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A simple method of self assembled nano-particles deposition on the micro-capillary inner walls and the reactor application for photo-catalytic and enzyme reactions

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Abstract

A simple method using self-assembly of colloidal particles was applied to modify a microcapillary inner surface. It was possible to arrange the particles on to the capillary inner wall and to control particle layer thickness and layer patterning of by choosing adequate combinations of solvents and drying temperature. Furthermore, anatase type TiO_2 coated SiO_2 composite particles were shown to be applicable for the particle arrangement process in the microreactor to carry anatase type TiO_2 catalyst. This process was applied as a simple catalyst carrying method onto the micro-reactor inner wall. It was applied for a few catalytic reaction systems including enzyme reaction and photocatalytic reaction. Enzyme reaction was enhanced because of the increase in the reactor surface area. Furthermore, reasonably good enhancement of the photocatalytic reaction was observed for a reaction in a micro-reactor.

Keywords: Colloidal particles; TiO_2 catalyst; Microreactor technology; Monodispersed particles; Self-assembly; Letero coagulation

1. Introduction

Smart, integrated microreactor technology has become a new and very promising field within a very short time in the fields of chemistry, process engineering, and biotechnology [1]. Microchannels have been utilized as important components in microreactor systems to operate many reactions with precise temperature and time control, higher production rate, etc. [2–5]. A micro-reactor is attractive for catalytic reactions because of its large surface to volume ratio and precise temperature control. Sol–gel and CVD methods are often used to introduce a heterogeneous catalyst in a microchannel [6,7]. However, these procedures are not simple; they often require treatments at high temperature. This restriction limits the variety of reactor and catalyst materials.

In this study, we applied a particle arrangement method to modify the capillary inner wall. Since the late 1990s, many researchers have undertaken particle arrangement on a planar substrate: so-called colloidal crystals [8–11]. A two-dimensional colloid crystal can be obtained for the solvent evaporation method and its thickness can be controlled through concentration of the suspension and repeated processing [8,12,13]. However, an open environment is usually chosen to prompt solvent evaporation and to obtain a high-quality particle array. Differently from the open system, an evaporated molecule must pass along an increasing distance to exit from a capillary during the arrangement process. These capillary characteristics augment the difficulty of solvent molecules to escape from a capillary. Although Vos et al. allowed silica sphere sediments and the suspending liquid to slowly evaporate in 400-μm-thick and 4-mm-wide glass capillaries [14], that process requires several weeks to fill the entire capillary with colloidal crystals. Moreover, it is not possible to control the particle layer thickness.

On the other hand, preparation methods of composite particles, including coated particles, have been studied quite intensively for the last two decades. Many researchers have conducted preparation methods for such composite particles [15–18]. Among them, the hetero-coagulation method, which utilizes an electrostatic attractive force between surfaces of opposite signs of electric charge, can utilize nanocrystals directly to prepare composite particles with porous shell structures. The surface charge is the fundamental source of problems because this method utilizes a physical force; principally, there are no difficulties in choosing deposition conditions according to the material that is used. The surface charge can be altered by pH

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and surfactants such as polymer electrolytes. Especially, polymer electrolytes can modify the surface charge while maintaining its colloidal stability. Therefore, it is possible to build up an arbitrary structure of core-shell particles [19].

From this point of view, we aimed to develop a simple and versatile method to carry particle layer on micro-reactor using a colloidal crystal method in this study. Then, we tried to carry an enzyme to modify the surface layer and thereby verify that surface roughness can affect the efficiency of the micro-reactor as an enzyme reactor. In addition, we tried to utilize a core/shell type composite particle (SiO_2/anatase type Titania), which has only rarely been applied for the self-assembly process. Composite particles are considered to be suitable for wider choices and combinations of catalysts. Moreover, its support materials and simple setting up procedure can be realized. We investigated its photocatalytic activity toward photocatalytic reduction of organic dye. Here, we utilized a micro-capillary because it is a widespread material for gas chromatography and is easy to obtain. Moreover, the thinness and smoothness of the capillary glass wall was effective for preventing serious loss of light intensity for photo-catalytic reactions. The thin glass wall also facilitates quick and exact temperature control [4] and integration of the reactor.

