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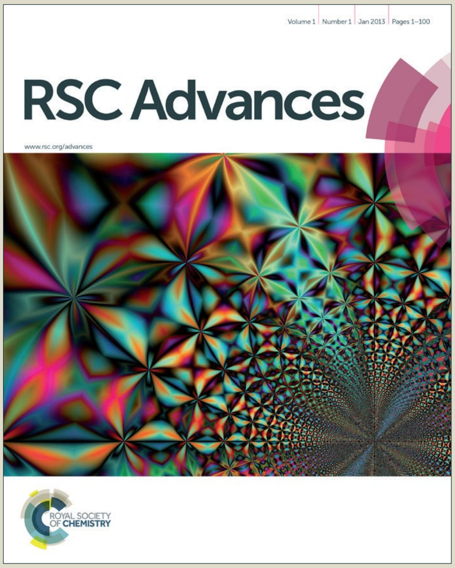

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Fabrication of highly fluorescent CdSe quantum dots via solvent-free microfluidic spinning microreactors

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The available method for *in-situ* fabrication of highly fluorescent hybrid materials prepared *via* microfluidic spinning technology (MST) has been demonstrated. Initially, we applied MST to construct one dimensional microfibers, then utilized line-line junctions and knots as the microreactors, *in-situ* synthesizing highly fluorescent CdSe quantum dot (QD) hybrid through solid-solid contact reaction. After grinding the as-prepared CdSe hybrid fibers to powders, we facilely used them as the phosphor to successfully prepare white light-emitting diode (WLED). Also, we applied the CdSe QD arrays as "test paper" for detection of Pb^{2+} and Cu^{2+} contents, which are similar to "touch spots" of neural network. This strategy shows not only green synthesis of fluorescent QD hybrid, but also a great prospect on large scale synthesis of fluorescent materials with energy saving.

1. Introduction

Semiconductor quantum dots (QDs) have been continuing promising candidates in the fields like optoelectronics,[1] photovoltaics,[2-4] light emitting diodes (LEDs),[5] biomedical imaging and sensing[6-8] owing to their narrow-band, highly efficient and widely tunable emission. So far, large-scale preparation of photoluminescent (PL) QDs with high performance in most cases has replied on heavy metal compounds such as cadmium[9] or lead chalcogenides,[10] which may bring up a number of heavy metal ions waste water during manufacturing process, limiting them to be further scaled up in the industry.

Recently, the strategy for the preparation of QDs via microfluidic technology has attracted considerable attention due to its advantage for environment and public health.[11-14] Very recently, the construction of QDs with knot microreactors via microfluidic spinning technology (MST) was reported,[15] which could be called green synthesis of CdS nanocrystals without heavy metal ions waste water. However, there is still a broad research space in the synthesis of QDs by MST method.

Herein, we demonstrated a simple, rapid and green strategy for the preparation of highly fluorescent CdSe/polyvinyl pyrrolidone (PVP) powders via MST method for the first time. This method is of the following advantages: (1) we set up a new kind of line-line one dimensional (1D) fiber microreactors (noted as $1D_L$-$1D_L$), which can facilely produce QDs through fiber-fiber contact reaction without waste water generation. (2) In contrast with traditional method (reaction temperature over 300 °C), the formation conditions of CdSe QDs herein are simple, energy saving and mild (reaction temperature 110 °C) as well as the PL arrays of the microfiber can be simultaneously generated. (3) This solid-solid reaction between two microfibers via MST provides an easy platform to produce CdSe QD powders in large scale. Besides, we further constructed quantum dots doping microarray via knot contact reaction (noted as $1D_k$-$1D_k$), which can be applied in selective detection toward different kinds of metal ions including Zn^{2+}, Mn^{2+}, Pb^{2+}, Cu^{2+}. For practical application, we grinded in-*situ* CdSe QDs microfibers to produce CdSe hybrid powders, which can be applied in construction of white light-emitting diode (WLED). Therefore, the MST paves a new way for large scale realization of robust QD powders, which is applicable in nanocrystal phosphors, sensor, display and biological field.

2. Experimental

2.1 Materials

Cadmium acetate dihydrate ($Cd(Ac)_2·2H_2O$, 98.5%), polyvinyl pyrrolidone (PVP, M_n=1.3x10^6, K88-96), ethanol (99.7%), selenium powder (Se, 99.9%), tributylphosphine (TBP, 90%), zinc acetate dihydrate ($Zn(Ac)_2·2H_2O$, 99.0%), manganese(II) chloride tetrahydrate ($MnCl_2·4H_2O$, 99.0%), cupric chloride dihydrate ($CuCl_2·2H_2O$, 99.0%), leadacetate trihydrate ($Pb(Ac)_2·3H_2O$, 99.5%) were purchased from standard commercial suppliers, all chemicals were used as received.

