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Application of ultrasound-aided method for the synthesis of CdS-incorporated three-dimensional TiO_2 photocatalysts with enhanced performance

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ABSTRACT

In this study, an ultrasound-aided hydrothermal–impregnation method was used to synthesize three-dimensional (3D) urchin-like CdS–TiO_2 nanostructures (UCTs) with variable CdS content. The photocatalytic efficiencies (for degrading limonene and toluene vapor) of UCTs synthesized using the ultrasound-aided process were greater than those of UCTs fabricated without ultrasound treatment. In addition, the photocatalytic efficiencies of ultrasound-treated UCTs were greater than those of zero-dimensional ultrasound-treated CdS–TiO_2 particles, which, in turn, were greater than those of untreated 3D TiO_2. These results indicate that ultrasonication is an amicable process for the synthesis of UCTs with high photocatalytic activity. The enhanced activity of ultrasound-treated photocatalysts is ascribed to the greater charge carrier efficiency, adsorption capacity, and light absorption efficiency of these materials. The photocatalytic efficiencies of ultrasound-treated UCTs increased as the CdS loading was increased from 0.1% to 0.3%, gradually dropping as the loading was further increased to 3.0%, which indicated the existence of an optimum CdS loading. UCT photocatalytic efficiencies depended on the input concentration of target pollutants, relative humidity, and air flow rate. The photocatalytic efficiency for the decomposition of limonene mixed with 2-propanol was lower than that for limonene alone, likely due to the radical scavenging properties of 2-propanol. However, the photocatalytic degradation efficiency of the latter alcohol was not changed upon admixture. Toluene exhibited the same behavior. The mineralization ratios of both target compounds were lower than their decomposition ratios, indicating formation of byproducts due to incomplete oxidation. In addition to CO, three organic compounds were observed as photocatalytic decomposition byproducts of limonene (acetic acid, limonene oxide, and methacrolein) and toluene (benzene, benzaldehyde, and *p*-xylene). UCTs synthesized by the ultrasound-aided hydrothermal–impregnation method could be used to decompose organic vapors with an efficiency of up to 98%, depending on operating conditions.

1. Introduction

Application of the widely used TiO_2 semiconductor to the photocatalytic decomposition of environmental pollutants is effective only if it is activated in the ultraviolet (UV) region [1–3]. Practical utilization of TiO_2 is also restricted by its low quantum efficiency due to the high recombination rate of charge carriers [1,3]. To tackle these drawbacks, substantial effort has been devoted to the modification of the surface characteristics of TiO_2. Surface modification by sensitization with narrow band gap semiconductors is an attractive strategy for extending the light absorption of TiO_2 into the visible region [4,5]. CdS is a promising semiconductor for this purpose, owing to its narrow band gap (~2.4 eV) [6]. A combination of TiO_2 with CdS (CdS–TiO_2) induces efficient charge separation by electron migration from the conduction band of CdS to that of TiO_2 upon exposure to visible light, improving the quantum efficiency [5]. CdS in CdS–TiO_2 is also stabilized against photocorrosion in humid environments, which occurs due to the oxidation of surface sulfide ions by the photoproduced charge carriers [7]. Several research groups [6,8–12] have demonstrated that zero-dimensional (0D) CdS–TiO_2 particles (CTPs) activated by visible light can be used to degrade environmental pollutants and generate hydrogen by water splitting.

Structural dimensionality of photocatalysts is an important parameter for determining photocatalytic efficiency, since it influences light absorption, surface properties, and the transport of

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charge carriers [13]. Three-dimensional (3D) nanostructures have a high surface area-to-volume ratio, which enhances charge carrier mobility, adsorbate transfer into the nanostructure, and light absorption efficiency [13,14]. Owing to these properties, 3D TiO_2-based structures show better photocatalytic performance in the degradation of water contaminants (such as 4-nitrophenol, methyl orange, alizarin red S, and *p*-chlorophenol) compared to 0D spherical TiO_2-based structures [15–17]. However, applications of 3D CdS–TiO_2 nanostructures in the treatment of environmental pollutants are hardly reported.

