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Preparation of three-dimensional interconnected mesoporous anatase TiO₂-SiO₂ nanocomposites with high photocatalytic activities

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ABSTRACT

In this article, we report the preparation of a three-dimensional (3D) interconnected mesoporous anatase TiO₂-SiO₂ nanocomposite. The nanocomposite was obtained by using an ordered two-dimensional (2D) hexagonal mesoporous anatase 70TiO₂-30SiO₂-950 nanocomposite (crystallized at 950 °C for 2 h) as a precursor, NaOH as an etchant of SiO₂ via a “creating mesopores in the pore walls” approach. Our strategy adopts mild conditions of creating pores such as diluted NaOH solution, appropriate temperature and solid/liquid ratio, *etc.* aiming at ensuring the integrities of mesopores architecture and anatase nanocrystals. XRD, TEM and N₂ sorption techniques have been used to systematically investigate the physico-chemical properties of the nanocomposites. The results show that the intrawall mesopores are highly dense and uniform (average pore size 3.6 nm), and highly link the initial mesochannels in a 3D manner while retaining mesostructural integrity. There is no significant change to either crystallinity or size of the anatase nanocrystals before and after creating the intrawall mesopores. The photocatalytic degradation rates of rhodamine B (RhB, 0.303 min⁻¹) and methylene blue (MB, 0.757 min⁻¹) dyes on the resultant nanocomposite are very high, which are 5.1 and 5.3 times that of the precursor; even up to 16.5 and 24.1 times that of Degussa P25 photocatalyst, respectively. These results clearly demonstrate that the 3D interconnected mesopores structure plays an overwhelming role to the increments of activities. The 3D mesoporous anatase TiO₂-SiO₂ nanocomposite exhibits unexpected-high degradation activities to RhB and MB in the mesoporous metal oxide-based materials reported so far. Additionally, the nanocomposite is considerably stable and reusable. We believe that this method would pave the way for the preparation of other 3D highly interconnected mesoporous metal oxide-based materials with ultra-high performance.

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1. Introduction

Ordered mesoporous metal oxide-based materials have at-

tracted a wealth of interest because of their large and uniform mesopore size, high specific surface area, particularly the unique electronic optical and catalytic properties relating to

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applications in photocatalysis, catalysis, advanced batteries and water purification, *etc.* [1–27]. It is well-known that the pores dimensionality is of paramount importance since it can exert a profound effect on the accessibility, adsorption and diffusion behavior of guest molecules within the pore network, *etc.* [9–11]. 3D interconnected mesoporous networks have shown numerous advantages over 2D and 1D counterparts, such as: (1) considerably benefiting ingress/egress of guest species because of possessing far more openings to the internal porous network at the surface, (2) extremely enhancing diffusion efficiencies of guest molecules within the interconnected mesopore networks, (3) largely elevating both the accessibility and availability of the inner surfaces, (4) allowing light to irradiate more inner surfaces through the openings and interlinked mesopore architectures, which can lead to an immense increment of $\cdot\text{OH}$ radical in number, and (5) enhancing light harvesting efficiency due to the multiple scattering of light in the interpenetrated mesopores [28–30]. The combination of such prominent characteristics can significantly improve photocatalytic oxidation performance.

The syntheses of ordered mesoporous metal oxide-based materials can be roughly divided into “soft template” and “hard template” methods. The syntheses of 3D interconnected mesoporous networks in metal oxide-based materials employing the “soft template” approach have hitherto not been reported, to the best of our knowledge. Conversely, there have been multiple reports detailing the preparation of mesoporous metal oxide-based materials with 3D interlinked voids or mesopores using the “hard template” method [31–35]. However, the main shortcomings of the latter approach are [7]: (1) it is difficult to completely fill the pores of the hard template (such as mesoporous silica or mesoporous carbon), even when multiple impregnation steps are used, and (2) the synthetic approach involves multiple and tedious steps requiring time to generate the template followed by its subsequent removal, *etc.* Hence, the simple preparation of 3D metal oxide-based materials possessing well-established interconnected mesochannels remains a challenge.

