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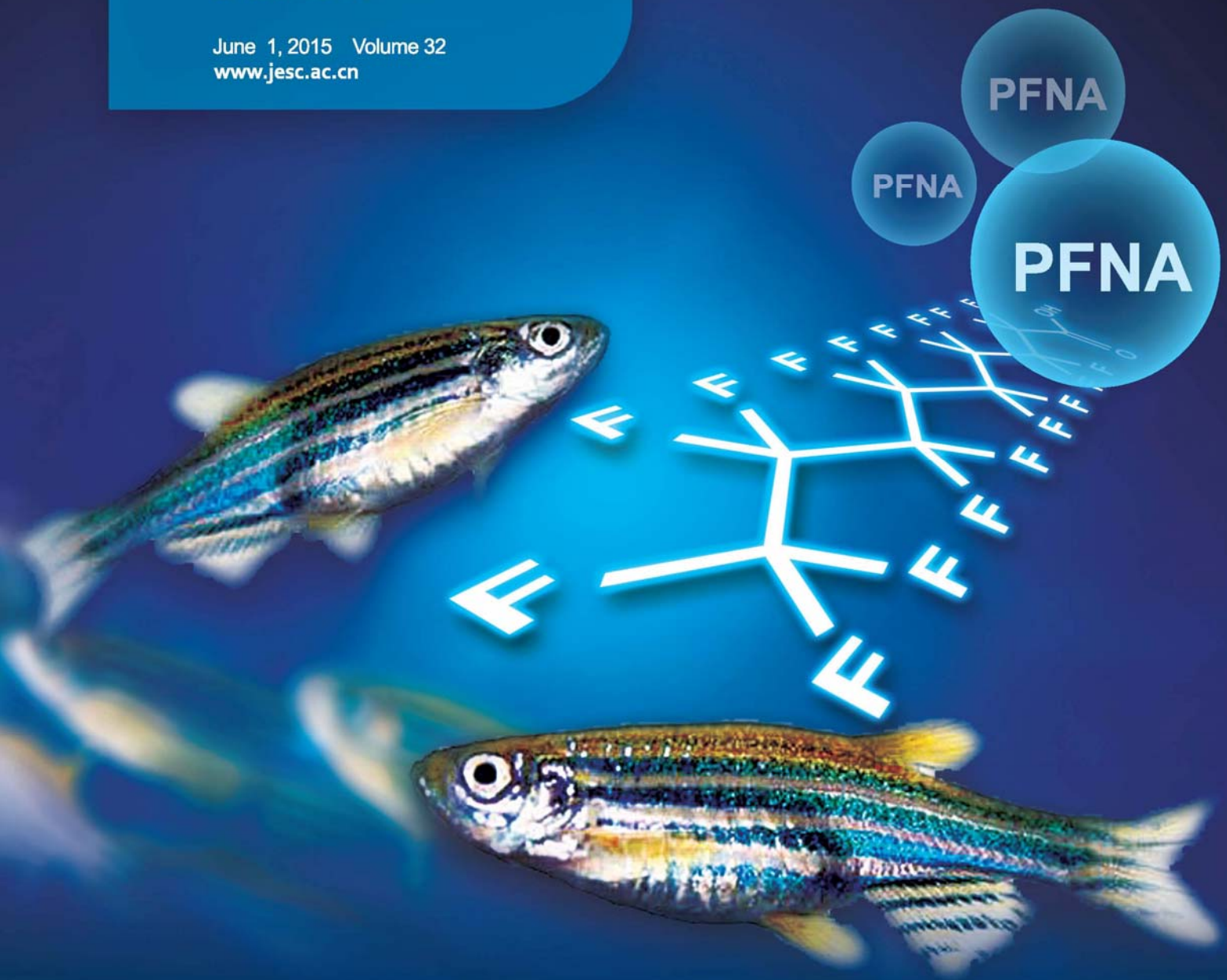

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Tricrystalline TiO_2 with enhanced photocatalytic activity and durability for removing volatile organic compounds from indoor air

