Fabrication of Uniform Anatase TiO$_2$ Particles Exposed by {001} Facets

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Uniform anatase TiO$_2$ particles exposed by {001} facets were successfully synthesized by using EDTA together with F as morphology controlling agents. The crystallographic structure as well as the growth mechanism of anatase TiO$_2$ particles was investigated systematically by XRD, SEM, TEM and XPS, respectively.

Titanium dioxide (TiO$_2$) has been extensively studied due to its many industrial applications such as photovoltaic cells, photo-/electrochromics, photocatalysis, photonic crystals, smart surface coatings, and sensors.[1-3] TiO$_2$ has commonly three types of polymorphs, namely, anatase, rutile, and brookite. Among them anatase TiO$_2$ is the most promising photocatalyst because of its appropriate electronic band structure, photostability, chemical inertness and commercial availability.[1,2] Photoactivity of anatase TiO$_2$ is largely dependent on its crystallinity, size, surface state, and electronic structure.[3] Both theoretical simulations and experimental results indicate that (001) surface of anatase TiO$_2$ is more photoactive than (101). However, due to its high surface energy, clean {001} facets diminish rapidly during the crystal nucleation and growth.[4,5] Thus according to Wulff construction, the mostly exposed surface of anatase TiO$_2$ is thermodynamically stable (101), which normally contains more than 94% of total crystal surface.[6,7]

Recently Yang and co-workers successfully synthesized macro-sized anatase TiO$_2$ single crystals with a large percentage of {001} facets using fluorine to lower the surface energy of {001} facets.[8,9] Then Xie's group further synthesized nano-sized anatase nanosheet with 89% of {001} facets by using the similar strategy.[10] Following these breakthroughs, more works in this area have been reported recently,[11-14] where some other techniques such as microwave-assisted hydrothermal route involving F containing ionic liquid[15] or anodization followed by hydrothermal treatment[11] were used. However, all these methods used F-containing compounds as capping agents to control the morphology of anatase TiO$_2$, which is highly toxic and corrosive in the forms of gas or liquid state. Thus it is highly desirable to develop a new synthesis strategy using less fluorine containing compounds as capping agents to prepare anatase TiO$_2$ with dominant high-reactive {001} facets.

Herein, we report a new hydrothermal process to synthesize uniform anatase TiO$_2$ particles exposed by a large percentage of {001} facets without using additional fluorine-containing compounds such as hydrofluoric acid (HF) as capping agent. In a typical experiment, 6 mL of TiF$_4$ aqueous solution (0.04 M), 20 mL of disodium ethylene diamine tetraacetate aqueous solution (EDTA, C$_{10}$H$_{14}$N$_2$O$_8$Na$_2$·2H$_2$O, analytical grade, 6 mM), and 34 mL of deionized water were added into a Teflon-lined stainless steel autoclave. The autoclave was kept at 170 - 200 °C for 4 - 10 h in an electric oven. After reaction, the products were separated by centrifugation, washed with deionized water for 5 times and then dried in vacuum at 60 °C for 7 h. This synthetic strategy is different from those processes reported[11-16] and the morphology of the final product is also quite unique. The resulting particle is uniform multi-twined anatase TiO$_2$ crystal dominated with {001} facets. Furthermore, chelating agent EDTA played a role as a synergistic capping agent on the formation of these uniform anatase TiO$_2$ particles and it can co-adsorb on anatase surface together with F to stabilize reactive (001) surfaces, which were evidenced experimentally in this work.

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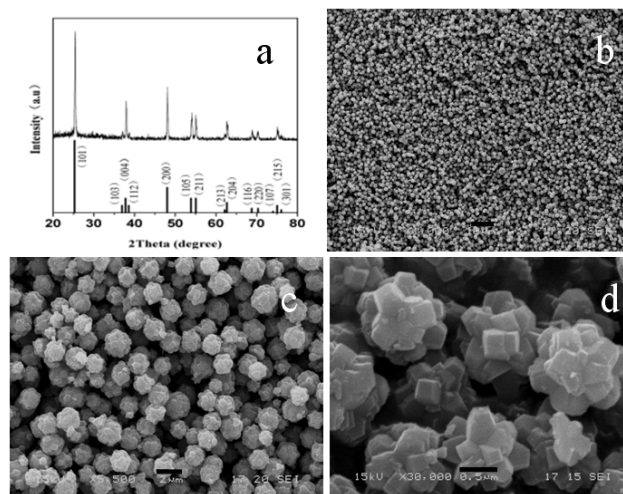† Electronic Supplementary Information (ESI) available:

