

# Facile synthesis of high-temperature (1000 °C) phase-stable rice-like anatase TiO<sub>2</sub> nanocrystals

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**Abstract** High-temperature phase-stable rice-like anatase TiO<sub>2</sub> nanocrystals were synthesized by one-pot solvothermal method using soluble titania xerogel and isopropyl alcohol (IPA) as the precursor and the solvent, respectively. Sample characterization was carried out by powder X-ray diffraction, high-resolution transmission electron microscopy, field emission scanning electron microscope, X-ray photoelectron spectroscopy, and N<sub>2</sub> adsorption–desorption isotherms. The results showed that TiO<sub>2</sub> nanocrystals had rice-like shapes with an average size of 5 nm in width and 35 nm in length. The BET surface area was 153 m<sup>2</sup>/g. Unexpectedly, the rice-like TiO<sub>2</sub> nanocrystals exhibited high-temperature phase stability, which could remain as pure anatase phase after calcinations at 1000 °C. Growth mechanism investigation revealed that the IPA solvent played a key role in nucleation and growth of rice-like anatase TiO<sub>2</sub> nanocrystals. The photodegradation of rhodamine B demonstrated that rice-like anatase TiO<sub>2</sub> nanocrystals exhibited enhanced photocatalytic activity under visible light irradiation.

**Keywords** Nanocrystals · Rice-like · Anatase · TiO<sub>2</sub> · Phase stability · Functional nanomaterials

## Introduction

Over the past several decades, TiO<sub>2</sub> nanocrystal has been recognized as one of the most promising semiconductor materials owing to its wide band gap, low cost, chemical stability, and environmental friendliness. These properties make it one of the most extensively investigated semiconductor oxides, which can be used as photocatalysts, photovoltaic electrodes, and gas sensors (Bai et al. 2014; Chen and Mao 2007; Fujishima et al. 2000; Nisar et al. 2013). As is well known, the relative properties of TiO<sub>2</sub>-based functional materials are mainly dependent on its microstructure and physical properties, such as morphology, crystal structure, surface area, and crystallinity. In general, TiO<sub>2</sub> exists mainly in three crystal phases in nature: anatase, brookite, and rutile. Although rutile is the most thermodynamically stable phase at ambient pressure, anatase possesses the best photocatalytic activity because of the large band gap (3.2 eV) and strong oxidizing power. A high crystallinity of anatase TiO<sub>2</sub>, which possesses fewer surface defects, is one of the well-known critical factors in improving the photocatalytic performance. Thermodynamically, rutile is the most stable phase among diverse polymorphs of titania, and anatase can be readily transformed into rutile via a solid-state

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phase transformation (usually by calcination at above 550 °C in air). Although the high thermal treatment (>700 °C) could improve the crystallinity of TiO<sub>2</sub>, it leads to undesirable grain growth and the anatase–rutile phase transformation. Various attempts have been made to improve the crystallinity of anatase TiO<sub>2</sub> and resist the anatase–rutile phase transformation, such as metal or nonmetal doping, or surface modification with metal oxides (i.e., Al<sub>2</sub>O<sub>3</sub>, NiO, and ZnO). For example, Sun et al. (2012) synthesized stable biphasic porous TiO<sub>2</sub> nanoparticles with high crystallinity, large surface area, and small particle size through a post-treatment of ethylene diamine molecules, which are stable up to 800 °C. Grover et al. (2014) recently reported a pure and stable anatase TiO<sub>2</sub>, which could retain the anatase crystal phase (~100 %) by calcination at elevated temperatures (800–900 °C). However, synthesis of anatase TiO<sub>2</sub> with thermal stability at higher temperature (≥1000 °C) is still a challenge.

Morphology control with well-defined shape is the other key factors role in determining the properties of designed devices (D'Arienzo et al. 2011; Zhou et al. 2011). Recently, rice grain-shaped anatase TiO<sub>2</sub> nanocrystal has attracted increasing attention due to its high thermal stability and enhanced photoelectrochemical performances (Grover et al. 2014; Sun et al. 2012). Parmar et al. (2011) reported rapid synthesis of unique anisotropic single-crystalline rice-shaped TiO<sub>2</sub> nanoparticles utilizing a mixture of Ti-isopropoxide [Ti(OPr)<sub>4</sub>], acetylacetone, and deionized water by a microwave-assisted hydrothermal procedure. The TiO<sub>2</sub> nanorice exhibited an excellent photovoltaic efficiency of higher than 8 % as an anode of a dye-sensitized solar cell. Very recently, Li et al. (2014) prepared size-controllable and thermally stable rice-like brookite TiO<sub>2</sub> particles with high phase purity through a hydrothermal process. They found that the rice-like brookite TiO<sub>2</sub>-scattering layers could improve the performances of the P25 film-based solar cells. Despite the above-mentioned successful demonstrations, there is still need to develop a new, convenient, and economic synthesis procedure that can readily produce rice-like anatase TiO<sub>2</sub> nanocrystals with improved phase stability.

