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The broadened and red-shifted photoluminescence spectral emission of poly(*N*-vinylcarbazole) nanoparticles

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ABSTRACT

The emission of poly(*N*-vinylcarbazole) nanoparticles, prepared from tetrahydrofuran solution using a reprecipitation method, differed to those of the particles in both solution and film. The photoluminescence spectra of the nanoparticles was broader and red shifted in comparison to those in solution and film. Repulsion between carbazole groups and solvent favours the adoption of a fully overlapped, sandwich-like configuration of neighboring carbazole groups in the nanoparticles. The decay times of the excimers in the nanoparticles were shorter than those in solution.

1. Introduction

Semiconducting polymer nanoparticles have attracted much attention owing to their excellent optical and electronic properties as well as their potential application in low-cost, nano-optoelectronic devices [1–7]. High performance photoelectronic devices, such as polymer light-emitting diodes (PLEDs) and thin-film transistors, have been successfully prepared by using semiconducting polymer nanoparticles as active layers [8,9]. Poly(*N*-vinylcarbazole) (PVK) has been widely researched and employed as hole-transporting or emission layers in PLEDs [10–13]. Recently, PVK nanoparticles with of wide diameter range 50–200 nm have been prepared by emulsion polymerization [14]. The excited states in PVK have been considered as excimers owing to the closed carbazole groups. Two configurations are responsible for the excimers in PVK namely, an excimer with a low-energy emission band (430 nm) that comprises an overlapping, sandwich-like configuration of two carbazole groups and an excimer in which the partial overlap of two carbazole groups is responsible for the observed, high-energy emission band (380 nm) [15–17]. The 380-nm emission band has been found to be dominant in the photoluminescence (PL) spectra of syndiotactic PVK, whereas, the intensity of the 430-nm emission band increases with increasing mole fraction of the isotactic diads in PVK [16]. Thus, the emission spectrum of PVK can be controlled by its configuration. The fully overlapped configuration in PVK can also be formed by exposure to either UV light or an electrical field [18,19]. The overlapped configuration results in high conductivity because of strong, intrachain, π-stacked interactions. PLEDs fabricated from UV-irradiated PVK exhibit higher efficiencies than those secured using non UV-irradiated PVK [18].

The optical properties of semiconducting polymers are often influenced by their conformation, which, in turn, are effected by the environment that surrounds the polymer chains. This work concerns the broadening and red shift of emissions from PVK nanoparticles imparted by changes in the polymer chain conformation. The optical properties of the PVK nanoparticles were investigated by adjusting the concentration of the polymer solution used for preparation. Internal, C–C rotation within the polymer backbone leads to fully overlapped, sandwich-like configurations between the neighboring carbazole groups in the polymer nanoparticles, results in the observed broadened and red-shifted emissions.

2. Experimental

PVK (from Acros Organics) was used as received without any purification. PVK was dissolved in distilled tetrahydrofuran (THF) to

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prepare the solutions with the concentrations of 2, 1, 0.5, and 0.1 mg/mL. The PVK nanoparticles were prepared via the reprecipitation method. In a typical preparation, 100 μL of the PVK THF solution was rapidly injected into 10 mL of deionized water with vigorous stirring, and then the aqueous PVK nanoparticle suspension was subjected to ultrasonic for 20 min. Mixing of THF with water rapidly changes the character of the solvent and induces nucleation and growth of the polymer nanoparticles. PVK film was spin-coated on a clear glass substrate using the PVK solution with concentration of 2 mg/mL. The PVK films were treated with ultrasonic for 10–20 min in deionized water or air, respectively. The morphologies of the polymer nanoparticles were characterized by transmission electron microscopy (TEM, JEM-200CX). The PL and PL excitation (PLE) spectra were obtained by using the FluoroMax-2 fluorescence spectrophotometer. The time-resolved fluorescence decay data were measured on an Edinburgh FLS 920 fluorophotometer equipped with a time correlated single-photon counting (TCSPC) card. All the experiments and measurements were performed at room temperature.

3. Results and discussion

The morphologies of the PVK nanoparticles can be characterized by TEM. Fig. 1 shows the TEM images of the PVK nanoparticles prepared from the PVK solutions with different concentrations. It can be seen that the colloidal polymer nanoparticles adhere to each other after water volatilizes and the densities of PVK in the polymer nanoparticles are different. The results imply that the polymer nanoparticles are composed of incompact polymer chains and some of water in aqueous suspensions. The sizes of the polymer nanoparticles are increased from 30 nm to 80 nm with increasing the concentration of the PVK solution. As the PVK THF solution is rapidly injected into water under strong stirring, the solution is divided into many droplets by strong shearing force. Simultaneously, THF molecules quickly diffuse into water to make the PVK chains exposed to water, and then the PVK chains become coiled to form nanoparticles. Obviously, the number of the PVK chains in the droplets depends on the concentration of the polymer solution. Numbers of the polymer chains in the droplets contribute to large nanoparticles for using the PVK solution with high concentration to prepare the polymer nanoparticles.