Additionally, controlling the crystallinity, phase, and crystal size of the pore walls is an important factor, which determines their performance in practical applications [9,10]. For example, titania has three crystalline phases with the anatase polymorph showing the highest photocatalytic activity [12,17,36]. Both high crystallinity and large nanocrystals can obviously enhance activity [11,17,37,38]. Fortunately, designing ordered mesoporous $\text{TiO}_2\text{-SiO}_2$ nanocomposites with complete anatase crystallization, large nanocrystals and high specific surface areas can be readily achieved as a function of crystallization temperature and time, and Ti/Si ratio. Furthermore, tailored silica nanoparticle sizes residing in the pore walls can also be realized.

In this study, we report the simple preparation of a 3D interconnected mesoporous anatase $\text{TiO}_2\text{-SiO}_2$ nanocomposite. The 3D mesoporous nanocomposite was obtained by using an ordered 2D hexagonal mesoporous anatase $70\text{TiO}_2\text{-}30\text{SiO}_2$ nanocomposite (crystallized at 950°C for 2 h, abbreviated as $70\text{TiO}_2\text{-}30\text{SiO}_2\text{-}950$) as a precursor, NaOH as an etchant of silica *via* a “creating mesopores in the pore walls” approach. Our

strategy adopts moderate conditions of creating mesopores such as diluted NaOH solution, appropriate temperature and solid/liquid ratio, in order to ensure the integrities of mesoporous structures and anatase crystals. Under these conditions, the dense and uniform intrawall mesopores with an average size of 3.6 nm were obtained, which highly connect the initial 2D arranged mesochannels into a 3D network. Meanwhile, the mesostructures are retained in the integrity. Rhodamine B (RhB) and methylene blue (MB) dyes were chosen as probe molecules to evaluate the resulting nanocomposite. The 3D interconnected mesoporous nanocomposite exhibits unexpectedly high photocatalytic degradation activities to RhB and MB—significantly higher than that for the precursor sample and a commercial Degussa P25 photocatalyst, in addition to being quite stable and reusable. We believe that this method is generally applicable to other ordered mesoporous metal oxide-based materials, such as niobium and tantalum oxides, opening up a new avenue to design 3D highly interconnected mesoporous architectures with ultra-high performances.

2. Experimental

2.1. Chemicals

Titanium isopropoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, TIPO, $\geq 97\%$) and tetraethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS, $\geq 96\%$) were purchased from Fluka. Pluronic P123 ($M_w = 5800$, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) was received from Sigma-Aldrich. Ethanol (absolute), concentrated HCl (36.5 wt%) and P25 photocatalyst (a commercial nano-crystalline TiO_2 consisting of *ca.* 80% anatase and 20% rutile; BET surface area is *ca.* $50\text{ m}^2/\text{g}$) was kindly supplied by Degussa Corp. RhB ($\text{C}_{28}\text{H}_{31}\text{ClN}_3\text{O}_3$) was bought from Sigma-Aldrich and MB ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}\cdot 3\text{H}_2\text{O}$) was purchased from Sinopharm. The molecular structures of RhB and MB are shown in Fig. 1, each prepared into $2.5 \times 10^{-5}\text{ mol/L}$ aqueous solutions with deionized water, respectively. All the chemicals were used as received without any further purification. The pH values of RhB and MB solutions were neither adjusted nor buffered.

2.2. Preparation

The ordered 2D hexagonal mesoporous $70\text{TiO}_2\text{-}30\text{SiO}_2$ nanocomposite was synthesized according to our previous procedure [39]. The as-synthesized sample was calcined at 350°C for 6 h in air to remove the organic template and subsequently crystallized at 950°C for 2 h in air with a heating rate of $1^\circ\text{C}/\text{min}$. The obtained ordered 2D hexagonal mesoporous anatase $\text{TiO}_2\text{-SiO}_2$ nanocomposite with a Ti/Si ratio of 70/30

Fig. 1. Molecular structures of RhB and MB.

