Anatase TiO₂ Mesocrystals Enclosed by (001) and (101) Facets: Synergistic Effects between Ti³⁺ and Facets for Their Photocatalytic Performance

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Titanium dioxide (TiO₂), is among the most widely investigated materials for its unique properties and many promising applications in environmental and energy areas.^[1] Particularly, TiO₂ is extensively utilized in photocatalysis.^[1a,2] In general, the properties and operational performances of TiO₂ are strongly dependent on its crystal phase, crystallinity, morphology, surface area, and architecture.^[3] The structural integrity of the photocatalyst also plays an important effect on the photocatalytic activity of the photocatalysts.^[3] Defects in bulk and interface between subunit nanoparticles can affect the photocatalytic activity; this can be attributed to the capture of the photoinduced electrons and holes by the defects and the transfer block of the electrons and holes by the interface. Therefore, the construction of the architecture of the particles can control the photocatalytic activity.

In addition, for the same crystal phase and composites, such as anatase TiO₂ single crystal (SC), it is found that the photocatalytic activity of the TiO₂ is highly influenced by the (101)/(001) facet ratio.^[4] This can be contributed to the potential barriers of the reactions, which take place in the valence band and conduction band, and the arrangement of the atoms exposed on the various facets.^[3,5] Recently, it has been found that the average surface energy of anatase is $0.90~J\,m^{-12}~$ for $~(001)\,{>}\,0.53~J\,m^{-12}~$ for $~(100)\,{>}\,0.44~J\,m^{-12}~$ for (101), and it is expected that the higher surface energy (001)has higher chemical activities, and the (001) facet therefore is defined as the active facet.^[2f,3,6] More recently, however, Cheng and co-workers have proved that the photocatalytic reactivity order of (001), (010), and (101) is $(101) \approx (010) >$ (001) in their experiments.^[4]

TiO₂ mesocrystal (MC), a highly ordered superstructure of crystals with mesoscopic size (1-1000 nm), which exhibits identical scattering pattern and behavior in polarized light to TiO₂ SC, can be regarded as an intermediate species between TiO₂ nanopolycrystal (NPC) and TiO₂ SC.^[7] TiO₂ MC was firstly synthesized by topotactic conversion of NH4TiOF3 MC in the presence of nonionic surfactants.^[8] Re-

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cently, there have been some efforts towards the direct mesoscale assembly of TiO₂ MCs as well as their photocatalytic reactivities.^[9,10] In the mesoscale assembly processes, however, surfactants,^[8] organic additives,^[9b] solid surfactant^[9f] or hydrofluoric acid^[10b] were used. MCs can be used as catalyst, photocatalyst, sensor, and electrode materials.^[9] High porosity (or stacking defects) and high crystallinity are both required when aiming at the best performance.^[7] There have been few studies reported on the photocatalytic activity of TiO_2 MC. Furthermore, the photocatalytic activity of TiO_2 MC with controllable proportion of (101) and (001) facets has not been exploited yet. It is, therefore, highly desirable to study the photocatalytic activities of TiO2 MC with different (101)/(001) facet ratios.

We have found that the photocatalytic activities enhance with increasing (101)/(001) facet ratio when the TiO₂ MCs exhibit identical surface areas, crystallinity and structural integrity. It is shown that the photocatalytic activity of TiO_2 is determined by the synergistic effect between the Ti³⁺ and (101)/(001) facet ratio; the structural integrity of the composed subunits as well plays an important role on the photocatalytic activity of the TiO₂ MCs, compared with TiO₂ nanoparticles.

We have synthesized regular shaped TiO₂ MCs enclosed with different proportion of (001) and (101) facets by a facile green approach. The TiO₂ MCs were prepared by using formic acid (FA) and titanium isopropoxide (TTIP) as original reactants without any other additives and surfactants at 160°C, and the (101)/(001) ratio of TiO₂ MCs was controlled by facilely varying the solvothermal treatment periods. The obtained materials were denoted as MC-t, where t represents the solvothermal periods (t=1, 2, 4, 6, 8,10 h; see the Supporting Information). The TiO₂ NPC particles, as a reference sample, were also synthesized by a similar procedure, with the original molar ratio of TTIP/FA 1:8 (Figure S1 in the Supporting Information); the commercial photocatalyst, Degussa P25, was also used as a reference sample.

