

Dimensionality-dependent photocatalytic activity of TiO₂-based nanostructures: nanosheets with a superior catalytic property

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Abstract TiO₂-based nanostructures usually possess excellent photochemical properties. However, the relationship between their dimensionality and photocatalytic activity was rarely investigated. In this study, a series of TiO₂-based nanostructures in various dimensionalities (such as nanosheets, nanotubes) were obtained by hydrothermal treatment of P25, and the process of structural evolution was also systematically investigated by TEM, BET, Raman, and XRD analysis. Much higher rate constant ($3.7 \times 10^{-2} \text{ min}^{-1}$) for the degradation of rhodamine B was found for nanosheets, comparing with those of three-dimensional P25 nanoparticles ($0.59 \times 10^{-2} \text{ min}^{-1}$) and one-dimensional nanotubes ($0.85 \times 10^{-2} \text{ min}^{-1}$). It is found that the hydrothermally prepared TiO₂-based nanosheets possess small thickness (ca. 5 nm) and plentiful surface hydroxyl groups, and the reason why TiO₂-based nanosheets possess superior photocatalytic activity is also discussed in detail from the microstructure and surface chemical states. In addition, TiO₂-based nanosheets exhibit good reusability in the cyclic experiments, implying a potential application for photocatalytic degradation of organic pollutants.

Introduction

TiO₂-based nanomaterials are widely used as photocatalysts because of their low-cost preparation, biologically inert, and excellent photochemical properties [1–3]. It is reported that the photocatalytic activity of photocatalyst is closely related to the morphology, which directly affects the specific surface area, crystal structure, and surface state such as surface hydroxyl density [4–8]. A lot of attempts have been made to the preparation of catalyst with excellent photocatalytic activity by morphological control [9, 10]. For example, through a hydrothermal treatment of crystal TiO₂ with concentrated NaOH solution, the produced nanostructures usually have higher specific surface area compared with the raw material [11, 12]. The higher specific surface area may provide more adsorption and reaction active sites for photocatalytic degradation. In recent years, TiO₂-based nanostructures obtained by this method have attracted increasing attentions.

Among such kind of materials, TiO₂-based nanotubes have been investigated considerably due to the high photochemical property and potential application in photocatalytic degradation of organic pollutants [13, 14]. The formation process of TiO₂-based nanotubes has also been studied and different viewpoints have been proposed [15–18]. Some researchers considered that TiO₂ nanoparticles in raw react with NaOH to form lamellar products first, and then the tubular structure is formed by rolling the exfoliated single nanosheets [19] or wrapping the multi-layer nanosheets [20]. Although other mechanisms such as oriented crystal growth model have also been proposed, nanosheets are still believed to be the essential for the formation of nanotubes. It is noteworthy that although the formation process was investigated considerably, the attention was mainly focused on the structures and

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properties of nanotubes and other similar preparations such as nanorods [21], nanobelts [22], etc. The structures and properties of the nanostructures obtained during the process (such as nanosheets formed in the initial stage), especially the relationship between the structural evolution and the photocatalytic activities of these nanostructures were rarely investigated, while the systematical investigation for these stages should be significant. It may be beneficial not only to further understand the evolution process, but also to explore the relationship between structure and property of the produced nanostructures.

In addition, two-dimensional (2D) photocatalysts usually exhibit excellent properties in photocatalytic degradation [23–26]. The researches for 2D TiO_2 mainly focus on TiO_2 nanosheets dominated by (001) facets according to our knowledge. While the preparation of this kind of TiO_2 nanosheets cannot be conducted without hydrofluoric acid, which is extremely corrosive and toxic and must be handled with extreme care [27]. Therefore, the preparation of TiO_2 -based nanosheets via an alkaline hydrothermal method is relatively safer and more convenient. As a 2D structure, TiO_2 -based nanosheets have larger ratio of width to height than nanoparticles. This will cause the decrease in the migration distance of photogenerated electron–hole pairs to the surface of catalyst, which may be beneficial to the increase of separation efficiency of electron–hole pairs [28, 29]. Furthermore, some properties of TiO_2 -based nanosheets may be similar to that of TiO_2 -based nanotubes due to their similar preparation conditions. Accordingly, TiO_2 -based nanosheets prepared by alkaline hydrothermal method may have potential application in photocatalytic degradation.

In this paper, various TiO_2 -based nanostructures (such as nanosheets and nanotubes) were prepared through an alkaline hydrothermal method. The dimensional evolution was systematically investigated by the changes of morphology, specific surface area, and the structure. The relationship between the structure and property of these nanostructures was evaluated by the degradation of rhodamine B (RhB). TiO_2 -based nanosheets were found to possess excellent photocatalytic activity. The factors influencing photocatalytic activity were also discussed in detail.

Experimental sections

Preparation

TiO_2 -based nanostructures were prepared via a hydrothermal method as follows: 0.8 g TiO_2 (Degussa P25) was dispersed in 50 mL of 10 M NaOH aqueous solution under intense stirring, and then the mixture was transferred into a

Teflon-lined autoclave (100 mL). After heating in an oven at 130 °C for 1–48 h, the autoclave was cooled down by tap water to room temperature, and the resultant white powder was washed with distilled water until a pH value near 8 was reached. Then, the white powder was treated with 60 mL of 0.1 M HCl solutions twice, 1 h for each time, to achieve a complete ion exchange. Finally, the powder was washed with distilled water for several times and then dried at 70 °C for 12 h.

