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To cite this article: Z D Dai *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **479** 012120

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Controlled synthesis of TiO₂ nanosheets with exposed {001} facets for enhanced photocatalytic activity

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Abstract. Tailor-made TiO₂ nanocrystals with well-defined exposed facets have attracted increasing research interest recently. The exposed facets greatly determine the reactive activity of TiO₂ nanocrystals and dominate their application potential. Size-controllable TiO₂ nanosheets with highly reactive {001} facets were synthesized by a conventional hydrothermal synthesis process. The particle sizes ranged from 25 nm to several micrometres and a tuneable percentage of {001} surface area ranged from 50 % to 90 % according to the particle size. The photocatalytic activity of TiO₂ nanosheets smaller than 100 nm was much higher and very stable, comparing to the commercial TiO₂ photocatalysts.

1. Introduction

Nanostructured TiO₂ with a high percentage of reactive {001} facets has currently attracted significant interest among materials researchers [1-6]. The {001} facet of anatase TiO₂ is more reactive than the {101} facet [7, 8], which promises a wide range of applications from high-performance photocatalysts, Li-ion battery cells [9-14]. Towards to these multidisciplinary applications, it is requested to improve the performance of nanostructured TiO₂. It is reported that the {001} surface of anatase TiO₂ is the oxidation site, whereas the {101} surface is the reduction site [15, 16]. The shape-tailored TiO₂ has strict boundary for {001} and {101} surfaces, which is greatly helpful for promotion of the space-induced electron-hole separation [17, 18]. Therefore, the shape control of TiO₂ is an effective approach to improve photocatalytic activity. On the other hand, it is well known that the photocatalytic activity of TiO₂ also depends on particle size [19]. Small size offers a large surface area for light absorption and numerous photocatalytic reaction active sites, so that small nanosheets exhibit high photocatalytic activity, mostly by influencing charge-carrier dynamics, adsorption rate, and the adsorbed amount of reaction species. Therefore, controlling both the size and morphology of nanostructured TiO₂ is necessary to effectively improve the photocatalytic activity and comprehensively evaluate the performance.

Recently we synthesized the size-controllable TiO₂ nanosheets with highly exposed {001} facets by a conventional hydrothermal synthesis process. The particle size of produced TiO₂ nanosheets ranged from 25 nm to submicrometers [20]. In order to avoid the high safety risk of hydrofluoric acid that generally used as fluorine-containing tailoring materials to protect the {001} surfaces during the crystal growth [1], we selected a minimally toxic reagent, ammonium hexafluorotitanate, as an F⁻ ion source to synthesize TiO₂ nanosheets by the hydrothermal method. We used another reagent,



titanium(IV) butoxide, as a Ti source to adjust the F/Ti molar ratio. By carefully adjusting the F/Ti molar ratio, we succeeded in controlling the particle size and tuning the percentage of {001} surface area of TiO₂ nanosheets. In this paper, we focus on the size and morphology control of anatase TiO₂ nanosheets synthesized by the above approach. We report the size-controlled synthesis of anatase TiO₂ nanosheets with exposed {001} facets with particle sized ranging from 25 nm to several micrometers. We also report the morphology control of anatase TiO₂ nanosheets, including in regular nanosheets, mesoporous nanosheets, and highly-level mesoscopic microspheres assembled from regular sheets.

2. Experimental

2.1. Synthesis of TiO₂ nanosheets

Ammonium hexafluorotitanate (1 g; 99.99% purity) was dissolved into 5 ml of hydrochloric acid (5 M). Titanium(IV) butoxide (97% purity) was then added to the above solution under strong stirring in a controlled amount such that the total F/Ti molar ratio was 1.0, 1.2, 1.5, 1.8, or 2.0. White gels formed under continuous stirring. The gels were placed into a 50 ml Teflon tube for a 6-hour hydrothermal reaction at 180 °C. The products of the hydrothermal reaction were washed with ultrapure water (resistance = 18.2 MΩ) three times and by methanol once, all with subsequent centrifugal separation (10,000 G, 10 min). The samples were named NS-1, NS-2, NS-3, NS-4, NS-5, corresponding to the F/Ti molar ratio of 1.0, 1.2, 1.5, 1.8, and 2.0, respectively.

