# A Facile Hydrothermal Method for Controllable Synthesis of TiO2 Nanocrystals with Tunable Shapes

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<td>Nie, shengcao; Wuhan University of Technology, Key Laboratory of Silicate Materials Science and Engineering Zhao, Xiujian; Wuhan University of Technology, Key Laboratory of Silicate Materials Science and Engineering Liu, Baoshun; Wuhan University of Technology, School of Material Science and Engineering</td>
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### RSC Advances

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A Facile Hydrothermal Method for Controllable Synthesis of TiO$_2$ Nanocrystals with Tunable Shapes

Shengcao Nie, Xiujian Zhao, and Baoshun Liu*

The controllable preparation of anatase TiO$_2$ nanocrystals with tunable shapes has drawn much attention recently. The general method to prepare such nano-TiO$_2$ involves the use of HF as a surfactant. However, the use of HF is top-risk, which should be avoided in experiments. Therefore, the development of facile and friendly methods to controllably synthesize anatase TiO$_2$ nanocrystals is important. In this research, instead of the general titanium precursors, titanium peroxide sol was used as the source material to synthesize anatase TiO$_2$ nanocrystals due to its high stability in water. Oleic acid and oleylamine were used as capping surfactants, a hydrothermal method without using top-risk HF was developed to prepare the uniform anatase TiO$_2$ nanocrystals with various shapes, which can be tuned from octahedral bipyramid, to truncated octahedral bipyramid, and then to nano-sheet. The ratios between {001} and {101} surface can be easily tuned by changing the amounts of oleic acid and oleylamine. The photocatalytic activity of these anatase TiO$_2$ nanocrystals was also evaluated through the crystal violet photo-degradation under UV light illumination. It was shown that the anatase TiO$_2$ nanocrystals can present the photocatalytic activity comparable to commercial P25.

Introduction

Nowadays, nano-TiO$_2$ has become a key functional material in the fields of photocatalysis, dye-sensitized solar cells (DSSCs), lithium batteries, and the others.\textsuperscript{1-10} It was shown that the its properties are closely dependent on the morphologies and the structure.\textsuperscript{13-19} For example, it was reported that the controllable synthesis of anatase TiO$_2$ nanocrystals with various exposed facets is important for improving the photocatalytic activity.\textsuperscript{20-26} From the viewpoint of thermodynamic, anatase TiO$_2$ has the shape of truncated octahedral bipyramid that is surrounded with eight \{101\} facets and two \{001\} facets. This is a very popular crystal shape in nature. Moreover, theoretical studies showed that the order of average surface energy is $\gamma$\{110\} (1.09 J m$^{-2}$) > $\gamma$\{001\} (0.90 J m$^{-2}$) > $\gamma$\{100\} (0.53 J m$^{-2}$) > $\gamma$\{101\} (0.44 J m$^{-2}$).\textsuperscript{27} The high energy \{001\} facets may be more reactive for dissociative adsorption of reactant molecules than that of the \{101\} facets, so it was shown that the TiO$_2$ with highly-exposed \{001\} facets should present better performances for both photocatalysis and DSSCs.\textsuperscript{28-31} From this viewpoint, the synthesis of such anatase TiO$_2$ nanocrystals is still interesting for us.

