

# Synthesis of truncated anatase bipyramids with exposure of {111} facets

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**Abstract:** Polyhedrons of truncated anatase bipyramids with exposure of {111} facets were hydrothermally synthesized from hydrolysis of  $\text{TiF}_4$  in the presence of  $\text{NH}_4\text{F}$ ,  $\text{HCl}$ , and tri-block copolymer P123 using citric acid monohydrate as a stabilizer. The phase, crystal structure, morphology, chemical composition and property of the anatase polyhedrons were characterized by various techniques of X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), selected area electron diffraction (SEAD), energy-dispersive X-ray spectrometry (EDX) and UV radiations, and their high performances in photo-degradation of methylene blue (MB) under alkaline conditions were specifically recognized.

**Key words:** anatase polyhedrons; oriented growth; hydrothermal synthesis; photocatalyst

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## 暴露{111}面的截顶点四棱双锥锐钛矿多面体的制备

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**摘要:**以四氟化钛为前驱物、P123为表面活性剂、柠檬酸为稳定剂、盐酸为酸性调节剂、氟化铵为添加剂,利用水热方法首次制备出暴露{111}面的截顶点四棱双锥锐钛矿多面体。通过XRD, SEM, TEM, HRTEM, SEAD和EDX对所制备的多面体的组成、结构和形貌进行了分析和表征。结果显示:柠檬酸和氟化铵的使用,有利于锐钛矿多面体的取向生长和{111}晶面的保留。同时研究发现,所制备的多面体在碱性和紫外光照条件下对亚甲基蓝(MB)具有很好的催化活性和降解效果,显示出潜在的应用价值。

**关键词:**二氧化钛多面体;取向生长;水热合成;光催化剂

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## 0 Introduction

Anatase has been proved to be a more active crystal phase of titania than rutile in most photo-oxidative applications<sup>[1]</sup>. The photoreactivity order of the recognizable facets of anatase is  $\{010\} > \{101\} > \{001\}$ , as introduced in the literature<sup>[2-3]</sup>. So, the phase control of titania with specific crystal facet(s) is a key factor in addressing the photocatalytic property generally. As a result, both the structure and facet of titania influence the catalytic properties and practical performances<sup>[4]</sup>.

Up to now, varied shapes of  $\text{TiO}_2$  have been well controlled via different strategies, which are available for the investigation of photo-oxidative properties<sup>[5]</sup>. In general, additives are often employed for the control of targeting materials. For example, HF was investigated to induce the growth of anatase polyhedral crystals with selective facets<sup>[6-8]</sup>, and citric acid, as an acidity regulator and stabilizer, was explored to reveal the impacts on the growth behavior of anatase  $\text{TiO}_2$  nanoparticles<sup>[9-10]</sup>.

In the current work, we reported an alternative hydrothermal process to synthesize anatase  $\text{TiO}_2$ , which was hydrolyzed from  $\text{TiF}_4$  in the presence of  $\text{NH}_4\text{F}$ , HCl (adjusting pH to 2.5), and tri-block copolymer P123 using citric acid monohydrate ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ) as a stabilizer, and the shape was well controlled in truncated anatase bipyramids with exposure of  $\{111\}$  facets. To our knowledge, the truncated anatase bipyramids with exposure of  $\{111\}$  facets have not been well explored so far. Meanwhile, the photocatalytic activities of the as-prepared samples were investigated, and it was found that the polyhedrons calcined at  $600^\circ\text{C}$  exhibited a relatively high photoreactivity in the degradation of methylene blue (MB) under alkaline conditions.

## 1 Experimental

In a typical synthesis, 500 ~ 1 000 mg of triblock copolymer P123 (Aldrich) was dissolved

in 15.0 mL of ultrapure water in a 50 mL Teflon-lined autoclave under continuous stirring. A few minutes later, 79 mg of  $\text{TiF}_4$  (Alfa Aesar) was added into 8 mL of ultrapure water, followed by 81 mg of  $\text{NH}_4\text{F}$  and then 2.0 mL of hydrochloric acid (0.1 mol/L) with stirring to form a transparent solution, which was added into the autoclave with stirring. After that, 399 mg of citric acid monohydrate ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ) in 7.0 mL ultrapure water was further added into the above mixture with thorough stirring. Then, the autoclave was heated at  $180^\circ\text{C}$  for 10 h. When the autoclave was cooled down to room temperature naturally, the samples were centrifuged at 9 000 rpm for 3 min and washed with water and ethanol for several times.

