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Hierarchical Porous TiO_2 Templated from Natural Artemia Cyst Shells for Photocatalysis Applications

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Abstract: A novel hierarchical porous TiO_2 is successfully synthesized through a sol-gel method, using a natural cyst shell as hard template. The morphology characterization shows that the as-prepared TiO_2 with a hierarchical porous architecture is assembled by multiple-layered porous nanosheets. The degradation of methylene blue dye in water can rapidly reach 96% with as-prepared TiO_2 after 50 min, showing an improved photocatalytic efficiency of 13% as compared to commercial TiO_2.

Keywords: hierarchical porous; natural template; titanium dioxide; photocatalytic activity

Introduction

Titanium dioxide (TiO_2), a typical semiconductor with wide-band, has been extensively investigated owing to its promising applications in catalysts, photo-splitting of water[1], self-cleaning[2], gas sensors, and photovoltaic cells[3-9] etc. One of the most important applications of TiO_2 is as a photocatalyst in environmental protection due to its chemical stability, strong oxidation activity, chemical stability, and nontoxicity[10,11]. In practical application, the photocatalytic performance of TiO_2 is strongly influenced by the crystal structure, morphology, and crystallite size[12-15]. Thus, design and synthesis of nanocrystals with well-defined morphologies is significant in tailoring the properties.

Up to now, various morphologies of TiO_2, such as nanorods[16], nanowires[17], nanotubes[18,19], have been successfully developed through different methods. However, the low dimensional nanoscaled building blocks have more chances to aggregate in the process of synthesis and photocatalysis, leading to shrinkage of its specific surface and photocatalytic and photoelectrochemical performance. While three-dimensional (3D) hierarchical structured TiO_2 can avoid this problem. In addition, this kind of materials combines the catalytic properties of smaller pore systems and the available diffusion pathways of macroporous networks with high surface area[20-25]. Tao et al.[26] synthesized

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hierarchical nanostructured TiO_2 spheres via hydrothermal method in NaOH solution. Zhao et al.[27] prepared highly oriented hierarchical structured rutile TiO_2 nanoarrays through a hydrothermal method and assembled it to form dye-sensitized solar cells, harvesting a better fill factor and higher conversion efficiency. Liu et al.[28] synthesized nanostructured TiO_2 with different hierarchical morphologies via a hydrothermal route by, and their morphology-dependent photocatalytic performance for phenol degradation was evaluated.

In this work, a novel hierarchical porous TiO_2 was synthesized by a facile and low cost sol-gel method, in which a natural material, Artemia cyst shell (AS) was used as hard template, which was reported to possess with a hierarchical porous inner cortical structure[29]. The photocatalytic activity of the as-prepared TiO_2 was evaluated by degradation methylene blue (MB), showing an improved photocatalytic efficiency of 13% as compared to commercial TiO_2.

Experimental

The hierarchical porous TiO_2 was synthesized in an improved sol-gel approach. Specifically, 5 ml butyl titanate was dissolved in 10 ml anhydrous ethanol at 50 ^oC, the pH value was adjusted to 2 with concentrated hydrochloric acid. Subsequenly a mixture including anhydrous ethanol, glacial acetic acid and deionized water in the proportion of 5:2:1 (v:v:v) was dropped into the above solution slowly. Finally the ball-milled AS was added, the obtained system was drastically stirred for 1 h and kept overnight at room temperature to allow the thorough adsorption of titania sol into the AS structure. The as-prepared product was gently heated in an oven at 80 ^oC overnight. Finally, hierarchical porous TiO_2 was obtained after the AS template was removed upon subsequent heat treatment at 500 ^oC for 10 h in air.

Powder X-ray diffraction (XRD) patterns of samples were recorded on a D-max-2500/PC X-ray diffractometer (Japan, Rigaku, Cu Kα). The sample morphology was examined in a Hitachi-S4800 field emission scanning electron microscope (FESEM, Japan) and Hitachi-7650 transmission electron microscopy (TEM, Japan). The chemical composition of the product was characterized by EDS (Energy-dispersive X-ray spectroscopy, Horiba, 7539-H). The specific surface area (*SSA*) and pore size distribution were investigated with nitrogen cryosorption (Micromeritics, ASAP2020).