Characterization

Transmission electron microscopy (TEM) was obtained by JEOL JEM-2010-HT instrument at the accelerating voltage of 200 kV. Raman scattering spectra were collected on a LabRAM HR-800 (HORIBA JY) instrument. The samples were illuminated by a 488-nm laser with power of 6 mW. The spectra were acquired with a 1200 groove mm^{-1} grating. The Brunauer–Emmett–Teller (BET) surface areas (S_{BET}) were determined by nitrogen adsorption isotherm measurements at 77 K on a JW–BK system. X-ray diffraction (XRD) patterns were collected on a Bruker D8-advance X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. Data were recorded with a step interval of 0.02° and a scan rate of 2° min^{-1} in the 2θ range from 5° to 70° . An atomic force microscopy (NanoNavi Station, Seiko Instruments) was used to examine the surface morphology of nanosheets. The measurement was carried out in a tapping model, with a driving frequency of 130 kHz at a scan speed of 0.4 Hz using a silicon cantilever with a normal spring constant of 16 N m^{-1} . Fourier-transform infrared (FT-IR) spectra were recorded on a Thermo Fisher Nicolet Is10 Fourier-transform infrared spectrometer. ^1H NMR experiments were performed on a Varian Infinity-Plus400 NMR spectrometer equipped with a double channel 2.5 mm probe at a spinning frequency of 20 kHz. The samples were pre-treated at 130 °C for 12 h to remove the physically adsorbed water molecules.

Evaluation of photocatalytic performances

Photocatalytic activities of the catalysts were evaluated by the degradation of RhB. A 160 W high-pressure mercury lamp was positioned inside a photoreactor and the distance between the mercury lamp and the RhB solution was 15 cm. In a typical reaction, 0.1 g catalyst was added to 100 mL of 20 mg L^{-1} RhB solution and stirred in the dark for 1 h to reach the adsorption equilibrium. Then, the high-pressure mercury lamp was turned on. At regular irradiation intervals of 10 min, 1.6 mL sample was withdrawn from the dispersion and centrifuged to separate the catalyst.

The concentration of the residual RhB solution was detected by UV–Vis spectrophotometer. In the cyclic experiments of the catalyst, 0.1 g catalyst and 100 mL of 4 mg L⁻¹ RhB solution were used. The dispersion was withdrawn at a regular irradiation time intervals of 10 min and 30 min for TiO₂-based nanosheets and P25, respectively. After each cyclic experiment, 4 mL of 100 mg L⁻¹ RhB solution was added into the reactor to maintain the preliminary concentration of RhB solution.

Results and discussion

Dimensional evolution of TiO₂-based nanostructures

As shown in Fig. 1, the morphologies of samples prepared with different hydrothermal durations are displayed by TEM images. For Degussa P25 (Fig. 1a), granular crystals with diameters of 20–40 nm are observed. The SAED pattern indicates the diffraction lines representative of the polycrystalline phases, namely, (101), (004), (200), (204), (215) diffractions of anatase-phase and (211), (112) diffractions of rutile phase. In Fig. 1b and c, the morphologies of the samples are still granular and no obvious change is observed. However, nanosheet-like products were found after 2 h of hydrothermal treatment (Fig. 1d), which means that the TiO₂ nanoparticles began to strip into nanosheets. In Fig. 1e, the sample prepared with 3 h of hydrothermal treatment mainly consists of nanosheets with the length greater than one hundred nanometers and the width several tens of nanometers. The increasing scale of nanosheets implies the growth of small nanosheets stripped off from the granular crystals, due to the oxolation of the OH species at the edge of raw nanosheets [30, 31]. In addition, some large nanosheets began to scroll, implying the trend of further transformation into nanotubes. In Fig. 1f, large amounts of nanotubes with diameters of ca. 8 nm and length of 50–200 nm are observed and the diffraction rings cannot be indexed to any known phase of TiO₂. When compared the SAED pattern of nanotubes with that of P25, the initial diffraction rings all disappeared and some new diffraction rings with less distinct were observed, indicating the change of crystal structure and a poor crystallinity.

Figure 2 shows the N₂ adsorption–desorption isotherms and the corresponding BET-specific surface areas of the products prepared with different hydrothermal reaction times. It is found that the specific surface area of the prepared nanostructure changes subtly in the initial 1 h of hydrothermal process, and then increases rapidly from 60 to 348 m² g⁻¹ with the reaction time increasing from 1 to 5 h. After being treated for over 5 h, the BET surface area increases slightly and saturates gradually. Combined with the TEM and BET results, we can explain the process as

follows. At the early stage (within 1 h), only a small part of the Ti–O bonds are broken, which cannot cause the split of TiO₂ nanoparticles. Therefore, their morphologies and surface areas have no obvious change. With the reaction time increased from 1 to 5 h, plenty of Ti–O bonds are broken and TiO₂ nanoparticles are stripped into smaller particles and sheet-like products. The thin lamellar fragments also link with each other to form larger planar nanosheets, which successively begin to scroll into nanotubes. Therefore, the BET surface area increases rapidly during 1–5 h. After 5 h of hydrothermal treatment, the stripping process is almost finished and more TiO₂-based nanosheets are converted into nanotubes. It is well known that a larger specific surface of photocatalyst can provide much more adsorption and photocatalytic reaction sites for photocatalytic degradation.