2. Experimental procedures

2.1. Surface modification of micro-reactor

Fig. 1 shows the equipment we used. The silica-glass capillary (GL Science, Japan) had an inner diameter of 530, 320, or 200 μm, with a glass inner wall and polyimide coated outside. Silica spheres (Catalysts and Chemicals Ind. Co., Ltd., Japan) of 120 nm or 300 nm in the mixing solution of water and ethanol were used as raw material suspensions for particle arrangement. The silica suspension was injected into a 60 cm long capillary through a Teflon tube using a syringe. Bubbles were avoided. A part of the capillary (ca. 50 cm) was placed horizontally in an oven (temperature: 60–120 °C), as shown in Fig. 1. An interface (meniscus shape) is visible between the suspension and capillary wall. Air moved continuously along the capillary from the open side to the close side (the syringe side). No additional drawing force was applied in this study. The capillary was cut off from the Teflon tube after several hours of drying. After that, the capillary was additionally dried for 12 h at about 90 °C.

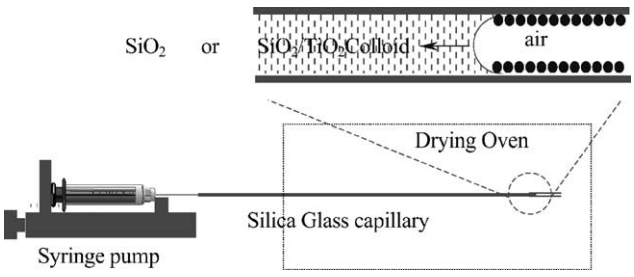

Fig. 1. Experimental set up.

An optical microscope was utilized to observe the meniscus movement and convective flux. In addition, scanning electron microscopy (SEM) (Alpha-25A; Akashi Beam Technology Co., Japan) showed arrangement of particles in the capillary.

In some case, the surface modification has applied for particle arrangement patterning. Inside of a dried capillary, a dilute solution of octadecyltrimethoxysilane in toluene was introduced and heated and then dried in an oven at 100 °C for 30 min to modify wettability of the capillary inner surface. The contact angle measurement showed that the surface became hydrophobic. The capillary was then placed under a 150 W mercury UV lamp for 10 days while masking some part of it. We tried to render the surface hydrophilic patterning.

2.2. Enzyme reactor

In this study, a hydrolysis reaction of umbelliferone acetate to umbelliferone by a hydrolysis enzyme, Lipase was demonstrated as a model reaction. A 20 cm length silica microcapillary tubing with 320 μm i.d. × 450 μm o.d. was used as the microreactor. Type II Lipase from porcine pancreas (Sigma, USA) was immobilized after the microcapillary was coated with SiO_2 in the manner mentioned above. We referred a successful implementation in literature [20] as shown schematically in Fig. 2. The particle layer surface and untreated capillary tube surface were treated with 3-aminopropyltrimethoxysilane. Then the reactor was treated further with succinic anhydride followed by active ester formation, 100 mg/ml porcine pancreatic lipase solution was flowed through the microcapillary.

The enzyme reactor activity was determined by verifying the hydrolysis rate of umbelliferone acetate to umbelliferone because the starting material and product were easily separated by HPLC. Products showed various reaction times, as indicated by residence time in microcapillary, which was calculated according to the flow rate of reactant. We determined their concentration by HPLC (separation module 2695, dual absorbance detector 2487, Waters Co., MA; column heater U-620 type 30, Sugai Co. Ltd., Japan; column Cosmosil C18 ∅4.6 × 150 mm; Nacalai Tesque, Inc., Japan); flow rate 1 ml/min; solvent A, 0.05% trifluoroacetic acid (TFA) in water; solvent B, 0.05% TFA in acetonitrile; 0–50% B in 30 min. Elution was monitored by absorption at 220 nm. The retention time of the product (umbelliferone) was 4.2 min. Concentration of umbelliferone was induced by the HPLC peak intensity. The yield was calculated by comparing the concentration with a stoichiometric concentration.

2.3. Photocatalytic reactor

Anatase type TiO_2 sol (TOsol, 0.85%; Kon Corporation, Japan), SiO_2 sol (d = 120 nm, purchased from Catalysts

