Hollow Fiber Membrane as a Low-cost and High-efficient Micromixer to Prepare CdS Nanoparticles

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Hollow fiber membrane was utilized to act as a new kind of micromixer. By controlling the nitrogen pressure, external reactant could quickly mix with the fluid in the fiber channel through the nanopores located on the wall of hollow fiber membrane. CdS nanoparticles with narrow size distribution have been produced in this microreactor system owing to the efficient mixing.

Microreactor technique has been widely used in organic and inorganic synthesis since the end of last century.[1–9] Reactions performed within a microreactor invariably generate relatively pure products in high yield, in comparison to the equivalent bulk reactions, in much shorter times and in sufficient quantities to perform full structural characterization. Besides the micropump, the micromixer is another important component in a microfluidic system because efficient and fast mixing is very important for many microfluidic applications. In the microspace, microfluidic mixing usually depends on the molecule diffusion because of the small Reynolds number and laminar flow, which is an unfavorable condition for some chemical synthesis, especially for fast reactions. If reactions start before the sufficient mixing of reactants, inhomogeneous reaction conditions will result in the inconsistent production properties. In order to reduce the mixing time and increase the mixing efficiency, researchers have designed a lot of micromixers, which meet the problems of complicated fabrication, expensive cost and frequent cleanout. Therefore, finding a low-cost and facile method to set up a microfluidic mixing system is still a meaning work for the development of the microreactor technique.

Hollow fiber membrane is a kind of roundness tubular membrane, which contains a lot of nanopores on its wall. From the SEM picture of hollow fiber cross section in Figure 1c, it can be observed that the wall of the hollow fiber membrane includes two kinds of pores: nanosized pores on the inner and outer surfaces and microsized pores in the medium of membrane, which is due to the pore forming reagent volatilization during the spinning. Hollow fiber membrane has been widely used for the desalination of sea water, artificial organ and waste water treatment, and so on. In this communication, hollow fiber membrane was utilized as basic materials to set up microchannel and micromixer first time, which avoids the complicated fabrication process that is necessary for most of ordinary mixers. Since a plenty of industrial applications, the price of hollow fiber membrane is cheap, and various hollow diameters and pore sizes are available. In this study, polyacrylonitrile hollow fiber membrane was chosen, of which the outer diameter is 530 μm, and the inner diameter is 330 μm. The pore size of the inner surface is about 20 nm.

In order to carry out the efficient mixing, a reaction system has been designed as shown in Figure 1. Its main part is a micromixer device, which was fabricated as follows: polyacrylonitrile hollow fiber membrane was inserted into an transparent poly(methyl methacrylate) (PMMA) pipe (diameter: 10 cm, length: 10 cm), through which the mixing state can be easily observed. On the wall of PMMA pipe, there is an entrance which can be used for adding reagents and applying gas pressure. Two ends of the hollow fiber membrane were connected with Teflon microcapillary. One kind of reactant was injected into Teflon microcapillary by the microsyringe pump and mixed with another reactant in the hollow fiber. During our study, nitrogen was used to press the reagent in the pipe into the hollow fiber through nanopores on the fiber wall.

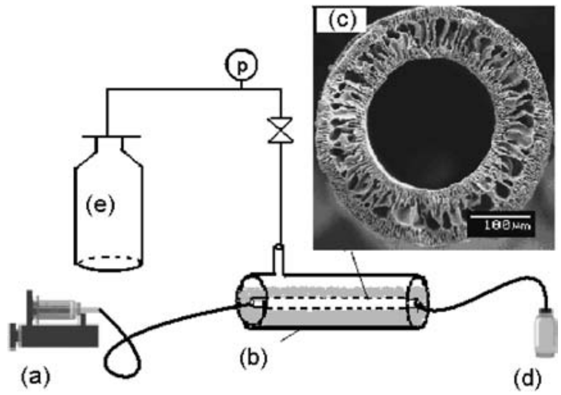

Figure 1. Schematic of the microreactor system: (a) Syringe pump, (b) PMMA pipe, (c) SEM of the hollow fiber membrane cross-section, (d) Receiving flask, (e) Nitrogen.

In the microfluidic channel, molecular diffusion driven by the concentration gradient plays a more important role in laminar flow. Larger contact surface per unit volume will result in more areas with different concentration; therefore, diffusion rate increases with the rise of the ratio of contact surface to unit volume between two liquids. Using hollow fiber membrane as a micromixer gets the idea from Ryo Miyake's work.[10] The mixer that they designed has a channel for the liquid, an inlet port for the reagent, and a 2.2 mm × 2 mm × 330 μm mixing area, and its bottom has 400 micronozzles (15 μm × 15 μm). Through these nozzles, a reagent is injected into the sample liquid, making many microplumes. These plumes increase the contact surface between the two liquids drastically and hasten the speed of the mixing by diffusion. In our work, the interesting pore structure of fiber walls can be regarded as many nanonozzles. When nitrogen valve opened, the reagent added into the container beforehand is pressed through nanopores on the wall of the hollow fiber membrane and mixes with the other reagent fluid in the hollow fiber pushed by the syringe pump. Owning to the big contact surface, mixing is faster than ordinary laminar flow. Compared with