Sonochemical treatment is an environmentally friendly method for synthesizing nanostructural materials, since it reduces the consumption of chemical reagents and energy, increases the specific surface area, and produces uniform and finely dispersed nanomaterials [18–21]. Sonochemical processing utilizes acoustic cavitation generated by the sudden collapse of bubbles in liquid phases to initiate chemical reactions and physical changes [18,22]. Previously reported [18,19,23], 0D nanospherical photocatalysts synthesized by ultrasound-aided processes exhibited enhanced photocatalytic efficiencies for the decomposition of aqueous dye pollutants. Shirsath et al. [18] reported that the photocatalytic efficiencies of methylene blue decomposition over 0D Ce-doped TiO_2, Fe-doped TiO_2, and unmodified TiO_2 synthesized by ultrasound-assisted processes were 84%, 77%, and 71%, respectively, while those for photocatalysts synthesized by conventional methods were 75%, 68%, and 61%, respectively. Li et al. [23] also reported that 0D Fe-doped TiO_2 nanoparticles prepared by an ultrasound-aided hydrothermal process exhibited more efficient methylene orange degradation than unmodified TiO_2. Hydrothermal treatment can also be used to prepare various 3D photocatalysts [15,24–26], and CdS can be easily incorporated into TiO_2 via an impregnation method [10]. Therefore, we suggest that an ultrasound-aided hydrothermal–impregnation process can be used to prepare 3D CdS–TiO_2 nanostructures with improved photocatalytic activity.

In this study, the ultrasound-aided hydrothermal–impregnation method was used to synthesize 3D urchin-like CdS–TiO_2 nanostructures (UCTs) and to assess their ability to decompose vapor-phase pollutants under various conditions. Four reference photocatalysts were examined in this study: 0D ultrasound-treated CdS–TiO_2 particles, two 3D TiO_2 samples prepared with and without ultrasound treatment, and a non-ultrasound-treated UCT. Limonene and toluene vapors were selected as model pollutants. Limonene is present in many household cleaning agents owing to its flavoring and cleaning properties and was chosen based on its prevalence in indoor environments and its reaction with oxidants (such as O_3, $^{\cdot}OH$, and $^{\cdot}NO_3$) that produce highly toxic formaldehyde and organic particulate matter [27,28]. Toluene is another hazardous indoor air pollutant widely employed to evaluate the performance of photocatalysts [29]. The effects of adding 2-propanol, a well-known OH radical scavenger [30], were evaluated by examining the photocatalytic efficiencies for mixtures of limonene/2-propanol and toluene/2-propanol using a representative UCT. The mineralization ratios and byproducts formed in the above photocatalytic reactions were also investigated.

2. Materials and methods

2.1. Preparation of photocatalysts

Procedures for the preparation of reference photocatalysts and UCT samples with various CdS contents are summarized as follows: preparation of TiO_2 powders, fabrication of 3D TiO_2 nanostructures with and without ultrasound treatment, incorporation of CdS into the above 3D TiO_2 nanostructures, and impregnation of CdS into 0D TiO_2 powder. TiO_2 powders were prepared under ultrasonication conditions using titanium tetraisopropoxide (TTIP, Sigma-Aldrich) as Ti precursor. Surfactant P-123 (Sigma-Aldrich, 1.0 g) was added to deionized water (200 mL) and stirred for 40 min, followed by the addition of TTIP (60 mL) and stirring for another 40 min. The solution was ultrasonicated for 80 min (for better dispersion) using an ultrasonic cleaner with a frequency of 40 kHz (Branson 5510), allowed to stand for 24 h in a clean room, and centrifuged at 1500 rpm for 15 min. The precipitates were dried at 85 °C for 12 h and heated at 500 °C for 2 h to afford TiO_2 nanopowders.

