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Shielding of surface photogenerated charges by SiO_2 coating for the photocatalytic degradation of air pollutants

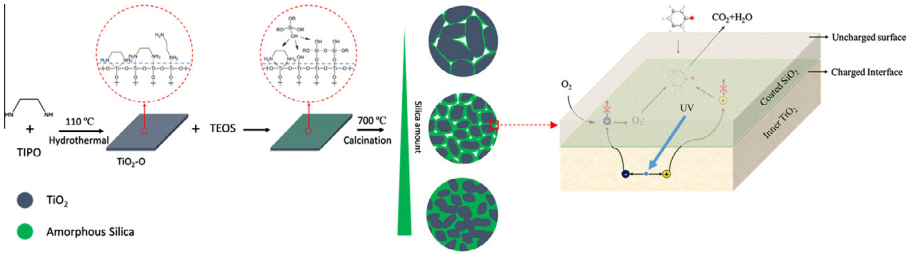
Jinze Lyu [a,b,c,*], Luna Sun [a], Junbo Zhong [d], Qiang Fu [a], Min Zhang [a], Shuo Wang [a,b,c], Ji Li [a,b,c]

[a] School of Environment and Civil Engineering, Jiangnan University, Wuxi, Jiangsu 214122, China
[b] Jiangsu Key Laboratory of Anaerobic Biotechnology, Jiangnan University, Wuxi, Jiangsu 214122, China
[c] Jiangsu College of Water Treatment Technology and Material Collaborative Innovation Center, Suzhou, Jiangsu 215009, China
[d] Key Laboratory of Green Catalysis of Higher Education Institutes of Sichuan, College of Chemistry and Pharmaceutical Engineering, Sichuan University of Science and Engineering, Zigong, Sichuan 643000, China

HIGHLIGHTS

- Novel SiO_2-coated TiO_2 nanocrystals was prepared.
- SiO_2 coating controlled the crystallinity and crystal size of inner TiO_2.
- SiO_2 coating efficiently shielded the photo-induced charges on the TiO_2 surface.
- SiO_2 coating did not inhibit the transfer of toluene.

GRAPHICAL ABSTRACT



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ABSTRACT

TiO_2 has promising applications in air purification and self-cleaning but is usually inactivated by floating particulate matters. The inactivation is due to the accumulation of photogenerated charges on TiO_2 surface. The surface charges significantly enhance the adsorption of particulate matters and thus block incident light. To shield photogenerated charges on TiO_2 surface, a series of nanocomposites composed of inner TiO_2 nanocrystals and SiO_2 coating was synthesized using ethylenediamine as SiO_2 coating assistant. XRD, N_2 adsorption/desorption, TEM, surface photovoltage, UV–vis, and GC-FID were used to study the effect of SiO_2 coating on the structure of inner TiO_2 nanocrystals, the ability of shielding surface charges, the adsorption of airborne particles, and the removal efficiency of toluene. The results showed that SiO_2 coating efficiently shielded the photogenerated charges on the TiO_2–SiO_2 interface and reduced the adsorption of airborne particles but did not diminish the transfer of toluene from air to photocatalytic sites on the TiO_2 surface. The crystallinity and crystal size of inner TiO_2 gradually decreased with increased amount of SiO_2 coating. TiO_2@SiO_2-50 with a small crystal size of 9.2 nm and relatively high crystallinity showed the best photoactivity. This work may provide a new strategy to overcome the problem of TiO_2 inactivation by haze pollution.

1. Introduction

With the fundamental properties of photocatalysis and photo-induced super hydrophilicity, TiO_2 can be widely used in many fields, such as environment purification, H_2 generation, and antifogging [1–7]. The market use of TiO_2 photocatalysis is predominantly through the application of TiO_2 in exterior building

* Corresponding author at: School of Environment and Civil Engineering, Jiangnan University, Wuxi, Jiangsu 214122, China.
E-mail address: ljz@jiangnan.edu.cn (J. Lyu).