The structure evolution process of TiO₂-based products prepared at different hydrothermal treatment times was characterized by Raman scattering spectra as shown in Fig. 3. For P25, there are five typical contributions of anatase-phase at 147 (*E_g*), 199 (*E_g*), 400 (*B_{1g}*), 522 (*B_{1g}/A_{1g}*), and 643 cm⁻¹ (*E_g*), which is in good agreement with the published data [32]. The Raman scattering spectrum of the product with 1 h of hydrothermal treatment is very similar to that of P25, which means that the product is still crystalline TiO₂. With 2 h of hydrothermal treatment, a weak Raman band at 279 cm⁻¹ is observed for the product. It is related to the break of symmetry in the bent TiO₆ layers [33]. The intensive Raman bands at about 496 cm⁻¹ is observed in the Raman scattering spectrum of the product for 3 h reaction, which reveals the presence of the 2D lepidocrocite-type TiO₆ octahedral layers [34]. The new Raman band at about 706 cm⁻¹ is found in Raman scattering spectrum of the product for 5 h reaction, which can be attributed to the bending of the TiO₆ octahedral layers during the rolling process [35, 36]. The typical Raman bands of TiO₂ crystalline begin to disappear after 5 h reaction, and the Raman bands at about 279, 496 and 706 cm⁻¹ are gradually obvious. These are consistent to the results of TEM images and BET-specific surface area data.

Figure 4 shows the XRD patterns of TiO₂-based nanostructures. For the raw material P25, the diffraction peaks can be indexed to anatase-phase TiO₂ (JCPDS No. 89-4921) and rutile-phase TiO₂ (JCPDS NO. 89-0552). The XRD patterns of the products prepared with 1 and 2 h reaction are very similar to that of P25. But after hydrothermal treatment for 3 h, the intensity of the typical TiO₂ peaks decreases markedly (Fig. 4a). The facts indicate that the phase component of TiO₂-based nanostructure begin to change obviously. When the reaction time is extended beyond 5 h, all the original diffraction peaks of P25 TiO₂ almost disappear. It indicates that the raw TiO₂ has been

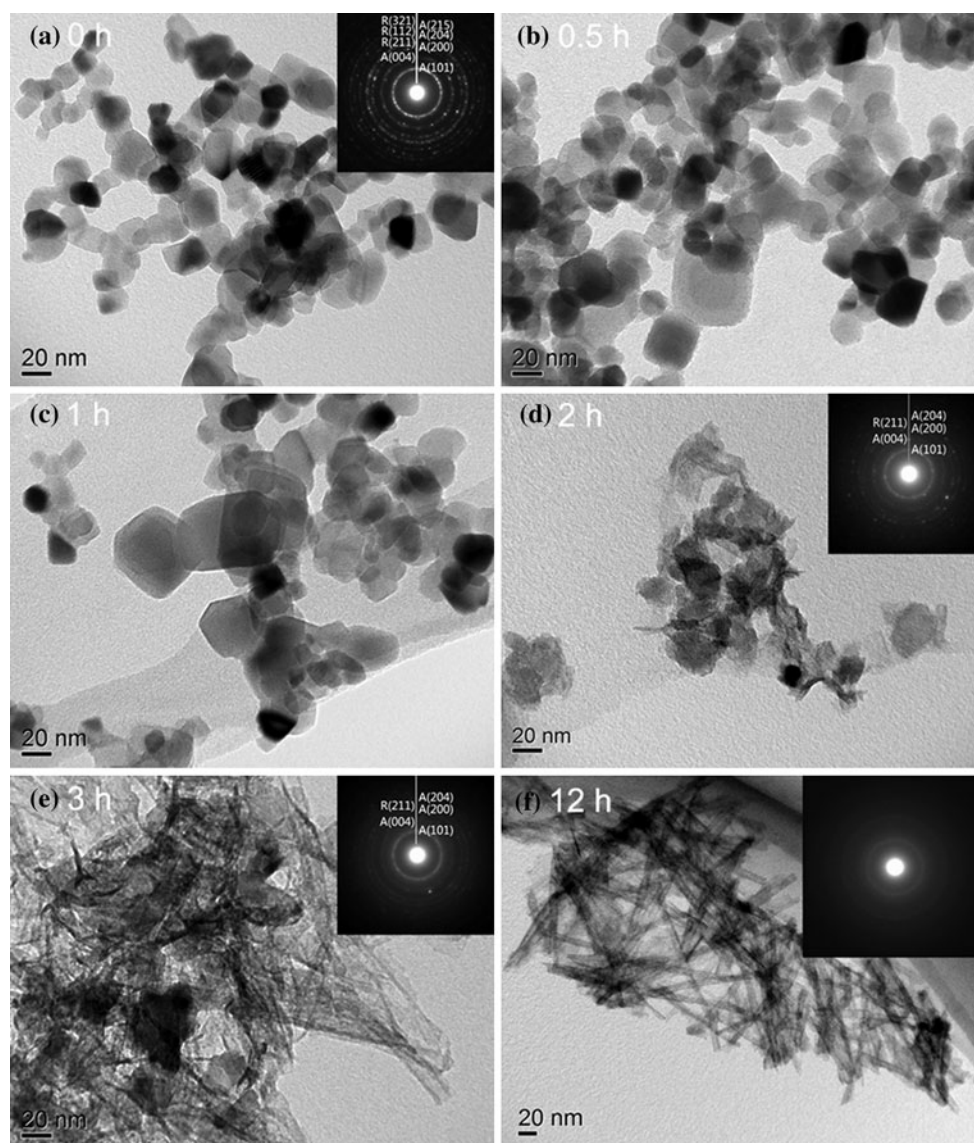


Fig. 1 TEM images and partial SAED patterns of the nanostructures prepared by hydrothermal treatment of P25 at 130 °C for **a** 0 h, **b** 0.5 h, **c** 1 h, **d** 2 h, **e** 3 h, and **f** 12 h

completely converted into a new crystal structure. As we reported before, the hydrothermal product may be ascribed to $\text{H}_2\text{Ti}_3\text{O}_7$ [37, 38]. The results confirm the structure transformation process observed in Raman scattering. Besides, the variation of crystal size calculated by the Scherer's equation is also estimated.

$$D = k\lambda / (\beta \cos\theta)$$

where D is the average crystal size, k is the Scherer coefficient (0.89), λ is the X-ray wavelength (0.15406 nm), β is the full width at half maximum (FWHM) in radians, and θ is the Bragg' angle [39, 40]. The crystal sizes of P25 and the products obtained with 1 and 2 h reaction are uniform with an average value of ca. 25 nm. While the crystal size of the sample prepared with 3 h of hydrothermal treatment

is distributed ranging from 7.4 to 86.3 nm, implying the exfoliation of nanoparticles and the growth of the exfoliated nanosheets. After hydrothermal treatment of 12 h, the crystal sizes of the products were decreased to ca. 8.9 nm.

