J|A|C|S
COMMUNICATIONS

Tunable Photocatalytic Selectivity of Hollow TiO_2 Microspheres Composed of Anatase Polyhedra with Exposed {001} Facets

Shengwei Liu,[†] Jiaguo Yu,*[,†] and Mietek Jaroniec*[,‡]

State Key Laboratory of Advanced Technology for Material Synthesis and Processing, Wuhan University of Technology, Luoshi Road 122#, Wuhan 430070, P. R. China, and Department of Chemistry, Kent State University, Kent, Ohio 44242

Received June 16, 2010; E-mail: jiaguoyu@yahoo.com; jaroniec@kent.edu

Abstract: A fluoride mediated self-transformation method is proposed for the synthesis of hollow TiO_2 microspheres (HTS) composed of anatase polyhedra with exposed ca. 20% {001} facets. Importantly, HTS exhibit tunable photocatalytic selectivity in decomposing azo dyes in water. The fluorinated HTS show preferential decomposition of methyl orange (MO) in comparison to methylene blue (MB). In contrast, the surface-modified HTS by either NaOH washing or calcinations at 600 °C favor decomposition of MB over MO. The surface chemistry and the surface structure at the atomic level are key factors in tuning the adsorption selectivity and, consequently, photocatalytic selectivity of HTS toward azo dyes.

Heterogeneous semiconductor photocatalysis is a potentially promising approach toward solving worldwide environmental and energy-related issues.[1] Titania (TiO_2) has proven to be the most versatile material among various oxide and nonoxide photocatalysts because of its high catalytic activity and long-term stability.[1] However, photocatalytic reactions on TiO_2 are often accompanied by formation of highly reactive radical species (e.g., $\cdot OH$) that are typically nonselective, resulting in insufficient photocatalytic selectivity. It is a great challenge to develop TiO_2 photocatalysts with desirable selectivity that is crucial for transformation and purification of targeted organics.[2]

Recently, the surface structure of TiO_2 photocatalysts has been intensively explored at the atomic level. Both theoretical and experimental studies of TiO_2 polymorphs indicate that the metastable {001} facets of anatase are more reactive than the other ones.[3] Since the pioneering work by Yang et al.,[3a] there is great interest in the synthesis of anatase TiO_2 micro-/nanosheets with a high percentage of {001} facets and in the exploration of these sheets in the photocatalytic decomposition of pollutants, hydrogen production, and so on.[3] Nevertheless, only a few attempts have been made toward creating higher-order and high-surface area microsized superstructures from primary anatase TiO_2 nanosheets.[4] In particular, to our knowledge, hollow microspherical assemblies consisting of anatase TiO_2 nanosheets with a high percentage of {001} facets have not been reported yet. Here we present a feasible strategy for the synthesis of hollow TiO_2 microspheres (HTS) composed of anatase polyhedra having ca. 20% {001} facets (Figure 1). Importantly, the photocatalytic selectivity of HTS toward decomposition of azo dyes in water can be tuned by varying the percentage of {001} facets as well as by modifying the surface of anatase polyhedra.

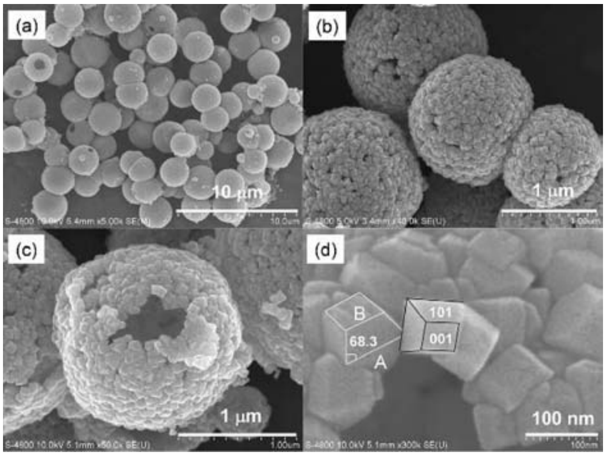

Figure 1. SEM images of the fluoride-mediated TiO_2 samples: (a) overall view of TiO_2 microspheres; (b) image of a few microspheres showing their unique structure consisting of primary TiO_2 nanoparticles; (c) a single microsphere showing its hollow nature; (d) a portion of the microsphere shell composed of nanosized polyhedra with exposed {001} facets.