3D TiO_2 nanostructures were prepared by hydrothermal and ultrasonic treatment of TiO_2 nanopowders. Titanium tetrachloride ($TiCl_4$, Sigma-Aldrich, 40 mL), 10 M NaOH (Sigma-Aldrich, 60 mL), and 30% H_2O_2 (Sigma-Aldrich, 20 mL) were added to deionized water (280 mL). TiO_2 nanopowders (200 mg) were added to the mixture, followed by hydrothermal treatment in an autoclave at 85 °C for 4 h. After centrifuging the resulting solution at 10,000 rpm for 10 min, the precipitates were mixed with aqueous HCl (Sigma-Aldrich, 400 mL) and sonicated three times for 40 min using an ultrasonicator (Sonics & Materials VCX750: power, 750 W; frequency, 20 kHz; pulse, on; tip diameter, 19 mm; amplitude, 29 μm). The products were successively washed with distilled water and ethanol (Sigma-Aldrich), dried at 50 °C for 20 h, and heated at 500 °C for 2 h to produce a 3D TiO_2 nanostructure (denoted 3D TiO_2). The 3D TiO_2 synthesized without ultrasound treatment is denoted NU-3D TiO_2.

UCTs were prepared by impregnating 3D TiO_2 nanostructures with CdS. A predetermined amount of cadmium acetate [$Cd(CH_3COO)_2{\cdot}H_2O$, Sigma-Aldrich; 0.018, 0.053, 0.106, 0.177, or 0.533 g] was added to ethanol (100 mL) to prepare Mixture A. Mixture B was prepared by adding 3D TiO_2 nanopowder (1 g) to 3-mercaptopropionate ($HSCH_2CH_2CO_2H$, Sigma-Aldrich, 60 μL) and keeping the mixture at ambient conditions for 1 h. Mixture B was added to Mixture A to produce Mixture C. A specified amount of thiourea (NH_2CSNH_2, Sigma-Aldrich; 0.015, 0.046, 0.092, 0.152, or 0.457 g) was slowly added to Mixture C, followed by dropwise addition of 0.2 M NaOH to reach pH 10. The solution was kept at ambient conditions for 15 h and vacuum-filtered to isolate the precipitates, which were washed with deionized water and acetone and dried at 70 °C for 12 h to furnish the desired UCTs. The amounts of $Cd(CH_3COO)_2{\cdot}H_2O$ and NH_2CSNH_2 were adjusted to fabricate UCTs with CdS/TiO_2 ratios of 0.1, 0.3, 0.6, 1.0, and 3.0, denoted UCT-0.1, UCT-0.3, UCT-0.6, UCT-1.0, and UCT-3.0, respectively. UCT-0.3 synthesized without ultrasound treatment is denoted NU-UCT-0.3. The CTP-0.3 photocatalyst was synthesized by impregnating 0D TiO_2 powders with CdS to produce a CdS/TiO_2 ratio of 0.3 following the procedure used for the preparation of ultrasound-treated UCT-0.3.

The samples were examined using X-ray diffraction (XRD, Rigaku D/max-2500 diffractometer), scanning electron microscopy (SEM, Hitachi S-4300), high resolution field emission transmission electron microscopy (TEM, FEI company Titan G2 chemiSTEM Cs Probe TEM), photoluminescence emission spectroscopy (PL, Acton Research SpectraPro 2150i), UV–visible spectroscopy (Varian CARY 5G), and N_2 physisorption (ASAP 2020, Micromeritics).

2.2. Photocatalytic efficiencies

The efficiencies of the photocatalysts in the degradation of limonene and toluene were determined using a Pyrex tube reactor (3.7 cm inside diameter × 26.5 cm length). Another Pyrex tube (2.7 cm outer diameter × 26.5 cm length) was allocated inside the reactor. A cylindrical fluorescent daylight lamp (8 W, 1.5 cm outer diameter × 24.5 cm length) was placed inside the latter tube. The inner surface of the reactor was covered with 0.20 mg cm^{-2} of

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