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Highly photoreactive TiO₂ hollow microspheres with super thermal stability for acetone oxidation

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ABSTRACT

TiO₂ hollow microspheres (TiO₂-HMSs) have attracted much attention because of their high photoreactivity, low density, and good permeability. However, anatase TiO₂-HMSs have poor thermal stability. In this study, surface-fluorinated TiO₂-HMSs were assembled from hollow nanoparticles by the hydrothermal reaction of the mixed Ti(SO₄)₂-NH₄HF-H₂O₂ solution at 180 °C. The effect of the calcination temperature on the structure and photoreactivity of the TiO₂-HMSs was systematically investigated, which was evaluated by photocatalytic oxidation of acetone in air under ultraviolet irradiation. We found that after calcination at 300 °C, the photoreactivity of the TiO₂-HMSs decreases from 1.39 × 10⁻³ min⁻¹ (TiO₂-HMS precursor) to 0.82 × 10⁻³ min⁻¹ because of removal of surface-adsorbed fluoride ions. With increasing calcination temperature from 300 to 900 °C, the building blocks of the TiO₂-HMSs evolve from truncated bipyramidal shaped hollow nanoparticles to round solid nanoparticles, and the photoreactivity of the TiO₂-HMSs steady increases from 0.82 × 10⁻³ to 2.09 × 10⁻³ min⁻¹ because of enhanced crystallization. Further increasing the calcination temperature to 1000 and 1100 °C results in a decrease of the photoreactivity, which is ascribed to a sharp decrease of the Brunauer–Emmett–Teller surface area and the beginning of the anatase–rutile phase transformation at 1100 °C. The effect of surface-adsorbed fluoride ions on the thermal stability of the TiO₂-HMSs is also discussed.

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1. Introduction

Semiconductor photocatalysis has attracted much attention because of its potential applications in solving the problems of environmental pollution and energy shortage, such as photocatalytic degradation of organic pollutants [1–4], H₂ production by photocatalytic water splitting [5–7], photocatalytic reduction of CO₂ [8–11], and dye-sensitized solar cells [12]. TiO₂ is a typical semiconductor photocatalyst, and is the most studied

photocatalytic material because of its excellent semiconducting properties, low cost, non-toxicity, and long-term stability [13–18]. In nature, TiO₂ mainly exists in three crystal forms: anatase, rutile, and brookite, of which rutile is the most stable form [19]. It is generally accepted that the photoreactivity of anatase TiO₂ is much higher than that of rutile, although some studies have reported a higher photoreactivity for rutile TiO₂ than anatase. Investigation of brookite TiO₂ is limited because pure brookite TiO₂ is difficult to synthesize [20].

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Several research groups have recently investigated hollow structured TiO_2 , such as TiO_2 hollow microspheres (TiO_2 -HMSs) [12,21–30]. This is because TiO_2 -HMSs have high reactivity, low density, and good permeability, and are easy to recycle [31–34]. However, highly photoactive anatase TiO_2 transforms to the less reactive rutile phase at temperatures higher than 600 °C under normal conditions, which limits the commercial applications of TiO_2 -HMSs in high temperature situations [35]. Doping TiO_2 with metal ions to improve the thermal stability of anatase TiO_2 has been investigated. For example, Shutilov *et al.* [36] prepared Al-doped anatase TiO_2 nanoparticles by incipient-wetness impregnation of xerogel (anatase) with *tert*-butyl aluminum solution, and they retained the anatase phase even when calcined at 950 °C. However, a trace amount of Al_2O_3 also formed during calcination. Kumari *et al.* [37] showed that the thermal stability of anatase TiO_2 nanoparticles could be improved by using 1-thioglycerol as a capping agent during preparation. However, the thermal stability of the TiO_2 nanoparticles only improved from 500 to 650 °C.