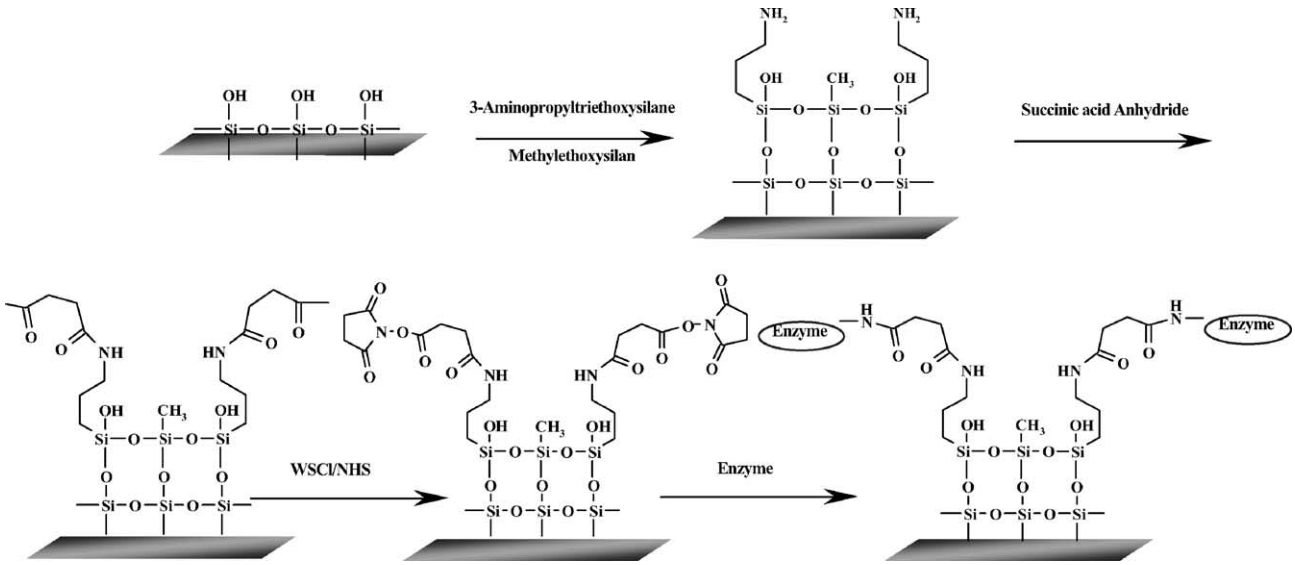

Fig. 2. A schematic diagram of enzyme immobilization.

and Chemicals IND. Co., LTD), and polyethylenimine (PEI; Aldrich, WI) were used without no additional purification. Heterocoagulated SiO_2/PEI/TiO_2 was obtained using surfactant PEI (polyethylenimine) to alter surface potentials of the SiO_2: 0.5 g PEI was dissolved in 5 ml H_2O and stirred intensely for 1 h. The resultant solution was added into 10 ml SiO_2 sol and stirred for 1 h. The mixture was centrifugally separated to remove excess surfactant. It was then water-washed by centrifugation for several times, and finally dispersed into 20 ml H_2O. The resultant SiO_2/PEI solution showed ca. pH 9.20. A solution with ratio below 1:0.05 (in wt.) of SiO_2/PEI: TOsol was obtained by dripping TOsol into the SiO_2/PEI solution. On the other hand, a weight ratio above 1:1 could be obtained when SiO_2/PEI was added into the TOsol solution.

A 5-cm silica capillary tubing with 530 μm i.d. × 600 μm o.d. was used as the microreactor. The microcapillary was cleaned with piranha solution (70:30 (v/v) mixture of concentrated H_2SO_4 and 30% H_2O_2) for 12 h at room temperature, and then rinsed with pure water. One end of the capillary was connected with a syringe; the other end of the microcapillary was soaked into the precursor solution. The microcapillary was filled with the solution by drawing the syringe. With one end closed by the syringe, the capillary was dried at 88 °C for 12 h. Particle arrangement on the capillary inner-wall was observed by SEM.

Methylene blue, which has its main absorption peak at 611 nm, can be reduced by a photocatalytic reduction to leucomethylene blue, which has no absorption at 611 nm. We mounted the photocatalyst microreactor onto a UV-lamp. Using the TiO_2 or SiO_2/TiO_2 modified microreactors and non-treated microcapillary, a photocatalytic reduction of methylene blue under UV (254 nm) irradiation was performed. Absorbance of 611 nm of light of the sample passed through the reactor was utilized to determine concentration of the remaining methylene blue after UV irradiation for a particular time to obtain a reduction rate curve. An initial slope of the reduction curve induced the initial reaction rate.

3. Results and discussion

3.1. Formation of silica particle layer on inner wall of micro-reactor

Microscope observation showed that the inner surface of a silica glass capillary was hydrophilic because the contact angle of water or ethanol on the silica surface was much less than 90°. A thin solvent film exists naturally in the front of the colloid suspension because of surface tension. According to results obtained by Denkov et al. [10,11], colloids start to assemble in a thin liquid film when its thickness becomes comparable or slightly smaller than the particle. Therefore, in a capillary, when the surface of the suspension starts to move along the capillary as a consequence of solvent evaporation, silica particles will self-assemble on the capillary inner wall. Thereby, no additional drawing force or process is needed.

