



Enhanced visible light photocatalytic activity of Pt/I-TiO₂ in a slurry system and supported on glass packing



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ABSTRACT

Highly photoactive I/TiO₂, Pt/I-TiO₂ nanocomposites were obtained using a hydrothermal and wet impregnation method. The incorporation of iodine and modification with 0.05 mol% of platinum leads to enhanced photocatalytic activity as compared to singly doped TiO₂ due to the presence of impurity energy level in the structure of TiO₂. X-ray diffraction, TEM microscopy, UV-Vis spectroscopy, X-ray photoelectron spectroscopy and BET methods showed that the most active photocatalyst had anatase structure, 187 m²/g specific surface area, absorbed UV-Vis light and contained 3 nm platinum particles. XPS analysis revealed that iodine exists in the form of I⁻ and IO₃⁻ species and platinum was present as Pt and PtO₂. The photocatalytic activity of Pt/I-TiO₂ nanocomposite was maintained after 4 runs, suggesting stability and reusability of the obtained photocatalyst. The efficiency of degradation of model organic compound was measured in a slurry type photoreactor as well as in a fixed-bed photoreactor equipped with parabolic mirror with Pt/I-TiO₂ immobilized on glass beads or glass Raschig rings.

1. Introduction

Titanium (IV) oxide is one of the most important photocatalytic materials in the area of environmental purification [1,2]. However, the photocatalytic activity of TiO₂ is limited by its inefficient exploitation of visible light. For TiO₂ the band gap is equal from 3.0 to 3.2 eV depending on the crystal structure, thus it only absorbs ultraviolet light, which constitutes only 3–5% of the solar light.

For the effective and large-scale utilization of visible light, which makes up as much as 45% of the total solar energy a variety of organic [3] and inorganic compounds [4] were examined as dopants or surface modifiers. Recently, noble metal nanoparticles (Ag, Au, Pt, Pd) have attracted attention, since they possess the ability to absorb visible light due to localized surface plasmon resonance (LSPR) and may enhance the transfer of photogenerated electrons extending the lifetime of charge carriers [5,6]. Among noble metal nanoparticles, platinum produce the highest Schottky barrier that facilitate electron capture and therefore hinders the recombination rate between electrons and holes [7]. Surface modification by deposition of platinum nanoparticles on the semiconductor surface is interested not only because of extension of UV-Vis light absorption but also ascribed to the effective charge separation [8]. Although platinum nanoparticles are very promising modifiers, taking into consideration their high cost, trace amounts of

this metal should be used in photocatalysis. Accordingly, reducing the amount of Pt without compromising their photocatalytic performance can be achieved by modification with other metal into bimetallic structure [9,10] or co-doping of TiO₂ with nonmetal element [11,12].

Recently, co-doped TiO₂ with two different elements, especially non-metal and metal elements has become a rapidly growing field of interest in photocatalysis. The impurity doping into the lattice of metal oxide semiconductor with the appropriate nonmetal element could modify the properties of semiconductor and enhance the separation of charge carriers [13]. Kim et al. reported that co-doping of Fe and N inhibit the recombination of the photogenerated electron and hole. The Fe³⁺ ion can trap the photoexcited electron, while N can trap a part of photoinduced holes, prolonging the charge carriers lifetime [14]. Introduction of a small amount of carbon, nitrogen and sulfur into the lattice of TiO₂ and modification with Pd nanoparticles enhanced photocatalytic activity towards the removal of acetylsalicylic acid and effective generation of ·OH radicals [15]. The carbonate species and doped sulphur species created additional two impurity levels by replacing Ti⁴⁺ below the conduction band of TiO₂, and the doped nitrogen species also generated a new impurity level above the valence band of TiO₂. Moreover, deposition of palladium generate the Schottky barrier on TiO₂ surface, which trapped electrons and suppressed electron-hole recombination [15]. Previously, we have also reported that

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compared to N-TiO₂ and Pt-TiO₂ samples, the photocatalytic activity of Pt-N/TiO₂ was improved, regarding the observed synergistic effect of co-dopants [16]. Higher photoactivity of Pt-N/TiO₂ nanoparticles resulted from the efficient interfacial electron transfer from the conduction band to oxygen species.

In the present paper, we report a novel platinum modified and iodine, carbon co-doped TiO₂ photocatalysts (Pt/I,C-TiO₂) prepared through a combined hydrothermal and wet-impregnation method. Surface modification with platinum and co-doping of iodine and/or carbon into titanium (IV) oxide has been proposed to both extend the absorption and enhance efficiency of pollutants degradation under visible light irradiation. The effect of iodine, carbon co-doping and platinum modification on the photocatalyst structure, surface area, crystallinity, and efficiency of phenol degradation under Vis ($\lambda > 420$ nm) and UV-Vis light irradiation was investigated.

Another important issue in application of photocatalysis in wastewater treatment is separation of photocatalyst after purification process. Sedimentation for separation of the photocatalyst is usually insufficient. Even, when the coagulation, flocculation or centrifugation is proceed, there is often a residue of suspended photocatalyst in supernatant. Photocatalyst flocculation depends on the wastewater matrix and is hardly predictable [17]. Therefore, another set of experiments was made using Pt/I-TiO₂ immobilized on solid substrate. Immobilization of photocatalyst eliminate the need for subsequent filtration and particle recovery and facilitate photocatalyst regeneration. Non transparent porous materials such as zeolites, ceramic beads, activated carbon used as TiO₂ support are much less efficient compared to glass supports due to light transmission limitation in photocatalytic reaction. Therefore, in this study glass beads and glass Raschig rings were used for the first time as the substrates for immobilization of Pt/I-TiO₂ photocatalyst.

