

Sharp fluorescence nanofiber network of CdSe/CdS core-shell nanoplatelets in polyvinylpyrrolidone

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ABSTRACT: In this work, a novel nanofiber network of colloidal semiconductor CdSe/CdS nanoplatelets (NPLs)/polyvinylpyrrolidone (PVP) with characteristics of porous membranes has successfully been fabricated via the electrospinning technique, in which NPLs and PVP were used as fluorescence agent and fiber matrix, respectively. Firstly, the CdSe core NPLs with quasi 2D geometry was synthesized, and the epitaxial growth of the CdS shells was performed by the atomic layer deposition (c-ALD) method at room temperature. CdSe/CdS core-shell NPLs with a narrow, ca. 20 nm photoluminescence band were blended with PVP dissolved in ethanol-trichloroethylene mixture; and hybrid polymer-NPLs fibers were obtained through the electrospinning technique. The final nanofiber network exhibits the excellent optical properties of the NPLs, which has potential for separation and absorption of pollutants and isolation of microorganisms.

KEYWORDS: semiconductor nanoplatelets, polymer, electrospinning, hybrid materials, fluorescence nanofiber network

INTRODUCTION

In recent years, microporous membranes have attracted the attentions for separation and absorption of pollutants and for isolation of microorganisms [1]. The latest publications [2] indicated the possibility that this structure can be fabricated from nanofiber networks, with the advantages of controllable porous size from tens of nanometers to micrometers [3]. In the past decade, there are publications on the methodology, whereas [4], it is not possible to know the degree of pollution, harmfulness or toxicity through this kind of porous structure. Thus, it is necessary to design a structure that can impart this microporous structure to sense these dangerous matters. Thus, fluorescence sensing is ideal strategy to meet this task [5].

Colloidal semiconductor quantum dots (QDs) are the promising next-generation units for the application advantages of cost-effective production, superior color purity, high quantum yield (QY), and precisely tunable emission wavelength through the whole visible to the near infrared range [6–9]. Such advantages have encouraged much efforts to de-

velop sensing applications [10]. However, spherical CdSe QDs suffer from the size sensitivity to broaden spectra and to shift emission wavelengths with the change of their diameter scale and distribution [11]. Whereas, CdSe nanoplatelets (NPLs) have zero size deviation along their normal direction along which the quantum confinement occurs [12]. Therefore, CdSe NPLs demonstrate narrower absorption and emission bands. As compared to QDs, CdSe NPLs can potentially exhibit weaker Coulomb interaction between carriers, which allows for more efficient charge injection without affecting confinement and recombination regimes [13, 14].

Electrospinning is an effective and low-cost technology for preparing polymer fibers with diameter range from tens of nanometers to a few micrometers [15, 16]. The high surface-to-volume ratio of electrospun fibers has encouraged extensively on tissue engineering scaffolds, energy storage, sensors and drug delivery [17–20]. The sensitive 2,4-dinitrotoluene fluorescence sensors based on porous electrospun fibres and porous membranes prepared from pyrene-doped poly (methyl methacrylate), polyvinyl chloride, polystyrene, and

co-polymers from these polymers have been successfully developed [21]

So far, there are just few studies on QDs/polymer composite fibers by direct mixing method [22, 23]. And recently, the ultrafine fibers of the QDs doped in polymer hosts illustrated successes of electrospinning method for electronic and optoelectronic devices [24, 25]. Reports indicated that there are two methods to introduce QDs into polymer fibers, i.e. *in situ* formation method and direct blending [26]. Although the *in situ* formation method has a precise control of the size distribution, the formation process usually leads to increases of surface defects resulting in poor optical properties [27]. The QDs/polymer direct mixing method can solve the problems mentioned above and achieve ultrafine fibers with excellent optical properties and narrow size distribution [28, 29].

Herein, novel hybrid luminescent nanofiber network based on the CdSe/CdS core-shell NPLs/polyvinylpyrrolidone (PVP) was demonstrated. The NPLs have been introduced into the PVP solution by addition of trichloroethylene to the polymer solution. Compared with similar work in the past, this new type of network was doped with NPLs that have high quantum yield (QY) and extremely narrow full-width at half-maximum (FWHM). The different novel hybrid luminescent nanofiber network maintains sharp fluorescence as usual after electrospinning. This work provided a new hybrid nanofiber network with great potential applications for sensing and detecting.