HTS were synthesized by using a modified fluoride-mediated self-transformation strategy.[5] Ethanol was selected to promote the stabilization of {001} facets of anatase polyhedra (building blocks for the HTS formation). The resulting HTS sample (denoted E2; see details in the Supporting Information) having *ca.* 20% of {001} facets was used to collect all data shown in both figures of this work. The X-ray diffraction (XRD) pattern (Figure S1 in the Supporting Information) of the resulting sample matches the highly crystalline anatase phase of TiO_2 (JCPDS NO. 21-1272). The low magnification scanning electron microscopy (SEM) image of HMS (Figure 1a) shows that this sample mainly consists of TiO_2 microspheres having diameters of 1−2 μm, except for a small fraction of dispersed TiO_2 nanocrystals. The fraction of these microspheres in the sample is *ca.* 60%, which can be further improved by adding an appropriate amount of urea (as a basic catalyst) to the synthesis mixture.[5b] The SEM image of a few microspheres (Figure 1b) shows that they are composed of primary nanoparticles, which make their surface rough and porous. The latter was additionally confirmed by the pore analysis based on N_2 adsorption measurements (Figure S2 in the Supporting Information). The SEM image (Figure 1c) of a broken microsphere revealed the hollow nature of these microspheres, which is consistent with the corresponding transmission electron microscopy (TEM) images (Figure S3 in the Supporting Information). The high magnification SEM image (Figure 1d) of a portion of the TiO_2 microsphere shell shows that the shells of HTS mainly consist of TiO_2 polyhedra having sizes between 50 and 100 nm (typically, truncated bipyramids or decahedra). The remaining rounded or irregular nanopar-

---

[†] Wuhan University of Technology.
[‡] Kent State University.

10.1021/ja105283s

ticles resemble also truncated bipyramids. These nanosized building units are similar in shape but smaller in size than the TiO_2 decahedra reported by Yang et al.[3a] According to the symmetries of anatase TiO_2 crystals, the two flat and square surfaces should be {001} facets and the eight hexagonal surfaces should be {101} facets of these crystals, respectively.[3] Moreover, an angle of *ca.* 68.3° (Figure 1d) between the aforementioned surfaces is also consistent with the interfacial angle between {001} and {101} facets of anatase TiO_2 crystals. The average aspect ratio (B/A) (Figure 1d) is 0.5−0.6, corresponding to nearly 20% exposure of {001} facets to the total exposed facets.[3d]

It is noteworthy that the template-free formation of HTS resembles the recently proposed fluoride-mediated self-transformation mechanism.[5] In contrast to the previously studied systems,[5] in which an outward hollowing process was normally accompanied by a gradual decrease in the shell thickness, the current case follows an inward hollowing process via a sphere-in-shell intermediate (Figure S4 in the Supporting Information). Clearly, due to the possible influence on the diffusion and adsorption of active F ions and the dissolution of the interior space, ethanol added to the present synthesis mixture seems to be responsible for the observed difference in the formation of hollow microspheres; also, its addition is crucial for increasing the percentage of exposed {001} facets.[3b] Note that the average size of shell-building nanoparticles increases with the increasing amount of ethanol in the mixture of solvents (Table S1), and simultaneously, their shape evolves toward faceted polyhedra (Figure S5 in the Supporting Information). It was proposed that F^- can interact strongly with {001} facets, reducing the surface energy and kinetically inhibiting the crystal growth, which favors the formation of {001} facets.[3a] The presence of Ti−F surface species was confirmed by a high resolution X-ray photoelectron (XPS) spectrum of F1s with a binding energy of ca. 684 eV (Figure S6 in the Supporting Information). Moreover, the amount of Ti−F surface species increases indeed to some extent with the increasing amount of ethanol in the mixed solvent (Figure S6 in the Supporting Information); a higher percentage of these Ti−F species can be accounted for the higher percentage of exposed {001} facets.