Non-metal ion dopants, such as S [38], N [39], and F [35,40,41], have also been used to increase the anatase–rutile phase transformation temperature, among which fluoride is effective for obtaining high thermal stability anatase TiO_2 . According to the study of Yu *et al.* [42], the presence of fluoride ions can efficiently prevent the anatase–rutile phase transformation. Pillai and co-workers [43] prepared high thermal stability anatase TiO_2 (up to 900 °C) with high photocatalytic activity using trifluoroacetic acid. Retention of the anatase phase at high temperatures was attributed to the presence of small amounts of fluorine in the lattice. Our group prepared high thermal stability anatase TiO_2 nanosheets with exposed high energy (001) facets, which were prepared by the hydrothermal reaction of a mixed solution of tetrabutyl titanate and hydrofluoric acid [35]. The high thermal stability of the anatase TiO_2 nanosheets was attributed to the strongly adsorbed fluoride ions on the surface. However, fabrication of highly photoreactive TiO_2 -HMSs with high thermal stability has not been reported.

In this study, TiO_2 -HMSs were prepared by hydrothermal treatment of a mixed $\text{Ti}(\text{SO}_4)_2\text{-NH}_4\text{F-H}_2\text{O}_2$ solution according to our previously reported method [44]. Considering that surface-fluorinated TiO_2 -HMSs should possess high thermal stability, the effect of the calcination temperature on the structure and photocatalytic activity of the as-prepared TiO_2 -HMSs was investigated, where the photocatalytic activity was evaluated by photocatalytic oxidation of acetone under ultraviolet (UV) irradiation.

2. Experimental

2.1. Sample preparation

The surface-fluorinated TiO_2 -HMS precursor was prepared in the presence of fluoride ions according to our previously reported method [44]. First, 7.5 mmol of $\text{Ti}(\text{SO}_4)_2$ and 7.5 mmol of NH_4F were dissolved in 65 mL of water under magnetic stirring. Second, 10 mL of H_2O_2 (30 wt%) was added dropwise into

the mixed solution. Third, the dark-brown solution that formed was transferred to a 100-mL Teflon-lined autoclave and maintained at 180 °C for 3 h. After cooling to room temperature, the precipitate was collected, washed with distilled water, and then dried in a vacuum oven.

The obtained white powder (TiO_2 -HMS precursor) was then calcined at different temperatures (300–1100 °C) for 2 h. For simplicity, the samples are denoted Tx, where x is the calcination temperature (see Table 1).

2.2. Characterization

X-ray diffraction (XRD) was performed with a D8 Advance X-ray diffractometer (Bruker, Germany). The accelerated voltage and applied current were 15 kV and 20 mA. The morphology and structure of the samples were characterized by field emission scanning electron microscopy (FE-SEM, s-4800, Hitachi, Japan) with an acceleration voltage of 10 kV and transmission electron microscopy (TEM, Tecnai G20, USA) with an acceleration voltage of 200 kV. The nitrogen adsorption–desorption isotherms were obtained with an ASAP 2020 accelerated surface area and porosimetry system (Micromeritics Instruments, USA). All of the samples were degassed at 150 °C prior to the measurements. The Brunauer–Emmett–Teller (BET) specific surface area (A_{BET}) was determined by the multipoint BET method and the pore size distribution was obtained by the Barrett–Joyner–Halenda method. The nitrogen adsorption volume at $P/P_0 = 0.994$ was used to determine the pore volume and average pore size. The UV–visible (UV–vis) diffuse reflectance spectra were obtained with a UV–vis spectrophotometer (LambdaBio 35) using BaSO_4 as the reference. The surface chemical state of the samples was analyzed by X-ray photoelectron spectroscopy (XPS) using a Multilab 2000 XPS system with a monochromatic Al source and a charge neutralizer. All of the binding energies were referenced to the C 1s peak of surface adventitious carbon at 284.4 eV.

2.3. Photocurrent measurements

The photocurrent measurements were performed with an Electrochemical Station 5 (CHI660D, China). A 3-W light-emitting diode (LED) lamp mainly emitting at 365 ± 5 nm was used as the light source for excitation of the FTO/ TiO_2 electrode. The measurements were performed with a standard three-electrode assembly. The FTO/ TiO_2 electrode, a Pt plate, and a saturated calomel electrode (SCE) electrode were used as the working, counter, and reference electrodes, respectively. The FTO/ TiO_2 electrode was prepared using the as-prepared TiO_2 sample as the TiO_2 precursor by the doctor-blade method. Na_2SO_4 solution (0.4 mol L^{-1}) was used as the electrolyte and saturated with air.

2.4. Photocatalytic oxidation of acetone

The photocatalytic activities of the TiO_2 -HMSs were evaluated by photocatalytic mineralization of gaseous acetone under UV light irradiation in a 15-L reactor at ambient temperature

Table 1

Physical properties of the photocatalyst.

