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Article

Effects of crystallinity, {001}/{101} ratio, and Au decoration on the photocatalytic activity of anatase TiO₂ crystals

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ABSTRACT

Anatase TiO₂ nanocrystals and sub-microcrystals with truncated octahedral bipyramidal morphologies were prepared by direct calcination of TiOF₂ precursors. The as-prepared TiO₂ samples were thoroughly characterized by X-ray diffraction, Raman spectroscopy, field-emission scanning electron microscopy, N₂ adsorption-desorption isotherms, X-ray photoelectron spectroscopy, and UV-visible diffuse spectroscopy. It was found that the crystallinity, grain size, and {001}/{101} ratio of the samples can be increased by raising the calcination temperature from 500 to 800 °C. The higher crystallinity and {001}/{101} facet ratio resulted in an increase in both aqueous and gas-phase photocatalytic activities, by inhibiting the recombination and separation of electrons and holes. After selecting two TiO₂ samples with high crystallinity and {001}/{101} ratio, Au nanoparticles were decorated on their surfaces, and the photocatalytic activity of the resulting samples under visible light illumination was studied. It was found that the visible light-induced photocatalytic activity increased by 2.6 and 4.8 times, respectively, upon Au decoration of the samples prepared by calcination of TiOF₂ at 700 and 800 °C.

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1. Introduction

TiO₂ has attracted great attention since the demonstration of its excellent photoelectrochemical activity for water splitting in 1972 [1]. Under light illumination, TiO₂ materials can be used for both renewable energy generation and pollutant degradation [2,3]. In addition, TiO₂ itself is a clean, stable, nontoxic, and low-cost material; hence, it is often used as a prototype material for photocatalytic applications [4–6]. These advantages highlight the importance of further studies aimed at

improving the photocatalytic activity or visible light utilization of TiO₂. Many factors, including crystalline structure [7], specific surface area [8], exposed facets [9–14], morphology [15–17], and defects [18,19], can affect the photocatalytic activity of TiO₂ materials. Surface decoration with noble metal nanoparticles [20–22] and doping [23–27] are the two main approaches used to enhance the visible light utilization of TiO₂ photocatalysis [28,29].

The photocatalytic activity of TiO₂ materials is associated with their crystallinities. It was shown that increasing the crys-

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tallinity of anatase TiO_2 (a- TiO_2) can result in an enhancement of its photocatalytic activity [30,31]. Synthesizing highly crystalline anatase TiO_2 or, equivalently, increasing the anatase-rutile transition temperature, appears as a suitable way to improve the photocatalytic properties of this material. It was shown that highly crystalline TiO_2 materials exhibit high photocatalytic activities for hydrogen generation and reactive brilliant red X3B degradation [20,32]. By using TiOF_2 as precursor, the presence of F^- ions can inhibit the anatase-to-rutile phase transition during the calcination process, and can thus be used to prepare highly crystalline anatase TiO_2 . Although TiOF_2 is often used as a precursor to prepare nanostructured TiO_2 materials [32–36], its role as a precursor of highly crystalline anatase TiO_2 and its effect on the photocatalytic properties have not been thoroughly investigated [31]. Controlling the $\{001\}/\{101\}$ ratio in anatase crystals is also important for enhancing the photocatalytic activity, owing to the roles of $\{001\}$ and $\{101\}$ exposed facets as hole and electron collectors, respectively, which can effectively promote the spatial separation of electrons and holes. In addition, the special surface heterojunction formed by $\{001\}$ and $\{101\}$ facets can further prevent the recombination between holes and electrons in the $\{001\}$ and $\{101\}$ surfaces, respectively [9]. Therefore, another attractive task involves the preparation of highly crystalline anatase TiO_2 crystals with controlled $\{001\}/\{101\}$ ratios. Because F^- ions are well-known surfactants limiting crystal growth along the $\{001\}$ direction, it is possible to obtain TiO_2 materials with the above features by direct annealing of TiOF_2 precursors.