Typical field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) images of a mesocrystal sample (MC-4) are shown in Figure 1. The morphology of the sample is a highly truncated bipyramid with about 200 nm in thickness and 500 nm in length (Figure 1a). As can be seen from Figure 1b, the assemblies are composed of subunits of about 30-40 nm in diameter with similar shape to that of the assembly, which in-

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Figure 1. Representative images of TiO_2 MCs (MC-4): a), b) FESEM images; inset a) TiO_2 MC particle enclosed by (101) and (001) facets; c) TEM image; d) HRTEM image; insets: the SAED along the [001] zone axis.

dicates the formation of TiO₂ mesocrystals.^[11] Furthermore, an angle of 68.3° between the top and lateral facets (Figure 1 a, inset), which is consistent with the interfacial angle between the (001) and (101) facets, is observed on the assembly, suggesting that the assemblies are enclosed by (001) and (101) facets.^[2f] There are, however, some defects on the surface of the assembly particles, as shown in the FESEM images (Figure 1b); this is in agreement with the characteristics of mesocrystals.^[7] Nitrogen absorption/desorption analysis further shows the existence of micropores among the subunits in the assemblies (Figure S2a in the Supporting Information), which is also a characteristic of the mesocrystals.^[11] X-ray diffraction (XRD) patterns (Figure S2b in the Supporting Information) show that the obtained product (MC-4) is of anatase phase with high crystallinity (JCPDS No.: 21-1272). Further analysis of the peak broadening of (101) reflection by the Scherrer equation indicates the average crystal size of 38 nm, suggesting that the TiO₂ mesocrystal particles are composed of nanocrystal subunits.^[9e] The high resolution TEM (HRTEM) images further prove the formation of mesocrystals with high crystallinity, which is consistent with the XRD result. As shown in Figure 1d, the distance between the lattice fringe is 0.19 nm, corresponding to the (001) crystal planes, and the patterns of the selected area electron diffraction indexed as the [001] zone axis diffraction indicates that the top and bottom square surfaces are the (001) facets. The study on the morphology of MC-10 further proves the formation of TiO₂ mesocrystals. The HRTEM images of MC-10 reveal that the assemblies are composed of subunits (Figure S3 in the Supporting Information). The nanounits exhibit clear lattice fringes and the selected area electron diffraction (SAED) is distorted to a certain extent, showing that the distortions came from small mismatches between boundaries of the nanounits, which is a typical characteristic for mesocrystals.^[11] Mesocrystals with typical defects and inclusions, such as boundaries and surface defects, have been observed for various systems as kinetically metastable species or as intermediates in a crystallization reaction leading to single crystals.^[11]

To obtain the growth mechanism of the TiO_2 MCs, samples were collected and investigated at various reaction periods. When titanium tetraisoproxide was introduced dropwise into formic acid the transparent liquid immediately transformed into a milk-like suspension. The obtained products observed with TEM are composed of disordered amorphous nanoparticles (Figure 2a); the XRD as well confirms the amorphous phase of the obtained material (Figure S2b in



Figure 2. SEM images of products synthesized by solvothermal reaction of TTIP and FA for various periods: a) 1, b) 2, c) 4, d) 6, e) 8, and f) 10 h.

the Supporting Information). After solvothermal treatment for 2 h (Figure 2b), the morphology of the products converts into nanosheets, and anatase phase occurs as proven by XRD (Figure S2b in the Supporting Information). Highly truncated-bipyramid-shaped assemblies emerge when the solvothermal treatment time reaches 4 h (Figure 2c). As the solvothermal reaction period reaches 6 h (Figure 2d), the assembly particles grow continuously along the [001] direction, resulting in the decrease in the percentage of (001) facets and the increase of (101) facets. As solvothermal time is prolonged, the assemblies grow further along the [001] direction and eventually they grow into the bipyramid shaped particles at reaction time of 10 h (Figure 2e, f). The morphologies of the products at different intervals indicate that 4 h of reaction time is sufficient for the formation of mesocrystals and the TiO₂ MCs grow along the [001] zone axis.

