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Synergistic effect of Fe_2O_3/Ho_2O_3 Co-modified 2D-titanate heterojunctions on enhanced photocatalytic degradation

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ABSTRACT

TiO_2-based nanosheets (TNSs) co-modified by Fe_2O_3 and Ho_2O_3 were synthesized by one-pot hydrothermal method using $Fe(NO_3)_3$ and $Ho(NO_3)_3$ as precursors compositing with TiO_2. The Fe_2O_3/Ho_2O_3-TNSs heterojunctions possessed a thickness of approximately 3–4 nm, large specific surface area of 210–310 cm^2/g, with Fe_2O_3 and Ho_2O_3 nanoparticles highly dispersed over the surface of the nanosheets. The crystallization of the samples gradually increased with the amount of Fe_2O_3 nanoparticles, which was confirmed by the XRD, BET and Raman spectra, indicating that Ho_2O_3 and Fe_2O_3 influenced the crystallinity and structure evolution of the TNSs, besides, led to an improved the visible-light absorption. Surface photocurrent and fluorescence spectral studies revealed that the photo-generated charge carrier separation efficiency could be efficiently improved by an appropriate amount of modification. The Fe_2O_3/Ho_2O_3-TNSs exhibited synergistic effect on photocatalytic degradation of RhB as well as MO under visible light. The highest efficiency was obtained by 0.05%-Fe_2O_3/Ho_2O_3-TNSs (Fe:Ho:Ti = 0.05:1:100), which was 8.86 and 6.72 times than that of individual 1.0%-Ho_2O_3-TNSs (Ho:Ti = 1:100) and 0.05%-Fe_2O_3-TNSs (Fe:Ti = 0.05:100), respectively. The possible mechanism for enhanced visible-light-induced photocatalytic activity was proposed. Ho_2O_3 introduced in the photocatalysts may act as the hole capture while Fe_2O_3 may share the same Fermi levels with TNSs and serve as the electron capture center in the n-n-p system, which reduced the recombination rate of photo-induced electron-hole pairs.

1. Introduction

Organic pollutants in wastewater is one of the most serious pollution sources around the world. Thus removal and degradation of organic pollutants has been a matter of considerable interest [1]. Nowadays, more and more researchers pay great attention to some oxides as the semiconductor photocatalysts, such as the predominant catalysts like TiO_2, ZnO, and CeO_2 for their highly photocatalytic activity [2–4]. Among the various oxide semiconductor photocatalysts, TiO_2 has been widely investigated for photocatalytic degradation of organic pollutants due to its strong photocatalytic ability, high stability, non-toxicity and low cost. However, there still exists certain defects exist about TiO_2 restricting the wide application. For example, the large band gap ($E_g = 3.2$ eV) requires that only near-UV light can be used in photocatalysis. Unfortunately, in solar energy applications only ca. 3% of the solar light is available. The relatively high rate of electron-hole recombination often results in a poor efficiency of photocatalytic reactions with low quantum yield [5]. Besides, the relative small surface area of TiO_2 (about 50 m^2/g) nanoparticles also limits catalyst to absorb organic pollutants. Therefore, many attempts have been made to reduce the recombination of photo-generated electrons and holes, and to extend the light absorption of TiO_2 into visible light region [6–8]. Introduction metallic oxide into photocatalytic, as one of the most efficient and convenient ways for surface modification, has been tried by many researchers [9,10]. Deposited by metallic oxide, the optical absorption region of TiO_2 could be extended into visible light and meanwhile the generation rate of the electron-hole pairs may be improved [11]. Among the metallic oxide, Fe_2O_3 has received special concern due to the narrow band gap and the remarkable improvement in the photocatalytic activity of modified TiO_2 [12,13].

In addition, modification TiO_2 by lanthanide metallic oxide is

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increasingly being considered to maximize its photocatalytic efficiency due to the formation of lattice distortion of titanium dioxide, which could accept more photo-excited holes and produce stronger surface free radicals to oxidize absorbed molecules [14]. Many studies have focused on lanthanide metals oxide modification on TiO_2, such as Ce_2O_3 [15], Er_2O_3 [16], Gd_2O_3 [17], and the research about Ho_2O_3-modified TiO_2 has been made by our group [14], the result showed that the Ho_2O_3 significantly improved the photocatalytic degradation efficiency compared with pure TiO_2, which is 3.95 times higher than pure TiO_2 in UV–vis light. However, the photocatalytic degradation efficiency of this catalyst in visible light range is still required to be improved, which gives us a hint that TiO_2 co-modified by Fe_2O_3 and Ho_2O_3 may generate a synergistic effect to improve the separation of photo-generated electrons and holes, and thus enhance the photocatalytic activity [14]. Recently, three-component junction systems, e.g. TiO_2 co-modified by Fe_2O_3 and Ce_2O_3 [18], Fe_2O_3 and Er_2O_3 [1] have attracted considerable interest since these systems can result in higher photocatalytic activity and unique characteristics, compared with pure TiO_2 or two-component junction systems.

Besides, the restricted morphology of TiO_2 nanoparticles somewhat limits the synergistic effect of Fe_2O_3 and Ho_2O_3 composite due to either the small specific surface area or the high aggregation rate of the catalyst may caused. As a consequence, morphology control of TiO_2-based photocatalysts also attracts the attention of the public. Comparing with other morphologies of TiO_2-based photocatalysts, TiO_2 nanosheets (TNSs) possess a high specific surface area and small thickness. For example, satisfactory results have been reported by hydrothermal method [19,20], with the specific surface area as high as 339 m^2/g and the thickness as thin as 5 nm. It is known that a larger specific surface can expose photocatalysts to more light and contact with more pollutant molecules for photocatalytic reaction, and a small thickness of photocatalysts is beneficial to enhance the separation of photo-generated electrons and holes.