(70TiO₂-30SiO₂-950) was finely ground and used as the precursor. The precursor was then treated with 0.5 mol/L NaOH solution at 40 °C with a solid/liquid ratio of 1/10 (g/mL) [40]. The mixture was isolated and vigorously stirred for 12 h prior to the suspension being centrifuged to recover the solid. The solid was again impregnated with fresh NaOH solution under the same conditions as described. This procedure was repeated a further two times (total 36 h). The final solid was thoroughly washed with deionized water under stirring, centrifuged and dried at 100 °C for 24 h before being activated at 300 °C for 3–6 h in air at a heating rate of 3 °C/min.

2.3. Characterization

Small-angle X-ray powder diffraction (SAXRD) patterns were recorded on a German Bruker D4 X-ray diffractometer with Ni-filtered Cu-K α radiation (40 kV, 40 mA). Wide-angle X-ray diffraction (WAXRD) patterns were collected on a Rigaku D/MAX-rB X-ray powder diffractometer using a high-power Cu-K α ($\lambda = 0.15418$ nm) source operating at 40 kV and 60 mA with a graphite monochromator filter. The average anatase nanocrystal size was estimated using the Scherrer equation at the half-height width of the (101) diffraction peak with silicon as a standard for the instrumental line broadening. The crystallinity of anatase nanocrystals was expressed as a function of the intensity or area of the (101) diffraction peak. Transmission electron microscopy (TEM) images were obtained on a JEM-2011 transmission electron microscope (JEOL Company) combined with energy-dispersive X-ray spectroscopy (EDX) operating at 200 kV. For TEM measurements, the samples were prepared by sonication in ethanol and suspended onto holey carbon grids. The atomic wt% of Ti and Si in the sample were examined using EDX. N₂ adsorption-desorption isotherms were collected on a Micromeritics ASAP 2010 Adsorption Analyzer at -196 °C. All samples were degassed at 250 °C for at least 5 h before analyses. The Brunauer-Emmett-Teller (BET) specific surface areas were calculated from adsorption data at a relative pressure range from $p/p_0 = 0.057$ –0.20. The total pore volumes (V_T) were calculated at a relative pressure of $p/p_0 = 0.976$. Pore size distributions were calculated from adsorption branches using the Barrett-Joyner-Halenda (BJH) model.

2.4. Adsorption and photocatalytic reaction

Adsorption and photocatalytic oxidation of RhB and MB on mesoporous anatase-silica nanocomposites were investigated in air in a quartz vessel at room temperature according to our previous method [41,42]. Fifty mL of an aqueous dye solution and 50.0 mg of the finely ground catalyst powders were placed in the quartz vessel, which formed a suspension under stirring. For comparison, all the experiments were performed under identical conditions. First, the suspensions were vigorously stirred in the dark for a desired time to evaluate the adsorption performance. After establishing the adsorption-desorption equilibrium, photocatalytic reactions were initiated by subjecting the suspension to UV light irradiation from a 25-W low-pressure mercury lamp ($\lambda = 254$ nm). The radiant flux was measured with a photometer (International Light Model IL1400A). A 1.0-mL aliquot of the suspension was taken at specific time intervals and centrifuged at 15000 r/min for 15 min. Dye concentration was analyzed using a JASCO V-550 UV-Vis spectrophotometer. For comparison, the performance of a commercial P25 photocatalyst was also measured.

Stability and reusability were investigated by repetitive adsorbing and degrading RhB. After the dye was adsorbed and photocatalytically degraded each time, the sample was separated by centrifugation, followed by activating at 300 °C in air for 3–6 h. Subsequently, the material was re-used under the same RhB solution concentration.

3. Results and discussion

3.1. SAXRD and WAXRD

The SAXRD pattern of the parent sample (70TiO₂-30SiO₂-950) displays only one peak centered at $2\theta = 1.08^\circ$ (Fig. 2(a)), which can be indexed as the (100) diffraction of a typical 2D hexagonal mesostructure ($p6mm$ space group) [39], demonstrating an ordered arrangement of mesopore channels with a cell parameter (a_0) of 9.4 nm. After creating mesopores in the pore walls, both the peak position ($2\theta = 1.07^\circ$) and intensity of the resulting sample have no obvious variation (Fig. 2(a)), indicating that the integrity of the mesostructure remains unchanged.

