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PREPARATION AND OPTICAL PROPERTIES OF WAVELENGTH MODIFYING SEMICONDUCTING NANOPARTICLES (CdS, CdSe, ZnS, ZnS:Mn^{2+})

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Nanoparticles of CdS, CdSe, ZnS and ZnS:Mn^{2+} were synthesized by thermal treatment using autoclave method using sodium oleate as effective stabilizers. Photoluminescence of the synthesized nanoparticles showed wavelength modification into visible region when excited at UV light. The lifetime of a film such as PVA and LDPE is reduced by a degradation of the double bonds of C=O and C=C in the polyolefin films by ultraviolet (UV). As a result, the physical properties of the films are changed. This is suppressed by doping wavelength modifying nanoparticles into the films to absorb UV light which gives damage on films. Absorption, fluorescence, X-ray diffraction and transmission electron microscopy were employed for the characterization.

Keywords: CdS; CdSe; photoluminescence; ZnS; ZnS:Mn^{2+}

INTRODUCTION

Colloidal nanoparticles have attracted broad attention from researchers in various disciplines [1]. Nanoparticles have their unique properties due to the quantum size effect and size-dependent characteristics [2,3].

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Semiconductor nanoparticles have been applied to many different technological areas including biological labeling and diagnostics, light-emitting diodes, electroluminescent devices, photovoltaic devices, lasers and single-electron transistors [4]. Although many synthetic techniques for such nanoparticles have been developed, nanoparticles are still obtained as aggregated state in organic or inorganic media. A new direction for synthetic methods and an understating of the mechanisms on how the size and shape of the nanocrystals which can be easily varied are key issues in nanochemistry. In this paper, we demonstrate a new synthetic method for CdS, CdSe, ZnS, ZnS:Mn^{2+} nanoparticles using sodium oleate. Sodium oleate has been used as specific stabilizer for the synthesis of CdS, CdSe, ZnS and ZnS:Mn^{2+} nanoparitlces having various properties such as dispersion ability and stability in the polymer resins such as PVA and LDPE for the preparation of functional nanocomposite films.

EXPERIMENTAL

Materials and Analytical Methods

Cadmium chloride hemipentahydrate ($CdCl_2 \cdot 5/2H_2O$, Aldrich), sodium oleate ($C_{17}H_{33}COONa$, Junsei), sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 98^+%, Aldrich), manganese(II) nitrate ($Mn(NO_3)_2$, 98%, Aldrich) and zinc chloride($ZnCl_2$, extra pure, Junsei) were used in their commercial form. NaHSe powders were prepared by the reaction between selenium and sodium borohydride in water. Acetone and iso-octane were all of the highest quality commercially available. Distilled water was passed through a six-cartridge Barnstead Nanopure II purification train consisting of Macropure treatment. UV-vis absorption spectra were taken by using a Varian, Cary 1 C. Photoluminescence spectra were recorded on a Perkin-Elmer, LS50B. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images were obtained by using a Jeol, JEM-2010 and Hitach H-7500, respectively. X-ray powder diffraction (XRD) spectra were obtained using a Philps, X'Pert-MPD system.

Synthesis of CdS, CdSe, ZnS and ZnS:Mn^{2+} Nanoparticles

The synthesis of CdS and CdSe nanoparticles was achieved by reacting Na_2S and NaHSe in an aqueous solution. All of the materials were the highest quality commercially available. In a typical procedure, 80 mL of mixed solution containing 0.125 M sodium oleate and water was prepared and stirred for 20 min. Then, a 5.0 mL of 6.25×10^{-2} M $CdCl_2$ was added. The resulting solution was allowed to be stirred for 30 min and 6.25×10^{-2} M $Na_2S \cdot H_2O$ was added and followed by stirring for 2 hrs to form yellow

solution. This solution was put into a autoclave of 100 mL capacity and maintained at 300°C for 2 hrs and air-cooled to room temperature. Precipitation occurs to form nanoparticles of CdS. Afterward, the precipitates were washed with acetone and filtered to remove the residues of impurities. The bright yellow product was dried at room temperature. ZnS and CdSe nanoparticles were synthesized with the same method. The synthetic method of ZnS:Mn^{2+} was similar to that of ZnS. Before the addition of Na_2S, a desired amount of $Mn(NO_3)_2$ and sodium oleate was added to zinc oleate solution.