2.2 Preparation of CdSe/PVP microfibers via $1D_L$-$1D_L$ microreactor

There are numerous polymers used as a carrier for microfluidic spinning such as polyvinylpyrrolidone (PVP), polycaprolactone (PCL), polylactic acid (PLA), polyurethane (PU) and polymethyl methacrylate (PMMA). Herein, we chose water-soluble PVP as the carrier. Meanwhile, ethanol was selected as solvent of PVP, because of its good solubility with TBP and the appropriate viscosity of PVP ethanol solution. First of all, 3.0 g PVP powders were dissolved in 10.0 g ethanol. After 2 hours mechanically stirring, a uniform and transparent 23 wt% PVP solution was obtained at room temperature. Subsequently, 2.0 g 23 wt% PVP solution and 0.2 g cadmium acetate dihydrate ethanol solution (0.2 mol L^{-1}) were transferred into a 5 mL beaker, mixed well to prepare PVP-Cd^{2+} spinning solution. Se-TBP was prepared by dissolving 0.0132 g selenium powders in 1 mL TBP and the corresponding Se-TBP spinning solution was formed by mixing 0.2g Se-TBP and 2g 23% PVP solution. Then two kinds of spinning solutions were respectively loaded into two syringes (10 mL) with 20G stainless steel needle. A clean glass as a collector installed in the stepmotor as closely as possible from the needle, the flow velocities of polymer phase and the motor speed were fixed at 0.1 mL h^{-1} and 600 rad min^{-1} under a constant voltage, respectively. Through optimization of the process, PVP-Cd^{2+} microfibers were formed and used as the first layer. The second layer Se-TBP microfibers with the same diameter were covered on the PVP-Cd^{2+} microfibers, then Cd^{2+} and Se-TBP were mixed at the fiber-fiber contact area. Exposure to 110 ^{o}C, they diffused into close enough proximity to undergo chemical reaction. After 30 min, highly fluorescent CdSe QD lines were observed under fluorescence microscope. What's more, holding the diameter of PVP-Cd^{2+} microfibers unchanged, "Janus microfibers" could be obtained by augmenting the motor speed to 800 rad min^{-1} to fabricate Se-TBP microfibers with thinner diameter. The microfiber diameters and motor speed relations are referred to the reported literature.[15]

2.3 Synthesis of CdSe QD microarrays *via* $1D_k$-$1D_k$ microreactor

The preparation method of spinning solution followed the same steps specified above. Ordered PVP-Cd^{2+} microfibers were received on a rotating motor-driven slide glass substrate as the first layer. Adjusting the position of the glass, Se-TBP microfibers were used as the second layer aligned in the vertical direction to form approximate orthogonal cross-over microarrays. The microarrays, on the one hand, served as mixing junction of two microfibers, on the other hand, acted as a microreactor, when the microarrays heated at 110 ^{o}C for 30 min, chemical reaction occurred to produce fluorescent CdSe QDs *in-situ*.

2.4 Fluorescent response of CdSe QDs toward metal ions

Firstly, 0.1 mol L^{-1} (M) zinc acetate, manganese chloride, cupric chloride and lead-acetate ethanol solutions were prepared, respectively. Subsequently, a certain amount of cadmium acetate was added to form 0.2M cadmium acetate ethanol solutions. Eventually, 0.01M, 0.05M, 0.1M of lead-acetate and 0.01M, 0.03M, 0.05M of cupric chloride respectively mixed with 0.2M cadmium acetate ethanol solutions were produced. Analogously, Se-TBP and spinning solution were prepared completely following the same steps as above. Metal ions doped CdSe QDs were fabricated in the same manner using $1D_k$-$1D_k$ microreactors. These knots were taken to fluorescence measurements.

2.5 Preparation of WLED

The blue GaN-based LED chip with the peak wavelength centered at 460 nm was attached on the bottom of the LED bases. The two threads on LED were prepared to connect to the power supply. Afterwards, the thermocurable resin was mixed with the CdSe/PVP powders and put in a vacuum chamber to remove the bubbles. The CdSe/PVP/silicone mixtures were dispensed on the LED chip and thermally cured at 120 ^{o}C for 1 h. ZWL-600 instrument with integral sphere was used to measure optical performances.

2.6 Characterization

1.1.1 Transmission electron microscopy (TEM)

TEM images were taken using JEOL JEM-2100 transmission electron microscope. Taking off the CdSe QD lines and dissolving them in water, a drop of the solution was deposited onto a copper grid, afterwards transferring it into the TEM sample chamber. The size of CdSe QDs was estimated by averaging individual particles using Gatan Digital Micrograph software (Gatan, Pleasanton, CA).