Fig. 2. Small-angle (a) and wide-angle (b) XRD patterns of the samples before (1) and after (2) creating mesopores in the pore walls.

The WAXRD pattern of the parent sample exhibits the characteristic diffraction peaks of anatase [39] displaying the intense and narrow (101) peak (Fig. 2(b)). The area and intensity of the (101) diffraction peak are ~ 323 and ~ 288 , respectively, and the average size of the nanocrystals is calculated to be ~ 10.8 nm, which is larger than the cell parameter a_0 (9.4 nm). Such sized nanocrystals implies a degree of partially or fully blocked mesochannels as the nanocrystals may protrude into the cylindrical mesochannels. After creation of the intrawall mesopores, the area and intensity of the 101 peak have no significant alterations (345 and 288, respectively), illustrating that the crystal size and crystallinity are not essentially altered (Fig. 2(b)).

3.2. TEM observations

TEM micrographs show that the precursor has ordered 2D hexagonal mesopore channels without intrawall pores (Fig. 3(a) and (b)). The cell parameter (a_0) is evaluated to be ~ 9.5 nm, essentially the same as the value (9.4 nm) calculated from SAXRD. The mesochannel sizes are uniform and the average size is *ca.* 4.1 nm. High-resolution TEM images reveal that the crystals are randomly oriented and link with the amorphous silica nanoparticles to form a “brick-mortar-like” framework structure. The majority of crystals align in the pore wall direction, while some crystals protrude into the mesochannels to produce ink-bottle-shape or blocked channels (Fig. 3(b)). The average nanocrystal size is measured to be *ca.* 11.3 nm, slightly larger than that (10.8 nm) calculated from WAXRD. The lattice fringes of the nanocrystals can be clearly observed and an av-

erage d -spacing is measured to be ~ 0.34 nm, which is indexed as the 101 reflection of anatase structure—in agreement with the d_{101} spacing (0.35 nm) calculated from the WAXRD patterns. The reason for non-transformation of the anatase phase into rutile polymorph when subjecting the material to temperature as high as 950 °C is a direct result of the role of SiO_2 [39,40]. Similar results have also been reported previously in the literature [43].

After creating pores in the pore walls, the TEM micrographs of the resultant sample show homogeneously distributed dense pores in the walls connecting the mesochannels to form 3D hexagonal bimodal interconnected mesoporous networks (Fig. 3(c)–(d)). Along the [001] direction, there is evidence of “peanut-shell-like” channel openings. Although the intrawall pores are random in orientation, they always link the 2D mesochannels to form 3D mesoporous networks. The pore size distribution is rather narrow (3.1–4.3 nm), averaging ~ 3.6 nm. The amorphous SiO_2 nanoparticles linking the anatase nanocrystals clearly disappear, leaving voids in the pore walls along the pore direction. The high-resolution TEM micrographs reveal that some obstructed mesochannels are opened by the intrawall mesopores (marked area in Fig. 3(c)), forming ink-bottle-shaped pores. The average size of the main mesochannels is measured to be 4.2 nm, essentially the same as that of the parent sample. EDX analysis shows that the Ti/Si atomic ratio of the resulting sample is 85.0/15.0 (Fig. 3(c), inset).

3.3. N_2 adsorption-desorption isotherms

The N_2 adsorption-desorption isotherm of the precursor

Fig. 3. Representative transmission electron microscopy (a, c) and high-resolution TEM (b, d) images of the samples before (a, b) and after (c, d) creating the intrawall mesopores, respectively; viewed along [001] (a, b and d) and [110] (c) directions. Inset, EDX spectrum.