2.2. Photocatalytic activity characterisation

The obtained TiO₂ nanosheets were dried under air atmosphere at 80 °C. For evaluation of the photocatalytic activity of the TiO₂ nanosheets, 200 mg of TiO₂ was mixed and dispersed in 200 ml of a solution containing methylene blue (5 mg/l). The mixture solutions were irradiated by a low-pressure mercury arc lamp (210 W) for 5 hours, and the samples were collected every 30 min. The concentrations of methylene blue were determined by UV-Vis absorption measurements after two centrifugations for 30 min each. Control experiments that used two types of commercial TiO₂ nanoparticles, ST-01 (Ishihara Sangyo, Japan) and P25 (Degussa AG, German), which are both well-known high-performance photocatalysts, were also performed to evaluate the photocatalytic activity.

3. Results and discussion

Figure 1 shows typical transmission electron microscopy (TEM) images of the synthesized TiO₂ nanosheets. TiO₂ nanosheets have a square shape with an average size of 25 nm, which is the {001} surface of anatase TiO₂ (Figure 1a). A side view of the nanosheets shows clearly a rod shape which is composed of {001} and {101} surfaces. Figures 1b, 1c and 1d show that all TiO₂ nanosheets are square shape and have highly exposed {001} facets in various F/Ti molar ratio. The average size of is 30 nm for NS-2 (Figure 1b), 50 nm for NS-3 (Figure 1c) and 120 nm for NS-4 (Figure 1d), respectively. A larger F/Ti molar ratio results in larger particle size, suggests that concentration of Ti source determine the particle size [21]. In addition, the commercial TiO₂, P25 and ST01, were also shown in Figure 1e and 1f as control. P25 TiO₂ has an irregular shape and an average size of about 30 nm. ST01 has a much smaller size than other TiO₂ samples. The average size is about 5 nm, which resulting in a very high specific surface area.

We measured the specific surface area of TiO₂ nanosheets by a standard BET method. The data were summarized in Table 1. It was found that the specific surface area of nanosheets decreased gradually with the increasing size. We estimated carefully the percentage of {001} surface area to the total surface area in TiO₂ nanosheets. The ratio of the {001} facets to total surface area can be calculated from the degree of truncation, which have been suggested by Lu [1]. The percentage of nanosheets was also summarized in Table 1. The percentage increased gradually from 52% to 75% with the increasing size. Because {001} and {101} surfaces are contributed to the photocatalysis in function of oxidation and reduction site respectively [15, 16], an appropriate ratio of {001}/{101} is speculated to be of great benefit for high photocatalytic activity.

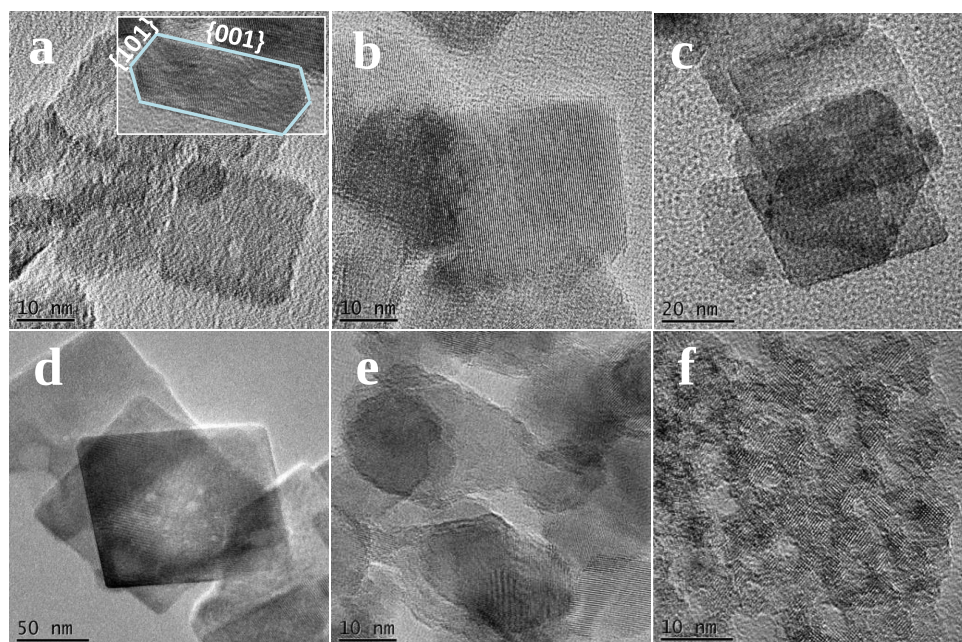


Figure 1. TEM images of (a) NS-1, (b) NS-2, (c) NS-3, (d) NS-4, (e) P25, and (f) ST01, respectively. Inset is a side view of NS-1 nanosheet.

