Development of Monodisperse Mesoporous Microballs Composed of Decahedral Anatase Nanocrystals

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Abstract: Mesoporous monodisperse microballs of amorphous titania were prepared from solution of absolute ethanol, tetrabutyl titanate (TBOT) and potassium chloride via a sub-zero sol–gel route. The as-obtained microballs were used as the precursor in an alcohothermal (ethanol with a small amount of water) process to synthesize monodisperse mesoporous microballs built of decahedral anatase nanocrystals. FE-SEM observation and XRD analysis have confirmed that the formed decahedral anatase-rich powder retained the original spherical morphology of the precursor. Importantly, a hierarchical structure composed of faceted anatase has been achieved under “green” conditions, i.e., fluorine-free. Additionally, the hysteresis loops (BET results) have confirmed the existence of mesopores. Interesting, faceted microballs show noticeable photocatalytic activity under UV/vis irradiation for hydrogen generation without any co-catalyst use, reaching almost forty times higher activity than that by famous commercial titania photocatalyst—P25. It has been proposed that enhanced photocatalytic performance is caused by mesoporous structure and co-existence of two kinds of facets, i.e., {001} and {101}, and thus hindered charge carriers’ recombination.

Keywords: anatase nanocrystal; decahedral anatase; faceted titania; heterogeneous photocatalysis hierarchical structure; mesoporous microballs; {001} facets; {101} facets; TiO$_2$

1. Introduction

The micrometer-sized spherical titania particles with crystalline framework, and thus high photocatalytic performance, have shown a potential for various technological applications. The specific morphology could significantly improve not only the photocatalytic efficiency, but also the recycling/reuse ability of photocatalysts that is essential for “green” technology [1–5]. However, the preparation of monodisperse (non-aggregated) titania microballs under pure aqueous conditions is still challenging. In comparison to the complex mechanism in water, non-aqueous (or tiny-aqueous) processes offer the possibility of better control of the reaction pathways at the molecular level, enabling the synthesis of materials with well-defined and uniform particle morphologies. Therefore, the sol–gel routes to prepare metal oxide nanoparticles (NPs; including also TiO$_2$) in organic solvents under exclusion (or in the presence of small amount) of water have become a versatile alternative to the pure aqueous methods [6–8]. Spherical titania structures with tailored properties, e.g., particle sizes [9], monodispersity [10], porosity [11], and surface properties [12], have been successfully prepared by utilizing this fabrication strategy.

Furthermore, titania nanocrystals with exposed facets have attracted extraordinary attention due to high photocatalytic activity [13–17]. For example, morphology-governed activity has been proven for octahedral anatase particles (OAP) with eight equivalent {101} facets [18,19], i.e., samples prepared under ultrasonic-assisted hydrothermal synthesis with almost same physical properties (specific surface area, crystallinity, crystalline size, total
electron traps’ (ETs) density) but different only in morphology (the content of OAPs in the product) have shown the direct correlation between the morphology and the photocatalytic activity. Accordingly, it has been proposed, based on photoacoustic spectroscopy (PAS) and time-resolved microwave conductivity (TRMC), that faceted samples contain shallow rather than deep ETs, and thus high mobility of charge carriers’ instead of their recombination results in the high photocatalytic activity [18,19]. Moreover, the presence of additional facets might result in further enhancement of photocatalytic performance. For example, decahedral anatase particles (DAPs), with two additional \{001\} facets, have been shown to be the most active titania photocatalyst among various commercial and self-synthesized titania materials [20,21], possibly due to intrinsic separation of charge carriers, i.e., electron and hole migration to \{101\} and \{001\} facets, respectively [22,23].

There are various methods of the anatase nanocrystals’ formation from amorphous titania. Generally, the hydrothermal process has been suggested as more reasonable and successful than other methods, e.g., calcination [24,25]. However, some studies suggest that the alcohothermal (a suspension of ethanol and a small amount of water) process is recommended, especially for the preparation of monodisperse mesoporous microballs composed of fine titania nanocrystals [26,27].

In this study, a facile alcohothermal synthesis approach employing ethanol as both the crystal growth stabilizer and morphology control agent have been developed to prepare a hierarchical monodisperse microballs, composed of decahedral anatase nanocrystals with exposed \{001\} and \{101\} facets.