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materials, interior building materials, and air purifiers. TiO_2 used in these fields could oxidize air pollutants, such as NO_x and volatile organic compounds (VOCs), to keep building surfaces clean [1,8]. However, the application of TiO_2 for air purification is seriously limited by particulate air pollution. The floating particulate matters easily adsorb onto the TiO_2 surface, thus filtering part of incident light. Therefore, the amount of photogenerated charge carriers decreases with the intensity of incident light. Nowadays, particle pollution [9–11] is very common in Southeast Asia and India. Therefore, technology needs to be developed in these areas to inhibit the inactivation of TiO_2 by adsorbed particulate matters. Most floating particles in the air can be mechanically blocked by filters set in front of photocatalytic units in air purifiers. This method has been proven effective and is widely used in air purifiers. However, the application of TiO_2 on self-cleaning construction materials still faces the challenge induced by particulate air pollution.

Under light irradiation, photogenerated electrons and holes accumulate on the TiO_2 surface; this accumulation significantly enhances the adsorption of floating particles and causes the inactivation of TiO_2. Coating the surface of TiO_2 with a nanofilm to isolate floating particles is a possible solution. However, the coated film must meet three needs: i) the film should be an insulator to shield photogenerated charges on the TiO_2 surface, ii) most light in the UV band can penetrate the film to excite electron-hole pairs in TiO_2, and iii) the film can block floating particles but does not influence the transfer of gaseous pollutants from the air onto the TiO_2 surface. Amorphous SiO_2 is a typical insulator with a band gap of 9 eV, which means SiO_2 does not adsorb light with a wavelength >137 nm. SiO_2 can also form a porous structure in nanoscale [12–14], to allow the selective isolation of floating particles from gaseous pollutants. SiO_2 is mostly used as the support of TiO_2 or the frame material of mesoporous SiO_2–TiO_2 composites [12,15,16]; only a few studies have considered SiO_2-coated TiO_2. Several works have reported that TiO_2–SiO_2 nanocomposites can efficiently decompose organic stains deposited on its surface and thus show a promising self-cleaning effect [16,17]. Hupp et al. [18] deposited insulating and transparent SiO_2 onto the open areas of a nanoparticulate TiO_2 surface to retard electron recombination at the photoelectrode interface of dye-sensitized solar cells; in their study, deposited SiO_2 reduced the transfer of electrons onto the TiO_2 surface to the electrolyte. Grosso et al. [19] deposited an SiO_2 film with a thickness of 20 nm onto a TiO_2 film to prevent the degradation of a polymer layer by radical species onto the TiO_2 surface. However, to the best of our knowledge, little research has been conducted on SiO_2 coating's shielding effect on photogenerated charges on the TiO_2 surface for air purification or self-cleaning applications. To study the shielding effect, surface charges on the catalyst surface have to be detected. Surface photovoltage (SPV) spectroscopy is a contactless technique applied to characterize optical-electronic properties of semiconductors. SPV is very sensitive to the change in surface potential of catalysts caused by photogenerated charge carriers under room temperature. Therefore, SPV can be used to identify the amount of charges accumulated at catalysts surface under light irradiation.

The present study provides a simple and replicable synthetic method for SiO_2-coated TiO_2 nanocrystal composite. The effect of SiO_2 coating on the structural properties of inner TiO_2 in the crystallization process was studied by adjusting the amount of added tetraethyl orthosilicate (TEOS). SPV technology was first used to test the shielding effect of SiO_2 film. Toluene was selected as the model VOC to study the performance of the prepared composites for photocatalytic degradation of air pollutants at different relative humidity (RH). The present work provides a novel idea to deal with the challenge of haze pollution in the photocatalytic degradation of air pollutants.