Adsorption and photocatalytic performances of TiO_2 -based nanostructures

Since photocatalytic reaction process occurs on catalyst surface, the adsorption ability of photocatalyst may play an important role in the degradation of organic pollutants. The adsorption performances of the nanostructures were evaluated through the adsorption percentage value of RhB after adsorption equilibrium was achieved in the dark. As shown in Fig. 5, the adsorption percentage for nanostructures

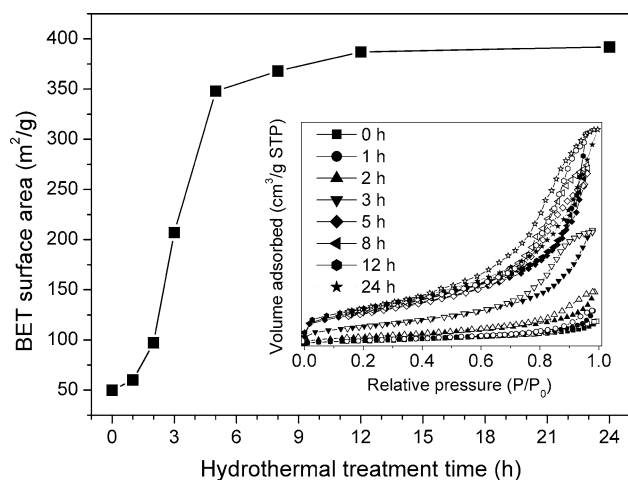


Fig. 2 BET-specific surface areas of the nanostructures prepared by hydrothermal treatments of P25 for different hydrothermal treatment times. Inset: the corresponding N_2 adsorption-desorption isotherms of the nanostructures

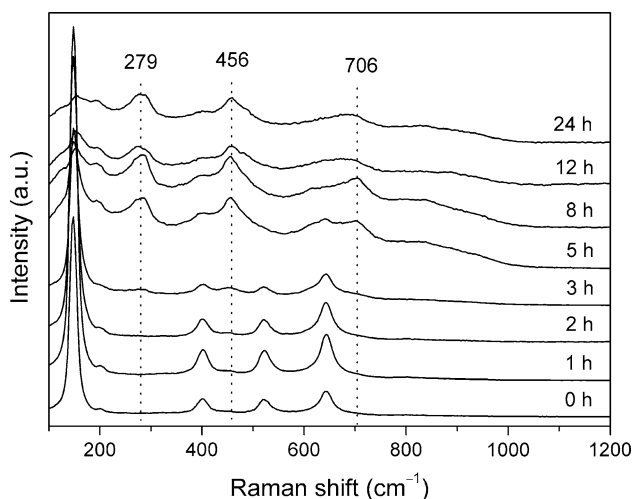


Fig. 3 Raman spectra of the specimens obtained from hydrothermal treatment of P25 for various reaction times

prepared with 1 h or 2 h reaction is less than 1 %, which is lower than that of P25 (4 %). It may be resulted from the broken part of TiO_2 crystal structure. While for TiO_2 -based nanosheets prepared for 3 h, the adsorption percentage is 17 %. The remarkable increase of the adsorption capacity is mainly ascribed to the formation of hydroxyl groups on trititanate surface, which can provide strong electrostatic attraction for cationic dyes [41]. For nanostructures prepared over 5 h, the adsorption percentage increases gradually. It is ascribed to the formation of increasing number of nanotubes, because material with porous structure usually has much higher adsorption capacity than other structural materials.

Photocatalytic activities of the TiO_2 -based nanostructures prepared with different hydrothermal durations were

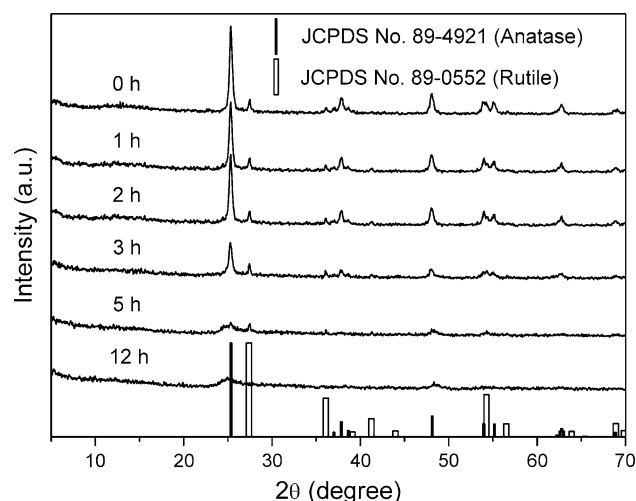


Fig. 4 XRD patterns of the specimens prepared with various reaction times

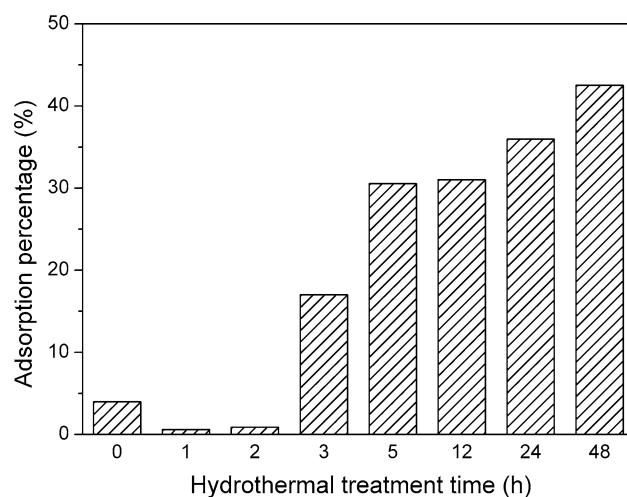


Fig. 5 Adsorption performances of the nanostructures prepared with different hydrothermal treatment times: the adsorption percentage of RhB after adsorption equilibrium in the dark

