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Microreactor Arrays

Microarrays Formed by Microfluidic Spinning as Multidimensional Microreactors**

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Abstract: *The exploration of methods allowing chemical reactions to be carried out at ultrasmall scales is of great scientific and technological interest. We report herein a microfluidic spinning technique for the fabrication of softened-polymer microarrays for use as multidimensional microreactors and the application of these microreactors in the synthesis of fluorescent nanocrystals. Highly aligned microarrays and controlled-angle grids were readily constructed from microfluidically spun polyvinylpyrrolidone (PVP) microfibers. One–zero dimensional (1D–0D), one–one dimensional (1D–1D), and one–two dimensional (1D–2D) microreactors were then produced by the intersections between microfibers and droplets, crossed microfibers, and microfibers and a PVP film, respectively; each component can be doped with different reagents. Specific examples show that these multidimensional microreactors enable the in situ generation of fluorescent nanocrystals without ligands within minutes.*

Micro-/nanostructured fibers have received increasing interest[1] owing in part to their promising applications in sensors,[2] display devices,[3] and specific materials.[4] Until now, efforts to create highly ordered fibrous arrays in an effective manner have mainly focused on electrostatic spinning,[5] a template method,[6] direct drawing,[7] and lithographic printing.[8] Recently, microfluidic spinning technology (MST) has emerged as a powerful platform for the fabrication of micro-/nanofibers with high alignment ratios; this technology shows wide adaptability for a variety of polymers. For example, Kang et al. employed MST to continuously create microfibers with tunable morphological, structural, and chemical features.[9] However, the fabrication and application of polymer hybrid microarrays based on this MST still remain scarce, especially for the design of diverse patterns and new microreactors.

Herein, we present a simple and rapid strategy based on MST for the fabrication of softened-polymer microarrays, and their extension to multidimensional microreactors for the first time. MST offers a straightforward platform for the facile organization of polyvinylpyrrolidone (PVP) into one-dimensional (1D) microstructures. The fluorescent-dye-doped PVP microfibers were readily woven to afford multicolor patterns of parallel arrays and grids. These microfibers could also be loaded with reactants; in this way, three kinds of microreactor arrays, namely 1D–0D, 1D–1D, and 1D–2D microreactors, were constructed at the intersections between microfibers and droplets, crossed microfibers, and microfibers and a PVP film, respectively. Each mixed junction of two components doped with different reagents can serve as an ultrasmall-volume reactor. It is highly desirable to carry out reactions at ultrasmall scales for both fundamental and applied research.[10] Much effort has been devoted to the fabrication of microreactors on the basis of continuous-flow microreactors,[11] microspheres,[12] microfibers,[13] knot reactors,[14] and the template method,[13b] whereas the construction of microreactors by MST has not been reported previously. Moreover, by doping two reagents, a cadmium (or zinc) source and a sulfide source, into the two components, fluorescent nanocrystals (NCs) could be produced directly within these microreactors at ambient temperature. To the best of our knowledge, this is the first example of the in situ generation of fluorescent NCs by diffusion at solid–liquid and solid–solid interfacial junctions in multidimensional microreactors. This MST-based method, which enables chemical reactions to form NCs to be carried out at ultrasmall scales and ambient temperature in a controllable fashion, is potentially important for the development of an environmentally friendly and ligand-free route to fluorescent NCs and may offer fundamental insight into chemistry in confined microreactors.

Figure 1a shows schematically our procedure for the construction of various multicolor fluorescent patterns of microfibrous arrays by MST. Through the optimization of the process parameters (see Figures S1 and S2 in the Supporting Information), the flow velocity of the polymer phase and the motor speed were fixed at $0.1\,\mathrm{mL\,h^{-1}}$ and $800\,\mathrm{rad\,min^{-1}}$, respectively. By the use of MST, parallel alignments and rectangular grids of polymer microfibers doped with different fluorescent dyes can be readily woven at room temperature (Figure 1b–e; see the experimental section in the Supporting Information). Unlike electrostatic spinning,[15] this method is not limited to the use of some uninsulated polymer feedstocks, and no high voltage or heat is required. Besides, grids can be edited with controlled angles by MST to arrange parallel, orthogonal, and arbitrary-angle microarrays (Fig-