Water, ethanol, and a mixture of water and ethanol were adopted to test the possibility of particle arrangement in a long capillary. Each solvent had its own critical temperature: above this temperature, the suspension meniscus can move along quite a long distance; below this temperature, the meniscus will stop near the open side, or move very slowly. The rate of meniscus motion is directly proportional to the solvent evaporation rate. When the surface was far from the open side, the evaporated molecule had to overcome resistance (random molecule movement, wear with the inner wall, etc.) to escape from the capillary. Because resistance

will increase with the length, an evaporated molecule should have sufficient driving force to reach the open side. We inferred that the solvent vapour pressure acts as the driving force for evaporated molecule movement. A higher temperature produces a higher pressure of evaporated vapour; therefore, the rate of meniscus motion has a relationship to temperature. According to our experiment, with a 530 μm capillary, this critical temperature for water as the solvent should be above 98 °C; it is above 77 °C for ethanol. In this study, we mostly utilized a solvent whose molar ratio of water to ethanol was 4:6. The critical temperature for the solvent was between 78 and 88 °C. At 78 °C, the drying rate was decreased with time and stopped at a certain point, whereas at 88 °C, the drying rate was constant for a few days to obtain 10 m long particle arrangement. Such conditions make the particle arrangement in a capillary not only applicable in a lab. They also meet potential demands from industry.

Fig. 3 shows SEM pictures of the inner surface of a capillary with particle arrangement. Particle arrangement can be obtained over the whole inner surface of the capillary with uniform thickness. A hexagonal array can be obtained in most cases and the particle layer has a meso-porous structure. The pore size can be calculated as a few 10 nm. An experimental measurement based on Mercury porosimeter of a similar particle layer prepared by a solvent evaporation method in a open environment showed