MATERIALS AND METHODS

Materials

Cadmium acetate dehydrate ($\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 99.99%), ammonium sulfide ($(\text{NH}_4)_2\text{S}$, 40%), myristic acid, selenium powder (Se, 99.99%), 1-octadecene (1-ODE, 90%), oleylamine (OAm, 80–90%), oleic acid (OA, 90%), and PVP (Mw = 1300000 g/mol) were purchased from Aladdin, Shanghai, China. Methanol, hexane, isopropanol, ethanol, trichloroethylene (C_2HCl_3), toluene, and acetonitrile were from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. N-methylformamide (NMF, 99%) was from Macklin, Shanghai, China. All chemicals were used as received and without further purification.

Characterization

UV-vis absorption of NPLs solution was recorded by PerkinElmer Lambda 750S spectrophotometer in the

range of 200–2300 nm using a glass cuvette with a 1 mm \times 1 mm optical path. Photoluminescence (PL) spectra and fluorescent optical microscopic photographs were measured with Cary Eclipse fluorescent spectrometer and OLYMPUS BX41 universal microscope with a UV lamp emitting in the wavelength range of 340–380 nm, respectively. The morphologies of NPLs and hybrid fibers were characterized by transmission electron microscopy (TEM, JEM-2000 Ex) and scanning electron microscopy (SEM, Tescan-Vage3). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 5700 infrared spectrophotometer in the range of 4000–400 cm^{-1} .

Preparation of CdSe and CdSe/CdS NPLs

Twenty mmol of $\text{Cd}(\text{OAc})_2 \cdot 2(\text{H}_2\text{O})$ was dissolved in 50 ml of methanol and mixed with 45 mmol of myristic acid dissolved separately in 300 ml of methanol. The white precipitate was filtered out from the solution and washed with methanol three times to remove the excess precursors. The final $\text{Cd}(\text{myr})_2$ powder was dried under vacuum at 40 °C overnight. Then, $\text{Cd}(\text{myr})_2$ (140 mg), Se powder (24 mg) and 1-ODE (15 ml) were introduced into a three-neck round-bottom flask and degassed under vacuum at 100 °C for 30 min with stirring. After degassing, the reaction mixture was heated up to 240 °C under nitrogen atmosphere. When the temperature reached 195 °C, 80 mg of $\text{Cd}(\text{OAc})_2 \cdot 2(\text{H}_2\text{O})$ were rapidly added into the reaction mixture. After the temperature reached 240 °C, the reaction mixture was stirred for 8 min, then 2 ml of OA were added and the solution cooled down to 80 °C. To overgrow CdSe core NPLs with CdS shell by ADL method [30], 1 ml of CdSe cores in 4 ml hexane dissolved in 3 ml hexane, and the first monolayer was deposited by adding 12.5 μl of $(\text{NH}_4)_2\text{S}$ in 5 ml NMF and vigorously stirring until complete the phase transfer of NPLs from hexane to NMF phase. The S-coated CdSe NPLs were precipitated from NMF by adding a mixture of toluene and acetonitrile, centrifuged at 10000 rpm and re-dispersed in 5 ml of NMF. Then, the monolayer of Cd was deposited by introducing 1.5 ml of 0.25 M solution of $\text{Cd}(\text{OAc})_2 \cdot 2(\text{H}_2\text{O})$ in NMF, the mixture was stirred for 3 min, after which the CdSe/CdS core-shell NPLs were precipitated by adding the mixture of toluene and acetonitrile (toluene:acetonitrile = 1:1, v/v). To further increase the CdS shell thickness, the above procedure was repeated three times and the final core-shell NPLs with different thickness were dispersed in trichloroethylene with the addition of OAm.

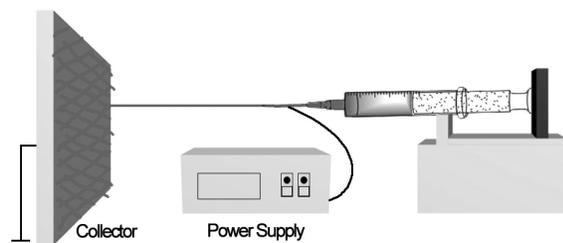


Fig. 1 Schematic diagram of the electrospinning process.

