

Preparation and Reduction Effect of Volatile Compounds of TiO₂ Hemispheres

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Since titanium dioxide (TiO₂) was first used in photocatalytic reactions for degrading contaminants in water and air by Fujishima and Honda,¹ TiO₂ has been extensively studied as a photocatalyst for environmental application.^{2–7} However, the general use of TiO₂ as a photocatalyst has been limited because TiO₂ requires ultraviolet (UV) irradiation under the wavelength of 380 nm for its activation due to the wide band gap of 3.2 eV.⁸ To overcome this limitation, much effort has been devoted to the development of visible-light-induced photocatalysts by doping TiO₂ with transition metals such as Cr, Zn, Cu, Mn and Fe.^{9–14} It has been recently found that visible-light-induced photocatalysts brought out efficient decomposition of organic compounds, and could be anti-bacterial and viral agents.^{15–18}

Hollow sphere nanoparticles have been known as potentially excellent materials for contaminated pollutants removal.^{19,20} TiO₂ hollow nanospheres with chromium ion were shown to improve the photocatalytic activity and photodecompose methylene blue (MB) under visible light irradiation.²⁰ Thus, because photocatalysts of TiO₂ hollow nanospheres with Cr³⁺ are activated by visible-light rather than UV and have more spacious superficies than any flat layer array, they can be used effectively for the decomposition of volatile organic compounds (VOCs) in air. In this work, TiO₂ hemisphere nanostructures with Cr³⁺ were synthesized with polystyrene-methyl acrylic acid (PSA) latex particles as templates and characterized by FESEM (field emission scanning electron microscope). And the reduction extent of VOCs (toluene and trimethylamine) and ammonia by ABS (acrylonitrile butadiene styrene) copolymer coated with the prepared TiO₂ hemispheres under fluorescent light irradiation was evaluated.

TiO₂ hemisphere nanostructures were obtained by using PSA latex particles as templates. Fig. 1 shows the SEM image of TiO₂ hemispheres with 0.5% Cr³⁺, which were formed by rupture according to abrupt temperature change from RT to 600 °C during calcination. The diameter (~300 nm) of the PSA polymer was smaller than that of the prepared

hemispheres. This result revealed that TiO₂ spheres were successfully coated on PSA particles and PSA was removed by calcination in air at 600 °C.

Hydroxyl radicals generated from the photocatalytic reactions were considered to be very potent oxidants and non-selective in reactivity for the oxidation of organic substances (Fig. 2).²¹ The reduction effect of VOCs and ammonia by ABS copolymer coated with 0.5% Cr/Ti hemispheres was assayed with Gastec detector tube method. The extent of photodecomposition of VOCs and ammonia under fluorescent light was shown in Table 1 and Fig. 3.

The concentration of toluene was decreased to 22 ppm by addition of a TiO₂ hemisphere-coated ABS copolymer, whose deodorization rate was 45% (denoted as sample 1). A deodorization rate of 62.5% was achieved for toluene by addition of a pretreated and hemisphere-coated ABS, in which an ABS was first pretreated with a corrosive strong acid and dipped in TiO₂ hemisphere solution (denoted as sample 2). This value was 17.5% higher than the deodorization rate of 45% of toluene obtained by the use of a hemisphere-coated ABS. The first treatment of an ABS with a

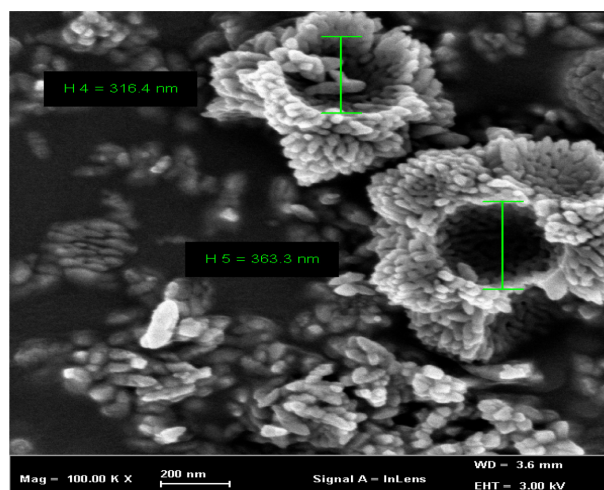


Figure 1. SEM image of TiO₂ hemispheres with 0.5% Cr³⁺ calcinated at 600 °C.