Fig. 4. N₂ adsorption-desorption isotherms (a) and pore size distributions (b) of the 2D (1) and 3D interconnected (2) mesoporous anatase crystal-silica nanocomposites.

shows a typical type IV isotherm with one capillary condensation step at relative pressures (p/p_0) of 0.40–0.58 (Fig. 4(a)), suggesting a narrow mesopore size distribution. The hysteresis loop displays H2 type, suggesting an ink-bottle-shaped mesopore geometry. This may be related to any mesochannel blockage from the protruding anatase nanocrystals [39], being in agreement with TEM observations (Fig. 3(b)). The mean pore size is *ca.* 4.0 nm (Fig. 4(b)), close to the value (4.1 nm) evaluated from high-resolution TEM observations. The calculated BET specific surface area and pore volume are 75 m²/g and 0.091 cm³/g, respectively.

It is of interest to observe the presence of two distinct uptake patterns in the resulting sample on the adsorption curve (Fig. 4(a)), which evidently suggests two sets of mesopores of varying size. The new minor N₂ uptake at low p/p_0 (0.39–0.44) indicates the existence of a smaller mesopores possessing a well-defined pore size distribution. The N₂ uptake in the 0.44–0.58 p/p_0 region is relatively steep, implying an increment of the mesochannels, which probably come from the opened mesochannels. It is interesting that the desilicated material isotherm consists of two convoluted hysteresis loops. The loop relating to the low p/p_0 region results from the intrawall mesopores. The drop of desorbed amount in 0.39–0.48 p/p_0 region is sharper than that of the precursor, suggesting an increase of the ink-bottle-shaped mesochannels, which may be ascribed to the opened channels. The pore size distribution curve exhibits two discrete and well-resolved peaks (Fig. 4(b)). The minor peak located at *ca.* 3.4 nm is sharp, clearly indicating the uniformity of the intrawall mesopore size. The mesochannel mean size (*ca.* 4.1 nm) is almost the same as that of the precursor. The BET surface area and pore volume (121 m²/g and 0.141 cm³/g) are obviously larger than that of the parent sample, respectively. The textural properties of the materials are in good accordance with those from the TEM and SAXRD measurements.

3.4. Preparation of 3D interconnected mesoporous architectures

Using ordered 2D hexagonal mesoporous anatase

70TiO₂-30SiO₂-950 nanocomposite as a precursor, NaOH as an etchant of silica, the 3D bimodal interconnected mesoporous nanocomposite can successfully be prepared *via* a “creating mesopores in the pore walls” method (Fig. 5). The precursor was synthesized according to our modified evaporation-induced self-assembly (EISA) process with post heat treatment [39]. The as-synthesized nanocomposite has a uniform and homogeneous framework with well-dispersed silicate. Upon calcination at 350 °C to remove the template, the amorphous framework begins to crystallize. At this moment, phase separation occurs and anatase nanocrystals are randomly embedded in the matrices of amorphous TiO₂ and SiO₂. Increasing the crystallization temperature and/or time results in further growth of the TiO₂ nanocrystals [39]. Simultaneously, the amorphous SiO₂ nanoparticles also enlarge, which serve as a glue linking the nanocrystals firmly together to form a unique “brick-mortar-like” framework. Furthermore, the silica nanoparticles play a key role in stabilizing the mesoporous structure and limiting the nanocrystals quickly coarsening. In this article, we control pore wall crystallinity, nanocrystal size and the size of the silica nanoparticles by fixing the crystallization temperature (950 °C) and time (2 h) of the precursor. Under such conditions, we can obtain high crystallinity, large anatase nano-

Fig. 5. Scheme for the preparation of the 3D interconnected mesoporous system by creating mesopores in the pore walls. (a) The ordered 2D hexagonal mesoporous anatase crystal-silica nanocomposite without intrawall pores; (b) The anatase crystal-silica nanocomposite with 3D interconnected mesopores.

crystals and sufficiently large silica nanoparticles (which is the decisive factor to yield intrawall mesopores). Additionally, the use of mild conditions of creating the intrawall mesopores, such as 0.5 mol/L NaOH concentration and 40 °C *etc.*, allows both retention of the mesopore structural integrity and high photocatalytic performance.