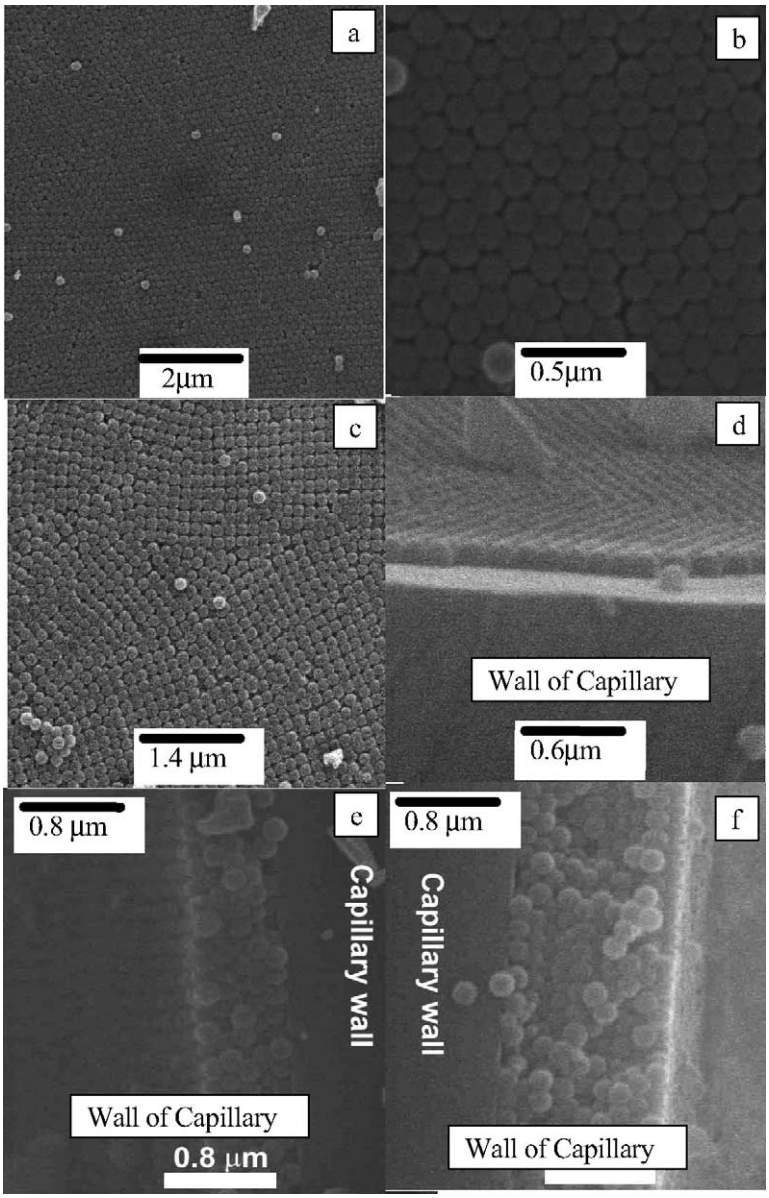

Fig. 3. Top view and cross-section of silica particle layer on wall of capillary. (a and b) Hexagonal arrangement. (c) Cubic arrangement. (d) Monolayer of silica particle arrangement (concentration of SiO_2: 3.8 mg/l). (e) Five layer of silica particle arrangement (concentration of SiO_2: 7.6 mg/l). (f) Ten layer of silica particle arrangement (concentration of SiO_2: 19 mg/l).

a good correspondence with the calculation [8]. Occasionally, a cubic structure was also able to be visible. Silica particle concentration affected the arrangement thickness: more condensed suspensions yielded thicker particle layers. Monolayers and multilayers can be controlled using different suspension concentrations, as shown in Fig. 3.

The particle layer stability was checked. The as-prepared capillary with a particle layer was soaked in various pH aqueous solutions for 3 days; alternatively, the solution was flowed into the capillary with a 200 μl/min flow rate for 3 h. Then the particle layer of the inner surface was observed by SEM. We found that the particle arrangement was stable in both static and dynamic water. In addition, some samples were heat-treated at 600 °C for 1 h. The silica did not fuse and ordered particles remained. These results allow the particle arrangement produced by our method to be used under environments where physical and thermal stabilities must be considered.

It is possible to design the vertical structure on the inner wall of a capillary with our method layer by layer because the particle arrangement is stable in an aqueous solution. We first made a large particle layer with 300 nm silica, then used 120 nm silica spheres to produce the second layer. As shown in Fig. 4, small particles occupy voids of the large particles. Such voids with different sizes and positions can be obtained in the second layer. Another advantage of our method was to make the particle pattern on the inner wall of a capillary. In our method, the thin solvent film in the front of the meniscus is a necessary condition to make a particle arrangement. Without this thin film, such as on the hydrophobic surface of a capillary, no particles can be found. Therefore, we utilized a silane coupling agent, such as octadecyltriethoxysilane, to modify the hydrophilic silica surface of a capillary to hydrophobic. Then we rendered some areas hydrophilic again using mercury UV lamp irradiation and a mask. As the contact angle become large for the hydrophobic area, as shown in Fig. 5a, the particle layer did not deposit on the hydrophobic surface. On a surface with this kind of pattern, particle arrangement can only be found on the hydrophilic area, as seen in Fig. 5c. The above results suggest the possibility of producing a composite catalyst or of designing a device on the inner wall of a capillary using our method.

3.2. Fabrication of the enzyme reactor and its catalytic activity

As reported by Miyazaki et al. [20], the enzyme reaction can be enhanced in a micro-reactor with a sol–gel layer. In our work, one benefit is the further increase the ratio of surface to volume that is anticipated with the coating of particle layer in a microcapillary. Therefore, we tried to carry an enzyme into a silica-particle-treated micro-reactor.

A 320-μm silica glass capillary was surface treated with monodispersed silica as described in the experimental section. As mentioned in the former section, the thickness (monolayer to tens of layers) of the resultant close-packed structure could be controlled by size and concentration of particles. For comparison, the same process of enzyme immobilization was also performed on a microcapillary inner wall without SiO_2 coating. To gain insight into the surface amount of lipase, measurement was based on UV determination of the coated amino group according to Gisin's method [21]. As expected, results showed that the amount of the amino group also enlarged to about 1.5 times with SiO_2 coating; this was proportional to the enlarged inner surface area of the capillary.