2. Experimental

2.1. Preparation of photocatalysts

All the reagents used in the experiments are of analytical grade (purchased from Aldrich) and used without further purification. Photocatalysts I/TiO₂, Pt/I-TiO₂ and Pt/I,C-TiO₂ were obtained using a hydrothermal and wet-impregnation method, as presented in Fig. 1A in Supporting materials.

Pt/I-TiO₂ photocatalysts were obtained without addition any carbon source by hydrothermal treatment method. In this regard, precursor of iodine (HIO₃ or KI) was dissolved in deionized water and dropwise added to titanium (IV) butoxide. After mixing for 30 min a certain amount of K₂PtCl₄ was added into titania sol. The resulting colloid was transferred into a 200 cm³ Teflon lined stainless steel autoclave.

Hydrothermal reaction was performed at 110 °C for 12 h and then the obtained suspension of the photocatalyst was centrifuged (2000 rpm for 5 min), dried at 70 °C to dry mass and calcinated at 300 °C for 3 h. The Pt/TiO₂ was prepared with the same method except no adding precursor of iodine.

Pt/I,C-TiO₂ photocatalysts were obtained by mixing titanium (IV) butoxide with acetylacetone and ethanol in proportion 1:1:2 and dropwise addition of ethanolic solution of TiO₂ precursor to aqueous dispersion containing certain amount of precursor of iodine and acetylacetone. The mass ratio of water to acetylacetone and ethanol equaled to 1:1:2. After 1 h of mixing aqueous solution of K₂PtCl₄ was added into titania sol and then obtained suspension of the photocatalyst was transferred into a 200 cm³ Teflon lined stainless steel autoclave. Hydrothermal reaction was performed at 110 °C for 12 h. Precipitated Pt/I,C-TiO₂ particles were centrifuged (2000 rpm for 5 min), dried at 70 °C to dry mass and calcinated at 300 °C for 3 h.

2.2. Characterization of photocatalysts

XRD analysis were performed using a Rigaku Intelligent X-ray diffraction system SmartLab equipped with a sealed tube X-ray generator. Data acquisition conditions were as follows; 2 θ range: 20–80°, scan speed: 1 min⁻¹ and scan step 0.01°. Crystallite size of the photocatalysts in the direction vertical to the corresponding lattice plane was determined using Scherrer's equation based on the corrected full width at half maximum (FWHM) of the XRD peak and angle of diffraction. Subtraction of the FWHM of standard was employed as correction method.

To evaluate light-absorption properties of modified photocatalysts, diffuse reflectance (DR) spectra were recorded, and the data were converted to obtain absorption spectra. The band gap energies of photocatalysts were calculated from the corresponding Kubelka–Munk function, F(R), which is proportional to the absorption of radiation, by plotting F(R)^{0.5}E_{ph}^{0.5} against E_{ph}, where E_{ph} is photon energy. The measurements were carried out on Jasco V-670 spectrophotometer equipped with PIN-757 integrating sphere.

Nitrogen adsorption–desorption isotherms were recorded at liquid nitrogen temperature (77 K) using Micromeritics Gemini V (model 2365) instrument and the specific surface areas were determined using the Brunauer–Emmett–Teller (BET) method.

XPS analysis was conducted on multichamber ultrahigh vacuum (UHV) system, (Prevac).

Fluorescence spectra of generated 2-hydroxyterephthalic acid were measured on a Perkin Elmer LS55 fluorescence spectrophotometer. The employed excitation light in recording fluorescence spectra was 315 nm.

High-resolution transmission electron microscopic (HRTEM) images were made with FEI Europe, Tecnai F20 X-Twin transmission electron microscope.

2.3. Measurements of photocatalytic activity

The photocatalytic activity of Pt/I,C-TiO₂ powders under UV-Vis and Vis light was estimated by measuring the decomposition rate of phenol in an aqueous solution. Phenol was selected as a model pollutant since it is a non-volatile, common contaminant frequently present in industrial wastewaters. The mechanism of phenol decomposition is also well established. Photocatalytic oxidation was carried out in two reaction systems (1) in suspension of photocatalyst and (2) in a fixed bed reactor with photocatalyst immobilized on glass beads or glass Raschig rings. The experimental setups used for photocatalytic measurements are presented in Fig. 2A in Supporting materials.

Firstly, the suspension of photocatalyst was irradiated using a Xenon lamp (6271 H, Oriel), emitting both UV and Vis light. The light flux at UV range (310–380 nm) was 30 mW/cm². The 25-cm³ photoreactor of 3-cm thickness of exposure layer was equipped with a quartz window. The optical path included a water filter and a cut-off glass filter (GG 420, $\lambda > 420$ nm). The temperature of the aqueous phase during irradiation was kept at 20 °C using a water bath. Aliquots of 1.0 cm³ of the aqueous suspension were collected at regular time periods during irradiation and filtered through syringe filters ($\varnothing = 0.2 \mu\text{m}$) to remove the photocatalyst particles.

In the experimental setup presented in Fig. 2A-b (see in Supporting materials) the photoreactor, made of a cylindrical quartz tube (i.d. 44 mm, length 130 mm), was filled with TiO₂-coated glass beads or glass Raschig rings with diameter of about 0.5 cm and positioned over an aluminum parabolic mirror. 0.5 dm³ of phenol solution (C₀ = 0.2 mmol/dm³) was pumped in a loop with a flow rate of 5 cm³/min. The fixed bed was irradiated by UV-Vis light using a 125 W Xenon lamp (Oriel) with irradiation flux 15 mW·cm⁻². Phenol concentration was estimated by colorimetric method using a UV-Vis spectrophotometer (DU-7, Beckman). Photocatalytic degradation runs were preceded by blind test in the absence of a photocatalyst or illumination.

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