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Preparation and Optical Properties of CdS/PVK Nanocomposites based on CdS Nanorod Arrays

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Abstract. Well-defined CdS nanorod arrays were pepared via a facile one-step hydrothermal approach and Poly (N-vinyl carbazole) (PVK)/CdS nanocomposites were fabricated by spin-coating chloroform solution of PVK on the surface of CdS film. A variety of techniques including scanning electron microscopy (SEM), optical absorption and photoluminescence (PL) were employed to investigate the surface morphology and optical properties of PVK/CdS nanocomposites. Photoluminescence efficiency of nanocomposites decreases compared to pure PVK and CdS nanorod arrays due to quenching through high photocharge generation quantum efficiency and high charge transport between inorganic semiconductor and conducting polymer.

Introduction

As a class of electronic and optoelectronic materials, nanocomposites consisting of semiconductor nanocrystals and organic polymers have attracted a great attention as an alternative of polymer solar cells [1~6]. Indeed, it has been reported several types of hybrid solar cells composed of conjugated polymers and n-type inorganic nanocrystals, such as CdSe [7], TiO_2 [8], ZnO [9] and CdS [10], which exhibited a highly power conversion efficiency.

CdS is the most promising inorganic semiconductor to be applied in organic–inorganic hybrid photovoltaic devices due to its primary band gap of 2.4eV(~516nm) and good electron acceptable [11]. As a well-known hole transport organic semiconducting polymer, Poly(N-vinyl carbazole)(PVK) is often used as an electronic and optical materials [12]. The preparation and photoluminescence properties of hybridized CdS/PVK nanocomposites has been studied [13-15], and exhibited advantages of both the excellent carrier generation efficiency and mobility of the CdS inorganic semiconductor and processibility of the organic polymer. In such a composite, the CdS semiconductor cluster acts as a sensitizer for the photogeneration of carriers and the polymer serves as the carrier-transporting medium [16].

It's worth noting that CdS/PVK nanocomposites reported previously was prepared simply mixing PVK and CdS nanocrystal. This kind of nanorod arrayed mussily inside composite film, which resulted in disadvantage of charge transportation between vertical electrodes. In this paper, we prepared CdS/PVK nanocomposite film based on CdS nanorod perpendicular to ITO substrate, and studied their optical properties.

Experimental Section

Preparation of CdS/PVK Nanocomposites. The preparation of CdS nanorod arrays was adopted from the literature [17]. The etched ITO glass was placed vertically to the bottom of the Teflon-lined stainless-autoclave, and then the solution composed of 1 mmol of cadmium nitrate, 3 mmol of thiourea, and 0.6 mmol of glutathione was added. After reaction of 3.5h at 200 °C, the film was rinsed with distilled water. Prepared chloroform solution of PVK with the concentration of 20, 40, 60mg/ml respectively, and then spin-coated on the surface of CdS film at the speed of 3000r/s.

Characterization. Field emission scanning electron microscopy (FESEM) images were taken on a FESEM-4800 scaning electron microscope. The absorption spectra were recorded by the PE UV-Vis LAMBDA 25 ultraviolet-visible absorption spectrometer. The photoluminescence spectra were measureed by F-4500 luminescence spectrophotometer from Hitachi. The thin film samples were excited at 300nm and 420nm respectively.

Results and Discussion

Fig. 1 shows the typical scanning electron microscopy (SEM) images of the as-prepared CdS nanorod arrays and CdS/PVK composite film. It is seen that the whole ITO glass is covered with uniform CdS nanorod arrays which was composed of uniform rods about 100 nm in diameter(see Fig. 1(a) and 1(b)). In addition, Fig. 1(b) shows the distance between the CdS rods is approximately 100nm and leaves large opening space in the array for the complementary polymer to interpenetrate.