Fig. 1 (a) X-ray diffraction pattern of the as-synthesized anatase TiO$_2$ particles (top), which is in good agreement with calculated diffraction pattern of bulk anatase (bottom). (b-d) are SEM

images of anatase TiO_2 particles with different magnifications. (Scale bars in (b), (c), and (d) are 10 µm, 2µm, and 0.5µm, respectively)

As shown in Fig. 1a, all X-ray diffraction (XRD) peaks of the product synthesized at 200 °C for 4 h match well with the crystal structure of the anatase TiO_2 phase (space group $I4_1/amd$, PDF 21-1272)[8] and no other phases can be detected. The relative diffraction intensity of (004) peak is much higher than that of calculated diffraction patterns of bulk anatase, indicating that as-prepared anatase TiO_2 particles are exposed by {001} facets. Figs. 1b-d show scanning electron microscope (SEM) images of the anatase TiO_2 particles. The prepared anatase TiO_2 particles have an average size around 1.2 µm and the size distribution is very narrow. As revealed in Fig. 1d, each anatse TiO_2 particle contains few multi-twinned and highly truncated bipyramidal TiO_2 single crystals, which act as the primary building blocks. The well faceted morphology of these building blocks displays the high crystallinity of the anatase TiO_2 particles. According to symmetries of anatase TiO_2 crystals, for a single truncated pyramid in each anatase TiO_2 particle, the top flat and square surface should be {001} facets and the four trapezoidal surfaces should be {101} facets.[8] Thus the percentage of {001} facets can be derived directly from this regular geometry, which is 22.8% statically. Detailed structural information of the macro-sized anatase TiO_2 particles was also investigated by transmission electron microscope (TEM) and selected area electron diffraction (SAED), and the high-resolution TEM (HRTEM), as shown in Fig. 2. On the external edge of the anatase TiO_2 particles shown in Fig. 2a, flat regions (indicated with white dashed lines) can be easily identified, which are {001} facets confirmed by SEM (Fig. 1d) and HRTEM (Fig. 2c) images.
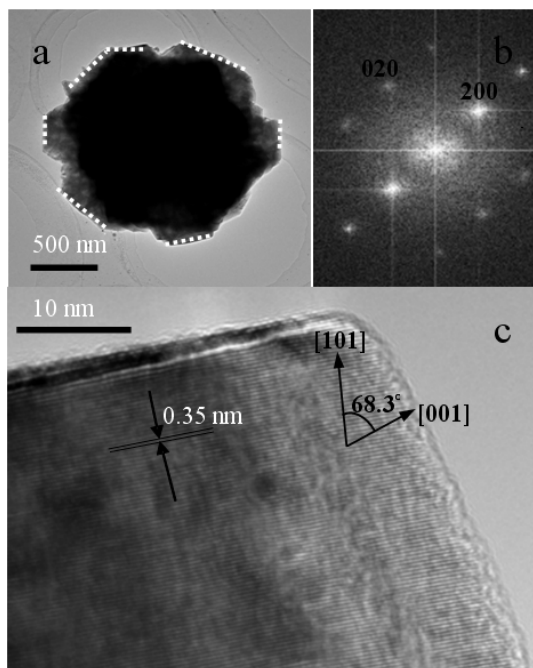

Fig. 2 (a) Typical TEM image of anatase TiO_2 particle; (b) corresponding SEAD pattern and (c) HRTEM image.