Synthesis of PVA/CdS, ZnS:Mn^{2+} and LDPE/CdS, ZnS:Mn^{2+} Nanocomposite Films

A 16 g of PVA pellet was dissolved in 50 ml of acetone to make PVA solution. As the same method, a 1×10^{-3} g of CdS or ZnS:Mn^{2+} nanoparticle was added in 1 ml of acetone. A 4.0 ml of PVA solution was mixed with 0.09 wt% of resulting CdS or ZnS:Mn^{2+} dissolved in acetone and loaded into a round container. In accordance with the concentration, 0.87 and 2.62 wt% of CdS or ZnS:Mn^{2+} dissolved in acetone were added in PVA solution. The mixture was left for 24 hrs at room temperature. Finally, the transparent PVA composite film containing CdS or ZnS:Mn^{2+} was obtained. In case of LDPE, a 10 g of LDPE was added in 100 ml of toluene and then heated at 80°C for 2 hrs. CdS solution dissolved in toluene was added in LDPE solution and then leaved at 40°C until make the LDPE composite. The synthesized LDPE composite was prepared to be film with press machine.

RESULTS AND DISCUSSIONS

Figure 1 shows the X-ray powder diffraction (XRD) pattern of the synthesized nanoparticles. The XRD patterns showed that the crystallinites of the samples. All the peaks of CdS in Figure 1 were indexed as the cubic structure of CdS, which are consistent with the reported data for CdS (JCPDS Card File No. 80-0019). The CdSe diffraction patterns exhibit peak positions corresponding to their cubic structures (JCPDS Card File No. 19-0191). The case of ZnS:Mn^{2+} was ZnS of wurtzite phase (JCPDS Card File No. 75-1534) and the synthesized ZnS was consistent with that of Sphalerite phase. TEM was employed to obtain direct information on the size and shape of the produced nanoparticles. The TEM images in Figure 2 show the CdS (a) and CdSe (b) nanoparticles with diameters of 2.6–7.8 nm and 6–13 nm, respectively. The particle shape is spherical and triangle. Especially, the triangle shape is made by synthetic conditions of high

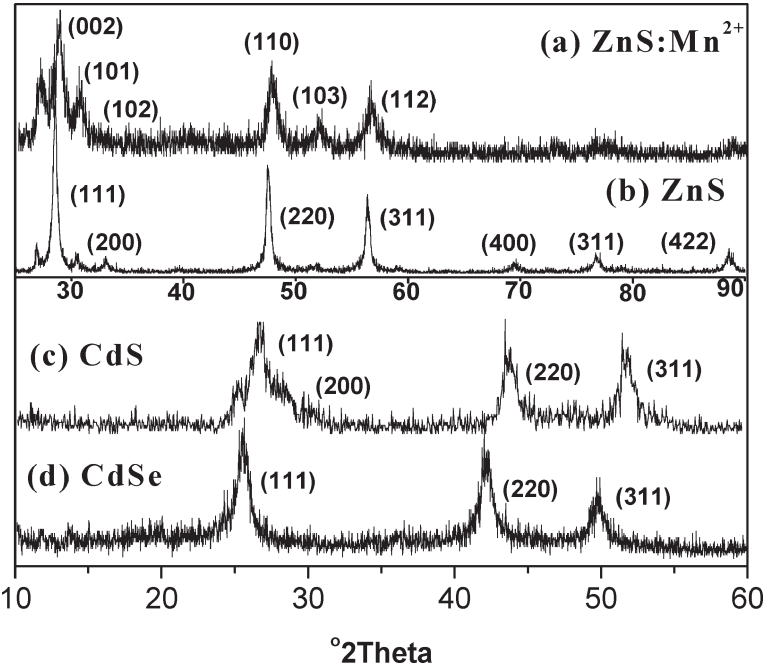

FIGURE 1 X-ray powder diffraction (XRD) patterns of nanoparticles. These nanoparticles are capped with sodium oleate as a surfactant.

temperature and pressure. The nanoparticles of ZnS (c) and ZnS:Mn^{2+} (d) were depicted in the TEM image. The diameter was determined as about 8–13 nm. As shown in Figure 2, the synthesized ZnS:Mn^{2+} nanoparticles were monodispersed and had spherical shape.

Figure 3 presents the absorption spectra of the synthesized nanoparticles prepared in aqueous solutions. Sodium oleate has been used as effective stabilizer for the synthesized nanoparticles. The absorption spectra in Figure 3 display an absorption range from 300 to 520 nm for CdS nanoparticles. Both ZnS and ZnS:Mn^{2+} absorbed UV light at $\lambda_{max.} = 312$ nm. Compared with the band gap of the characteristic absorption (>500 nm) of bulk CdS, a blue-shift to 490 nm is indicative of size quantization.[5,6].CdSe nanoparticles had no peculiar characteristics, but it showed that absorption of general range. This is caused by the broad particle size distribution.