Herein, we report a facile solvothermal synthesis of elongated rice-like anatase TiO<sub>2</sub> nanocrystals with high-temperature (1000 °C) stability using soluble titania xerogel (STX) as a precursor and isopropyl

alcohol (IPA) as a solvent. The rice-like anatase TiO<sub>2</sub> nanocrystals exhibited higher photocatalytic activity than that of P25 under visible light irradiation. To the best of our knowledge, this is the first time IPA is used as solvothermal solvent to synthesize high thermally stable, rice grain-shaped anatase TiO<sub>2</sub> nanocrystals.

## Materials and methods

All reagents used in our experiments are of analytic purity and used without further purification. The STX was synthesized following our previous work (Meng et al. 2012). Briefly, 15 mL of tetrabutyl titanate (TBT) was added into 15 mL of trifluoroacetic acid (TFA) solution (50 wt%) under stirring in ice-bath. After stirring for 3 h, a clear solution was obtained. The solution was placed at room temperature for 3 days and a yellowish gel was obtained. Then, the yellowish gel was dried at 60 °C overnight to obtain the STX. Subsequently, 0.1 g of STX was dissolved in 30 mL IPA at room temperature and then the solution was transferred into a Teflon-lined autoclave and heated at 180 °C for 24 h. After cooling down to room temperature, white products were collected by centrifugation and washed for several times with distilled water and ethanol. The final product was dried at 70 °C for 10 h and labeled as I180-24. The samples synthesized in IPA at 160 and 180 °C for 5 h were labeled as I160-5 and I180-5, respectively. For comparison, TiO<sub>2</sub> nanoparticles were synthesized using different solvents including water, *n*-propanol, and ethanol. In order to investigate the phase stability, solvothermally synthesized TiO<sub>2</sub> samples in IPA were calcined at 900–1000 °C for 2 h under ambient conditions using a muffle furnace at a heating rate of 5 °C/min and labeled as I180-900 and I180-1000.

The crystal phases of the resulting products were characterized by powder X-ray diffraction (XRD, Rigaku D/max 2400 diffractometer with Cu K $\alpha$  radiation,  $\lambda = 1.54178 \text{ \AA}$ ) at a scanning rate of 2°/min. The morphologies and sizes of the TiO<sub>2</sub> nanoparticles were observed on a JEOL S-4300F field emission scanning electron microscope (SEM) at 15 kV and JEOL JEM-2010 transmission electron microscope at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCA Lab 250Xi using 200 W monochromated Al K $\alpha$  radiation. The 500  $\mu\text{m}$  X-ray spot was used for

XPS analysis. The base pressure in the analysis chamber was about  $3 \times 10^{-10}$  mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing.  $N_2$  adsorption–desorption isotherms were obtained by means of a Micromeritics ASAP 2040 system at liquid nitrogen temperature (77 K). Before carrying out the measurement, 0.1 g sample was out-gassed under vacuum for 6 h at 250 °C. Pore volume and size distributions were derived from the desorption branches of the isotherms by the Barrett–Joyner–Halenda (BJH) model, and the Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area from the adsorption data.

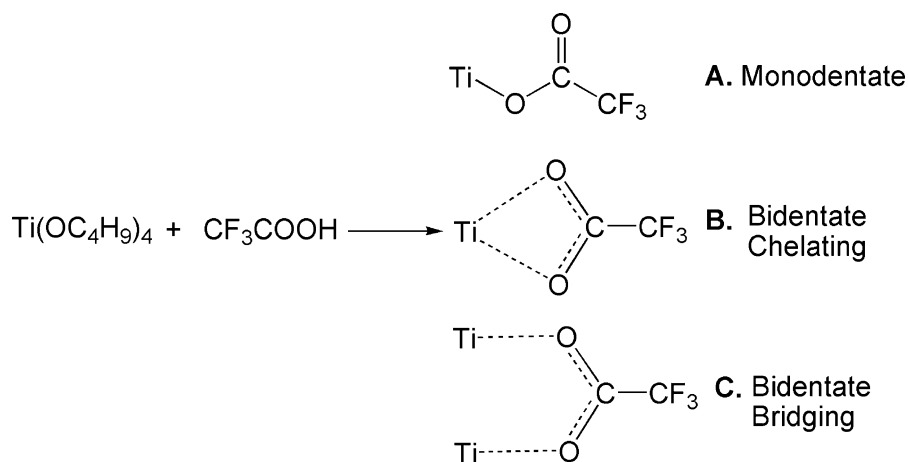
The photocatalytic activity was evaluated by degradation of rhodamine B (RhB) under visible light irradiation. 30 mg of  $TiO_2$  nanocrystals was added into 30 mL of aqueous solution of RhB (30 mg/L) in a 100-mL-Pyrex glass vessel. Prior to irradiation, the suspension was kept in the dark overnight to insure the establishing of an adsorption/desorption equilibrium, and the equilibrium concentration was fixed as the initial concentration ( $C_0$ ). The irradiation source was a 300 W Xe lamp (Philips) with a 420-nm cutoff filter to ensure irradiation by visible light only. At given intervals of illumination (every 0.5 h), the RhB concentration variations ( $C_t$ ) were monitored using Shimadzu UV1601-PC UV–Vis spectroscopy at the maximum absorption wavelength of 554 nm. For comparison, commercial  $TiO_2$ , Degussa P25, and RhB solution without any photocatalysts were also examined under an identical condition.

