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Noble metal modified TiO_2 microspheres: Surface properties and photocatalytic activity under UV–vis and visible light

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ABSTRACT

Composite photocatalysts that consist of TiO_2 and noble metal nanostructures have been considered to be the promising and pivotal material for accessible enhancement of the efficiency in the photocatalytic process carried out in the aqueous and gas phases. In this work we fabricated porous TiO_2 microspheres through a hydrothermal process followed by photochemical reduction of noble metal nanoparticles at the TiO_2 surface. The morphology and structure of M-TiO_2 spheres (M = Ag, Au, Pt and Pd) were studied with the use of various techniques, including transmission electron microscopy (TEM), X-ray powder diffraction analysis (XRD), photoluminescence (PL) and UV–vis diffuse-reflectance spectroscopy (DRS). The effect of metal amount (from 0.1 to 1 wt.%.) on the photocatalytic activity during toluene degradation in gas phase and phenol degradation in aqueous phase was investigated. Additionally, the photocatalytic activity of the M-TiO_2 samples was evaluated by measuring the formation rate of photo-induced hydroxyl radicals (•OH) under UV–vis light irradiation using coumarin as a probe. The obtained results indicated that toluene could be mostly removed from the air over TiO_2 microspheres modified with Ag, Au, Pt, and Pd nanoparticles. UV-mediated photoreactivity was almost similar for all samples obtained by loading metals from solutions consisting of 0.1 and 1 wt.% of metal precursors. Under visible light, except for Au, in gas phase toluene oxidation, the optimized loading of the metals was 0.1 wt.-% (photoreactivity changed in order: Ag-TiO_2 ≈ Pd-TiO_2 > Pt-TiO_2 » Au-TiO_2). In case of phenol degradation in the aqueous phase, in the presence of UV irradiation the highest amount of metal (1.5 wt.%) was profitable, while under the Vis light reaction the medium amount of metal (0.5 wt.%) was beneficial. Additionally, it was noticed that phenol was degraded not only via oxidation by •OH radicals but probably also in direct reaction with the photogenerated carriers (e^-/h^+), particulary in the presence of TiO_2 spheres loaded with Au and Ag nanoparticles.

1. Introduction

Heterogeneous photocatalysis has been proposed as a promising process to remove pollutants from air and water streams due to possibility of organic pollutants oxidation to CO_2 and H_2O in the presence of semiconductors [1–10]. TiO_2 is one of the most promising materials for environmental remediation due to its non-toxicity, photo-stability and relatively low cost [11]. However, the wide band gap (3.2 eV for anatase) and the rapid recombination of photogenerated charge carriers mainly limit further applications of anatase [12]. To improve the photocatalytic reactivity of TiO_2 and to extend its light absorption into the visible region, substitution of non-metal atoms, transition metal doping, reduced forms of TiO_x, coupling some semiconductors with narrow bandgap were proposed [12–17]. Among these techniques, noble metal nanoparticles (especially Au, Pt, Pd and Ag) modification of TiO_2 is also used to inhibit recombination of electron- hole recombination process and to extend absorption properties of TiO_2 into visible region due to surface plasmon resonance(SPR) [18,19]. Noble metal nanoparticles absorb and scatter light in the visible range as a result of SPR, where the resonant wavelength strongly depends on the particle size, shape, assembly state and surrounding dielectric environment [20–22]. Furthermore, it has been found that various TiO_2 with different morphology and size, such as nanosheet, nanofibers, nanotube and microspheres, possess good adsorptive and photocatalytic properties [23–25]. The fabrication of TiO_2 3D structures,

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such as microspheres has recently attracted enormous attention due to their low density, high surface-to-volume ratio, high surface area, good surface permeability and high photocatalytic activity [26–29]. Thus, it could be expected that higher energy conversion efficiency and photocatalytic activity could be achieved by using TiO_2 microspheres as photocatalysts [29].

Controlling of volatile organic compounds in the atmosphere is a major environmental problem now. Toluene is a volatile liquid (22 mm Hg at 20 °C) and it is released into atmosphere by industrial and consumer uses [30]. The largest sources of toluene effluents are the evaporation from gasoline, paints, paint thinners, fingernail polish, lacquers, adhesives, rubber, cigarette smoke and some printing and leather tanning processes [31]. Toluene is an irritant to the skin and mucous membrane, and can act as an anesthetic to the central nervous system [32,33]. Thus, one of the challenges in the field of photocatalytic air treatment systems is the development of photoactive materials activated by low powered and low cost irradiation sources (such as LEDs) to remove VOCs, such as toluene.

Toluene from the gas phase was efficiently removed over LED-irradiated TiO_2 nanotube arrays, obtained by anodic oxidation of titanium foil in ethylene glycol-based electrolytes [1]. It was found that the preparation conditions affected the TiO_2 nanotubes morphology (length of tubes, top-opened or clogged and wall smoothness) as well as their photocatalytic activity in the air purification process. The highest photoactivity in toluene degradation reaction was observed for longer (4.3-μm- and 5.9-μm-long nanotube arrays) obtained by Ti-foil anodization in ethylene glycol-based electrolyte. 30-min of irradiation by twenty five UV-LEDs (λ_{max} = 375 nm, 63 mW per diode) was enough to complete the removal of toluene (C_0 = 100 ppm) from the gas phase in the presence of TiO_2 nanotube [1].