investigated through the degradation of RhB under UV-Vis irradiation. Degussa P25 (0 h) was used for comparison. Figure 6a shows the relation between irradiation time and C/C_0 of RhB, where C is the concentration of RhB at irradiation time t , and C_0 is the concentration of RhB after adsorption equilibrium in the dark. The corresponding rate constant (k) of the nanostructures was shown in Fig. 6b. For Degussa P25, the k value is $0.59 \times 10^{-2} \text{ min}^{-1}$. After hydrothermal treatment, the photocatalytic activities of prepared catalysts enhance with the stripping of nanoparticles to nanosheets. When hydrothermal treated for 3 h, the prepared TiO_2 -based nanosheets show the highest k value of $3.7 \times 10^{-2} \text{ min}^{-1}$. With further extension of hydrothermal treatment time, the k decreases gradually. It indicates that the photocatalytic activities of the prepared

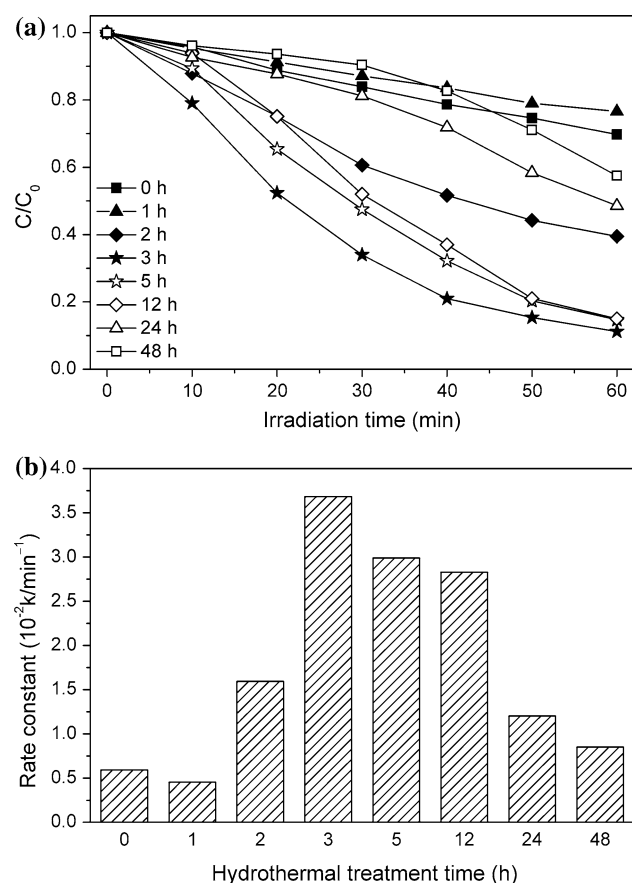


Fig. 6 **a** Photocatalytic degradation of RhB under UV-Vis light irradiation by nanostructures prepared with different hydrothermal treatment times and; **b** comparison of rate constant k of the nanostructures

nanostructures are strongly dependent upon the morphology and dimensionality.

Through the comparison of the variation trend of rate constant and adsorption capacity, it can be found that a suitable adsorption for pollutants is beneficial to photocatalytic reaction, while excess adsorption is harmful. TiO_2 -based nanosheets (2D) have good adsorption ability and exhibit much higher photocatalytic activity than nanoparticles (3D) and nanotubes (1D).

Effect of microstructure and surface states on photocatalytic activity

Due to the high photocatalytic activity for degradation of RhB dyes, the microstructures and surface chemical states of TiO_2 -based nanosheets were further investigated. Atomic force microscopy (AFM) was utilized to analyze the surface morphology and thickness of TiO_2 -based nanosheets. As shown in Fig. 7a, TiO_2 -based nanosheets have a large surface size of ca. 1–3 μm , which is far larger than the size of unexfoliated nanoparticles (20–40 nm). It

implies the growth of nanosheets stripped off from granular TiO_2 crystals. The stripping of granular TiO_2 results in the formation of high specific surface area, and the growth of exfoliated nanosheets is beneficial to the separation and recovery of photocatalyst after photocatalytic degradation because of its large scale. In fact, it was found that the separation and recovery of TiO_2 -based nanosheets were more convenient than that of P25 in the degradation experiments. Besides, TiO_2 -based nanosheets possess the thickness of 4–5 nm as shown in Fig. 7b, which is much thinner than that of the raw TiO_2 nanoparticles. The small thickness causes the decrease of the diffusion path for photogenerated carriers reaching to nanosheets surface, which is beneficial to the enhancement of photoelectric efficiency and the improvement of photocatalytic activity.