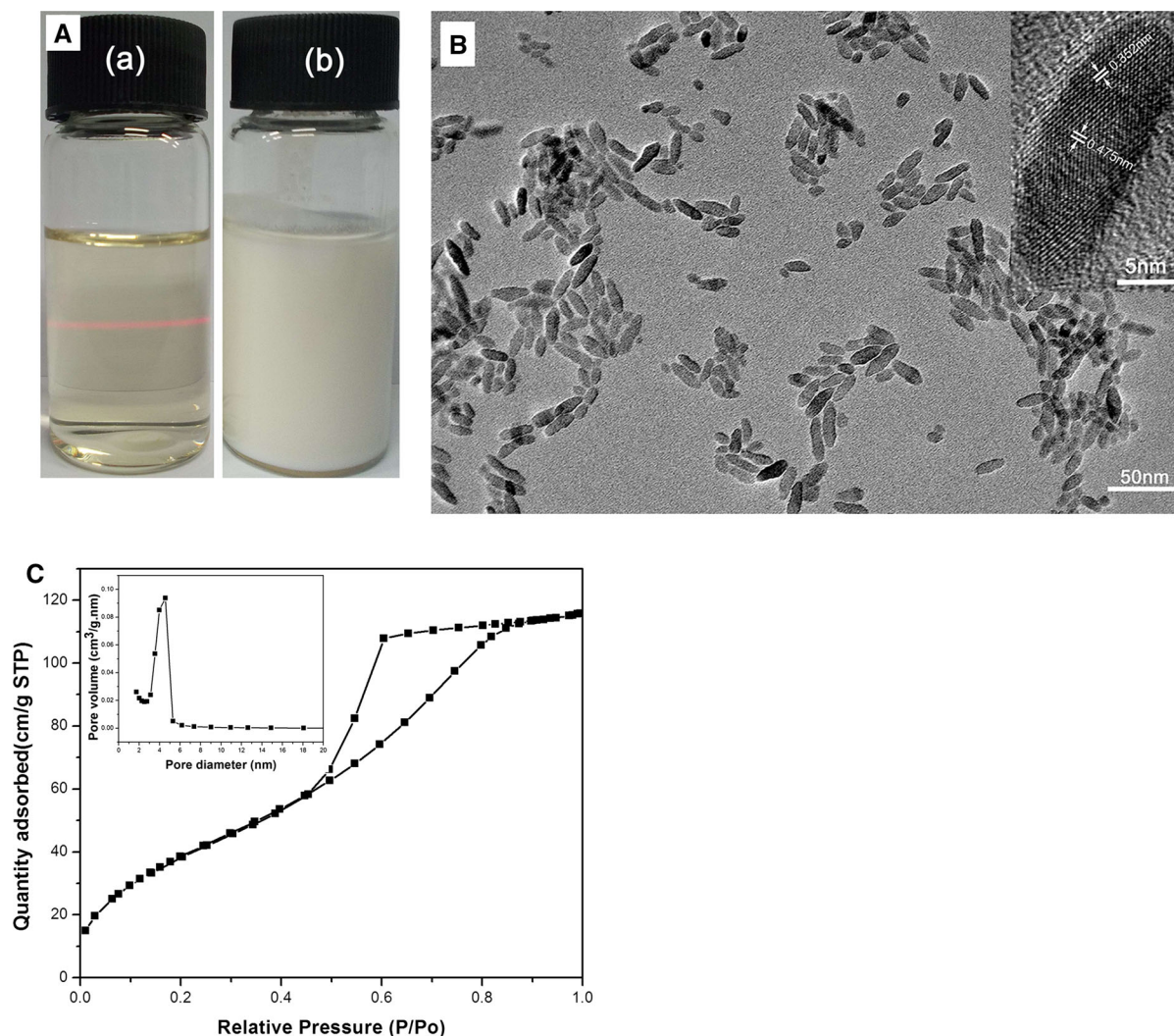
## Results and discussions

Soluble titania xerogel synthesized in the present work can be quickly dissolved in IPA, water and other polar organic solvents, such as ethanol, acetone, tetrahydrofuran, and so on. In our previous work, we have proved that TFA bonded to the titanium center in a bidentate bridging or chelating fashion (see Scheme 1B, C) in xerogel samples (Meng et al. 2012). The solubility of STX in organic solvents provides a large amount of manipulation variety for controlling synthesis of  $TiO_2$  nanoparticles via solvothermal method due to the slow hydrolysis and condensation rate under nonaqueous condition.