Although intensive research has focused on TiO_2 for many years, its visible light utilization is still an important issue that needs to be resolved. Although new types of semiconductors such as $g\text{-C}_3\text{N}_4$ and Cu_2O -based materials [37–39] have attracted considerable attention in recent years, enabling the visible light utilization of TiO_2 materials in photocatalytic applications still represents a significant challenge. Although a highly crystalline structure may be beneficial to improve the UV light-induced photocatalytic applications of TiO_2 , the photocatalytic properties of these materials are still unresponsive to visible light; as a consequence, the preparation of highly crystalline TiO_2 with visible light activity represents an important goal. Surface decoration with noble metals [40] is an efficient way to enable the use of visible light by TiO_2 photocatalysts, due to the local surface plasmon resonance (LSPR) absorption [41]. In particular, gold is a viable choice for the decoration because of its remarkable light absorption at wavelengths around 550 nm. Even small amounts of Au decoration can provide intense absorption of visible light.

Herein, we first synthesized TiOF_2 materials by a traditional hydrothermal route; the samples were then calcined at different temperatures to obtain nanocrystals and sub-microcrystals of TiO_2 with different crystallinities and $\{001\}/\{101\}$ facet ratios. The relation of the photocatalytic activity with the crystallinity and the $\{001\}/\{101\}$ facet ratio was investigated. Au nanoparticles were also decorated on highly crystalline TiO_2 surfaces to enhance their photocatalytic activities in the visible region.

2. Experimental

2.1. Catalyst preparation

TiOF_2 precursors were prepared using a simple one-step hydrothermal method, using 15 mL titanium tetrabutoxide (TBOT) and 6 mL HF solution (40%) as raw materials, operating with great caution due to the strongly corrosive nature of the HF solution. The hydrothermal reaction was performed at 180 °C for 24 h. After being cooled to room temperature, the as-prepared TiOF_2 materials were washed several times with deionized water as well as alcohol, and then dried at 80 °C for further use. Finally, a- TiO_2 samples were synthesized by calcination of the as-prepared TiOF_2 at different temperatures for 2 h. The samples were labeled T0, T500, T600, T700, and T800, where the number denotes the calcination temperature. For example, T600 represents TiO_2 calcined from TiOF_2 at 600 °C.

The deposition-precipitation (DP) method [42] is a common approach used for decorating metal Au nanoparticles on TiO_2 surfaces. In particular, in our work, 1.5 mL of 0.1 mol L^{-1} HAuCl_4 solution was added to 1 g TiO_2 (T700 and T800) in 20 mL containers. Then, 10 mL water was added and the reactants were fully mixed by magnetic stirring. After that, the solution was kept in the dark at room temperature for 1 h to deposit Au nanoparticles. The precipitates obtained by filtering the suspensions were washed several times with deionized water and alcohol, followed by drying at 80 °C in air. The resulting samples were labeled Au-T700 and Au-T800.

2.2. Structural characterization

X-ray diffraction (XRD) patterns were obtained through a D8 Advance (Bruker, Germany) diffractometer using $\text{Cu K}\alpha$ irradiation with a scan rate of 0.02° s^{-1} . The phase compositions and relative crystallinities were determined from the XRD patterns. A Raman microscope spectrometer (InVia, Renishaw, England) was used to record the Raman scattering spectra. Brunauer-Emmett-Teller specific surface areas (S_{BET}) were measured using a multichannel surface area and porosity analyzer (TriStar II 3020, Micromeritics, USA). Surface morphologies were inspected by field-emission scanning electron microscopy (FESEM, Ultra Plus, Zeiss, Germany) with an acceleration voltage of 5 kV and a working distance of 4 mm. UV-vis diffuse reflectance spectra were recorded by an UV-vis spectrophotometer (UV-2600, Shimadzu, Japan). X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Scientific, USA) with an analyzer pass energy of 30 eV was used to determine the binding energies of the material surface.

2.3. Photocatalytic degradation of methylene blue (MB) and volatile organic compounds (VOCs)

2.3.1. Aqueous photocatalytic activity

A MB aqueous solution was chosen as target pollutant to evaluate the aqueous photocatalytic activity. A 0.1 g amount of TiO_2 powder was dispersed in a ϕ 60 mm glass container, followed by the addition of 15 mL of 1×10^{-5} mol L^{-1} MB solution.

The solutions containing TiO₂ powders were first placed in the dark for 1 h to reach adsorption-desorption equilibrium, after which the solutions were exposed to the UV light illumination provided by four UV fluorescent tube lamps with emission centered at 375 nm. The temperature and light intensity were kept at ~25 °C and ~4.5 mW cm⁻² in all experiments. To follow the changes in MB concentration, the UV-vis absorption spectra were monitored for 10 min using a UV-vis spectrometer (UV-2600, Shimadzu, Japan). The apparent rate constants (k_{app}) were evaluated by linearly fitting the time-dependent $\ln(C_t/C_0)$ parameter (where C_0 and C_t are the initial and reacted MB concentrations, respectively) according to quasi-first order kinetics.