## 2 Results and discussion

X-ray diffraction (XRD, on a Philips X' Pert Pro Super diffractometer) pattern of the sample prepared at  $180^\circ\text{C}$  for 10 h was depicted in Fig. 1 (a), and all diffraction peaks were well indexed to anatase phase, as shown in standard JCPDS card (No. 21-1272, with space group:  $\text{I}4_1/\text{amd}[141]$ ). The relative intensity of (004) diffraction peak over (101) facet of the sample prepared under hydrothermal conditions was 32.29%, which was somewhat higher than that of the standard card (30%), showing an anisotropic growth of the sample. To increase the purity and improve the

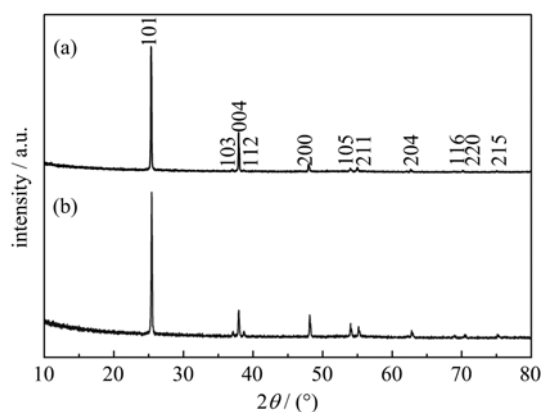
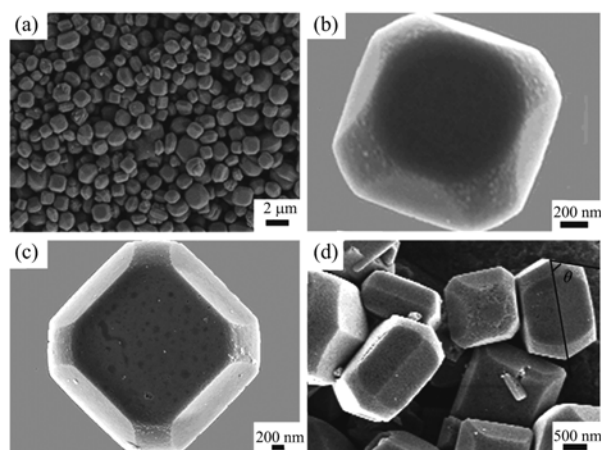


Fig. 1 The typical X-ray diffraction (XRD) patterns for the sample hydrothermally prepared at  $180^\circ\text{C}$  for 10 h (a) and the calcined one at  $600^\circ\text{C}$  for 90 min (b)

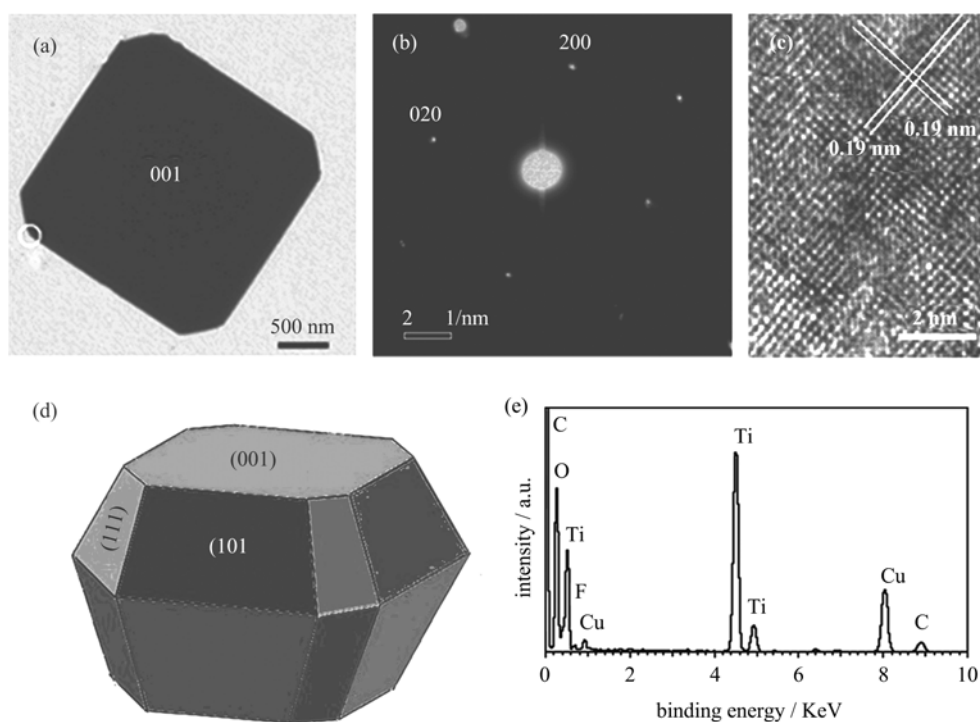
catalytic property of the sample, it was calcined at 600 °C for 90 min by removing the absorbed species, especially  $F^-$  ions<sup>[6]</sup>, from the surfaces of the crystals. Interestingly, the sample remained anatase phase after such calcinations (Fig. 1(b)).