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ABSTRACT

It is important to develop efficient and economic techniques for removing volatile organic compounds (VOCs) in indoor air. Heterogeneous TiO_2-based semiconductors are a promising technology for achieving this goal. Anatase/brookite/rutile tricrystalline TiO_2 with mesoporous structure was synthesized by a low-temperature hydrothermal route in the presence of HNO_3. The obtained samples were characterized by X-ray diffraction and N_2 adsorption–desorption isotherm. The photocatalytic activity was evaluated by photocatalytic decomposition of toluene in air under UV light illumination. The results show that tricrystalline TiO_2 exhibited higher photocatalytic activity and durability toward gaseous toluene than bicrystalline TiO_2, due to the synergistic effects of high surface area, uniform mesoporous structure and junctions among mixed phases. The tricrystalline TiO_2 prepared at R_{HNO3} = 0.8, containing 80.7% anatase, 15.6% brookite and 3.7% rutile, exhibited the highest photocatalytic activity, about 3.85-fold higher than that of P25. The high activity did not significantly degrade even after five reuse cycles. In conclusion, it is expected that our study regarding gas-phase degradation of toluene over tricrystalline TiO_2 will enrich the chemistry of the TiO_2-based materials as photocatalysts for environmental remediation and stimulate further research interest on this intriguing topic.

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Introduction

Volatile organic compounds (VOCs) are a group comprising the most abundant organic pollutants in indoor air, with concentrations ranging from 0.005 to 4600 μg/m^3 (Barro et al., 2009). They are emitted from various sources such as combustion by-products, cooking, construction materials, office equipment, and consumer products (Gallego et al., 2008; Weschler, 2009). Many VOCs are toxic or carcinogenic to humans, even at low concentrations (Missia et al., 2010). For instance, exposure to formaldehyde, benzene or toluene may cause skin irritation, rhinitis, headache, fatigue, and allergic reactions (Bernstein et al., 2008; Gallego et al., 2009); and benzene derived from aromatic molecules can show carcinogenic or mutagenic activity (Missia et al., 2010).

A number of techniques have been developed to remove VOCs from indoor air, such as adsorption techniques and oxidation techniques (Parmar and Rao, 2009). The former are conventional methods; gaseous pollutants are transferred from air to a solid phase with various adsorbents, *e.g.*, activated carbon (Liu et al., 2004). In contrast, heterogeneous photocatalysis using semiconductors as photocatalysts, an advanced oxidation

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technique, has greater potential. In the photocatalytic processes, an array of VOCs can be destroyed and even completely mineralized into CO_2 and H_2O (Demeestere et al., 2007; Nakata and Fujishima, 2012). While compared to other oxidation technologies like electron beam and plasma treatments, heterogeneous photocatalysis is more effective and economical, and suitable for wider application scope.

Among all semiconductor photocatalysts, TiO_2 (primarily existing in three crystal phases, *i.e.*, anatase, brookite, and rutile) is the most efficient and applicable, because of its wide band-gap energy, durability against photocorrosion, low toxicity and low cost (Demeestere et al., 2007; Wang et al., 2007). However, the photocatalytic applications of TiO_2 are limited by its low quantum efficiency due to the fast recombination between the photogenerated electrons and holes (Chen and Mao, 2007). The formation of phase junctions has been demonstrated as an effective strategy for inhibiting photogenerated electron-hole recombination (Li and Gray, 2007). In practice, tricrystalline TiO_2 has been synthesized by thermohydrolysis of $TiCl_4$ (Di Paola et al., 2008, 2009) and with solvothermal treatment of titanium tetrabutoxide (TBOT) in toluene (Liao et al., 2012). In the aqueous phase, the tricrystalline TiO_2 exhibited higher photocatalytic activity for organic pollutants than bicrystalline TiO_2.

However, the photocatalytic performance and durability of tricrystalline TiO_2 have not been tested in the gas phase. Due to the accumulation of strongly bound reaction intermediates on the TiO_2 surface (Demeestere et al., 2007; Hu et al., 2006), deactivation of TiO_2 during photodegradation of organic pollutants was much more frequently observed in the gas phase than the aqueous phase. Additionally, the existing methods for synthesizing tricrystalline TiO_2 are energy-consuming, and usually require high-temperature (≥400°C) (Lopez et al., 2001), long-time (≥48 hr) treatments (Di Paola et al., 2008, 2009), or toxic toluene (Liao et al., 2012).