2.3.2. Gas-phase photocatalytic activity

The gas-phase photocatalytic properties of the present materials were evaluated by studying the oxidation of formaldehyde and acetone, which are the main indoor pollutants harmful to human health [43]. A 0.1 g amount of TiO₂ powder was ultrasonically dispersed in a ϕ 60 mm glass container containing 10 mL deionized water and then dried at 80 °C in a dry box, to form a thin coating on the bottom of the glass container after removing water. Before the photocatalysis experiments, the sample was pretreated with UV light illumination for 24 h to remove surface carbonate contaminants. A photoacoustic multi-gas monitor (Model 1312, Innova Air Tech Instruments, USA) and a gas chromatograph (GC 2014, Shimadzu, Japan) were used to record the concentration of CO₂ generated from formaldehyde and acetone by the original and Au-decorated samples, respectively. The experimental device is shown in Scheme 1. Before starting the photocatalytic reactions, dry air was allowed to flow through the reactor for at least 10 min to drain out CO₂, until the CO₂ concentration was lower than 20 ppm. A 2 μ L aliquot of liquid formaldehyde was then injected into the reactor for photocatalytic oxidation. After dark adsorption for 30 min, an Hg lamp (SP9, Ushio, USA) was switched on to start the photocatalytic reaction under UV light illumination at 15 mW cm⁻² and 365 nm. The reaction temperature was maintained at 40 °C with a heater. The photocatalytic rate was estimated by linearly fitting the CO₂ evolution profiles. The photocatalytic oxidation of acetone by the Au/TiO₂ samples under

Scheme 1. Schematic diagram of the photocatalytic set-up for formaldehyde degradation.

visible light illumination was investigated following the same procedure, with the difference that a Xe lamp (PLS-SXE300, PerfectLight, China) was adopted as the light source using a 420 nm short-cut optical filter, which only allows the transmittance of long-wavelength light. The light intensity was adjusted to 270 mW cm⁻².

3. Results and discussion

3.1. Effect of crystallinity

The XRD patterns of the TiO₂ samples obtained from the calcination of TiOF₂ at different temperatures are shown in Fig. 1a, which also indicates the crystal planes corresponding to each peak [44]. The characteristic peaks of T0 match well with those of TiOF₂ (JCPDS No. 01-0490), which indicates the TiOF₂ phase of the hydrothermal product. On the other hand, all XRD peaks of the annealed samples correspond to diffractions of the anatase TiO₂ planes (JCPDS No. 99-0008), revealing that TiOF₂ transformed into the anatase TiO₂ phase after calcination. The weak peak observed for the sample calcined at 800 °C corresponds to the (110) diffraction of rutile TiO₂ (JCPDS No. 88-1175), which indicates that that rutile phase was also present in this sample. To confirm the presence of the rutile phase, Fig. 1b shows enlarged views of the T700 and T800 patterns in the 24°–28° region. Compared to that from the pure anatase

Fig. 1. (a) XRD patterns of samples T0 to T800; (b) Partially magnified XRD patterns of T700 and T800.

Table 1Summary of physical properties and photocatalytic activities of as-prepared TiO₂ samples.

Sample	Phase	Relative crystallinity	Size (nm)	S_{BET} (m ² g ⁻¹)	{001}/ {101}	k_{app} of MB (m ⁻² min ⁻¹)	k_{app} of HCHO (ppm m ⁻² min ⁻¹)
T0	Anatase	—	—	30.2	—	0.001	0.2
T500	Anatase	1	55.4	6.3	0.7%	0.026	17.8
T600	Anatase	1.16	66.4	6.2	8.4%	0.023	25.2
T700	Anatase	1.24	65.4	5.6	13.1%	0.032	36.4
T800	Anatase, Rutile	1.09	71.3	5.7	18.7%	0.030	27.7