The morphology of the samples was investigated by SEM, on a JEOL JSM-6700F. Fig. 2 (a) illustrated that the hydrothermally prepared sample was composed of dispersed polyhedrons, and the polyhedral shape looked as top-truncated bipyramids with side facets cut-off (Fig. 2(b)), which could be determined as  $\{111\}$  planes. The size was about 2  $\mu\text{m}$  in diameter, and the shape of the calcined polyhedrons did not change after calcinations except for the sharpening of edges (as seen in Fig. 2 (c), (d)). The interfacial angle between two black lines ( $\theta$  in Fig. 2(d)) was about  $(68.3 \pm 0.3)^\circ$  on average, which was close to the angle of  $\{001\}$  and  $\{101\}$  crystal planes of anatase. This result was



**Fig. 2 SEM images for the polyhedrons: hydrothermally prepared in large areas (a) and a typical individual crystal of the polyhedrons (b) and the corresponding calcined polyhedron(s) with shape edges (c), (d)**

consistent with the previous report<sup>[11]</sup>, and it also implied that the calcinations did not alternate the structure and the shape of the polyhedrons but cleaned up the fluorinated surfaces. The TEM (on a JEOL-2010) image (Fig. 3(a)) showed a typical



(a) TEM image of the polyhedron with exposed  $\{111\}$  facets, viewed along  $[001]$  direction. (b) Electron diffraction (ED) pattern of the circled area in (a), and (c) the corresponding HRTEM image, projected from  $[001]$  zone axis. (d) Schematic diagram for a single crystalline polyhedron. (e) EDX spectrum of a polyhedron without calcinations

**Fig. 3 Structure characterization of a typical individual anatase polyhedron**

polyhedron, projected along the  $[001]$  direction (Fig. 3(b)), and the corresponding HRTEM (on a JEOL-2010) image (Fig. 3(c)) showed that the lattice spacings of (200) and (020) crystal facets were both 0.19 nm with an interfacial angle of  $90^\circ$ , which confirmed the above investigation. To vividly illustrate the structure of the anatase polyhedrons, a schematic diagram was depicted in Fig. 3(d). The average percentage of  $\{001\}$ ,  $\{101\}$  and  $\{111\}$  facets of the current polyhedrons was estimated at 32%, 47% and 21%, respectively, according to the polyhedral crystal shown in Fig. 2(c) and Fig. 3(d). The chemical composition of the polyhedrons was revealed, and the fluoride ions on the facets were removed completely after calcinations even though there was about 2% F element detected by EDX spectrum on the surfaces of the crystals before calcinations (Fig. 3(e)).

As it is known,  $F^-$  ions could induce the growth of anatase crystals with shape of truncated bipyramids<sup>[6]</sup>, which were isolated by the facets of  $\{001\}$  and  $\{101\}$  while there were not any  $\{111\}$  planes observed in the truncated bipyramids with only addition of  $F^-$  ions. In the current work, the use of citric acid could mostly stabilize the  $\{111\}$  facets due to its spatial structure and coordination effect, which has been observed in other oxide systems<sup>[12-15]</sup>. Meanwhile, the use of P123 would promote the growth of polyhedrons with uniform size kinetically, and such phenomena have been observed in different cases<sup>[14-18]</sup>. As a result, the truncated bipyramids were formed with exposure of  $\{101\}$ ,  $\{111\}$ , and  $\{001\}$  crystal facets, and they looked as if their side faces of  $\{111\}$  were cut off from the ones in Ref. [6], as seen in Fig. 3(d).

In addition, the photodegradation performance of MB over the calcined anatase polyhedrons was investigated in the work with light sources from high-pressure mercury lamp (HPML, 250 W). The degradation of the dye mixture was monitored with an UV-3600 spectrometer (Shimadzu, Japan) using a quartz cell of 10 mm layer thickness and 1 nm resolution, and blank trials were also

performed at the same time for easy comparison. In Fig. 4, it was found that the present polyhedrons showed higher photoreactivity than that of the self-degradation of MB under UV radiation generally. With the addition of NaOH in solution (pH 11~12), the degradation of MB was promoted accordingly since that oxygen free radicals and  $\cdot OH$  radicals could be easily produced under alkaline conditions<sup>[19-20]</sup>.

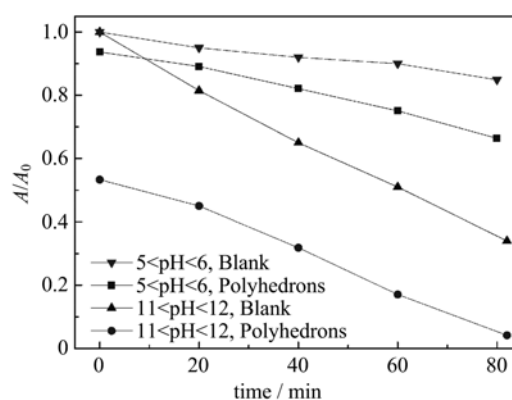


Fig. 4 The photo-degradation rate of MB over the calcined anatase polyhedrons compared with the self-degradation rate of MB under the same UV radiations

### 3 Conclusion

In conclusion, the polyhedrons of truncated anatase bipyramids isolated by  $\{001\}$ ,  $\{101\}$  and  $\{111\}$  facets were hydrothermally synthesized from hydrolysis of  $TiF_4$  mainly with the use of citric acid monohydrate as a stabilizer. The shape, structure, possible growth mechanism and property of the anatase polyhedrons were explored, and it was found that the calcined polyhedrons possessed relative high performances in photodegradation of MB under alkaline conditions.

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