The preparation of anatase TiO$_2$ nanocrystals with highly-exposed \{001\} facets is difficult as high-energy facets generally diminish during TiO$_2$ nanocrystal growth.\textsuperscript{32} Some special surfactants or source materials are needed to prohibit the preferable growth along \{101\} direction, in order to get nano-TiO$_2$ with highly-exposed \{001\} facets. After the first synthesis of TiO$_2$ nanocrystals with high-exposed \{001\} facets from TiF$_4$ solutions through hydrothermal method,\textsuperscript{33} much effort have been taken due to their great interest. In additional to pure materials, nitrogen doped anatase TiO$_2$ nanocrystals with highly-exposed \{001\} facets were also prepared by the hydrothermal treatment of TiN powder in HF solution.\textsuperscript{34} Generally, high-concentrated HF solution is needed to grow the anatase TiO$_2$ nanocrystals with highly exposed \{101\} facets. Lu et al. obtained the anatase TiO$_2$ microcrystals with 64 \% \{001\} facets exposed by using HF as shape controlling agent;\textsuperscript{29} this method can be used to further increase the percentage of exposed \{001\} to 89 \%, resulting in the formation of nano-sheets.\textsuperscript{34, 35} The big problem is that HF is
undesirable due to its high toxicity. The HF-induced TiO₂ nanocrystals also always have large size, which inevitably reduces the specific surface area and limits their applications. In addition to HF, other surfactants were also attempted. For example, Zhao et al. got mesoporous TiO₂ microspheres covered dominantly with {001} facets with using H₂SO₄ as surfactants through hydrothermal method. 36 Xia et al. obtained uniform tiny TiO₂ nanocrystals with exposed {101} facets by treating the electrospinned TiO₂-polyvinylpyrrolidone (PVP) complex materials by hydrothermal reaction. 37 It was shown that the shape of TiO₂ nanocrystals depends on the pH. In comparison with the HF-induced method, the TiO₂ nanocrystals prepared by Xia et al. have much smaller size. With diethylenetriamine and isopropyl alcohol being used as the surfactants, Chen et al. got the hierarchical spheres that are composed of ultrathin anatase TiO₂ nanosheets with nearly 100 % exposed {001}. This material has specific surface area of 170 m²/g. 38 Do et al. reported a non-aqueous solvothermal method to prepare the anatase TiO₂ nanocrystals with rhombic, truncated rhombic, spherical, and dog-bone shapes. 39 In this method, ethanol, titanium butoxide (TBT), oleic acid (OA), and oleylamine (OM) were used as solvent, titanium precursor, and capping surfactants, respectively. Water vapour was used as the hydrolysis agent of TBT to control the reaction rate.

The controllable growth of TiO₂ nanocrystals with perfect shapes needs low reaction speed, so non-aqueous condition was favorable. However, non-aqueous condition affect product yield of TiO₂ nanocrystals due to low water amount and low reaction speed. From this viewpoint, the development of a green and risk-less hydrothermal method to prepare such TiO₂ materials is necessary and attractive. This needs that the titanium precursor should have low reaction speed. Our previous researches showed that titanium peroxide sol is very stable in air, which can kept for several months. 39, 40 It is a good titanium precursor to grow anatase TiO₂ nanocrystals without using any reaction inhibitors through hydrothermal routine. In the present research, with using OA and OM as the capping surfactants, a facile harmless hydrothermal method was invented to prepare anatase TiO₂ nanocrystals with the exposed {101} facets. The {001}/ {101} ratio can be well controlled, and the shapes of the anatase TiO₂ nanocrystals can be tuned from octahedral bipyramids, to truncated octahedral bipyramids, and then to nano-sheets. The application of them in photocatalysis was also studied through the photo degradation of crystal violet (CV) under UV light illumination. It was shown that the anatase TiO₂ nanocrystals present the photocatalytic activity that can be comparable to the commercial P25.

**Experimental**

**Titanium peroxide sol preparation:** 8 mL TiCl₄ was added in 500 mL ice-cold distilled water (ca. 0-5 °C) under continuous magnetron stirring. Several hours later, the TiCl₄ water solution became transparent. Then, 1:5 ammonia was slowly added in the TiCl₄ water solution to produce Ti(OH)₄ participate until the pH of ca. 7. The Ti(OH)₄ sedimentation was kept for ca. 12 h, and then it was filtered and cleaned for several times by the ionized water. The cleaned Ti(OH)₄ sedimentation was dispersed in cold distilled water (~4 °C) again, and then 80 mL H₂O₂ was slowly added. The mixed water solution was kept stirring until it became a yellow transparent titanium peroxide sol.