Fig. 2 shows the normalized PL and PLE spectra of the PVK film, PVK nanoparticles, and PVK solution with concentration of 0.5 mg/mL. The PVK nanoparticles are prepared from the solution with concentration of 0.5 mg/mL. The structured PLE spectra of the three samples are similar except slight red shift in the PVK film. In the film, the interaction between molecules widens the energy bands of the polymer to result in a narrow energy gap, corresponding to the red-shifted PL and PLE spectra. The PLE results indicate that the carbazole groups in PVK act as individual molecules for light absorption. It can be seen that the PL peak of the PVK solution and the film are at 377 and 405 nm, respectively. The results are consistent with other reports [10,11]. Compared to the PVK solution and film, the PL spectrum of the PVK nanoparticles becomes wide and its PL peak red shifts to 430 nm. The 430 nm PL band has been considered to be connected with intrachain excimers, in which the two neighboring carbazole groups in one polymer chain form a full overlapping, sandwich configuration [15–17]. During the preparation of the polymer nanoparticles, a small quantity of the PVK THF solution is injected into a great quantity of water. The extended conformations of the polymer chains in THF become the coiled conformations in water due to the internal rotations of the C–C bonds. The repulsion between the carbazole groups and the poor solvent overcomes the steric hindrance of the carbazole groups in PVK. As a result, the fully overlapping configurations are formed in the PVK nanoparticles.

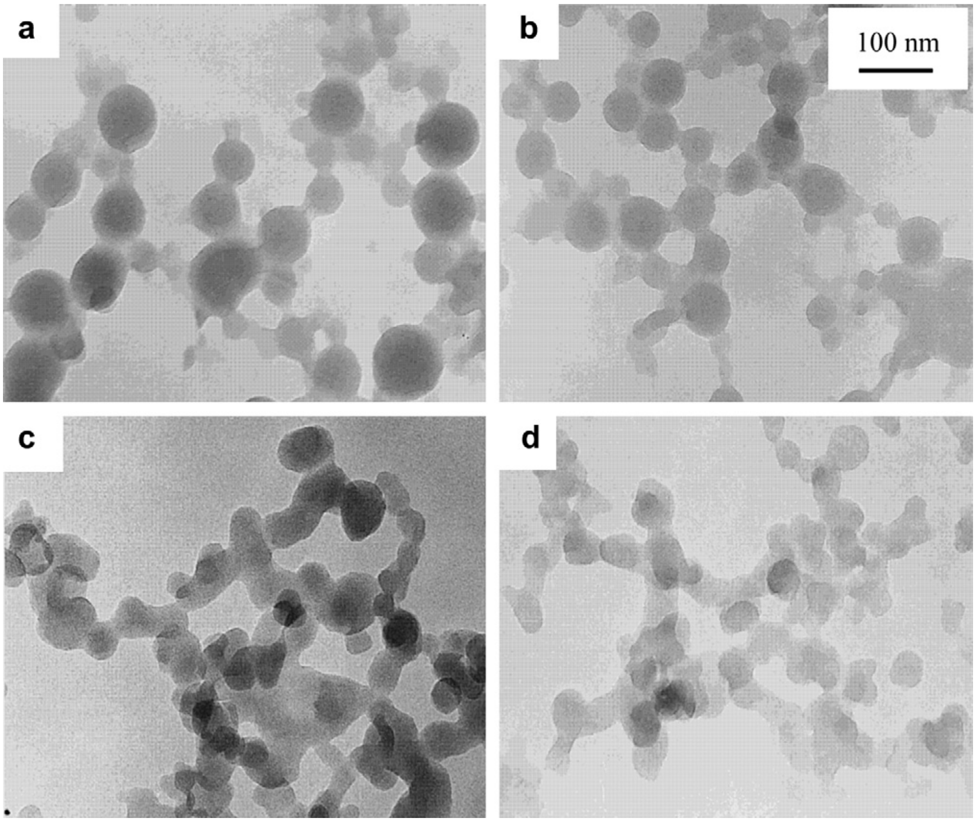

Fig. 1. TEM images of the PVK nanoparticles prepared from the PVK solutions with the concentration of (a) 2, (b) 1, (c) 0.5, and (d) 0.1 mg/mL.