phase of T700, a weak XRD peak at 27.5° arising from rutile TiO₂ can be clearly seen in T800. However, the amount of rutile phase is much lower than that of anatase phase. T500 was selected as reference sample with a relative crystallinity (RC) of 1, and the RC of the other samples was estimated based on the intensity of their {101} peak relative to that of T500. Table 1 shows that the RC increases with an increase in annealing temperature. The RC of T800 shows a slight decrease due to the phase transformation from anatase to rutile. The samples maintain an almost pure anatase structure at the calcination temperature of 800 °C, much higher than the 600 °C value generally associated with the transformation from anatase to rutile. F⁻ ions in the samples are considered to play an important role in inhibiting the anatase-to-rutile transformation [45], increasing the phase transition temperature by about 200 °C. The average sizes of anatase TiO₂ crystallites were estimated from the {101} peak using the Scherrer equation, which yielded values of 55.4, 66.4, 65.4, and 71.3 nm for the T500, T600, T700, and T800 samples, respectively. Because the presence of F⁻ ions favors the formation of {001} exposed facets, the ratios of {001} to {101} exposed facets were calculated and are shown in Table 1. In order to calculate the {001}/{101} ratio, a schematic diagram of the anatase TiO₂ structure [46] is shown in Fig. 3f.

Fig. 2a shows the Raman scattering spectra of the synthesized samples. The Raman peaks at 396.2, 515.0, and 638.2 cm⁻¹ reveal the formation of anatase TiO₂ after calcination, which is in full agreement with the analysis of the XRD patterns. These peaks correspond to the Raman-active B_{1g}, A_{1g}, and E_g lattice vibration modes, respectively. No Raman signals corresponding to the rutile phase were detected for the T800

sample; this is due to the very low amount of this phase, even though it was observed in the XRD patterns. The intensities of these peaks show a trend similar to that of the XRD patterns, with an initial increase with an increase in calcination temperature, followed by a slight decrease due to the phase transition in the T800 sample. In terms of the specific vibration modes involved, it has been reported [47] that the E_g, B_{1g}, and A_{1g} peaks mainly originate from the symmetric stretching vibration (SSV), symmetric bending vibration (SBV), and antisymmetric bending vibration (ABV) of O–Ti–O linkages, respectively. The {101} facets contain saturated 6c-Ti and 3c-O as well as unsaturated 5c-Ti and 2c-O sites, while the {001} facets only contain unsaturated 5c-Ti and 2c-O atoms. When the percentage of {001} facets increased, the intensity associated with the SSV mode decreased, while that of the SBV and ABV modes increased. The XRD analysis shows that the {001}/{101} ratios tend to increase with an increase in calcination temperature, which may also affect the Raman spectra. Fig. 2b shows the normalized Raman scattering spectra of the samples, with the insets displaying partially enlarged view of the B_{1g} (396.2 cm⁻¹) and A_{1g} (515.0 cm⁻¹) peaks. The figure does not show a regular variation in the intensity of the E_g mode relative to that of the A_{1g} and B_{1g} modes, which may be due to the low percentage of exposed facets. Increasing crystallinity and {001}/{101} ratios result in an increase in the intensity of the B_{1g} mode (396.2 cm⁻¹) relative to that of the A_{1g} mode (515.0 cm⁻¹). The T0 sample does not show any Raman signals, due to its TiOF₂ form.

Figs. 3a–e show the FESEM images of T0, T500, T600, T700, and T800, respectively. Fig. 3a shows that TiOF₂ exhibits an irregular morphology and multiple crystal sizes. The calcined samples show the presence of truncated octahedral bipyramids

Fig. 2. As-measured (a) and normalized (b) Raman spectra of samples T0, T500, T600, T700, and T800.

Fig. 3. SEM images of samples T0 (a), T500 (b), T600 (c), T700 (d), and T800 (e); (f) Schematic diagram of truncated octahedral bipyramids.

with high-energy $\{001\}$ facets, indicating the transformation from TiOF_2 to anatase. The formation of the regular truncated octahedral bipyramids is ascribed to the presence of F^- ions during the calcination process; these ions have been reported to be effective capping agents to form the exposed $\{001\}$ facets [48]. As the calcination temperature increases from 500 to 800 °C, the ratio of truncated octahedral bipyramids to irregular particles increases. When the calcination temperature increases to 800 °C, Fig. 3e shows that the truncated octahedral bipyramids become smooth and unclear compared to those of the other calcined samples. The grain size distributions of the samples are not uniform and their sizes increase with an increase in temperatures, in good agreement with the XRD analysis. The S_{BET} values and other properties of the as-prepared samples are shown in Table 1. A rapid decrease in S_{BET} is observed when TiOF_2 transforms into anatase. In the case of the TiO_2 materials, the calcination temperature cannot have a strong impact on the S_{BET} values, although the grain size shows a clear increase, which may be due to the aggregation of TiO_2 particles. The T700 sample shows the most regular morphology in the form of truncated octahedral bipyramids, despite the different sizes

of its particles.

