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## ARTICLE

## TiO<sub>2</sub> nanosheet array thin film for self-cleaning coating

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A simple hydrothermal method is developed to directly grow TiO<sub>2</sub> nanosheets on the bare glass substrate. By tuning the reaction conditions, the thickness of TiO<sub>2</sub> nanosheets layer can be tuned from tens to hundreds of nanometer. This TiO<sub>2</sub> nanosheets layer exhibits good transparency due to the air pocket exists inside of the thin film layer between nanosheets. On the other hand, the TiO<sub>2</sub> layer has good hydrophilic surface and good wettability, especially under UV light illumination. The degradation of dye (Rhodamine B) results indicate that the TiO<sub>2</sub> nanosheets coating has excellent photocatalytic activity. All these results demonstrate TiO<sub>2</sub> nanosheets coating could be a high transparent self-cleaning coating.

### Introduction

A coating with self-cleaning properties would be interesting and attractive since it could save a lot of time and cost for maintenance of building and solar panel.<sup>1</sup> Self-cleaning coatings are primarily categorized into hydrophobic and hydrophilic,<sup>2-7</sup> and both these types clean the surfaces by their different behavior towards water. The former makes the water droplets to slide and roll over the surfaces, thereby carrying the dirt away with them to mimic natural lotus leaf. Much effort has been devoted to try to mimic the self-cleaning property of the lotus leaf.<sup>8,9</sup> The latter uses appropriate metal oxides with hydrophilic surface to sheet the water that removes the dirt from the surface.<sup>7,10</sup> In addition to the sheeting effect, metal oxides have an additional property of chemically breaking down organic dirt deposits by a sunlight-assisted cleaning mechanism, i.e. photocatalytic effect of TiO<sub>2</sub>. Among all kinds of metal oxides, TiO<sub>2</sub> has been one of the most investigated engineering materials during recent decades, especially in the arena of energy and environmental applications, due to its advantage of good photocatalytic activity and photostability and low cost.<sup>11-13</sup> The photocatalytic property of TiO<sub>2</sub> relies on the access of high energy facets such as (001) and surface area. Making TiO<sub>2</sub> coating with large surface area and high-energy facet will enhance its photocatalytic activity.<sup>14</sup>

TiO<sub>2</sub>-based coatings can be applied easily on transparent substrates such as glass and plastics to provide a self-cleaning function. However, the coatings developed thus far always enhance the surface reflection of transparent substrates due to the large refractive index of TiO<sub>2</sub> ( $n \approx 2.52 - 2.76$ ). Reflection at the air-glass interface is about 4% for normal incident light;

whereas at the air-TiO<sub>2</sub> interface reflection for normal incident light could be as high as 20%.<sup>15</sup> For some applications, such as solar cells, windows, a high transmittance for visible light is desirable.<sup>14,16</sup> Developing nanostructural TiO<sub>2</sub> coating is an effective route to lower the refractive index of TiO<sub>2</sub> layer and reflectivity of interface. Fujishima and coworkers reported the TiO<sub>2</sub>/SiO<sub>2</sub> multiple layers for the self-cleaning coating with antireflective properties.<sup>14,15</sup> Recently our group developed TiO<sub>2</sub> and ZnO@TiO<sub>2</sub> nanowire array for the self-cleaning coating, exhibiting good photocatalytic performance and stability.<sup>10,17</sup> However, FTO was often employed as a substrate for the nanowires array growing in both cases. Herein, we further develop TiO<sub>2</sub> nanosheets array directly grown on the bare glass. By tuning the reaction conditions, the thickness and density of TiO<sub>2</sub> nanosheets can be finely adjusted. This TiO<sub>2</sub> nanostructure enhance the transmittance of glass accompanying with excellent photocatalytic properties due to porous TiO<sub>2</sub> nanosheet exposed with (001) facet structures. The wettability of the TiO<sub>2</sub> nanosheet array was characterized by contact angle measurement. Although the contact angle increases with the increasing of density of TiO<sub>2</sub> nanosheet, it clearly decreases after illuminate with UV light irradiation. That indicates that the TiO<sub>2</sub> nanosheet layer has a good hydrophilic property. This route shows great potential for self-cleaning application in the solar cells and windows.

