecules attached to the surface of the nanocrystals

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