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<tr>
<th>Group-1</th>
<th>OA (mL)</th>
<th>OM (mL)</th>
<th>Titanium peroxide sol (mL)</th>
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**Synthesis of the TiO₂ nanocrystals:** 20 mL yellow titanium peroxide sol was placed in a Teflon-closed steel autoclave. The OA and OM were dissolved in 33 mL ethanol. Afterwards, the OA and OM ethanol solutions were mixed with the titanium peroxide sol in the autoclave, which was then kept stirring for some minutes. The mixed solution was hydrothermally treated at 150 °C for 18 h to get the final product. The amounts of titanium peroxide sol and ethanol were kept unchanged, and the amounts of OA and OM were adjusted for various experiments, which were classified as three groups, as shown in Table 1. Lastly, the TiO₂ products were washed and cleaned by ethanol for several times to remove the physically-adsorbed residual organic surfactant, and then were dispersed in toluene for the further characterization.

**Characterization:** X-ray diffraction (XRD) patterns of the anatase TiO₂ nanocrystals were checked using a D/Max-IIIA X-ray diffraction meter in a 20 mode from 10° to 80°. High-resolution transmission electron microscopy (HR-TEM) images were observed using a transmittance electron microscopy (HITACHI, H-600 STEM/EDX PV910). The thermo-gravimetric analysis (TG-DTA) was carried out under a flow of air with a temperature ramp of 5 °C min⁻¹ by using a thermal analyser (Germany, NETZSCH, STA449C/3/G). Infrared absorption spectra were recorded by using Nexus fourier
transform infrared spectroscopy (FT-IR) in the range of 400-2000 cm⁻¹ (America, Thermo-Nicolet company)

**Photocatalytic measurement:** Firstly, 0.04 g TiO₂ nanocrystal powders were mixed with ethanol in a 40 mL glass container, which was then ultrasonically dispersed for ca. 30 min. The ethanol was removed by heated at 70 °C, and then 50 mL crystal violet (CV, 6 mg L⁻¹) was slowly added in the glass container. The adsorption and photocatalytic abilities of the TiO₂ samples were evaluated by measuring the UV-Vis absorption spectra of the CV aqueous solutions for different reaction intervals. A 15 W (TOSHIBA, 365 nm) UV fluorescent lamp was used as light source. The UV light intensity was measured to be ca. 1.0 mW cm⁻².

![Fig. 1](image1.png)

Fig. 1 shows the pictures of the titanium peroxide sol (A), the mixed solution after hydrothermal reaction (B), and the toluene solution that contains the TiO₂ nanocrystals (C). The titanium peroxide sol is a yellow transparent water sol, which is very stable and can be kept for several months at room temperature and air atmosphere. After hydrothermal treatment, it can be seen that the yellow transparent solution changed to a mixture solution with three layers, as shown in Fig. 1 (B). The top, middle, and bottom layers are the OA and OM ethanol solution, the white TiO₂ nanocrystal solution, and the water-ethanol solution, respectively. The TiO₂ nanocrystals should be capped with OA and OM molecule, so they are both hydrophobic and oleophilic, which makes the TiO₂ sample locate between the oil and water layers. After the solutions of top and bottom layers were carefully removed, the middle layer that contains the TiO₂ sample was left, which were then washed by ethanol for several times to remove the physically-absorbed OA and OM molecule. The white TiO₂ sample was lastly dispersed in toluene for the further TEM checking, which can form an optical transparent solution, as shown in Fig. 1 (C).