1.1.2 Spectroscopy

The fluorescence images and microstructures of fluorescent microfibers were obtained using a Zeiss AXIO 5 imager optical microscope. Fluorescence spectrum was measured on a laser scanning confocal microscope (LSCM). Time-resolved fluorescence decay curves were acquired based on the leica SP5 FLIM system using a 405 nm laser as the excitation source.

1.1.3 SEM measurement

The morphology of knot was observed by scanning electron microscopy (SEM) using a Hitachi S-4800 scanning electron microscope.

1.1.4 EDS measurement

Energy dispersive X-ray spectroscopy (EDS) data were obtained from the samples prepared for TEM.

3. Results and discussion

MST provides an excellent platform for the facile organization of polymer solution and nanoparticles into 1D organic-inorganic hybrid materials (panoramic image see Fig. S1 in the Supporting Information). The formation process of highly fluorescent CdSe QDs by MST method under 110 ^{o}C is illustrated in Fig. 1. Particularly, there exist no cadmium solution appearing in this process, and fluorescent CdSe QDs are still done by MST, being more desirable for health and environment. Fig. 1a shows the synthesis of CdSe/PVP microfibers by using $1D_L$-$1D_L$ contact QD microreactor. The highly fluorescent CdSe/PVP microfibers were then grinded to be the powders, serving as phosphors for constructing WLED. Another model for synthesis of CdSe QD arrays is with help of knot microreactors derived from junctions of fiber lines (Fig. 1b). As seen in Fig. 1b, these knots containing CdSe QDs can be applied to detect different kinds of metal ions, serve as a role of "test paper". Fluorescence quenching was observed when Pb^{2+} ions appeared in the knots. Nevertheless, when mixing Cu^{2+} ions, partially fluorescent quenching and red shift of characteristic peaks (about 50 nm) simultaneously appeared. The method offers an available strategy for green synthesis of CdSe QDs in a controllable fashion.

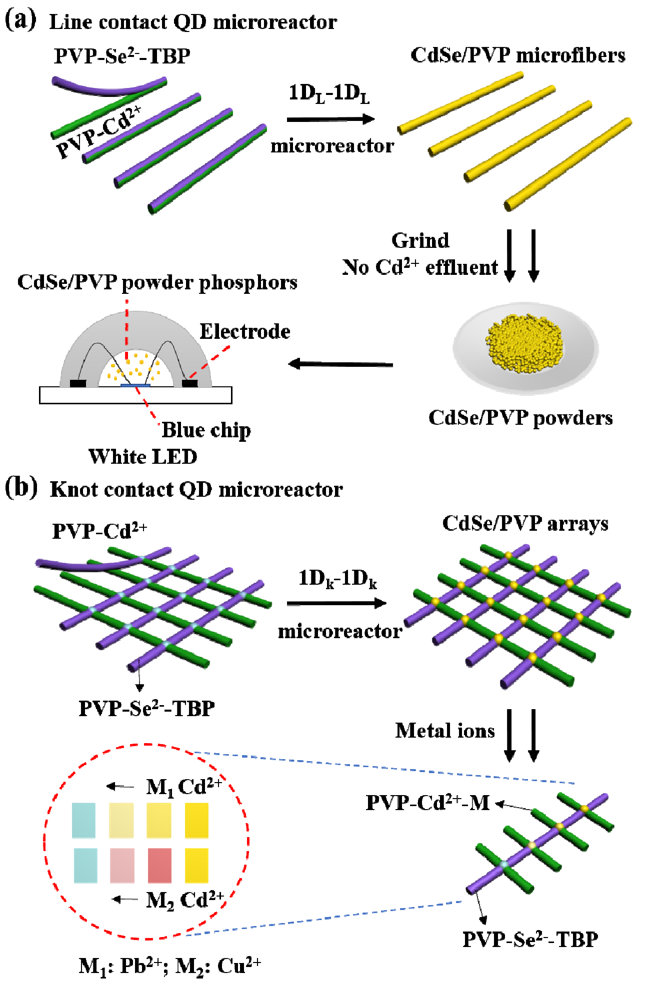

Fig. 1 Schematic representation of the route for the synthesis of PL CdSe QDs. (a) The weaving of $1D_L$-$1D_L$ microreactors to prepare CdSe/PVP microfibers and their application in WLED. (b) Illustration of the specific procedure for preparing CdSe QD arrays on $1D_k$-$1D_k$ microreactors and their applications in sensitive and selective detection to metal ions.