The UV-vis diffuse reflectance spectra of the samples are shown in Fig. 4. The Tauc plots of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ shown in the inset of the figure were used for estimating the bandgap energies. The transformation from TiOF_2 to anatase TiO_2 is accompanied by a clear red shift of the optical absorption edges. However, the absorption edges hardly change with the calcination temperature when the samples are in the anatase phase. The estimated bandgap energies of TiOF_2 (3.10 eV) and anatase TiO_2 (3.04 eV) are indicated in the inset of Fig. 4. The bandgap energy of the anatase TiO_2 phase is lower than its theoretical value of 3.2 eV, possibly due to the effect of F^- ions, which has been theoretically [49] and experimentally [50] proved. The T800 sample shows an increased intensity between 380 and 420 nm, attributed to the existence of a small amount of rutile, which is a direct bandgap material. The UV-vis diffuse reflectance results are in good agreement with the XRD and Raman analyses.

Fig. 5a shows the time dependence of $\ln(C_0/C_t)$ during the photocatalytic degradation of MB under UV light illumination of the T0, T500, T600, T700, and T800 samples. TiOF_2 shows the lowest photocatalytic activity, while the calcined samples present much higher activity. The k_{app} values of the different samples, normalized to the S_{BET} values, were estimated from Fig. 5a and are shown in Fig. 5b. The figure shows that the photocatalytic activity for the photodegradation of MB aqueous solutions is not significantly affected by the crystallinity. The T700 material shows the highest photocatalytic activity among the investigated samples.

Fig. 6a shows the CO_2 evolution profiles during the photocatalytic oxidation of formaldehyde under UV light illumination, which exhibit an almost linear increase in the CO_2 amounts. Fig. 6b shows the increasing trend of the rate constants of CO_2 evolution, normalized to the S_{BET} values. The data corresponding to commercial P25 is also shown for comparison. As shown in the figure, the photocatalytic activity of the calcined samples first increases with the calcination temperature, and then decreases for the T800 sample. The T700 presents the best photocatalytic activity among all calcined sam-

Fig. 4. UV-vis diffusion reflectance spectra of T0–T700 samples; the inset shows the corresponding plots used to calculate the bandgaps.

Fig. 5. (a) MB degradation profiles under UV light irradiation and (b) corresponding k_{app} values measured for samples T0, T500, T600, T700, and T800.

Fig. 6. (a) CO₂ evolution curves during UV light-induced photocatalytic oxidation of formaldehyde and (b) corresponding k_{app} values measured for samples T0, T500, T600, T700, and T800.

ples, whereas TiOF₂ shows the lowest activity due to the absence of the anatase phase. After taking the specific surface area into account, the activity of all as-prepared TiO₂ samples is higher than that of commercial P25, measured under the same experimental conditions. The k_{app} value of T700 is about six times higher than that of commercial P25, which denotes a substantially improved performance in the degradation of formaldehyde.

3.2. Effect of Au decoration

Fig. 7 shows the UV-vis diffuse reflection spectra of the T700 and T800 samples and of their Au-decorated counterparts. The inset shows a partial magnification of the curves in Fig. 7. The absorption peaks at ~595 nm for T700 and Au-T800 are ascribed to the local surface plasmon resonance of Au nanoparticles, which shows that metal Au nanoparticles were successfully loaded on the TiO₂ samples, resulting in their absorption in the visible region.

In addition, the XPS technique was used to determine the surface chemical composition of the Au-TiO₂ samples and confirm the presence of metallic Au. Figs. 8a–d show the O 1s, Ti

2p, C 1s, and Au 4f core-level XPS spectra of Au-T700 and Au-T800. The C 1s peaks shown in Fig. 8c arise from contamination from surface carbonate, which was used as reference for the XPS calibration. According to Chen's work [51], the O 1s, Ti 2p_{3/2}, and Ti 2p_{1/2} peaks located around 530, 459, and 465 eV,

Fig. 7. UV-vis diffuse reflectance spectra of T700, T800, Au-T700, and Au-T800 samples, with partial magnifications shown in the inset.