Table 1. Specific surface area (SA) and {001} percentage of TiO₂ nanosheets.

TiO ₂	Size (nm)	SA (m ² /g)	Percentage (%)
NS-1	25	116.99	52
NS-2	30	85.28	55
NS-3	50	71.96	58
NS-4	120	40.70	64
NS-5	550	11.60	75

Figure 2a shows the X-ray diffraction (XRD) patterns of as-synthesised TiO₂ nanosheets. It is clear shown that all the as-synthesized TiO₂ nanosheets were anatase crystalline. The diffraction peaks have been indexed in Figure 2a. All diffraction peaks are in good agreement with the standard XRD profile (# JCPDS 84-1286). The crystallinity of TiO₂ nanosheets was improved with increased particle size from NS-1 to NS-5. 550 nm-sized TiO₂ nanosheets of NS-5 shows very sharp and strong diffraction peaks, which indicates the perfect crystallinity of such TiO₂ nanosheets. Raman spectroscopy of as-synthesised TiO₂ nanosheets is shown in Figure 2b. All the samples show clearly Raman vibration peaks at of 147, 394, 515, and 634 cm⁻¹, which have been assigned to E_g, B_{1g}, A_{1g}, and E_g, the four characteristic Raman vibration modes of anatase TiO₂ [22].

We evaluated the optical property of the as-prepared nanosheets by transmission spectra. From the Figure 2c, the transmittance of nanosheets increased with the change of wavelength. It was clearly observed that the transmittance shifted to low energy regions, which suggested that the band gap of nanosheets would reduce with the increasing size. The main absorption bands were located in UV region, indicating that the as-prepared TiO₂ nanosheets with exposed {001} facets have high photocatalytic activity under UV light irradiation.