^1H NMR spectrum of TiO_2 -based nanosheets was measured to investigate the types of protons and the relative content of surface hydroxyl groups. The ^1H NMR spectra of P25 and TiO_2 -based nanotubes were also obtained for comparison. As shown in Fig. 8, several characteristic proton resonance peaks can be identified at 6.8, 4.8, 4.0, 2.8 ppm in the ^1H NMR spectrum of TiO_2 -based nanosheets. The chemical shifts at 4.8 and 4.0 ppm are associated with the physically absorbed water [42, 43], whereas the signals near 6.8 and 2.8 ppm can be ascribed to bridging and terminal surface hydroxyl groups, respectively [42, 44]. The ^1H NMR spectrum of TiO_2 -based nanosheets is similar to that of TiO_2 -based nanotubes. Comparing the spectra of TiO_2 -based nanosheets and P25, the intensity of the proton peak at 6.8 ppm increases markedly, while the signal intensity of the peak at 2.8 ppm changes very slightly, which indicate that the hydroxyl groups formed on TiO_2 -based nanosheets surface are mainly bridging hydroxyl groups.

Besides, FT-IR spectra of the samples were also obtained to further investigate the variation of hydroxyl groups on catalyst surface. As shown in Fig. 9, two peaks at 1630 cm^{-1} and at around 3300 cm^{-1} can be observed in the spectrum of P25, which are attributed to the binding vibration of H–O–H and the stretching vibration of O–H, respectively [45–47]. For TiO_2 -based nanosheets and nanotubes, the intensity of the peak (at around 3300 cm^{-1}) associated to hydroxyl groups increased greatly compared to that of P25, which indicates the existence of plentiful hydroxyl groups on TiO_2 -based nanosheets surface. It is documented that surface hydroxyl group of photocatalyst is an important factor to affect its adsorption and photocatalytic performances, because the surface hydroxyl groups can attract cationic dyes to photocatalyst surface and capture $h\nu_{\text{ph}}$ to generate Ti-OH^+ radicals [24, 41]. Therefore, the high concentration of bridging surface hydroxyl groups may play an important role on the adsorption and photocatalytic activity of TiO_2 -based nanosheets.

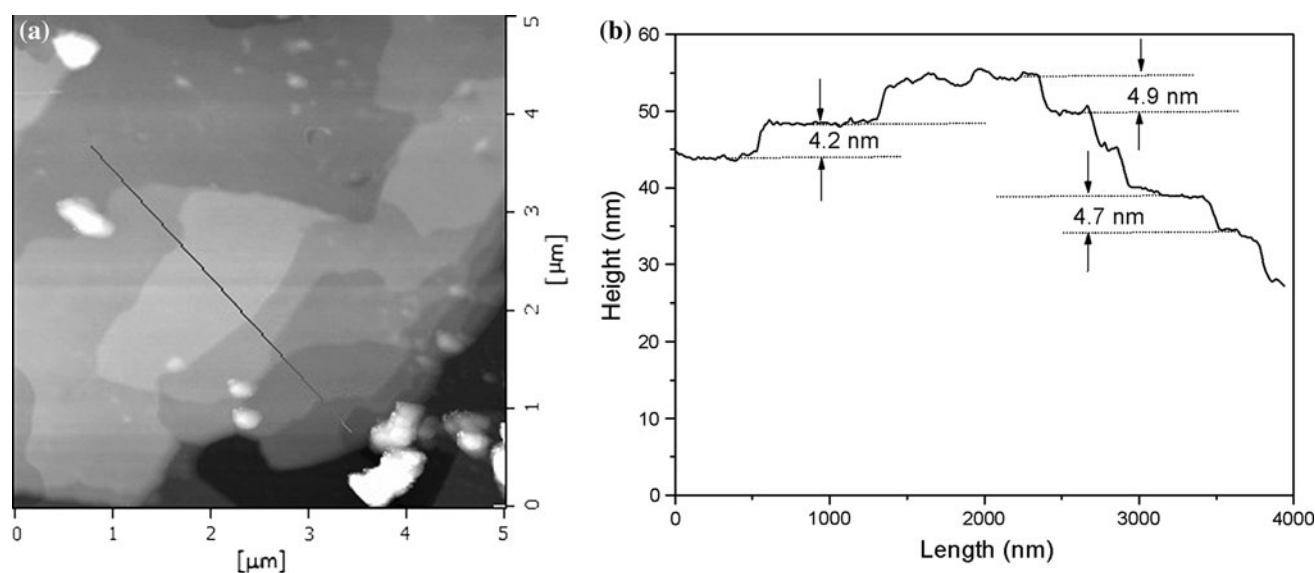


Fig. 7 **a** AFM image of TiO_2 -based nanosheets prepared with 3 h of hydrothermal treatment; **b** line profile showing the height of the nanosheets

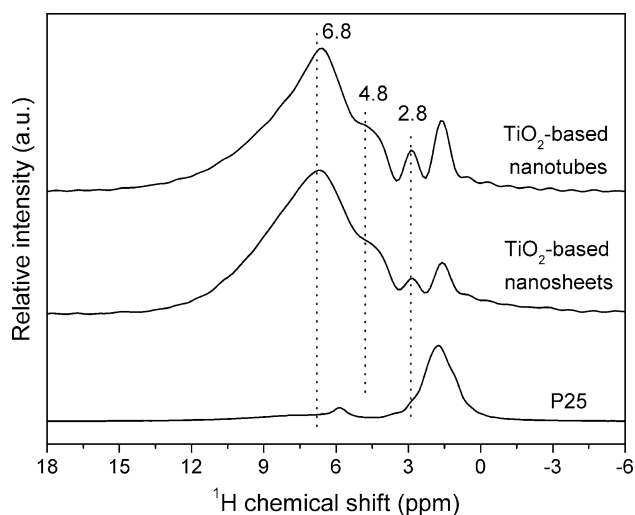


Fig. 8 ^1H NMR of P25, TiO_2 -based nanosheets, and TiO_2 -based nanotubes

As discussed above, microstructure and surface states of TiO_2 -based nanostructures are closely related to their dimensionalities, which play an important role on the photocatalytic activity of the TiO_2 -based nanostructures. On the one hand, the hydrothermally prepared products have increasing BET surface area with the gradually exfoliation of nanoparticles into nanosheets, which can provide much more adsorption sites for organic molecules to be degraded. TiO_2 -based nanosheets have smaller thickness and plentiful hydroxyl groups as compared with nanoparticles, which are beneficial to the improvement of photoelectron efficiency. On the other hand, the adsorption capacity of the prepared products increases with the increasing transformation of nanosheet to nanotubes, while