The photoluminescence spectrum (PL) was measured at room temperature using a 365 nm excitation (Fig. 4). PL studies of the synthesized nanoparticles indicated excitonic transition. The line shape of the PL spectrum is essentially given by the inhomogeneous broadening which is due to the

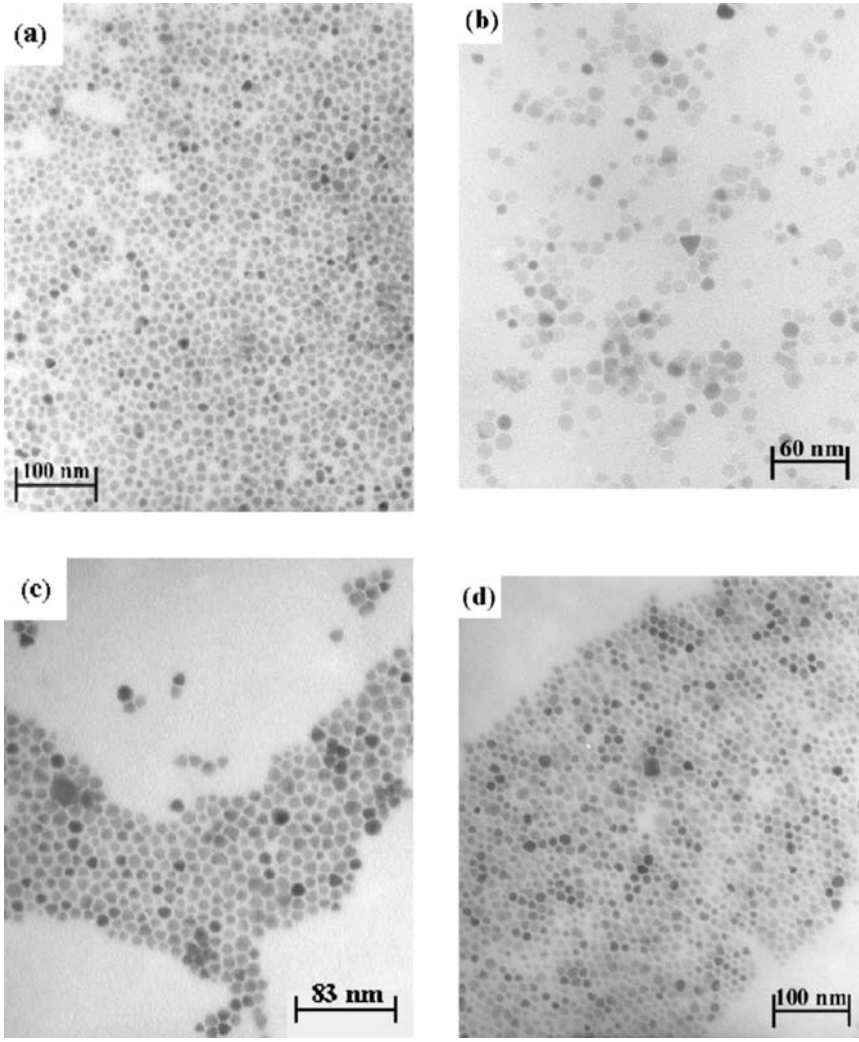

FIGURE 2 Transmission electron microscopy (TEM) images of (a) CdS, (b) CdSe, (c) ZnS and (d) ZnS:Mn^{2+} nanoparticles.

size distribution of the crystallites. The PL spectra of CdS and CdSe in Figure 4 show a narrow emission band at 520 and 600 nm, respectively. The CdS nanoparticles stabilized with sodium oleate showed PL emission at lower wavelengths. This is presumably due to somewhat smaller size of particles. Thus, the use of sodium oleate as stabilizing agent allows the synthesis of highly crystalline CdS nanoparticles. This is well shown