3.1 Synthesis and characterization of CdSe hybrid fibers

In the first part of the experiment, we investigated the fluorescent CdSe QDs, which were synthesized via $1D_L$–$1D_L$ microreactor (Fig. 2). Initially, PVP-Cd^{2+} (23 wt%) microfibers were spun as the first layer on a glass substrate. The PVP-Se-TBP (23 wt%) microfibers with the same diameter were used as the second layer and arranged in parallel on PVP-Cd^{2+} microfibers (Fig. 2a). Then fluorescent CdSe QDs with bright yellow fluorescence were formed along the microfibers at 110 °C for 30 min (Fig. 2c) and the diameter of these fluorescence microfibers is as small as 30 μm. In addition, by adjusting the motor speed, relatively thinner PVP-Se-TBP (23 wt%) microfibers with a diameter of 20μm were fabricated. Interestingly, we obtained Janus microfibers by arranging the thinner PVP-Se-TBP microfibers on the top of thick PVP-Cd^{2+} microfibers (Fig. 2b). After the reaction between two kinds of fibers, CdSe QD fluorescent microfibers were gradually formed on the overlapping section (Fig. 2d). Based on the above results, we speculated that the $1D_L$-$1D_L$ microreactors may furnish a new approach to fabricate versatile fluorescent arrays, and the method might be applied in the manipulation of fluorescent hybrid fibers and QD hybrid powders.

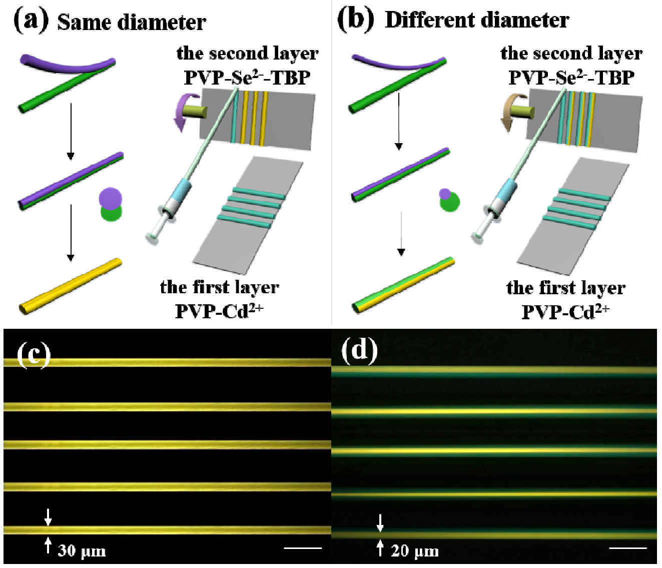

Fig. 2 (a, b) Schematic illustration of the principle for synthesizing CdSe QDs from $1D_L$–$1D_L$ microreactor. Fluorescence microscope images of $1D_L$–$1D_L$ microreactors for the fabrication of CdSe QDs loaded fluorescent microfibers: PVP-Cd^{2+} microfibers and PVP-Se-TBP microfibers of the same diameter (c) and different diameter (d). Scale bar: 100 μm.

To further understand this procedure, the optical properties of as-synthesized CdSe QDs were measured using LSCM. The PL spectra of PVP microfiber and CdSe QDs were studied (Fig. 3a), and the PL emission peak with the maximal intensity of the CdSe QDs focus on 550 nm. However, the PVP microfiber, which was not participated in the reaction, exhibits a feeble blue fluorescent of organic material ($\lambda_{em} = 490$ nm). In addition, to gain more insight into their PL emission mechanism, a multidimensional time-correlated single-photon counting (TCSPC) methodology was employed to evaluate the fluorescence lifetime of the CdSe QDs. As seen in Fig. 3b the decay traces for the CdSe QDs were evaluated by biexponential functions Y(t) based on nonlinear least-squares analysis which can be expressed by the followed function:[16, 17]

$$Y(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2)$$

Where α_1, α_2 are fractional contributions of time-resolved decay lifetimes τ_1, τ_2. The average lifetime $\bar{\tau}$ was calculated using equation:

$$\bar{\tau} = \frac{\alpha_1\tau_1^2 + \alpha_2\tau_2^2}{\alpha_1\tau_1 + \alpha_2\tau_2}$$

