

Preparation and electrorheological characteristic of CdS/Polystyrene composite particles

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Abstract Cadmium sulfide/polystyrene (CdS/PS) hybrid particles were synthesized and their physical characteristics including electrorheology were examined. Monodisperse CdS/PS nanocomposite particles with diameters of 2 μm were obtained via dispersion polymerization. To form cadmium sulfide nanoparticles onto the PS surface, 2-(dimethylamino)ethyl methacrylate was used as a functional monomer for coordinating with Cd^{2+} ions. Finally, cadmium sulfide nanoparticles with size <10 nm were formed with the release of S^{2-} ions from thioacetamide. The morphology of the as-prepared CdS/PS nanocomposite particles clearly showed that the CdS particles are present on the surface of the PS. The optical properties were also studied. In addition, their electrorheological characteristics were confirmed by using optical microscopy with applied electrical field. Recently, dielectric properties of CdS nanoparticles were already reported; however, electrorheological characteristics of CdS/PS nanocomposite particles were investigated for the first time.

Keywords CdS/Polystyrene · Microspheres · Hybrid particles · Electrorheological fluid

Introduction

Polymer-semiconductor nanoparticles have attracted considerable attention during the past decade due to their numerous possibilities of applications such as photoelectric devices, optical limiting, and sensors. Recently, many researches have been directed towards investigation of nanometer-sized semiconductor materials, especially II-VI nanocrystals (cadmium sulfide (CdS), CdTe, and CdSe), because of their unique physical properties depending on dimensionality [1–3]. In general, organic-inorganic nanocomposites are low cost in terms of both materials and processing techniques compared to expensive materials of the conventional semiconductor processing industry. This enables easy production of large area devices like solar cells from organic-inorganic nanocomposites [4–7].

Lately, many methods have been developed to synthesize a CdS/polymer composite because CdS, a direct band gap semiconductor with $E_g=2.4749$ eV, is a prospective material for photoelectric conversion in solar cells among nanometer-sized semiconductor materials [8]. In nanocomposites, organic polymer cannot only stabilize the nanoparticles in a solid matrix but also effectively combine the peculiar features of CdS, thus resulting in novel properties. Elashmawi et al. prepared CdS/poly(vinyl alcohol) nanocomposites using a solvothermal method which employed ethylenediamine as a reaction medium and poly(vinyl alcohol) as the polymer controller matrix [9]. Jin et al. synthesized CdS-coated polystyrene (PS) composites by an in situ synthesis method. The PS spheres adsorbed polyelectrolytes, which were coordinated with Cd^{2+} reacted with sulfions released through the hydrolysis of thioacetamide in an aqueous bath [10]. In almost the

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same way, Cheng et al. obtained nano-CdS/PS composite particles via surfactant-free emulsion polymerization. 2-(Dimethylamino)ethyl methacrylate (DMEMA) was used as an auxiliary monomer [11]. In this paper, we prepared PS microspheres through dispersion polymerization with poly(vinyl pyrrolidone; PVP) as a steric stabilizer first. Our group already reported the effect of the steric stabilizer in dispersion polymerization. We verified that the PVP as the stabilizer can support a formation of perfect inorganic shell structure [12]. It made possible to obtain stable and mono-disperse particles in our experiment. Then, we formed CdS nanoparticles onto PS seed using DMEMA as a “pickering” emulsifier, Cd^{2+} aqueous solution, and thioacetamide (TAA) to release S^{2-} ions.

Many researchers also have reported about the dielectric properties of CdS nanoparticles. Abdulkhadar et al. studied the dielectric properties of CdS nanoparticles over a temperature range from 300 to 500 K [13]. Zhou also revealed dielectric and dielectric loss properties of the nanoparticles and conventional powders of CdS in the frequency range 10^2 – 10^8 Hz at room temperature [8]. However, electrorheological characteristic of CdS has not been reported to date. An electrorheological (ER) fluid usually consists of microscopic dielectric particles in insulating liquid [14]. They exhibit sudden and reversible change in their viscosity or even solidification as a result of an applied electric field because the dispersed dielectric particles are polarized and interacted to each other to form chain or fiber structures aligned in the direction of the applied electric field. ER fluid is denoted “smart” fluid since they can turn many devices such as clutches, valves, dampers, etc. into active mechanical elements capable of responding to environmental variations [15–17]. In this research, as-prepared CdS/PS composite particles were dispersed in silicone oil, and then examined by observing through optical microscope under an electric field to confirm their ER behavior.

