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Hierarchically porous TiO₂/SiO₂ fibers with enhanced photocatalytic activity[†]

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While TiO₂ nanoparticles are one of the most promising photocatalysts, their applications have been greatly hindered by easy aggregation. One of the effective routes to solve this problem is to incorporate them on/in a solid carrier. In this paper, we report the fabrication of hierarchically porous TiO₂/SiO₂ fibers *via* an electrospinning technique combined with subsequent high-temperature calcination treatment, in which the hierarchically porous SiO₂ fibers confer a platform to assemble TiO₂ nanoparticles with a uniform spatial distribution. The resultant hierarchically porous TiO₂/SiO₂ fibers have shown an enhanced photocatalytic activity with ~95% degradation of rhodamine B as compared to ~75% using our synthesized TiO₂ nanoparticles and ~77% using commercially available Degussa P25 after 120 min illumination.

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1. Introduction

Titanium dioxide (TiO₂) is considered as one of the most promising semiconductor photocatalysts due to its high efficiency, low cost, chemical inertness, and photo-stability.1 In particular, nanoscale TiO₂ particles exhibit a high photocatalytic activity due to their high specific surface areas.² However, TiO₂ nanoparticles could be easily aggregated to reduce their surface areas, thus greatly lowering their performance. Moreover, suspended TiO2 nanoparticles are difficult to be separated from the reaction solution after the photocatalytic process, which inevitably brings the second pollution to the treated water. Typically, surface modification,³ size-controlled TiO₂ nanoparticles⁴ and assembling nanosized photocatalyst on/in a solid carrier⁵ are often used to overcome these shortcomings. Among these strategies, the third one is regarded as the promising effective route, and thus many efforts have been devoted to assemble TiO₂ nanoparticles on/in various supports such as thin films,⁶ nanotubes,⁷ porous fibers,⁸ dendrimers,⁹ and so forth.

Hierarchically porous fibers are deemed as an excellent candidate for catalyst supports, owing to their high surface area

and attendant dispersion of catalyst functions, and superior mass transport.¹⁰ The key point is to select a proper material as the carrier support. SiO₂ could be an excellent one owing to its chemical inertia, thermal stability, and high transmissivity to the UV radiation.¹¹ Up to date, a rich variety of methods have been exploited for the fabrication of porous SiO₂ fibers.¹² However, the inner structures of the reported SiO₂ porous fibers are ordinary solid.

In present work, we report the fabrication of hierarchically porous TiO_2/SiO_2 *via* electrospinning technique, in which the hierarchically porous SiO_2 fiber framework services as the ideal platform to assemble. As compared to the reported work,¹³ the present TiO_2/SiO_2 fibers possessed a novel hierarchically hollow structure and the TiO_2 nanoparticles were well dispersed on/in the amorphous SiO_2 matrix. The photodegradation of rhodamine B (RhB) as a simulate reaction were investigated and the electrospun TiO_2/SiO_2 hierarchically porous fibers show a significantly enhanced photocatalytic activity compared to TiO_2 nanoparticles and Degussa P25.

2. Experimental procedure

TiO₂/SiO₂ porous fibers were synthesized *via* calcination of electrospinning polyureasilazane (PSN), polyvinylpyrrolidone (PVP) and tetrabutyl titanate (TBOT) hybrid fibers. In a typical experimental procedure, 5.0 g of PSN (Ceraset, Kion Corporation, USA), 4.0 g of PVP ($M_W \approx 30\,000$, Ares, Scientific Instruments Company, Ningbo, China) and 2.5 g TBOT (Aladdin, Reagent Company, Shanghai, China) were commercially were commercially available and directly used without further purification. For electrospinning of polymeric precursor fibers, 9.5 ml of absolute ethyl alcohols were used as the solvent. The

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[†] Electronic supplementary information (ESI) available: (1) SEM images of the electrospun polymer precursor fibers, pure TiO_2 nanoparticles and P25; (2) XRD pattern and EDS analysis of the pure TiO_2 nanoparticles and P25. (3) The spectra changes of RhB in dark and over P25 photocatalyst. See DOI: 10.1039/c4ra02285h

mixtures of PSN/PVP/TBOT were firstly vigorous stirred for 12 h, and then transformed into a plastic syringe with a stainless steel nozzle (anode, diameter: 0.2 mm). The tip of the stainless steel nozzle was placed in the front of a metal cathode (collector) with a fixed distance of 20 cm between the nozzle and the collector. An electrical potential of 20 kV was applied for electrospinning PSN/PVP/TBOT fibers. The resultant polymeric fibers were located in an Al_2O_3 crucible (99% purity) with a piece of graphite paper as the cover, and then placed at the centre of a tube furnace. Subsequently, the samples were pyrolyzed in air at the desired temperature of 900 °C for 2 h with a heating rate of 5 °C min⁻¹, followed by furnace-cool to ambient temperature. For comparison, TiO₂ nanoparticles were prepared via the traditional sol-gel process combined with subsequent calcination treatment. Typically, 2.0 g of TBOT was firstly mixed with an amount of deionized water and vigorous stirred for 12 h for the formation of TiO₂ gelatin, which were dried by an incubator and subsequently calcinated with the similar pyrolysis procedure of the TiO₂/SiO₂ porous fibers as mentioned above. Degussa P25 was commercially available, and used directly for the photocatalytic activity characterization (Aladdin, Reagent Company, Shanghai, China).