Fig. 8. O 1s (a), Ti 2p (b), C 1s (c), and Au 4f (d) core-level XPS spectra of Au-T700 and Au-T800 samples.

respectively, are attributed to the lattice O^{2-} and Ti^{4+} ions. The additional O 1s peaks at 531.8 eV (Au-T800) and 531.0 eV (Au-T700) are ascribed to the hydroxyl (OH^-) species on the TiO_2 surface [52]. The Au 4f peaks located at binding energies around 86 eV (Au $4f_{5/2}$) and 83 eV (Au $4f_{7/2}$) reveal the presence of metallic Au on the TiO_2 surface [53]; the Au/Ti atomic ratios were calculated to be 1.0% for Au-T700 and 0.3% for

Au-T800. The different location of the Ti 2p, O 1s, and Au 4f peaks in the Au-T700 and Au-T800 samples is due to their different annealing temperature.

Figs. 9a and b show the CO_2 evolution profiles of TiO_2 and Au/ TiO_2 samples under visible light illumination and a comparison between the CO_2 evolution rate constants of the two samples, respectively. The non-decorated samples show very

Fig. 9. (a) CO_2 evolution curves from visible light photocatalytic oxidation of acetone and (b) corresponding k_{app} values measured for samples T700, T800, Au-T700, and Au-T800.

Scheme 2. (a) Schematic diagram for the separation of UV light-induced electrons and holes on {001} and {101} facets and (b) separation of visible light-induced electrons and holes in Au-decorated TiO₂.

low photocatalytic activities, which substantially increase after Au decoration. In particular, the photocatalytic activities of T700 and T800 increase by 2.6 and 4.8 times, respectively, after Au modification. This Au-induced visible photocatalytic activity is likely due to the local surface plasmon resonance absorption of Au nanoparticles.

3.3. Proposed mechanism

The observed increase in photocatalytic activity with an increase in calcination temperature may be due to two reasons. First, the higher crystallinity may inhibit the electron-hole recombination; second, the increase in the {001}/{101} ratios is another important factor, as shown in Scheme 2a. The FESEM images highlight the increased proportion of truncated octahedral bipyramidal structures with an increase in calcination temperature. In addition, the XRD analysis also shows an increase in the {001}/{101} ratio with an increase in calcination temperature. Because the surface energies of the {001} and {101} facets (0.90 and 0.44 J m⁻², respectively) are different [54], electrons tend to assemble on the low-energy {101} facets while holes transfer to the high-energy {001} facets, which favors the separation between holes and electrons. In photocatalysis, the consumption of electrons by O₂ leads to chemisorbed O₂⁻ species [55], which are considered important reactive oxygen species for organic oxidation. However, if the electron and hole accumulation sites are not well separated from each other, the generated O₂⁻ species can be consumed by holes on the TiO₂ surface, resulting in the desorption of gaseous O₂. Therefore, the coexistence of {001} and {101} facets can reduce the probability for holes to consume O₂⁻ species through the separation of electrons and holes into different facets, finally resulting in an enhanced photocatalytic activity. It is worth noting that Yu and coworkers [9] suggested the existence of a heterojunction between the {001} and {101} facets, belonging to the traditional heterojunction type, whose occurrence in a crystal is caused by the presence of two energy states. The presence of this heterojunction enables further separation of electrons and holes accumulated in different facets.

The above results show that the Au decoration accelerates the degradation of acetone in TiO₂ samples, compared to that in the undecorated materials. The visible light-induced photo-

catalytic mechanism is illustrated in Scheme 2b. The local surface plasmon resonance absorption of the decorated Au nanoparticles can result in the generation of hot electrons. The latter can move to the conduction band (CB) of TiO₂ and reduce O₂ to O₂⁻, which is one of the factors promoting the photocatalytic oxidation of acetone. In addition, the hot holes left behind in the excited Au nanoparticles could accept electrons from the organic species and also lead to acetone oxidation. Owing to these reasons, Au decoration can enhance the photocatalytic activity under visible light illumination.