Fig. 6 showed the reaction time versus yield for umbelliferone, which is a hydrolysis product of the enzyme reaction. The reaction completed at about 10 min in the microcapillary with SiO_2 coating. The reaction rate was enhanced for the silica particle coated one, which is reasonable by the fact that larger surface area and larger amount of enzyme which

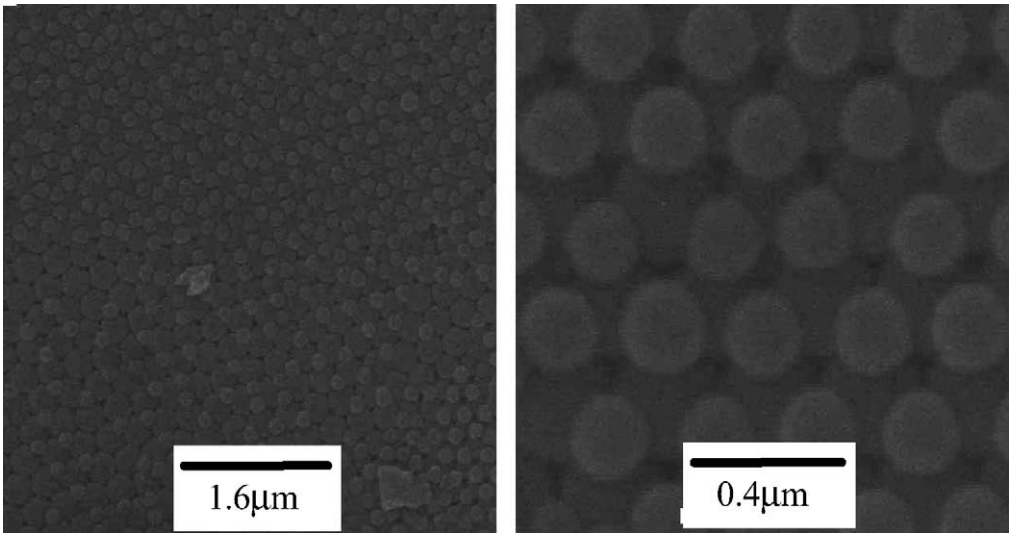

Fig. 4. Two layer arrangement of different size of particles. Particle size: 300 nm (under layer), 120 nm (upper layer).

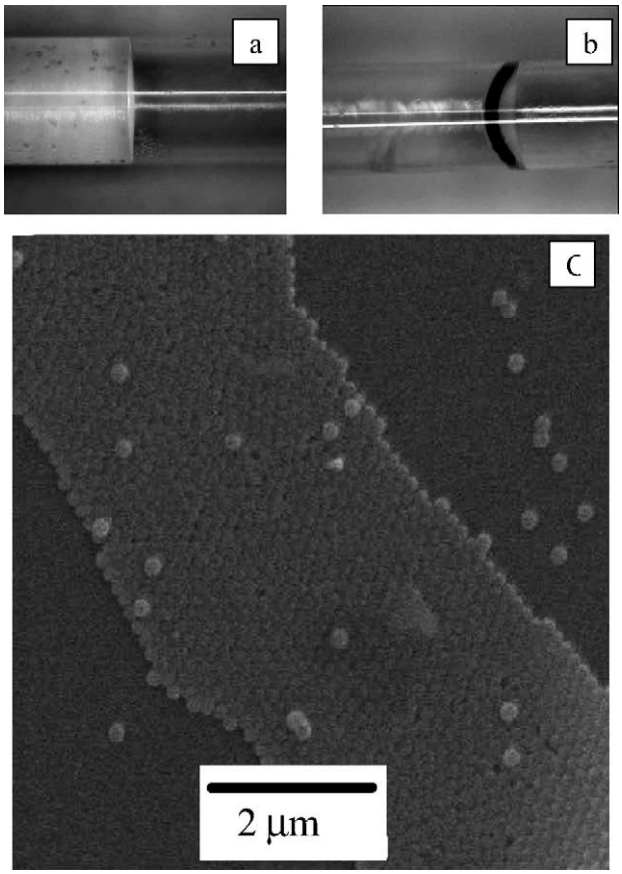

Fig. 5. Patterning of particle arrangement. (a) Hydrophobic surface treated with octadecyltriethoxysilane. (b) Hydrophylic surface. (c) Patterning of silica particle arrangement.