The photocatalytic properties of hierarchical porous TiO_2 were investigated, by using high pressure xenon lamp as the light source, and MB solution as the degradation target. Prior to illumination, 100 ml of MB aqueous solutions (10 mg/L) containing 0.03 g samples were magnetically stirred in the dark for 30 min to achieve adsorption/desorption equilibrium and better dispersion. During irradiation, a series of samples were taken from the reactor every 10 min and the

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degree of MB degradation was determined via UV-Vis. According to the degree of MB degradation, the photocatalytic activity of the as-prepared TiO_2 was evaluated.

Results and Discussion

The XRD pattern of commercial TiO_2 and the as-prepared hierarchical porous TiO_2 is shown in **Figure 1**, which indicates the synthesized sample displays a good crystallinity. The characteristic peaks of tetragonal anatase TiO_2 (JCPDS NO.21−1272, space group 141/amd (141)) were observed. The morphology of the AS template and as-obtained TiO_2 was observed under FESEM and TEM as shown in **Figure 2**. **Figure 2a** and **2b** demonstrate the microstructure of the AS before and after ball milling respectively. The net-like hierarchical porous structure on the AS is fairly exposed after ball-milling, which can be easily duplicated. SEM image of the as-prepared TiO_2 calcined at 500 ^oC are shown in **Figure 2c**, it indicates that the product shows a net-like 3-D hierarchical porous structure with good connectivity between pore walls. The structure is multi-layered, from which macropores, ranging in diameter mainly from 200 to 700 nm, can be obviously observed. TEM images further proved the hierarchical porous architecture of our obtained TiO_2, as shown in **Figure 2d** and **Figure 2e**, and indicated that the pore wall was assembled by TiO_2 nanoparticles. **Figure 2f** is a typical high-resolution TEM (HRTEM) image on the pore walls, which reveals the presence of many nanocrystals showing anatase lattice fringes, indicating that the wall of the pores is assembled by such TiO_2 nanocrystals, and the average crystallite size is about 5 nm. The interplanar spacing is measured to be 0.35 nm, which is consistent with that of the anatase (101) crystal faces. EDS analysis of the as-prepared TiO_2 indicates the existence of element Fe, S and Ca besides Ti and O (**Figure 3a**), these heteroatoms should be resulted from the natural Artemia cyst shell, which could be self-doped to the hierarchical porous TiO_2.

The nitrogen adsorption-desorption isotherm plot and the corresponding pore-size distribution curve for as-prepared TiO_2 are shown in **Figure 3b**. It reveals that the nitrogen sorption isotherm presents a reverse "S" shape, which is identified as IV-type according to the Brunauer classification[30]. The BET specific surface area is measured to be 124 m^2/g. This value is high enough and comparable to those reported porous TiO_2 from literature[31, 32]. Barrett-Joyner-Halenda (BJH) analysis (**Figure 3b** inset) reveals that most of the pores fall into the size range of 2-4 nm, suggesting the coexistence of micropores ($\leqslant$ 2 nm) and mesopores (2~50 nm). Macropores ($\geqslant$50 nm) detected in SEM picture cannot be accurately measured through BJH method. This hierarchical porous structure facilitates the efficient diffusion and transportation of the degradable organic molecules in photochemical reaction, which will contribute to the photocatalytic activity of TiO_2

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material[33].

The possible formation mechanism of the hierarchical porous structure can be explained by a surface sol-gel coating process[34, 35]. At the initial stage of sol-gel synthesis, titanium ion was chemisorbed onto AS surface which is abundant with hydroxylated groups. After the addition of water, $Ti(OH)_4$ colloids as the precursor of TiO_2 nano-particle in the pore wall formed due to a hydrolysis of $Ti(OC_4H_9)_4$. During this sol-gel process, anhydrous ethanol was used as solvent, and glacial acetic acid was added dropwisely to adjust the acidity of the reaction system. After further nucleation and growth, the TiO_2 nanocrystals were assembled into hierarchical architectures of AS. And the target sample was obtained after AS template was removed by calcination treatment.