3.5. Adsorption and photocatalytic degradation of RhB and MB

The adsorption of RhB on the parent sample proceeds slowly, taking *ca.* 30 min to essentially reach adsorption-desorption equilibration [Fig. 6(a)]. The saturated adsorption amount is ~58.4%. Interestingly, the fast adsorption process observed on the nanocomposite with 3D interconnected mesopores [Fig. 6(a)] achieves a rate ~6 times faster than that of the precursor. The increased adsorption rate is ascribed to the improved diffusion efficiency contributed by the 3D mesoporous architecture [40]. The transport efficiency enhancement resulting from the interlinked mesopores was also observed in the mesoporous silica, SBA-15 material. The diffusivity of *n*-heptane in SBA-15 with smaller mesopores being dominant in the walls connecting the larger mesopores of the main channels is 3–4 times higher than that in SBA-15 possessing a high content of intrawall micropores linking the mesochannels [44]. The saturated adsorption amount (44.8%) is obviously lower than that on the parent sample and displays a negative correlation with increased surface area and pore volume. This phe-

nomenon results from the decrease of silica composition, which plays an overwhelming role in cationic dye adsorption [41,42]. Similar trends are also observed with MB [Fig. 6(b)]. When subjecting the materials to UV irradiation, the concentration of RhB drops exponentially with photocatalytic degradation time on the precursor, and a pseudo-first-order reaction is observed [Fig. 6(a), (c)]. The degradation rate is 0.0597 min⁻¹. The degradation rate observed on the 3D interconnected mesopore sample is extremely high (0.303 min⁻¹), as much as 5.1 times that of the precursor and 16.5 times that of the P25 photocatalyst (0.0184 min⁻¹). Significantly, similar trends also occur with MB [Fig. 6(b), (d)]. The degradation rate of MB on the 3D interconnected mesoporous sample is ~5.3 and 24.1 times that of the parent sample and P25 photocatalyst [Fig. 6(d)], respectively. These results fully demonstrate that the 3D interconnected mesoporous structure exhibits unexpectedly high activities to RhB and MB dyes. It is worth noting that both the 3D and 2D nanocomposites exhibit higher catalytic activities for MB photodegradation than for RhB photodegradation. This is related to the higher MB saturated adsorption amounts on both the 3D and 2D nanocomposites compared with RhB, which probably result in the synergistic role of the coupled adsorbing and photocatalytically degrading MB to be closer to the synchronicity. Our previous results have demonstrated that the synchronous role of the coupled adsorption and photocatalytic oxidation generates the optimal activity [41].

Fig. 6. Adsorption and photocatalytic degradation of RhB (a) and MB (b) before and under UV light irradiation in the presence of samples, respectively; here, C is the concentration of organic pollutants at the time t and C_0 is the initial concentration. Photocatalytic degradation rates of RhB (c) and MB (d) on the samples. (1) The parent sample; (2) the sample with 3D interconnected mesopores; (3) Degussa P25 photocatalyst.

3.6. Stability and reusability

The stability and reusability of the 3D interconnected mesoporous anatase $\text{TiO}_2\text{-SiO}_2$ nanocomposite were investigated using RhB. Prior to subjecting the sample to UV light irradiation, the adsorption of RhB onto the sample is rapid, taking only ~ 5 min to essentially reach adsorption-desorption equilibration in the first cycle (Fig. 7). The saturated adsorption amount is $\sim 44.5\%$. After UV light irradiation, the concentration of RhB declines exponentially with time and the degradation percentage reaches 99.8% within 20 min. After nine additional cycles, the equilibrium time remains at *ca.* 5 min, while the saturated adsorption amount is in the range of 41.3%–48.1%, which has no significant change. All degradation percentages are higher than 99.7%. These results fully illustrate that our 3D interconnected mesoporous nanocomposite is quite stable and reusable.