In this study, we aim to promote the application of tricrystalline TiO_2 in photocatalytic elimination of indoor VOCs. Anatase/brookite/rutile tricrystalline TiO_2 was synthesized using a low-temperature hydrothermal method with the assistance of HNO_3. The photocatalytic activity and durability in the photodegradation of toluene were analyzed and compared to P25 TiO_2 (a widely used benchmark model photocatalyst). Toluene is one of the most abundant VOCs found in indoor air (Greenberg, 1997; Wang et al., 2007) and is not easily degraded due to the relative stability of its aromatic ring against oxidation and reduction processes (Hodgson et al., 2007).

1. Materials and methods

1.1. Synthesis

Anatase/brookite/rutile tricrystalline TiO_2 was prepared as follows. 4.4 mL TBOT (Aladdin Reagent Co.) was slowly added to 50 mL of a 10 mol/L NaOH solution under vigorous stirring, yielding an amorphous TiO_2 suspension. After 5 hr stirring, the suspension was separated by centrifugation, washed three times with deionized water and redispersed in 39 mL deionized water. Then, a concentrated HNO_3 solution (65%) was added under stirring. The molar ratios of HNO_3 to TBOT (R_{HNO3}) were varied from 0.2 to 1.2 at intervals of 0.2 by varying the volume of HNO_3 solution. The mixture was sealed in a Teflon autoclave and maintained at 180°C for 24 hr. Finally, the resulting precipitate was separated by centrifugation, washed with deionized water until the washing solution reached pH 7 and then dried at 50°C. The TiO_2 powders were labeled as TiO_2-a. For example, TiO_2 nanocrystals prepared at $RHNO_3$ = 0.8 were denoted as TiO_2-0.8.

1.2. Characterization

The synthesized products were characterized in three aspects, including the X-ray diffraction (XRD) pattern, specific surface area and pore size distribution. First, the XRD patterns were explored between 20° and 90° (2θ range, Δ2θ = 0.02°) with a D/MAX 2550 PC using Cu Kα radiation (Rigaku, Tokyo, Japan). The phase contents of the TiO_2 samples were calculated from the integrated intensities of anatase (101), rutile (110), and brookite (121) peaks (Luo et al., 2003; Zhang and Banfield, 2000). The average diameters (*d*) of the crystallites (*i.e.*, anatase, rutile and brookite) were calculated from the full-width at half-maximum of the respective XRD patterns using the Scherrer formula (Patterson, 1939). Second, the specific surface areas were estimated using N_2 adsorption experiments based on the classical Brunauer–Emmett–Teller (BET) method, which were conducted in the relative pressure range of 0.01 to 0.1 with a NOVA 2000e surface area analyzer (Quantachrome, Florida, U.S.A.). The pore size distributions of the TiO_2 nanocrystals were calculated from the desorption branch of the nitrogen isotherms using the Barrett–Joyner–Halenda (BJH) method (Barrett et al., 1951).

1.3. Photocatalytic activity

The photocatalytic activity of tricrystalline TiO_2 was evaluated by the photocatalytic degradation of toluene in air under UV irradiation, with P25 as a reference. The photodegradation of gaseous toluene was conducted in a cylindrical quartz photoreactor operating in continuous flow mode (Fig. 1). The carrier gas generated from a clean-air generator was split into three streams. The first stream was bubbled through water to set the humidity for the reaction (20% ± 3%), and the second stream was used to generate a gaseous stream of toluene passed through a permeation tube filled with pure liquid toluene cooled in an ice-water bath. These two streams then converged with the clean air branch (the third stream) in a 1.5 L-cylindrical-chamber. The toluene/air mixed vapor was fed to the catalyst dish at a total flow rate of 1 L/min, and the concentration of toluene was 1 ppm, which is a typical level in indoor air environments. The catalyst dish was prepared by coating 20 mg of TiO_2 onto a piece of quartz wool with an area of 11 × 20 cm^2 using 20 mL of a TiO_2/ethanol suspension. A 6 W UV lamp with a dominant wavelength of 254 nm was used as the irradiation source. The distance between the catalyst dish and the lamp was 1.5 cm. The concentrations of toluene were determined using an online gas chromatograph (GC, Fuli 9790, Wenling, China) equipped with a stainless steel packed column (2.5% dinonyl phthalate + 2.5% bentane, length: 3 m, diameter: 3 mm) and a flame ionization detector. Prior to photodegradation, adsorption equilibrium of toluene on the photocatalyst was achieved in 4 hr without irradiation.

