Preparation, characterization and electroluminescence of ZnS nanocrystals in a polymer matrix

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ZnS nanocrystals have been synthesized in polymer matrices. Absorption spectrum and small-angle X-ray scattering studies showed that the size of the ZnS nanoparticles was *ca.* 3.0 nm. Electron diffraction results showed that the ZnS nanocrystals have hexagonal structure. A ZnS nanoparticle/polymer composite as an emitter was used to fabricate a single layer structure electroluminescent device with a low turn-on voltage ($\leqslant 4$ V) and blue electroluminescence was observed at room temperature.

Nanometre-sized semiconductor clusters are representative of a state of matter intermediate between individual molecules and bulk species, which have attracted growing interest during the last decade.[1–3] Because the electronic and optical properties of semiconductor nanocrystals differ from those of both molecules and bulk materials, this class of new material shows a number of striking effects such as size quantization,[4–6] nonlinear optical behaviour[7,8] and unusual fluorescence,[9] and they exhibit novel optical and transport properties which are potentially useful for technological applications. Recently, by taking advantage of developments in the preparation and characterization of direct-gap semiconductor nanocrystals, and of electroluminescent polymers, Colvin *et al.*[10] and Dabbousi *et al.*[11] have constructed a hybrid organic–inorganic electroluminescent (EL) device and realized electroluminescence from CdSe nanocrystals. ZnS is a semiconductor, the photoluminescence and electroluminescence of which have been studied in detail.[12,13] The preparation and optical properties of colloidal ZnS have also been reported.[14–16] Previous studies have addressed the preparation of semiconductor nanocrystals in a wide variety of matrices, but it has proved difficult to control particle size and also to obtain optical-quality films. Polymers are expected to provide good mechanical and optical properties conferring high kinetic stability on nanometre-sized semiconductor particles. In our group, PbS,[17] PbI_2,[18] Fe_2O_3,[19] CdS[20] and ZnS have been synthesized in polymer matrices using a variety of methods. In this paper, the synthesis of ZnS nanocrystals in polymer matrices is described. As the ZnS nanocrystals–polymer composites possess excellent film processability, good optical-quality thin films of the composite can be obtained readily by the spin-coating method. By taking advantage of thespecific electronic and optical properties of ZnS nanocrystals and the excellent film processability of the composite, an EL device was fabricated and the photoluminescence and electroluminescence of the composite are reported.

Experimental

The synthesis of the ZnS nanocrystals–polymer composite (ZnSP) is similar to the method reported in ref. 17.

Styrene (St), zinc oxide (ZnO), azoisobutyronitrile (AIBN), methacrylic acid (MA), methanol and tetrahydrofuran (THF) were all analytical grade reagents; St and MA were both distilled at a pressure of 5 Torr. AIBN was recrystallized twice from ethanol.

Zinc methacrylate [$Zn(MA)_2$] was prepared from ZnO and MA. It is known that there are two C=C bonds in each $Zn(MA)_2$ molecule, so in copolymerization with St, it works as a cross-linking agent. St (40 ml) and $Zn(MA)_2$ (1.649 g) were dissolved in 100 ml THF in a tempered glass vessel and AIBN (3.276 g) was added as an initiator. The copolymerization was carried out at 60 °C under an N_2 atmosphere for 3 h. A lightly cross-linked Zn^{2+}-containing microgel (ZnP) precipitation was obtained by pouring the above solution into a beaker containing 1000 ml of methanol. The molecular mass of the microgel was found to be 3.2×10^4 by GPC. The mass percentage of zinc in this composite microgel was *ca.* 4.3, as determined using atomic absorption.

ZnP (0.1 g) was dissolved into 2 ml chloroform and then reacted with H_2S gas (molar ratio $H_2S:Zn^{2+}$, 1:1) in a sealed container. A ZnSP organosol was formed. The organosol was colourless with no precipitation even after a year.

The UV–VIS absorption spectrum of ZnSP was measured with a Shimadzu UV-3100 UV–VIS spectrophotometer. The photoluminescent and electroluminescent spectra of ZnSP were recorded with a Hitachi model 850 fluorescence spectrophotometer. Optical measurements were all carried out at room temperature under ambient atmosphere.