The visible-light-active 2D-nanosheets modified by Fe_2O_3 and Ho_2O_3 were synthesized using a simple one-pot hydrothermal method in this work. Several characterization methods were used to investigate the influence of the modification on TNSs and the synergistic effects of the three-component junction systems were studied. RhB and MO solution were selected to be the pollutant model under visible light irradiation, the results showed the products with some new and attractive properties, which are expected to obtain enhanced photo-catalytic activity with respect to commercially available TiO_2 photocatalyst.

2. Experimental section

2.1. Preparation

Degussa P25 (TiO_2, 20% rutile and 80% anatase) was purchased from Degussa Co., Ltd. NaOH, Ho_2O_3, $Fe(NO_3)_3 \cdot 9H_2O$, RhB, MO and HCl were provided by Sinopharm Chemical Reagent Co., Ltd. All the reagents were analytical grade and used without further purification. Deionized water with a resistance of 4.25 MΩ cm was used in the whole experiments process.

Degussa P25 was dispersed in 50 mL of 10 mol/L NaOH solution under intense stirring. A certain amount of $Ho(NO_3)_3$ and $Fe(NO_3)_3$ solution was dropped slowly into the suspension. After magnetically stirred for half an hour, the mixture was treated at 130 °C for 3 h in a 100 mL Teflon-lined autoclave. Then the autoclave was water-cooled to ambient temperature, and the resultant powders were separated by high-speed centrifugation and washed by deionized water for several times until neutral condition was obtained. After that, proton exchanging was carried out in 250 mL HCl solution (0.1 mol/L) under magnetic stir for 2 h. Finally, the powders were washed again until pH value of the rinsed water reached about 7 and then dried at 65 °C for 12 h. A series of Fe_2O_3/Ho_2O_3-TNSs were prepared by changing the concentration of $Fe(NO_3)_3$ solution, while the atomic ratio of Ho to Ti was fixed at 1.0%. The obtained samples were denoted as x-Fe_2O_3/Ho_2O_3-TNSs, where x (x = 0.025%, 0.05%, 0.075%, 0.1%, 0.25%, 0.5%, 1.0% and 1.5%) represents the atomic ratio of Fe to Ti. For comparison, single Ho_2O_3 composite nanosheets (Ho_2O_3-TNSs) were also prepared using the same method without adding Ferric source.

2.2. Characterization

The morphological features of the samples were characterized by transmission electron microscopy (TEM, JEOL JEM-2010) and high-resolution transmission electron microscopy (HRTEM, JEM-2010FEF) with an energy dispersive spectroscope (EDS). The X-ray diffraction (XRD) patterns were collected on a Bruker D8 advance X-ray diffractometer by monochromatic Cu Ka radiation ($\lambda = 1.5406$ Å). The Brunauer-Emmett-Teller specific surface areas (S_{BET}) were measured at 77 K (JW-BK, China). Raman spectra were obtained by a Horiba LabRAM HR Raman spectrometer with an excitation wavelength of 448 nm and output power of 5 mW. X-ray photoelectron spectroscopy (XPS) measurements were collected on a Thermo VG Multilab2000 using Al Ka as the excitation source. Ultraviolet–visible (UV–vis) light were collected on a Shimadzu UV-2550 spectrophotometer using barium sulfate as a reference. A Hitachi FL4600 florescence spectrometer (FL) with 500 V voltage and 300 nm excitation wave-length was used to study the recombination efficiency of electrons and holes. The record ranged from 450 to 520 nm.

2.3. Photocatalytic activity

The photocatalytic activities of samples were evaluated by degradation of RhB and MO solution under a 350 W xenon lamp. The irradiation distance between the lamp and the sample was about 15 cm. The intensity of luminous power was detected by a light intensity meter, the luminous power intensity was approximately 45.6 mW, and the light power density detected was 67.1 mW/cm^2. The reaction suspensions were obtained by adding 0.05 g photocatalysts into 50 mL of 20 mg/L dyes solution in a cylindrical glass vessel and stirred for 30 min to reach equilibrium absorption. The reactor temperature was controlled by a cooling fan and the cylindrical glass vessel was placed in a water tank to prevent the temperature from increasing during irradiation. Every 10 min during visible-light irradiation with a cut off filter ($\lambda < 400$ nm) covering the beaker, about 1.6 mL of reaction liquid was withdrawn and centrifuged and then analyzed for residual RhB or MO concentration by UV–vis absorbance spectra. In all photocatalytic tests, P25 was used as a reference.

2.4. Hydroxyl radicals test

The fluorescence-coumarin method was used to detect hydroxyl radicals (•OH) efficiency in the visible light. 0.20 g catalyst was dispersed in 100 mL coumarin solution (10^{-3} mol/L), and stirred in dark for 30 min to reach the adsorption stability. The photocatalytic activities were evaluated by the same route introduced above. It is known that the coumarin is easily to react with •OH to generate a strong fluorescent effect of 7-hydroxycoumarin (7-HC), therefore the generation rate of •OH on the catalyst surface can be derived by comparing the fluorescence intensity of the solution.