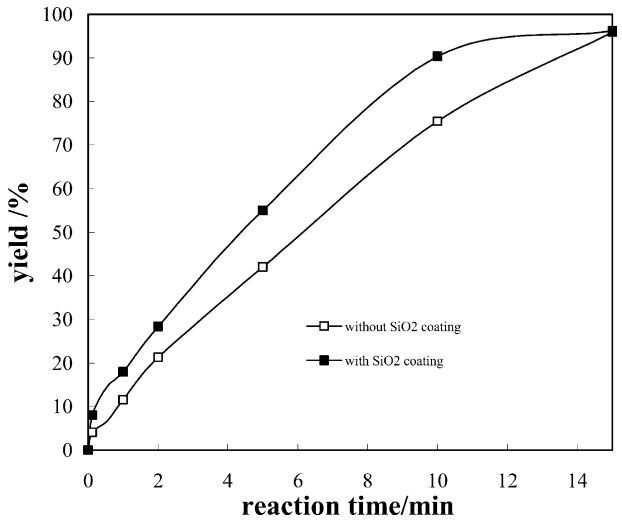

Fig. 6. Effect of surface area enlargement by silica surface treatment on hydrolysis rate of umbelliferone acetate catalyzed by Lipase. Reaction yield was determined from the yield of the hydrolyzed product, umbelliferone.

stabilized on the reactor surface. In this study, it was not possible to heat the enzyme because of the inherent possibility of degradation. Therefore, we had to carry the enzyme after we prepared the silica coating layer. The silica coating layer has a rougher surface than a plane wall of the glass capillary. Simple calculation indicates that the top surface area of silica particle layer is about 1.5 times larger than that of flat wall of glass, which shows a good correspondence with the amount of the enzyme increased after surface treatment with silica particles. This corresponds to the difference in the amount of enzyme carried on the particle layer and the difference in enzyme reaction kinetics.

3.3. Fabrication of an anatase type titania reactor and its photocatalytic activity

A photocatalytic reaction can used for environmental and energy applications. Because the specific dimension of microreactor is much smaller than that of the other reactors, application for photocatalytic reaction is expected to be effective: the loss of light energy by absorption and scattering by the solid catalyst in a reaction solution would be reduced. Anatase type Titania is a very popular catalyst for photocatalytic reaction; it can be used for environmental reactions to decompose hazardous organic or inorganic molecules by UV irradiation [22]. As described in the introduction part, anatase type titania is often carried onto a microreactor by a sol–gel or CVD methods. Therefore, anatase type titania was heterocoagulated in this study onto monodispersed silica. Then it was arranged on a capillary tube to obtain a photocatalytic microreactor. Regarding concentration of pure SiO_2 particle layers, the molar ratio of SiO_2 to TiO_2 was adjusted to 1.28:1 (about 0.01 g ml^{-1} SiO_2 particles). Fig. 7 shows an SEM image of modified surface of a 530 μm diameter micro-capillary. An overall well-arranged hexagonal array was obtained (Fig. 7a) with a thickness of four layers in the 5 cm capillary. Thickness was not completely consistent with that of the SiO_2 layer with the same concentration described before. This may be the result of effects of the surfactant and rough surface of the core-shell structure. The same process of catalyst immobilization was performed on the inner wall of a microcapillary without a SiO_2 layer for comparison to elucidate the role of the SiO_2 coating. When the TiO_2 catalyst was used as the sole modification material, the TiO_2 particle layer was a single layer and not closely packed, as shown in Fig. 7b. This may result from the TiO_2 particles' irregular shape and high colloidal stability. A similar coating was also obtained in a 200 μm capillary.

The photocatalytic reaction was performed by injecting the methylene blue solution through the microcapillary controlled by a syringe pump. Using microcapillaries, TiO_2-coated inner surface, and SiO_2/TiO_2 modified inner surface as the reactors, we found that reduction of methylene blue (0.1 mM) assisted by TiO_2 photocatalysis under an UV-irradiation wavelength of 254 nm was a function of the reaction time. That reaction time was inferred to be the