### Experimental

#### Chemicals and materials

Isopropanol (AR grade) was purchased from the Tianjin Fuyou fine Chemical Co. Ltd. Ethanol (AR grade) and hydrochloric acid (AR grade) were purchased from the Beijing Chemical

factory. Tetrabutyl orthotitanate (AR grade) was purchased from the Tianjin Guangfu Chemical Reagent Co. Ltd. And other reagents, Titanium (IV) isopropoxide (TIP, AR grade), diethylenetriamine (DETA, AR grade) and rhodamine B (RhB, AR grade), are purchased from the Aladdin Reagent Company. All of the materials in these experiments were used without further purification.

### Synthesis of TiO<sub>2</sub> nanosheet thin film

Firstly, we dip-coated a layer of dense TiO<sub>2</sub> from TiO<sub>2</sub> sol-gel precursor on the bare glass substrates (25 x 25 mm<sup>2</sup>), which were ultrasonically cleaned with deionized water, ethanol, acetone and isopropanol, at speed of 20 mm/min. TiO<sub>2</sub> sol-gel precursor was prepared by stirring the mixture of 30 mL isopropanol, 1.2 mL hydrochloric acid and 2.04 g tetrabutyl orthotitanate over 30 minutes. The amorphous TiO<sub>2</sub> was transferred into TiO<sub>2</sub> nanocrystal seeds layer by thermal-treating the pre-coated glass in an electric oven at 450 °C for 4h. Next, after 15 min plasma surface treatment, the glass with TiO<sub>2</sub> seed layer was placed into a Teflon lined stainless steel autoclave, which contained 30 μL DETA, 30 mL isopropanol and a variable amount (200 - 400 μL in this study) of TIP. The sealed autoclave was heated to 180 °C for 18 h in an electric oven. Then, the reaction was naturally cooled to room temperature. The as-prepared samples were gently rinsed with ethanol and dried at room temperature. Finally, the samples were annealed at 400 °C for 1h to form the crystal.

### Characterization

The morphology of the samples was measured with a JEOL JSM 4800F field emission scanning electron microscope (FE-SEM). Transmission electron microscopy (TEM) images were taken from a FEI Tecnai G2 transmission electron microscopy. X-ray diffraction patterns were obtained on Bruker AXS D8 Focus Diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The UV-Vis transmittance spectra were carried out by a Shimadzu UV-3600 UV-Vis scanning spectrophotometer. The contact angle (CA) were measured by a KRUSS GH-100 universal surface tester, and the CA photos were recorded by a CCD camera interfaced with an optical microscope, which was arranged in a goniometric setup.

### Rhodamine B (RhB) photo-degradation activity measurements

RhB ethanol solution of 5000 ppm was prepared for dye degradation in the experiment. Three selected samples (marked as TIP-200, TIP-300, TIP-400 prepared from 200, 300 and 400 μL TIP as Ti source, respectively) were compared for photocatalytic reaction. All samples were dipped in RhB ethanol solution and kept out of the light for 24 hours. Then the samples were removed and dried naturally so that a layer of RhB formed on the sample surface. The photocatalytic activity of the samples was evaluated by monitoring the decolorization of rhodamine B (RhB) irradiated by a 300W UV-light xenon lamp (AM1.5) at 15 cm distance. The samples without any previous treatment were covered with Al foil from any other light source before irradiation. When irradiated for the specified

time, the maximum peak (553 nm) of absorbance band was monitored by a Shimadzu UV-3600 UV-Vis spectrophotometer to estimate the amount of RhB.