When STX was added into IPA, a clear solution was obtained within several minutes (Fig. 1A). The observation of Tyndall light scattering demonstrated the formation of colloidal dispersion. The colloidal solution can remain stable for 6 months without precipitating. After the solvothermal treatment at 180 °C for 24 h, a milk-like suspension was obtained. Figure 1B clearly shows the typical TEM image of  $TiO_2$  nanocrystals. It can be easily seen that rice-like  $TiO_2$  nanocrystals with a uniform size distribution are obtained. The  $TiO_2$  nanocrystals have an average particle size of 8 nm in width and an average of 25 nm in length. HRTEM image (insert in Fig. 1B) shows clear crystalline lattice fringes, 0.352 and 0.475 nm, which correspond to the (101) and (002) atomic planes of anatase  $TiO_2$ , respectively. Figure 1C shows the nitrogen adsorption–desorption isotherms and the corresponding pore size distribution curves of rice-like  $TiO_2$  nanocrystals. The isotherm exhibits typical

**Scheme 1** Chemical sequence of TBT hydrolysis in TFA-bonding modes





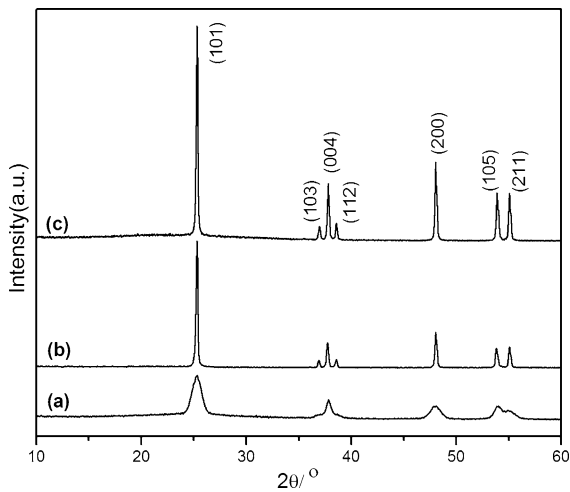
**Fig. 1** **A** Photographs of titania sol in isopropanol before (a) and after (b) solvothermal treatment. **B** Low-resolution TEM image, high-resolution TEM image of I180-24. **C** Nitrogen

adsorption–desorption isotherms and corresponding pore size distribution curves (*inset*) of I180-24

type IV pattern with hysteresis loop, a typical characteristic of mesoporous materials. The pore size distribution calculated from the desorption branch of the nitrogen isotherm by the BJH method shows a narrow range of 3.0–5.0 nm with a maximum pore diameter of about 4.2 nm (see inset of Fig. 1C). These mesopores are formed by the aggregation of primary particles. The narrow pore distributions also imply that the prepared rice-like TiO<sub>2</sub> nanoparticles have a uniform particle size distribution. The BET surface area is measured to be 153 m<sup>2</sup>/g, which is about three times higher than that of P25 powder (50 m<sup>2</sup>/g). The results of nitrogen adsorption/desorption experiments

indicate that the rice-like TiO<sub>2</sub> nanocrystals synthesized in IPA have large specific surface area, which is helpful for the improvement of photocatalytic activity.

The structure of TiO<sub>2</sub> nanocrystals was further investigated by XRD. Figure 2a shows the XRD patterns of the rice-like anatase TiO<sub>2</sub> synthesized in IPA. It is clear that the solvothermally synthesized TiO<sub>2</sub> nanocrystals are pure anatase. According to the Scherrer's equation, the average particle size is about 25 nm, which is consistent with the TEM results. Figure 2b, c shows the XRD patterns of the calcinated samples at 900 and 1000 °C for 2 h, respectively. Unexpectedly, the rice-like TiO<sub>2</sub> nanocrystals

