A One-Step Approach to the Synthesis of High Aspect Ratio Titania Nanoflakes

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High aspect ratio TiO₂ nanoflakes are synthesized by a one-step modified surface hydrolysis method. Surface morphology and physical dimensions are characterized using scanning electron microscopy, laser diffraction analysis, and transmission electron microscopy. Microsized flakes having a thickness ≈40 nm are successfully synthesized by spreading an oil phase consisting of titanium tetraisopropoxide and a low surface tension hydrocarbon on the surface of water. Pure anatase phase crystalline titania nanoflakes are obtained by calcining at 400 °C without changing the shape and thickness of flakes. Relatively higher specific surface area (2–6 times) and less crystal defects enhance photocatalytic activities of nanoflakes due to more surface reaction sites and the suppression of fast recombination. By performing dye degradation under ultraviolet illumination, titania nanoflakes exhibit the higher photocatalytic efficiency over the commercial photocatalyst, Degussa P25. As far as it is known, this method is the most efficient and cost effective process for making low-dimensional nanomaterials in a continuous manner. These titania nanoflakes can be easily separated from the treated water by simply sedimentation or filtration and therefore is very suitable for water purification application.

Nanostructured titanium dioxide has attracted tremendous interest in the field of environmental purification, solar energy conversion, pigment, optics, gas sensing, and energy storage because of their unique physicochemical properties. Many scientific works have been focused on particle size down to the order of nanometer. However, using TiO₂ nanoparticles for water treatment is limited in practical application since it is very difficult to be removed from purified water due to very small mass. The conventional separation methods such as centrifuging, filtration, and sedimentation cannot be used to solve this problem efficiently and economically. Except for size control, shape control of particulates on nanometer scale is more difficult and starts to attract attention recently. Many nanomaterials, more specifically anisotropic nanostructures, have been successfully synthesized including nanotubes, nanowires, nanorods, nanofibers, and nanosheets. However, synthesis for titania nanomaterials with at least 1D close to the optimum size of photocatalyst will be a revolution of the whole titania fabrication.

In this study, micrometer sized titania flakes having a thickness ≈40 nm were successfully synthesized by spreading an oil phase consisting of titanium tetraisopropoxide and a low surface tension hydrocarbon on the surface of water. These nanoflakes were produced by restricting the hydrolysis of titania precursor within dimension of the organic thin film due to the difference of surface energy to water. The flakes were also calcined at 400 °C resulting in high purity anatase having near identical dimensions to the uncalcined material. Investigations have shown the described method to be efficient and economical at producing gram to kilogram quantities of material. This study examines these nanoflakes which were characterized by scanning electron microscopy (SEM), laser diffraction analysis, X-ray diffraction (XRD), transmission electron microscopy (TEM), physisorption techniques, and UV–visible spectrometer.

The surface morphology of synthesized titania nanoflakes was investigated using SEM images, shown in Figure 1. The major diameter of the flakes was found to be of the order of 10–20 µm (Figure 1A,B), and the thickness of these flakes was ≈40 nm (Figure 1C,D). The flakes were further treated by calcination at 400 °C for 2 h. Aggregation was not apparent when comparing these treated flakes (Figure 1B) with those obtained directly from synthesis (Figure 1A). Moreover, the thickness of calcined flakes did not change by the heat...
treatment (Figure 1D). Both the uncalcined and calcined flakes were transparent under the SEM (Figure 1B).

Particle size distributions of synthesized and calcined flakes were measured using laser diffraction. Laser diffraction particle size analysis alone is unsuitable for characterizing anisotropic particles as the analyzer assumes the particles conform to a spherical model. In combination with electron microscopic method it is possible to garner a better understanding of the synthesized particles morphology. The measured major dimension of the flakes was comparable to the dimensions obtained from the SEM images (Figure 1A,B). The statistics data of particle size distribution by volume were shown in Table 1. The synthesized material has a broad size distribution spanning from 1 to 100 µm with a \( D_{50} \) of 20.8 and 19.0 µm for the synthesized and calcined flakes respectively (Figure 2). Comparing the volume distributions it is evident some larger flakes break or crack during dehydration and crystallization. The average aspect ratio of the flakes is 1:500 which can be calculated from mean size (Table 1) divided by thickness.