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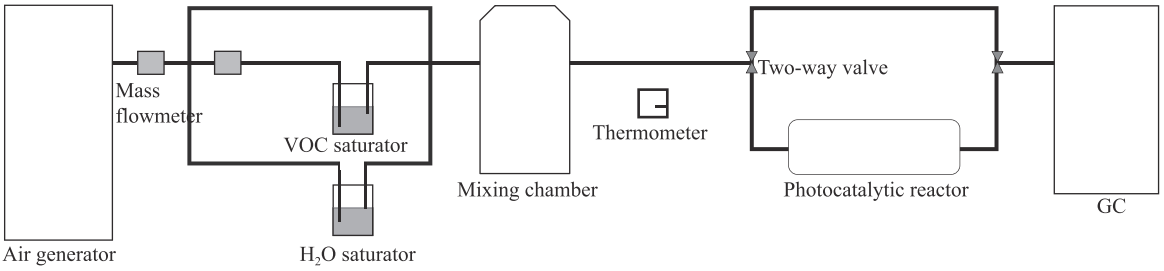

Fig. 1 – Photocatalytic device. (1) Air generator; (2) mass flowmeter; (3) VOC saturator; (4) H_2O saturator; (5) mixing chamber; (6) thermometer; (7) Two-way valve; (8) photocatalytic reactor; (9) GC.

The photodegradation rate of toluene was calculated by the following equation:

$$\eta_t = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

where η_t (%) represents the photodegradation rate at reaction time t, C_0 (mg/m^3) and C (mg/m^3) are the initial and the reaction concentration of toluene, respectively. The photocatalytic degradation of toluene on TiO_2 is a pseudo-first-order reaction and its kinetics can be expressed as follows (Demeestere et al., 2007):

$$1n\left(\frac{C_0}{C}\right) = k_{app}t$$

where, k_{app} (min^{-1}) represents the apparent kinetic constant.

1.4. *Hydroxyl radicals*

In order to explore the synergistic effects of anatase–brookite–rutile phases, the formation of hydroxyl radicals (·OH) during the UV irradiation of TiO_2 nanocrystals was studied. The amount of ·OH radicals generated on the surface of UV-irradiated TiO_2 was measured with the terephthalic acid (TA, Aladdin Reagent Co., Shanghai, China) fluorescence probe method (Hirakawa and Nosaka, 2002; Ishibashi et al., 2000b). TiO_2 5 mg was suspended in 50 mL of an aqueous solution containing 2 mmol/L NaOH and 0.5 mmol/L TA. The suspension was stirred in darkness for 30 min. Then, 3 mL of the suspension was exposed to UV light irradiation at a wavelength of 254 nm (using a 6-W UV lamp as the light source) for 5 min, followed by filtration through a 0.25 μm membrane filter. Finally, the fluorescence signal of 2-hydroxy terephthalic acid (TAOH) at 426 nm was recorded on a RF-5301pc spectrofluorophotometer (Shimadzu, Tokyo, Japan) at an excitation wavelength of 320 nm.

1.5. *Photocatalytic durability*

To explore the photocatalytic long-term durability advantage of the TiO_2 samples with the highest photocatalytic activity, five reuse cycles were tested for the photodegradation of gaseous toluene. Each cycle included 2 hr of light on and 4 hr of light off.

The possible gaseous intermediates (Demeestere et al., 2007), such as benzene, phenol benzaldehyde, benzyl alcohol and benzoic acid, were analyzed by collecting air samples at the reactor outlet in stainless steel tubes packed with 300 mg activated carbon during the photodegradation. The absorbed intermediates were extracted into carbon disulfide and measured by GC. CO_2 was converted into methane in a converter with nickel catalysts at a temperature of 350°C and also determined on the online GC. The concentration of toluene was maintained at 100 ppm in the intermediate and CO_2 identification tests, in order to improve the accuracy of test results.