![Fig. 2](image2.png)

**Fig. 2** shows TEM images of the as-prepared TiO₂ samples prepared according to the parameters of group-1 (Table 1). In these experiments, the OA amount was increased from 2 mL to 12 mL, and the OM amount was decreased from 12 mL to 2 mL. When 2 mL of OA and 12 mL of OM were used, it can be seen from Fig. 2 (A) that the hydrothermal product is composed of very small uniform TiO₂ nanocrystals, which present the shape of octahedral bipyramids. Obviously, they belong to anatase TiO₂ single nanocrystals. The nanocrystals are surrounded by eight {101} surface, and almost no {001} exposed facets can be seen. The ratio of exposed {001} and exposed {101} is near ca. 0. When the OA amount was increased to 5 mL, and the OM amount was decreased to 10 mL, the hydrothermal product changed to the uniform nanocrystals with the shape of octahedral bipyramids. These TiO₂ nanocrystals contain both exposed {101} and {001} facets (Fig. 2(B)). By selecting some nanocrystals, the average ratio between the exposed {001} and the {101} facets was calculated to be ~ 7 %. The further increase of OA amount to 8.5 mL and the further decrease of OM amount to 8.5 mL changed the shape of the hydrothermal sample to nanosheets with the thickness of ca. 6 nm (Fig. 2 (C)).

The high-resolution TEM image of one stood nanosheet was shown in the top-right corner of this Figure. It can be seen that TiO₂ nanosheet present the shape of truncated octahedrons. The {001}/[101] ratio of this sample is ~ 60 %. The continuous increase of OA amount and decrease of OM amount cannot change the shape of TiO₂ nanocrystals anymore, and they are still in the form of nano-sheets, but their size tends to become smaller. As no stood TiO₂ nano-sheets can be seen, although the thicknesses of these samples cannot be decided, they should be thinner than the sample shown in Fig. 2 (C). For comparison, the sample prepared without using OA and OM is shown Fig. 2(F), and it can be seen the TiO₂ nanoparticles has irregular shape. Therefore, the above results show that the OA and the OM are important to control the shape evolution of TiO₂ nanocrystals even in hydrothermal environments, in additional to the non-aqueous methods. It can be known that the OA tends to control the formation of {101} surface, and OM tends to limit the growth of TiO₂ nano-crystal along [001] direction. As a result, by using the titanium peroxide sol as the titanium precursor, the anatase TiO₂ nanocrystals with the tunable shapes and the controllable {001}/[101] ratio can be prepared by just using a facile hydrothermal method.
Fig. 3 shows the XRD patterns of the TiO$_2$ samples prepared according to the experimental parameters of group 1. All of the samples can be indexed as the anatase TiO$_2$. With the increase of the OA amount and the decrease of OM amount, the X-ray diffractive intensity of (004) lattice becomes weaker and weaker, showing that the thermodynamically preferable growth of TiO$_2$ nanocrystals along the [001] direction is limited. At the same time, it can be seen that the intensity ratio of (101) peak and (004) peak increase, suggesting that the shape of anatase TiO$_2$ nanocrystal shape should alter from the octahedral bipyramids, to the truncated octahedral bipyramids, and then to the nano-sheets, which accords to the TEM analysis.

To clearly show the role of OM in the controllable growth of anatase TiO$_2$ nanocrystals, the OM amount was kept unchanged at 7 mL during hydrothermal reaction, with the OA amount being changed from 0 mL to 9 mL, as shown in Table 1 (group 2). Fig. 4 shows the TEM images of the TiO$_2$ samples. When the OA was not used, the as-prepared anatase TiO$_2$ nanocrystals are in the shape of octahedral bipyramids (Fig. 4(A)), with less {001} surface being exposed. As the OA amount was increased to 3 mL, the shape of anatase TiO$_2$ nanocrystals transfers to truncated octahedral bipyramids (Fig. 4(B)). One nanocrystal was shown in Fig. 4(C), and the angle labelled is 68.3$^\circ$, which indicates a good anatase crystalline phase. The magnification of Fig. 4(C) is shown in Fig. 4(D), three sets of crystalline facets of anatase were labelled, which are corresponding to (-101), (002), and (101) crystalline lattices of anatase according to XRD analysis. We roughly estimate the percentage of exposed {001} facets of the TiO$_2$ nanocrystal in Fig. 3(C), which is ca. 8%. As the OA amount was increased to 6 mL, most of the TiO$_2$ nanocrystals are nanosheets (Fig. 4(E)), although it also contains some truncated octahedral bipyramids. When the OA amount was increased 9 mL, it can be seen from Fig. 4(F) that all of TiO$_2$ nanocrystals are in the shape of nano-sheets. The above results gave us a clear conclusion that OA plays an important role in the formation of the exposed {101} facets under the condition of hydrothermal reactions.