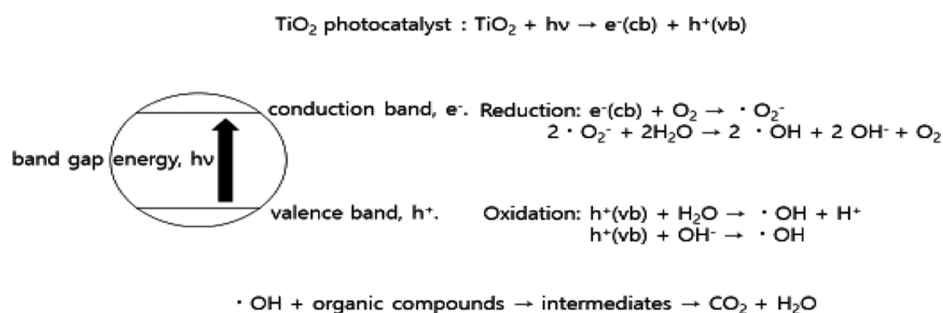


Figure 2. Mechanism proposed for the action of TiO_2 .

Table 1. Deodorization rate of toluene, trimethylamine and ammonia by an ABS copolymer coated with Ti/Cr hemispheres.

toluene	Initial concentration (ppm)	detected concentration (ppm)	deodorization rate (%)
Control	40	40	—
Sample1	40	22	45
Sample2	40	15	62.5
trimethylamine	Initial concentration (ppm)	detected concentration (ppm)	deodorization rate (%)
Control	20	20	—
Sample1	20	10	50
Sample2	20	8	60
ammonia	Initial concentration (ppm)	detected concentration (ppm)	deodorization rate (%)
Control	40	40	—
Sample1	40	19	52.5
Sample2	40	16	60

Sample1: an ABS coated with only TiO_2 hemispheres without any pretreatment
 Sample2: an ABS coated with TiO_2 hemispheres after pretreatment

strong acid before dipping in a photocatalytic solution improved both the coating efficiency of TiO_2 and the deodorization rate of toluene. Corrosive acid pretreatment is thought to activate surface energy state leading to strong binding between TiO_2 nanoparticle and ABS surface, and more nanoparticles are coated on ABS surface so that more photocatalytic active sites are made. The photo-catalytic degradation rate of toluene over Ce- TiO_2 thin film was 61.9% with illumination using a 254 nm light source for 8 h of irradiation time.²² So our Cr- TiO_2 hemisphere is thought to be practically more excellent in eliminating toluene in air because it does not need UV irradiation for its activation.

The concentration of trimethylamine (TMA) was decreased to 10 ppm by addition of a TiO_2 hemisphere-coated ABS copolymer, whose deodorization rate was 50%. A deodorization rate of 60% was achieved for TMA by addition of a pretreated and hemisphere-coated ABS. This value was 10% higher than the deodorization rate of 50% of TMA obtained by the use of a hemisphere-coated ABS. Like toluene, the first treatment of an ABS with a strong acid

before dipping in a photocatalytic solution improved both the coating efficiency of TiO_2 and the deodorization rate of TMA.

The concentration of ammonia was decreased to 19 ppm by addition of a TiO_2 hemisphere-coated ABS copolymer, whose deodorization rate of 52.5%. On the other hand, the addition of a pretreated and hemisphere-coated ABS resulted in a deodorization rate of 60% of ammonia. This value was 7.5% higher than deodorization rate of 52.5% of ammonia by a hemisphere-coated ABS. Similar to toluene and TMA, the first treatment of an ABS copolymer with a strong acid increased both the coating efficiency of TiO_2 and the deodorization rate of ammonia. This more deodorization rate was observed after the pretreatment of an ABC with a corrosive strong acid, followed by coating of the copolymer with the photocatalytic solution. These results suggest that TiO_2 hemispheres can be used for effective decomposition of VOCs under fluorescent light inside buildings so that indoor air quality could be improved.