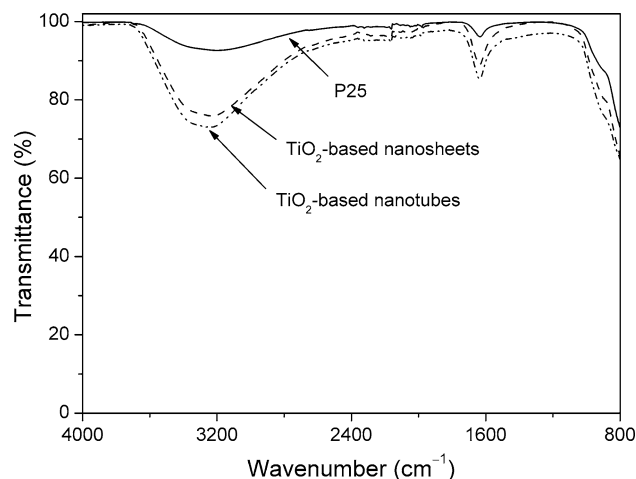


Fig. 9 FT-IR spectra of the catalysts for P25, TiO_2 -based nanosheets, and TiO_2 -based nanotubes

excess adsorption may cause the decrease of light energy reached to photocatalyst surface. That is why TiO_2 -based nanosheets possess much higher photocatalytic activity than nanoparticles and nanotubes, and the excellent microstructure and distinctive surface states may provide a potential application for this kind of nanosheets in photocatalytic degradation of organic pollutants.

Stability of TiO_2 -based nanosheets

The cyclic experiments were also carried out to investigate the stability of TiO_2 -based nanosheets in photocatalytic reaction process. Degussa P25 TiO_2 was used for comparison. As shown in Fig. 10, TiO_2 -based nanosheets exhibit much higher photocatalytic activity than P25 during

the cyclic degradation of RhB (4 mg L^{-1}). Furthermore, TiO_2 -based nanosheets still exhibit a relatively high photocatalytic activity after the fourth cycle, which is similar to that of commercial P25 TiO_2 . It indicates that the photocatalytic property of nanosheets is stable.

Conclusions

The morphological and structural evolution of TiO_2 -based nanostructures under alkaline hydrothermal conditions was investigated systematically. The TEM, BET, Raman, and XRD results clearly revealed the formation process of these nanostructures, especially nanosheet which has rarely been investigated. At the early stage (within 1 h), only a small part of Ti–O bonds are broken, which cannot cause the split of TiO_2 nanoparticles. Thus, the morphology and structure of P25 have no obvious change. With the reaction time increased, plenty of Ti–O bonds are broken and TiO_2 nanoparticles are stripped into smaller particles and sheet-like products. The small lamellar fragments also link with each other to form larger planar nanosheets, which successively scroll into nanotubes.

It is found that the photocatalytic activities of TiO_2 -based nanostructures are strongly dependent upon their morphologies and structures. TiO_2 -based nanosheets exhibit much higher photocatalytic activity than the 3D nanoparticles and 1D nanotubes. The high external specific surface area of nanosheets provides sufficient available surface for adsorption and photocatalytic degradation of dye pollutants, and the small thickness of nanosheets provides short diffusion path for photogenerated carries. In addition, TiO_2 -based nanosheets have suitable adsorption ability due to the plenty of surface hydroxyl groups and its

sheet-like structure. These may be the main reasons why TiO_2 -based nanosheets exhibit such superior photocatalytic activity. The good reusability of TiO_2 -based nanosheets in the cyclic degradation experiments implies a potential application for dealing with organic pollutants.