Crystalline structure changes of the titania flakes was monitored by powder XRD (Figure 3). The synthesized flakes show broadening and weak Bragg peaks which indicates the nature of flakes consist of partial amorphous material with a presence of the anatase phase (Figure 3A). After heat treatment, the expected phase transformation from amorphous to crystalline titania was confirmed by seven characteristic diffraction peaks (Figure 3B). The heat treated flakes were converted to a pure anatase phase [JCPDS: 21-1272] which is the most photoactive phase of titania.\(^{[18]}\) There was no indication of the rutile phase by XRD. The intensity of characteristics peaks was comparable to the commercial pure anatase standard materials (Figure 3C) which indicates nearly complete conversion of the amorphous titania. The average crystal grain size can be calculated by the Scherer equation

\[
d = \frac{k\lambda}{B\cos\theta_b}
\]

where \( d \) is the calculated grain size, \( \lambda \) is the wavelength of X-ray (Cu K\( \alpha \) 1.54 Å), \( B \) is the full-width at half-maximum intensity, and \( \theta_b \) is the half of the diffraction peak angle. The grain size was determined to be 4 and 9 nm for synthesized and calcined flakes respectively (Table 2).

**Table 1.** Particle diameter statistics for synthesized and calcined titania flakes under investigation.

| Sample            | \( D_{10} \) [µm] | \( D_{50} \) [µm] | \( D_{90} \) [µm] | Mean [µm] | Standard deviation [µm] |
|-------------------|-------------------|-------------------|-------------------|------------|-------------------------|
| Synthesized flakes| 5.2               | 20.8              | 81.6              | 39.1       | 58.9                    |
| Calcined flakes   | 5.1               | 19.0              | 51.8              | 24.7       | 20.9                    |

Figure 1. SEM images of titania nanoflakes: A) synthesized samples, B) calcined samples, C,D) edge views of (A) and (B), respectively. Images were obtained without conducting coating.
tion, several 2D titania nanomaterials were revealed having high 5–8 nm fine grains throughout the surface of flakes. In addition, and attributed to high aspect ratio (250:1 to 500:1) and averaged in conjunction with the Brunauer–Emmett–Teller (BET) model. The high specific surface area of titania flakes were expected in terms of the nitrogen absorption isotherms talline and consist of fine grains of anatase. Consequently, it is thought that the flakes are polycrystalline and had a separation distance of 0.35 nm, corresponding to the interplanar spacing of the (101) planes for anatase. Random orientation of individual grains over the both flakes was suggested from the concentric diffraction rings in the select area diffraction mode and consistent with the anatase (101), (004), (200), (105) for circles 1 to 4, respectively (the insets of Figure 4). On closer inspection, an amorphous layer can be seen surrounding the smaller circular crystallites in synthesized sample (Figure 4A). After calcination, some pores were developed due to local rearrangement and growth of crystal grains. Consequently, it is thought that the flakes are polycrystalline and consist of fine grains of anatase.

The specific surface area of synthesized and calcined titania nanoflakes was estimated using nitrogen absorption isotherms in conjunction with the Brunauer–Emmett–Teller (BET) model. The high specific surface area of titania flakes were expected and attributed to high aspect ratio (250:1 to 500:1) and averaged 5–8 nm fine grains throughout the surface of flakes. In addition, several 2D titania nanomaterials were revealed having high specific surface of 110 to 320 m² g⁻¹, respectively from exfoliation of a layered precursor[6] and lamellar micelle template.[20] It is desirable for photocatalytic materials to have higher specific surface area as this usually results in higher photoactivity since a large amount of adsorbed organic molecules at surface sites, increasing the reaction rate. However, high surface area powders are usually associated with large amounts of crystal defects favoring fast recombination of electrons and holes, ultimately leading to lower photocactivity. Compared to a commercial photocatalyst, Degussa P25, the surface areas of nanoflakes were 2–6 times higher (Table 3). The photocatalytic activity of these flakes was investigated by performing dye degradation experiments under ultraviolet activation.