3.7. Adsorption, diffusion and photocatalytic degradation processes

For the 3D interconnected mesoporous anatase $\text{TiO}_2\text{-SiO}_2$ nanocomposite, the anatase nanocrystals and silica nanoparticles co-exist predominantly inside the mesochannels and intrawall mesopores (Fig. 8(a)). During reactions, the RhB and MB molecules are first adsorbed overwhelmingly on the SiO_2 nanoparticles on the outer surfaces. Thereafter, the adsorbed molecules diffuse inside the mesopore channels in a quite short time (Fig. 8(b)). Meanwhile, the anatase nanocrystals surfaces generate $\cdot\text{OH}$ radicals under UV irradiation, which simultaneously react with the adsorbed molecules from all directions inside the mesopore network. As a result, the molecules are in no time degraded into smaller moieties, finally mineralized into CO_2 , H_2O , *etc.* [40–42]. Subsequently, CO_2 , *etc.* would depart very easily from the reaction site to the solution outside. All these processes carry out unexpectedly fast because of the 3D interconnected mesoporous architecture.

4. Conclusions

A 3D interconnected mesoporous anatase crystal-silica

Fig. 7. Stability and reusability studies of the 3D interconnected mesoporous nanocomposite.

Fig. 8. Adsorption and photocatalytic degradation process scheme of RhB and MB molecules on the 3D interconnected mesoporous anatase $\text{TiO}_2\text{-SiO}_2$ nanocomposite. (a) The nanocomposite; (b) the nanocomposite adsorbing and photocatalytically degrading organic pollutants.

nanocomposite has been successfully prepared by using ordered 2D hexagonal mesoporous anatase $70\text{TiO}_2\text{-}30\text{SiO}_2\text{-}950$ nanocomposite as a precursor, NaOH as an etchant of SiO_2 via a “creating mesopores in the pore walls” method. Our results show that the initial mesochannels in the resultant sample are highly connected by dense and uniform intrawall mesopores while retaining mesostructural integrity. The crystallinity and size of the initial anatase nanocrystals are not significantly altered after creating the intrawall mesopores. The BET specific surface area and pore volume of the sample possessing interconnected mesopores are remarkably higher than those of the precursor. The diffusion rates of RhB and MB molecules through the 3D mesopores system were greatly enhanced by a factor of more than four when compared with the 2D precursor without intrawall pores. The sample possessing interconnected mesopores exhibits significantly higher photocatalytic activity than the parent sample. Unexpectedly high degradation activities for RhB (0.303 min^{-1}) and MB (0.757 min^{-1}) in the 3D mesoporous architecture are as high as 5.1 and 5.3 times that of the precursor (0.0597 , 0.144 min^{-1}), respectively, even up to 16.5 and 24.1 times that of a commercial Degussa P25 photocatalyst (0.0184 , 0.0314 min^{-1}), respectively. These results fully demonstrate that the 3D interconnected mesoporous network plays a key role in the marked increase in activity. Our sample exhibits excellent photocatalytic degradation activities to RhB and MB when compared with other mesoporous metal oxide-based materials reported in the literature. Importantly, our sample is considerably stable and reusable. Furthermore, this approach paves the way for the preparation of other ordered mesoporous metal oxide-based materials with 3D interconnected mesopores, such as Nb_2O_5 and Ta_2O_5 , with excellent photocatalytic performances.

Notes

The authors declare no competing financial interest.

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Graphical Abstract

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Preparation of three-dimensional interconnected mesoporous anatase TiO₂-SiO₂ nanocomposites with high photocatalytic activitiesWeiyang Dong*, Youwei Yao, Yaojun Sun, Weiming Hua, Guoshun Zhuang
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An ordered mesoporous anatase-silica nanocomposite with 3D interconnected mesopores presents unexpectedly high photocatalytic degradation activities toward RhB and MB dyes, significantly higher than the corresponding non-interconnected mesoporous precursor and a commercial Degussa P25 photocatalyst.