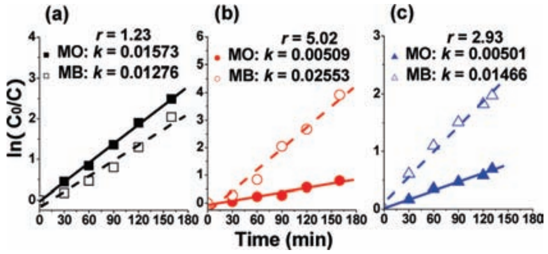

Figure 2. A comparison of photocatalytic decomposition of methyl orange (MO) and methylene blue (MB) by hollow TiO_2 microspheres (HTS) before and after surface modification: (a) as-prepared fluorinated HTS sample; (b) HTS modified by NaOH washing; (c) sample modified by calcination at 600 °C. The catalytic selectivity is defined as the ratio (*r*) of the apparent rate constants (*k*).

The photocatalytic selectivity of HTS toward decomposition of selected azo dyes is illustrated in Figure 2. Specifically, the sequential decolorization process of a mixed aqueous solution of methyl orange (MO) and methylene blue (MB) dyes by HTS was monitored under UV-light irradiation. Obviously, the photodegradation process of MO is much faster than that of MB by fluorinated HTS (Figure 2a), which is similar to the decolorization of these dyes with P25 commercial titania photocatalyst (Figure S8 in Supporting Information). This is not surprising because the chemical structure of MO favors its photodecomposition in comparison to MB.[6] Surprisingly, a major replacement of the surface-bonded fluoride species by hydroxyl groups due to NaOH washing (*ca.* 0.5 atom % of F remained; Figure S7 in the Supporting Information) reversed the photodegradation process as reflected in Figure 2b by the faster decomposition of MB in comparison to MO. This observation indicates the possibility of tuning the photocatalytic selectivity by simply modifying the surface of TiO_2 photocatalysts. Furthermore, an almost complete removal of the surface-bonded fluoride species by calcination at 600 °C in air for 90 min (<0.3 atom % of F remained; Figure S7 in the Supporting Information) resulted also in the sample favoring photodegradation of MB instead of MO (Figure 2c). In fact, the tunable photocatalytic selectivity of the HTS samples is related to the adsorption selectivity introduced by the aforementioned surface modifications. As can be seen in Figure S9 in the Supporting Information, the adsorption selectivity of HTS toward MB is significantly enhanced by surface modification with either NaOH washing or calcination. The surface rehydroxylation seems to promote the selective adsorption of MB molecules.[2b] Modification of the adsorption selectivity is a powerful technique for tuning catalytic selectivity.[2a] Usually, the preferentially adsorbed molecules can react more efficiently with photogenerated short-living •OH, which are on the TiO_2 surface and can be rapidly converted to catalytically inactive surface hydroxyls.

Notably, the degree of catalytic selectivity is related to the structural characteristics of HTS, including the percentage of exposed {001} facets. For instance, P25 titania, which has below 5% of the exposed {001} facets, favors the photocatalytic decomposition of MO, while the HTS sample calcined at 600 °C preferentially decomposes MB; this example indicates the importance of the surface structure in modifying the catalytic selectivity of titania. The latter can be also tuned by varying the fraction of ethanol in the mixed solvent; for instance, the catalytic selectivity of the as-prepared fluorinated HTS toward photodecomposition of MO decreased with the increasing fraction of ethanol in the synthesis mixture (Figure S8 in the Supporting Information). The aforementioned decrease correlates with increasing surface fluorination (Figure S6 in the Supporting Information). In contrast, the HTS samples modified by NaOH washing exhibited higher selectivity toward photodecomposition of MB (Figure S8 in the Supporting Information). Note that NaOH washing caused the conversion of abundant Ti−F species present on the {001} facets into Ti−OH species, which favor photodecomposition of MB.