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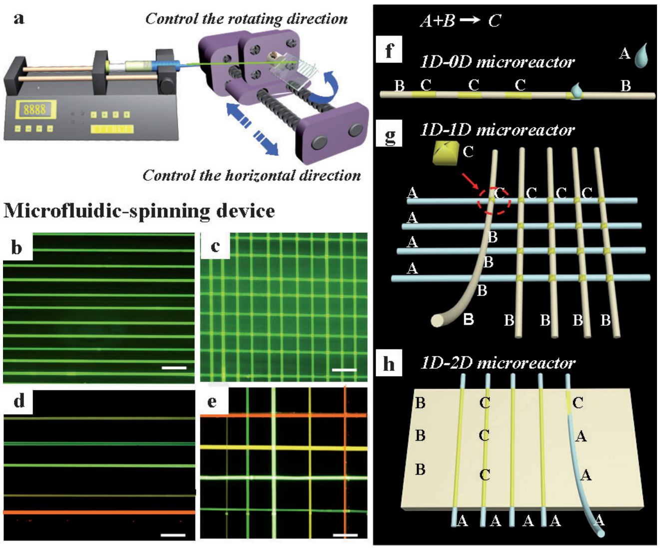

Figure 1. a) Schematic representation of the microfluidic-spinning device. b–e) Fluorescence microscope photographs of parallel microarrays (b,d) and orthogonal grids (c,e) doped with a single fluorescent dye (b,c) and diverse fluorescent dyes (d,e). Scale bars: 100 μm. f) 1D–0D, g) 1D–1D, and h) 1D–2D multidimensional microreactor arrays.

ure 1 b,c; see also Figure S3). For current advances in the fabrication of parallel arrays, the average alignment ratio and misalignment angle of the parallel fibers are 80–95 % and ±1°, respectively,[16] whereas those for the as-prepared aligned microarrays described herein are 99 % and ±1°, respectively. Therefore, this MST provides a more convenient procedure for the weaving of highly aligned and orthogonal PVP microarrays with controlled angles. Moreover, the combination of PVP with different fluorescein derivatives enabled the convenient construction of colorful fluorescent microfiber alignments and grids (Figure 1 d,e), which could have a variety of applications, for example, in molecular sensing, fluorescent display codes, and microreactors.

To construct multidimensional microreactors by MST, we made full use of softened PVP microfibers with a high-ratio surface area (Figure 1 f–h). For the fabrication of 1D–0D microreactors for a reaction $A + B \rightarrow C$, droplets loaded with one reagent (A) were dropped onto microfibers loaded with the other reagent (B) at equidistant intervals (Figure 1 f). A reaction occurs at the junction of droplets and fibers through solid–liquid interfacial diffusion to yield a reaction product (C). Similarly, 1D–1D and 1D–2D microreactors were created at the intersections between crossed microfibers and between microfibers and a PVP film, respectively (Figure 1 g,h). Solvent-vapor-mediated coalescence of the two polymer components at the intersections enables the fusion of the solid–solid interface to form a mixed junction.[10] The reaction happens at the knot junctions of grids in the 1D–1D microreactor (Figure 1 g) and at the line junctions formed between microfibers and the film in the 1D–2D microreactor (Figure 1 h). Specifically, by loading a nonfluorescent cadmium or zinc source (reagent A) into one component of the microreactor and a nonfluorescent sulfide source (reagent B) into the second component of the microreactor, fluorescent CdS or ZnS NCs could be generated in situ at these junctions at ambient temperature to form diverse fluorescent microarrays. The observation of fluorescence emission directly indicates the occurrence of chemical reactions. Typically, homogeneous-phase methods for the preparation of fluorescent NCs highly rely on the introduction of effective ligands. In contrast, this strategy takes full advantage of microreactors with a high specific surface area and a confined space, thus enabling the generation of fluorescent NCs without any ligands. Moreover, the formation of hybrid polymer microarrays with fluorescent patterns by the use of intersection microreactors may offer a new avenue for the construction of ordered multidimensional configurations for various applications, such as optical microsensor arrays[10a] and high-quality display devices.