Sample	Calcination temperature (°C)	Phase ^a	A_{BET}^b (m ² g ⁻¹)	PV ^b (cm ³ g ⁻¹)	APS ^b (nm)	CS ^c (nm)	R_c ^d
Precursor	—	A	20.8	0.11	21.7	79.0	1.00
T300	300	A	15.1	0.09	23.4	78.5	0.98
T500	500	A	11.4	0.07	21.4	79.8	1.12
T700	700	A	10.7	0.06	24.6	82.9	1.31
T900	900	A	10.0	0.05	25.9	84.4	1.38
T1000	1000	A	7.6	0.04	22.3	97.7	1.53
T1100	1100	81.6(A) 18.4(R)	3.2	0.01	11.4	93.7(A) 74.3(R)	0.95

^a A and R represent the anatase and rutile phase.^b BET surface area, pore volume, and the average pore size of the photocatalyst.^c Crystalline size of the photocatalyst according to Scherrer equation.^d Relative crystallinity of the photocatalyst based on the peak intensity of anatase (101) using TiO₂-HMSs precursor as the reference.

[35]. The prepared TiO₂-HMS samples (0.3 g) were first dispersed in 30 mL of double distilled water. The dispersions were then evenly transferred into three culture dishes with diameters of 7.0 cm. The TiO₂ samples were dried in an oven at 80 °C for about 2 h to evaporate water and then cooled to room temperature before use. After the dishes coated with TiO₂ powder were placed in the reactor, 10 μ L of acetone was injected into the reactor with a microsyringe. The acetone vapor was allowed to reach adsorption-desorption equilibrium with the catalyst in the reactor prior to UV light irradiation. The concentrations of acetone and CO₂ in the reactor were determined online by an INNOVA 1412 Photoacoustic IR Multigas Monitor (Air Tech Instruments). The initial concentration of acetone after reaching the adsorption equilibrium was about 300 ppm, which remained constant for about 5 min before UV lamp irradiation (15 W at 365 nm). Each set of experiments was performed for 120 min. The photocatalytic activity of the powders was evaluated by comparing the apparent pseudo-first-order reaction rate constant (K_{app}) based on $\ln(C_0/C) = k_{\text{app}}t$, where k_{app} is the apparent reaction rate constant, and C_0 and C are the initial and reaction concentrations of acetone, respectively.

3. Results and discussion

3.1. Phase structure

The structure is one of the most important factors that affects the photocatalytic activity of semiconductor photocatalysts. XRD was performed to investigate the changes of the phase structure and crystallite size of the TiO₂-HMSs with the calcination temperature. Fig. 1 shows the XRD patterns of the TiO₂-HMS precursor and TiO₂-HMS samples calcined at various temperatures. In the XRD pattern of the TiO₂-HMS precursor, there is a sharp peak at $2\theta = 25.3^\circ$ corresponding to the (101) plane diffraction of anatase TiO₂, indicating that it has good crystallinity [45,46]. After calcination at temperatures from 300 to 1000 °C, the peak intensities of anatase increase, which indicates enhancement of crystallization. From Table 1, the average crystalline size steady increases from 79.0 to 97.7 nm and the relative crystallinity of the nanocrystals increases from 1.00 to 1.53 with increasing calcination temperature from 300 to 1000 °C. However, with a further increase of the calcination

temperature to 1100 °C, a small peak at $2\theta = 27.4^\circ$ appears for the T1100 sample, which correspond to the (110) plane diffraction of rutile TiO₂ [41,47]. This indicates that anatase-rutile phase transformation begins at about 1100 °C. At this temperature, 18.4% of the anatase TiO₂ transformed to the rutile phase.

Anatase TiO₂ usually begins to transform to the low photo-reactivity rutile phase at about 600 °C [48,49]. However, in the present study, the prepared TiO₂-HMS precursor shows very high thermal stability with an anatase-rutile phase transformation temperature as high as 1100 °C, indicating that the TiO₂-HMSs can be used in high-temperature environments.