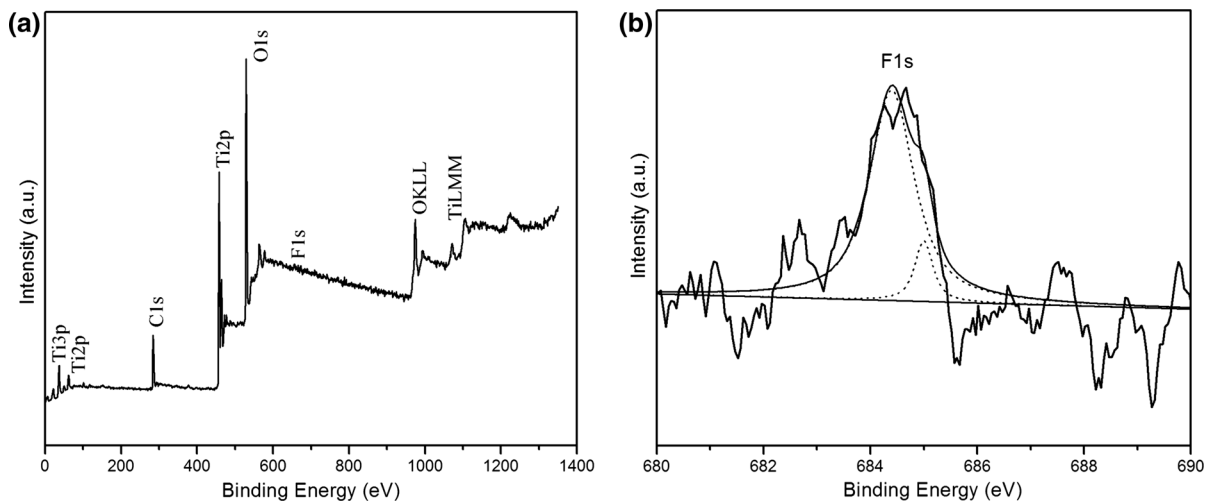


**Fig. 2** XRD patterns of **a** I180-24, **b** I180-900 and **c** I180-1000

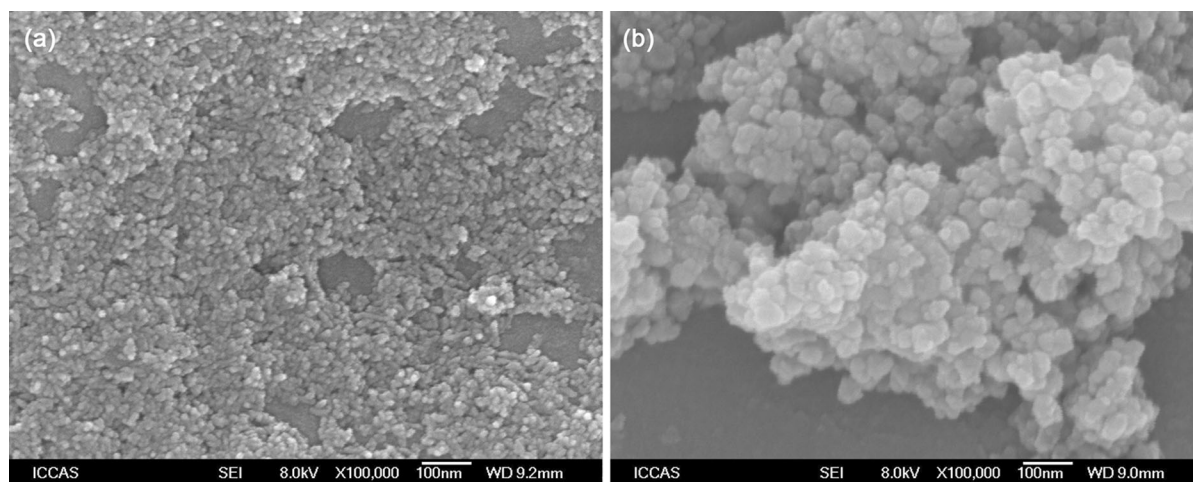
remained pure anatase phase calcinated at 900 °C for 2 h. More interestingly, no clear rutile characterized peak ( $2\theta = 27.4^\circ$ ) appeared even when the calcining temperature was increased up to 1000 °C. Only noticeable increase in intensity and decrease in broadness for the (101) peak at  $2\theta = 25.3^\circ$  were observed when the calcination temperature was increased from 900 °C to 1000 °C. The average particle size was increased from 25 to 47 nm after annealing at 1000 °C for 2 h calculated by Scherrer equation. This suggested that no anatase–rutile phase transformation occurred for rice-like TiO<sub>2</sub> nanocrystals when calcined at high temperature (1000 °C).

In general, the anatase–rutile phase transformation is kinetically defined, and the reaction rate is determined by parameters such as particle shape/size, purity, and reaction conditions. Anatase nanocrystals coarsen, grow, and then transform to rutile only when a critical size is reached. Therefore, phase transformation is dominated by factors such as defect concentration, grain boundary concentration, and particle packing. In the present work, there are two possible reasons for the high-temperature anatase stability of TiO<sub>2</sub> nanorices. One reason can be attributed to the presence of trifluoroacetate complex, which can cause the fluorination of the anatase crystals under thermal decomposition. Figure 3b shows the high-resolution XPS spectrum of F1s region. The F1s peak located at around 684.4 eV is a typical value for fluorinated TiO<sub>2</sub> systems such as ≡Ti–F species on the TiO<sub>2</sub> crystal surface. No signal for F in the lattice of TiO<sub>2</sub> (BE = 688.5 eV) is found, suggesting that F element only exists in surface fluoride (≡Ti–F). Therefore, the fluorinated clusters may repel each other and thus slow down the nuclear and growth rate of rutile phase.

Besides the effect of trifluoroacetate complex, the unique rice-like shape with fewer interfaces is another important factor in affecting the anatase to rutile phase transformation. A reduction in anatase–anatase interface can slow the phase transformation, especially when this transformation is governed by the interface nucleation. Figure 4 shows the SEM images of TiO<sub>2</sub>



**Fig. 3** XPS survey spectra of **a** I180-1000 and **b** high-resolution of F 1s



**Fig. 4** SEM images of TiO<sub>2</sub> nanorices **a** before and **b** after sintering at 1000 °C for 2 h

nanorices before and after sintering at 1000 °C for 2 h. The particle size was increased to about 50 nm after calcinations, which was consistent with XRD data. The packing characteristics of the rice-like TiO<sub>2</sub> nanocrystals limited the interface nucleation of the rutile phase and effectively retard the phase transformation at a relatively high temperature. Therefore, the rice-like shape TiO<sub>2</sub> with fewer interfaces played crucial roles in anatase–rutile phase transformation.