Equidistantly intermittent microarrays doped with fluorescent CdS or ZnS NCs were created with 1D–0D microreactors (Figure 2). Initially, a solution of PVP (30 wt %) and a cadmium source ($CdCl_2\cdot 2.5\,H_2O$; 0.2 M) in ethanol was microfluidically spun into a microfiber as a reactor substrate. Subsequently, droplets (0.5 mL) containing a trace amount (3.5 μL) of aqueous sulfide ($Na_2S\cdot 9\,H_2O$; 0.05 M) were dropped equidistantly onto the microfiber (Figure 2 a). To prevent excessive diffusion of the droplets on the microfiber, we chose volatile acetone as the solvent for the droplets. The 1D–0D microreactors (i.e. the junctions formed between the droplets and the microfiber) had a length of about 10–40 μm and a width of about 18 μm (Figure 2 d; see also Figure S4). After several minutes, yellow fluorescent CdS NCs were formed in the reactors, and a necklacelike structure was observed along with excellent optical properties (Figure 2 b,d). The formation of CdS NCs in the 1D–0D microreactors at room temperature in several minutes could be attributed to the high specific surface area of the microfiber and the confinement effect on ion diffusion. Also, the solvent-vapor-mediated coalescence

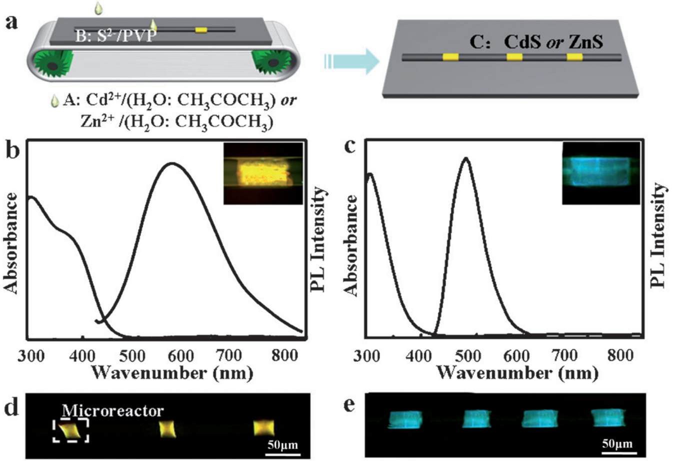

Figure 2. a) Schematic illustration of a 1D–0D array of microreactors for the generation of necklacelike sulfide NCs. b,c) PL emission and UV/Vis absorption spectra of CdS (b) and ZnS NCs (c). d,e) Fluorescence microscope images of CdS (d) and ZnS NCs (e). Scale bars: 50 μm. The insets in (b) and (c) show the corresponding magnified fluorescence images.

of the droplets and the microfiber at their intersections accelerates the fusion of the two reagents within an ultrasmall space (10^{-15} m^3) to induce the chemical reaction. On other hand, the frustration of ion diffusion in this microreaction further avoids the formation of large chunks of CdS crystals without fluorescence. The obtained PVP microfiber loaded with CdS NCs showed a broad photoluminescence (PL) peak centered at 532 nm (Figure 2b), which displayed a quantum effect characteristic of fluorescent CdS NCs.[17] An intense UV absorption peak was observed at 380 nm (3.31 eV; Figure 2b). According to the Brus formula, the particle size of the CdS NCs can be calculated to be 3.49 nm.[18] We similarly synthesized blue fluorescent necklacelike ZnS NCs with such 1D–0D microreactors. In this case, zinc acetate was loaded in the microfiber, and the sulfide source was dissolved in acetone and applied in droplets. The obtained ZnS NCs had a PL emission peak at 482 nm ($\lambda_{ex} = 405$ nm) and a continuous UV absorption from 300 to 400 nm (Figure 2c).[19] The images in Figure 2d,e further reveal visually the formation of bright fluorescent CdS and ZnS NCs within a limited space of approximately 10^{-15} m^3. These 1D–0D microreactors provide a confined liquid–solid interface for the fabrication of ordered necklacelike fluorescent microfibers; such an approach has not been reported previously.

The second set of experiments focused on the construction of microfiber grids by MST; in this case, the knot junctions of these grids were investigated as 1D–1D microreactors (Figure 3a). A solution of PVP (30 wt%) in ethanol containing M $CdCl_2$ was spun into lateral filaments of aligned microfibers as the first layer on a glass substrate, and a solution of PVP (30 wt%) in ethanol containing Na_2S (0.1M) was woven into fibers aligned in the vertical direction as the second layer to form orthogonal cross-over microarrays. After 10 min, the fluorescent products, CdS NCs, were formed at the knot junctions of the grids, and bright fluorescent microarray patterns were observed (Figure 3b–d). The size of the "weld" knots was as small as 20×22 μm^2 (Figure 3c,d; see also Figure S5). The formation of fluorescent NCs clearly confirms that at the knot junctions of grids, not only is the content of two microfiber types mixed, but the reagents also diffuse into close enough proximity to undergo chemical reaction. The generation of CdS NCs in the knots is further confirmed by the PL peak at 532 nm and the corresponding fluorescence confocal microscopy images (see Figure S6).