2. Experimental Part

The precursor, i.e., mesoporous monodisperse microballs of amorphous titania, was synthesized according to the procedure described previously [28]. In brief, 4 mL KCl (0.05 mol L\(^{-1}\)) (AR Macklin) aqueous solution was mixed with 100 mL absolute ethanol (AR Macklin) in a 200 mL round-bottomed flask, in which the temperature was precisely controlled at \(-10\) °C. Then, 4 mL tetrabutyl titanate (TBOT, AR Macklin) was rapidly added under continuous stirring. After sealing the neck of the round-bottomed flask with a septum, the suspension was kept under magnetic stirring for 5 min and then aged for 5 h, resulting in the attainment of a white precipitate that was washed (four times with ethanol and then four times with deionized water), centrifuged and freeze dried. The as-obtained precursor (mesoporous monodisperse microballs of amorphous titania) was named as S\(_{pm}\), and further used for the preparation of microballs composed of anatase nanocrystals.

In a typical synthesis procedure, 0.2 g of S\(_{pm}\) was added into a beaker containing 60 mL liquid phase and then kept under stirring for 2 h to obtain a uniform suspension. Various compositions (volume ratio) of ethanol to water (i.e., 60:0, 58:2, 56:4, 54:6 and 52:8, 50:10, 0:60) were used, and obtained samples were named accordingly as Et-0 mL, Et-2 mL, Et-4 mL, Et-6 mL, Et-8 mL, Et-10 mL and Et-60 mL. Subsequently, the suspension was transferred into a 100 mL Teflon-lined stainless-steel autoclave, and alcohothermal reaction was conducted at 200 °C for 24 h. After the reaction, the white precipitates were washed with alcohol five times, centrifuged, and freeze dried.

The obtained powder products were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi SU8010,1 kV) and powder X-ray diffraction (XRD, PANalytical, Empyrean, Cu Kα radiation, 40 kV, 40 mA). Crystalline sizes and the particle aspect ratio (PAR) were estimated from XRD data using the Scherer equation. The PAR (\(d_{001}/d_{101}\)) is defined as a ratio of average crystallite size (depth) vertical to \{001\} and \{101\} planes, estimated using a width of 004 and 101 diffraction peaks, respectively. The higher the PAR value is, the higher is the content of \{101\} facets. Nitrogen adsorption-desorption measurements were performed using a Micromeritics ASAP 2020Plus instrument. The specific surface area of the samples was calculated using the multiple-point Brunauer–Emmett–Teller (BET) method in the relative pressure range of \(P/P_0 = 0.05–0.3\), where the pore size distribution was estimated from the adsorption branch of the sorption isotherms using the Barret–Joyner–Halenda (BJH) method.
The photocatalytic activity was evaluated for hydrogen generation in a closed glass reaction system at 25 °C, a full glass automatic on-line trace gas analysis unit (Labsolar-6A, Beijing Perfectlight Technology Co., Ltd., Beijing, China). The photocatalyst (0.05 g) was uniformly dispersed in an aqueous solution (100 mL) containing triethanolamine (TEOA, 10 vol%) as a sacrificial electron donor. The reactor was evacuated with a vacuum pump, and then irradiated with the 300-W xenon lamp. The temperature of the reaction suspension was maintained at 5 °C by circulating water during the photocatalytic experiment. The generated hydrogen was determined by an on-line gas chromatography system (GC9790II), equipped with the highly sensitive thermal conductivity detector (TCD) using argon as a carrier gas.