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References

1. Yu JC, Yu J, Ho W, Zhang L (2001) *Chem Commun* 19:1942
2. Li FB, Li XZ, Hou MF, Cheah KW, Choy WCH (2005) *Appl Catal A* 285:181
3. Huang D, Liao S, Quan S, Liu L, He Z, Wan J, Zhou W (2007) *J Mater Sci* 42:8193. doi:10.1007/s10971-012-2823-6
4. Chang Z, Liu J, Liu J, Sun X (2011) *J Mater Chem* 21:277
5. Yu J, Liu S, Yu H (2007) *J Catal* 249:59
6. Jitputti J, Rattanavoravipa T, Chuangchote S, Pavasupree S, Suzuki Y, Yoshikawa S (2009) *Catal Commun* 10:378
7. Macak JM, Zlamal M, Krysa JK, Schmuki P (2007) *Small* 3:300
8. Das SK, Bhattacharyya AJ (2011) *Mater Chem Phys* 130:569
9. Wu N, Wang J, Tafen DN, Wang H, Zheng JG, Lewis JP, Liu X, Leonard SS, Manivannan A (2010) *J Am Chem Soc* 132:6679
10. Xie RC, Shang JK (2007) *J Mater Sci* 42:6583. doi:10.1007/s10853-007-1506-026
11. Qamar M, Yoon CR, Oh HJ, Lee NE, Park K, Kim DH, Lee KS, Lee WJ, Kim SJ (2008) *Catal Today* 131:3
12. Xiao M, Wang L, Wu Y, Huang X, Dang Z (2008) *Nanotechnology* 19:015706
13. Tang Y, Yang L, Chen J, Qiu Z (2010) *Langmuir* 26:10111
14. Lee CK, Liu SS, Juang LC, Wang CC, Lyu MD, Hung SH (2007) *J Hazard Mater* 148:756
15. Gao T, Wu Q, Fjellvåg H, Norby P (2008) *J Phys Chem C* 112:8548
16. Nakahira A, Kubo T, Numako C (2010) *Inorg Chem* 49:5845
17. Yang J, Jin Z, Wang X, Li W, Zhang J, Zhang S, Guo X, Zhang Z (2003) *Dalton Trans* 20:3898
18. Wang YQ, Hu GQ, Duan XF, Sun HL, Xue QK (2002) *Chem Phys Lett* 365:427
19. Chen Q, Zhou W, Du G, Peng LM (2002) *Adv Mater* 14:1208
20. Kukovecz Á, Hodos M, Horváth E, Radnóczy G, Kónya Z, Kiricsi I (2005) *J Phys Chem B* 109:17781
21. Lan Y, Gao X, Zhu H, Zheng Z, Yan T, Wu F, Ringer SP, Song D (2005) *Adv Funct Mater* 15:1310
22. Pu YC, Chen YC, Hsu YJ (2010) *Appl Catal B* 97:389
23. Han X, Kuang Q, Jin M, Xie Z, Zheng L (2009) *J Am Chem Soc* 131:3152
24. Xiang Q, Lv K, Yu J (2010) *Appl Catal B* 96:557
25. Tae EL, Lee KE, Jeong JS, Yoon KB (2008) *J Am Chem Soc* 130:6534
26. Chen JS, Liu J, Qiao SZ, Xu R, Lou XW (2011) *Chem Commun* 47:10443
27. Yang XH, Li Z, Liu G, Xing J, Sun C, Yang HG, Li C (2011) *CrystEngComm* 13:1378
28. Peng X, Chen A (2006) *Adv Funct Mater* 16:1355
29. Liang YT, Vijayan BK, Lyandres O, Gray KA, Hersam MC (2012) *J Phys Chem Lett* 3:1760

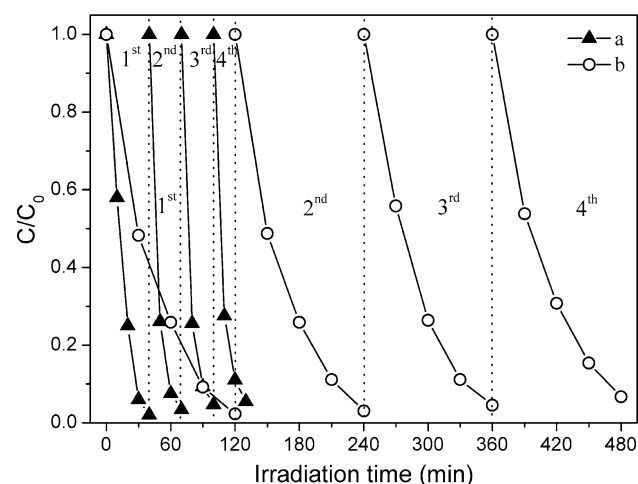


Fig. 10 Cyclic photodegradation of RhB under UV–Vis irradiation by **a** TiO_2 -based nanosheets obtained with 3 h of hydrothermal treatment and **b** P25 TiO_2

30. Yao BD, Chan YF, Zhang XY, Zhang WF, Yang ZY, Wang N (2003) *Appl Phys Lett* 82:281
31. Tsai CC, Teng H (2005) *Chem Mater* 18:367
32. Su W, Zhang J, Feng Z, Chen T, Ying P, Li C (2008) *J Phys Chem C* 112:7710
33. Yoshida K, Miao L, Tanaka N, Tanemura S (2009) *Nanotechnology* 20:405709
34. Gao T, Fjellvåg H, Norby P (2008) *J Phys Chem B* 112:9400
35. Gao T, Fjellvåg H, Norby P (2009) *Inorg Chem* 48:1423
36. Shen X, Zhang J, Tian B (2012) *J Mater Sci* 47:3855. doi: [10.1007/s10853-011-6241-x](https://doi.org/10.1007/s10853-011-6241-x)
37. Li Q, Xiao C, Li W, Zhang H, Chen F, Fang P, Pan M (2010) *Colloid Polym Sci* 288:1369
38. Li Q, Xiao C, Zhang H, Chen F, Fang P, Pan M (2011) *J Power Sources* 196:8250
39. Shukla VK, Yadav RS, Yadav P, Pandey AC (2012) *J Hazard Mater* 213–214:161
40. Kaviya S, Santhanalakshmi J, Viswanathan B (2012) *Mater Lett* 67:64
41. Asuha S, Zhou XG, Zhao S (2010) *J Hazard Mater* 181:204
42. Bavykin DV, Carravetta M, Kulak AN, Walsh FC (2010) *Chem Mater* 22:2458
43. Bavykin DV, Lapkin AA, Plucinski PK, Friedrich JM, Walsh FC (2005) *J Phys Chem B* 109:19422
44. Crocker M, Herold RHM, Wilson AE, Mackay M, Emeis CA, Hoogendoorn AM (1996) *J Chem Soc. Faraday Trans* 92:2791
45. Sun X, Li Y (2003) *Chem Eur J* 9:2229
46. Wang Z, Huang B, Dai Y, Liu Y, Zhang X, Qin X, Wang J, Zheng Z, Cheng H (2012) *CrystEngComm* 14:1687
47. Augugliaro V, Coluccia S, Loddo V, Marchese L, Martra G, Palmisano L, Schiavello M (1999) *Appl Catal B* 20:15