We assessed the fluorescence lifetime (τ) of the resulting CdS NC microarrays by time-resolved photoluminescence measurements. Decay traces for the samples (Figure 3d) were well fitted with the biexponential function $Y(t)$ based on nonlinear least-squares ($x^2 < 1.1$) by using the following expression:[20]

$$Y(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2) \quad (1)$$

in which α_1 and α_2 are fractional contributions of the time-resolved decay lifetimes τ_1 and τ_2. The average lifetime $\bar{\tau}$ could be calculated from Equation (2):[21]

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

For PVP hybrid microarrays doped with CdS NCs, the $\bar{\tau}$ value was 10.14 ± 0.05 ns, which is somewhat longer than that of a CdS NC control sample prepared by traditional methods.[22] The increased fluorescence-decay time further confirms that the microreactors based on the PVP polymer could effectively prevent the aggregation of NCs, decrease the amount of defects in the nanocrystals, and avoid nonradiative recombination.

As expected, knot junctions containing ZnS NCs could also be produced by this type of 1D–1D grid microreactor (Figure 3e; see Figure S8). The as-prepared ZnS NCs had an emission wavelength of 482 nm (see Figure S9) and a $\bar{\tau}$ value of 2.37 ± 0.05 ns (Figure 3f). Remarkably, these experiments suggest that the reactions taking place at the solid–solid interfacial junctions of the polymer microfibers are due to diffusion rather than activation-limited. This method for the synthesis of fluorescent NCs will be further explored to harness its advantages, such as the straightforward operating conditions and the mild, environmentally friendly reaction conditions without the need for ligands or solutions of poisonous heavy-metal ions.

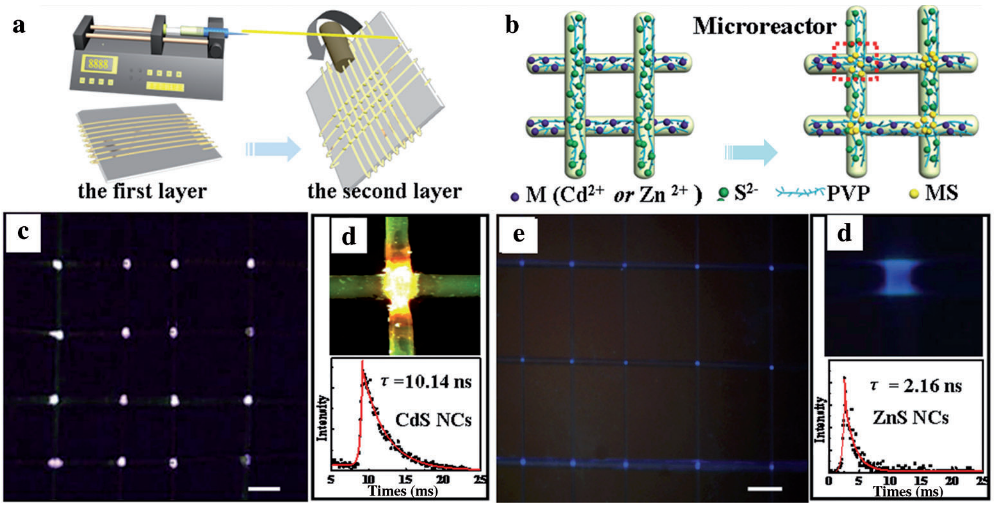

Figure 3. a) Schematic illustration of the weaving of orthogonal microarrays. b) Schematic illustration of the preparation of fluorescent NCs at the junctions of crossed microfibers. c,e) Fluorescence microscope images of 4×4 and 3×5 arrays of 1D–1D microreactors for the fabrication of CdS (c) and ZnS NCs (e), respectively. Scale bars: 100 μm. d,f) Magnified fluorescence images and time-resolved fluorescence decay curves of CdS (d) and ZnS NC knots (f).