Experimental

Materials

Styrene monomer in extra pure grade and TAA were obtained from Junsei (Japan). Potassium persulfate (Duksan Chemicals, Korea) was used as received. PVP ($M_w = 40,000$ g/mol) was supplied by Kanto Chemical Co., Japan. DMEMA (Tokyo Kasei Kogyo Co., Japan) was purified using a basic alumina inhibitor remover and then stored at 4 °C. Cadmium acetate dihydrate (0.1 mol/L aqueous solution for use) in reagent grade was purchased from Sigma-Aldrich (USA). High purity ethanol (Samchun, Korea) was used.

Methods

Synthesis of PS seed particles

PS microspheres were prepared by a conventional dispersion polymerization technique. 190.0 g ethanol, 20.0 g styrene monomer (10 wt.% to medium), and 2.0 g PVP stabilizer (10 wt.% to monomer) were charged into a 500 mL three-necked round-bottom flask equipped with stirrer, a reflux condenser, and N_2 inlet. The reaction system was deoxygenated by bubbling with nitrogen gas under 70 °C and a stirring rate of 300 rpm for 1 h. Then, 0.2 g AIBN dissolved in 10.0 g was injected. The reaction was continued for 24 h and a milky PS emulsion was obtained.

Synthesis of CdS/PS nanocomposites

Five grams of the synthesized PS particles, filtered with ethanol to remove residual monomer, initiator, and steric stabilizer (PVP) were re-dispersed into a 250 mL round-bottom flask with 100 mL distilled water. Then, 5.0 g Cd^{2+} solution (0.1 mol L^{-1}) and 0.5 g DMEMA were poured into the flask with a mechanic stirrer. The PS emulsion was stirred for 10 min at room temperature, and then temperature was elevated to 50 °C. Added to the reactants was 1.7 g TAA, and stirred for 1 h. By heating the TAA, S^{2-} ions were released and reacted with Cd^{2+} to form CdS particles onto the surface of PS particles. The milky emulsion turned into yellowish, and then allowed to cool to room temperature.

Characterization

Scanning electron microscopy (SEM), Hitachi S-4300, was employed on both PS particles and CdS/PS nanocomposites to determine their morphologies. The obtained particles were diluted with ethanol and dried on an aluminum foil and coated with platinum before characterization. The elementary analysis of the composite was performed using the energy dispersive X-ray spectroscopy (EDS) equipped in SEM. Transmission electron microscope (TEM) microphotographs was obtained by Philips CM 200. Powder X-ray diffraction (XRD) patterns were recorded by using Cu K_α irradiation on a Rigaku D/MAX 2200V/PC X-ray diffractometer. Thermogravimetry analysis was carried out using Perkin-Elmer Diamond TG/DTA Lab System with the heating rate of 20 °C/min. The ultraviolet-visible (UV-vis) absorption spectrum was recorded at room temperature on a Perkin-Elmer Lambda 25 UV-vis spectrophotometer. Finally, the ER fluid was prepared by dispersing the PS/CdS nanocomposite particles in silicone oil by means of an ultrasonic generator (Sonics & Materials, Inc. VC505, USA). Then, structural images of the ER fluid were obtained by optical microscopy (EG TECH, EGVM-35B).

Results and discussion

Preparation of CdS/PS composite particles

First, we have prepared PS particles via a conventional dispersion polymerization with poly(vinyl pyrrolidone) in ethanol. The PVP stabilized PS particles were used as templates to prepare CdS/PS composite particles. The shape of the particles is strongly dependent on the stabilizing surfactants used. The ideal amount of PVP in the formation of the PS particles is already revealed by Hong et al. [12]. When using the 10-wt.% PVP to the monomer as a stabilizer, the most stable emulsion and narrow range of size distribution could be obtained. Figure 1a shows TEM images of synthesized PS spheres with the diameter of about 1.5 μm . From the TEM images, we can see that the particles are very spherical and monodisperse. In addition, it could be seen from Fig. 1b that the PS particles have smooth surface.

