Supporting Information

Facile fabrication of structure tunable bead-shaped hybrid microfibers by a Rayleigh instability guiding strategy

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1. Experimental Section

1.1 Chemicals and Materials

Polylactic acid (PLA, $M_n = 100000$), dichloromethane (CH₂Cl₂), polyvinylpyrrolidone (PVP, $M_n = 1300000$), sodium sulfide nonahydrate (Na₂S·9H₂O), cadmium chloride (CdCl₂·2.5H₂O), ethanol (CH₃CH₂OH) and acetone were of analytical grade, commercially available and used without any further purification. Purified water with a resistance greater than 18 M Ω cm was used in all experiments. Polystyrene (PS) solution was controllably prepared using styrene by emulsion polymerization.¹ Fluorescent carbon quantum dots (CQDs) was synthesized by our previously reported methods.^{2,3}

1.2 Fabrication of bead-shaped microfibers via physical interaction

Polylactic acid was chosen as the polymer substrate. 3 g PLA was dissolved in 10 g CH_2Cl_2 to prepare 30 wt% solution at ambient temperature in an appropriate containers, and then PLA polymer fiber arrays was directly drew from the high concentration PLA/CH₂Cl₂ solution (length: 30 cm, diameter: 150 um) and used as a solid phase. The sliding liquid phase was fluorescent CQDs solution. Typically, a

CQDs loaded drop was put on the middle of the solid fiber phase. The drop broke up into many little droplets due to its surface tension, gravity and friction force between the droplets and fibers. After evaporation, the sliding liquid phase form solid bead along the microfiber, contributing bead-shaped fluorescent hybrid microfibers with cylindrical microstructures. When PS drop replaced CQDs solution as sliding liquid phase to fabricate functional fiber in the same way, bead-shaped hybrid microfibers with core/shell microstructures have been fabricated.

1.3 *In-situ* fabrication of QDs loaded fluorescent hybrid microfibers via 0D-1D dot-line contact reactor

A typical synthesis of dot-line contact reactor is as follow: 0.228 g CdCl₂·2.5H₂O was dissolved in purified water to form 0.1 M Cd²⁺ solution, and 0.5 mL Cd²⁺ solution was added into 10 mL asprepared 30 wt% PVP/CH₃CH₂OH solution. 0.224 g Na₂S·9H₂O was dissolved in 2 g of purified water in glass spawn bottle to prepare 0.1 M S²⁻ solution. According to above method, we drew a PVP polymer fiber containing Cd²⁺ in the vertical direction. And then, a sulfur source drop was put on the middle of Cd/PVP polymer microfibers. With the evaporation of the solvent, at the interface between the S²⁻ solution and Cd/PVP fiber, diffusion and reaction of Cd²⁺ and S²⁻ occurred. As a result, bead-shaped CdS/PVP hybrid microfibers with alternative fluorescent patterns and arrays were obtained.

1.4 Characterizations

The optical images were taken using an Olympus MVX10 stereomicroscope with color CCD camera. Photographs and observations of microstructures of fluorescent microfibers were obtained using a Zeiss AXIO 5 Imager optical microscope. Photographic images of the samples were captured by digital camera (100IS, Canon) or stereomicroscope (SZM45). Photoluminescence (PL) spectra and microscopic views of the fluorescent microfibers were achieved on a laser scanning confocal microscope (LSCM). The morphology of the microfibers were observed by scanning electron microscopy (SEM) with a QUANTA 200 (Philips-FEI, Holland) instrument at 20.0 kV. Transmission electron microscopy (TEM) observation was performed with a JEOL JEM-2010

transmission electron microscope. Reflection spectra of photonic crystals were taken by using an optical microscope equipped with a fiber optic spectrometer (Ocean Optics, USB4000).

2. Supplementary Figures

2.1 Rayleigh instability



Fig. S1 Schematic diagram of evolution of the fluid based on Rayleigh instability.

A fluid jet extruded from an orifice of radius R accelerates under the influence of gravity. Its shape is influenced both by the gravitational accelerationg and the surface tension. The cylindrical column of liquid (1) retains its circular cross-section but with diameter varying along its length (2). The changed surface curvature produces a change of pressure within the jet needed to balance the action of surface tension. Then, the external pressure is a maximum where the section is minimum (a) and a minimum where the section is maximum (b). The pressure gradient thus amplify the original disturbance. Lastly, the water jet breaks-up into discrete drops (3).⁴

The explanation of this Rayleigh instability begins with the existence of tiny perturbations in the stream. Whether a component decays or grows, and how fast it grows is entirely a function of its wave number and the radius of the original cylindrical stream. So we focus on the dependence on the two most important parameters, the wave number and the Weber number. By properly adjusting the driving frequency, we can choose a wavelength λ .