2. Results and discussion

2.1. *Phase composition*

The phase compositions of the obtained samples were sensitive to the molar ratios of HNO_3 to TBOT (R_{HNO3}). The XRD patterns show that the samples obtained at R_{HNO3} between 0.8 and 1.2 were anatase/brookite/rutile three-phase TiO_2 nanocrystals (Fig. 2). According to the standard diffraction data, the characteristic 2θ values at around 25.3°, 30.8° and 27.4° corresponded to the anatase (101) plane (JCPDS No. 21-1272), the brookite (121) plane (JCPDS No. 29-1360) and the rutile (110) plane (JCPDS No. 21-1276), respectively. The anatase content increased from 26.0% to 80.7% and the rutile content decreased from 54.8% to 3.7% when R_{HNO3} decreased from 1.2 to 0.8, whereas the brookite

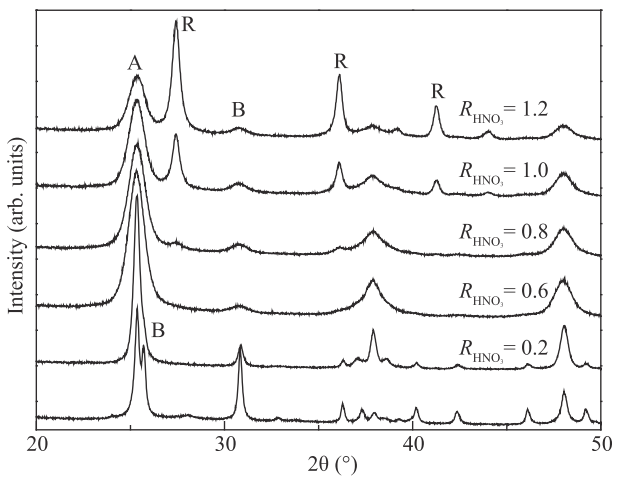

Fig. 2 – XRD patterns of TiO_2 nanocrystals. Peaks of anatase, brookite and rutile are identified as A, B and R, respectively. R_{NO3} is molar ratio of HNO_3 to titanium tetrabutoxide (TBOT) during the production process of TiO_2 nanocrystals.

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Table 1 – Physicochemical properties of TiO_2 nanocrystals and P25.

R_{HNO3} [a]	Anatase [b] (%)	Brookite [b] (%)	Rutile [b] (%)	*d* (anatase) [b] (nm)	*d* (brookite) [b] (nm)	*d* (rutile) [b] (nm)	S_{BET} (m^2/g^-)	Pore size [c] (nm)
1.2	26.0	19.2	54.8	19.2	8.70	23.3	92.10	8.6
1.0	59.5	14.5	26.0	8.60	7.60	21.3	112.9	6.3
0.8	80.7	15.6	3.70	8.20	7.50	19.2	136.6	5.4
P25	80.0	–	20.0	25.0	–	35.0	58.00	7.1

[a] Molar ratio of HNO_3 to titanium tetrabutoxide (TBOT) during the production process of TiO_2 nanocrystals.
[b] Determined by X-ray diffraction (XRD) patterns.
[c] Estimated using the desorption branch of the N_2 adsorption/desorption isotherm and the Barrett–Joyner–Halenda (BJH) formula.

content remained relatively steady (14.5–19.2%) (Table 1). These trends are consistent with previous reports (Tian et al., 2006; Yuan et al., 2004), which indicates that a dilute acid solution favored the formation of anatase, while a concentrated acid solution promoted the formation of rutile. The generation of the brookite phase might be attributed to the presence of Na^+ ions (Shen et al., 2013). The above results demonstrate an effective approach to the controllable fabrication of tricrystalline TiO_2 with a low-temperature hydrothermal treatment.

2.2. Photocatalytic activity

As shown in Fig. 3a, at the beginning of irradiation, adsorbed toluene on TiO_2 was preferentially degraded, after which more toluene could be adsorbed and degraded. During this period, toluene reacted rapidly. As the concentration of toluene was constant, the adsorption equilibrium and degradation equilibrium were easily reached, and the photodegradation rate of toluene leveled off. The photodegradation rate of toluene did not decrease and no deactivation was observed during a 2-hr test. It is unlikely that the leveling-off phenomenon was due to deactivation of the catalysts by the remaining intermediates, because if intermediates remained and occupied the active sites of the TiO_2 surface, the photodegradation rate of toluene would have decreased rather than leveling off. It could be clearly observed that the final degradation sequence followed the same order of the rate constants (Fig. 3b), which initially increased with decreasing R_{HNO3} and then decreased. Tricrystalline TiO_2-0.8 was proved to be the most efficient photocatalyst, with a photodegradation conversion of 89% and an apparent kinetic constant of 9.3×10^{-2} min^{-1}. In contrast, P25 only showed a photodegradation conversion of 44% and an apparent kinetic constant of 24×10^{-3} min^{-1}. Moreover, a decrease in the activity of tricrystalline TiO_2 was observed when R_{HNO3} became larger than 0.8, during which the ratio of anatase–brookite–rutile shifted away from its optimum.