To introduce Cd^{2+} ions onto the PS templates, Cd^{2+} solution was added into PS emulsion with DMEMA. It has been reported that the DMEMA can act as an effective emulsifier. Nagasaki and coworkers proposed that the electron donor atom in these monomers, such as DMEMA and 2-(trialkylsiloxy)ethyl methacrylates, increased the nucleophilicity of the alkoxide ion by chelation of the

alkali metal cation [18]. Therefore, when Cd^{2+} ions coordinated with it, an affinity of the Cd^{2+} ions with the prepared PS particles is more increased and strongly stable emulsion could be obtained effectively. After the addition of TAA to release S^{2-} ions to form CdS particles, the milky emulsion turned to yellowish, meaning the formation of CdS. Finally, CdS/PS composite emulsion was prepared and the CdS/PS composite particles are shown in Fig. 1c. The microphotograph, Fig. 1c, clearly shows that the CdS particles were synthesized on PS particle outer surface because the emulsifier DMEMA providing reacting location with Cd^{2+} ions encompassed only PS surface. As compared Fig. 1c with Fig. 1b, a large amount of nano-particles on the PS particle surface could be clearly seen. These nano-particles made the surface of the PS particle rough.

Figure 2 also shows the SEM images of the CdS/PS composite particles. In Fig. 2, one can confirm the formation of the CdS nano-particles through the rough surface of the particles. These TEM and SEM images indicate that the CdS/PS composite particles were successfully synthesized via dispersion polymerization.

X-ray diffraction analysis

The XRD analysis was used to characterize the crystalline structure of the resultants. XRD patterns of the as-prepared

Fig. 1 TEM images of the PS particles synthesized via dispersion polymerization (a) and (b) and TEM images of the CdS/PS composite by post-addition of Cd^{2+} and TAA (c)

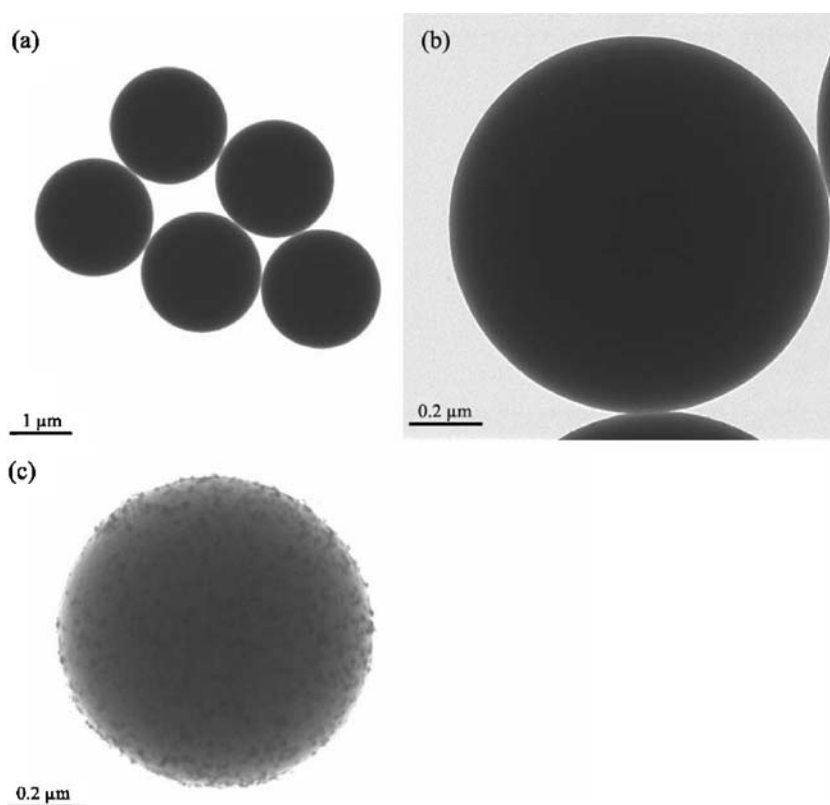
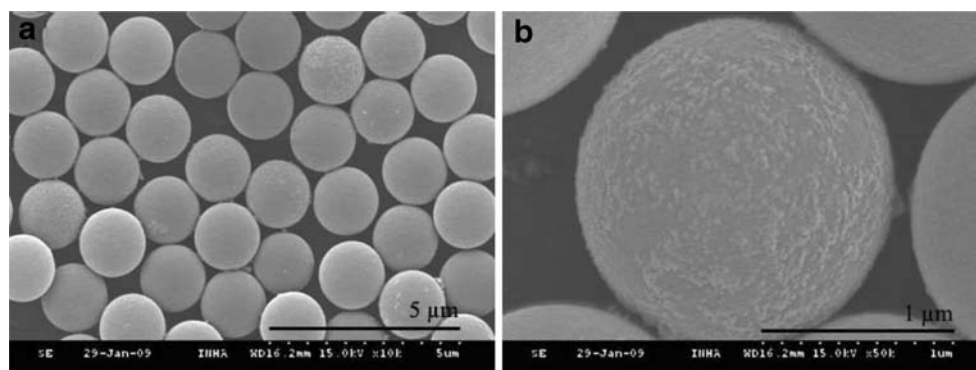