The wave number

$$x = \frac{2\pi R}{\lambda} \tag{1}$$

If x < 1, the jet is unstable to the corresponding perturbations, and at small viscosities, $x_R = 0.697$

the Rayleigh mode perturbations grow fastest. For x > 1 irregular breakup is observed.

The Weber number

$$We = \frac{\rho R U^2}{\sigma} \tag{2}$$

(ρ = density, U = basic velocity, R = nozzle radius, σ = surface tension) is of great importance because of the influence of the surface tension.⁵

2.2 Fabrication of bead-shaped CQDs/PLA fluorescent hybrid microfibers



Fig. S2 Two kind of cylindrical segment structures of CQDs doped RDBFs and their corresponding schematic diagrams and fluorescent micrographs (scale bar = $500 \mu m$).

Interestingly, by adjusting the flow velocity of sliding phase, two kind of bead-shaped microfibers with uniform bead structure and non-uniform bead structure have been obtained. Since water is the only liquid used in the experiment, the nozzle used in this work had a radius 1.2 mm, the only variable parameters remaining is the basic velocity U. Based on the above principles, by adjusting the flow velocity of sliding phase, we achieved two kind of bead-shaped microfibers with uniform bead structure and non-uniform bead structure.



Fig. S3 Optical image (a) and fluorescent micrograph (b) of alternative blue-and-red microfiber with blue CQDs and PLA microfibers doped with red fluorescence dyes (scale bar = 500μ m).

2.3 Fabrication of bead-shaped PS/PLA hybrid microfibers



Fig. S4 Optical micrographs of PS doped RDBFs array constructed by PS microspheres with diameter of 290 nm (a) and 320 nm (b) (scale bar = 1 mm). The reflection spectra of PS with diameter of 290 nm and 320 nm doped RDBFs.

Reflection peaks, named stop-band, are clearly visible and located at 578 and 605 nm, respectively.⁶ As an approximation, the wavelength of the reflection peak can be calculated considering a modified version of the Bragg's law:⁷

$$\lambda = 1.633 \, d(n_{\rm microspheres}^2 f + n_{\rm void}^2 (1 - f) - \sin\theta)^{1/2}$$
(3)

Where λ is the peak position, d is the diameter of the PS microsphere, microspheres and void are the refractive indices of the microspheres and voids (air in our case), respectively. f is the fraction, and the value is 0.74 in the structure. θ is the angle between the incident light and the normal to the (111) planes (at the surface of the PCs).



Fig. S5 Optical micrographs of bead-shaped core/shell PS doped RDBFs with uniform segment structure under different PS concentrations: 5%, 20% and 30% (scale bar = 500μ m).

As shown in Fig S5 ESI[†], at a low concentration of 5%, the bead-shaped hybrid microfibers with uniform segment structure presented core/shell microstructures. With the increase of the PS concentration, the diameter of PS beads along the fiber increased and bead-shaped core/shell microfibers with larger shell size were obtained.



Fig. S6 A schematic description of the fabrication process of bead-shaped hybrid microfibers. t_i : the time interval between two liquid drops; t_e : the time of the evaporation; ω : rotating motor speed; S_f : the rise distance of the fiber; S_b : the distance between two beads.

For a better description of the fabrication process of bead-shaped hybrid microfibers, we provided more details of the operation. As depicted in Fig. S6 ESI[†], every liquid drop would roll along the fiber with a distance of 15 cm. Once we dripped a drop, the next drop was dripped at the moment that the nethermost formed bead reached the middle of fiber, so the latter liquid drop would not affect or recoat the beads formed by the former liquid drop. Obviously, the time interval between two liquid drops was only impacted by the rising velocity of the fiber which was set by the rotating motor speed ω . The width of the glass substrate is 0.025 m, so the average rising velocity of the fiber is 0.05 ω and the time interval t_i between two liquid drops should be t_i=0.15/(0.05 ω)=3/ ω . Because the discrete droplets must have enough time to reach stable state before taken into arrays, the time of the evaporation t_e should less than t_i. At an extreme situation that just at the time the nethermost formed bead rose to the middle of fiber, its evaporation accomplished completely, namely t_i=t_e, the maximum of ω_m could be 3/t_e.



