



Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Trifunctional CdSe quantum dots-polymer composite film with electrochromic, electrofluorescent and light-induced coloration effects

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ARTICLE INFO

Keywords:

Electrochromic
Electrofluorescent
Light-induced coloration
Quantum dot
Conjugated polymer

ABSTRACT

A novel composite CdSe quantum dots (QDs)-polymer film achieving tri-function of electrochromic, electrofluorescent and light-induced coloration effects was deposited. Combining the advantages of both CdSe QDs and conjugated electrochromic polymers, the composite film presents excellent electrochromic properties with low redox potential, high optical contrast and fast response time. In addition, it achieves enhanced performance that the composite film could switch between non-fluorescent and fluorescent state, in which the photoluminescence (PL) intensity is more than twice that of pristine polymer film. Furthermore, the material can gradually become self-colored from bleached state under the irradiation of sunlight. Therefore, the trifunctional composite film may pave a new way for designing energy-saving electrochromic and electrofluorescent device in the future.

1. Introduction

Electrochromism, reversible optical transmittance change in response to an externally electrochemical anodic or cathodic polarization, has been developed over several decades [1,2]. Wherein conjugated polymers have gained much popularity due to the various colors, rapid response time, adjustable bandgap and high optical contrast. They are widely used in the fields such as large area “smart windows”, displays and anti-glazing mirrors [3,4].

Additionally, many researchers not only focus on the electrochromic properties of material, but also give importance to the combination with other special functions. For instance, Kim et al. prepared the conjugated polymer of propylenedioxythiophene-phenylene capable of electrochromic, electrofluorochromic, and chirality switching [5]; And Liou et al. successfully prepared flexible devices based on cyanoar-ylamine-containing polyimide which can synchronously achieve electrochromism and electrofluorescence [6]. The reversible switching of optical and fluorescent status by electric field can be achieved and it is a desirable field of investigation in optoelectronic device. Photoelectrochromic device (PECD) proposing the combination of WO₃-based electrochromic device (ECD) and polymer-based dye-sensitized solar cell was presented by Bella's group, the device can achieve self-powered electrochromism under sunlight with long term stability [7]. These works have explored a new road for the multi-functionalization of electrochromic materials. However, the focus of these works was on the individual properties of material itself, properties of composite material

formed by the corresponding material were seldom investigated. Moreover, the light-induced coloration electrochromic and fluorescent material was rarely reported, so we would like to design a novel composite material to realize the functions mentioned above, which can be applied for the light-induced electrochromic display or fluorescent indicator.

Quantum dots (QDs) have attracted much attention as these nanoparticles offer unique size-dependent absorption properties, photovoltaic conversion ability and enhanced photostability [8,9]. Furthermore, the surface of quantum dots can be modified for specific function, significant efforts have been devoted to the combination of QDs and other materials, such as QDs composite solar cell and QDs-LED screen [10]. Among various kinds of quantum dots, CdSe QDs are widely used in solar cell and photocatalytic water splitting fields, due to their tunable emission, enhanced photovoltaic conversion ability and feasible preparation means [11]. Thus, the CdSe QDs are promising to be the power source for our designed light-induced coloration composite material [12,13]. In addition, various conjugated polymer based functional materials with enhanced properties have been reported through different methodologies, which provides an available way to synthesize the mentioned composite film with multi-functions [14–18].

Our research group has been committed ourselves to electrochromic field over the past years, especially for conjugated polymer [3,19]. Recently, our research group have also investigated electrofluorescent-electrochromic bifunctional polymer and light-induced coloration electrochromic material [20,21]. As for both conjugated polymers

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<http://dx.doi.org/10.1016/j.solmat.2017.04.024>

Received 28 November 2016; Received in revised form 7 April 2017; Accepted 11 April 2017
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and QDs, their properties can be tuned individually to adapt to each other, therefore, the performance of QDs/polymer composite material may be superior to their corresponding individual properties [22–25]. In this article, a novel composite film containing CdSe QDs and soluble poly(3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine) has been developed. By virtue of excellent fluorescent and photo energy conversion ability of CdSe QDs and favorable electrochromic property of conjugated polymer, the formed composite film achieves electrochromic, electrofluorescent and light-induced coloration effects simultaneously via mutual interaction, which can pave a new way for the design and synthesis of efficient energy-saving electrochromic and electrofluorescent material.

2. Experimental

2.1. Materials

Cadmium oxide (CdO), 3-mercaptopropionic acid (MPA), sodium hydroxide, sodium sulfide, sodium sulfite, selenium powder, stearic acid, 1-octadecene (ODE), octadecylamine (ODA), tributylphosphine (TBP), tri-*n*-octylphosphine oxide (TOPO, 99%), Acetonitrile (ACN), lithium perchlorate (LiClO₄) chloroform and ethanol were purchased from Sigma Aldrich.