Fig. 2 SEM images of the CdS/PS composites in different magnifications: **a** 10 K and **b** 50 K



CdS/PS composite particles and PS particles are shown in Fig. 3. By comparison with the data from JCPDS file no. 10–454, the diffraction peaks at 26.44° , 43.56° , and 52.72° in Fig. 3b can be indexed as (111), (220), and (311) planes of the β -cubic crystal cadmium sulfide. For the PS, a typical amorphous polymer, the XRD diffraction peaks in Fig. 3b should be ascribed to the crystal structure of bulk CdS; therefore, the XRD pattern that is identical to that of pure CdS without other compounds indicates the formation of high-purity CdS onto the PS templates. When the resultants are hypothesized to pure cubic crystal CdS, the average crystallite size is estimated from the half width of the diffraction peaks using the Debye-Scherrer formula:

$$D = \frac{\alpha\lambda}{\beta \cos \theta}$$

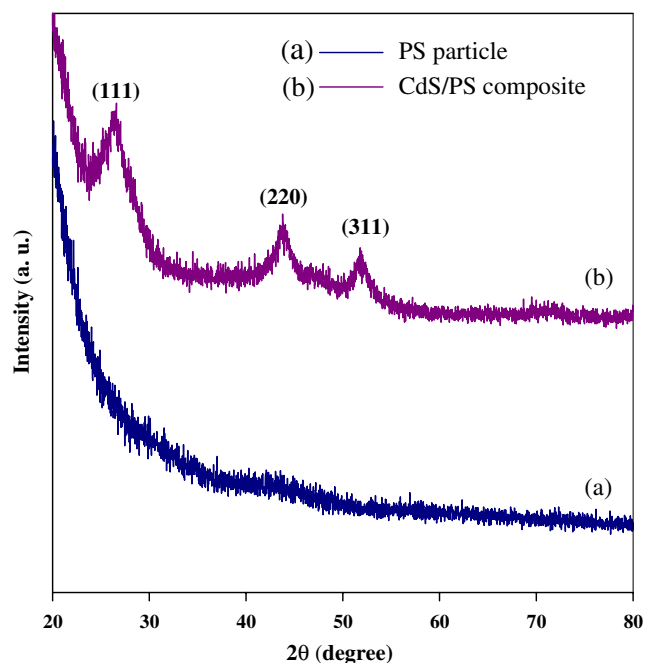


Fig. 3 XRD patterns of the pure PS templates (**a**) and the as-prepared CdS/PS composite particles (**b**)

Where D is the mean particle size, α is a geometric factor (0.94), λ is the X-ray wavelength used in experiments (here equal to $\text{CuK}\alpha = 0.1542 \text{ nm}$), β is the half-height width of the diffraction peak and can be measured from the XRD pattern, and θ is the degree of the corresponding diffraction peak [19]. Here, three θ values corresponding to (111), (220), and (311) planes are selected. The diameters estimates from the Debye-Scherrer formula are 3.92, 3.78, and 3.38 nm, respectively. The average crystallite size of the CdS particles is about 3.69 nm.