As a result, we calculated the average lifetimes of CdSe QDs to be 4.37±0.05ns, which is somewhat smaller than that of CdSe QDs control sample synthesized by traditional methods.[18] Typically, the shorter lifetime is caused by the intrinsic recombination of initially populated core states while the longer lifetime is ascribed to the involvement of the surface trap states located in the forbidden band, which is caused by dangling bonds or poorly passivated surfaces, generally leading to the tails of the PL spectra.[19, 20] Therefore, it indicates that the smaller PL lifetime of as-synthesized CdSe QDs was caused by the intrinsic recombination of excitons. In order to prove the existence and distribution of the CdSe QDs, we employed transmission electron microscopy (TEM) measurements to indicate their morphology. The as-prepared CdSe QDs, with a well disperse, are spherical (Fig. 3c). As shown in the inset of Fig. 3c, the high-resolution TEM (HRTEM) image of an individual QD reveals the well-resolved lattice fringes throughout the whole particle, confirming high crystalline structure of the CdSe QDs. Further corroboration from the energy dispersive X-ray spectroscopy (EDS) (Fig.2d) indicates the QDs are composed of cadmium and selenium. Fig. 3e presents the corresponding histogram of CdSe QDs size distribution. The average particle diameter was observed to be 2.8 nm.

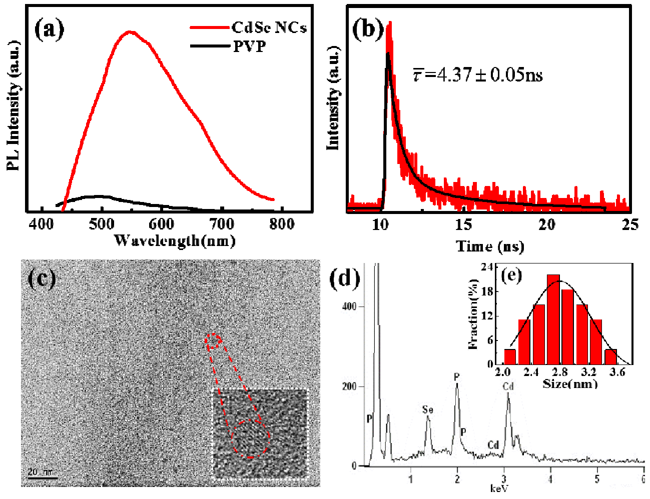

Fig. 3 (a) PL emission spectra and (b) time-resolved fluorescence decay curves of CdSe QDs prepared via $1D_L$–$1D_L$ microreactor. (c) TEM images of the as-prepared CdSe QDs, and the inset in (c) is the corresponding HRTEM image of a single QD (d) The EDS spectrum of CdSe QDs. (e) The size distribution histogram of CdSe QDs.

3.2 The optimum reaction conditions and stability

In order to obtain the best PL performance of CdSe QDs, the effects of different experiment conditions were thoroughly investigated, such as the reaction time, temperature and different molar ratios of Cd^{2+}/Se^{2-}. As shown in Fig. 4a, the PL intensity of the CdSe QDs improves with the increase of the reaction time. After 30 min, the increase of PL intensity of CdSe QDs is not obvious, so we could conclude that 30 min is the best reaction time. We can see from Fig. 4b that there is no reaction in the fiber junction containing Cd^{2+} and Se-TBP when the two overlapped microfibers are kept at ambient temperature. However, with the increase of temperature, the PL intensity at the overlapped fiber increases. Taking melting point of PVP into consideration, the ideal condition for producing CdSe QDs with good PL properties is 110 °C (Fig. 4b). In order to further optimize the PL performance of the CdSe QDs, we found that the CdSe QDs with a Cd^{2+}/Se^{2-} optimal molar ratio of 1.23:1 had the strongest PL emission intensity (Fig. 4c). In addition, CdSe QDs via $1D_L$–$1D_L$ microreactors have a good chemical stability (Fig. 4d). No obvious red shift of the PL emission peaks is observed by prolonging the exposure time in the air atmosphere, attributed to no particle growth of CdSe QDs in the room temperature. Besides, the confined space of microreactors prevents CdSe QDs from PL quenching.

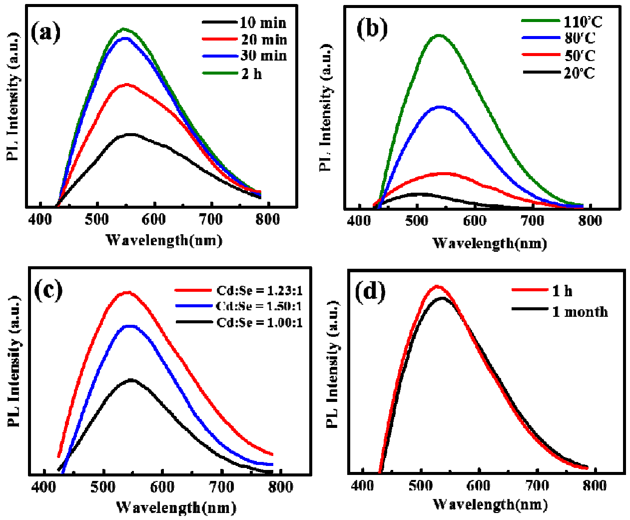

Fig. 4 PL emission spectra of CdSe QDs with different (a) reaction time; (b) temperature; (c) Cd^{2+}/Se^{2-} molar ratios and (d) exposure time.