3.2. Morphology evolution

Evolution of the morphology of the TiO₂-HMSs with the calcination temperature can be clearly seen in the corresponding scanning (Fig. 2) and transmission electron microscopy images (Fig. 3). The hollow interior of the TiO₂-HMS precursor is shown in Fig. 2(a), which shows that the hollow microspheres are composed of hollow truncated bipyramidal nanoparticles, indicating exposure of high energy (001) facets [50]. Lu and co-workers [51] reported synthesis of anatase TiO₂ microcrystals with 47% (001) facets on the surface by reversing the rela-

Fig. 1. XRD patterns of the photocatalysts for TiO₂-HMSs calcined at different temperatures, together with the expected diffraction peaks for anatase (AT) and rutile (RT) TiO₂.

Fig. 2. SEM images of TiO_2 -HMSs precursor (a and b) and the samples calcined at 300 °C (c, d), 900 °C (e, f) and 1100 °C (g, h) for 2 h. Arrows indicating the presence of nanopores.

tive stabilities of the (101) and (001) facets by doping with fluoride ions [51]. Therefore, it is not unusual to obtain TiO_2 -HMS assemblies from nanoparticles with exposed (001) facets. Formation of the hollow interior of the TiO_2 nanoparticles may be because of etching by fluoride ions [52].

With increasing calcination temperature from 300 to 1100 °C, the morphology of the hollow microspheres remains almost unchanged. However, the shape of the building blocks evolves from hollow truncated bipyramidal nanoparticles to solid nanospheres. It has been reported that almost all of the surface-adsorbed fluoride ions can be removed by calcination at 500 °C [51,53]. Therefore, the exposed high energy (001) facets of the TiO_2 nanoparticles disappear after calcination at high temperature, and the particles evolve into solid nanospheres to reduce the surface energy. Even after calcination at 1100 °C, the hollow microstructure of the photocatalyst is still clearly observed (Figs. 2(g) and (d)), further indicating the thermal stability of the TiO_2 -HMSs.

3.3. Nitrogen adsorption–desorption

The BET surface area and pore structure are important parameters that affect the photoreactivity of photocatalysts. Fig. 4

Fig. 3. TEM images of TiO_2 -HMSs for precursor (a), T300 (b), T900 (c), and T1100 (d). Inset of (a) showing the porous structure of the nanoparticles.

shows the nitrogen adsorption–desorption isotherms and corresponding pore size distribution curves of the TiO_2 -HMS samples. The isotherm of the TiO_2 -HMS precursor is type IV (Brunauer, Deming, Deming, and Teller classification) with a hysteresis loop at high relative pressures between 0.6 and 1.0, suggesting the presence of mesopores and macropores [54]. The corresponding pore size distribution (Fig. 4(b)) has a wide range from 4 to ca. 100 nm. The BET surface area and pore volume of the anatase TiO_2 -HMS precursor before calcination are 20.8 $\text{m}^2 \text{g}^{-1}$ and 0.11 $\text{cm}^3 \text{g}^{-1}$, respectively. The nanopores (or generation of hysteresis loops) are from aggregation of nanoparticles and the hollow interiors of the truncated bipyramidal nanocrystals (see the arrows in Fig. 2(b)) [55]. Such organized porous structures are extremely useful in photocatalysis because they provide efficient transport pathways for the reactant molecules and products.

After calcination, the adsorption isotherm of the photocatalyst shifts downward and the area of the hysteresis loops decreases, indicating that the photocatalyst has a smaller BET surface area and pore volume. From Table 1, with increasing calcination temperature from 300 to 1100 °C, the BET surface area decreases from 15.1 to 3.2 $\text{m}^2 \text{g}^{-1}$ and the pore volume decreases from 0.09 to 0.01 $\text{cm}^3 \text{g}^{-1}$.

3.4. Optical properties and XPS analysis

Fig. 5 compares the light-harvesting abilities of the TiO_2 -HMSs calcined at different temperatures. The T300 and T900 samples have similar optical properties with an absorption onset of 388 nm (bandgap of 3.2 eV), while the absorption onset of the T1100 sample begins at 431 nm (bandgap of 2.88 eV). The smaller bandgap of T1100 further confirms phase

Fig. 4. Comparison of the nitrogen adsorption-desorption isotherms (a) and the corresponding pore size distribution curves (b) of the TiO₂-HMSs before and after calcination at different temperatures.

transformation from anatase TiO₂ to the rutile phase [56], which is consistent with the XRD characterization results. Although the TiO₂-HMS precursor, T300, and T900 samples are the anatase phase, the TiO₂-HMS precursor shows absorption in the visible region (400–450 nm). The enhanced absorption is probably because of the complex reaction between H₂O₂ and titanium ions [44].