In conclusions, TiO_2 hemisphere nanostructures were obtained by using polystyrene-methyl acrylic acid particles as templates and by rupture according to abrupt temperature change during calcination. The reduction of VOCs and ammonia by an ABS copolymer coated with 0.5% Cr/Ti hemispheres was assayed with Gastec detector tube method. Deodorization rate showed 45% for toluene, 50% for TMA and 52.5% for ammonia. An ABS copolymer which was first pretreated with corrosive strong acid and then dipped in the photocatalytic TiO_2 solution showed the more deodorization rate of 62.5% for toluene, 60% for TMA and 60% for ammonia than without strong acid pretreatment.

EXPERIMENTAL

Preparation of TiO_2 Hemisphere Nanostructures with Cr^{3+}

TiO_2 hemisphere nanostructures with Cr^{3+} were prepared as follow: 180 μL of $\text{Ti}(\text{SO}_4)_2$ was added to 32 mL of distilled

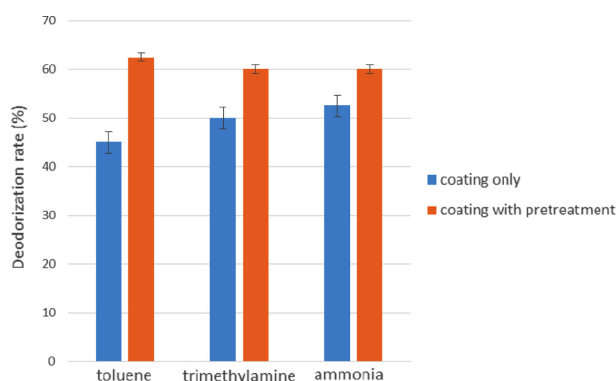


Figure 3. Difference in the deodorization rates of toluene, trimethylamine and ammonia by TiO₂ hemispheres with and without strong acid pretreatment. The values are the averages of three separated experiments.

water and stirred vigorously. 0.07 g of polystyrene (~300 nm) particles, 1.98 mL of CTACl (cetyltrimethylammonium chloride), 800 μ L of HCl and 0.36 mg of Cr₂(SO₄)₃·H₂O were added under the stirring condition. The mixture was agitated for 20 min and left at 70 °C with stirring overnight, then cooled and centrifuged for 10 min. The supernatant were discarded. And the precipitates were harvested and washed with distilled water and ethanol (1:1, v/v). The resulting solids were collected by centrifugation and dried at 60 °C overnight. The obtained sample was then put into oven and kept at 600 °C for 5 h. 1 g of the baked sample was added to 10 ml of ethanol and the mixture was sonicated for 30 min, followed by the addition of 300 μ L of ammonia solution and 500 μ L of distilled water. The mixture was then stirred at 300 rpm overnight, collected by centrifugation and dried at 60 °C overnight. 3 mL of methanol was added to 1 g of the resulting, dried sample and the mixture was stirred for 6 hr. Additive agent /leveling agent (0.3 part of the dried sample) was added to the mixture and agitated. ABS copolymer was coated by dipping in the above solution and dried in air.

SEM image was obtained using a field emission scanning electron microscope (ULTRA PLUS, Zeiss).

VOCs Assay

The effect of VOC reduction of the Ti/Cr hemisphere-coated ABS copolymer was tested with Gastec detector tube method. Ti/Cr hemisphere-coated resin and no coated resin were put in each 3L Tedlar bag, respectively and

exposed to each VOC (toluene and trimethylamine) and ammonia. After 2 h at (18±2)°C, the extent of VOC reduction was measured with each gas-detecting tube.

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