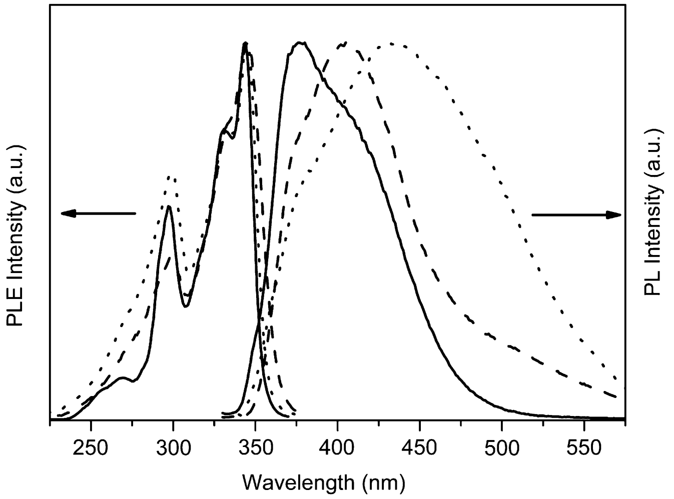

Fig. 2. Normalized PL and PLE spectra of the PVK solution (solid line), film (dashed line) and nanoparticles (dotted line). The PLE spectra of the PVK solution, film and nanoparticles were measured at the monitoring emission wavelength of 380, 405 and 430 nm, respectively.

Fig. 3 shows the PL spectra of the PVK nanoparticles prepared by using the PVK THF solutions with different concentrations. The relative PL intensity of the PVK nanoparticles increases and the PL peak is blue shifted from 442 nm to 422 nm with increasing the concentration of the PVK solution. The PLE spectra of the samples are shown in the inset of Fig. 3. There is no obvious difference for the shapes of the PLE spectra except different relative intensities. The results further indicate that the light absorption first occurs in the individual carbazole group. As one carbazole group is photoexcited, the excitation energy is delocalized over the excited carbazole group and the neighboring unexcited carbazole group, and then the excimer is formed. With increasing the concentration of the polymer solution, the number of the polymer chains is increased in one nanoparticle. In the case, the optical properties of the PVK nanoparticles will be close to those of the PVK film.

The emission properties of PVK have been proved to be affected by ultraviolet light or electrical field [18,19]. Here, we present the effects of ultrasonic on the emission properties of the PVK films, as shown in Fig. 4. Comparison with the pristine PVK film without ultrasonic treatment, the PL spectra of the PVK films treated with ultrasonic are slightly red shifted (several nanometers). The PL peaks of the treated PVK films are the same, independent of the time of ultrasonic and surroundings. Therefore, it is reasonable to believe that ultrasonic treatment cannot change the configurations of PVK. These results also imply that the fully overlapping configurations formed in the PVK nanoparticles are connected with the interaction between the poor solvent and the polymer chains during preparation.

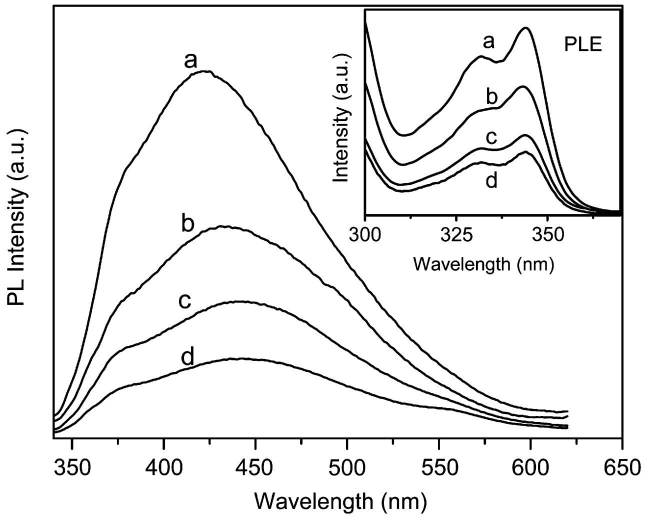

Fig. 3. PL spectra of the PVK nanoparticles prepared by using the PVK solutions with different concentrations, (a) 2, (b) 1, (c) 0.5, and (d) 0.1 mg/mL. The inset is the PLE spectra measured at the monitoring emission wavelength of 430 nm.