Similarly, in order to confirm the function of the OA for preparing the shape-controllable anatase TiO$_2$ nanocrystals, the OA was kept unchanged at 7 mL, with the OM amount being changed from 0 mL to 9 mL, as shown in Table 1 (group 3). Fig. 5 shows the TEM images of these TiO$_2$ samples. Differently, it can be seen that all of the anatase TiO$_2$ nanocrystals are in shape of nano-sheets, almost independent on the OM amount. Therefore, it seems that the OA should have a stronger effect in controlling TiO$_2$ nanocrystal growth, as compared to the OA, because the use of 9 mL of OM cannot induce the obvious change of TiO$_2$ nanocrystal shape, which is still in the form of nano-sheets.
Fig. 5 TEM images of TiO$_2$ nanocrystals according to groupF3. (A) oleic acid 0 mL, oleylamine 7 mL; (B) oleic acid 3 mL, oleylamine 7 mL; (C) oleic acid 6 mL, oleylamine 7 mL; (D) oleic acid 9 mL, oleylamine 7 mL;

Fig. 6 TG-DTA results of the TiO$_2$ sample prepared with using 5 mL OA and 10 mL OM. The TiO$_2$ sample (Fig. 2 (B)) was firstly dried at 30 °C, and then was balled as TiO$_2$ powder for TG-DTA analysis, as shown in Fig. 6. The first ~ 1.5 % weight-loss happening at 69.1 °C corresponds to an endothermic process, which is from the evaporation of the organic toluene. The second ~ 16.18 % weight-loss happening at 340.9 °C is an exothermic process, which is corresponding to the decomposition and oxidation of the OA and the OM adsorbed on TiO$_2$ surface. The exothermic peak at ~ 652.5 °C on the DTA curve is due to the anatase-to-rutile transition as there is no weight-loss at this temperature. In summary, the TG-DTA analysis showed that the TiO$_2$ sample contains ~16.2 % organic species. The FT-IR spectra of the TiO$_2$ samples prepared with and without using the OA and the OM are shown Fig. 7. If the OM and the OA were used during the hydrothermal treatment, four additional strong adsorption peaks at 1462, 1426, 2852, and 2922 cm$^{-1}$ appear at the spectrum (red line). The FT-IR absorption peak at 1462 cm$^{-1}$ is corresponding to the bending vibration of –CH bond, and the peak at 1526 cm$^{-1}$ is due to the vibration of N-H bond, which indicate the existence of the OM molecule on the TiO$_2$ nanocrystal surface. In addition, the peaks at 2852 and 1922 cm$^{-1}$ are from the stretching vibration of –CH$_3$, CH$_2$, or CH groups, also indicating the presence of OA on the TiO$_2$ surface. In order to remove these surface-capped organics, the TiO$_2$ sample (Fig. 2 (B)) was annealed at 450 °C for an hour, and the TEM image of the annealed TiO$_2$ sample was shown in Fig. 8. Although the annealing process can remove the adsorbed organics, it can be seen that the shape of truncated octahedrons were destroyed.