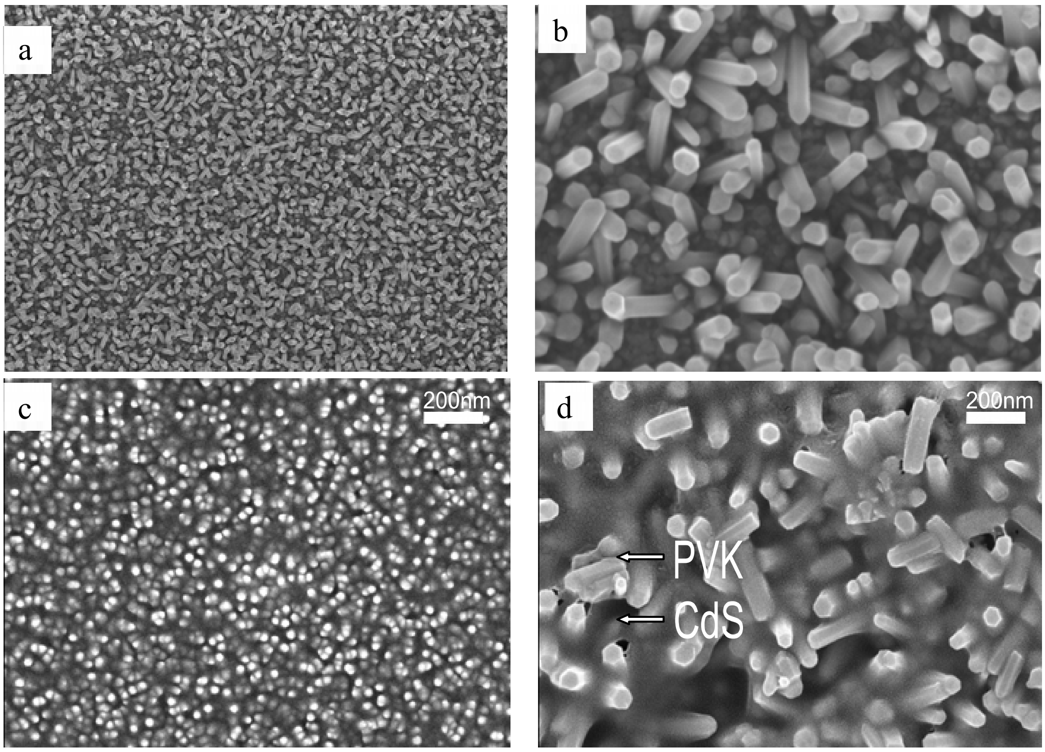

Fig. 1 SEM images of the as-prepared CdS nanorod arrays(a,b) and CdS/PVK composites film(c,d)

The SEM images of the CdS/PVK composite film (see Fig. 1 (c) and1 (d)) indicate that PVK interpenetrates inside the CdS nanorod arrays, finely disperses in the CdS nanorod arrays and embraces the nanorods from the root to the top. The PVK also deposits on the surface of the CdS nanorods and holds the extra space surrounding the nanorods, which contributes to the interface contact and charge transport between PVK and CdS nanorods.

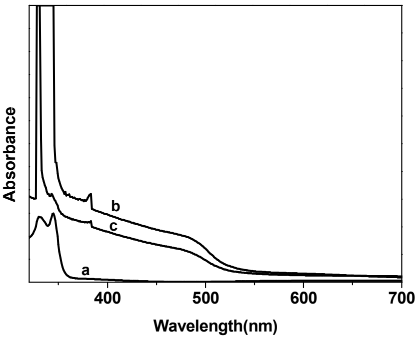

Fig. 2 UV-vis spectra of the PVK(a), CdS(b) and PVK/CdS nanocomposites(c)

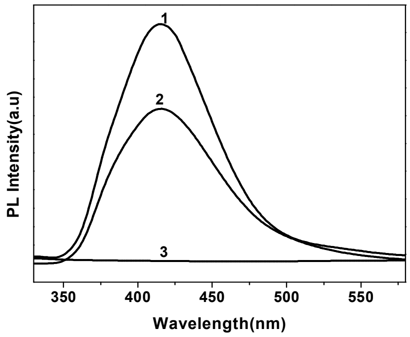

Fig. 3 Photoluminescence spectra of pure PVK(1), PVK/CdS(2) and pure CdS(3) (Ex=300nm)

Fig. 2 shows the UV-vis absorption speactra of the PVK (curve a), CdS (curve b) and PVK/CdS nanocomposites (curve c). The absorption of the PVK beyond 360nm was abvious and the absorption of CdS nanorods extends to 540nm. It is clear that the absorption spectra of PVK/CdS nanocomposites are virtually superpositions of the absorption spectra of pure PVK and CdS nanorods. For the PVK/CdS nanocomposites, the absorption starts at about 540nm and increases with decreasing wavelength.