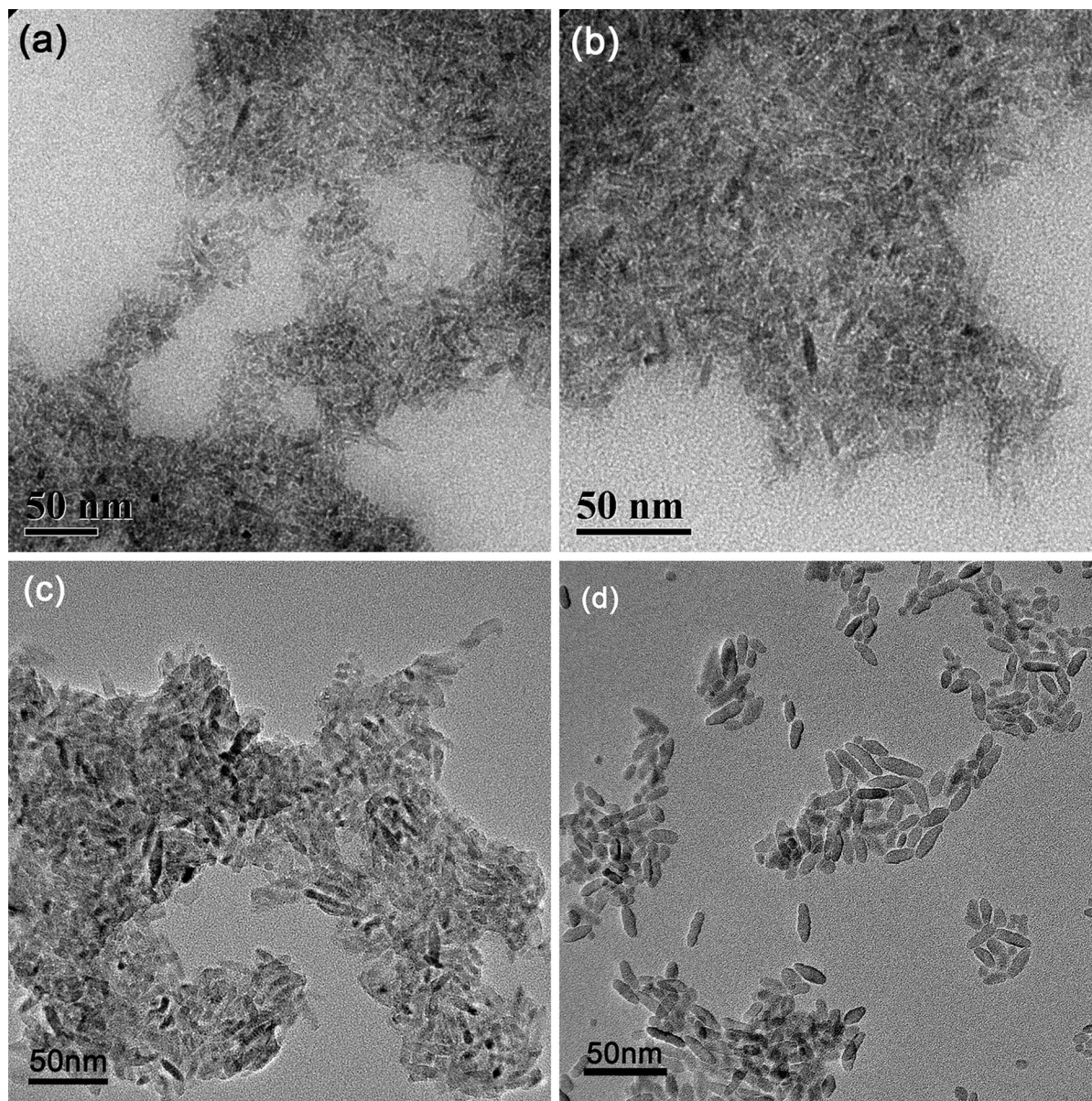
In order to investigate the growth mechanism of rice grain-shaped anatase TiO<sub>2</sub> nanocrystals, TiO<sub>2</sub> nanocrystals were synthesized at different temperatures and times in IPA. As shown in Fig. 5a, rice grain-shaped TiO<sub>2</sub> nanocrystals with size of an average of 3 nm in width and an average of 12 nm in length were formed at 160 °C for 1 h. With the increasing solvothermal temperature and time, the TiO<sub>2</sub> nanorice grew gradually, and the size increased to 5 nm in width and to an average of 20 nm in length (Fig. 5b, c, d). This suggests that IPA has a template effect on the nucleation of rice-like TiO<sub>2</sub> nanocrystals at the early stage of growth, which will be discussed in later section.

To further understand the unique role of IPA in the growth of TiO<sub>2</sub> nanorices, different solvent systems were used to synthesize the TiO<sub>2</sub> nanoparticles. Figure 6 shows the TEM images of TiO<sub>2</sub> nanoparticles prepared in *n*-propanol, ethanol, and water, respectively. In *n*-propanol, floccus-like structure was obtained, which was radically different from that in isopropanol. However, rectangular-shaped TiO<sub>2</sub> nanoparticles with uniform size were observed in ethanol, which have a

length of about 11 nm and a width of about 5 nm. In the case of water, TiO<sub>2</sub> nanoparticles with random shapes were obtained. The results show that IPA has a unique effect on the nucleation and the growth of rice-like TiO<sub>2</sub> nanocrystals.