Figure 4 (a) displays the room temperature absorbance spectra of commercial TiO_2 and hierarchical porous TiO_2. The data were recorded in the wavelength range of 200-800 nm and the absorption edges were approximately 380, 480 nm, respectively. It can be seen that the hierarchical porous TiO_2 shows a wide absorbance in the visible region and obvious red shift than that of the commercial TiO_2. The red-shift should be due to the elements doping of Fe and S inherited from the Artemia cyst shell during the material preparation[36-38]. The band gap of TiO_2 can be calculated from the Uv-vis absorbance data, via the equation $\alpha h\nu = k(h\nu - E_g)^m$, where α is the absorption coefficient, E_g is the optical band gap, k is a constant and $m = 1/2$. A typical plot of $(\alpha h\nu)^2$ versus $h\nu$was plotted using the data obtained from the optical absorption spectra (**Figure 4(b)**). The band gap of the as-prepared hierarchical porous TiO_2 is calculated to be 2.95 eV, showing an oblivious decrease compared to the commercial one (3.20 eV).

The photocatalytic activity of the samples was investigated by degrading a common organic dye methylene blue (MB) under weak alkaline condition. **Figure 4 (c)** presents the optical absorption spectra of MB aqueous solution (initial concentration: 10mg/L, 100 mL) with 30 mg of the as-prepared TiO_2 powders after exposure to high pressure mercury lamp for different time. The maximum absorption peak locates at 614 nm, corresponding to the MB molecules. And the absorption peak shrinks gradually with the extension of exposure time, until almost completely disappears after about 50 min. A series of color changes of MB solution during the irradiation are shown in the upper part of the inset photo in **Figure 4 (c)**. Notably, the intense blue color of the starting solution gradually fades with the extension of exposure time, which is corresponding to the sequential changes of the optical absorbance spectra.

The degree of MB degradation versus the exposure time from the optical absorbance measurement at 614 nm are shown in **Figure 4 (d)**. C_0 refers to the initial methylene blue

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concentration (after the dark reaction), and C is the concentration of methylene blue samples taken during the photocatalytic experiment. It indicates that the as-prepared TiO_2 shows a high photocatalytic activity, as the degration of MB can reach 96% at 50 min with the presence of as-prepared hierarchical porous TiO_2 catalyst. As contrast, the photocatalytic activity of commercial TiO_2 is also investigated under the same condition, of which the degration of MB only reaches 85%. The superior photocatalytic performance of the as-prepared TiO_2 can be ascribed to the special structure features. On one hand, the product has a perfect hierarchical structure, and it possesses a greater accessible specific surface area owing to its open and network structure features, which make the sample have more catalytically active sites. Besides, light would be reflected much more times among the hierarchical porous and the multiple reflections would extend the light propagation path, which is beneficial to the full utilization of incident light and enhance the photocatalytic property. On the other hand, the Fe and S element doping leads to red shift, thus broadens the absorbance range of light, and produces more photoproduction of electron and hole, thus the potocatalytic performance of the as-prepared TiO_2 can be enhanced. Furthermore, the bigger size of the hierarchical porous TiO_2 blocks can effectively prevent the aggregation and help enhance the photocatalytic activity[20]. A more detailed and deeper investigation of durability of the photocatalytic activity and the structure stability of the hierarchical porous TiO_2 is under progress.

Conclusions

In summary, the natural templating approach has been shown to provide a facile, environmental friendly and biomimetic method for the synthesis of hierarchical porous TiO_2. Owing to its special structure and self-doping of heteroatoms, such TiO_2 presents superior photocatalytic activity as compared to commercial TiO_2. This indicates that the as-prepared hierarchical porous TiO_2 could be a promising candidate for photocatalysis application or waste water treatment, because of the facileness in preparation, reproductivity and recycling.

Acklowdgement

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Figure Captions

Figure 1. XRD patterns of commercial TiO_2 and obtained hierarchical porous TiO_2.