Thermogravimetric analysis

Thermogravimetric analysis was performed to investigate thermal stability of as-prepared CdS/PS composites. The TG curves of pure PS templates and the CdS/PS composites are shown in Fig. 4. The thermal stability of the CdS/PS

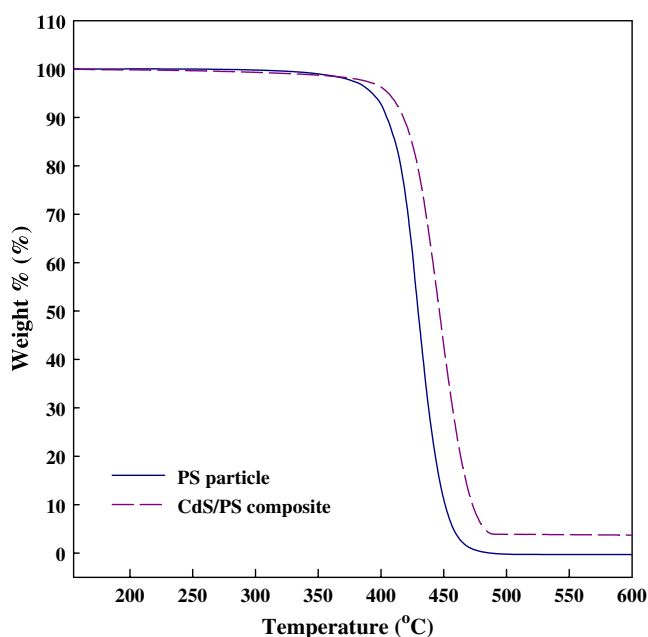


Fig. 4 TGA thermograms of the pure PS template (**a**) and the as-prepared CdS/PS composite particles (**b**)

composites can be compared with that of the pure PS. It can be seen that the introduction of the CdS nanoparticles improves the thermal stability of the pure PS [20]. The CdS/PS composite had a 0.3% weight loss at 250 °C, which was attributed to the evaporation of physically adsorbed water. The composites started to degrade from 405 °C and the decomposition was completed at 480 °C. Between 405 and 480 °C, the weight dropped very quickly and the weight loss of 94% was due to removal of the PS templates. The residual weight of 3.8% should be the weight of the CdS nanoparticles in this composite. This indicates the weight fraction of CdS in the CdS/PS composites should be calculated as

$$W_{\text{CdS}} = \frac{3.8}{94 + 3.8} \times 100\% = 3.89\%$$

Therefore, the calculated weight fraction of PS should be 96.11%.

Similar results had been obtained by EDS analysis. The Table 1 indicates that the detailed parameters for CdS/PS composite according to EDS analysis. One can confirm that the quantity of CdS particles is 3.4 wt.%. It is the almost same result calculated by X-ray analysis. The presence of thermally stable CdS particles in the composite prevents the diffusion of the volatile component during decomposition so that the thermal decomposition onset temperature of CdS/PS composite is higher than that of the pure PS. The formation of chemical bond due to the copolymerization between PS chains and the CdS capping agent resulted in the improvement of thermal stability in the hybrid materials [21].

UV-vis analysis

To obtain information of optical properties of as-prepared composite, the UV-vis absorption analysis of the PS particles and Cd/PS composites was carried out at room temperature and they are shown in Fig. 5 as curves (a) and (b), respectively. In the curve (a), no apparent absorption peak could be seen in the wavelength range of 420–900 nm. However, the absorption curve (b) shows a peak at 460 nm, which is assigned to the optical transition of the first excitonic state of the CdS nanoparticles [20]. The explicit blue shift of the absorption peak from 515 nm for

bulk CdS occurred due to the small size of the CdS quantum dots located on the surface of the PS particles. Based on their absorption wavelength in Fig. 5, we calculated their band gap values to be 2.69 eV for CdS. These features indicate the quantum-confined effect of the CdS/PS composites.