3.3 CdSe microfiber arrays

The second set of experiments was concentrated on the construction of microfiber arrays by MST. Fig. 5a is a schematic diagram illustrating the equipment of the microfluidic-spinning technique. During spinning, the spinning solution was placed into a digital fluid controller, and the fluid volume was accurately controlled by the syringe pump device. A slide glass as a collector was installed on a stepmotor, by optimizing motor speed parameters, parallel microfibers were obtained. In detail, PVP-Cd^{2+} (23 wt%) microfibers with a diameter of 30 μm were spun into lateral as the first layer on a glass substrate, and PVP-Se-TBP microfibers were woven in the vertical direction as the second layer. As expected, bright yellow fluorescent CdSe QD arrays were generated at the contact knots identified as $1D_k$-$1D_k$ microreactors (Fig. 5b). Fig. 5c, 5d are the fluorescence microscopy images corresponding to the phenomenon before and after reaction, directly showing bright yellow fluorescent CdSe QD 4x4 arrays. Similarly, CdSe QD 3x7 arrays were constructed with $1D_k$–$1D_k$ microreactors as depicted in Fig. 5e. Fig. 5f is an enlarged image of $1D_k$–$1D_k$ microreactor. The size of the knot is as small as 34x30 μm^2 and the corresponding chemical reaction is carried out within an ultra-small space (about 10^{-14} m^3). The formation process of fluorescent CdSe QDs clearly demonstrate that the knots not only serve as mixing junction of two microfibers, but also act as a microreactor. When heated, chemical reaction occurred to produce amounts of CdSe QDs *in-situ*. As shown in Fig. 5g, it is the typical SEM image of microfiber knot, and it shows that that PVP microfibers with a diameter of 30 um can be loaded with Cd^{2+} and Se-TBP, and that the knots formed between crossed microfibers can function as the microreactor.

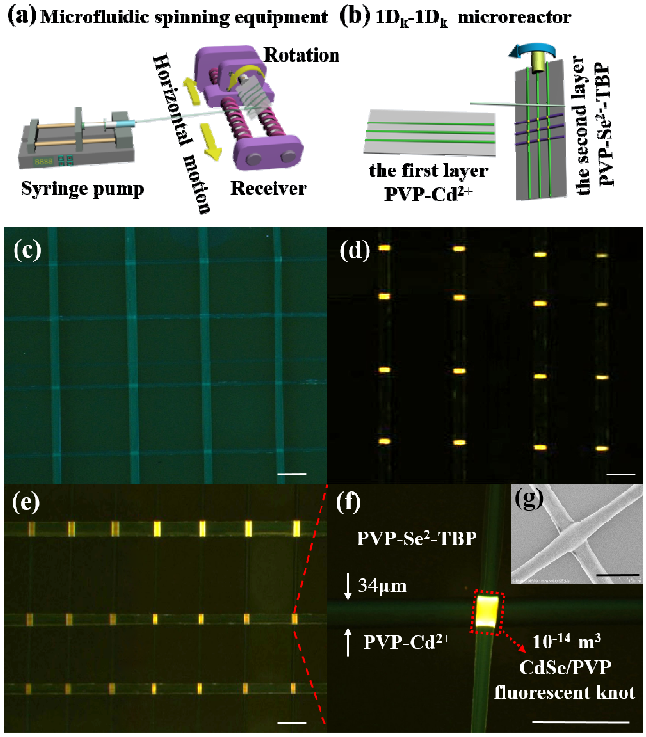

Fig. 5 (a) Schematic representation of the microfluidic-spinning device. (b) The principle of the preparation of fluorescent CdSe QDs at the knots of crossed PVP microfibers. (c, d) Fluorescence microscope images of 4x4 arrays for the fabrication of CdSe QDs before and after reaction (e, f) Fluorescence microscope images of 3x7 CdSe QD arrays and partial enlarged image; (g) SEM image of microfiber knot. Scale bars: 100 μm.