The obtained products were characterized with X-ray powder diffraction (XRD, D8 Advance, Bruker, Germany) with Cu K α radiation ($\lambda = 1.5406$ Å), field emission scanning electron microscopy (SEM, S-4800, Hitachi, Japan) and high-resolution transmission electron microscopy (HRTEM, JEM-2100, JEOL, Japan) equipped with energy dispersive X-ray spectroscopy (EDS).

The photocatalytic activity of the resultant products was evaluated for degradation of rhodamine B (RhB). The photocatalytic reaction is performed in an inner-irradiation quartz annular reactor with a Xenon lamp ($\lambda > 320$ nm, CEL-Hx F300, Beijing) and a water-cooled condenser. Typically, 90 mg of RhB and 800 mg of the as-prepared TiO₂/SiO₂ porous fibers were dispersed in 100 ml deionized water (the mole fraction of RhB is 3.5×10^{-4}). Prior to irradiation, the suspensions were magnetically stirred in dark for 30 min to ensure the establishment of an adsorption-desorption equilibrium between the photocatalyst and the RhB dye. An aliquot (3 ml) of the solution was taken at a certain time interval (10 min) during the reaction and analyzed on the UV-visible spectrophotometer (UV-3900, Hitachi, Japan). The change in RhB absorbance in the solution was used to monitor the extent of reaction at given irradiation time intervals. For comparison, 60 mg of as-prepared TiO₂ nanoparticles and P25 were also used as the photocatalyst for degradation of RhB with the same concentration and light conditions. Here, 60 mg TiO_2 nanoparticles is to keep the identical dosages of these two TiO₂ photocatalysts for the degradation of RhB, which is calculated based on the EDS results (Fig. 3). According to the EDS analysis, the atomic ratio of Si to Ti is: 29.07 : 1.84 = 15.8. Then the weight ratio of SiO₂ to TiO_2 within the porous fibers can be calculated as: $15.8 \times (28 +$ 16×2 : $1 \times (44 + 16 \times 2) = 948$: 76 = 12.5: 1. As for 800 mg porous TiO₂/SiO₂ fibers used as the photocatalysts, the dosage of TiO₂ nanoparticles should be fixed at: $800 \times 1/(12.5 + 1) = 60$ (mg).

3. Results and discussion

3.1 SEM and TEM characterizations of the as-prepared products

The as-spun precursor fibers are ranged in the size of several to dozens millimeters in length and averagely sized in \sim 2.5 µm in diameters with smooth surfaces (Fig. S1(a), ESI[†]) and circular solid cross-sections (Fig. S1(b), ESI⁺). Fig. 1 displays the typical SEM images of the calcinated fibers under different magnifications. The products are of high yields with well-defined fiber shapes (Fig. 1(a)). Fig. 1(b) shows the resultant fibers under a high magnification, suggesting that the fibers are averagely sized in \sim 1.6 µm in diameter with rough surfaces. Closer observation (Fig. 1(c)) of the fiber bodies under a higher magnification reveals that numerous tiny nanoparticles are assembled uniformly in the fiber matrix. Notably, the fibers possess a thoroughly porous structure throughout the entire bodies (Fig. 1(d and e)). As compared to the reported works on the fabrication of porous SiO₂ fibers,¹² our fibers exhibit a novel hierarchically porous structure. Their typical XRD pattern (Fig. 1(f)) discloses that the fibers are composed by major phases of amorphous SiO2 and rutile TiO2 (JCPDS card no. 21-1276). The minor peaks detected at $\sim 28^{\circ}$ and $\sim 32^{\circ}$ are attributed to the tiny SiO₂ nanoparticles, which might be transformed partly from the amorphous SiO₂ caused by the high pyrolysis temperature.

Fig. 2(a) is a typical TEM image of the obtained fibers under a low magnification, clearly suggesting that the fibers possess a thoroughly porous structure. A closer observation displays that a large amount of tiny nanoparticles are uniformly assembled in the porous fiber frameworks (Fig. 2(b)). Fig. 2(c) provides a typical selected area electron diffraction (SAED) pattern recorded from the marked area of A in Fig. 2(b), implying that the fibers are composed by amorphous phase and crystalline rutile TiO₂. Fig. 2(d) presents a representative HRTEM image of the as-synthesized fibers, suggesting that TiO₂ nanoparticles are irregularly shaped and typically sized in just several nanometers, which are isolatedly and homogeneously assembled in the amorphous framework matrix. The blue marked areas refer to the crystalline TiO₂ nanoparticles.