On the basis of the above-experimental results, the possible scheme for the formation of TiO_2 MCs is shown in the Figure 3. At the initial stage (step A) of the reaction, the titanium formate complexes, an intermediate, are formed immediately via the coordination of FA to titanium centers by ligand exchange/substitution, and subsequently the Ti–O–Ti bonds are formed by both hydrolysis-condensation and non-hydrolytic condensation. The intermediates then convert into TiO₂ nanocrystals by a classical nucleation and nano-



Figure 3. Proposed formation scheme of the TiO₂ MCs.

crystal growth; meanwhile they are temporarily stabilized by the FA molecules, leading to the formation of leaf-like nanosheets by orientation force in FA (step B). $^{\left[9a,\,10a\right] }$ The nanosheets then undergo a mesoscale oriented self-assembly process during which the FA molecules should be preferentially attached onto the specific (101) surfaces of the nanosheets, and therefore lead to strongly anisotropic mutual interactions between them, accompanied with further crystallinity enhancements (step C). Up to this period, nucleation and crystallization are the dominant processes. As the reaction time is prolonged, more subunits preferably adhere to the (001) facets of the assemblies and the mesocrystals grow along the [001] direction; this leads to the formation of truncated bipyramid-like assemblies (step D), and eventually octahedral assemblies form, which can contribute to the high surface energy of the (001) surface, often leading to assembly into the oriented nanocrystals along the [001] direction (step E). The process includes nucleation at the initial period and non-classical growth, that is, particle-mediated formation of mesocrystals, which is similar to the growth process defined by Cölfen and Antonietti.^[11] In the growth process, the proportion of (001) facets decreases and that of (101) increases; FA plays a critical role in the formation of TiO₂ MC and acts as a binding molecule.

The proportion of the (101) facet can be readily adjusted by the variation of the solvothermal periods. At intervals of 4, 6, 8, and 10 h, it is shown that the obtained TiO_2 MCs have a (101)/(001) facet ratio of 60:40, 75:25, 88:12, 98:2, corresponding to MC-4, -6, -8, and -10, respectively (Table S1 in the Supporting Information).

Nitrosobenzene (NSB) is a relatively stable substrate at room temperature, and it can be reduced photocatalytically on TiO₂ into aniline in the absence of molecular oxygen by using isopropanol as sacrifice reagent, and it can also be oxidized photocatalytically into nitrobenzene (NB) in the presence of molecular oxygen (Scheme 1). Furthermore, these reactions facilitate the determination of the products. NSB, therefore, was selected as a probe molecule to examine the photocatalytic activity of the TiO₂ MCs. The reaction between NSB and molecular oxygen in the photocatalytic oxidation reaction of NSB to NB is performed by holes in the valence band of TiO₂. Simultaneously, the photocatalytic reduction of the molecular oxygen to hydrogen peroxide (water molecule) by electrons in the conduction band happens. In the photoreduction of NSB, the reaction between NSB and isopropanol was also carried out. The NSB is re-



photoreduction reaction <---> photooxidation reaction

Scheme 1. Photocatalytic reduction and oxidation reaction of NSB under different conditions.

duced photocatalytically into aniline by electrons, and the isopropanol is oxidized into acetone by holes. These photocatalytic reactions are presented in the Scheme 1. The photocatalytic reactivity was also characterized by hydroxylation of terephthalic acid (TA) to salicylic acid (TAOH) in aqueous suspensions containing different photocatalysts. The conversion of TA was used to evaluate the photocatalytic reactivity. The hydroxylation of TA to TAOH is a photooxidation reaction, in which molecular oxygen acts as an oxidation reagent.

X-ray photoemission spectroscopy (XPS) was used to investigate the chemical composition of the particle surface. The Ti 2p_{3/2} features were observed at 459.20 eV for samples (Figure 4a). These features are all well-assigned to Ti⁴⁺, and indicate that no Ti³⁺ exists on the surface (the XPS technique characterizes the top 1–10 nm depth of the particle).^[12] The presence of Ti³⁺ was further investigated by low temperature electron paramagnetic resonance (EPR; Figure 4b). No EPR signals appear for a g-value of about 2.02 corresponding to O₂⁻ produced from the reduction of adsorbed O₂ by surface Ti³⁺, further confirming the absence of surface Ti³⁺ as for the NPC and SC samples.^[13] However, for the MC samples, the signals for O_2^- and Ti^{3+} are observed (Figure 4b), indicating the presence of Ti³⁺ in the bulk of MC samples. The Ti³⁺ can be formed by the situ-reduction of Ti⁴⁺ by formic acid, which is as a reducing agent, in an anaerobic system. The obtained product is blue in color and displays a visible absorption (Figure S6 in the Supporting Information), which is attributed to the existence of Ti³⁺.^[14] The quantity of the Ti³⁺ can be increased as the solvothermal treatment period is prolonged (Figure 4b). Moreover, the intensities of these signals enhance with an increase in the proportion of the (101) facets; this suggests the linear correlation between concentration of Ti³⁺ and the proportion of (101) facet in this system.

