Electronic Supplementary Material (ESI) for RSC Advances
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Supporting information

Carbonate ions-assisted syntheses of anatase TiO_2 nanoparticles exposed with high energy (001) facets

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1. Experimental Section

Reagents: The syntheses of different shapes of anatase TiO_2 nanoparticles were carried out using commercially available reagents. Potassium hydroxide (KOH, 90%), ammonium carbonate ($(NH_4)_2CO_3$, 99%), ammonium chloride (NH_4Cl, 99%), ammonium sulphate ($(NH_4)_2SO_4$, 99%), potassium carbonate (K_2CO_3, 99%) and methylene blue (MB, analytical reagent) were purchased from Sinopharm Chemical Reagent Co., Ltd. Degussa P25 was purchased from Shanghai Haiyi Co. All reagents were used as received without further purification.

Preparation of potassium titanate nanowires (KTNWs): KTNWs as the precursor were prepared via a hydrothermal reaction between a concentrated KOH solution and P25, according to the previous report [17b]. Typically, 44.8 g KOH were dissolved in 80 mL of distilled water, followed by adding 2 g P25 under magnetic stirring, and a white suspension formed. The resulting suspension was averagely transferred into three Teflon-lined stainless steel autoclaves with the capability of 50 mL, and then the autoclaves were kept at 200 °C for 24 h. After reaction, the white precipitate in the autoclaved mixture was collected by centrifugation, washed with distilled water and ethanol three times, and finally dried at the oven.

Synthesis of TiO_2 nanoparticles with different shapes

In a typical experiment for the synthesis of truncated tetragonal bipyramidal TiO_2 nanoparticles with exposed 60% (001) facets, KTNWs (0.01 g) and urea (20 mmol) were dispersed in the distilled water (16 mL) under intense ultrasonic treatment. The resulting solution was then transferred into a 25 mL Teflon-lined stainless-steel autoclave and was kept at 200 °C for 16 h. TiO_2 nanoparticles with other shapes were synthesized via a similar route, the (001) facets percentages of which were tuned by adjusting the amount of urea.

Characterization of TiO_2 nanoparticles with different shapes. The composition and phase of the as-prepared products were acquired by the powder X-ray diffraction (XRD) pattern using a Panalytical X-pert diffractometer with Cu Kα radiation. The morphology and crystal structure of as-prepared products were observed by scanning electron microscopy (SEM, S4800), and high-resolution transmission electron microscopy (HRTEM, JEM-2100) with an acceleration voltage of 200 kV. All TEM samples were prepared from depositing a drop of diluted suspensions in ethanol on a carbon film coated copper grid.

Photocatalytic degradation efficiency of TiO_2 nanoparticles with different shapes. Before measuring photocatalytic properties, the TiO_2 samples were calcined at the temperature 350 °C to remove the adsorbates. The photodegradation efficiency of methylene blue (MB) in aqueous solution was measured under the UV irradiation (50 W Hg lamp, 365 nm). All the experiments were carried out at the temperature of 25±2 °C. Typically, 2 mg of TiO_2 samples were dispersed in 40 mL of MB aqueous solution (4×10^{-5} M) under ultrasonic to form a suspension, and the suspension was magnetically stirred for 30 min in the dark. At regular irradiation time intervals, the dispersion was sampled and centrifuged to separate the TiO_2 photocatalyst. The photodegradation efficiency was monitored by measuring the absorbance of the centrifuged solutions at its maximum absorption wavelength of 662 nm with UV-vis spectroscopy (SHIMADZU, UV-2100) at room temperature.

2. Supplementary Results

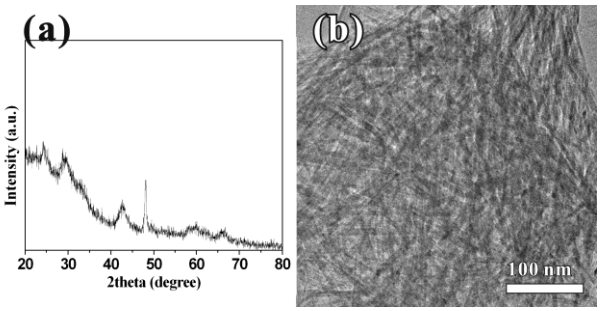

Figure S1. (a) Typical XRD pattern and (b) TEM image of the KTNWs precursor.