![Fig. 7 FT-IR spectra of the TiO$_2$ samples prepared with using and without using OA and OM in the hydrothermal reactions.](image)

The TiO$_2$ sample (Fig. 2 (B)) was firstly dried at 30 °C, and then was balled as TiO$_2$ powder for TG-DTA analysis, as shown in Fig. 6. The first ~ 1.5 % weight-loss happening at 69.1 °C corresponds to an endothermic process, which is from the evaporation of the organic toluene. The second ~ 16.18 % weight-loss happening at 340.9 °C is an exothermic process, which is corresponding to the decomposition and oxidation of the OA and the OM adsorbed on TiO$_2$ surface. The exothermic peak at ~ 652.5 °C on the DTA curve is due to the anatase-to-rutile transition as there is no weight-loss at this temperature. In summary, the TG-DTA analysis showed that the TiO$_2$ sample contains ~16.2 % organic species. The FT-IR spectra of the TiO$_2$ samples prepared with and without using the OA and the OM are shown Fig. 7. If the OM and the OA were used during the hydrothermal treatment, four additional strong adsorption peaks at 1462, 1426, 2852, and 2922 cm$^{-1}$ appear at the spectrum (red line). The FT-IR absorption peak at 1462 cm$^{-1}$ is corresponding to the bending vibration of –CH bond, and the peak at 1526 cm$^{-1}$ is due to the vibration of N-H bond, which indicate the existence of the OM molecule on the TiO$_2$ nanocrystal surface. In addition, the peaks at 2852 and 1922 cm$^{-1}$ are from the stretching vibration of –CH$_3$, CH$_2$, or CH groups, also indicating the presence of OA on the TiO$_2$ surface. In order to remove these surface-capped organics, the TiO$_2$ sample (Fig. 2 (B)) was annealed at 450 °C for an hour, and the TEM image of the annealed TiO$_2$ sample was shown in Fig. 8. Although the annealing process can remove the adsorbed organics, it can be seen that the shape of truncated octahedrons were destroyed.

![Fig. 8 TEM images of the annealed TiO$_2$ sample.](image)

The theory of Wulff construction tells us that the shapes of anatase TiO$_2$ nanocrystals are mainly controlled by the growth speed along [001] and [101] directions. Due to the high surface energy of {001} surface (0.9 J m$^{-2}$), anatase TiO$_2$ nanocrystals generally prefer to grow along the [001] direction, which leads to the disappearing of {001} surfaces. As indicated by our results and other study, the OA molecule should preferably adsorb on {001} surfaces, which prevents the TiO$_2$ nanocrystal growth along [001] directions, resulting in the formation of octahedral bipyramids. If the OM was also used during the hydrothermal reactions, our above observations indicate that the OM molecule can be preferably and strongly adsorbed on {101} surface, which limits the anatase TiO$_2$ nanocrystals growth along [101] direction. In this case, the anatase TiO$_2$ nanocrystals will grow along both [001] and [101] directions, which finally leads to the formation of the truncated octahedral bipyramids and the nano-sheets, as shown in Fig. 2. By altering the ratio between the OA amount and the OM amount, the {001}/{101} ratio of anatase TiO$_2$ nanocrystals can be altered.
Furthermore, our results show that the OA seems to be more highly-functional to control the anatase TiO\(_2\) nanocrystal shape as compared to the OM.

