

Quantum Dots/Conductive Polymer Nanocomposite

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ABSTRACT

The nanocomposite composed of CdSe quantum dots and conductive polymer (OC1C10-PPV) was investigated. The spherical 3.8-nm functionalized CdSe quantum dots were synthesized by a colloidal chemical method. The conductive polymer OC1C10-PPV was synthesized from 1-methoxy-4-(3,7-dimethyl-octanoxyl) benzene and 4-methoxyphenol. The quantum dots were mixed with OC1C10-PPV before and after polymerization. It was found quantum dots will affect the polymerization of OC1C10-PPV. The photoluminescence (PL) peaks from CdSe and OC1C10-PPV was 590 nm (FWHM~26 nm) and 555 nm (FWHM~50 nm), respectively. Photoluminescence spectra of nanocomposite displayed mixed characters of quantum dots and OC1C10-PPV.

Keywords: conductive polymer, nanoparticle, quantum dots

1 INTRODUCTION

There has been a great effort to develop luminescent materials such as quantum dots (QDs) in the past decade. The quantum confinement effect (QCE) has been demonstrated to exist on many types of materials while their dimension reduces to nanometer scale. For semiconductive QDs, the wavelength of the electron is close to the diameter of the crystallite so the matter wave of the carrier will be confined to form standing wave like a particle in a box. The confinement effect for the electron leads to a split of energy band edge, and therefore electronic, optical or magnetic properties of the QDs are different to those of bulk material [1]. For most of the semiconductors, the discrete band edge causes higher band gap energy (E_g). The E_g of the semiconductive QDs blueshifts to higher energy when the dimension of crystallite reduced [2-3]. Consequently, scientists can modify the band structure of materials by the change of particle size. Moreover, the optical properties of semiconductors can be altered by particle size [4-5].

The colloidal semiconductive QDs used as luminescent materials have been devoted recently. Alivisatos et al. used semiconductive colloidal QDs as biological tagging for

diagnostics and visualization. It has significant advantages compared to existing organic dyes such as a high luminescent efficiency, reduced photobleaching, multi-color labeling, parallel screening, infrared labels, blood diagnostics, and bio-compatible [6].

The luminescent conjugate polymer or conductive polymer also attracts much attention recently [7]. The advantage of the polymer-based product is the simple process. However the reliability of polymer is a challenge for the commercial applications. Some inorganic filler have been introduced into polymer to improve the thermal or optical properties [8]. On the other hand, the composite composed of luminescence QDs and luminescent conductive polymer is a new material for optical applications. The mechanisms of the material synthesis and luminescence are not clearly. In this study, the QDs/conductive polymer which QDs mixed with conductive polymer before/after polymer polymerization was investigated.

2 EXPERIMENTAL

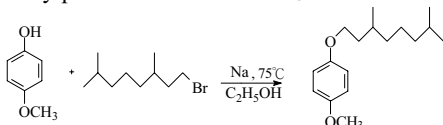
Cadmium oxide, selenium, trioctylphosphine (TOP), trioctylphosphine oxide (TOPO) and hexadecylamine (HDA) are supplied from Aldrich. 4-methoxyphenol was purchased from TCI. Acetic acid, tetrahydrofuran, n-hexane was obtained from Tedia. Paraformaldehyde and sodium hydroxide was purchased from Showa. All solvents were purified before it was used.

2.1 Preparation of CdSe QDs

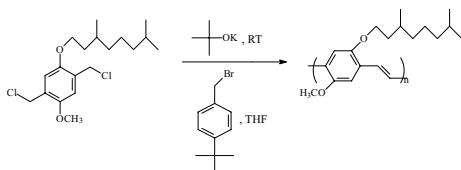
The CdSe QDs were synthesized from organometallic precursors via thermal decomposition. The selenium powder was dissolved in trioctylphosphine under nitrogen to form TOPSe stock solution. The cadmium oxide was mixed with the fatty acid and heated at ~100°C in a flask free of water and oxygen. TOPO and HDA were then added into the flask at 320 °C. After the clear liquid appeared, the TOPSe stock solution was injected into the flask. The ratio of cadmium to selenium is 1.2. The reaction time was 10 minutes. The slurry was washed by methanol and toluene for several times to separate TOPO-capped CdSe QDs.