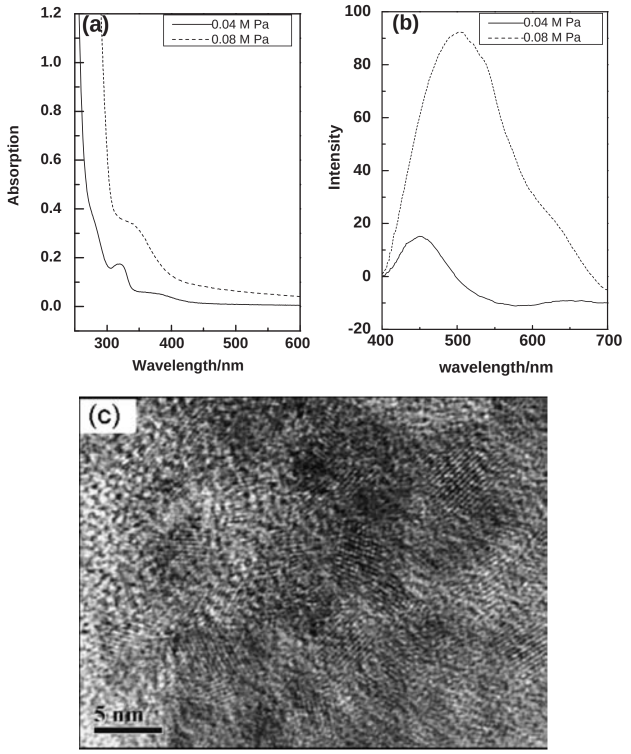

Figure 2. (a) UV–vis absorption spectrum of CdS nanoparticles obtained from the hollow fiber membrane microreactor system, (b) photofluorescence spectrum of CdS nanoparticles obtained from the hollow fiber membrane microreactor system (365 nm excitation wavelength), (c) high-resolution TEM picture of CdS nanoparticles.

Miyake's work, hollow fiber membrane as micromixer can be used without further fabrication process and exchanged without washing for low price.

Because microreactors can afford homogeneous reaction conditions, several groups have use microreactors to prepare low-polydisperse semiconductor nanocrystals.[2–4] Here, aqueous CdS synthesis experiment is used to conform the efficiency of our new fiber micromixer. 1×10^{-4} M $Cd(NO_3)_2{\cdot}4H_2O$ solution containing mercaptoacetic acid was injected into the hollow fiber membrane by the syringe pump, and 1×10^{-4} M Na_2S was added into the PMMA pipe first, then pressed through the nanopores to mixing with $Cd(NO_3)_2$ by nitrogen. Under the same $Cd(NO_3)_2{\cdot}4H_2O$ injecting volume of 100 µL min^{-1}, different nitrogen pressure were used to control the addition of Na_2S.

UV–vis absorption spectrum, photofluorescence spectrum and the high-resolution TEM were utilized to characterize the product. The CdS particle size is calculated using the effective-mass model.[11] In the absorption spectra of Figure 2a, the peak of CdS prepared under 0.04 MPa ranged from 340 nm (4.1 eV; 3.2 nm CdS in diameter) to 300 nm (3.6 eV; 2.8 nm CdS in diameter), and under 0.08 MPa ranged from 405 nm (3.05 eV; 4.6 nm CdS in diameter) to 310 nm (4.05 eV; 3.3 nm CdS in diameter). It indicates that lower nitrogen pressure is much likely to produce uniform nanoparticles. The fluorescence emission of the CdS also gives the same result (Figure 2b). Meanwhile it reveals that particles prepared under 0.04 MPa blue shift compared with that under 0.08 MPa, which indicates a smaller average particle size arising from low nitrogen pressure. TEM observation of the sample produced at 0.04 MPa (Figure 2c) indicates that the particle size was about 4 nm, and lattice image clearly shows the crystallized particles. Some references have shown that increasing Cd/S concentration ratio may result in small and uniform nanoparticles.[12,13] Nitrogen pressure can affect the mixing proportion, and change the ratio of Cd to S. Lower nitrogen pressure reduces the amount of Na_2S, therefore, gives narrower size-distributed CdS nanoparticles. Usually aqueous CdS nanoparticle synthesis is very sensitive to reaction conditions, and high-quality nanoparticles can only be obtained under the homogeneous mixing. In this reaction system, mixing length is only 10 cm, which is much shorter than the necessary length for the laminar flow,[5] but high-quality aqueous CdS can still be obtained, which proves that our hollow fiber mixer is efficient and feasible.

In conclusion, hollow fiber membrane has been used as a new kind of micromixer which can be utilized to produce narrow size-distributed CdS nanoparticles. The mixing portion and particle size can be controlled by nitrogen pressure. Compared with ordinary micromixers, expensive and complicated fabrication process is not necessary. Owing to the low price and the structure characteristics, hollow fiber membrane has great potential application in the combinatorial chemistry because different kinds of samples can be tested at the same time.

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