We further investigated the in situ synthesis of fluorescent NC hybrid microarrays by using 1D–2D microreactors constructed by the intersections between aligned microfibers and a PVP film. In a typical experiment, a series of wetted 1D microfibers were arranged in parallel on a 2D PVP film. The junction segments serve as 1D–2D microreactors. A solution of PVP (10 wt %) in ethanol containing Na_2S (0.05 M) was initially spin-coated onto a clean glass substrate to form a uniform PVP film (Figure 4 a). Subsequently, wetted aligned microfibers were uniaxially woven onto the above film from a solution of PVP (30 wt %) in ethanol containing $CdCl_2$ (0.1 M) by MST. The overlapping sections between microfibers and the PVP film layer offer a solid–solid interfacial surface for the reaction of the cadmium source with the sulfide source. In a similar process to that observed with the 1D–1D microreactors, yellow brightly fluorescent parallel microarrays containing CdS NCs were gradually formed in the 1D–2D microreactors after several minutes, as indicated by fluorescence microscopy (Figure 4 b; see also Figure S10). To further expand the application of the 1D–2D microreactors, we wove a uniform pentagram pattern by weaving a microfiber onto a PVP film; both components contained the same reagents as described above. A fluorescent pentagram pattern was obtained after 15 min (Figure 4 c). This experiment suggests that these microreactors offer a new avenue for the in situ fabrication of versatile fluorescent patterns and might be applied in the manipulation of fluorescent displays and optical sensor devices.

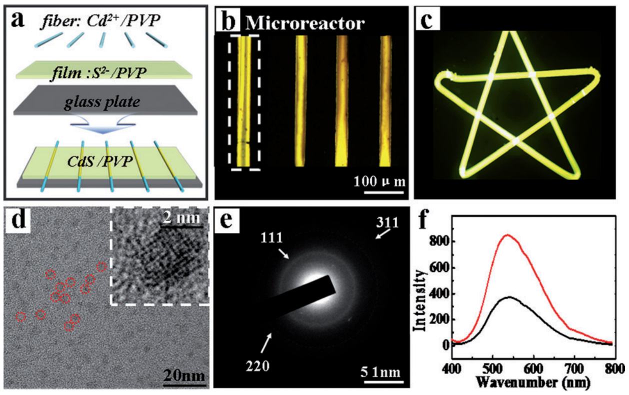

Figure 4. a) Schematic representation of a 1D–2D array of microreactors. b,c) Fluorescence microscope images of aligned CdS NC arrays (b) and a pentagram pattern (c) formed in 1D–2D microreactors. d) TEM image and e) SAED pattern of CdS NCs. The inset in (d) is the corresponding HRTEM image. f) PL spectra of the samples in (b: black) and (c: red).

To verify the existence and distribution of CdS NCs in the hybrid microarrays, we used transmission electron microscopy (TEM) to examine their morphology. CdS NCs had a well-dispersed dotlike nanostructure with an average size of 3.59 nm[23] (Figure 4 d; see also Figure S11). The high-resolution TEM (HRTEM) image shows the well-resolved lattice fringes of CdS NCs (inset of Figure 4 d; see also Figure S12). Three clear diffraction rings in the selected area electron diffraction (SAED) pattern correspond to the (111), (220), and (311) reflections (Figure 4 e) characteristic of a typical cubic blende structure of CdS NCs.[24] The clear diffuse rings further indicate the excellent monodispersion and high crystalline structure of the CdS NCs, without aggregation in the PVP microfibers. Additionally, both the aligned microarray and the pentagram pattern show PL emission of the CdS NCs at 532 nm (Figure 4 f). The fluorescent hybrid microarrays of ZnS NCs can also be fabricated in the same manner by using 1D–2D microreactors (see Figure S13). On the basis of these results, we believe that other similar reactions for the generation of fluorescent NCs should be possible by the use of microreactors of this type.

In summary, we have demonstrated a rapid and facile MST strategy for fabricating a variety of fluorescent polymer hybrid microarrays with versatile patterns, including necklacelike patterns, parallel arrays, and controlled-angle grid and pentagram patterns. More importantly, these microarrays can be readily edited by MST to give multidimensional 1D–0D, 1D–1D, 1D–2D microreactors, which provide solid–solid or liquid–solid interfacial reaction platforms for the in situ synthesis of fluorescent NCs under mild and environmentally friendly conditions. A variety of polymers are available that are compatible with the reagents, thus adding versatility to this straightforward and inexpensive method. Our results suggest that this facile approach based on multidimensional microreactors may be used to generate new hybrid materials with a variety of prospective applications, such as quantum dots, optical microsensor arrays, and fluorescent labeling codes.

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