2.2. Instruments

NMR spectra were measured by Bruker Avance AV400. The absorption spectra of films were measured with a UV–vis–NIR spectrophotometer (V-670; Jasco). The transmission electron micrograph was carried out by a Field Emission Transmission Electron Microscope (FETEM, JEOL JEM-2100F). Cyclic voltammetric (CV) measurements were carried out using a CHI 660D electrochemical workstation in a three-electrode cell with a working electrode (film coated on tin indium oxide (ITO) glasses, films area were approximately 0.7 cm × 3.0 cm), a pseudo-reference electrode (Ag/Ag⁺), and a counter electrode (platinum wire) in the electrolyte of 0.1 M LiClO₄/ACN. Spectroelectrochemical analysis was performed with electrolytic cells using a 1 cm UV-cuvette, films (0.7 cm × 3.0 cm) on ITO glasses as the working electrode, a platinum wire as the counter electrode, and a silver wire as the reference electrode. The fluorescent spectra and electrofluorochemical behavior of the composite film was characterized by OBIN YVON Fluorolog-3-TAV fluorescence spectrophotometer under AM 1.5 G illumination at 100 mW/cm². The dynamic spectra of the composite film under the irradiation of light were measured by Ocean Optics. The films (about 200 nm) were prepared by spraying chloroform solution of corresponding materials onto the ITO glass. Photographs of the films were collected with a Canon (IXUS 125 HS) digital camera. The transmittance change was measured. The fluorescence microscope images were collected with olympus u-HGLGPS.

2.3. Preparation of polymer

The polymer was synthesized according to the following steps (Scheme 1).

2.3.1. Compound 1

20 mmol of 3,4-dimethoxythiophene, 50 mmol of dibromoneopentyl glycol, 2 mmol of *p*-toluene-sulfonic acid, and 250 mL of toluene were added in a 500 mL flask equipped with a Soxhlet extractor with 4 Å type molecular sieves in a cellulose thimble. The mixture was reflux overnight, then it was cooled, and respectively extracted with saturated brine and anhydrous ether. The extracted solution was dried under vacuum, and the crude product was purified by silica gel column chromatography, with petroleum ether/chloroform (10:1) as eluent, white powder was obtained as compound 1. ¹H NMR (300 MHz, CDCl₃, ppm): δ 6.49 (s, 2H), 4.12 (s, 4H), 3.65 (s, 4H).

2.3.2. Compound 2

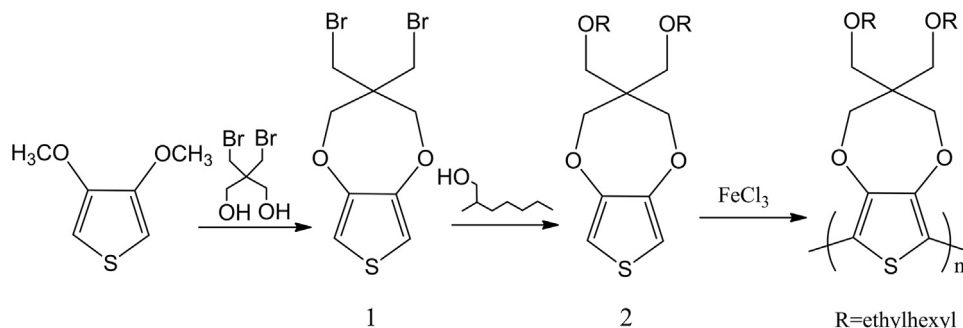
A dried round-bottom flask filled with 100 mL of DMF, 12 mmol of 2-ethyl hexanol (4 eq), and 18 mmol of NaH (6 eq) was heated at 90 °C for 3 h. Then 3 mmol of compound 1 was added and continued to react for 24 h at 95 °C. After reaction, the reaction mixture was cooled and extracted with saturated brine and anhydrous ether twice. The organic phase was dried over magnesium sulfate, and the solvent was removed by rotary evaporation under reduced pressure. The obtained crude product was purified by column chromatography with petroleum to give colorless oil. ¹H NMR (300 MHz, CDCl₃, ppm): δ 6.45 (s, 4H), 4.0 (s, 4H), 3.47 (s, 4H), 3.28 (d, 4H), 1.2–1.6 (m, 18H), 0.8–1.0 (m, 12H).

2.4. Polymer synthesis

The compound 2 was dissolved in a small amount of chloroform, then nitromethane solution dissolved with ferric chloride (5 eq) was added. With the addition, the reaction solution gradually turned green, the reaction was continued for 6 h, poured into 300 mL of methyl alcohol, filtered, and the filtrate was washed with Soxhlet extraction via methanol, hexane and chloroform respectively. The solvent was removed by rotary evaporation under reduced pressure to obtain the purple solid.

2.5. Preparation of TOPO-capped CdSe QDs

TOPO-capped CdSe QDs were prepared according to the modified method published by Peng [26]. Briefly, 0.2 mmol of CdO, 0.8 mmol of stearic acid and 2 g of ODE were placed in a three-neck flask, heated to 200 °C to give clear solution under inert gas protection. The reaction mixture was cooled to room temperature, 1.5 g of ODA and 0.5 g of TOPO were added and heated to 240 °C, a solution of selenium (0.158 g, 2 mmol, dissolved in 0.472 g of TBP and diluted by 1.37 g of ODE) was quickly injected into this hot solution. The mixture was allowed to react for 20 s, it was cooled to room temperature and then poured into CHCl₃/ACN (1:2), the precipitate was gained by centrifugation.



Scheme 1. The synthetic route of polymer.

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