The effect of alcohol solvent on synthesis of anatase TiO<sub>2</sub> nanocrystal has been reported by several authors. Wang et al. (2002) reported that the amount and configuration of CH<sub>2</sub> in alcohols played key role in controlling the crystal structures, grain sizes, and morphologies of the products. Liao et al. (2009) used peroxotitanate complex solution as precursor to prepare TiO<sub>2</sub> nanocrystal colloids with different shapes and sizes. They found that ethanol shows much stronger adsorption onto the (001) plane, which depressed the growth rate along the [001] direction, and the rectangular shape was formed. Recently, Wu and Tai (2013) investigated the solvent effects on the crystallization of anatase nanoparticles using eight different alcohols. The results showed that the solvent properties, such as the dielectric constant and boiling point, were considered in terms of their correlation to the crystallite size and shape. In our work, the selective adsorption of IPA on Ti-(OOCCF<sub>3</sub>)<sub>4</sub> octahedral complexes may play a key role in nuclear and growth of rice-like TiO<sub>2</sub> nanocrystals. The growth mechanism of TiO<sub>2</sub> nanocrystals using Ti-(OOCCF<sub>3</sub>)<sub>4</sub> octahedral complexes as precursor in different alcohol solvents is under further investigation.

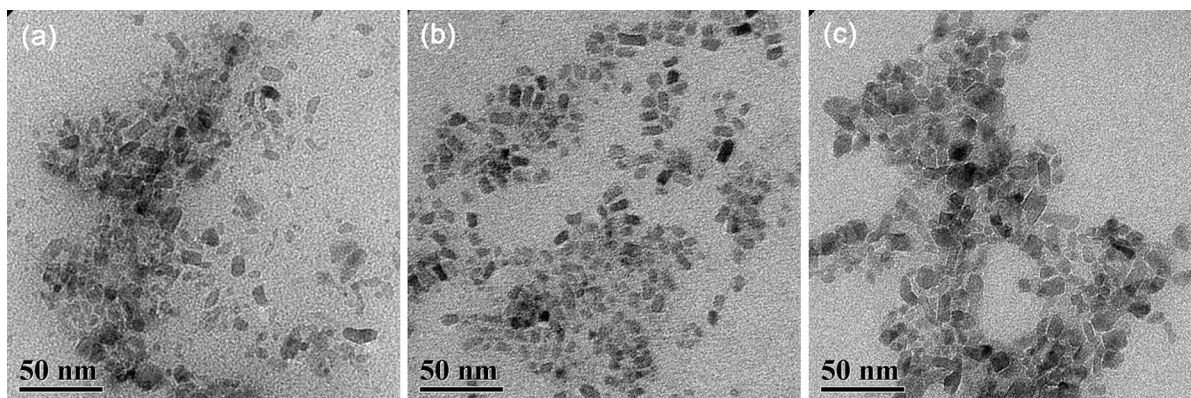
The thermal stabilities of the synthesized TiO<sub>2</sub> nanocrystals in different solvents are shown in Fig. 7.



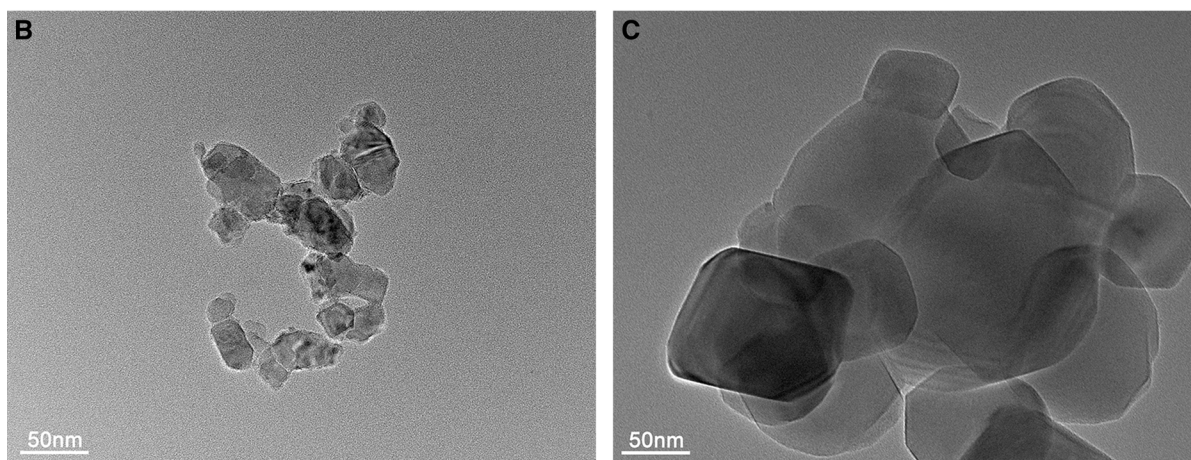
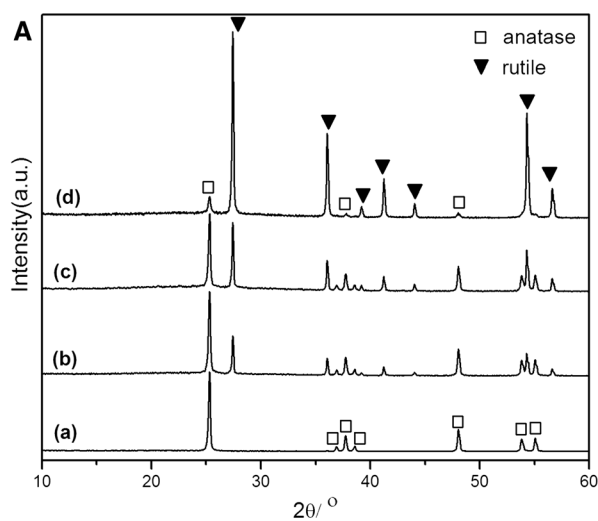
**Fig. 5** TEM images of TiO<sub>2</sub> nanocrystals **a** I160-1, **b** I160-5 **c** I180-5, and **d** I180-24