Figure 2. SEM image of (a) Artemia cyst shell, (b) AS debris (after ball milling), (c) the as-prepared hierarchical porous TiO_2; (d) TEM image of the as-prepared hierarchical porous TiO_2; (e) the corresponding local magnificent image of (d); (f) the corresponding HRTEM image.

Figure 3. (a) EDS patterns of the as-prepared TiO_2 and template AS (inset); (b) Nitrogen adsorption-desorption isotherms plots and pore size distribution plots of as-prepared TiO_2 (inset).

Figure 4. (a) UV-Visible absorption spectrum; (b) plot of $(\alpha h\nu)^2$ versus $h\nu$ for the TiO_2 samples; (c) Time-dependent color change and corresponding time-dependent absorption spectrum of MB in the presence of as-prepared TiO_2; (d) The degree of MB degradation with catalysts versus the exposure time, where C_0 refers to the initial methylene blue concentration (after the dark reaction).

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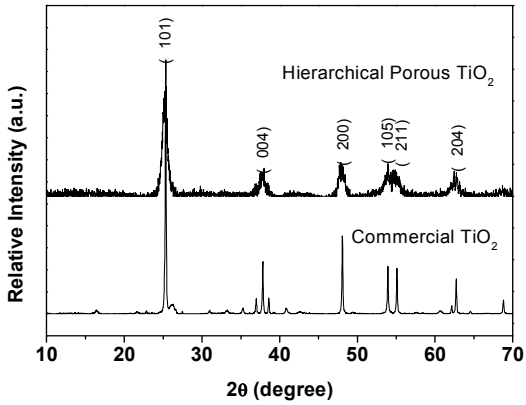

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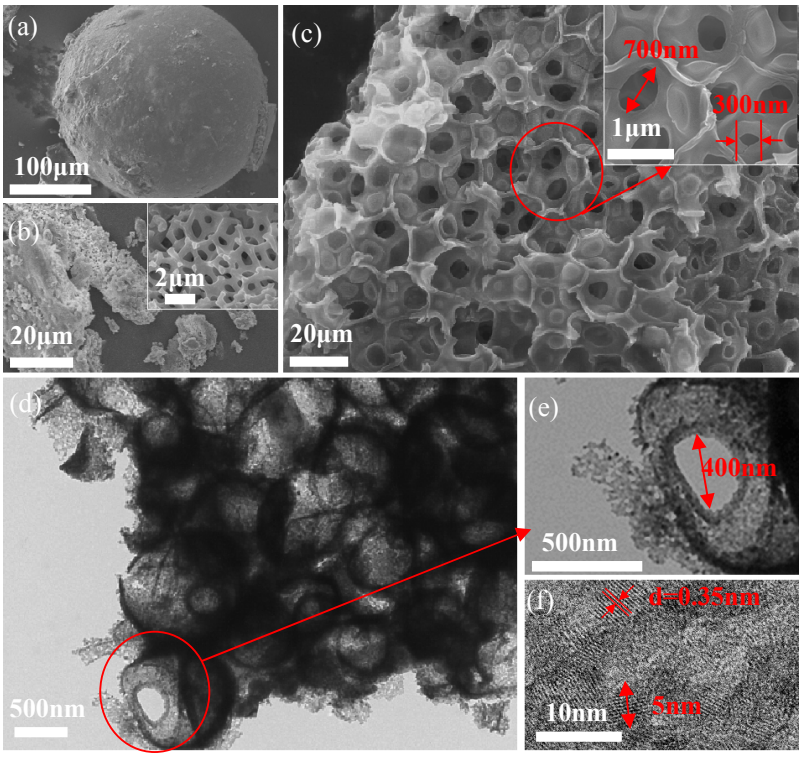