The XPS survey spectra of the TiO₂-HMSs before and after calcination are shown in Fig. 6(a). Both the TiO₂-HMS precursor and T300 sample contain Ti (458 eV), O (530 eV), C (284 eV), and F (684 eV) elements. The carbon peak is attributed to adventitious carbon from the XPS instrument [57]. However, the peak of the F element is not present in the XPS spectra of the T900 and T1100 samples. This is because of desorption of the fluoride ions from the surface of the TiO₂-HMSs with calcination. It has been reported that almost all of the adsorbed fluoride ions can be removed when the calcination temperature is higher than 500 °C [51].

The high-resolution Ti 2p XPS spectra of the samples are shown in Fig. 6(b). There are two peaks at binding energies of 458.6 and 464.4 eV, which correspond to the signals of Ti⁴⁺ 2p_{3/2} and Ti⁴⁺ 2p_{1/2} [58, 59]. The high-resolution XPS spectra in the F 1s region (Fig. 6(c)) only contain a single peak centered at 683.8 eV, which is from surface-adsorbed F ions. No signal corresponding to F doped in the lattice of TiO₂ is observed at a

binding energy of about 688.6 eV [42,60]. Therefore, the possibility of F doping in the TiO₂-HMSs can be excluded. Fig. 6(d) shows the high-resolution XPS spectra of TiO₂-HMSs in the O 1s region. The O 1s region is composed of two contributions. The main contribution (529.8 eV) is from lattice oxygen and the minor contribution (532.0 eV) is from surface-adsorbed oxygen (or -OH groups) [61,62]:

where $\square$ is an oxygen vacancy. The XPS signals of adsorbed oxygen are very weak for the TiO₂-HMS precursor and T300 sample compared with those for the T900 and T1100 samples. This is because of substitution of surface -OH groups by fluoride ions to (Eq. (1)) [63]. The surface-adsorbed fluoride ions can be removed by calcination, forming surface oxygen vacancies (Eq. (2)) [35]. However, oxygen vacancies can be recovered to produce surface adsorbed -OH groups by adsorption of water gas from air (Eq. (3)) [64]. Therefore, for the T900 and T1100 samples (Fig. 6(d)), it is not unusual that there are strong XPS signals for the -OH groups.

3.5. Photocurrent

Generally, the photocurrent indirectly reflects the semiconductor's ability to generate and transfer photogenerated charge carriers under irradiation [28,65]. Fig. 7 shows the photocurrent responses of the TiO₂-HMS samples coated on FTO electrodes in photoelectrochemical cells for several on-off cycles. Reproducible prompt photocurrents are generated when the FTO/TiO₂ electrodes are irradiated with an UV LED lamp. This indicates that most of the photogenerated electrons are transferred to the cathode (across the sample) to produce a photocurrent under irradiation. Note that there are initial anodic photocurrent spikes with irradiation of the samples, except for sample T900. The initial anodic photocurrent spikes originate from separation of the photogenerated electron-hole pairs within the photoelectrode. The holes are then transferred to the sample surface and trapped or captured by a reduced species in the electrolyte, while the electrons are transported to

Fig. 5. UV-vis diffuse reflection spectra of the TiO₂-HMSs samples.

Fig. 6. XPS survey spectra of the TiO₂-HMSs samples (a), and the corresponding high resolution XPS spectra in Ti 2p (b), F 1s (c) and O 1s (d) regions.

the cathode. After the spike current is attained, the photocurrent continuously decreases before reaching a constant current. This indicates that the holes accumulated at the sample surface competitively recombine with electrons rather than being trapped or are captured by a reduced species in the electrolyte [66]. No obvious spike photocurrent is observed for the T900 sample. This indicates that the number of accumulated holes on the surface of the TiO₂-HMSs of the T900 sample sharply decreases, indicating a low recombination rate of photogenerated electron–hole pairs. Notably, the TiO₂-HMS precursor shows the weakest photocurrent (less than 0.2 $\mu\text{A cm}^{-2}$),

while the T900 sample shows the largest photocurrent (1.2–1.6 $\mu\text{A cm}^{-2}$). This indicates that calcination favors efficient separation of the photogenerated carrier, enhancing the photocatalytic activity.