4. Conclusions

Highly crystalline anatase TiO₂ crystals were prepared by direct calcination of TiOF₂ precursors obtained through a simple hydrothermal method. The present systematic investigations show that a higher crystallinity can improve the UV light-induced photocatalytic activity toward both liquid MB solutions and gaseous formaldehyde. The F⁻ ions result in the formation of truncated octahedral bipyramidal morphologies after calcination; the increase in {001}/{101} ratio with the calcination temperature is considered beneficial for the separation of light-induced carriers and also contributes to enhancing the photocatalytic activity. The highly crystalline anatase TiO₂ samples decorated with Au, labeled T700 and T800, show 2.6 and 4.8 times higher photocatalytic activities, respectively, under visible light illumination compared to their undecorated counterparts. Our results indicate that combining high crystallinity and surface decoration may be a promising way to improve the visible photocatalytic properties of TiO₂ materials.

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Graphical Abstract

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Effects of crystallinity, {001}/{101} ratio, and Au decoration on the photocatalytic activity of anatase TiO₂ crystals

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The photocatalytic activity of anatase TiO₂ materials prepared by calcination of TiOF₂ can be substantially improved by increasing their crystallinities and {001}/{101} ratios; moreover, Au decoration can effectively enhance the visible light-induced photocatalytic activity.

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结晶度, {001}/{101}晶面比和Au负载对热处理TiOF₂制备的锐钛矿TiO₂光催化活性的影响

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摘要: TiO₂半导体由于具有清洁、无毒光催化性能优异和热稳定性好等优点, 一直是光催化理论及应用研究的一个热点材料, 但其较宽的禁带宽度(金红石3.0 eV, 锐钛矿3.2 eV)和较快的光生载流子复合速率限制着其进一步应用. 在本研究中, 我们通过直接煅烧TiOF₂前体成功制备出具有截断八面体形貌的锐钛矿TiO₂纳米及亚微米晶体, 并采用现代测试方法综合分析了煅烧温度对其结晶度、{001}/{101}晶面比例以及光催化性能的影响, 然后以高结晶度的TiO₂样品负载Au, 进一步探讨了负载Au对其可见光催化活性的提升.

X射线衍射图谱(XRD)和拉曼光谱表征结果表明, 未煅烧的样品为TiOF₂, 在700 °C以下煅烧的样品均呈纯锐钛矿相, 而800 °C煅烧的样品出现了少量金红石相, 表明以TiOF₂为前体制备的TiO₂锐钛矿相向金红石相的转变温度明显高于常规TiO₂材料. 同时, XRD峰强度随煅烧温度升高而增大, 表明样品结晶度提高, 因而我们认为700与800 °C煅烧的样品结晶度较高, 而且保持了纯的或大量的锐钛矿物相. 根据XRD谱得到的{001}与{101}晶面方向的平均尺寸计算了{001}/{101}晶面比例. 结果显示, 随着煅烧温度提高, {001}/{101}晶面比例增大. 通过场发射扫描电子显微镜观察到煅烧的样品具有较规则的截断八面体双锥形貌, 煅烧温度越高, 形貌越规则, 颗粒尺寸越大. N₂吸附-解吸等温线测试结果显示, 煅烧后样品的比表面积低于未煅烧的TiOF₂, 原因是煅烧后的样品团聚现象比较严重. 紫外-可见漫反射光谱显示煅烧样品的吸收边相比于未煅烧的TiOF₂发生明显红移. 不同样品在紫外光下降解甲基蓝与甲醛的性能研究表明, 700 °C煅烧的样品具有最高的光催化活性, 这可归因于其较高的结晶度及纯的锐钛矿相结构.

对于负载Au的高结晶度TiO₂样品(Au-T700和Au-T800), 紫外-可见漫反射光谱中在597 nm处出现了Au的等离子吸收峰, X射线光电子能谱中86与83 eV处Au 4f峰的出现也表明Au成功负载在材料表面. 丙酮可见光催化降解实验表明, 相比于未负载的700和800 °C下煅烧TiOF₂制备的TiO₂, 负载Au的样品的催化活性分别提高了2.6和4.8倍.

综上所述, 通过升高煅烧温度可提高TiO₂的结晶度、晶粒尺寸和{001}/{101}晶面比例. 而结晶度和{001}/{101}晶面比例的提高可以抑制电子和空穴的复合, 从而提高TiO₂液相和气相光催化活性. 在具有最高结晶度和{001}/{101}晶面比例的TiO₂上负载, 后其可见光催化活性进一步提高.

关键词: 高结晶度; 锐钛矿二氧化钛; 高能晶面; 金负载; 光催化

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