The physical properties of the various TiO_2 MCs facilitate us to investigate the respective photocatalytic activities (Table S1 in the Supporting Information). Little variation in particle size and surface area exists among MC-4–MC-10; the crystallinities of the TiO₂ MCs hardly change (Figure S2b and Table S1 in the Supporting Information). The variation in photoactivity can be attributed to the distinct proportion of (001) and (101) facets in the TiO₂ MCs. TiO₂ MCs exhibiting a higher proportion of (101) facets possess higher photo-oxidation and photoreduction activities (Figure 5); this is similar to the TiO₂ SCs with the different



Figure 4. Core Ti 2p: a) XPS spectra, and b) EPR spectra of the $\rm TiO_2$ NPC, SC, and MC samples.

(001)/(101) facet ratios explored by Cheng et al.^[4] The photocatalytic activity of hydroxylation of TA is also higher using TiO₂ MCs with a higher proportion of (101) facets (Figure S4 in the Supporting Information). These results can be attributed to both surface atom distribution and surface electronic band structure.^[3,6] The (001) facet is considered as 100% unsaturated Ti5c, which theoretically results in higher photoreactivity of (001) than (101), whereas the (101) facet possesses 50% Ti5c and 50% saturated Ti6c.^[6,15] On the other hand, the TiO₂ MCs that have a higher percentage of (101) facets exhibit a higher conduction band minimum than that of the (001) facet, indicating that more strongly reductive electrons can be generated on (101) facets; the valence band is identical, showing the similar mobility of charge carriers (Figure S5 in the Supporting Information).^[4]

In addition, the hole-trapped probability on the (101) facet is higher than that of (001); this leads to a lower recombination of electron-hole on the (101) facet than (001), thus the photocatalyst possessing the higher proportion of (101) facet exhibits the higher photocatalytic activity.^[16] The



Figure 5. The photocatalytic activity of different TiO₂ MCs with various proportion of (001) and (101) facets; The photo-oxidation reaction was performed with nitrosobenzene (5.0 mM) and photocatalyst (1.0 gL^{-1}) under ultraviolet visible light irradiation.

existence of oxygen vacancies can shift the valence band maximum downwards as a result of band bending effects, as well as the introduction of Ti³⁺ defects in band gap, which facilitates the generation of strongly reductive electrons, as proved by EPR (Figure 4b).^[3,17] The Ti³⁺ in the bulk of TiO₂ MCs can be eliminated by calcination in the atmosphere and the color of the products alters from blue to white (Figure S6 in the Supporting Information). The crystallinity of the TiO2 MC after calcination does not alter evidently compared with the one before calcination. The photocatalytic activities of the TiO₂ MCs follow the same sequence (Figure S7 in the Supporting Information) and are lower than those of the corresponding unsintered samples. These results further confirm the existence of synergetic effect between Ti³⁺ and the (101)/(001) facet ratio. Consequently, the synergistic effects of the two factors are responsible for the higher photocatalytic activity of the TiO₂ MCs with higher proportion of (101) facets.

In addition, the normalized photocatalytic activity of TiO₂ is higher than that of TiO₂ NPC and P25 (Figure S8 in the Supporting Information). The highly ordered junction between the subunits of TiO₂ MCs plays a crucial role in the photocatalytic activity. The highly ordered subunits of TiO₂ nanoparticles assemble into TiO₂ mesocrystals and the crystal plane of (101) match well between the subunits (Figure S9 in the Supporting Information). The junctions should be more regular than that of TiO₂ NPC and P25 particles. The photoinduced electrons and holes can more readily migrate across the well-match junctions than in those irregular junctions in TiO₂ NPC and P25, and the holes migrate much faster than the excited electrons in the anatase phase; this reduces the recombination of holes and electrons, and thereby improves the photocatalytic activity.^[3,6] Additionally, the high degree of crystallinity of TiO₂ MCs is higher than that of NPC and P25; this is indicative of a lower concentration of bulk defects (oxygen and/or titanium vacancies) in the subunits of MCs, and leads to lower hole-electron recombi-

nation rate, and further results in the higher specific photocatalytic activity than that of NPCs.^[3] Therefore, it is reasonable that the photocatalytic activity of TiO_2 MCs is higher than that of NPCs with the identical normalized surface areas.