2. Materials and methods

2.1. Catalysts preparation

5.36 mL ethylenediamine (98%, Aldrich, USA) was added into 40 mL absolute ethanol (>99.8%, Aldrich, USA), followed by 30 min stirring. A solution of 400 mmol/L titanium(IV) isopropoxide (TIPO, 97%, Aldrich, USA) in 50 mL absolute ethanol was dropped to the ethylenediamine-ethanol solution under vigorously stirring for 30 min. After that, 40 mL deionized water was added, and the mixture was stirred for another 2 h. Then, the solution was transferred into a 200 mL autoclave and heated at 110 °C for 24 h. After cooling down to room temperature, the mixture was centrifuged. The obtained solid was washed with absolute ethanol twice and dispersed into 400 mL absolute ethanol, followed by adding 60 mL deionized water and 16 mL ammonium hydroxide solution (28%, Aldrich, USA) under continuously stirring. The solution was equally divided into five parts, and 0, 0.1, 0.25, 0.5, and 1 mL tetraethyl orthosilicate (TEOS, 99.0%, Aldrich, USA) was added drop by drop to each part, respectively, followed by 3 h stirring. Then, the solution was centrifuged. The obtained solids were dried at room temperature and heated at 700 °C for 30 min. After cooling down naturally, the prepared samples, named as TiO_2@SiO_2-0, TiO_2@SiO_2-10, TiO_2@SiO_2-25, TiO_2@SiO_2-50, and TiO_2@SiO_2-100, were ready for the successive experiments. The mole ratios of Si added to Ti were 1:50, 2.5:50, 5:50, and 10:50 for TiO_2@SiO_2-10, TiO_2@SiO_2-25, TiO_2@SiO_2-50, and TiO_2@SiO_2-100, respectively. To discuss the electron shielding effect of the SiO_2 coating, TiO_2-HF was obtained by removing the SiO_2 coating of TiO_2@SiO_2-50 in HF solution. The sample which followed exactly the same synthesis process except for heating at 700 °C was named as TiO_2-O.

2.2. Photocatalytic experiment

The detailed information of the photocatalytic experiment has been reported in our earlier works [20,21]. A single-pass reactor was used to test the removal efficiency of toluene. The prepared samples were coated onto uniform glass rods (diameter, 4.1 mm; length, 140 mm) by dipping method until the weight of each sample reaching 5.0 ± 0.2 mg. The photocatalytic reactor was a quartz tube (internal diameter, 5.0 mm; length, 155 mm). The irradiation light came from four UV lamps (8 W, 254 nm, PHILIPS) surrounding the reactor with the complementary wavelength at 183 nm being filtered. The carrier gas was produced by a clean-air generator (GA-5000A, Beijing Zhongxinghuili, China). Three mass flow rate controllers (S48-32/MT, Horiba Metron Instruments, China) were used to adjust the concentrations of toluene and water vapor. RH was set as 20%, 50%, and 80%, respectively. To simulate the level of indoor air pollutants, the concentration of inlet toluene was kept constant at 387 ± 20 μg/m^3. The photodegradation experiments were performed at a higher toluene concentration of 22 ± 0.3 mg/m^3 to characterize the difference of the prepared catalysts in photoactivity. The gas system was placed in an incubator (LRH150F, Shanghai Yiheng, China) at a constant temperature of 25 ± 0.5 °C. The concentrations of toluene from the inlet and outlet were detected by GC-FID (GC9790II, Zhejiang Fuli, China).

2.3. Characterization of catalysts

The data of N_2 adsorption-desorption curves was obtained by an Autosorb-1MP-VP surface area analyzer (Quantachrome, USA). All the samples were degassed at 378 K for 8 h before the N_2 adsorption-desorption measurements. A JEM-2010(HR) instrument (JEOL, Japan) was used to obtain the transmission electron microscopy (TEM) images at an accelerating voltage of 200 kV. An X-ray diffraction (XRD) instrument D/MAX 2550 PC (Rigaku,