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Modified micro-space using self-organized nanoparticles for reduction of methylene blue

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By using silica layers bound to the surface of the inner wall of the microchannel *via* a self-assembly technique which relies on capillary forces to organize the colloids, TiO_2 particles were attached to the inner surface of a micro-capillary. The reduction rate of methylene blue increased by more than 150 times in the SiO_2/TiO_2 modified micro-space compared to that in a batch system.

Microreactor technology has gained a great deal of attention over the last several years.[1] For wider applications, recent progress in this field suggests the development of a functional microchannel inner surface. Much effort has been devoted to impregnate a catalyst onto agglomerated particles or the support layer. However, these methods are quite complicated, and not easy to control in the micro-space.[2–5] In our previous study,[6] we developed a simple technique to obtain well-organized SiO_2 layers in a microcapillary using an SiO_2 colloid as the resource solution. Silica particles could self-assemble on the inner wall of a capillary without any additional drawing force. The structure produced by this method enhances the possibility of a catalytic reaction by exploiting its larger surface area, while pure SiO_2 has a lower catalytic ability. TiO_2, one of the most widely used photocatalysts,[7,8] was used to produce an arrangement in the microchannel on the target surface in the present study. However, it is absurd to use pure TiO_2 to produce such an arrangement in a microchannel, because of the difficulty in obtaining monodispersed spherical TiO_2. The core–shell structure is the usual method to prepare spherical particles with a functional surface.[9–11] Therefore, we tried to produce self-organized TiO_2-coated SiO_2 with a core–shell structure on the inner wall of the microreactor. Based on implementation techniques in the literature[12] using a surfactant to generate a surface charge on the particles, in the present study, a simple method to prepare TiO_2-coated SiO_2 colloid using the surfactant PEI (polyethylenimine) to alter the surface potential of the SiO_2 at pH 9 was developed. Our result proved that it was possible to arrange the monodispersed particles even though the spheres had rough surfaces. The coated catalyst shell significantly increased the reduction rate of methylene blue.

SiO_2 colloid (d = 120 nm) and anatase TiO_2 sol were used in the present study. The colloid solution was prepared by slowly adding TiO_2 sol (0.85 wt%) into a pre-synthesized SiO_2/PEI solution. Fig. 1 shows the schematic for preparing the SiO_2/TiO_2 colloid solution. The anionic TiO_2 became readily attached to the surface of the cationic PEI-covered SiO_2 and gradually neutralized it. A clear solution was obtained before precipitation at zero electric potential.

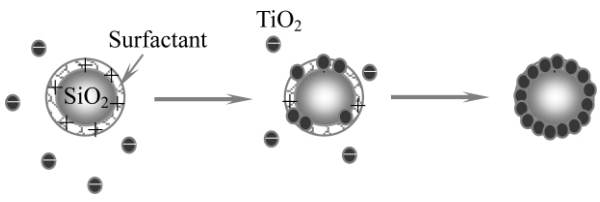

Fig. 1 Schematic for preparing SiO_2/TiO_2 core–shell particles.

Silica capillaries of length 5 cm and 530 and 200 μm I.D. with a glass inner wall were used as the microreactors. The inner surfaces of the microcapillaries were washed with piranha solution (70:30 *v*/*v* mixture of concentrated H_2SO_4 and H_2O_2) for 12 hours at room temperature, and then rinsed with pure water. One end of the capillary was connected to a syringe, while the other end of the capillary was placed in the colloid solution. The capillary was filled with solution by drawing a vacuum with the syringe. With one end closed, the capillary was dried overnight at 88 °C (Fig. 2). Using this method, TiO_2 was introduced and coated on the inner wall of the microcapillary by the self-organization of SiO_2.

Fig. 3 shows the SEM image of the modified surface of a 530 μm diameter microcapillary. Based on the method from our

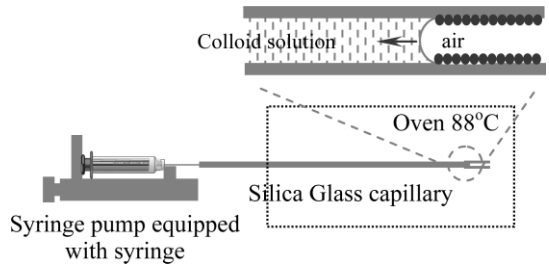

Fig. 2 Experimental outline. Microscope image showed the self-assembly of particles on the inner wall of the capillary.

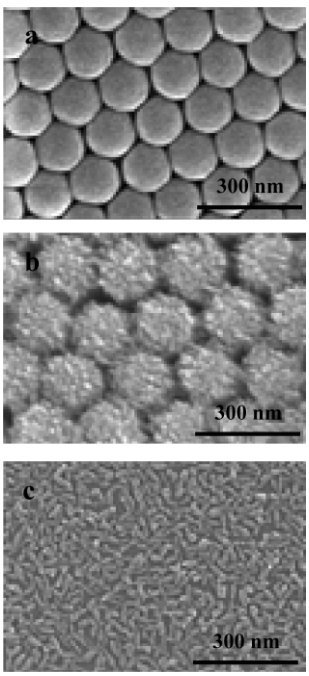

Fig. 3 SEM images of modified capillary. (a) Hexagonal SiO_2 array on the inner wall of a 530 μm capillary. (b) SiO_2/TiO_2 layer with a core–shell structure in a 530 μm capillary. (c) TiO_2-coated 530 μm capillary.

