



Carbon decorated $\text{In}_2\text{O}_3/\text{TiO}_2$ heterostructures with enhanced visible-light-driven photocatalytic activity



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ABSTRACT

Titanium dioxide (TiO_2) has been observed to solve environmental pollution and energy crisis, but its large band gap and high rate of charges combination impede its application. Narrowing band gap and enhancing separation of photoinduced electron-hole pairs are still a challenging task. Creating the heterojunction between different substances is an effective method. Meanwhile, doping TiO_2 with carbon is an efficient technique to reduce band gap and facilitate charges' transfer. In this study, carbon modified $\text{In}_2\text{O}_3/\text{TiO}_2$ heterostructures are prepared via a facile incipient wet impregnation method. Doping TiO_2 with carbon produces an additional carbon-doping level above valence band (VB) of TiO_2 causing it to be excited under visible light, and forms heterojunction between In_2O_3 and TiO_2 , which suppresses recombination of photoexcited electrons and holes and promotes migration of charge at the interface. Furthermore, ternary nanocomposite exhibits an effective separation and migration performance of photoinduced electrons and holes, and it shows enhanced photoactivity compared with pure P25 when it is applied to photocatalytically remove elemental mercury (Hg^0) under visible light irradiation. The possible charge transfer and photocatalytic reaction mechanism are proposed based on characterization and experimental results. In view of the enhanced photocatalytic performance of as-prepared sample, combination of carbon and In_2O_3 doped into TiO_2 support is a promising method to improve the photoactivity. Meanwhile, this method has a tremendous assist on designing and preparing newly effective photocatalyst and large-scale industrial applications.

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1. Introduction

Mercury, due to hypertoxicity and persistence, has gained considerable attention in recent years [1]. In addition, its heavy diffusivity has attracted global attention because mercury can spread the whole world for several years after it releases in the atmosphere [2,3]. The largest anthropogenic fountainhead of mercury is coal-fired power station, thus many emission standards have been constituted. In January 2013, Minamata Convention on Mercury, the first international legally binding treaty, was authorized by delegates from 147 countries [4]. It proposed a strict emission standard for coal-fired power plants. Therefore, it is imminent to explore efficient technologies to control mercury emissions from coal-fired power plants.

Mercury in coal-fired power plant flue gas exists in three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particulate-bound mercury (Hg^p) [5,6]. Hg^p can be easily captured by fabric filter (FF) or electrostatic precipitator (ESP), and Hg^{2+} can be removed by wet flue-gas desulfurization (WFGD) due to its water-soluble (especially in acidic conditions). However, Hg^0 is the most difficult speciation to be removed by existing air pollutant control devices in coal-fired power plants. The common Hg^0 removal techniques comprise physical adsorption, oxidant injection, and catalytic oxidation. Zhang et al. reported that the gas-phase mercury is adsorptively removed by oxygen non-thermal plasma modified activated carbon [7]. Fang et al. investigated the mercury oxidatively adsorbed by $\text{CaCO}_3/\text{KMnO}_4$ solution [8]. Zhao et al. found that Hg^0 could be perfectly catalytic oxidized by Mn/CNT at low temperature [9]. Compared with common techniques, the burgeoning photocatalysis owns high oxidation efficiency and satisfactory recyclable characteristics without secondary pollution.

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Consequently, photocatalytic oxidation of Hg^0 removal from coal-fired power plant flue gas has great potential development.

Titanium dioxide (TiO_2), one of the best-known semiconductor photocatalysts, has been observed to solve environmental pollutant and energy crisis owing to its strong oxidative property, non-toxicity, and high chemical stability [10]. Nevertheless, its large band gap (3.02 eV for rutile, 3.20 eV for anatase) impedes the application of TiO_2 photocatalysts, which can be excited in the ultraviolet light [11]. Furthermore, photoexcited electrons and holes are more easily recombined and difficult to migrate, which leads to a limited photooxidation rate [12]. To improve photocatalytic activity of TiO_2 support, many studies have been conducted to modify it to improve its optical properties and expand the absorption edge to visible light. These studies include surface modification [13], incorporating metal or nonmetal ion [14,15], and combining with metal oxides [16].

Combining metal oxides with TiO_2 host is a noticeable means to promote the migration of photoexcited electrons and holes and to narrow its band gap [17]. Indium oxide (In_2O_3), an important n-type semiconductor, which indirect band gap is about 2.6 eV, has been adopted to narrow the band gap of host [18,19]. Meanwhile, the formation of $\text{In}_2\text{O}_3/\text{TiO}_2$ heterojunction can effectively promote the interfacial charge transfer and the separation of the photoexcited electron-hole pairs, and in turn improve the photoactivity. Moreover, the conduction band (CB) levels of combined semiconductors in the proper place can promote the migration of photoexcited electrons [20]. The band gap of In_2O_3 is lower than that of TiO_2 , but the CB of In_2O_3 (E_{CB} for $\text{In}_2\text{O}_3 = -0.63$ V versus NHE, which means the CB potential and can be determined as the x-intercept of Mott-Schottky curve.) is higher than that of TiO_2 (E_{CB} for $\text{TiO}_2 = -0.4$ V versus NHE). Therefore, the formed heterostructure is an efficient junction to promote the separation of photoinduced electron-hole pairs when coupling In_2O_3 and TiO_2 together. Despite combining metal oxides with TiO_2 support can improve its activity, the introduced additional metallic ions also act as a recombination center, which causes excited electrons and holes to be combined once again. According to previous works [21,22], doping non-metal with TiO_2 support, such as carbon, nitrogen and sulfur, is an efficacious measure to extend the absorbing edge to the visible light region for TiO_2 and suppress recombination of the excited electrons and holes. Doping carbon with host shows sizeable potential superiorities compared with other genres of non-metal doping especially [23]. Carbon not only can act as adsorbent or support, but also can act as sensitizer, which can promote electrons migrating to the semiconductors [24]. Hence, it is propitious to utilize the synergistic functions of metal oxides and non-metal for extending the absorbing edge and promoting the separation of excited electrons and holes. Using In_2O_3 and carbon co-doped TiO_2 support as a photocatalyst system is an effective method for solving environmental pollutant and energy crisis.