2.2 Synthesis of OC1C10-PPV

1-methoxy-4-(3,7dimethyl-octanoxyl) benzene was synthesized from 3,7-dimethyl-1-bromooctane and 4-methoxyphenol in alcohol at 75°C.



1-methoxy-4-(3,7dimethyl-octanoxyl) benzene was transferred to 4-methoxy-2,5-chloromethyl-(3,7dimethyl-octanoxyl) benzene at 75 °C in mixture of acetic acid, hydrochloric acid and paraformaldehyde. Then 4-methoxy-2,5-chloromethyl-(3,7dimethyl-octanoxyl) benzene polymerized to OC1C10-PPV in THF at room temperature. OC1C10-PPV was orange with naked eye.



2.3 Preparation of QDs/OC1C10-PPV

For Sample A, the CdSe QDs were dispersed in OC1C10-PPV in toluene (QDs = 5 wt %). An orange solution was obtained after it stirred in dark at room temperature for 3 hours.

For Sample B, QDs added into the precursor (4-methoxy-2,5-chloromethyl-(3,7dimethyl-octanoxyl) benzene) before polymerization and then polymerized to OC1C10-PPV (QDs = 5 wt %). An orange solution was obtained after the reaction.

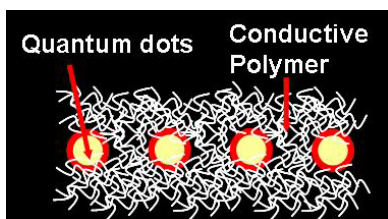


Figure 1 QDs/conductive polymer nanocomposite

2.4 Characterization

The size of QDs was analyzed by transmission electron microscope (JEOL JEM-2010). Photoluminescence spectra were measured by Hitachi F-4500 fluorescence spectrophotometer. The molecular weight distribution was determined by gel permeation chromatography (Waters, GPC).

3 RESULTS AND DISCUSSION

Monodispersed CdSe QDs were obtained without any size selection. The size of CdSe QDs is about 3.8 nm, as shown in Fig. 2. The XRD patterns for the CdSe QDs are shown in Fig. 3. The peaks are broad since the crystallites are in nanoscale.

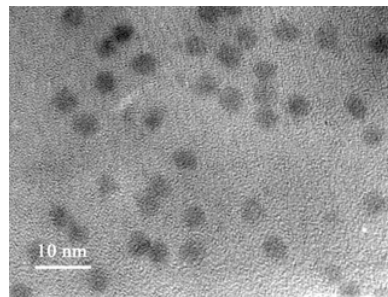


Figure 2 TEM image of the CdSe QDs. The darker spots were CdSe QDs.

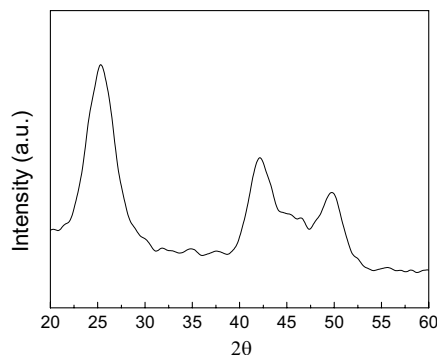
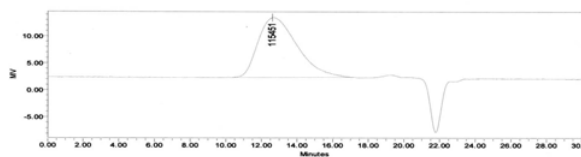
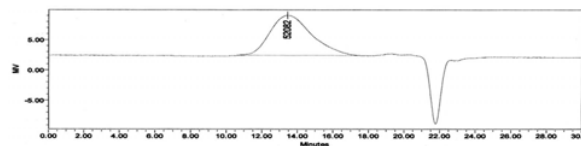


Figure 3 XRD of CdSe QDs.