Figure 5A shows typical UV-visible diffuse reflectance spectra in the wavelength range of 250–500 nm for the synthesized flakes together with the calcined flakes. The sharp decrease in the diffuse reflectance in the UV region results from the fundamental light absorption of the semiconductor materials and a blue shift of the onset of reflectance occurred at calcined sample due to heat treatment. In semiconductor physics, the general relation between the absorption coefficient and the band gap energy is given by

\[(\alpha h\nu)^m = h\nu - E_g\]  

(2)

where m is an index depending on the nature of the electron transitions, \(\alpha\) is the absorption coefficient, h is the Planck constant, \(\nu\) is the frequency of electromagnetic radiation, and \(E_\text{g}\) is band gap energy of the semiconductor. To estimate band gap energies of both nanoflakes, \(\alpha\nu\) data in Figure 5A was plotted as \((\alpha h\nu)^m\) versus \(h\nu\) and the optical absorption energy was determined via extrapolation. An increase in band gap from 3.25 to 3.33 eV, i.e., a blue shift, is mostly likely due to the quantum confinement effect of higher crystallinity after calcination and thin flaky morphology.[21] The atomic structure at the grain boundary is different from that in the amorphous area, leading to larger free carrier concentrations and the existence of potential barriers at these boundaries. Therefore, an electric field is built up, the band gap energy increases, and the absorption limit shifts to shorter wavelength range.

Figure 6 compares the photocatalytic activity of P25, synthesized and calcined titania nanoflakes by removing the methylene blue form water under UV light irradiation. Degussa P25 was used as a reference material. It has a mean diameter of 30 nm which is comparable to the minor dimension of nanoflakes (40 nm). It was observed that calcined flakes exhibited the highest photocatalytic efficiency on the degradation of methylene blue among all tested samples. Besides, titania flakes in this study demonstrated not only higher photocatalytic activity on removing methylene blue from water but the easier fabrication against the state of art titania nanomaterials such as

| Sample             | \(\theta_0\) [°] | \(d\) [nm] |
|--------------------|----------------|-----------|
| Synthesized flakes | 25.91          | 4.1       |
| Calcined flakes    | 25.35          | 8.7       |

Table 2. Grain size calculation by the Scherer equation for both nanoflakes.
nanofibers, nanotubes, nanocomposite. The main photocatalysis reactions were identified by laser flash photolysis and listed as follows:

- Charge-carrier generation

\[
\text{TiO}_2 + h^+ \rightarrow h^+_{\text{VB}} + e^-_{\text{CB}} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldos
carried out by annealing the sample at 450–500 °C.\(^{30,33}\) Higher density of OH groups for synthesized and calcined flakes were attributed to the higher specific surface area comparing to the Degussa P25. Hydroxyl radical, one of the most reactive species in the photocatalysis process, is strongly related to the hydroxyl group concentration at titania surface. Therefore, we could expect that better photocatalytic performance could be achieved by the sample showing the larger OH component in the XPS oxygen 1s signal.

Three titania samples demonstrated similar dye adsorption in the dark within 2 h which suggested photocatalysis is the main reaction instead of physical adsorption (Figure 7A). A first order rate reaction was shown in Figure 7B which indicates dye concentration is the limiting factor. In contrast, significant enhancement was observed when agitation was added to the system in the form of introducing air bubbles into the system continuously (Figure 7C). The reaction with added turbulence presented a pseudo first order fashion and much higher efficiency especially for the flake systems. One possible explanation of these differences may be correlated to oxygen depletion during the photocatalysis process. From the results of XRD and TEM, both flakes consisted of very small nanocrystallites which imply a large amount of defects (grain boundaries) within both materials. Consequently, fast recombination of photoassisted charge carriers preferentially occurs at these local defect sites and dominates the reaction. The flake samples have much higher surface area than P25. However, the photocatalytic performance is not proportional to surface area without supplying oxygen to the system. By introducing air into the system, dissolved oxygen will primarily become an electron accepter and may form superoxide radicals.\(^{34}\) Dissolved oxygen adsorbed at titania surface to trap the electrons in order to prevent the harm of charge–carrier recombination through the following reaction.

\[
O_2 + e^- \rightarrow O_2^+ \quad (12)
\]

The highly reductive species, superoxide radicals, was detected directly by the electron spin resonance technology.\(^{35}\) Besides, the partial pressure of oxygen in the solution was revealed to be a vital factor in the heterogeneous photocatalysis.\(^{36–38}\) Therefore, aeration process remarkably increase the photocatalytic reaction rate through better charge separation and reduction ability. More importantly, fast recombination, the rate limiting step, could be depressed by eliminating excited conduction band electron for higher efficiency.