In summary, selective adsorption and photocatalytic decomposition of azo dye molecules were accomplished by using HTS with exposed {001} facets and designed surface chemistry. The proposed methods for controlling hierarchical assembly, crystallinity, and surface chemistry of TiO_2 materials open new avenues for the design of advanced photocatalysts with desirable catalytic selectivity beyond reactivity and stability.

Acknowledgment. This work was supported by the NSFC (50625208, 20773097 and 20877061) and 973 Program (2007CB613302).

Supporting Information Available: Experimental details of synthesis, surface modification, characterization, and photocatalytic testing; nine figures with XRD, nitrogen adsorption and pore size distribution, SEM, TEM, XPS, dye adsorption, and photocatalytic data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37. (b) Park, J. H.; Kim, S.; Bard, A. J. *Nano Lett.* **2006**, *6*, 24. (c) Grätzel, M. *Nature* **2001**, *414*, 338.

(d) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69. (e) Carp, O.; Huisman, C. L.; Reller, A. *Prog. Solid State Chem.* **2004**, *32*, 33.

(2) (a) Shiraishi, Y.; Saito, N.; Hirai, T. *J. Am. Chem. Soc.* **2005**, *127*, 12820. (b) Higashimoto, S.; Okada, K.; Morisugi, T.; Azuma, M.; Ohue, H.; Kim, T. H.; Matsuoka, M.; Anpo, M. *Top Catal.* **2010**, *53*, 578. (c) Zhan, S. H.; Chen, D. R.; Jiao, X. L.; Song, Y. *Chem. Commun.* **2007**, 2043.

(3) (a) Yang, H. G.; Sun, C. H.; Qiao, S. Z.; Zou, J.; Liu, G.; Smith, S. C.; Cheng, H. M.; Lu, G. Q. *Nature* **2008**, *453*, 638. (b) Yang, H. G.; Liu, G.; Qiao, S. Z.; Sun, C. H.; Jin, Y. G.; Smith, S. C.; Zou, J.; Cheng, H. M.; Lu, G. Q. *J. Am. Chem. Soc.* **2009**, *131*, 4078. (c) Han, X. G.; Kuang, Q.; Jin, M. S.; Xie, Z. X.; Zheng, L. S. *J. Am. Chem. Soc.* **2009**, *131*, 3152. (d) Zhang, D. Q.; Li, G. S.; Yang, X. F.; Yu, J. C. *Chem. Commun.* **2009**, 4381. (e) Xiang, Q. J.; Lv, K. L.; Yu, J. G. *Appl. Catal., B* **2010**, *96*, 557. (f) Amano, F.; Prieto-Mahaney, O. O.; Terada, Y.; Yasumoto, T.; Shibayama, T.; Ohtani, B. *Chem. Mater.* **2009**, *21*, 2601.

(4) (a) Zheng, Z. K.; Huang, B. B.; Qin, X. Y.; Zhang, X. Y.; Dai, Y.; Jiang, M. H.; Wang, P.; Whangbo, M. H. *Chem.—Eur. J.* **2009**, *15*, 12576. (b) Chen, J. S.; Tan, Y. L.; Li, C. M.; Cheah, Y. L.; Luan, D. Y.; Madhavi, S.; Boey, F. Y. C.; Archer, L. A.; Lou, X. W. *J. Am. Chem. Soc.* **2010**, *132*, 6124.

(5) (a) Yu, J. G.; Liu, S. W.; Yu, H. G. *J. Catal.* **2007**, *249*, 59. (b) Liu, S. W.; Yu, J. G.; Mann, S. *Nanotechnology* **2009**, *20*, 325606. (c) Yu, J. G.; Guo, H. T.; Davis, S. A.; Mann, S. *Adv. Funct. Mater.* **2006**, *16*, 2035.

(6) Guillard, C.; Lachheb, H.; Houas, A.; Ksibi, M.; Elaloui, E.; Herrmann, J. M. *J. Photochem. Photobiol. A* **2003**, *158*, 27.

JA105283S