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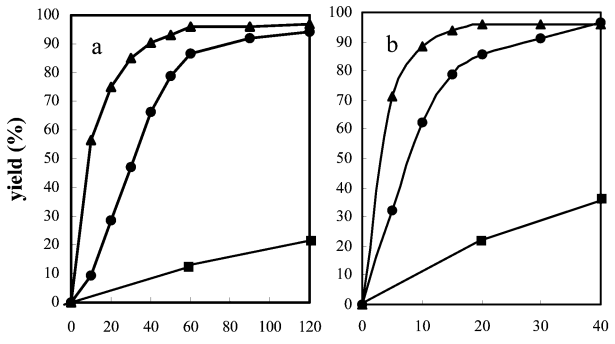
previous study,[6] an SiO_2 arrangement can be obtained over the entire inner surface of the capillary (Fig. 3(a)). By reference to the concentration of the pure SiO_2 particle layers, the molar ratio of SiO_2 to TiO_2 was adjusted to 1.28 : 1 (about 0.01g ml^{-1} SiO_2 particles). An overall well-arranged hexagonal array was obtained (Fig. 3(b)) with a thickness of four layers in the 5 cm capillary. The thickness was not completely consistent with that of an SiO_2 layer with the same concentration[6] possibly caused by the effect of the surfactant and the rough surface of the core–shell structure. To investigate the role that the SiO_2 coating could play, the same process of catalyst immobilization was also performed on the inner wall of a microcapillary without an SiO_2 layer for comparison. When the catalyst TiO_2 was used as the only modification material, the TiO_2 particle layer was a single layer and not closely packed, as shown in Fig. 3(c). A similar coating was also obtained in a 200 μm capillary.

Using microcapillaries (with the original glass inner surface, TiO_2-coated inner surface and SiO_2/TiO_2 modified inner surface, respectively) as the reactors, the reduction of methylene blue (0.1 mM) assisted by TiO_2 photocatalysis under a UV-irradiation wavelength of 254 nm was investigated as a function of the reaction time (residence time in microcapillary, which was calculated according to the flow rate (Fig. 4)). The reaction was performed by injecting the methylene blue solution through the microcapillary controlled by a syringe pump.

For comparison, a batchwise reaction was initially carried out. A 3 ml, 0.1 mM methylene blue solution containing 2 mg TiO_2 was irradiated by a UV lamp. An increased yield with a longer reaction time making the reduction go a step further was observed. The reaction was finished in about one hour, and the conversion rate was about 0.09% s^{-1}.

Products in the microcapillary after different reaction times were obtained and measured by the UV method. The results of the reaction in the presence and absence of TiO_2 under UV irradiation are shown in Fig. 4, and the conversion rates of the photocatalytic reduction of methylene blue in the micro-capillary are listed in Table 1.

The results in Fig. 4(a) showed the remarkable catalytic effect of TiO_2. Without the TiO_2 catalyst, the conversion rates were 0.2% s^{-1} (in a 530 μm capillary) and 1.2% s^{-1} (in a 200 μm capillary). On the other hand, as we expected, the results showed that the microreaction system reduced the reaction time to minutes compared to the batchwise reaction. In the microcapillary with TiO_2 as a catalyst, 2 min is enough to finish the reaction in the 530 μm capillary (conversion rate is 1.5% s^{-1}), and a faster conversion rate of 6.3% s^{-1} was found in the narrower 200 μm capillary in which the reaction was completed in 40 s. With specific efforts to introduce TiO_2 into the microcapillary using core–shell structure layers, the arranged SiO_2 layers offered an increased inner reaction field in the capillary, which is also capable of introducing a higher amount of catalyst. In this way, an additional effect was found that the reduction of methylene blue was completed in only 40–50 s using the SiO_2/TiO_2-coated 530 μm capillary at the fairly rapid rate of 5.7% s^{-1}, and even only 20 s (reaction rate of 14.2% s^{-1}) is sufficient in the 200 μm capillary. One the other hand, considering the absorption property of SiO_2, the SiO_2 layered inner surface not only provided a larger ratio of surface to volume in the microreactor, it could also be said that it also promoted the reaction efficiency by absorbing reactants near it.



a	Reaction time (sec)	10	20	30	40	50	60	100	120
	Flow rate (μL min^{-1})	65.9	33.0	22.0	16.5	13.2	11.0	6.6	5.5
b	Reaction time (sec)	5	10	15	20	30	40		
	Flow rate (μL min^{-1})	18.8	9.4	6.3	4.7	3.1	2.3		

Fig. 4 Reaction yield *vs* reaction time for 0.1 mM methylene blue according to UV results in (a) a 530 μm capillary and (b) a 200 μm capillary. ■, Without any coating; ●, TiO_2 coated; ▲, SiO_2/TiO_2 coated.

Table 1 The conversion rate as a function of modification

	Modification	Conversion rate/% s^{-1}
530 μm capillary	Without coating	0.2
	TiO_2 coating	1.5
	SiO_2/TiO_2 coating	5.7
200 μm capillary	Without coating	1.2
	TiO_2 coating	6.3
	SiO_2/TiO_2 coating	14.2

In summary, the present work extended the potential application to modify a microreactor with core–shell structure particles. Highly dispersed TiO_2-coated SiO_2 with a core–shell structure was prepared as a modification resource. Although it has a rough surface, a hexagonal arrangement on the inner surface of the microcapillary was obtained. A significantly high reduction yield of methylene blue is reasonably obtained because of the highly active catalytic system.

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