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Preparation of titania particles utilizing the insoluble phase interface in a microchannel reactor

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A stable interface between two insoluble currents in a microchannel reactor has been obtained by selecting the solvents and adjusting the flow rate; titania particles with a size of less than 10 nm could be prepared continously on this interface; this new method shows great advantage for the control and measurement of particle sizes.

Microreactor technology has recently become a new and very promising field within a very short time in the fields of chemistry, process engineering and biotechnology. The advances in the past few years in microreactors have demonstrated that the miniaturization of chemistry has significant advantages with respect to cost, safety, throughput, kinetics and scale-up. This has prompted the investigation of chemical reactions and syntheses using microreactors with the emphasis on the nature of reactions, the manufacture of reactors and application to the development of functional materials and drugs.[1–5]

The preparation of nanoscale particles is an important field in nanomaterials science. Many methods have been utilized to produce nanoparticles without agglomeration,[6–9] such as the microemulsion method,[10] in which droplets (*i.e.* reaction chamber) provide control of the rate and the extent of particle formation. Recently, Edel *et al.* has described a microfluidic procedure to produce cadmium sulfide nanoparticles,[11] and they showed the nanoparticles can be obtained in a continuous microfluidic system. Here we also use a microfluidic system to produce nanoparticles, which is beneficial in discouraging coalescence of the newly formed nanoparticles. Meanwhile, we utilize the interface between two immiscible liquids to control the particle size, and not only the microchannels. According to the previous study,[12] a lamellar flow mode can be observed in the microchannel reactor when two insoluble phases are introduced through a Y-shape inlet using microsyringe pumps. Some researchers have studied the interface between two immiscible liquids.[13,14] and they believed its width was only 1 nm or several angstroms. Their results also showed the existence of a packing effect of each liquid against the opposite phase in this region, which means that a type of mixing exists on the interface. Therefore, the interface between the lamellar flow can also be regarded as a type of 'nanospace' like reaction chamber because the reactants can only contact each other at this interface and react. Based on this idea, in this study, the particles are designed to occur on the interface between two insoluble liquid currents in the microchannel reactor. Some special characteristics are expected to be obtained because the particle growth mechanism on the interface may be different from that in beakers.

A ceramic microchannel reactor was used in this study: a 9 cm long microchannel (depth: 200 μm, width: 360 μm) was carved on the ceramic substrate by a drill, and sealing glass powder was used to bond this carved ceramic substrate with a glass cover. A sketch of the microfluidic system is shown in Fig. 1.

Several solvents have been tested to obtain a stable interface in the microfluidic system. It was found that appropriate flowing rates and similar viscosities were important to produce a stable interface. As shown in Table 1, two insoluble liquid systems were used in this study:1-hexanol/formamide and cyclohexane/water.

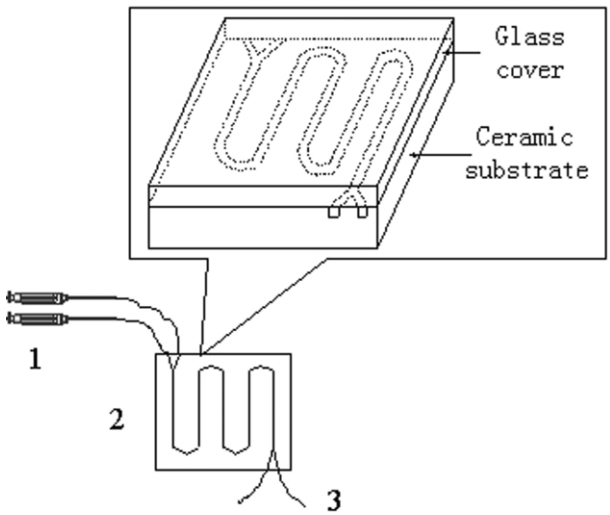

Fig. 1 Schematic of the microfluidic system: 1, syringe and pump; 2, the microchannel reactor; 3, the outlet.

It is well known that titania can be prepared by the hydrolysis of titanium alkoxide and the reaction rate is very fast (beneficial in terms of completion of the entire reaction in the microchannels).[7] Therefore, titania was selected to check the feasibility of producing nanoparticles on the interface in a microchannel reactor. In the hexanol/formamide system, 0.147 ml TTIP (0.05 M titanium tetraisoproxide) was dissolved in 10 ml of 1-hexanol, and 1.8 ml of distilled water (10 M) was added to 10 ml of formamide as the reactants. The water/alkoxide molar ratio is 200. Through two syringes, 1-hexanol containing TTIP and formamide containing distilled water were injected into the microchannel. By adjusting the injection rate, a stable interface could be obtained in the microchannel, as shown in Fig. 2. The products were collected in two bottles. Similarly, in the cyclohexane/water system, 0.005 ml TTIP (0.0017 M) was dissolved in 10 ml of cyclohexane as the organic phase, the other phase was 100% distilled water.