3.4 CdSe QDs sensing of metal ions

We also demonstrated the as-prepared CdSe QDs exhibit sensitive and selective detection to different metal ions as "test paper", including Zn^{2+}, Mn^{2+}, Pb^{2+} and Cu^{2+}. Fig. 6a depicts the fluorescence microscope images when adding 0.1M Zn^{2+}, Mn^{2+}, Pb^{2+} and Cu^{2+} into spinning solution. In Fig. 6a, we could clearly find that the addition of Zn^{2+} results in a faint enhancement of the PL intensity of CdSe QDs, which might be attributed to the surface passivation of these inorganic nano-materials.[21] For Mn^{2+}, a feeble decrease of PL intensity was observed. Whereas, when the same concentration of Pb^{2+} or Cu^{2+} present in the spinning solution, PL intensity of CdSe QDs was almost entirely quenched. This PL quenching could be ascribed to the competitive TBP binding between the QD core and Pb^{2+} or Cu^{2+}. The relative fluorescence intensity $[(I-I_0)/I_0]$ of CdSe QDs with the addition of Zn^{2+}, Mn^{2+}, Pb^{2+} and Cu^{2+} in the spinning solution, where I_0 and I are the PL intensity in the absence and presence of metal ion in the spinning solution are shown in Fig. 6b. The corresponding PL emission spectra of CdSe QDs response to different metal ions are shown in Fig. 6c. To further use the "test paper", different concentrations of Pb^{2+} and Cu^{2+} were prepared and added to the spinning solution. As a result, the degree of fluorescence quenching is enhanced with a rise in the concentration of Pb^{2+}. However, the presence of Cu^{2+} in the spinning solution not only results in the same phenomenon above, but also causes the emission peak red shift to longer wavelength, which may be attributed to the quantum confinement effect of an electron−hole pair.[22] Fig. 6d, 6g intuitively show this phenomenon. Fig. 6e, 6h and Fig. 6f, 6i are the corresponding fluorescent histograms and PL emission spectra of CdSe QDs response to Pb^{2+} and Cu^{2+}, respectively. The selective response toward different ions, especially toward Pb^{2+} and Cu^{2+}, prompted us to assume that the CdSe QDs could be suitably used as metal ion probes.

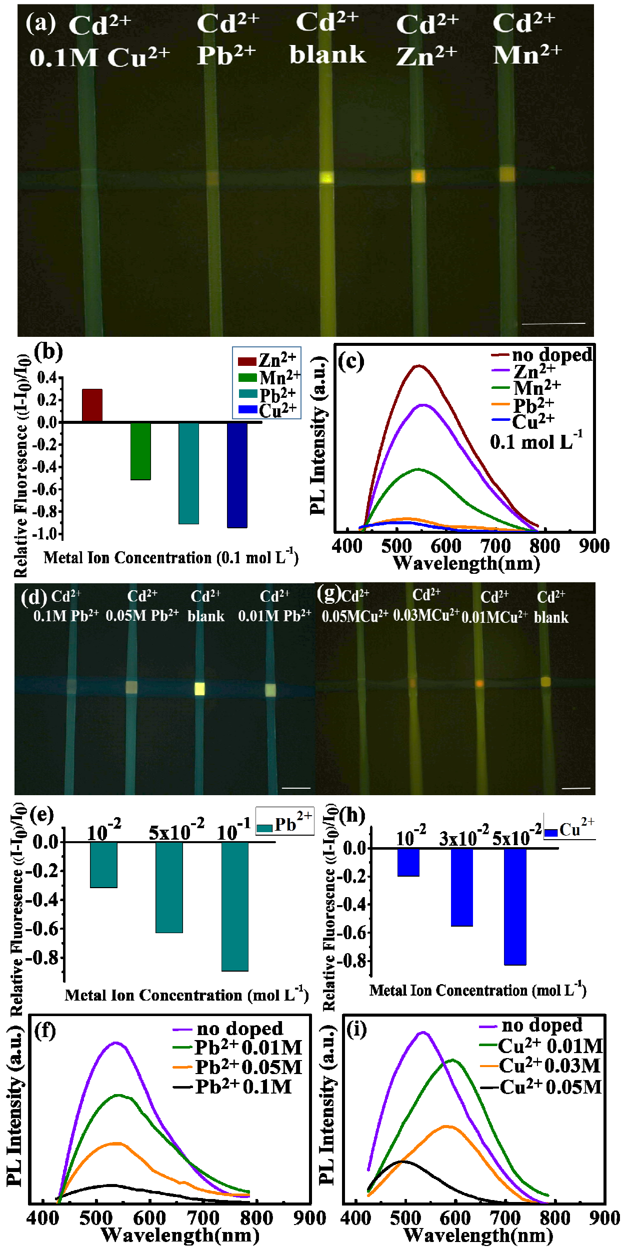

Fig. 6 (a, d, g) Fluorescence microscope images of CdSe QDs sensitive to different metal ions. (b, e, h) Fluorescent histogram. (c, f, i) Corresponding PL emission spectra of CdSe QDs. Scale bars: 100 μm