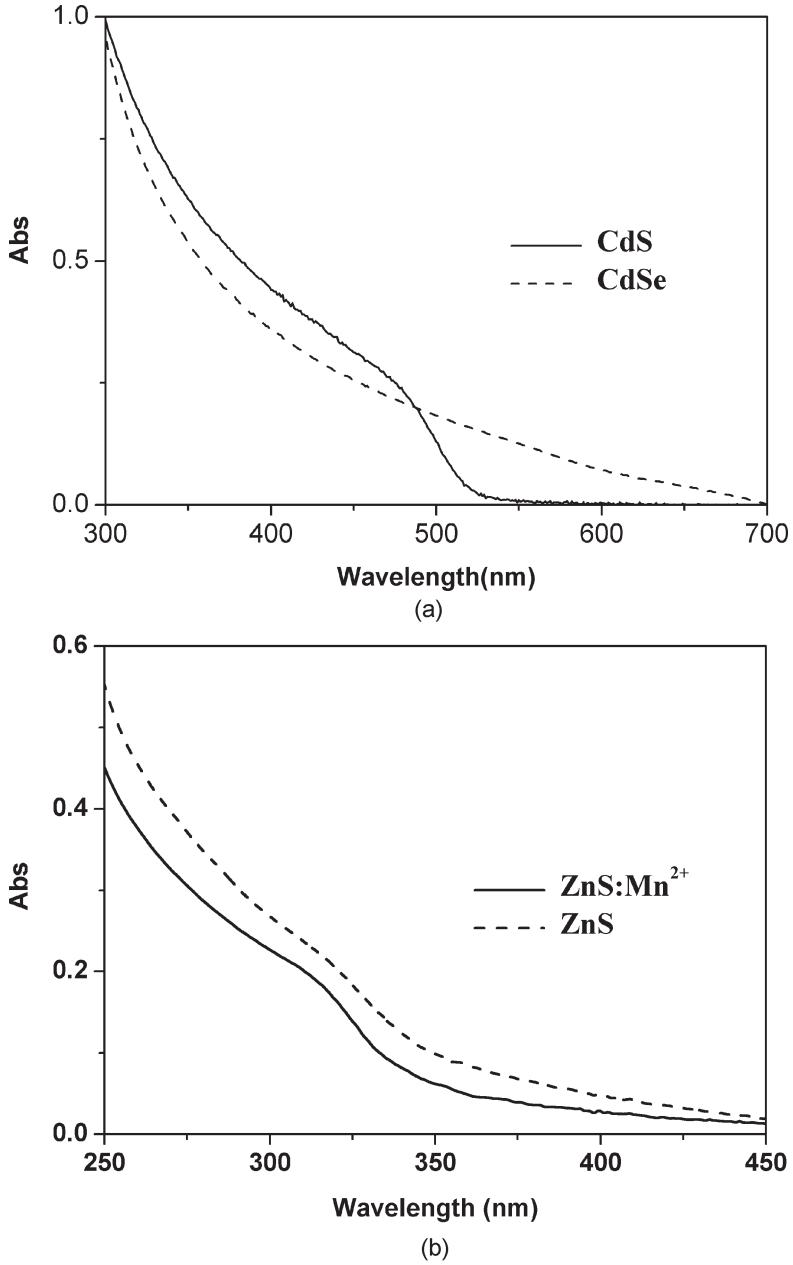

FIGURE 3 UV-vis spectra for the synthesized nanoparticles dispersed in iso-octane.