## Results and discussion

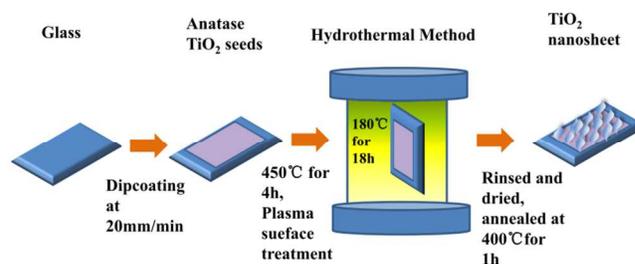
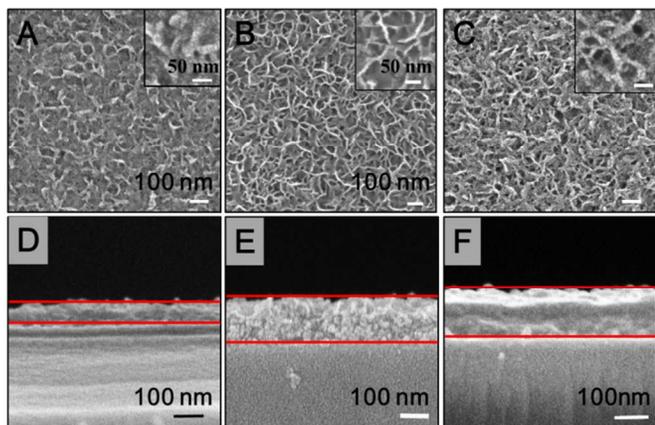


Fig. 1 Schematic diagram of the preparation procedure for the TiO<sub>2</sub> nanosheets array on the bare glass substrate through hydrothermal route.

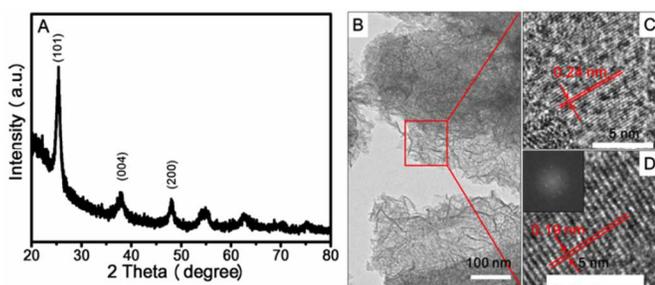
Recently, Lou *et al.* developed a simple hydrothermal route to synthesize TiO<sub>2</sub> spheres composed of nanosheets with exposed highly reactive (001) facets, which possessed high surface area and good photocatalytic activity.<sup>18</sup> We have demonstrated the TiO<sub>2</sub> nanosheets can grow on the ZnO nanowire surface.<sup>19</sup> This provides an opportunity to fabricate TiO<sub>2</sub> nanostructure on the substrate like glass, FTO and ITO and so on. In this report, we developed TiO<sub>2</sub> nanosheets array grown on the glass through modified Lou's route. As shown in the Fig. 1, a layer of TiO<sub>2</sub> seed was firstly applied on the bare glass substrate to obtain uniformly and fully covered TiO<sub>2</sub> nanosheet array. TiO<sub>2</sub> nanosheets array was then grown in the TIP and DETA solution at 180 °C for 18 hours. The plan and cross-section view of as-grown TiO<sub>2</sub> nanosheets arrays were displayed in the Fig. 2. From the top view FE-SEM images, the TiO<sub>2</sub> nanosheets density increases with the initial TIP amount. Some TiO<sub>2</sub> spheres will attach on the surface of substrate when TIP amount is too high. That may lead to scattering and loses the transmittance of glass. From the cross-section FE-SEM images (Figure 2-D-F), the thicknesses of the TiO<sub>2</sub> nanosheets array are 80, 130 150 nm for the TIP-200, 300 and 400, respectively. It should be noted that the thickness contain the ~30 nm of TiO<sub>2</sub> seed layer. We also investigate the effect of reaction time on the TiO<sub>2</sub> layer. The TiO<sub>2</sub> nanosheets can not fully cover the substrate when the reaction time is less than 8 hours and the thickness has slightly different for the 12 to 18 hours when other reaction conditions keep same as TIP-300.