3.5 Applications of CdSe/PVP hybrids in WLED

The present approach for synthesis of CdSe QDs by aid of solid-solid microfiber contact microreactors is simple, green, along with no residual heavy metal waste water. After reaction, the products with bright PL property could be easy to produce hybrid PL powders by simply grinding. We employed these powders as the phosphor for the construction of WLED. Fig. 7a, 7b are the digital photos of CdSe/PVP powders under daylight and UV light, bright yellow fluorescent CdSe/PVP powders could be intuitively observed. As shown in Fig. 7c, bright white light produced by LED lamp illuminates an image in the dark. We used CdSe/PVP powders in coating on a 460 nm UV chip and acting as light converters. The blue light emitted from GaN chip can be changed into white light when passing through the CdSe/PVP/silicone mixtures and the color rendering index (CRI) up to 69.9 at 350 mA. The coordinate of the WLED is located at (0.3410, 0.3317) (Fig. 7d), belonging to the white gamut. Two peaks are observed from emission spectrum of the WLED (Fig. 7e). One comes from the CdSe/PVP powders and another originated from GaN bule chip. Thus it can be seen that these CdSe/PVP powders are promising candidate of phosphor for WLED. More importantly, these CdSe/PVP powders produced by MST are easily scaled up, along with no Cd^{2+} effluent generation, which might have extensive industrial application.

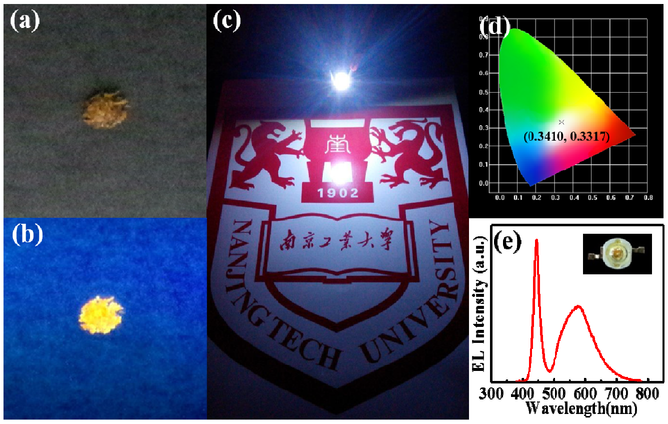

Fig. 7 The digital photos of CdSe/PVP powders under daylight (a) and UV light (b). (c) The photograph of as-prepared WLED device in the dark. (d) Placement of the WLED emission spectra on the CIE 1931 chromaticity chart. (e) EL spectrum of WLED based on CdSe/PVP powders operated at 350 mA, inset: photographs of WLED under daylight.

4. Conclusions

In summary, we have demonstrated a rapid, facile and green strategy to produce solvent-free bright fluorescent CdSe QD hybrid fibers and arrays *via* MST. Compared with CdSe QDs from traditional hot injection method, the MST approach could effectively reduce the synthesis temperature from 300 °C to 110 °C, making this way energy saving and easy to perform without any metal ions waste water. These as-prepared CdSe QDs had a well-dispersed spherical nanostructure with a mean size of 2.8 nm. Moreover, we found that CdSe QD arrays are responsive to different kinds of metal ions including Zn^{2+}, Mn^{2+}, Pb^{2+}, Cu^{2+}, especially on particularly selective fluorescence sensing toward Pb^{2+}, Cu^{2+}. More importantly, we can facilely grind the CdSe/PVP microfibers into hybrid fluorescent powders, allowing them to be as phosphors for fabrication of the WLED. The method is versatile, and various hybrid QDs loaded microfiber arrays can utilize this principle and may yield good examples to fabricate other hybrid fluorescent powder with robust applications, such as sensors, LED, fluorescent label and biological field.

Acknowledgements

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ARTICLE

Fabrication of highly fluorescent CdSe quantum dots via solvent-free microfluidic spinning microreactors

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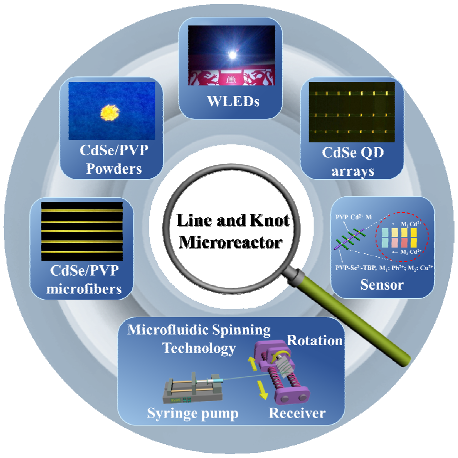

The available method for *in-situ* fabrication of highly fluorescent hybrid materials prepared *via* microfluidic spinning technology (MST) have been demonstrated.