The EDS analysis shows that the fibers mainly consist of Si, O, Ti (Fig. 3(a)). The detected C and Cu come from the carbon film and copper grid used to support the TEM sample, respectively. The atomic ratio of Si to O, within the experimental limit, is close to 1:2, implying that the amorphous matrix frameworks are SiO₂ (Fig. 3(b), ESI[†]). The element mappings confirm that the assembled TiO₂ nanoparticles exhibit a very uniform spatial distribution within the porous SiO₂ frameworks (Fig. 3(c)–(e)).

3.2 The proposed formation mechanism

The possible mechanism for the formation of inner porous structure is schematically illustrated in Fig. 4. Before electrospinning, TBOT will be easily hydrolyzed in ethanol *via* the reaction as bellow:



Fig. 1 (a and b) Typical SEM images of the hierarchically porous TiO_2/SiO_2 fibers under different magnifications. (c) Closer observation of the fiber surface. (d and e) Typical SEM images of the destroyed body and cross-section of the products, showing their hierarchically porous nature throughout the entire fibers. (f) A respective XRD pattern of the as-synthesized hierarchically porous TiO_2/SiO_2 fibers.

$$Ti(O-Bu)_4 + H_2O \rightarrow Ti(OH)_4 + C_4H_9OH$$
(1)

As a result, Ti(OH)₄ would exist as a droplet phase and dispersed in the PVP/PSN solutions, which favors the formation of a microemulsion. The dispersed droplet phase experiences only by the acting surface forces from the continuous phase of PVP/PSN solution sucked into the jet due to the electric forces. Thus, in the case of the electric force strong enough, a jet will be stretched from the PVP/PSN and Ti(OH)₄ drop tip, making the formation of a discontinued jet and, ultimately, discontinued fibers.14 The resultant discontinued structure plays as the template for the formation of the hierarchically porous fibers by the convention of $Ti(OH)_4$ to TiO_2 caused by the calcination in air. Additionally, the formation of the hierarchically porous fibers can be attributed to the selective evaporation-calcination process due to the distinctively different thermal properties between PVP and PSN.15 Thus, PSN would be converted to SiO2 and retained for constructing the hierarchically porous fibers

under calcination at 900 °C, and $Ti(OH)_4$ would be transformed to rutile TiO_2 , which consequently make TiO_2 nanoparticles be assembled in SiO_2 hierarchically porous fibers.

3.3 Photocatalytic activity

The photodegradation of rhodamine B (RhB) used as a simulate reaction was investigated to explore the photocatalytic activity of the hierarchically porous TiO_2/SiO_2 fibers. Prior to irradiation, the mixture is maintained in dark and no obvious photodegradation can be observed after 120 min (Fig. S3, ESI†), suggesting that the reaction should be photocatalytic rather than physical adsorption. As disclosed in Fig. 5(a), the UV-visible adsorption peaks centered at ~554 nm of RhB over TiO_2/SiO_2 porous fibers undergoes a fairly evolution with the increase of the irradiation time, suggesting the dye concentrations decreased during the photocatalysis process.¹⁶ However, the spectra changes of RhB (Fig. 5(b)) over TiO_2 nanoparticles (SEM image and XRD pattern of the fabricated







Fig. 2 (a and b) Typical TEM images of the obtained fibers under different magnifications. (c) A typical SAED pattern of the fiber recorded from the marked area of A in (b). (d) A representative HRTEM image of the fiber recorded form the marked area of B in (b).

 TiO_2 nanoparticles, see Fig. S2, ESI[†]) exhibit an evolution quite different from that of TiO_2/SiO_2 porous fibers. Notably, the adsorption peaks experience a gradually decrease at the early stage of the reaction time of ~70 min, whereas there is negligible changes with the further increase of the irradiation time. This could be ascribed to the aggregation of the TiO_2 nanoparticles after long time work induced by the minimization of the surface energy, which results in the photocatalyst deactivation. The aggregation of nanoparticles would lead to following negative influences: (i) inhibit the interparticle charge transfer; (ii) lower the capacity of the adsorption of reactants and desorption of products, ultimately result in the deactivation of the photocatalysis behavior. Furthermore, for comparison, the photocatalytic efficiency of commercial TiO₂ nanoparticles (Degussa P25) (SEM image and EDS pattern, see Fig. S4, ESI⁺), which are a widely used standard photocatalyst, is also measured under the same experimental conditions. The



Fig. 3 (a) A typical EDS spectrum of the porous fibers. (b) Detailed chemical compositions (at%) of the porous fiber. (c-e) The element mapping of Si, O, and Ti within the honeycomb mesoporous fibers.