As we know, anatase TiO<sub>2</sub> has the best photocatalytic activity among the three crystalline phase- anatase, brookite and rutile. In order to transfer the TiO<sub>2</sub> nanosheets into anatase phase, the samples were calcined at 400 °C for 1 hour. X-ray diffraction (XRD) pattern, as shown in Fig. 3A, shows the diffraction peaks at 25.3, 37.8, 48.0 corresponding to anatase TiO<sub>2</sub> (JCPDS no. 21-1272) (101), (004) and (200), respectively. Furthermore, we can confirm the crystalline TiO<sub>2</sub> from transmission electron microscopy (TEM) images. Fig. 3B shows that the TiO<sub>2</sub> thin film contains thin petal-like TiO<sub>2</sub> nanosheet structures. High

resolution TEM images exhibit that the nanosheet structures have clear crystalline lattice structures. It can be observed that there is a set of lattices with an equal interfringe spacing of 0.24 and 0.19 nm, corresponding to the anatase (020) and (200) planes. According to previous reports<sup>17, 20</sup>, the TiO<sub>2</sub> nanosheets are bound by (001) facets on both of the exposed sides.



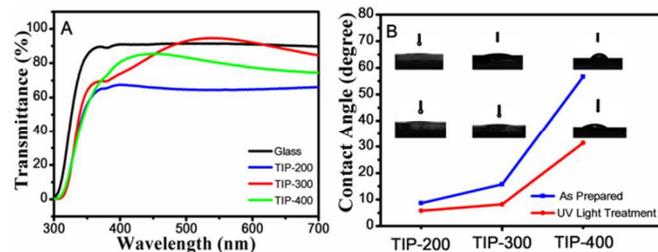
**Fig. 2** FE-SEM images (plan view A–C and cross-sectional view D–F) of TiO<sub>2</sub> nanosheets array thin film prepared from TIP-200 (A, D), TIP-300 (B, E) and TIP-400 (C, F) in 30 mL isopropanol with 30  $\mu$ L DETA, respectively. The insets in A, B and C are high magnification images for A, B and C.



**Fig. 3** Electron microscopy and XRD characterization of anatase TiO<sub>2</sub> nanosheet synthesized from 300  $\mu$ L of TIP and 30  $\mu$ L of DETA in 30 mL isopropanol at 180 °C for 18 hours. (A) XRD patterns of anatase TiO<sub>2</sub> nanosheet on glass. (B) Transmission electron microscopy (TEM) graphs of porous anatase TiO<sub>2</sub> nanosheets. The insets are high resolution TEM images of the selected area. (C and D) High resolution TEM image of the red square shown in A. The top inset in D shows a fast Fourier transform micro-graph of the image area in (D).

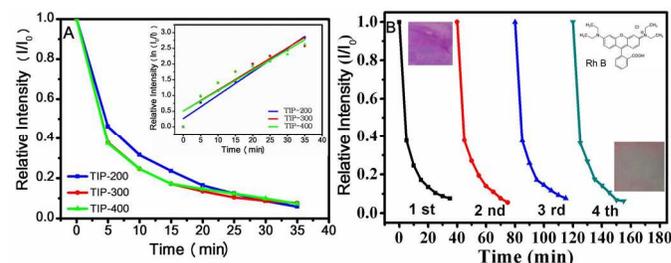
Due to TiO<sub>2</sub> has large refractive index ( $n=2.5-2.7$ ),  $\sim 20\%$  reflectivity at air-TiO<sub>2</sub> interface make the transmittance of glass loss too much. For the windows and solar cells applications, high transparency is highly desired. Fig. 4A shows the transmittance of the bare glass substrate coated with the TiO<sub>2</sub> nanosheets thin films of different thickness. The bare glass shows  $\sim 90\%$  transmission. The TIP-200 shows low transparency ( $\sim 60\%$ ), which is close to the glass coated with dense TiO<sub>2</sub> thin film. The TIP-200 shows looser nanosheet structures and thinner coating thickness. That is the reason why TIP-200 displays low transparency. When the thickness of TiO<sub>2</sub> nanosheets array increases to 150 nm, the transmittance of TIP-300 is close to that of bare glass. The main reason is that the dense TiO<sub>2</sub> nanosheets structure possesses huge amount air pocket in the thin film, which effectively decreases the