Electrorheological fluid characteristic

ER fluid is a colloid of conductive or polarizable and monodispersed solid particles in insulating fluid such as silicone oil [17]. A heuristic description of the ER effect is as follows. Owing to the dielectric constant contrast between the solid particles and the liquid in a colloid, each solid particle would be polarized under an electrostatic field, with an effective dipole moment. The induced dipole-dipole interaction means that the particles tend to aggregate and form columns along the applied field direction [15].

The dielectric properties of CdS nanoparticles are already revealed in many researches but ER fluid characteristic of the CdS/PS composite has not been reported. To investigate the ER characteristic of the as-prepared CdS/PS composite, we prepared the ER fluids by sonication to the dried CdS/PS composites dispersed in silicone oil (10 vol%). No stabilizers were added to the dispersion in the silicone oil. In the theoretical models of ER fluids, the suspended ER particles are normally assumed to be monodisperse and spherical particles. Therefore, we expected that the as-prepared CdS/PS composites would make good ER fluid because they have a uniform spherical form and polymeric microspheres in the range of size from 1 to 10 μm are known to exhibit superior ER performance provided that they all have similar electrical properties. A DC high voltage source was used to apply a voltage to the sample and the applied electric field was maintained for a few minutes at room temperature to obtain an equilibrium columnar structure.

The microstructure image of the ER fluid in Fig. 6 was obtained using an optical microscope. In Fig. 6b, the formation of a microsphere chain was demonstrated under an applied electric field of 1.47 kV/mm. The gap between the two parallel electrodes was fixed precisely at 450 μm. The formation of columns is the reason why the high-field state of an ER fluid exhibits increased viscosity and is able

Table 1 The detailed parameters for the as-prepared CdS/PS composites obtained from EDS analysis

Element	Apparent Concentration	Intensity Correction	Weight.%	Weight.% Sigma	Atomic%
C	448.32	0.6372	96.60	0.10	99.38
S	5.23	0.8001	0.90	0.04	0.35
Cd	11.71	0.6426	2.50	0.10	0.28
Total			100.00		