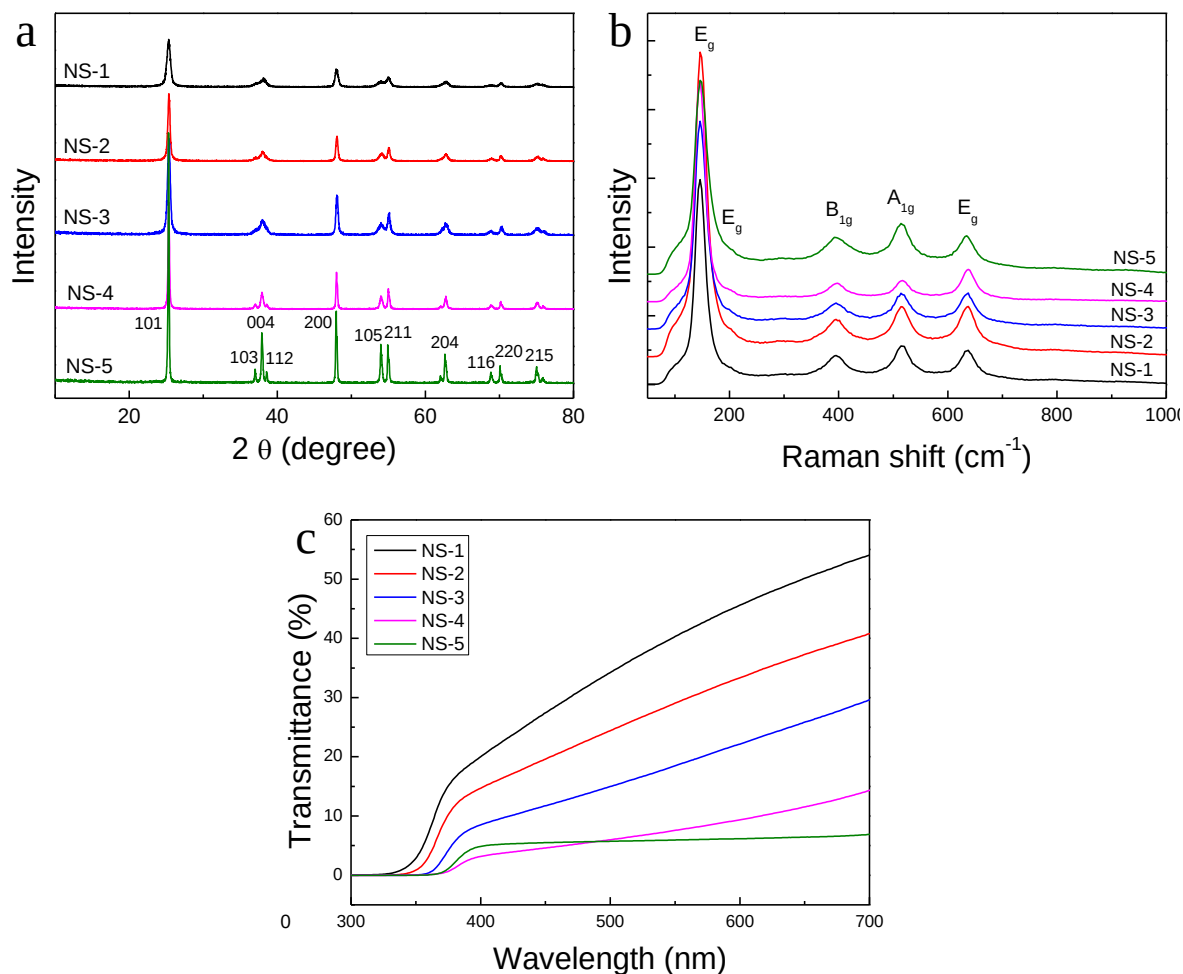


Figure 2. (a) XRD patterns and (b) Raman spectroscopy of {001} TiO_2 nanosheets.

The photocatalytic activity of size-controllable TiO_2 nanosheets with highly exposed {001} facets were evaluated in the degradation of dyes. Figure 3a shows the change in the concentration of methylene blue with ultraviolet irradiation time. In the absence of TiO_2 photocatalysts, methylene blue was degraded slowly by ultraviolet irradiation. After 5 hours irradiation, only approximately 20% of the methylene blue had decomposed. In the presence of TiO_2 photocatalysts, the degradation rates were greatly enhanced. The photocatalytic degradation of methylene blue was completed within 1.5 hours when using NS-1 nanosheets as a catalyst. The complete reaction time increased synchronously with TiO_2 nanosheet size. The smallest TiO_2 nanosheets (approximately 25 nm) had the highest photocatalytic activity, which indicates that particle size greatly affects photocatalytic activity. Most TiO_2 nanosheets were better than commercial photocatalysts in the photocatalytic degradation of methylene blue.

The pseudo-first-order rate constant k_{app} is a characteristic kinetic parameter for photocatalytic activity at very low dye concentration since the rate of the photocatalytic degradation of dyes by TiO_2 fits the Langmuir-Hinshelwood model [23]. Figure 3b shows $\ln(C_0/C)$ changed as a function of reaction time. The slope of the line, i.e., k_{app} , decreased with increasing TiO_2 nanosheet size. However, the k_{app} of nanosheets were almost higher than those of commercial TiO_2 ; only TiO_2 nanosheets with a size of ca. 550 nm showed slopes lower than those of P25 and ST01.