Fig. 3 shows the photoluminescence spectra of pure PVK, PVK/CdS and pure CdS excited at a wavelength of 300nm. It can be seen that there is no emission for pure CdS nanorods. And the photoluminescence peak of pure PVK was narrow with only one emission maximum at 416nm attributed to the transition in the carbazole groups of PVK. From the figure it is clear that the photoluminescence spectrum did not change when PVK solution was spin-coated onto CdS film, but the intensity was decreased compared with that of the pure PVK solution with the same concentration.

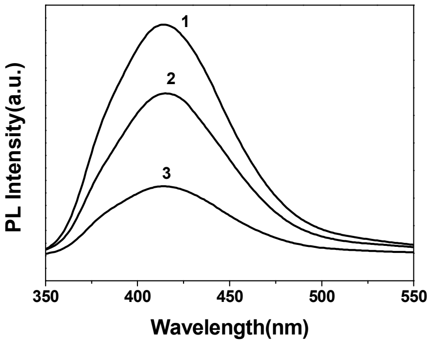

Fig. 4 Photoluminescence spectra of CdS/PVK nanocomposites with the PVK concentration of 60mg/ml(1), 40 mg/ml(2), 20mg/ml (3) (Ex=300nm)

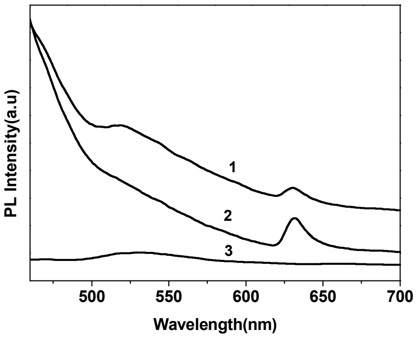

Fig. 5 Photoluminescence spectra of pure CdS (1), PVK/CdS(2) and pure PVK (3) (Ex=420nm)

Fig. 4 shows the photoluminescence spectra of CdS/PVK nanocomposites with the PVK concentration of 60mg/ml, 40 mg/ml, 20mg/ml respectively excited at a wavelength of 300nm. It can be seen that the emission maximum has no change, while the intensity increases with the increasing of PVK concentration.

When excited at a wavelength of 420nm, the photoluminescence spectra of pure PVK, PVK/CdS nanocomposites and pure CdS are shown in Fig. 5. It is conclude that the photoluminescence peak of PVK/CdS nanocomposites is mainly corresponding to the band emission of CdS nanorods, and the emission of pure PVK is very poor. It is because the band-gap energy of PVK is 3.6eV, which is higher than visible light of 420nm, not enough to exciting the electron from valence band to conduction band.

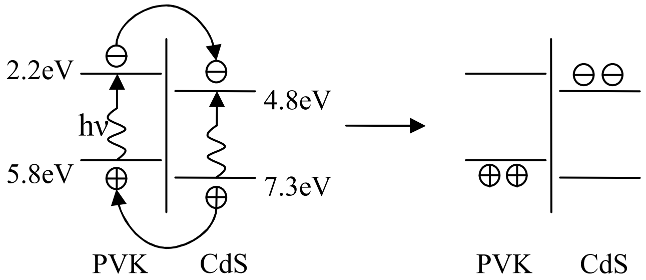

Fig. 6 Interfacial charge transfer and separation between PVK and CdS nanocomposites

The quenching of the fluorescence of PVK in the PVK/CdS nanocomposite results from the charge carrier transport between polymer and nanorods. Fig. 6 shows the interfacial charge transfer and separation in PVK/CdS nanocomposites[13]. From the figure we can see that the HOMO and LUMO of PVK are both higher than that of CdS nanorods. Therefore the photo-excited electrons in PVK will move to be surface of the CdS nanorods. This kind of interfacial charge transfer reduced the recombination of electron-hole pairs in PVK, increased the lifetime of hole in PVK and electron in CdS nanorods, thus brings down the transition probability from LUMO to HOMO and reduces the PVK photoluminescence.

In this work, we synthesized well-defined CdS nanorod arrays and fabricated PVK/CdS nanocomposites. The surface morphology detected by SEM shows that PVK is finely dispersed in the CdS nanorod arrays. Surveying by photoluminescence spectrum, photoluminescence efficiency of nanocomposites decreases compared to pure PVK and CdS nanorod arrays results from high charge carrier transport between polymer and nanorods.

Acknowledgments

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