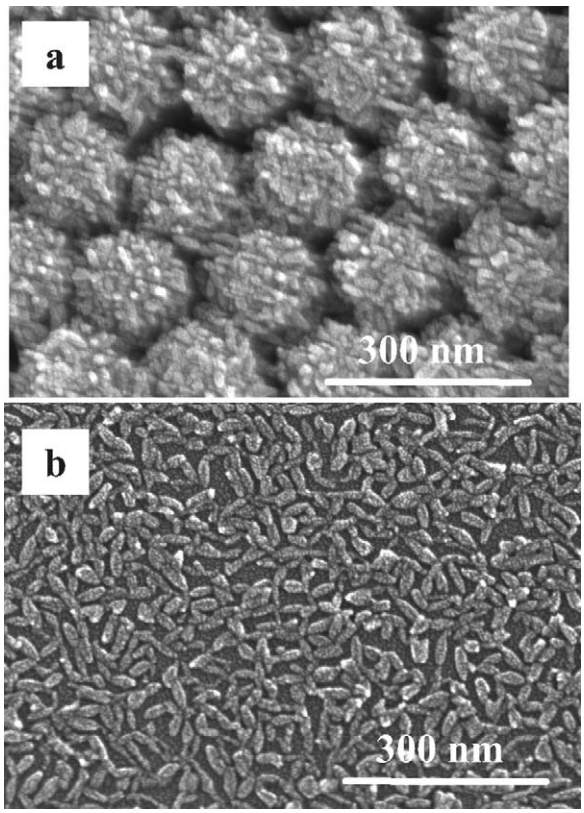

Fig. 7. Particle layer deposited on inner wall of capillary. (a) Anatase type TiO_2 coated SiO_2 layer. (b) Anatase type TiO_2 layer.

residence time in the microcapillary, which was calculated according to the flow rate.

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

Table 1
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

Concentration of methylene blue can be determined by light absorption of the UV treated sample. Therefore, products were obtained in the microcapillaries after different reaction times and measured by the UV method. Results of the reaction in the presence and absence of TiO_2 under UV irradiation are shown in Fig. 8. The conversion rates of the photocatalytic reduction of methylene blue in the microcapillary are listed in Table 1.

The results in Fig. 8a showed the remarkable catalyst effect of TiO_2. Without the TiO_2 catalyst, the initial reaction 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 a few minutes. In the microcapillary with TiO_2 as a catalyst, 2 min is sufficient to complete the reaction in the 530 μm capillary (initial reaction rate: 1.5% s^{-1}). Furthermore, reducing the capillary diameter to 200 μm improved the initial reaction rate to 6.3% s^{-1}; 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

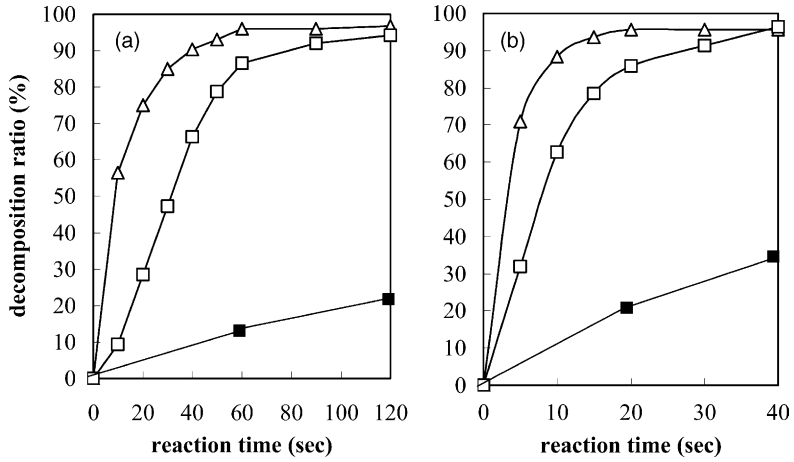

Fig. 8. Decomposition kinetics of 0.1 M methyleneblue under a UV irradiation. (a) 530 μm capillary and (b) 200 μm capillary. (△) TiO_2/SiO_2 particles, (□) TiO_2 particles, (■) No catalized.

20 s (reaction ratio 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 the photocatalyst.

4. Summary

Self-arrangement of colloidal particles was utilized to modify the microreactor inner wall. This method can modify the inner surface of capillary merely by drying after putting a colloid solution into capillary. Particle layers were generated at the menisci and developed with as the menisci moved. Choosing an adequate drying temperature and solvent, it was possible to make the moving rate constant by this condition. Thereby, we obtained homogeneous particle layer thickness for up to 10 m inside the microreactor. Thickness was controlled by concentration of colloid and from the particle layer from a monolayer to a few micrometers of thickness was obtained.

The silica particle coated microreactor was applied for enzyme reaction in a micro-reactor. We expected that a designable solid support for biomolecules offers special properties, such as larger surface area. In this study, an immobilized enzyme preserving reasonable activity, a modification of capillary with self-organized SiO_2 particle layers, was coupled to the enzyme reaction. In low concentration of the substrate region, the higher yield is reasonable by the fact that the pre-modification of SiO_2 is beneficial for immobilizing a larger amount of the enzyme than that directly immobilized on the microcapillary wall. Although no very large surface area by coating SiO_2 particles was obtained, a new way from present work is put forward here that biochemical active layers can be patterned by designing the well-organized solid support.

Also, the present work extended the potential application to modify the microreactor with core-shell structure particles. The 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 markedly high reduction yield of methylene blue is obtained with this highly active catalytic system.

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