SAED pattern in Fig. 2b can be indexed as the [010] zone axis diffraction and the selected area for electron diffraction is located within a single crystalline TiO_2. Moreover, HRTEM image in Fig. 2c shows the (101) atomic planes with a lattice spacing of 0.35 nm. The interfacial angle of 68.3^0, which is shown in Fig. 2c, indicates that the external flat surface should be (001).[8] Thus, based on these structural analyses, it can conclude that the as-prepared anatase TiO_2 particles are exposed with high-reactive {001} facets.
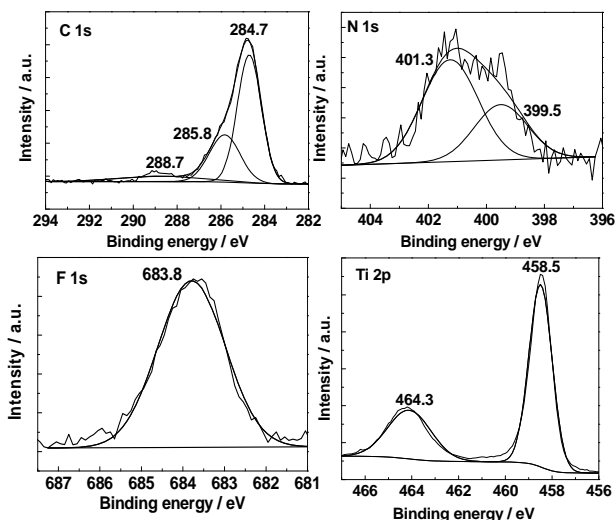

Fig. 3 X-ray photoelectron spectra of anatase TiO_2 particles, showing the four characteristic peaks of C 1s, N 1s, F 1s, and Ti 2p.

In order to verify the surface binding states of the chelating agent EDTA, X-ray photoelectron spectroscopy (XPS) was used to analyze the freshly prepared anatase TiO_2 particles, and the results are shown in Fig. 3. Binding energies for all the elements were referenced to the C 1s peak (284.7 eV) arising from adventitious carbon. Prior to the peak deconvolution, X-ray satellites and inelastic background (Shirley-type) were subtracted for all spectra. For C 1s, binding energy of 285.8 eV can be ascribed to N-C bond of EDTA, and another tiny peak at 288.7 eV should be caused by carboxylate.[9,12] For N 1s, generally the more positive N in the compounds, the higher the electron binding energy is (e.g., 408 eV in $NaNO_3$).[18] Furthermore, for nitrogen doped anatase TiO_2 using triethylamine as nitrogen source, the states of nitrogen on anatase surface are various and coexist in the forms of N-Ti-O and Ti-O-N, which have a binding energy of 399.2 eV and 401.2 eV, respectively.[19] Moreover, for synthesized nitrogen doped titania, Burda et al assigned N 1s position centred at 401.3 eV to O-Ti-N bond and they believed that N atoms substitute O atoms in the initial structure O-Ti-O.[18] Thus N 1s with a binding energy ranging from 399.5 to 401.3 eV in Fig. 3 can be deemed to be coexistent in the forms of N-Ti-O and Ti-O-N. Compared with the binding energy of F in solid solution $TiO_{2-x}F_x$ (688.8 eV, typically), F 1s with a binding energy of 683.8 eV in Fig. 3 is quite close to that of fluorinate TiO_2 system such as $\equiv$Ti-F species on the TiO_2 crystal surface.[20] The oxidation state of Ti

element (Ti 2p3/2, binding energy 458.5 eV; Ti 2p1/2, binding energy 464.3 eV) is identical to that of bulk TiO_2, as reported previously.[8] From these XPS results, we can safely conclude that EDTA is bonded on the surface of anatase TiO_2 particles to act as a capping agent.

To further confirm the functionalities of EDTA ligands in the formation of the uniform anatase TiO_2 particles with large percentage of {001} facets, some control experiments were carried out without adding EDTA in the reaction media (see ESI for the detailed experimental information). The results showed that the macro-sized anatase particles with dominant {101} facets were obtained (Figs. S2 in ESI) and the particles produced have rough surfaces, which are comparable to the previously reported results using a similar method (Figs. S2 and S3 in ESI).[8] From these results and our previous findings,[8,9] it can be concluded that both F and EDTA play a key role as capping agents to stabilize the high-active {001} facets of anatase TiO_2. Considering that $EDTA^{4-}$ can form very stable complexes with most of the transition metals and the resulting coordination compounds usually adopt octahedral geometry, after being bound and extensively enveloped by EDTA, metal ions such as Ti(IV) in solution exhibit a diminished hydrolysis capability, which generally makes the nucleation and crystal growth more controllable. Furthermore, because the pH value of the reaction medium in this work is close to 7.0, the complexes should be predominant in the form of stable $[TiO(EDTA)]^{2-}$,[21] which is quite different from complex fluoro ions stabilized in aqueous phase without EDTA. More importantly, once solid phase of crystal TiO_2 forms in the solution, $EDTA^{4-}$ is more likely to be adsorbed on (001) surface through a surface coordination process. Thus the growth rate on [001] crystal direction is suppressed significantly because under-coordinated 5c-Ti amount on (001) surface is 2 times higher than that of (101) surface. As a consequence, the prepared anatase TiO_2 has a large percentage of high reactive {001} facets.