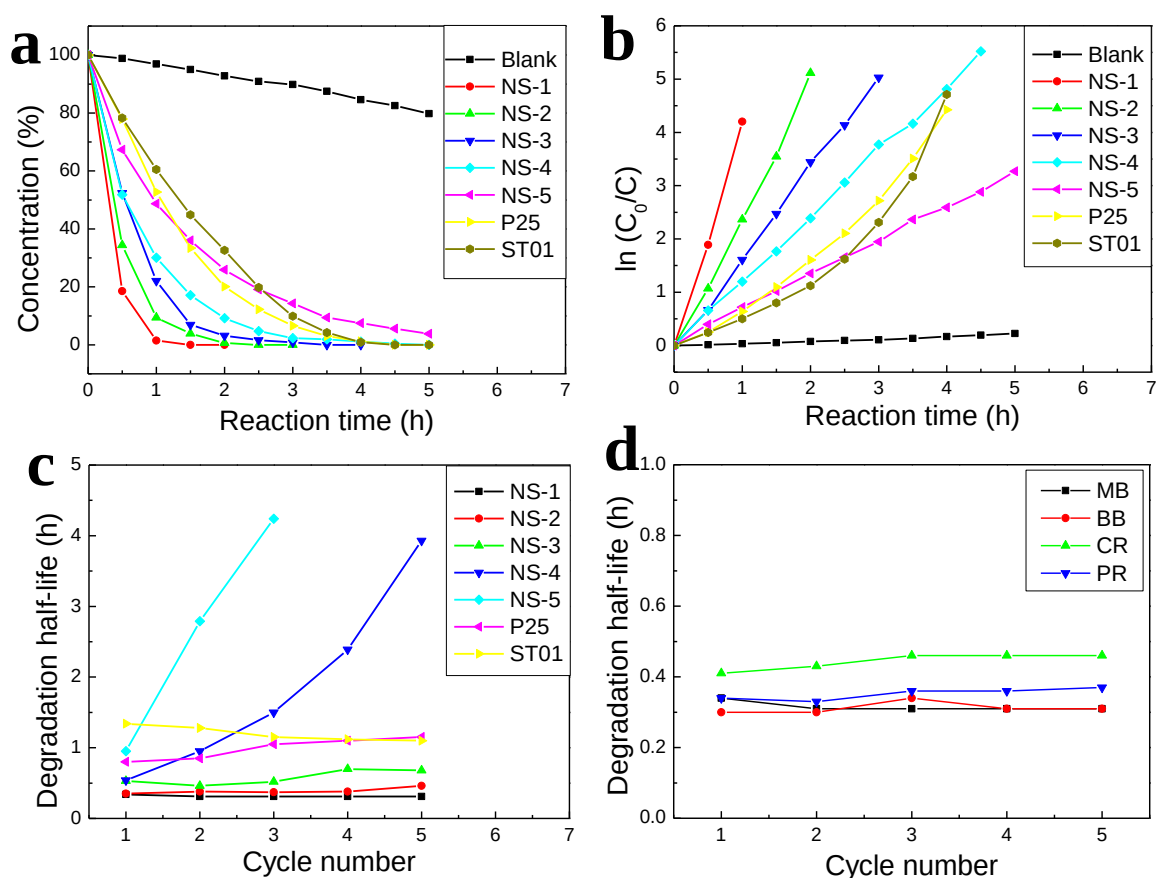


Figure 3. (a, b) Variation of concentration and $\ln(C_0/C)$ of methylene blue with reaction time. (c) Degradation half-life in five cycles with different TiO₂ variants in the photocatalytic degradation of methylene blue. (d) Degradation half-life of various dyes in five cycles with approximately NS-1 nanosheets.

We compared the specific surface area and k_{app} of the as-synthesised TiO₂ nanosheets and the commercial TiO₂. All data were summarised in Table 2. The k_{app} of TiO₂ nanosheets decreased with decreased specific surface area. TiO₂ nanosheets with size of smaller than 100 nm had higher k_{app} for the degradation of methylene blue than the commercial TiO₂ photocatalysts P25 and ST01. The smallest TiO₂ nanosheets (ca. 25 nm) had the highest real photocatalytic activity. TiO₂ nanosheets with a size of ca. 550 nm had the overall largest k_{app} per unit surface area. The normalised k_{app} per unit surface area of approximately 550 nm TiO₂ nanosheets was approximately 3 times higher than that of TiO₂ P25 and more than 13 times higher than that of TiO₂ ST01. The small TiO₂ nanosheets had high total photocatalytic activity when normalised by unit mass, whereas the large TiO₂ nanosheets had high photocatalytic activity when normalised by unit surface area.

Four types of organic dye were used to examine the photocatalytic activity of TiO₂ nanosheets: methylene blue (MB), bromothymol blue (BB), cresol red (CR), and phenol red (PR). Table 3 summarises the experimental k_{app} and normalised k_{app} per unit surface area of NS-1 nanosheets and ST01 TiO₂. The k_{app} of NS-1 nanosheets was superior to that of ST01 TiO₂ in the photocatalytic degradation of all selected dyes, regardless of whether it was normalised by unit mass or by unit surface area. The k_{app} of NS-1 nanosheets was 3.6, 2.2, 1.9, and 1.6 times higher than that of ST01 TiO₂ in the photocatalytic degradation of methylene blue, bromothymol blue, cresol red, and phenol red, respectively, and the normalised k_{app} per unit surface area for these four dyes was 8.8, 5.6, 4.7, and 4.0 times higher than that of ST01 TiO₂.