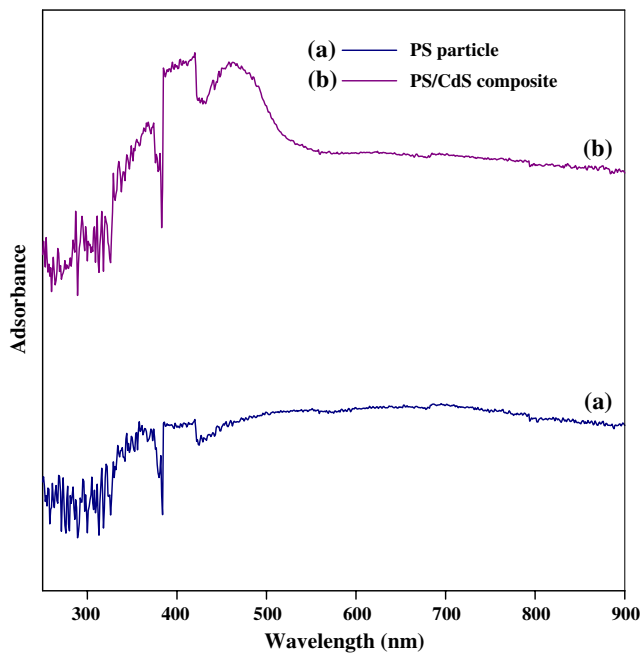
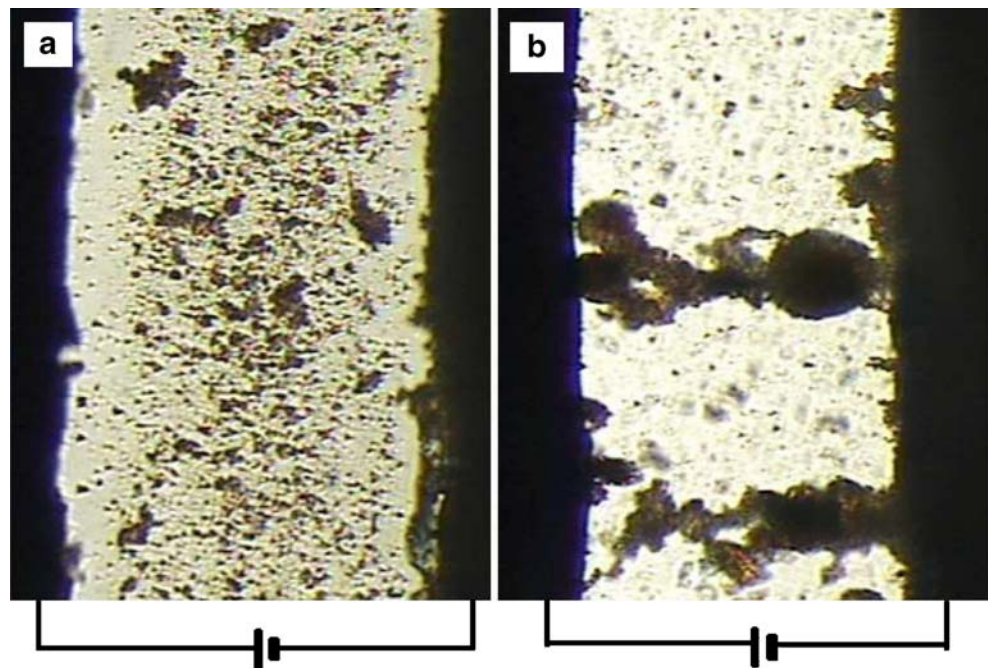


Fig. 5 UV-vis absorption spectra of the neat PS (a) and as-prepared CdS/PS composite particles (b)

to sustain shear in the direction perpendicular to the applied electric field. Therefore, the appearance of microstructure image shown in Fig. 6b is due to the electrostatic interaction between the conductive particles, which is caused by the mismatch of the dielectric constants between the conductive particles and oil. The CdS/PS composites form chains of particles within seconds after the application of an electric field, and the chain-like structure remained

Fig. 6 Optical microscopic images of the CdS/PS composite particles dispersed in silicone oil before (a) and after the application of an electric field strength of 1.47 kV/mm (b). The gap distance between the two parallel electrodes was 450 μm



stable as long as the electric field was applied. We also observed the aggregated particles in the chain. It is possible that the induced dipole-dipole interaction made the particles aggregate. Moreover, the fibrillated chain structures might provide a path for the transport of electrons, and thereby contribute to the conducting behavior of the ER fluids.

Conclusion

To prepare CdS/PS composite, PS microspheres prepared by dispersion polymerization with PVP as a stabilizer were firstly used as the seed. DMEMA was used as an auxiliary monomer that co-polymerized with styrene. DMEMA could act as an emulsifier in the procedure of polymerization, which leads to the improvement of affinity between Cd^{2+} ions and PS particles. By the addition of TAA under a heating reaction condition, S^{2-} ions were released and reacted with Cd^{2+} ions located on the surface of PS particles to produce CdS. Therefore, the CdS/PS composites could be synthesized easily. The TEM, SEM, XRD, TGA, and UV-vis spectrum results confirmed that the CdS nanoparticles were successfully fabricated on the PS seed particles. Using the as-prepared CdS/PS composites, we investigated the ER fluid characteristic. The as-prepared CdS/PS composite particles were dispersed in silicone oil by ultrasonic generator to prepare the ER fluid. In this work, the as-prepared CdS/PS composite particles exhibited ER properties. The chain-like structure was demonstrated under an applied electric field of 1.47 kV/mm. In principal, this result could be employed to have large applications in scientific research and industry.

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