3. Results and Discussion

The morphologies of amorphous precursor (S_{pm}) and anatase products are presented in Figure 1. It is clear that microballs of precursor are monodisperse, spherical and non-aggregated, as shown in Figure 1a. Moreover, a high-magnification FE-SEM image, shown in Figure 1b, reveals that the microball surface is relatively rough, which indicates that the particles are porous, and titania NPs are 3D interconnected, forming mesoporous networks. Interestingly, the morphology of microballs was maintained after the thermal treatment at 200 °C for 24 h. However, nano-building blocks were changed from irregularly shaped NPs (Figure 1a) to nanocrystals with diameters of around 20–80 nm, as shown in Figure 1d,f,h. It was observed that with a decrease in volume ratio of ethanol to water, both the average crystalline sizes and particles aspect ratio (PAR) decreased. It is proposed that a decrease in crystallite sizes is caused by the fact that a larger water volume promotes the dissolution–redeposition mechanism to form more critical nucleus. The content of the exposed [001] facet gradually decreased with an increase in water volume, possibly because the [001] facet has larger content of coordinated unsaturated Ti atoms. The alcohol molecules might selectively adsorb on the [001] facet, forming alkoxy groups with Ti^{4+}, which causes a decrease in the surface energy and inhibition of the growth on <001>, and thus exposing the [001] facet. The polarity of alcohol molecules is lower than that of water molecules, and thus addition of water might destroy the selective adsorption of alcohol on [001], and thus decrease the content of the exposed [001] facet [29]. Furthermore, the high magnification of FE-SEM images (Figure 1d,f,h) indicates that the microballs consist mainly of titania polyhedral particles, typically, truncated bipyramids (decahedron), and these nanosized building units are similar in shape.

According to the anatase symmetry, the two square and eight trapezoid surfaces should be [001] and [101] facets, respectively, as presented in the inset of Figure 1f [13,30–32]. It should be mentioned that simple calcination of the S_{pm} precursor despite obvious conversion of amorphous titania to the crystalline forms (anatase first and then anatase/rutile mixture) does not result in the formation of faceted-based microballs [28]. Accordingly, it might be concluded that alcohothermal treatment is necessary both to form perfectly shaped nanocrystals and to keep spherical morphology.

The crystalline properties of samples were investigated by XRD, and exemplary patterns are shown in Figure 2. The lack of any diffraction peak in the pattern of S_{pm} sample indicates its amorphous nature. However, the alcohothermal treatment results in phase transition from amorphous titania to anatase, as clearly observed by characteristic diffraction peaks at 25.3°, 37.8°, 48.0°, 53.9°, 55.1° and 62.7° corresponding to {101}, {004}, {200}, {105}, {211} and {204} facets, respectively.

The crystallite sizes and PAR values, estimated from XRD analysis (by Scherrer equation [33] and a ratio of [001]/[101], respectively), for the most active samples are summarized in Table 1. It can be seen that the average crystalline sizes decrease with an increase in alcohol/water volume ratios, which is consistent with morphology data (Figure 1).
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Figure 1. FE-SEM images of: (a,b) precursor Spm microballs, and (c–f) faceted microballs: Et-4 mL (c,d), Et-6 mL (e,f) and Et-8 mL (g,h); and (inset in f) the schematic illustration of decahedral anatase particles.
Figure 2. XRD patterns of precursor (S<sub>pm</sub>) and crystalline products (Et-4 mL, Et-6 mL and Et-8 mL).

Table 1. The preparation parameters (EtOH/H<sub>2</sub>O), crystallite sizes, particle aspect ratios (PAR) and specific surface areas (SSA) of precursor (S<sub>pm</sub>) and crystalline products (Et-4 mL, Et-6 mL and Et-8 mL).

<table>
<thead>
<tr>
<th>Sample</th>
<th>EtOH/H&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>(001)/nm</th>
<th>(100)/nm</th>
<th>PAR</th>
<th>SSA/m&lt;sup&gt;2&lt;/sup&gt; g&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>S&lt;sub&gt;pm&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Et-4 mL</td>
<td>56:4</td>
<td>48.6</td>
<td>131.1</td>
<td>1.07</td>
<td>29.2</td>
</tr>
<tr>
<td>Et-6 mL</td>
<td>54:6</td>
<td>43.2</td>
<td>57.4</td>
<td>0.51</td>
<td>35.9</td>
</tr>
<tr>
<td>Et-8 mL</td>
<td>52:8</td>
<td>38.9</td>
<td>32.8</td>
<td>0.46</td>
<td>38.3</td>
</tr>
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</table>