Fig. 5 (a and b) Temporal UV-visible adsorption spectral of the RhB solution with the irradiation time over TiO_2/SiO_2 porous fibers and TiO_2 nanoparticles, respectively. (c and d) Digital pictures of the color changes with the irradiation time of TiO_2/SiO_2 porous fibers and TiO_2 nanoparticles, respectively. (e and f) Photocatalytic activities and the first order kinetic plots of TiO_2/SiO_2 porous fibers, TiO_2 nanoparticles and P25, respectively. The black line in (e) responds to the photocatalytic activity of TiO_2/SiO_2 porous fibers in dark.

results suggest that the photocatalytic activity of P25 is similar to our present TiO_2 nanoparticles (Fig. 5(d) and (e) and S5(a), ESI[†]), implying the P25 photocatalyst also can not work steadily with high-efficiency. That is to say, the hierarchically porous SiO₂ fibers have been serviced as a good carrier for TiO₂ nanoparticles to limit their aggregation, which, in turn, enhances their photocatalytic activities. Fig. 5(c and d) and S5(b), ESI[†] show the color changes of RhB solutions by using these three photocatalysts corresponding to the UV-visible adsorption changes, respectively. It seems that the colors of the suspensions catalyzed by TiO₂/SiO₂ porous fibers (Fig. 5(c)) changed gradually from pink to almost colorless, suggesting the nearly complete photodegradation of RhB. Nevertheless, the suspensions catalyzed by TiO₂ nanoparticles (Fig. 5(d)) and P25 (Fig. S5(b), ESI[†]) still show an obvious light pink color after 120 min illumination. Fig. 5(e) presents the time-dependent degradations of RhB of these three photocatalysts (C and C_0 refer to the real time RhB concentration and initial RhB concentration, respectively). As for TiO₂/SiO₂ porous fibers, it exhibits a favorable linear relevance with a degradation quantity of ~95% after 120 min illumination. Otherwise, the degradation quantities of TiO₂ nanoparticles and P25 are \sim 75% and \sim 77%, respectively. Fig. 5(f) shows the first order constants of k derived form the linear fitting of the plots. The k of the photocatalysts of TiO2/SiO2 porous fibers, TiO2 nanoparticles and P25 are cal. 0.0227, 0.0125 and 0.017, respectively.



Fig. 6 Schematic illustration for RhB photodegradation over SiO $_2/$ TiO $_2$ porous fibers under light irradiation.

These results confirm the enhanced photocatalytic activities of hierarchically porous TiO_2/SiO_2 fibers as compared to TiO_2 nanoparticles.

3.4 The proposed photodegradation mechanism

The mechanism of RhB photodegradation over the hierarchically porous TiO₂/SiO₂ fibers is schematically illustrated in Fig. 6. Typically, current theory has pointed out that the reaction process of RhB photodegradation can divide into two types. One is deethylation with the obvious adsorption peak shifts, and the other is cycloreversion with insignificant peak transformation.17 Based on the present UV-visible adsorption (Fig. 5(a) and (b)), the reaction can be attributed to the second type. In general, TiO₂ particles firstly absorb the UV light to generate electron/ hole pairs once the energies are higher than the band gap energy. Then, part of the valence band holes (h^{+}) will directly cleavage the chromophore structure (cycloreversion) of RhB. Anther part of the holes will be trapped by the surface bound HO^- (or by H_2O) to yield 'OH radicals and H^+ cations. Concomitantly, the conduction band electrons (e⁻) are scavenged by the adsorbed oxygen molecules to yield superoxide radical anions (O2.) and combine with H⁺ cations to generate 'OOH radicals. Subsequently, 'OH and 'OOH radicals would attack on the positions of highest electron density in RhB molecules through photooxidation.

4. Conclusions

In summary, we have demonstrated the fabrication of hierarchically porous TiO_2/SiO_2 fibers *via* electrospinning polymeric precursor containing polyureasilazane, polyvinylpyrrolidone and butyl titanate combined with subsequent high-temperature calcination treatment. The obtained fibers are composed of hierarchically porous SiO₂ frameworks and tiny TiO₂ nanoparticles. The results suggest that the hierarchically porous SiO₂ fiber frameworks could confer an ideal platform to assemble the TiO₂ nanoparticles with a uniform spatial distribution. The resultant hierarchically porous TiO₂/SiO₂ fibers exhibit an enhanced photocatalytic activity with ~95% degradation of rhodamine B as compared to ~75% of our synthesized TiO₂ nanoparticles and ~77% of commercial available P25. It is expected that current work could provide a facile strategy for the exploration of photocatalysts with high performance.

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