Two factors are essential during gas–solid photocatalysis: the adsorption of pollutant molecules and the separation/transport of electrons and holes. The adsorption is usually related to the surface area and the pore structure of TiO_2. The tricrystalline TiO_2-0.8 had the largest surface area (136.6 m^2/g) because it had the smallest crystallite size (Table 1). Also, this TiO_2 nanomaterial exhibited a type IV isotherm with a hysteresis loop of type H2 over the relative pressure range of 0.5 to 0.8 (Fig. 4), indicating the presence of ink-bottle-like pores with narrow necks and wider bodies (Dai et al., 2012; Yu et al., 2003). These mesopores resulted from the aggregation of primary particles, with the smallest average pore size of approximately 5.4 nm (Fig. 4). A larger surface area favors TiO_2 adsorbing more gaseous reactants, such as H_2O, O_2 and organic pollutants, onto the surface, and the uniform mesopores allow for the rapid diffusion of these reactants and various products during the photocatalytic reaction, thereby enhancing the photocatalytic activity (Ismail and Bahnemann, 2011; Yu et al., 2006). However, the kinetic constant with normalized by surface area for tricrystalline TiO_2 (0.68×10^{-3} $g/(min \cdot m^2)$) was still

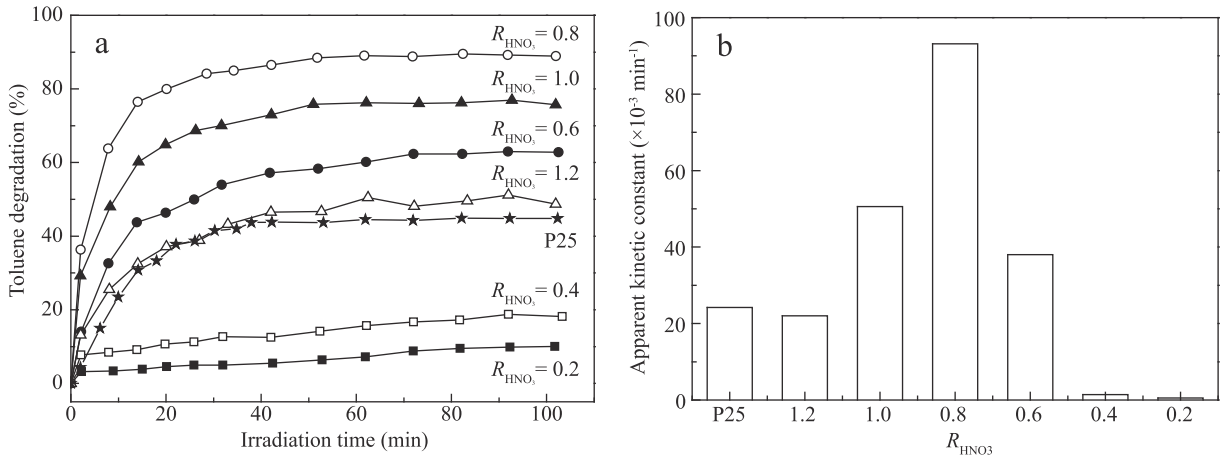

Fig. 3 – Photodegradation of gaseous toluene on TiO_2 nanocrystals and P25 as degradation rate (a) and apparent kinetic constant (b).

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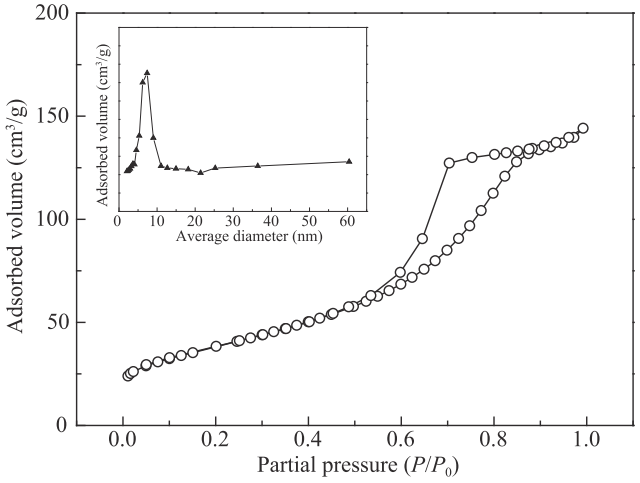

Fig. 4 – Nitrogen adsorption–desorption isotherm of tricrystalline TiO_2-0.8. The inset was the pore size distribution curve calculated from the desorption branch of the nitrogen isotherm using the BJH method.