As a summary, by using a chelating agent EDTA and F as synergistic capping agents, uniform anatase particles enclosed with {001} facets were successfully synthesized. The multi-twined particles are comprised of highly truncated pyramids of anatase TiO_2 single crystals. The formation of stable $[TiO(EDTA)]^{2-}$ complexes and surface-selective coordination of $EDTA^{4-}$ on anatase TiO_2 might be the core steps for the nucleation and crystal growth of anatase particles with dominant {001} facets. This new synthetic method may pave the way to prepare other metallic or semiconducting functional materials with favoured high-reactive facets by using non-toxic, non-corrosive and low-cost chelating agents such as EDTA.

Notes and references

1. X. L. Hu, G. S. Li and J. C. Yu, *Langmuir,* 2010, **26**, 3031.
2. A. L. Linsebigler, G. Q. Lu and J. T. Yates, *Chem. Rev.*, 1995, **95**, 735.
3. G. Liu, L. Z. Wang, H. G. Yang, H. M. Cheng and G. Q. Lu, *J. Mater. Chem.*, 2010, **20**, 831.
4. A. S. Barnard and L. A. Curtiss, *Nano Lett.*, 2005, **5**, 1261.
5. A. Vittadini, A. Selloni, F. P. Rotzinger, M. Grätzel, *Phys. Rev. Lett.*, 1998, **81**, 2954.
6. M. Lazzeri, A. Vittadini and A. Selloni, *Phys. Rev. B,* 2001, **63**, 155409.
7. U. Diebold, N. Ruzycki, G. Herman and A. Selloni, *Catal. Today,* 2003, **85**, 93.
8. H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng and G. Q. Lu, *Nature,* 2008, **453**, 638.
9. H. G. Yang, G. Liu, S. Z. Qiao, C. H. Sun, Y. G. Jin, S. C. Smith, J. Zou, H. M. Cheng and G. Q. Lu, *J. Am. Chem. Soc.*, 2009, **131**, 4078.
10. X. G. Han, Q. Kuang, M. S. Jin, Z. X. Xie and L. S. Zheng, *J. Am. Chem. Soc.*, 2009, **131**, 3152.
11. X. Y. Hu, T. C. Zhang, Z. Jin, S. Z. Huang, M. Fang, Y. C. Wu and L. D. Zhang, *Cryst. Growth Des.*, 2009, **5**, 2324.
12. G. Liu, C. H. Sun, H. G. Yang, S. C. Smith, L. Z. Wang, G. Q. Lu and H. M. Cheng, *Chem. Commun.*, 2010, **46**, 755.
13. G. Liu, H. G. Yang, X. W. Wang, L. Cheng, J. Pan, G. Q. Lu and H. M. Cheng, *J. Am. Chem. Soc.*, 2009, **131**, 12868.
14. M. Liu, L. Y. Piao, L. Zhang, S. T. Ju, Z. J. Yan, T. He, C. L. Zhou and W. J. Wang, *Chem. Commun.*, 2010, **46**, 1664.
15. D. Q. Zhang, G. S. Li, H. B. Wang, K. M. Chan and J. C. Yu, *Cryst. Growth Des.*, 2010, **10**, 1130.
16. M. Liu, L. Y. Piao, W. M. Lu, S. T. Ju, L. Zhao, C. L. Zhou and W. J. Wang, *Nanoscale.*, in press [DOI: 10.1039/c0nr00050g].
17. H. S. Hamid and F. Eric, *Minerals & Materials Characterization & Eng.*, 2006, **5**, 21.
18. X. B. Chen and C. Burda, *J. Phys. Chem. B.*, 2004, **108**, 15446.
19. Y. Cong, J. L. Zhang, F. Chen and M. Anpo, *J. Phys. Chem. C.*, 2007, **111**, 6976.
20. J. C. Yu, J. G. Yu, W. K. Ho, Z. T. Jiang and L. Z. Zhang, *Chem. Mater.*, 2002, **14**, 3808.
21. B. Karadakov and P. Nenova, *J. Inorg. Nucl. Chem.*, 1971, **33**, 2541.