In the hexanol/formamide system, the TiO_2 colloid was always found on the hexanol side. However, in the cyclohexane/

Table 1 Properties and the flowing rate of solvents

Solvent	Water solubility[15]	Viscosity at 25 °C[15]/mPa s	Flow rate/μl min^{-1}
1-Hexanol $C_6H_{14}O$	Slight	4.58	80
Formamide CH_3NO	Miscible	3.34	80
Cyclohexane C_6H_{12}	Slight	0.89	200
Water H_2O		0.89	100

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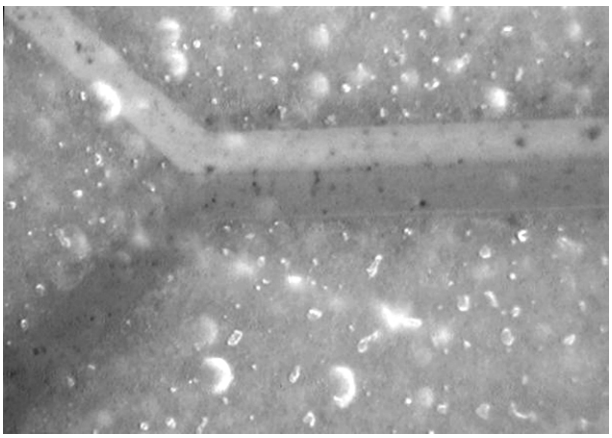

Fig. 2 The stable interface of cyclohexane and water in the microchannel (red ink was added to water to show it distinctly).

water system, the TiO_2 colloid can be found on both sides, which should result from the surface characteristics of TiO_2 (including many –OH groups).

The TiO_2 colloid collected at the outlet of the reactor was immediately monitored using a UV spectrometer. The UV spectra showed that the onset of absorption appears at $\lambda_{os} \approx 340$ nm, which is almost the same as the value Kormann *et al*. observed in a beaker after mixing $TiCl_4$ with water at 1 °C for 1 min.[16] They believed that extremely small quantum-size TiO_2 particles ($d < 3$ nm) that possess the anatase structure had been prepared. Compared with their method, our experiment utilizing the microchannel reactor is very simple.

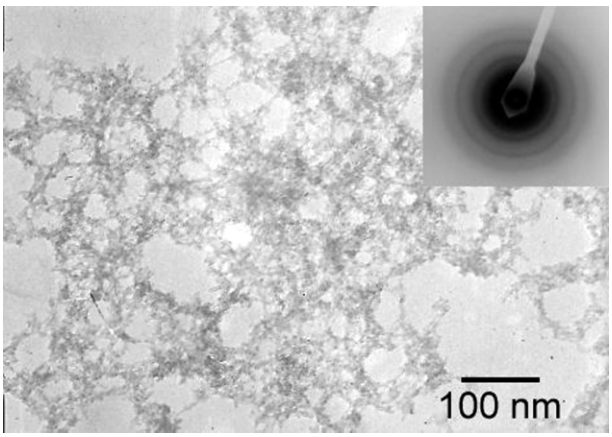

Fig. 3 TEM image and electron diffraction pattern of TiO_2 prepared from the cyclohexane/water system.

To prepare TEM samples, a drop of the colloidal suspension from the outlet of the microchannel reactor was applied to a copper mesh covered with a carbon film and subsequently dried by a vacuum desiccator. TEM observation indicated that titania particles of < 10 nm could be produced on the interface in the microchannel as shown in Fig. 3. The electron diffraction pattern showed the presence of the anatase polymorph.

These experiments showed that nanoparticles can be produced on the insoluble interface in the microchannel reactor. Compared with the microemulsion method, no surfactant is needed. As a flow system, this method shows an advantage for studying the growth mechanism of particles because particles can be immediately obtained at the outlet of the microchip with different reaction times. Due to the small volume, the microchannel reactor method also has the great potential of precisely controlling the reaction temperature and other conditions, such as the magnetic field strength, which will benefit the preparation of nanomaterials.

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