3.6. Photocatalytic oxidation of acetone

The photocatalytic activity of the TiO₂-HMSs was evaluated by photocatalytic oxidation of acetone. Fig. 8(a) shows the degradation profile of acetone and simultaneous formation of CO₂ in the reactor using the T900 sample as a photocatalyst. The photocatalytic oxidation of acetone is based on

From Fig. 8(a), about 40 ppm acetone decomposes and a stoichiometric amount of CO₂ (about 120 ppm) is produced after irradiation for 120 min. The molar ratio of acetone to CO₂ is nearly 1:3, indicating complete mineralization of acetone over the irradiated TiO₂-HMSs rather than a simple adsorption process.

Fig. 8(b) shows the relative photocatalytic activities of the TiO₂-HMSs calcined at different temperatures. After calcination at 300 °C, the photocatalytic activity of the TiO₂-HMSs slightly decreases from 20.8 (TiO₂-HMS precursor) to 15.1 min⁻¹ (T300) (a 40.1% decrease). This can be interpreted by desorption of surface fluoride ions from the surfaces of the TiO₂-HMSs (Eq. (2)). It has been reported that surface fluorination enhances the photocatalytic activity of TiO₂ by formation of mobile free $\cdot\text{OH}$ radicals ($\cdot\text{OH}_{\text{free}}$), which are more reactive than

Fig. 7. Transient photocurrent responses of TiO₂-HMSs based films for precursor (a), T300 (b), T900 (c) and T1100 (d) samples.

Fig. 8. Photocatalytic mineralization of acetone under UV light irradiation using T900 as photocatalyst (a), and the effect of calcination temperature on the photoreactivity of TiO₂-HMSs (b).

surface-adsorbed $\bullet\text{OH}$ radicals ($\bullet\text{OH}_{\text{ads}}$) [67,68]:

According to the XPS characterization results, the adsorbed fluoride ion contents of the TiO₂-HMS precursor and T300 sample are 2.89 and 2.18 at%, respectively. Therefore, it is understandable that the photoreactivity of the T300 sample is less than that of the TiO₂-HMS precursor.

With increasing calcination temperature from 300 to 900 °C, the photoreactivity of the TiO₂-HMSs steadily increases. This can be ascribed to enhanced crystallization (Fig. 1 and Table 1). However, with a further increase of the calcination from 900 to 1100 °C, the reactivity of the photocatalyst decreases. This can be attributed to the sharp decrease of the BET surface area (Table 1) and the appearance of the rutile phase.

3.7. Reasons for the high thermal stability of the TiO₂-HMSs

Anatase TiO₂ will transform to the low photoreactivity rutile phase when calcined at a temperature higher than 600 °C. However, in the present study, the thermal stability of the anatase TiO₂-HMSs is as high as 1100 °C (Scheme 1). The high thermal stability of the TiO₂-HMS precursor is attributed to surface fluorination during preparation:

It has been reported that fluoride ions show a strong affinity for TiO₂ by forming a layer of fluorine species ($\equiv\text{Ti}-\text{F}$, Eq. (1)) [63,69]. The strong adsorption of fluoride ions on the surface of

TiO₂ makes them difficult to remove. After calcination at 300 °C, the adsorbed fluorine content only decreases from 2.89 (TiO₂-HMS precursor) to 2.18 at% (T300, Fig. 6(c)). According to the literature, adsorbed fluorine can only be completely removed at calcination temperatures higher than 500 °C [51]. Removal of the surface-adsorbed fluoride ions results in formation of surface oxygen vacancies (Eq. (2)), which inhibits growth of TiO₂ nanocrystals by preventing formation of $\equiv\text{Ti}-\text{O}-\text{Ti}\equiv$ chains between neighboring TiO₂ nanoparticles (comparing Eqs. (7) and (8)) [35]. Therefore, a higher temperature is needed for diffusion of lattice oxygen to the oxygen vacancy. Fusion of neighboring TiO₂ nanoparticles then begins, and phase transformation occurs. Although adsorption of fluoride ions efficiently prevents the anatase–rutile phase transformation, crystallization of TiO₂ nanocrystals is greatly improved during calcination at high temperature. Therefore, high photoreactivity TiO₂-HMSs with high thermal stability are obtained.