Fig. S7 The evolution of a droplet from the moment of coating on the fiber to stable state along with time (scale bar = $100 \mu m$). The concentration of PS is 10 %.

For example, as shown in Fig. S7 ESI[†], once we used PS with concentration 10 % and diameter of 290 nm, the droplet took $t_e = 6.25$ s (0.104 min) to achieve a stable green color, the maximum of ω_m could be 3/0.104=28.8 rad/min. In our manuscript the rotating motor speed was set at 10 rad/min, and then in this case, t_i=18 s.

In order to better investigate the structure of the bead-shaped microfiber, we fixed the polymer phase flow rate at 0.1 mL·h⁻¹ and mainly studied the effects of rotating motor speed on the distance between two neighboring beads. As we descried before, every liquid drop would roll along the fiber with a distance of 15 cm, so the time one drop undergoes is $\sqrt{0.15 \times 2/g} = 0.173$ s (2.88×10⁻³ min) (ignoring the effect of friction between drop and fiber). The rising velocity of the fiber is 0.05ω , so after one drop finished its journey, the rise distance of the fiber S_f is $0.05\omega \times 2.88 \times 10^{-3} = 1.44 \times 10^{-4}\omega$. When ω was set at 10 rad/min, S_f would be 1.44 µm. As shown in the manuscript, the distance between two neighboring beads S_b is about 500 µm. Apparently, the rise distance of the fiber S_f is much more less than the distance between two beads S_b . In other words, among the progress of fabricating bead-shaped hybrid microfibers, the movement of fiber (rotating motor speed: 5-25 rad·min⁻¹) has little influence on the distance between two neighboring beads. As a result, the distance between the beads remain unchanged in a falling process.

2.4 In-situ fabrication of bead-shaped CdS/PVP fluorescent hybrid microfibers



Fig. S8 Optical micrographs of 0D-1D microreactors: (a) reacted and (b) unreacted CdS QDs (scale bar = 1 mm).



Fig. S9 Time-resolved fluorescence decay curve of the corresponding fluorescent CdS QDs doped RDBFs.

Decay traces for the samples were well fitted with biexponential function Y(t) based on nonlinear least-square, using the following expression.⁸

$$Y(t) = \alpha_1 \exp\left(-t / \tau_1\right) + \alpha_2 \exp\left(-t / \tau_2\right) \tag{4}$$

Where α_1 and α_2 are fractional contributions of time-resolved decay lifetimes τ_1 , τ_2 . And, average lifetime could be concluded from the equal (5):

$$\overline{\tau} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2}$$
(5)



Fig. S10 The HRTEM images of CdS QDs.

The well-resolved lattice fringes in the HRTEM picture (Fig. S8 ESI[†]) further indicate excellent monodispersion and finely preserved crystalline structures of QDs in PVP polymer microfibers.

Table S1 The particle size distributions and its corresponding frequency.

x/nm	f
2.3-2.6	3
2.6-2.9	5
2.9-3.2	10
3.2-3.5	30
3.5-3.8	32
3.8-4.1	10
4.1-4.4	7
4.4-4.7	3

The coefficient of variation (CV) of the CdS QDs particles can be calculated.

$$S = \sqrt{\frac{\sum fx^2 - (\sum fx)^2 / \sum f}{\sum f - 1}}$$

$$(4)$$

$$\overline{x} = \frac{\sum fx}{\sum f}$$

$$(5)$$

$$CV = \frac{S}{\overline{x}}$$

$$(6)$$

Where x is mid-value in every particle size group, f is frequency, s is variance of mean and x is

mean particle size.

The size-distribution diagram and a coefficient of variation (CV) of these nanoparticles of about 12.3% further indicates that the QDs have relatively narrow size distribution.



Fig. S11 Fluorescent properties of CdS QDs doped RDBFs ($\lambda_{ex} = 405$ nm) via 0D-1D microreactor at different reaction time: (a) fluorescence confocal microscopy images (scale bar = 500 µm) and (b) the corresponding PL emission spectra of CdS QDs within 0.5 h, 7 days and 4 months.

3. References

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