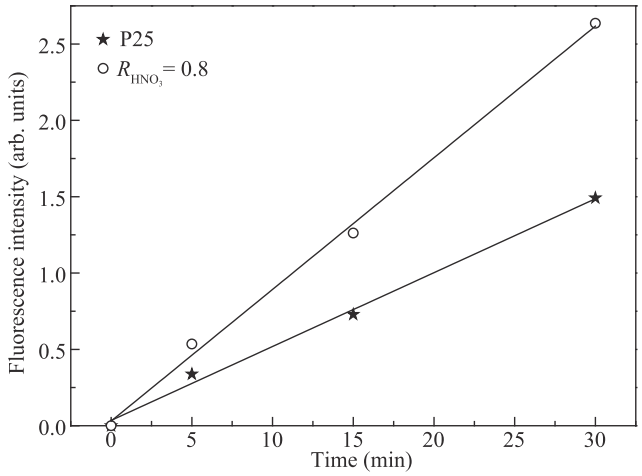

Fig. 5 – Fluorescence intensity changes observed during the irradiation of tricrystalline TiO_2-0.8 and P25 in a 0.5 mmol/L aqueous NaOH solution of terephthalic acid (excitation at 320 nm).

higher than that of P25 (0.42×10^{-3} g/(min·m^2)), clearly demonstrating that surface area is not the only influential factor for photocatalytic activity in this system.

Therefore, the other crucial factor for enhancing the photocatalytic activity of TiO_2 is the efficient charge separation and transfer, which could be evaluated by the formation of ·OH radicals during the UV irradiation of TiO_2 nanocrystals in TA solutions (Lv et al., 2010; Xiang et al., 2010; Yu et al., 2009). The absorption of a photon with energy higher than the band gap energy results in the formation of a valence band hole and a conduction band electron. It is commonly acknowledged that adsorbed water or hydroxide ions can be trapped by the holes to produce ·OH radicals, which are known to be a strong oxidizing species. Electrons are trapped at the surface after reacting with adsorbed molecular oxygen to produce superoxide anion radicals, which then form more ·OH radicals. The yield of ·OH radicals depends on the competition between the above reactions and electron-hole recombination. Therefore, the higher the formation rate of ·OH radicals, the higher the separation efficiency of electron-hole pairs achieved can be. Fig. 5 shows the changes in fluorescence spectra with irradiation time for TA solutions. No increase in fluorescence intensity was observed in the absence of UV light or TiO_2 nanocrystals, indicating that the fluorescence was caused by the chemical reaction of TA with ·OH that formed on the TiO_2/water interface *via* photocatalytic reactions (Hirakawa et al., 2007; Ishibashi et al., 2000a). On the contrary, in the presence of TiO_2 nanocrystals, the fluorescence intensity as a result of UV irradiation in TA solutions increased linearly as a function of time. Thus, it could be inferred that the number of ·OH radicals produced at the TiO_2 surface was proportional to the irradiation time and that this reaction obeyed zero-order reaction rate kinetics. Tricrystalline TiO_2-0.8 showed a much greater formation rate than P25, suggesting that the three-phase composite (anatase/brookite/rutile) enhanced the production of ·OH radicals. The two-phase structure of anatase and rutile with a suitable ratio has been reported to be beneficial in reducing the recombination rate of photo-generated electrons and holes, thereby enhancing the rate of ·OH formation (Lv et al., 2010). This enhancing relationship also applies to tricrystalline TiO_2. The coupled anatase, brookite and rutile phases possessed different redox energies for their corresponding conduction and valence bands (Shibata et al., 2004; Yin et al., 2010). Heterojunctions were thus formed, allowing an easier transfer of photogenerated electrons from one phase to another, which could suppress the recombination of photogenerated electrons and holes and consequently enhance the production of ·OH radicals. In summary, the high photocatalytic activity of tricrystalline TiO_2-0.8 could be attributed to the combined effects of high specific surface area, uniform mesoporous structure and junctions among mixed phases.