Cao et al. found, that toluene could be selectively photooxidized to benzaldehyde in the presence of TiO_2 hollow spheres [34]. They observed that TiO_2 hollow spheres exhibited higher photo-efficiency than commercial TiO_2 Degussa P-25 and the conversion of toluene gradually increased from 9.0% to 21%, when the hydrothermal time of the synthesis increased from 20 min to 6 h. It was attributed to higher UV absorbance and lower recombination of free carriers of these hollow TiO_2 spheres with exposed {001} facets due to their unique high surface crystallinity [34].

Phenols are generally considered to be one of the important organic pollutants discharged into the environment causing unpleasant taste and odor of drinking water [4]. Recently, the TiO_2 microspheres have an attractive advantage in water treatment due to the high light-harvesting capacity and easy mass transportation [27,35,36]. Yang et al. prepared WO_3/TiO_2 hollow microspheres by a spray drying method and observed that WO_3/TiO_2 photocatalyst shows higher photocatalytic activity than pure TiO_2 in photodegradation of phenol [35]. Photocatalytic activity of TiO_2 microspheres was measured by Wang et al. in the photodegradation process of sulfosalicylic acid (SSA), phenol, and 2,4-Dichlorophenoxyacetic acid (2,4-D) [27]. The results showed that TiO_2 microspheres had strong adsorption ability, which significantly contributed to the overall degradation rate of all three organic compounds [27].

Herein, we modified the surface of TiO_2 microspheres (obtained *via* hydrothermal route) with noble metal nanoparticles using the photodeposition method. The M-TiO_2 photocatalysts (M = Ag, Au, Pt and Pd) were studied for photodegradation of toluene in the gas phase using low-powered irradiation source (light-emitting diodes, λ_{max} = 375 and 415 nm) and phenol in aqueous phase under UV–vis and visible irradiation. Moreover, in the second part of our research hydroxyl radical formations were investigated. Fluorescence of irradiated coumarin solution was used as a method of •OH radical detection. Coumarin readily reacts with generated hydroxyl radicals forming hydroxycoumarins. Although the major hydroxylation product is 5-hydroxycoumarin, only 7-hydroxyproduct of coumarin hydroxylation emits fluorescent light [37,38]. Thus, this method was used only for hydroxyl radical detection, but not for determining concentration of hydroxyl radicals.

To our best knowledge, correlation between surface properties of such new composites – TiO_2 microspheres decorated with noble metal nanoparticles- and photoactivity, including: (a) toluene degradation in the gas phase, activated by light-emitting diodes (LEDs), (b) phenol degradation in the aqueous phase, and (c) •OH radicals formation was done for the first time. The effect of the type and size of noble metal nanoparticles on the photoactivity of M-TiO_2 was also discussed. Because of the fact that LEDs are low-powered and low-cost irradiation sources, there exists a promising possibility of reducing power consumption and costs of photocatalytic process.

2. Experimental

2.1. Chemicals and materials

All chemicals were analytical grade and used without further purification. The Degussa P-25 TiO_2 was supplied by Evonik Industries, and used as obtained. Titanium (IV) butoxide (TBT) (97%, Sigma-Aldrich) was used as titanium source for the preparation of TiO_2 microspheres. $KAuCl_4$ (98%), $Pd(C_5H_7O_2)_2$ (99%), H_2PtCl_6 (99%) and $AgNO_3$ (99%) from Sigma-Aldrich were used as a metal source in the preparation procedure. Coumarin was purchased from Sigma–Aldrich Co. (Germany) and phenol was obtained from POCh S.A. (Poland).

2.2. Preparation of TiO_2 microspheres

TiO_2 microspheres were prepared according to the procedure described by Zheng et al. [39]. The hydrothermal technique is an important tool to obtain advanced nanostructural materials. Moreover, by using this method it is possible to synthesized TiO_2 with homogeneity, high purity, crystal symmetry, metastable compounds with unique properties and narrow particle size distributions [40]. In the next step, 70 cm^3 of 99.8% ethanol (alcohol was used as hole scavenger [41]), solution containing TiO_2 microspheres (1 g) and metal precursor (0.1, 0.5 or 1% m/m Ag, Au, Pt, and Pd, respectively) was sonicated for 10 min, stirring in the dark for 10 min, degassed with nitrogen in the dark for 20 min and finally illuminated by 250 W Xe lamp (light flux 30.8 mW/cm^2) used as an irradiation source for 1 h. Initial concentrations of noble metal precursors in ethanol were: 7.33; 3.67 and 71.45×10^{-4} mol/dm^3 for $KAuCl_4$, 0.14; 6.78 and 1.34×10^{-4} mol/dm^3 for $Pd(C_5H_7O_2)_2$, 7.40; 3.70 and 73.31×10^{-4} mol/dm^3 for H_2PtCl_6 and 0.13; 6.65 and 1.32×10^{-4} mol/dm^3 for $AgNO_3$. Obtained samples were rinsed with deionized water and dried at 40 °C, without calcination. On the basis of literature data and our own experience it is known that the photodeposition method is a powerful technique to obtain metal nanoparticles of controlled size and shape in solution and deposited at the surface of different matrix [42,43]. Under UV light irradiation, the illuminated anatase TiO_2 generates in aqueous medium photoexcited electrons and positive holes. Afterwards, noble metal ions adsorbed on the surface of TiO_2 particles can react with the photogenerated e^- to form Ag^0, Au^0, Pt^0 and Pd^0. The description of the as-prepared photocatalysts is shown in Table 1. The amount of silver, gold, platinum and palladium precursors taken for photocatalyst preparation was calculated on the assumption that the content of Ag, Au, Pt, and Pd in the photocatalysts after synthesis should be equal to 0.1–1% m/m of the photocatalyst dry mass.