Figure S1a shows the typical XRD pattern of the as-prepared KTNWs precursor, which can be consistent with the monoclinic structure of $K_2Ti_6O_{13}$ (JCPDS no. 40-0403). The TEM observation (Figure S1b) indicates that the as-prepared KTNWs precursor consists of a large quantity of nanofibers with diameters of 7~10 nm and lengths of 500~1000 nm.

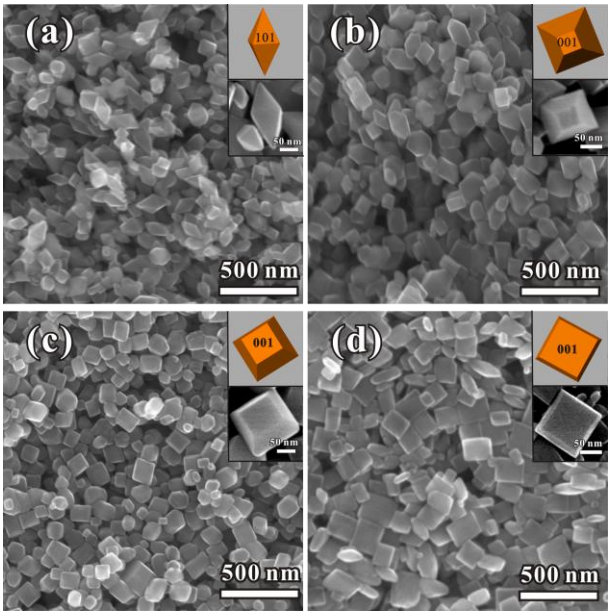

Figure S2. SEM images of TiO_2 nanoparticles synthesized by using 0.01 g KTNWs as precursor in the presence of (a) 0 mmol urea (Sample A), (b) 5 mmol urea (Sample B), (c) 10 mmol urea (Sample C), (d) 20 mmol urea (Sample D).

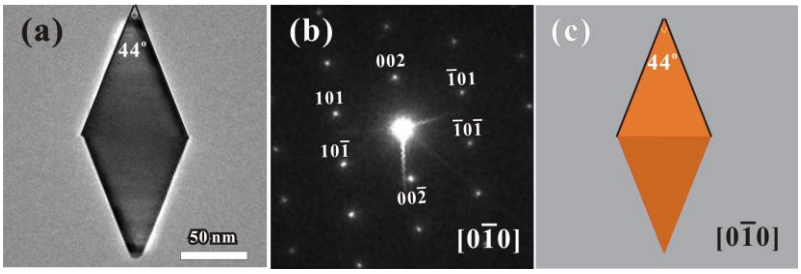

Figure S3. (a) Typical TEM image and (b) corresponding SEAD pattern of single TiO_2 bipyramid, (c) the schematic model of an ideal TiO_2 tetragonal bipyramid exposed with {101} facets projected from $[0\bar{1}0]$ direction.

Figure S3a presents a low-magnification TEM image of TiO_2 bipyramidal nanoparticles. The corresponding SAED pattern (Figure S3b) indicates that the TiO_2 tetragonal bipyramid is a single crystal, the axis of which is along the [001] direction. It should be noted that the interfacial angle of the opposite surfaces is ca. 44°, agreeing well with the theoretical value of the angle between the two opposite {101} facets in the TiO_2 tetragonal bipyramid exposed with {101} facets (Figure S3c).

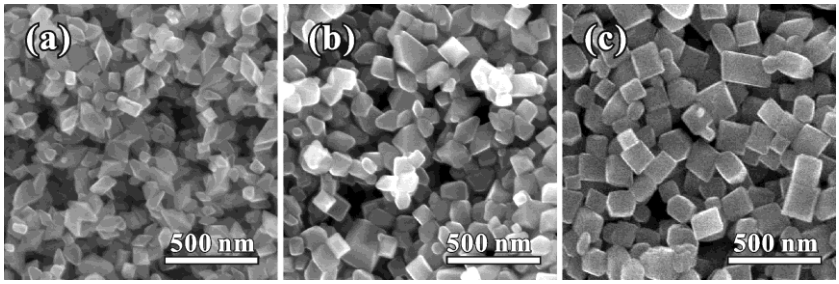

Figure S4. SEM images of TiO_2 nanoparticles synthesized by using KTNWs (0.01 g) as precursor in the presence of (a) 1 mmol $(NH_4)_2CO_3$, (b) 5 mmol $(NH_4)_2CO_3$, and (c) 10 mmol $(NH_4)_2CO_3$.