The other titanium precursors, such as tetrabutyl titanate and titanium isopropoxide, will suffer from the fast hydrolysis during the hydrothermal reaction in the present of much water if no acid is used. The hydrolysed product locates at the bottom of the autoclave, which prevents the good contact among titanium, OA, and OM. This disadvantage limits the accurate controlling of the anatase TiO\(_2\) nanocrystal shape. As we have discussed above, the no-aqueous methods were generally used to prepare these TiO\(_2\) samples. For example, Wu et al. used OA and titanium isopropoxide as capping surfactants and titanium precursor to prepare TiO\(_2\) nanosheet and TiO\(_2\) nanocrystals with highly-exposed \{001\} and \{001\} facets through the no-aqueous solvothermal method, with tiny water being used as the oxygen source;\(^{34}\) Dinh et al. used tetrabutyl titanate as titanium source to prepare TiO\(_2\) nanocrystals with various shapes through no-aqueous solvothermal method, with the OA and the OM being also used as the capping surfactants.\(^{38}\) As only low amount of water is allowed during the non-aqueous solvothermal reaction, the controllable growth of anatase TiO\(_2\) nanocrystals can be realized. However, it is difficult to achieve the large-quality production of anatase TiO\(_2\) nanocrystals due to the presence of tiny water. Compared with tetrabutyl titanate and titanium isopropoxide, titanium peroxide sol is much stable, which can be kept for several months without obvious change. Under the heating, titanium peroxide sol slowly decomposes and transfers to titanium oxide clusters, which can be uniformly crystallized during hydrothermal treatment at the natural condition without using the inhibitor to suppress reaction speed. The slow reaction speed allows the anchoring of OA and OM molecule on the TiO\(_2\) cluster surface, which finally controls the shapes of anatase TiO\(_2\) nanocrystals. As much water exists during the hydrothermal reaction, so the reaction speed should be faster than that of the no-aqueous solvothermal method and the high production yield can also be realized. From this viewpoint, the facile hydrothermal method without using the highly-toxic HF to control the anatase TiO\(_2\) nanocrystal shapes is feasible if the titanium peroxide sol is used as the titanium precursor. The formation mechanism of anatase TiO\(_2\) nanocrystals is shown in Fig. 9.

The application of such TiO\(_2\) nano-crystals in photocatalysis was evaluated. Three anatase TiO\(_2\) nanocrystal samples with different exposed \{001\}/\{101\} ratios were choosen to study the photocatalytic activity, with commercial P25 being used as the reference. Considering that the CV photo degradation is a complicated process in which the adsorption on a TiO\(_2\) surface is the first step, the adsorption experiment was carried out to compare the adsorption ability of different samples. Fig. 10 (A) shows the change of CV concentration after different periods of dark adsorption. The adsorption of CV on TiO\(_2\) surface almost reaches the equilibrium after ~2 h. P25 TiO\(_2\) has the lowest adsorption capacity, while the our samples show obvious adsorptions. The adsorption abilities decrease as the \{001\}/\{101\} ratio increases. It was considered that the capped surfactants on the anatase TiO\(_2\) nanocrystals should play an important role for CV adsorption.

Fig. 10 (B) shows the dependences of C/C\(_0\) of CV solutions on the time of UV light irradiation. All of the samples present photocatalytic activity. It was observed that the sample with the highest \{001\}/\{101\} ratio has the lowest photocatalytic activity, i.e., the photocatalytic activity decreases as the \{001\}/\{101\} ratio increases. This result is different from other researches, which reported that highly-exposed \{001\} facets is favourable for photocatalysis. In the present research, the OA adsorbing on \{001\} surface of anatase TiO\(_2\) nanocrystals may change the surface energy and structures, which limits the positive function of \{001\} surfaces. Combined the result of Fig. 10 (A), it was

![Fig. 8 TEM image of the annealed TiO\(_2\) sample prepared by the hydrothermal treatment with using 5 mL of OA and 10 mL of OM](image)

**Fig. 8** TEM image of the annealed TiO\(_2\) sample prepared by the hydrothermal treatment with using 5 mL of OA and 10 mL of OM

![Fig. 9 Diagram of anatase TiO\(_2\) growth along [001] and [101] direction.](image)

**Fig. 9** Diagram of anatase TiO\(_2\) growth along [001] and [101] direction.
also considered that the adsorption of TiO$_2$ nanocrystals for CV may also have an effect on the photocatalytic activity, as high adsorption ability can capture more CV molecule on TiO$_2$ surface. Fig. 10 (B) also shows that the photocatalytic activity of our sample can be comparable to commercial P25 TiO$_2$.

Fig. 10 (A) CV dye adsorption for TiO$_2$ sample A (OA: 2 mL, OM : 12 mL), B ( OA: 5 mL, OM : 10 mL), C (OA: 8.5 mL, OM: 8.5 mL), and the commercial P25; (B) their photocatalytic performance in degradation of CV in comparison with the commercial P25

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**Notes and references**