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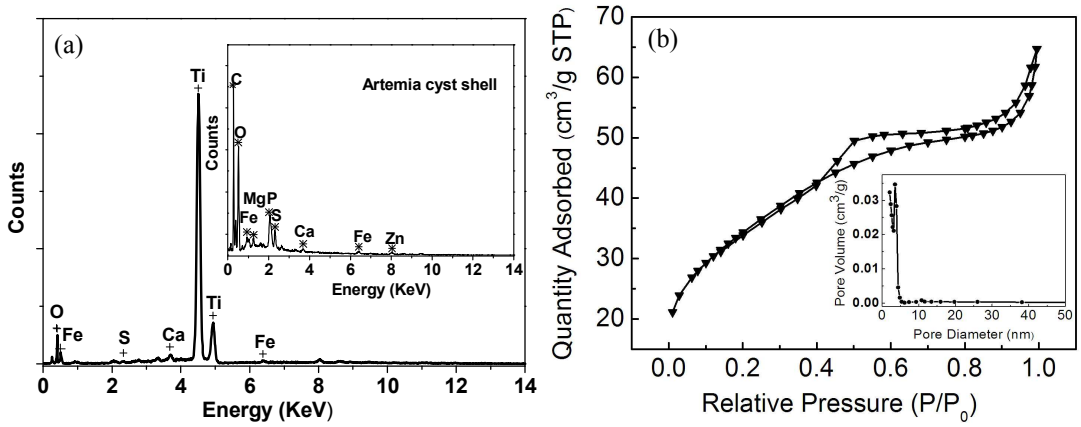

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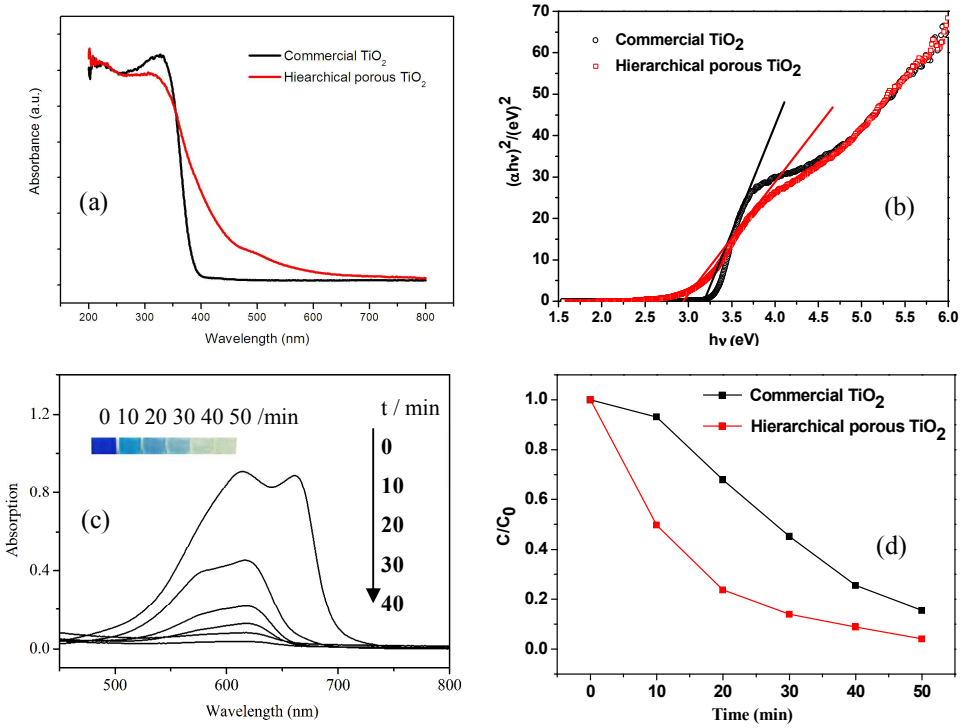

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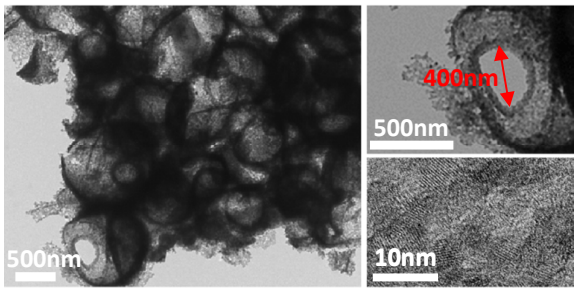
A novel hierarchical porous TiO_2 is synthesized using a natural Artemia cyst shell as template, showing improved photocatalytic performance.



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