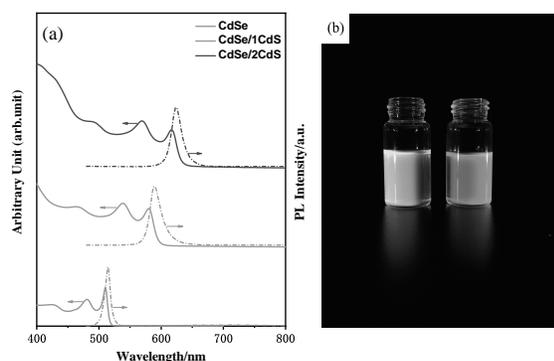


Fig. 2 (a) Absorption and photoluminescence spectra of CdSe core and CdSe/CdS core-shell NPLs with 1 ml and 2 ml thick CdS shell in hexane; (b) sample picture of CdSe core and CdSe/CdS core-shell NPLs. The photoluminescence spectra are obtained by excitation at 460 nm.

Fabrication of NPLs/PVP hybrid nanofiber network

To prepare the polymer solution, 10 g PVP was dissolved in the mixture of ethanol and C_2HCl_3 (ethanol: C_2HCl_3 = 2:1, v/v) and stirred for 12 h to obtain a homogeneous solution of 10 wt% PVP solution. Then, different contents of NPLs were added into the PVP solution and the mixture was continuously and vigorously stirred and sonicated strongly to avoid aggregation of NPLs. The as-prepared solutions with different contents (1 wt%, 3 wt% and 5 wt%) of NPLs were loaded into 5 ml plastic syringes attached with stainless steel needles. During the electrospinning process, using aluminum foil as the positive electrode collector, the applied voltage was 10 kV and the distance between the spinneret tip and the collector was kept at 20 cm. All of these processes were demonstrated under ambient conditions (Fig. 1).

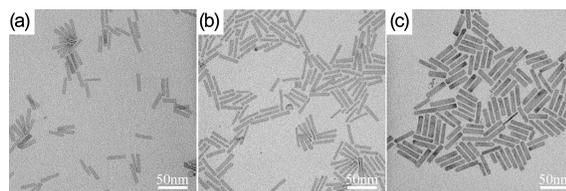


Fig. 3 TEM images of CdSe core and CdSe/CdS core-shell NPLs: (a) core CdSe NPLs, (b) CdSe/1CdS NPLs, (c) CdSe/2CdS NPLs.

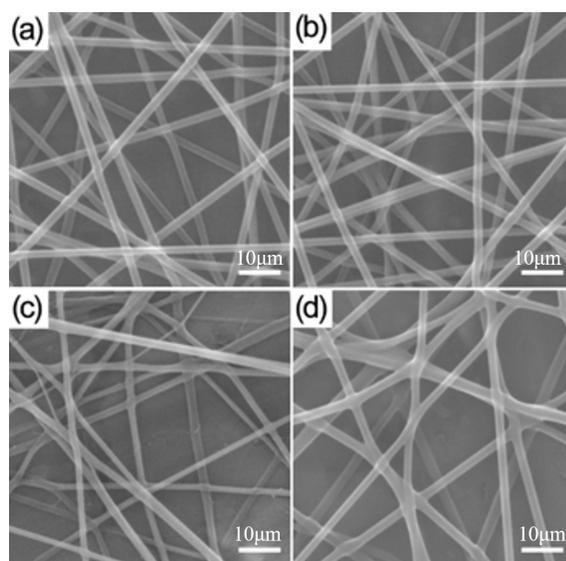


Fig. 4 SEM images of nanofiber network with different NPLs contents: (a) 0 wt%, (b) 1 wt%, (c) 3 wt%, (d) 5 wt%.

RESULTS AND DISCUSSION

Fig. 2(a) shows the absorption and emission spectra of as-prepared CdSe core, CdSe/1CdS and CdSe/2CdS core-shell NPLs in hexane solutions at the room temperature. During deposition of CdS shell, the heavy-hole absorption peak shifts from $\lambda = 510$ nm to 617 nm after 2 c-ALD cycles, while the stokes shift increases from 4 nm to 7 nm. Introduction of CdS shell resulted in broadening of PL spectrum to a FWHM ≈ 20 nm. The PL QYs of the CdSe/1CdS and CdSe/2CdS core-shell NPLs were about 20% and 40%, respectively. Fig. 2(b) is the sample picture, the left one is the CdSe core and the right one the CdSe/CdS core-shell NPLs.