Table 2. SA, k_{app} , and k_{app}/SA of TiO₂ nanosheets and commercial TiO₂.

TiO ₂	SA (m ² /g)	k_{app} (h ⁻¹)	k_{app} / SA
NS-1	116.99	4.20	0.0359
NS-2	85.28	2.56	0.0300
NS-3	71.96	1.61	0.0224
NS-4	40.70	1.23	0.0302
NS-5	11.60	0.65	0.0560
P25	58.11	1.10	0.0189
ST01	289.72	1.18	0.0410

Table 3. SA, k_{app} , and k_{app}/SA of as-synthesised NS-1 and commercial ST01 in the degradation of MB, BB, CR, and PR.

TiO ₂	SA (m ² /g)	k_{app} (h ⁻¹)		k_{app} / SA	
NS-1	116.99	MB	4.20	MB	0.0359
		BB	3.72	BB	0.0318
		CR	2.64	CR	0.0226
		PR	3.19	PR	0.0273
		MB	1.18	MB	0.0041
ST01	289.72	BB	1.66	BB	0.0057
		CR	1.4	CR	0.0048
		PR	2.00	PR	0.0069

The stability of the photocatalytic activity was also examined. Figure 3c shows the degradation half-life of five cycles of TiO₂ nanosheets in the photocatalytic degradation of methylene blue. TiO₂ nanosheets with size of smaller than 100 nm (NS-1, NS-2, NS-3) showed high photocatalytic activity, which superior to that of commercial TiO₂ photocatalysts. However, when they were larger than 100 nm (NS-4 and NS-5), the TiO₂ nanosheets were poisoned very quickly, and the photocatalytic activity became worse than that of the two commercial products. In contrast to a previous report [24], the P25 and ST01 commercial TiO₂ variants were quite stable under our experimental conditions. The degradation half-life in five cycles of NS-1 nanosheets for a variety of dyes is shown in Figure 3d. The degradation half-life showed no obvious change in five cycles. Such TiO₂ nanosheets smaller than 100 nm are very stable and show high photocatalytic activity for a long time. The size effect also plays an important role in catalytic stability.

How about the photocatalytic activity of micrometre-sized TiO₂ single crystals with exposed {001} facets in comparison to that of submicrometre-size TiO₂ nanosheets? We synthesised micrometre-sized anatase TiO₂ single crystals with exposed {001} facets by a similar hydrothermal process. The only parameter changed was the addition of 50 ml of a hydrochloric acid solution that allowed slow nucleation of TiO₂ and resulted in synthesis of large single crystals (Figure 4a). By changing the temperature, the size of the TiO₂ single crystal can also be controlled from 1 μ m to 5 μ m (Figure 4b). The percentage of {001} surface area ranged from 80% to 90% according to the particle size. As shown in Figure 4c, such micrometre-sized TiO₂ single crystals had much lower real photocatalytic activity than ST01 TiO₂ in the photocatalytic degradation of methylene blue. When normalised by unit surface area, the photocatalytic activity of micrometre-sized TiO₂ single crystals was higher than that of ST01 (Figure 4d) but still lower than that of submicrometre-sized TiO₂ nanosheets.