refractive index of the whole coating layer. The maximum transmittance is 94.6% at 531 nm, which is better than the bare glass. When the TiO<sub>2</sub> nanosheets array further increases to 180 nm, the transmittance of TIP-400 decreases to 80%. From FE-SEM top image, the density of TIP-400 is the densest among the three samples, which has less air pocket. That results in TIP-400 has higher refractive index than that of TIP-300.



**Fig. 4** (A) The transparency of the glass substrate and thin films of TiO<sub>2</sub> seeds with different thicknesses of TiO<sub>2</sub> nanosheets. (B) The contact angle of the TiO<sub>2</sub> nanosheet thin films coated with different thicknesses. The insets show the contact angle optical images.

The wettability is another important factor for hydrophilic type self-cleaning coatings. Normally, the nanostructure may induce hydrophobic due to the fine air pocket.<sup>21</sup> Fig. 4B shows the contact angle of TIP-200, 300 and 400. It clearly shows the contact angle increase from 8.69°, 15.76° to 56.64° for TIP-200, 300 and 400, respectively. After UV light illumination, the contact angle can be severally decreased to 5.79°, 8.20° and 31.27°. These results indicate the TIP-300 coating has good hydrophilic property for self-cleaning coating.



**Fig. 5** (A) Comparison of the photocatalytic degradation rates of rhodamine B (RhB) of the selected samples. Inset: In-plot of the degradation rates of the TiO<sub>2</sub> nanosheet thin film with different thicknesses (B) Cycling degradation curves of the TiO<sub>2</sub> nanosheet thin film (TIP-300) sample with optical pictures of the initial and final state in the cycle. The inset at right-up corner is the chemical structure of Rh B.

The photocatalytic activity of the coating layer is a key issue for hydrophilic self-cleaning coatings. Rhodamine B (Rh B), as a common dye mole, is often chosen as a model molecule for the study of organic molecules degradation. It is also suspected to be carcinogenic compound need be removed from drinking water. We chose Rh B as a model dye molecule to demonstrate the photocatalytic activity of the TiO<sub>2</sub> nanosheet thin films in this report. Fig. 5A shows the degradation of RhB on the TiO<sub>2</sub> nanosheet thin films with different quantities of TIP. We can see the three curves are at similar degradation rate. And it's a little slow for TIP-200. After 35 minutes illumination under UV-Vis light, about 98% RhB was degraded by the TiO<sub>2</sub>

nanosheet thin films. The substrate turned from dark purple to transparent under the light illumination. Fig. 5B shows the durability of the TiO<sub>2</sub> nanosheet thin films for the photocatalytic degradation of RhB under UV-Vis irradiation. After each recycle experiment, the photocatalytic activity remains unchanged. These results indicate that the TiO<sub>2</sub> nanowires array exhibit good photocatalytic performance and durability.

## Conclusions

In summary, we developed a simple synthesis route to fabricate the TiO<sub>2</sub> nanosheet array on the glass substrate. After 400 °C calcination, TiO<sub>2</sub> nanosheets are in anatase crystalline phase exposed with high-energy (001) facet. TiO<sub>2</sub> nanosheet array coating exhibits good transmittance due to the introduction of air pocket in the TiO<sub>2</sub> thin film. The contact angle obviously decreases after irradiation of UV-Vis light, indicating that the wettability of TiO<sub>2</sub> nanosheet array coating is improved. The degradation of RhB indicates that TiO<sub>2</sub> nanosheet array has excellent photocatalytic performance. All these results imply that TiO<sub>2</sub> nanosheet array could be a high performance self-cleaning coating. The conclusions section should come at the end of article, before the acknowledgements.

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## Notes and references

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## Graphic Abstract