GPC Results							
SampleName	Retention Time	Mn	Mw	MP	Mz	Polydispersity	
1	031001	12.610	45059	108975	115451	188234	2.418473

Figure 4 GPC result of OC1C10-PPV



GPC Results							
SampleName	Retention Time	Mn	Mw	MP	Mz	Polydispersity	
1	030928	13.446	25216	62168	52082	123694	2.465480

Figure 5 GPC result of OC1C10-PPV/CdSe QDs

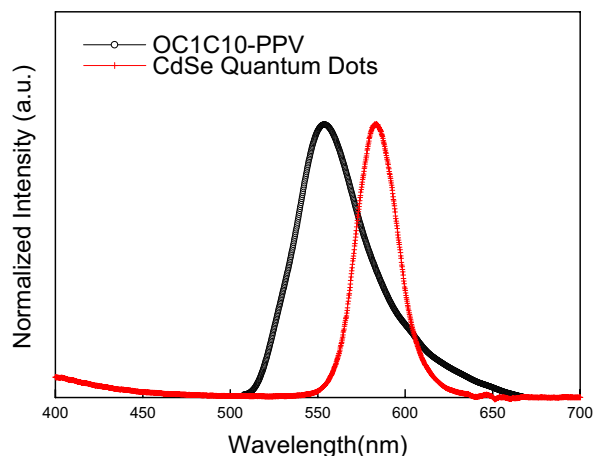


Figure 6 PL from OC1C10-PPV and CdSe quantum Dots, respectively.

From GPC measurement, the molecular weight and polydispersity of OC1C10-PPV were confirmed to 115,451 and ~2.42, respectively, as shown in Fig. 4. The molecular weight and polydispersity of QDs/OC1C10-PPV (Sample A) were similar to those of OC1C10-PPV. It displayed that the addition of QDs with OC1C10-PPV does not affect the molecular weight or distribution of OC1C10-PPV. On the other hand, if the QDs were added into the precursor before OC1C10-PPV polymerization, the molecular weight of QDs/OC1C10-PPV decreased and has a wider distribution than that of OC1C10-PPV, as shown in Fig. 5. The phenomenon implies the CdSe QDs maybe disturb the polymerization of OC1C10-PPV.

PL spectra of QDs and OC1C10-PPV were shown in Fig. 6. The peak positions of OC1C10-PPV and CdSe QDs were 555 nm (FWHM~50 nm) and ~590 nm (FWHM~26 nm), respectively. The PL spectra of QDs which mix with OC1C10-PPV before and after polymerization were shown in Fig. 7. The PL spectra displayed mixed characters of QDs and OC1C10-PPV. The PL from Sample B has a wider band than that of Sample A. The phenomenon indicates the molecular weight distribution of sample B is larger than that of Sample A, and implies the QDs influence the OC1C10-PPV polymerization and broaden the molecular weight distribution. The result is consistent with the previous data measured from GPC.

4 CONCLUSION

The CdSe QDs/OC1C10-PPV nanocomposite was fabricated. The QDs were mixed with OC1C10-PPV before and after polymerization. It was found that the molecular weight of QDs/OC1C10-PPV was similar to that

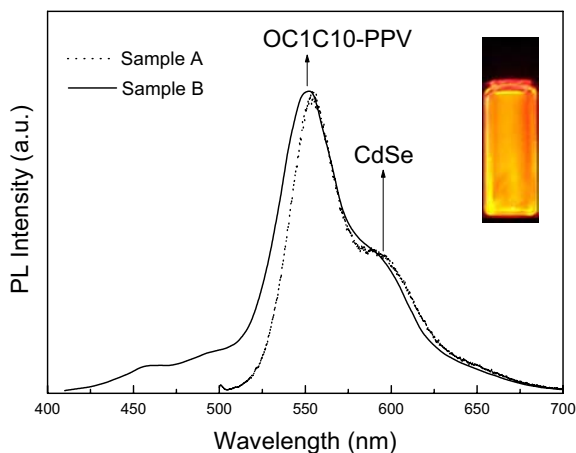


Figure 7 PL from QDs/OC1C10-PPV. The content of QDs is 5 wt%. The picture is the specimen under UV excitation.

of OC1C10-PPV while QDs directly mixed with OC1C10-PPV. However, QDs will decrease the molecular weight and broaden the molecular weight distribution of QDs/OC1C10-PPV while QDs were added into the precursor before polymerization of OC1C10-PPV. The PL peaks from CdSe and OC1C10-PPV was 590 nm (FWHM~26 nm) and 555 nm (FWHM~50 nm), respectively. PL spectra of nanocomposite displayed mixed characters of QDs and OC1C10-PPV.

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