In this paper, a series of mole percentage of indium and stationary carbon co-modified TiO_2 ternary materials were prepared by a facile incipient wet impregnation method. Doping TiO_2 with carbon can produce an additional carbon-doping level above the valence band (VB) of TiO_2 , meanwhile, an efficient heterojunction between In_2O_3 and TiO_2 is formed also. In this ternary nanocomposite, band gap is narrowed, and photoinduced electrons and holes are effectively separated. The synergized In_2O_3 and carbon co-doped TiO_2 photocatalyst was applied to photocatalytically remove gas-phase Hg^0 and it shows enhanced photocatalytic activity compared with pure P25. On the basis of characterization and experimental results, the possible transfer mechanism of photoexcited electrons and holes and possible reaction mechanism between ternary nanocomposites and Hg^0 are investigated.

2. Materials and methods

2.1. Chemicals and materials

$\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ and glucose (analytical grade) were sourced from Guoyao Chemical Reagent (Shanghai, China) and set as the precursors for indium oxide and carbon respectively. Degussa P25 (85 wt% anatase, 15 wt% rutile) was purchased from Jianghu Chemical Company in Shanghai, China. Absolute ethanol and distilled water were used for the preparation of ternary nanocomposites.

2.2. Preparation of carbon modified $\text{In}_2\text{O}_3/\text{TiO}_2$ heterostructure

The modified photocatalysts were prepared with stationary carbon contents (maintain the carbon precursor contents fixed) and different In/Ti molar ratios ranging from 0:1 to 0.09:1 by a facile incipient wet impregnation method. In a typical preparation procedure (In/Ti molar ratio was 0.02:1, i.e., 2 mol%), 20 mL distilled water and 30 mL absolute ethanol were blended in a beaker with continuous stirring for 5 min to obtain solution A. Then, P25 TiO_2 (25 mmol, 1.997 g) was added into solution A with continuous stirring for 30 min to get suspension B. Afterwards, glucose (0.5 g) and $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ (0.1910 g, 0.5 mmol) were mixed into the suspension B to obtain suspension C. The suspension C was continuously stirred for 30 min and dried at 120 °C in a ventilation oven overnight. After that, the obtained sample was ground in an agate mortar with pestle. The obtained powder was calcined in a muffle furnace with heating rate 5 °C/min until 400 °C and maintained this temperature for 3 h. Finally, the carbon modified $\text{In}_2\text{O}_3/\text{TiO}_2$ nanocomposite was obtained and named as C-In/Ti-2. We name 0, 1, 3, 6, and 9 mol% of In-doped TiO_2 nanocomposites with carbon modification as C-P25, C-In/Ti-1, C-In/Ti-3, C-In/Ti-6, and C-In/Ti-9 respectively, and the sample C-In/Ti-2 without carbon doped as In/Ti-2. In_2O_3 was prepared by the same method.

2.3. Characterizations

The crystalline phases of as-prepared nanocomposites were characterized by X-ray diffraction (XRD) using Cu K α radiation (BRUKER D8 ADVANCE Diffractometer, Germany), of which scanning angle range was initiated from 10° to 90° (scan rate 2 °min⁻¹). To further identify the elemental composition, X-ray photoelectron spectroscopy (XPS) analysis was implemented with Al K α X-ray (hm = 1486.6 eV) radiation operating at 250 W (PHI5300, USA). To observe surface structure and morphology, scanning electron microscope (SEM, Phillips XL-30 FEG/NEW) was performed. The shape and microstructure was confirmed by transmission electron microscopy (TEM, Phillips Model CM200). The crystalline structures of the as-prepared samples were further characterized by high resolution TEM (HRTEM). The energy-dispersive X-ray spectroscopy (EDS) was adopted to confirm the composition of the samples. The specific surface areas of the as-prepared samples were computed from the N_2 adsorption/desorption data on the basis of the Brunauer-Emmett-Teller (BET) method (Micromeritics ASAP 2020), whose error bars are 1% of the measurement result. Fourier transform infrared (FTIR) spectra were attained using Nicolet Nexus spectrometer with potassium bromide disks over the range of 4000–400 cm⁻¹. The optical absorption properties of the as-prepared samples were collected in the range of 350–800 nm on UV–vis diffuse reflectance spectra (UV–vis DRS) (SHIMADZU UV-3600 Plus). BaSO₄ was used as a reflectance standard in the UV–vis DRS experiment. Photoluminescence (PL) measurements of the samples were performed on a fluorescence spectrophotome-

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