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孔道三维相互连通锐钛矿 TiO_2 - SiO_2 纳米复合介孔材料的制备及其高光催化活性

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摘要: 本文报道一种孔道三维相互连通锐钛矿 TiO_2 - SiO_2 纳米复合介孔材料的制备。该介孔材料是以两维六方有序结构、直孔道、锐钛矿 70TiO_2 - 30SiO_2 -950纳米复合介孔材料(于950 °C晶化2 h)为前驱体, NaOH为 SiO_2 的刻蚀剂, 通过“在孔壁内造孔”的方法获得。我们的策略是采用温和的造孔条件, 如稀NaOH溶液, 合适的温度与固/液比等。采用X射线衍射(XRD), 透射电镜(TEM)和低温 N_2 吸附等技术对样品的介孔结构进行了系统表征。结果表明, 墙内孔的密度非常高, 孔径均一(平均尺寸3.6 nm), 且在三维网络高度连通原孔道, 但介孔结构仍保持其完整性。锐钛矿纳米晶粒的结晶度和大小在墙内造孔前后基本保持不变。该材料光催化降解罗丹明B(0.303 min^{-1})与亚甲基蓝(0.757 min^{-1})的活性相当高, 此活性分别是其母体材料的5.1和5.3倍, 甚至是Degussa P25光催化剂的16.5和24.1倍。这充分表明三维连通孔道结构对活性的大幅提高起了关键作用。孔道三维连通式锐钛矿 TiO_2 - SiO_2 纳米复合介孔材料对上述污染物展现出意想不到的高降解活性, 显著高于迄今已报道的金属氧化物基介孔材料对上述污染物的降解活性。更重要的是, 该光催化剂具有相当高的稳定性和重复使用性。相信, 本方法将为具有超高性能的孔道三维相互连通其它金属氧化物基介孔材料的制备铺平了道路。

小角XRD结果表明, 母体材料的孔道是两维六方有序结构, 在孔壁内造孔之后, 样品原有的介孔结构仍保持其规整性。宽角XRD结果显示, 二氧化钛的晶相是锐钛矿, 晶粒尺寸为10.8 nm。造新孔之后, 锐钛矿纳米晶粒的结晶度和大小与母体样品的相比变化不大。TEM结果显示, 母体样品的孔壁内没有孔。孔道是两维六方有序排列的直孔道, 孔径大小均一(平均尺寸4.1 nm)。高分辨透射电镜(TEM)观察揭示, 锐钛矿纳米晶粒(平均大小11.3 nm)在孔壁内随机排列, 并与无定形 SiO_2 纳米颗粒相互连接, 相间共存, 形成类似“砖块-水泥砂浆”砌成的孔壁, 这种独特的复合骨架结构赋予其很高的稳定性。当一些 SiO_2 纳米颗粒被去除之后, TEM观察显示, 孔壁内有密集分布的孔, 这些孔取向随机, 并在三维方向连通原孔道, 但介孔骨架结构仍保持其完整性。墙内孔的大小范围很窄(3.1–4.3 nm), 平均大小为3.6 nm。高分辨TEM观察显示, 锐钛矿晶粒大小与母体材料内的相比基本未变。上述结果与XRD结果一致。低温 N_2 吸附表征结果显示, 母体样品内只有一种孔道, 孔径为4.0 nm。去除部分 SiO_2 后的样品内有两种孔道, 孔径分别是3.4和4.1 nm。这些结果与TEM的观察吻合。罗丹明B与亚甲基蓝在造孔前后样品内扩散速率评价结果显示, 其在三维连通孔道内的扩散速率很高, 大约是其母体材料内的5倍以上。这表明相互连通的孔道网络结构非常有利于客体分子在其内扩散。光催化降解性能评价结果显示, 罗丹明B与亚甲基蓝在相互连通孔道内降解的速率相当高, 分别是其在不连通孔道内的5.1和5.3倍。这充分证明孔道三维相互连通对活性的大幅提高起了关键作用。我们对材料的稳定性和重复使用性作了评价, 经过10次循环使用孔道三维相互连通锐钛矿 TiO_2 - SiO_2 纳米复合介孔材料, 其吸附与光催化降解罗丹明B的性能变化不大。这充分证明本文制备的孔道连通复合介孔材料的性能是相当稳定的和可重复使用的。该方法可用于制备具有超高性能的孔道三维相互连通其它金属氧化物基介孔材料, 如 Nb_2O_5 , Ta_2O_5 等。

关键词: 二氧化钛; 二氧化硅; 纳米复合介孔材料; 三维连通式介孔结构; 光催化降解; 有机污染物

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