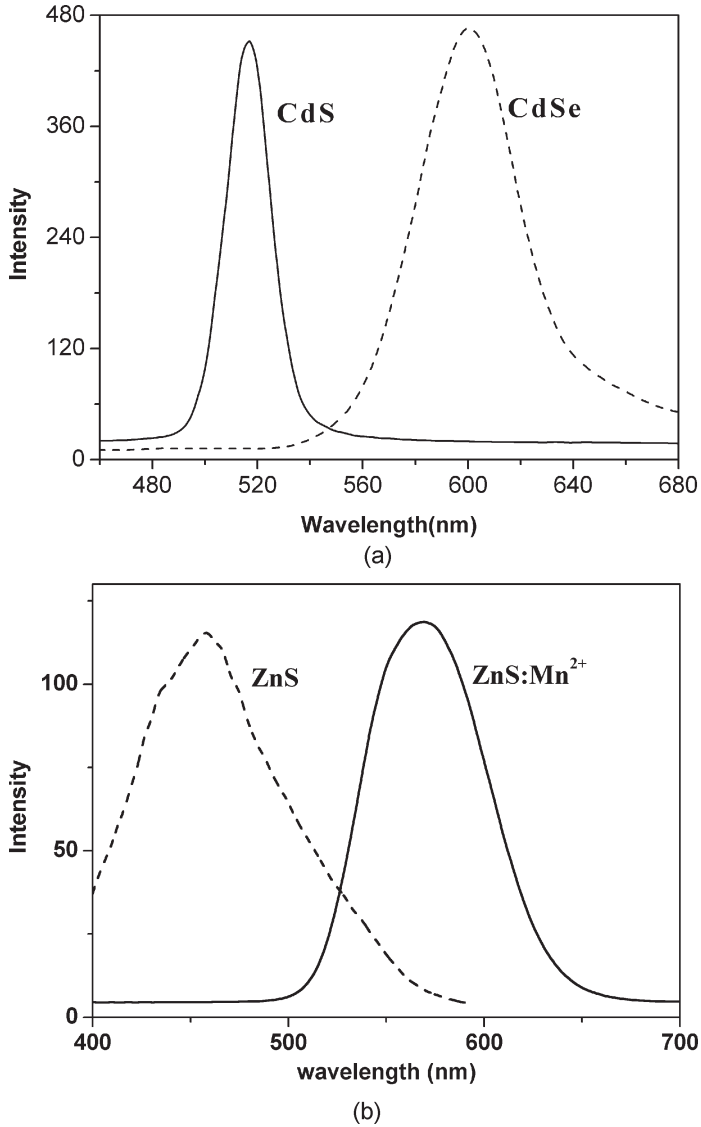

FIGURE 4 Photoluminescence (PL) spectra for the synthesized nanoparticles.

by strong band-edge of PL. ZnS and ZnS:Mn^{2+} emitted visible light at 457 nm ($\lambda_{ex} = 319$ nm) and 575 nm ($\lambda_{ex} = 312$ nm), respectively. The orange emission bands of ZnS:Mn^{2+} were attributed to the Mn^{2+}, $^4T_1 \rightarrow {}^6A_1$ transition of the ZnS nanocrystal host [7]. Photoluminescence of the

synthesized nanoparticles showed wavelength modification into visible region when it was excited at UV light.

Figure 5 shows the PL spectra of PVA (a) and LDPE nanocomposite films (b) containing CdS or ZnS:Mn^{2+} nanoparticles. The PL spectra are

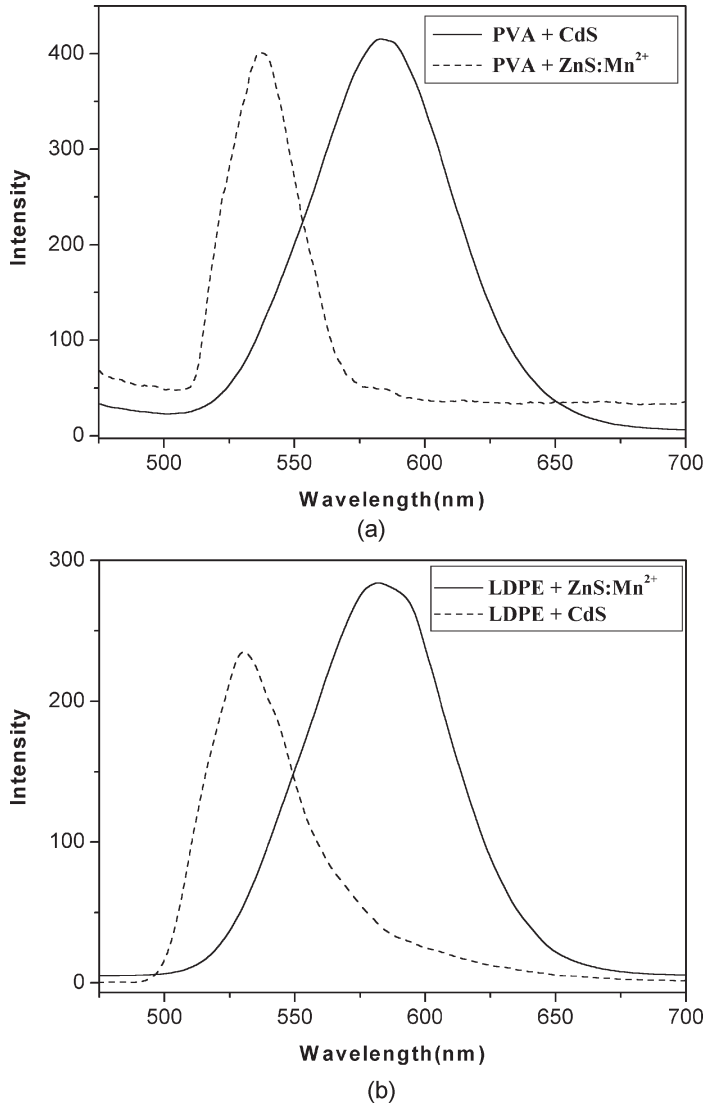

FIGURE 5 Photoluminescence (PL) spectra for PVA film (a), LDPE film (b) containing CdS and ZnS:Mn^{2+}.