The geometric morphology of the NPLs before and after shell growth was characterized by TEM. Fig. 3 shows the TEM images of core and core-shell NPLs. TEM images show that CdS shell uniformly

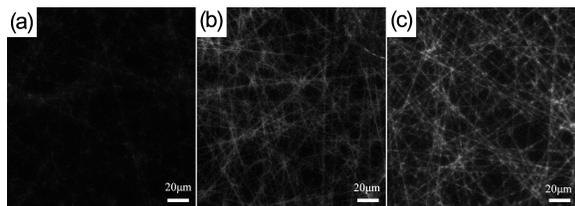


Fig. 5 Microscopy images (under the UV light) of CdSe/1CdS NPLs/PVP nanofiber network with different NPLs contents: (a) 1 wt%, (b) 3 wt%, (c) 5 wt%. White scale bar is 20 μm .

coated core NPLs resulting in the increase of lateral dimensions from 38 nm \times 9 nm to 41 nm \times 10 nm for 1 ml of CdS and 44 nm \times 11 nm for 2 ml of CdS.

The reason for choosing the CdSe/2CdS NPLs as the fluorescence agents to fabricate the NPLs/PVP hybrid fibers is its higher QY when compared to the CdSe core and the CdSe/1CdS NPLs. Therefore, an approach was developed to prepare NPLs/PVP hybrid fibers with different NPLs contents, in which the trichloroethylene plays a vital role as a dispersing medium during the electrospinning process. SEM images of hybrid fibers with different contents of CdSe/2CdS NPLs were shown in Fig. 4. It can be seen that the ultrafine hybrid fibers were fabricated successfully; and the morphology of these hybrid fibers is similar to that of the original PVP fibers. These fibers are smooth and continuous with 2 μm diameter. There was no significant change of the topography of these hybrid fibers, which indicates that the contents of NPLs have no obvious influence on the diameter of the hybrid fibers. The diameters of hybrid fibers became thicker slightly with the increase of NPLs content.

In order to demonstrate their fluorescence properties, the nanofiber networks obtained with different NPLs contents were characterized by microscopy under the UV light. Fig. 5 shows the microscopic images of CdSe/2CdS NPLs/PVP nanofiber networks on the glass substrates under the UV light. And the fiber networks exhibited strong and consequent red-color, which indicated that the NPLs were introduced homogeneously over the whole PVP fibers. Obviously, the NPLs content of 1 wt% was too small to get bright luminescence in doped sample (Fig. 5a), while the content of 3 wt% showed strong luminescence intensity (Fig. 5b). This indicates that as the NPLs contents increase, the luminescence intensity of the nanofiber network enhances.

Fig. 6 is a TEM image of the nanofibers. The existence and distribution of the NPLs can be clearly

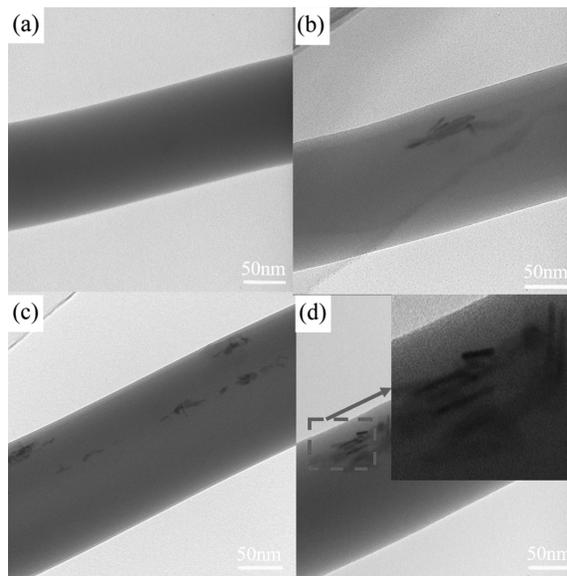


Fig. 6 TEM images of nanofibers with different NPLs contents: (a) 0 wt%, (b) 1 wt%, (c) 3 wt%, (d) 5 wt%.

seen in the figures. Obviously, zero doped nanofiber does not have a smooth surface (Fig. 6a), and all the doped nanofibers have the same smooth surfaces (Fig. 6b,c,d). The only difference between the two groups fibers is that there are NPLs inside the doped fibers. The spinning process did not destroy the morphology of the NPLs and maintained their excellent properties. The optical properties of the prepared NPLs/PVP nanofibers with NPLs content of 3 wt% have been further investigated and the nanofibers still remain the ideal fluorescence properties of the NPLs. As shown in Fig. 7, the absorption and emission of the CdSe/2CdS NPLs and nanofibers exhibited similar characteristics. The nanofibers exhibited the same first two excitonic transitions at the 572 nm and 618 nm (Fig. 7a), and a narrow emission peak at 628 nm (Fig. 7b), which had a slight red shift compared with the NPLs at 570 nm and 616 nm for absorptions (Fig. 7a) and at 624 nm for emission (Fig. 7b). It indicated that the emission peak was slightly redshift (4 nm) from the solution photoluminescence measured on the NPLs. The possible reason should relate to the slight additional energy relaxation due to coordination effect of oxygen atoms at carboxyl groups on PVP skeleton onto the surface of NPLs [31].