In summary, a high aspect ratio titania nanoflakes has been synthesized. Compared to other methods for making low-dimensional nanomaterials, this spreading film process could

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**Figure 5.** A) Diffuse reflectance spectra and B) the dependence of \((ahv)^2\) on the photon energy for synthesized and calcined titania flakes.

**Figure 6.** A) XPS O 1s peak fitting of synthesized flakes. B) OH/Otot XPS surface ratio of the titania samples.
Experimental Section

Synthesis: Titania nanoflakes were fabricated by spreading a mixture of stearic acid (Fisher, 99%), low surface tension hydrocarbon (for example, octane, Fisher, 97%), and titanium tetraisopropoxide (Aldrich, 97%) on the surface of solution consist of high purity water (Barnstead Nanopure Infinity, 18 MΩ cm⁻¹), nitric acid, and sodium dodecyl sulfate (Fisher, 99%). Stearic acid and the hydrocarbon were used to decrease the viscosity of titania precursor and enhance the spreadability of the mixture. The thickness of nanoflakes could be manipulated by varying the volume ratio of titania precursor and hydrocarbon. Typically, a ratio of 1:8 of titanat tetraisopropoxide to hydrocarbon was used to produce titania nanoflakes with thickness about 40 nm. The resulting slurry was washed with Nanopure water and then centrifuged (Begman BH-2) at 3000 rpm for 15 min to concentrate the slurry. The particles were then resuspended in isopropanol and centrifuged to remove further impurities. This was repeated a total of five. Finally, the nanoflakes were dried by a supercritical fluid drying process described elsewhere.[39]

Characterization: The surface morphology and thickness of titania nanoflakes were observed by a cold field emission SEM (JEOL 6335). Samples were made by depositing titania slurry on a smooth silicon wafer as substrate and placed to a vacuum oven for drying. XRD patterns were obtained on dried powders using a Philips APD 3720 diffractometer (Cu Kα radiation, λ = 1.54 Å). Particle size distributions were measured with a laser diffraction particle size analyzer (Beckman Coulter LS 13 320). When using a differential volume distribution of the flakes, the larger dimension of nanoflakes was estimated by dispersing both flakes in deionized water with liquid modules. HR-TEM images were obtained using a JEOL 2010F. The specimens were prepared by dispersing materials in isopropanol and placed on a lacy carbon grid. Specific surface area, pore size distribution were evaluated using a 5 point BET analysis with a Quantachrome NOVA 1200.

Photocatalysis: Dye decomposition experiments were performed inside a cylinder UV reactor equipped with 6 UVA lamps, RPR-3500A which emit light in a band between 300 and 420 nm with an approximately Gaussian distribution centered at 350 nm (Southern New England Ultra Violet Company, Branfield, CT). The light intensity of photocatalytic reactor was around 10 mW cm⁻² monitored using LI-250a light meter (Model Pyranometer, LICOR, Biosciences, USA). A 150 mL Erlenmeyer flask containing dye solution with TiO₂ particles at the constant concentration of 1:8 of titania precursor and hydrocarbon. Typically, a ratio of 1:8 of titanat tetraisopropoxide to hydrocarbon was used to produce titania nanoflakes with thickness about 40 nm. The resulting slurry was washed with Nanopure water and then centrifuged (Begman BH-2) at 3000 rpm for 15 min to concentrate the slurry. The particles were then resuspended in isopropanol and centrifuged to remove further impurities. This was repeated a total of five. Finally, the nanoflakes were dried by a supercritical fluid drying process described elsewhere.[39]

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