consistent with those of synthesized CdS or $ZnS:Mn^{2+}$ nanoparticles. The polymeric resin such as PVA or LDPE is subject to attack by UV light because of the organic nature of the polymer. UV lights are readily absorbed by certain organic functional group and excited to a higher energy state and then free radicals are formed, the degradation process has begun. In the process, free radicals react with atmospheric oxygen to generate peroxy radicals. These very quickly form hydroperoxide which in turn generate a radical on the polymer backbone itself. The weak hydroperoxide will cleave easily in the presence of heat and sunlight and produce more radicals. Polymer absorbs UV light to generate a photoexcited state. Peroxyradical abstracts a hydrogen from adjacent molecules. As this process occurs, the polymers are slowly degraded and broken down. To suppress this process, the synthesized nanoparticles are doped into the polymeric resin. UV light can be converted into visible light by nanoparticles. The synthesized PVA or LDPE composite films absorb the ultraviolet region wavelength light (< 400 nm) and emit the visible wavelength light. Thus, these composite films have various advantages. SEM image shows the section of LDPE composite containing CdS nanoparticles as Figure 6.

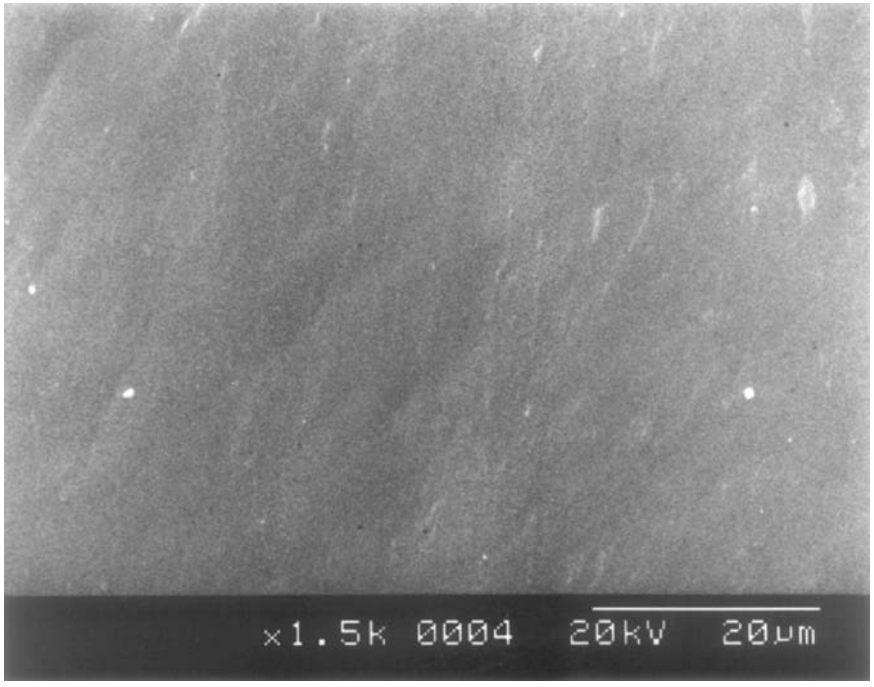

FIGURE 6 SEM images of LDPE master batch CdS nanoparticles.

This image has not aggregation of added nanoparticles, so it shows good dispersion of nanoparticles and stability of films.

CONCULSIONS

We synthesized semiconducting nanoparticles of CdS, CdSe, ZnS and ZnS:Mn^{2+} by thermal treatment using sodium oleate as surfactant and PVA or LDPE composite film containing the synthesized nanoparticles. The synthesized particles and composite films show strong band-edge of photoluminescence. These nanoparticles absorb the UV light ($200 \sim 400$ nm) and emit visible light ($400 \sim 700$ nm). For the structural characterization, sodium oleate was successfully used to replace the surfactant molecules on surface of nanoparticles. The synthetic procedures developed in the present study offer several important advantageous features for the synthesis of nanoparticles. The synthetic process is very easy and inexpensive. Also, the synthetic method is a generalized process that can be applied to synthesize different kinds of semiconducting nanoparticles. The dispersion and stability in the PVA and LDPE was also studied and determined as excellent.

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