2.3. Photocatalytic durability

The toluene conversion on tricrystalline TiO_2-0.8 was maintained at 89% ± 1% without significant deactivation for up to five repeated cycles, while P25 gradually lost its activity (Fig. 6). A

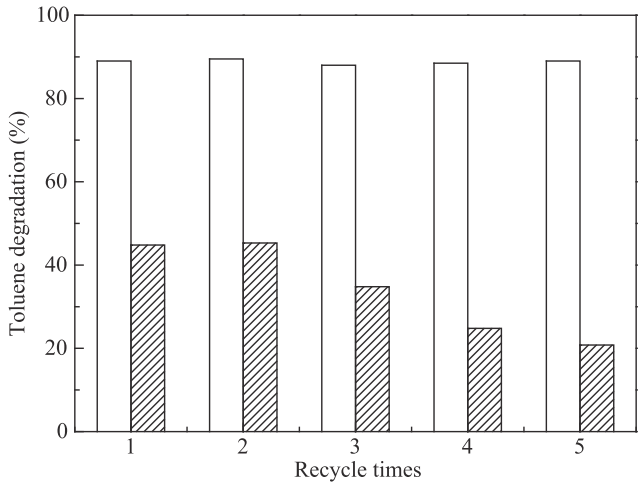

Fig. 6 – Recycling test over tricrystalline TiO_2-0.8 (blank) and P25 (filled) for five repeat uses.

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Table 2 – Comparison of intermediates and CO_2 resulted from toluene degradation by tricrystalline TiO_2-0.8 and P25.

R_{HNO3}	Intermediates [a] (mg/m^3)			CO_2 yield (%)
	Benzyl alcohol	Benzaldehyde	Benzoic acid	
0.8	0.17	42.00	n.d. [b]	56.3
P25	0.61	376.4	0.01	20.9

[a] Concentrations of intermediates in the extracts.
[b] Not detected.

color change of P25 from white to yellow was observed after the third reuse cycle. These results could be attributed to the more effective decomposition of toluene and refractory intermediates by the tricrystalline TiO_2-0.8. As intermediates, benzyl alcohol and benzaldehyde were identified for both tricrystalline TiO_2-0.8 and P25, whereas benzoic acid was identified only for P25 (Table 2). It is clear that the oxidation of toluene took place at the methyl group for both photocatalysts. The concentrations of three main intermediates for tricrystalline TiO_2-0.8 were much lower than those for P25, while the yield of CO_2 for tricrystalline TiO_2 was higher than that for P25 (56.3% and 20.9%, respectively), confirming that tricrystalline TiO_2-0.8 enhanced the photocatalytic degradation of both toluene and its intermediates.

In an attempt to increase the TiO_2 lifetime, other researchers have carried out catalyst regeneration, focusing on the destruction of presumed intermediates. Two main types of regeneration methods have been reported (Cao et al., 2000; Demeestere et al., 2007; Lewandowski and Ollis, 2003). First, thermal regeneration of TiO_2 deactivated after toluene degradation was applied (Cao et al., 2000). Temperatures as high as 420°C for at least 2 hr were required to "burn out" strongly bound intermediates and to recover the initial activity completely. A second type of regeneration method involves exposure of deactivated TiO_2 to contaminant-free, humidified air and UV irradiation (Lewandowski and Ollis, 2003). However, these methods require high regeneration temperature or long regeneration time, costing much energy. Based on the photocatalytic activity and reuse tests, this tricrystalline TiO_2-0.8 was not only highly efficient but also quite durable for prolonged use.

3. Conclusions

With the assistance of HNO_3, anatase/brookite/rutile tricrystalline TiO_2 with high crystallinity, large surface area (136.6 m^2/g) and uniform mesopores (5.4 nm) was successfully prepared using a low-temperature hydrothermal method. Compared to the existing methods, this route was more energy-saving, and the phase structure could be finely controlled by adjusting the amount of HNO_3. The three-phase TiO_2 nanocrystals showed much higher photocatalytic activity and durability in the degradation of gaseous toluene than the commercial anatase/rutile P25, mainly because of their superior properties in the adsorption of pollutant molecules and the separation/transport of electrons and holes. It is expected that our study regarding gas-phase degradation of toluene over tricrystalline TiO_2 can enrich the chemistry of TiO_2-based materials as photocatalysts for environmental remediation and stimulate further research interest on this intriguing topic.

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