Small-angle X-ray scattering was carried out on a D/max-rA X-ray diffractometer using Cu-Kα radiation.

Particle crystallinity was identified by electron diffraction on a TEM Hitachi H-8100IV instrument. A droplet of ZnSP solution was dripped onto a copper grid for TEM detection.

Result and Discussion

Fig. 1 shows the absorption spectrum of ZnS nanocrystals in the polymer matrix. From this, a minor absorption shoulder peaking at 290 nm (4.28 eV) is observed, which can be regarded

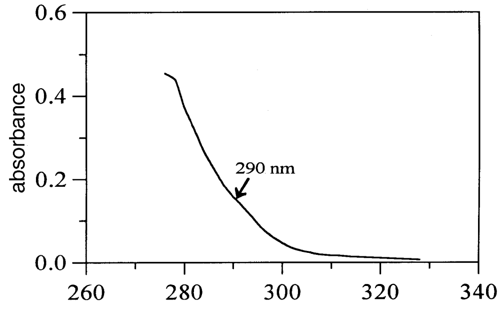

Fig. 1 Absorption spectrum of ZnSP in chloroform solution. The reference solution is ZnP in chloroform.

as an exciton peak. The absorption edge of ZnS nanocrystals in the polymer matrix is at *ca.* 300 nm (4.14 eV, determined by fitting the absorption data to the equation: $\sigma h\nu = A(h\nu - E_g)^{1/2}$, where σ is the absorption coefficient, $h\nu$ is the photon energy, and E_g is the direct bandgap.) Compared with the absorption edge of bulk ZnS which is *ca.* 338 nm (3.71 eV), the large blue shift can be understood as a quantum size effect due to confinement of the electron and hole in a small volume. According to a tight-binding calculation and research work carried out previously on ZnS colloids,[14–16] we can estimate the particle size of the ZnS nanocrystals to be *ca.* 3.0 nm. This result fits well with that obtained by SAXS measurement.

Typically, the relationship between the scattering intensity and the scattering angle for spherical particles is given as follows:

$$\ln I = \ln(I_e N n^2) - 4\pi^2 R^2 \varepsilon^2 / 5\lambda^2 \qquad (1)$$

where I is the scattering intensity, N is the Avogadro constant, I_e is the scattering intensity of a single electron, n is the electron number of a single nanoparticle, here ln $(I_e N n^2)$ is a constant, ε is the scattering angle, $\lambda = 0.15418$ nm is the wavelength of X-rays from the Cu-Kα target, and R is the radius of the particle. From the relationship between ln I and ε^2, the particle size is determined to be *ca.* 3.0 nm with a very narrow distribution (nearly 99.8% of the particles are 3.0 nm in size).

Data obtained from the diffraction pattern (Fig. 2) are given in Table 1. The diffraction values of 2.282 and 1.414 Å show that the structure of ZnS nanocrystals is not cubic. Compared with the standard data,[21] all these diffraction values belong to the hexagonal structure. Therefore, the structure of ZnS nanocrystals is hexagonal.

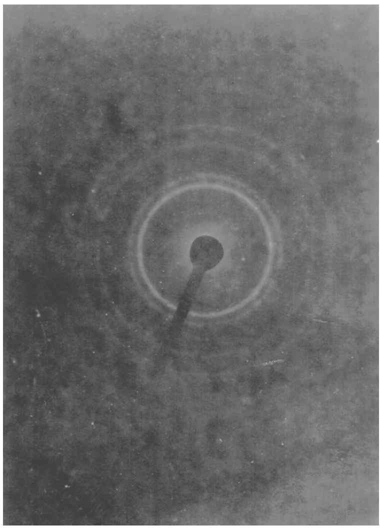

Fig. 2 Electron diffraction image of ZnS nanocrystals in a polymer matrix

Table 1 Diffraction data for ZnS nanocrystals measured by electron diffraction

nd	experimental data/Å	standard data/Å	*hkl*
1	2.282	2.273	102
2	2.008	1.911	110
3	1.414	1.414	104
4	1.206	1.210	114