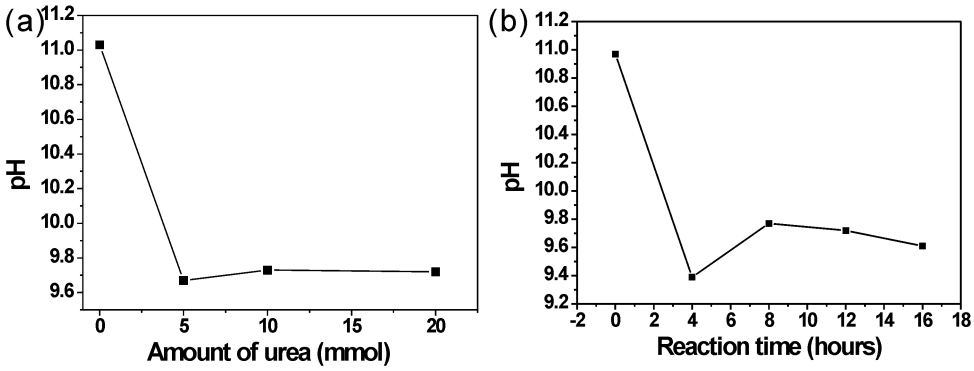

Figure S5. (a) pH change of reaction solution as a function of amount of urea, (b) pH change of reaction solution as a function of reaction time in the presence of urea of 20 mmol.

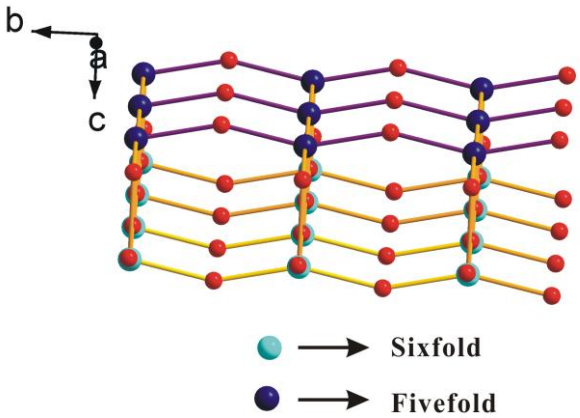

Figure S6. The surface atom arrangement on the (001) surface of anatase TiO_2.

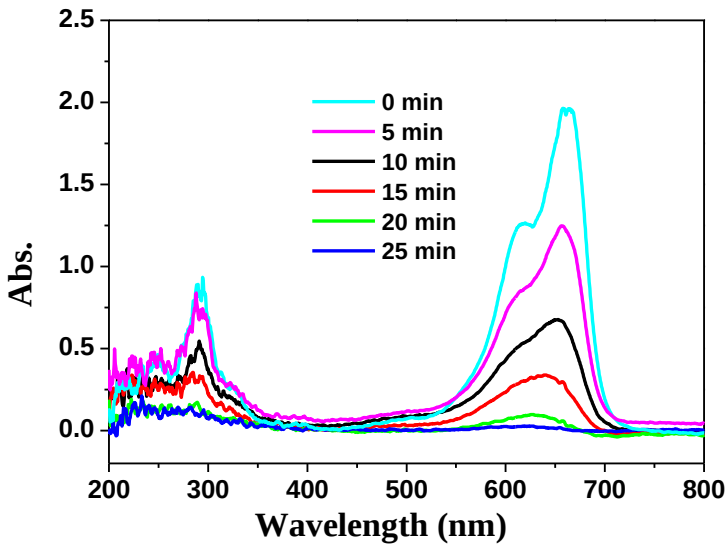

Figure S7. UV-vis absorption spectra of MB with UV light irradiation time in the presence of TiO_2 Sample.

In our study, MB is chosen as model pollutant to compare the ability of photodegradation of TiO_2 particles with different percentages of {001} facet. Previous study has demonstrated that the degradation of MB may follow two different mechanisms. One is the oxidative degradation of MB to CO_2, and the other is the two electron reduction to its colorless form, whose production should be accompanied by the absorbance at 256 nm.[1] In our study, it was observed that the absorbance peaks at 291 and 663 nm associated with MB decreased with irradiation time, whereas the absorbance band at 256 nm assigned to colorless intermediate did not appear at all. Therefore we think that the MB discoloration observed in this experiment should be due to the oxidative degradation, not to the de-coloring process.

[1]. T. Y. Zhang, T. Oyama, A. Aoshimaa H. Hidaka, J. C. Zhao, N. Serpone, *J. Photochem. Photobiol., A* 2001, **140,** 163.