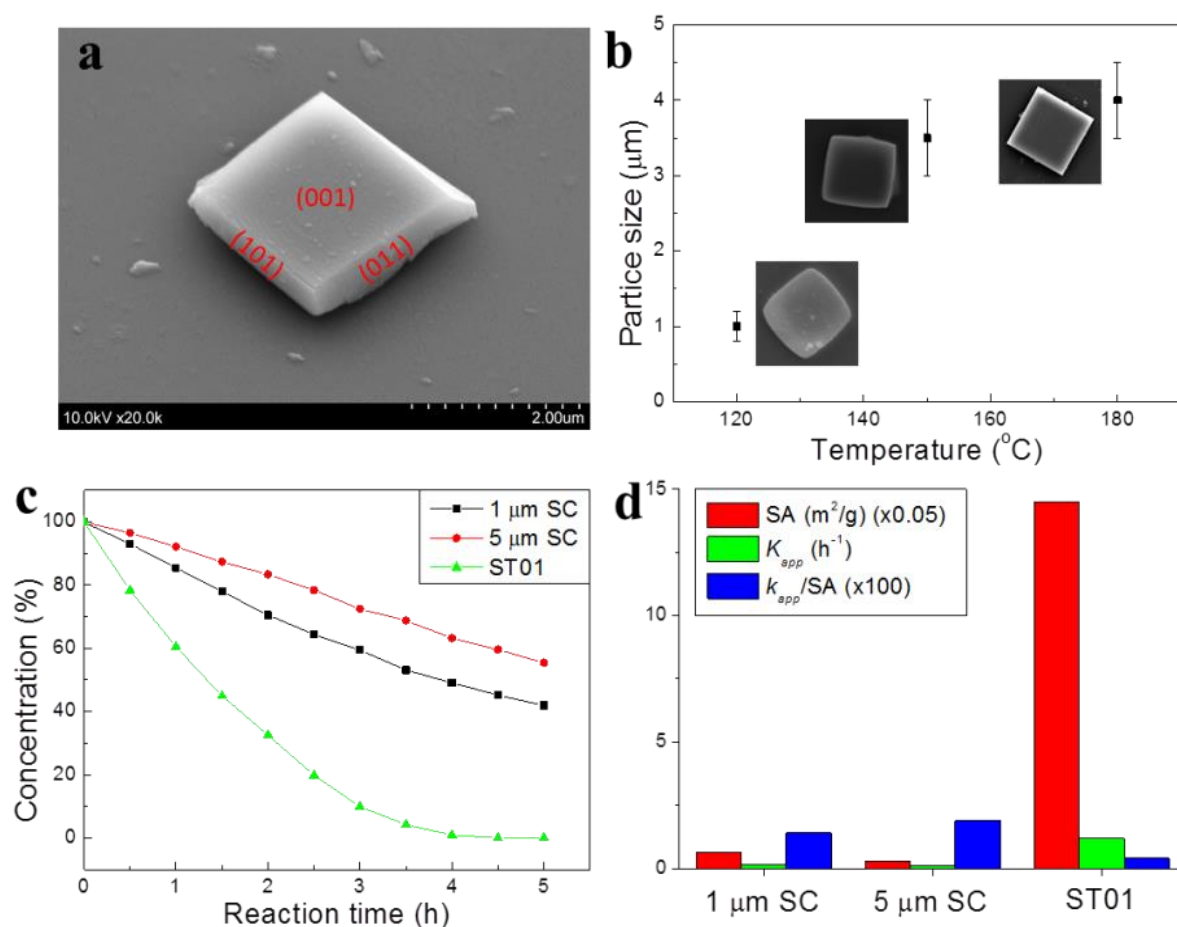


Figure 4. (a) SEM image of a micrometre-sized TiO₂ single crystal with a high percentage of exposed {001} facets from a 45° view. (b) Size distribution of micrometre-sized TiO₂ single crystals prepared at various hydrothermal temperatures. (c) Variation of concentration of methylene blue with reaction time when TiO₂ single crystals are used as photocatalysts. (d) Specific surface area and k_{app} of TiO₂ single crystals in the photocatalytic degradation of methylene blue.

4. Conclusions

We succeed in synthesis of size-controlled anatase TiO₂ nanosheets and single crystals with highly exposed {001} facets. The particle size of anatase TiO₂ sheets is controlled ranging from 25 nm to several micrometers by carefully adjusting the F/Ti molar ratio during the hydrothermal process. The percentage of {001} facets ranges from 52% to 90%, which we found it is according to the particle size of TiO₂ sheets. Anatase TiO₂ nanosheets smaller than 100 nm had higher photocatalytic activity when normalised by unit mass and were more highly stable, whereas large TiO₂ nanosheets had higher photocatalytic activity normalised by unit surface area. Our results provide clear evidence that the particle size of TiO₂ nanosheets plays an important role in photocatalytic activity. These size-controlled TiO₂ nanosheets show great potential for applications in photocatalysts, dye-sensitised solar cells, gas sensors, and biomedical applications.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21571028, No. 21601027), the Fundamental Research Funds for the Central Universities (No. DUT16TD19, No. DUT17LK33, No. DUT18LK28), and the Education Department of the Liaoning Province of China (LT2015007).

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