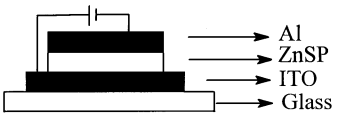

Fig. 3 Structure of the ZnSP single-layer structure EL device

The single layer structure EL device employed in this study consists of an indium tin oxide (ITO) anode, a ZnSP emitter layer and an Al cathode (Fig. 3). The ZnSP film was spin-coated onto an ITO-coated glass substrate with a sheet resistance of 20 Ω □$^{-1}$. The thickness of the ZnSP layer was *ca.* 100 nm. A 300 nm thick aluminium electrode was vacuum-deposited onto the ZnSP film at 10^{-6} Torr. The deposition rate was maintained at 0.1–0.2 nm s^{-1} and the emitting area was 2×2 mm^2. Fig. 4 presents the photoluminescent (PL) and EL spectra of the ZnSP thin film. The photoluminescence [Fig. 4(a)] peaks at 415 nm with an excitation wavelength of 350 nm, while the electroluminescence [Fig. 4(b),(c)] reaches a maximum at 435 nm which is red shifted compared to the photoluminescence. On one hand, this is probably a result of local Joule heating from the large current flux and poor thermal conductivity. On the other hand, many studies on the interaction between metal and polymer show that some metal can react with the polymer substrate, especially for Al.[22] So we deduce that during the vacuum deposition of the Al electrode onto the ZnSP substrate, a certain amount of Al diffuses into the ZnSP layer, acting as impurities. The luminescence arises from the radiative recombination of electrons and holes at defect levels brought about by Al,[12,13] and red-shifted electroluminescence is observed. The PL and EL spectra have the same shape and half-width indicating that the particles' electroluminescence and photoluminescence are from the same state, which is from some deep traps luminescence. So the external quantum efficiency of the EL device is very low. The current *vs.* voltage (*I–V*) characteristics are shown in Fig. 5. The turn-on voltage is <4 V. While ramping the applied

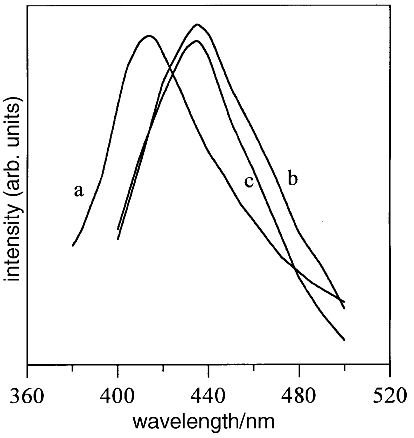

Fig. 4 PL and EL spectra of ZnSP thin film. (a) PL spectrum of ZnSP thin film on a quartz substrate, excitation wavelength 350 nm; (b) and (c) are the EL spectra of ZnSP single-layer structure EL device, (b) fresh ZnSP sample (aged for 1 h), (c) ZnSP sample aged for one month

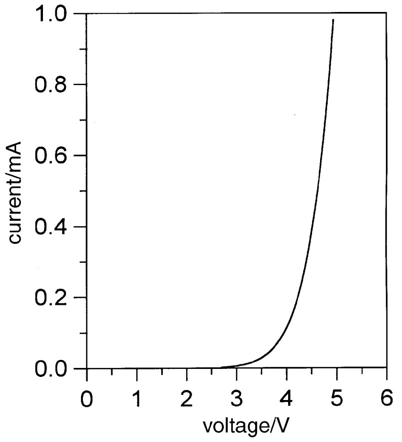

Fig. 5 Current–voltage characteristics for an ITO–ZnSP–Al device

bias, blue light becomes visible just below 5 V forward bias (no light is observed under reverse bias).

In Fig. 4, curves (b) and (c) present the EL spectra from the fresh ZnSP and ZnSP aged in the dark at room temperature for one month, respectively. There is little difference between these spectra. This indicates that ZnS nanocrystals prepared in polymer matrices possess good stability.

We gratefully acknowledge the support of the National Natural Science Foundation of China, and the Polymer Physics Laboratory of Changchun Institute of Applied Chemistry, Chinese Academy of Sciences.

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Paper 6/03555H; *Received* 21*st May*, 1996