In summary, TiO₂ MCs have been synthesized by a facile green approach, with the use of TTIP and FA as the original reactants. The obtained TiO₂ MCs are enclosed by (001) and (101) facets, and the proportion of (101) facet can be tuned by adjusting the solvothermal periods. The TiO₂ MCs exposing a high proportion of (101) facets possess higher photocatalytic activity than those with a lower proportion; this can be attributed to the synergistic effect of Ti³⁺ and the proportion of (101) facets. In addition, the normalized photocatalytic activity of TiO₂ MCs is higher than that of NPCs when the proportion of (101) facets is equal; this indicates that the structural integrity of crystal plays a key role in the photocatalytic activity.

Experimental Section

Synthesis and characterization of TiO_2 mesocrystals: Formic acid (FA) and titanium isopropoxide (TTIP) were purchased from Alfa Aesar Company. The mesocrystal was fabricated by simple solvothermal treatment of a mixture of formic acid and titanium isopropoxide at 160°C, and the morphology of the TiO2 mesocrystals was controlled by variation of solvothermal treatment periods. In a typical synthesis, titanium isopropoxide (0.75 mL) was introduced dropwise into formic acid (50 mL) under vigorous stirring. The obtained milky suspension was transferred into a Teflon-lined autoclave (100 mL) and solvotreated at 160 °C for a desired period. The products were collected by centrifugation, washed with ethanol four times, dried at 60 °C in a vacuum box for 12 h. The obtained materials were denoted as MC-t, where t represents the solvothermal periods (t=1, 2, 4, 6, 8, 10 h). The TiO₂ nanopolycrystal (NPC) was synthesized in a similar procedure with a molar ratio of TTIP/FA 1:8. The morphology of the TiO₂ NPCs is shown in Figure S1 in the Supporting Information.

The morphology of obtained materials was characterized by field emission scanning electron spectroscopy (FESEM, Hitachi, 4300 and 4800) and high resolution transmission electron spectroscopy (HRTEM, Tecnai, F20). The crystal structure of the samples was recorded on an X-ray diffractometer (Advance Bruker Axs diffractometer with Cu_{Ka} irradiation, 40 kV and 100 mA). The BET surface areas of the samples were measured with a physical absorptometer (Tristar 3000, Micromeritics). The obtained photocatalytic reaction products were analyzed by gas chromatography/mass spectroscopy (Agilent 4975) and liquid chromatography/mass spectroscopy (Agilent 6310).

Photoactivity measurements: Photocatalytic oxidation activity was evaluated by photo-oxidation of nitrosobenzene in an aerobic TiO₂ suspension by using acetonitrile as a solvent. Photoreduction was examined by photoreduction of nitrosobenzene in an anaerobic TiO₂ suspension by using isopropanol as both solvent and sacrifice reagent. The original concentrations of nitrosobenzene and photocatalysts were 5.0 mmol L⁻¹ (mM) and 1.0 gL⁻¹, respectively. PLS-SXE-300/300UV (Trustech China) was used as a light source in the photocatalytic reactions and the distance between the reaction system and light lamp was 10 cm, and the light intensity was about 0.3 mWcm². Photocatalytic hydroxylation of terephthalic acid (TA) to salicylic acid (TAOH) was performed in an aqueous suspension containing different photocatalysts, the original concentration of TA was 0.5 mM and contained sodium hydroxide (2.5 mM), which favored the solubility of TA in water. The determination of conversion of TA was carried out by LC/MS (Aligent 6300).

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Let's facet it: TiO₂ mesocrystals (MCs; see figure) enclosed by (101) and (001) facets can be synthesized by a facile green approach and the ratio of (101)/ (001) can be tuned simply by adjusting the solvothermal periods. The photocatalytic activity of TiO_2 MCs exposing high proportions of (101) facets possess higher photocatalytic activity than those with lower one; this can be attributed to the synergistic effect of Ti^{3+} and the (101)/(001) facet ratio.



Catalysis

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