As discussed above, only anatase peaks appeared in the sample synthesized in IPA after calcinations at 900 °C for 2 h (Fig. 7A, a). However, both anatase and rutile peaks were observed in the samples synthesized in ethanol, *n*-propanol, and water due to anatase–rutile phase transformation (Fig. 7A, b, c, d). This suggests that the samples synthesized in ethanol, *n*-propanol and water have lower thermal stability, especially in water. Most of anatase phase transformed into rutile phase for the sample synthesized in water

after calcinations. The TEM images (Fig. 7B, C) clearly show that the particle size is less than 50 nm for the sample prepared in IPA, while the particle size is more than 100 nm for the sample obtained in water due to the anatase–rutile phase transformation and the growth of rutile phase. The above results demonstrate that IPA can induce the growth of rice-like TiO<sub>2</sub> nanocrystals, and the unique shape in turn endows the anatase TiO<sub>2</sub> nanocrystals with high thermal stability and retard the anatase–rutile phase transformation.

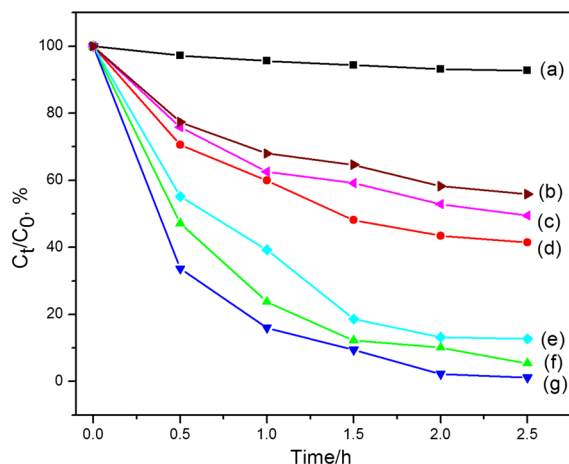


**Fig. 6** TEM images of TiO<sub>2</sub> nanoparticles synthesized in **a** *n*-propanol, **b** ethanol, and **c** water



**Fig. 7** A XRD patterns of TiO<sub>2</sub> nanocrystals synthesized in *a* isopropanol, *b* ethanol, *c* *n*-propanol, and *d* water after calcination at 900 °C for 2 h. TEM images of TiO<sub>2</sub> nanocrystals synthesized in isopropanol (**B**) and water (**C**) after calcination at 900 °C for 2 h





**Fig. 8** Photodegradation RhB dye under visible light irradiation: *a* blank, *b* I180-1000, *c* I180-900, *d* P25, *e* I180-5, *f* I160-1, and *g* I180-24

The photocatalytic performances of rice grain-shaped anatase TiO<sub>2</sub> nanocrystals were evaluated by photodegradation of RhB under visible-light irradiation. Figure 8 compares the photocatalytic activity of rice-like TiO<sub>2</sub> nanocrystals synthesized at different temperatures and times. As shown in Fig. 8, the rice-like anatase TiO<sub>2</sub> nanocrystals prepared in IPA exhibited higher RhB photodegradation rate than that of P25, and the sample synthesized at 180 °C for 24 h showed the highest photoactivity. As mentioned above, the rice-like TiO<sub>2</sub> nanoparticles have large surface area, which facilitated the adsorption and decomposition of pollutant. Meanwhile, the rice grain-shaped TiO<sub>2</sub> nanocrystals with sharp corners and edges have more active sites on the surfaces, which also can enhance the photocatalytic activity (Peng et al. 2010). Moreover, the photocatalytic activity is slightly enhanced when increasing the solvothermal temperature from 160 °C to 180 °C, which may be due to the higher crystallinity. After calcinations, the samples I180-900 and I180-1000 show lower photoactivity than P25 because the particle size was greatly increased during the heating process. Other calcined samples synthesized in ethanol, *n*-propanol, and water (not shown here) also exhibited lower photoactivity than P25, regardless of the ratio of anatase to rutile.

## Conclusion

In summary, we have developed a facile route for the synthesis of high-temperature phase-stable rice-like

anatase TiO<sub>2</sub> nanocrystals via solvothermal method. The IPA played a template-effect for the nucleation and growth of rice grain-shaped anatase TiO<sub>2</sub> nanocrystals. The rice grain-shaped anatase TiO<sub>2</sub> nanocrystals with large surface area exhibited higher photocatalytic activity for RhB degradation under visible light irradiation.

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