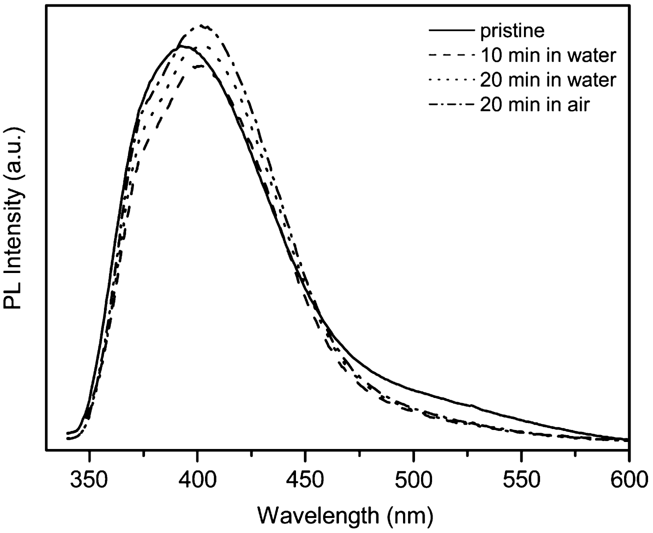

Fig. 4. Normalized PL spectra of the pristine PVK film (solid line), the PVK films treated with ultrasonic for 10 min (dashed line) and 20 min (dotted line) in deionized water and the PVK film treated with ultrasonic for 20 min in air (dashed and dotted line).

Fig. 5 shows the time-resolved fluorescence spectra of the PVK solution and nanoparticles. Obviously, the time-resolved fluorescence spectra of the two samples are multiexponential for probing

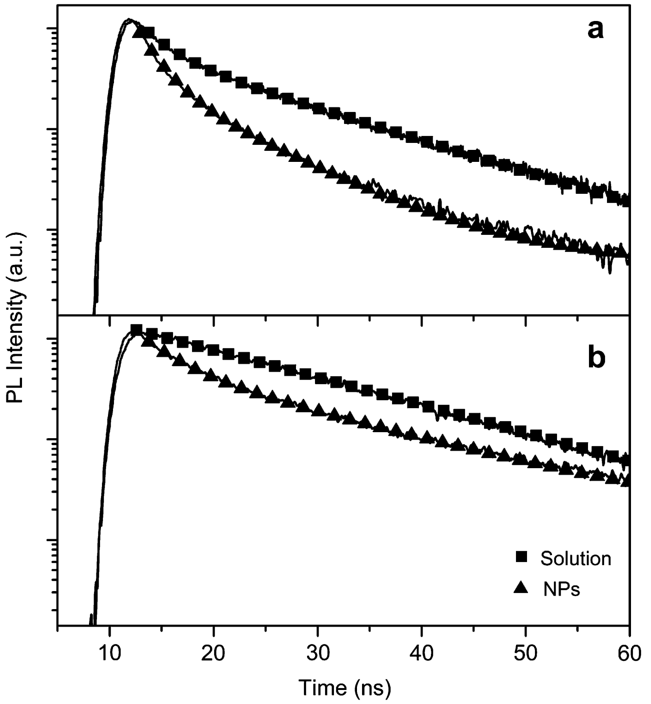

Fig. 5. Time-resolved fluorescence spectra of the PVK THF solution and the PVK nanoparticles obtained by pumping at 345 nm and probing at (a) 380 nm and (b) 430 nm.

at 380 nm. The average decay times of the 380-nm intrachain excimers in the solution and nanoparticles are 6.22 and 2.93 ns, respectively. The time-resolved fluorescence spectrum of the PVK solution is monoexponential for probing at 430 nm, and the decay time of the 430-nm intrachain excimer is calculated to be 16.36 ns. Different from the PVK solution, the time-resolved fluorescence spectrum of the PVK nanoparticles is multiexponential for probing at 430 nm. The average decay time of the 430-nm excimer in the PVK nanoparticles is only 7.1 ns, which is much shorter than that in the PVK solution. The above results indicate that the decay times of the two kinds of the excimers in the PVK nanoparticles are shorter than those in the PVK solution. One reason for the short decay time of the excimers in the PVK nanoparticles is correlative to the coiled conformations of the PVK molecules. In the THF solution, the PVK chains are extended, but the polymer chains become coiled in the nanoparticles due to the repulsion between the poor solvent and the polymer chains. So, the densities of the excimers in the nanoparticles are higher than those in the THF solution. The closed excited states usually give rise to excimer–excimer annihilation, which contributes to shortening the decay time of the excimers in the PVK nanoparticles. Another reason for the short decay time of the excimers in the nanoparticles is the circumstance around the PVK molecules. The PVK nanoparticles are dispersed in aqueous solution and the polymer chains are exposed to the polar solvent. In addition, some defects close to the excimers also contribute to the short decay time of the excited states in the PVK nanoparticles.

4. Conclusions

The PL spectra of the PVK nanoparticles differed to that in both solution and film, becoming broader and red-shifted. Repulsion between the carbazole groups and the solvent overcomes the steric hindrance of the carbazole groups, resulting in fully overlapped, sandwich-like configuration in the PVK nanoparticles. The decay times of the excimers in the PVK nanoparticles were shorter than those in the PVK solution because of the complex photophysics of the former.

Acknowledgments

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