4. Conclusions

Highly photoactive TiO₂-HMSs have been fabricated by assembly of hollow nanoparticles. The TiO₂-HMSs show very high thermal stability with an anatase–rutile phase transformation of as high as 1100 °C. Adsorbed fluoride ions are considered to be the most important factor for the high thermal stability of the TiO₂-HMSs. The present study provides a new way to design (photo)catalysts with high thermal stability.

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Scheme 1. Effect of calcination temperature on the morphology and phase structure of TiO₂ hollow microspheres (TiO₂-HMSs).

Graphical Abstract

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Highly photoreactive TiO₂ hollow microspheres with super thermal stability for acetone oxidation

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Anatase TiO₂ hollow microspheres (TiO₂-HMSs) were fabricated by hydrothermal treatment of the mixed solution of Ti(SO₄)₂-NH₄F-H₂O₂. The prepared TiO₂-HMSs show excellent photoreactivity in oxidation of acetone and high thermal stability with anatase-to-rutile phase transformation temperature of 1100 °C.

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高热稳定性TiO₂空心微球高效光催化氧化丙酮

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摘要: 空心结构材料具有低密度、高通透性和易于回收的优点, 因此人们对空心球的TiO₂, 如TiO₂空心微球(TiO₂-HMSs)的制备非常感兴趣。但是普通TiO₂-HMSs的热稳定性较差, 一般在600 °C以上就由活性较高的锐钛矿相相变成活性很差的金红石相。考虑到氟离子能够抑制TiO₂相变, 因此我们以Ti(SO₄)₂为钛源, 在NH₄F和H₂O₂的共同作用下, 于180 °C水热制备了由空心颗粒自组装成的表面氟化的TiO₂-HMSs, 并考察了其热稳定性与光催化氧化分解丙酮的性能。

研究发现, 当焙烧温度从300 °C上升到1000 °C时, TiO₂平均粒径从79.0 nm逐渐增大到97.7 nm, 结晶度从1.00增大到1.53。这是由于热处理促进了TiO₂颗粒的晶化。当进一步升温到1100 °C时, XRD谱开始出现金红石相TiO₂的特征衍射峰, 此时约18.4%的锐钛矿相开始向金红石相转化。因此, 本文制备的二氧化钛锐钛矿相可以稳定到1000 °C, 显示出优良的高热稳定性。

扫描电镜显示, 水热制备的TiO₂-HMSs是由高能(001)面暴露的TiO₂十面体纳米晶组装而成。随着焙烧温度提高到900 °C, 空心微球外观没有显著改变, 但是组装体纳米晶暴露出来的空洞逐渐变小, 晶粒变得圆滑; 至1100 °C时, 空心微球组装体的纳米晶变成了球形颗粒, 但是空心微球的空心结构没有坍塌, 空心微球结构依然得到保留。

我们用丙酮的紫外光催化氧化分解来评价不同温度焙烧的TiO₂空心微球的光催化活性。结果显示, 前驱体TiO₂空心微球于300 °C焙烧2 h, 丙酮的氧化速率从 $1.39 \times 10^{-3} \text{ min}^{-1}$ (前驱体)降至 $0.82 \times 10^{-3} \text{ min}^{-1}$ (T300样品), 这是因为样品表面吸附的氟离子受热挥发所致; 当焙烧温度从300 °C提高到900 °C时, 催化剂活性从 $0.82 \times 10^{-3} \text{ min}^{-1}$ 升至 $2.09 \times 10^{-3} \text{ min}^{-1}$, 这是由于焙烧促进了TiO₂的晶化; 进一步升至1000和1100 °C时, 催化剂活性显著下降, 这是由于催化剂的比表面积急剧减小和金红石相的生成。

总之, 本文利用氟离子的化学诱导作用制备出表面氟化的空心颗粒自组装TiO₂空心微球, 该TiO₂空心微球显示出超高热稳定性与高光催化活性, 因此在高温环境中具有实际应用前景。

关键词: 二氧化钛空心微球; 光催化氧化; 丙酮; 氟化; 热稳定性

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