To check the surface properties of obtained microballs, nitrogen adsorption–desorption isotherms were estimated using nitrogen gas sorption, and obtained data are shown in Figure 3 and Table 1. It is obvious that the precursor microballs possess a hierarchical structure with mesoporous networks, as indicated by a typical hysteresis loop for S<sub>pm</sub> at the relative pressure of 0.48–1.0. The specific surface area of the precursor reaches almost 90 m<sup>2</sup> g<sup>-1</sup>, but the alcohothermal treatment reduced it by ca. 2–3 times (30–40 m<sup>2</sup> g<sup>-1</sup>). However, the isotherms show high adsorption at high relative pressure (P/P<sub>0</sub>) range (approaching 1.0), indicating the formation of large mesopores and macropores. The pore size distribution curves (inset of Figure 3) present both mesopores (<13 nm size) and sufficient content of macropores (<100 nm size) in all analyzed samples, confirming a significant crystal growth (as seen in both FE-SEM and XRD analyses).
Next, the photocatalytic activity of all samples was investigated during hydrogen generation under UV/vis irradiation, and obtained data are shown in Figure 4. For comparison, the famous P25 photocatalyst with one of the highest photocatalytic activities among self-synthesized and commercial titania samples, and thus commonly used as a standard [21,34,35], was also analyzed. Interestingly, with an increase in water content during sample preparation, the activity of samples first increases, reaching the best performance for Et-6 mL sample, and then decreases. It should be pointed out that Et-6 mL sample does not exhibit best surface properties, i.e., not the largest BET area and not the smallest crystallites. Therefore, it is thought that PAR is detrimental for photocatalytic activity. It was proposed that, in the case of decahedral anatase particles, electrons and holes migrate to the opposite facets, and thus the “right” ratio between {001} and {101} is crucial [36–42]. Moreover, Yu’s group has proposed the formation of a “surface heterojunction” by exposing a certain proportion of {001} and {101} facets together, which could efficiently facilitate the charge carrier separation and thus significantly enhance the photocatalytic activity [32,33]. Interestingly, the sample prepared without ethanol addition, i.e., hydrothermal treatment (Et-60 mL), with the lowest PAR value exhibits the worst activity probably due to the low content of {001} facets and low crystallinity. It must be pointed out that the famous P25 photocatalyst is almost inactive, which is typical for titania samples for hydrogen evolution, as hydrogen molecules are efficiently formed on the surface of co-catalyst, e.g., platinum deposits [43–45]. Therefore, ca. 40 times higher activity of bare microballs (also without co-catalyst) indicates their high potential for photocatalytic reactions.
4. Conclusions

Monodisperse mesoporous microballs composed of decahedral anatase nanocrystals were successfully prepared by alcohothermal (ethanol with a small amount of water) process from mesoporous monodisperse microballs of amorphous titania, synthesized from solution of absolute ethanol, tetrabutyl titanate (TBOT) and potassium chloride via a sub-zero sol–gel route. It was found that alcohothermal treatment does not destroy an original sphere morphology. Moreover, a hierarchical structure was formed with decahedral anatase nanocrystals as nano-building blocks. It should be pointed out that faceted microspheres were prepared without addition of fluorine-compounds, commonly used for the preparation of titania with exposed facets, and thus the synthesis method could be classified as environmentally friendly. Moreover, faceted microballs show high UV/vis activity for hydrogen evolution without addition of any co-catalyst. The co-existence of both types of facets, i.e., \{001\} and \{101\}, hindering charge carriers’ recombination, and large size of microballs (micro), allowing easy and cheap recycling after reaction, indicate the high potential of faceted microballs for practical applications.

Author Contributions: Conceptualization, Z.W.; methodology, Z.W.; investigation, Y.C.; J.J.; resources, Z.W.; writing—original draft preparation, Y.C.; writing—review and editing, Z.W.; E.K.; visualization, J.J.; supervision, Z.W.; E.K.; funding acquisition, Z.W.; APC, E.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Natural Science Foundation of China (NSFC) (51802087 and 51004046), the Natural Science Foundation of the Hubei province of China (2019CFFB524 and 2010CDH05806), the Green Industry Leading Program of Hubei University of Technology (XJKY2021002), and “Yugo-Sohatsu Kenkyu” for an Integrated Research Consortium on Chemical Sciences (IRCCS) project from the Ministry of Education and Culture, Sport, Science and Technology-Japan (MEXT).

Data Availability Statement: The data presented in this study are available on request from corresponding author (Z.W.).

Conflicts of Interest: The authors declare no conflict of interest.