The functional groups of the PVP and nanofiber network were identified by FTIR spectra (Fig. 8). It could be seen that there was no obvious difference between the PVP and nanofiber network be-

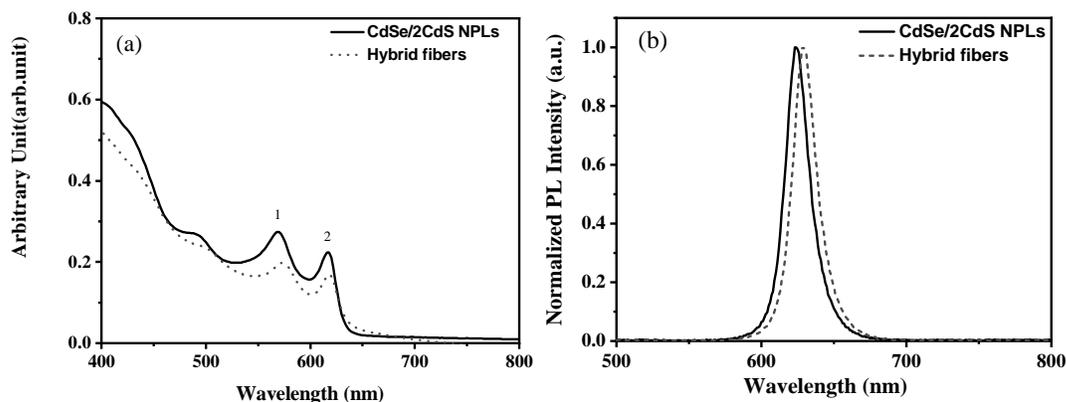


Fig. 7 (a) Absorption and (b) photoluminescence spectra of CdSe/2CdS NPLs and NPLs/PVP nanofibers. The PL emission spectra were collected with an excitation of 460 nm.

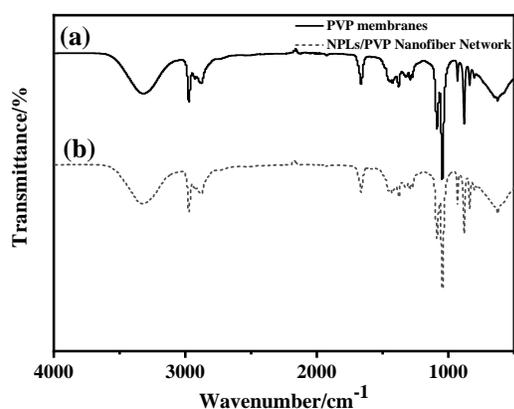


Fig. 8 FTIR spectra of the PVP and NPLs/PVP membranes: (a) PVP membranes, (b) NPLs/PVP nanofiber network.

cause the embedding content of NPLs was very low. There were a number of absorption characteristics of PVP observed in the FTIR curves, the bond at 1663 cm^{-1} is assigned to the C=O vibration of the amide groups, and the bond located at 1439 cm^{-1} and 1391 cm^{-1} were assigned with the cyclic C–H structures of pyrrolidine in PVP [32]. Moreover, the peaks at 2982 cm^{-1} and 2875 cm^{-1} were related to the stretching vibration of C–H and the broad band from 3583 cm^{-1} to 3081 cm^{-1} related to the overlap of the stretching vibrations of O–H group with N–H group [33].

CONCLUSION

Nanofiber networks, with a narrow photoluminescence based on the CdSe/CdS NPLs and PVP, have been fabricated via electrospinning technology for the first time, using oil-soluble NPLs as

the fluorescence material and PVP as the matrix. The CdSe core and CdSe/CdS core-shell structure were synthesized first, and then nanofiber networks of NPLs/PVP with different NPLs contents were fabricated by electrospinning. The as-prepared nanofiber network still maintained the excellent optical properties of the NPLs. As the content of NPLs increased, the photoluminescence intensity of nanofiber network enhanced. NPLs aggregation was occurred at the 5 wt% content.

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