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Regular Article

Synthesis of a novel narrow-band-gap iron(II,III) oxide/titania/silver silicate nanocomposite as a highly efficient and stable visible light-driven photocatalyst

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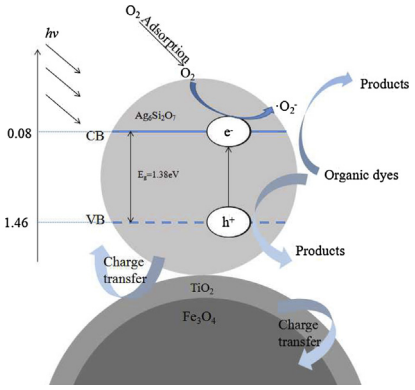
HIGHLIGHTS

- A $Fe_3O_4/TiO_2/Ag_6Si_2O_7$ nanocomposite was prepared to serve as a visible light-driven photocatalyst.
- The narrow-band-gap photocatalyst showed excellent photocatalytic activity.
- The photocatalyst exhibited good stability after several reaction cycles.
- The photocatalyst was magnetically separated from the treated solution.
- The holes should be the predominant active species during the photocatalytic reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

$Ag_6Si_2O_7$, a visible light-driven photocatalyst, has attracted considerable attention owing to its enormous environmental remediation potential. In this work, a magnetic iron(II,III) oxide/titania/silver silicate ($Fe_3O_4/TiO_2/Ag_6Si_2O_7$) nanocomposite was synthesized by anchoring TiO_2 and $Ag_6Si_2O_7$ on the surface of Fe_3O_4 nanoparticles. The morphology, crystal structure, as well as the spectroscopic, magnetic, and photocurrent properties of the as-prepared $Fe_3O_4/TiO_2/Ag_6Si_2O_7$ nanocomposite were studied. Methylene blue (MB) was used for evaluating the photocatalytic performance under simulated visible light. The Brunauer–Emmett–Teller (BET) surface area, total pore volumes, and average pore diameter of the $Fe_3O_4/TiO_2/Ag_6Si_2O_7$ nanocomposite were calculated to be 33.077 m^2/g, 0.099 cm^3/g, and 15.45 nm, respectively. The $Fe_3O_4/TiO_2/Ag_6Si_2O_7$ photocatalyst showed a narrow-band-gap (1.38 eV) while exhibiting excellent photocatalytic performance with a photocurrent of 9.4 $\mu A/cm^2$ under simulated visible light. Furthermore, the nanocomposites showed high resistance to degradation (i.e., more than 80%) after 5 reaction cycles and as a result of high saturation magnetization (25.51 emu/g), the spent material was easily separated upon application of a magnetic field. Meanwhile, the photogenerated holes (h^+) and superoxide ions ($\cdot O_2^-$) were confirmed as the main active species. This novel photocatalyst is expected to provide a new insight into the design of photocatalysts with excellent recyclability, high performance, and good stability.

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1. Introduction

Since the discovery of photocatalytic water splitting on TiO_2 in 1972 [1], photocatalysis has attracted enormous attention, being extensively studied for hydrogen evolution [2], water disinfection [3,4], air purification [5,6], and degradation of organic pollutants [4,7] applications. Among the various materials tested, TiO_2 has been the most widely studied photocatalyst owing to its low cost, non-toxicity, and abundance [8,9]. However, the practical applications of TiO_2 are significantly hindered by its wide band gap energy (E_g = 3.2 eV), which restricts absorption to the ultraviolet (UV) range (ca. 4% of the overall spectrum), seriously limiting the utilization of solar light [10–12]. To overcome this limitation, other semiconductors, metallic, or nonmetallic elements have been used to expand the absorption of TiO_2 to higher wavelengths, while novel photocatalysts with visible light absorption capabilities have been also prepared [13–17]. Apart from the above limitation, micro- or nano-scale photocatalysts are difficult to separate after the photocatalytic reaction by classic separation methods, requiring prolonged operations, and complex equipments, leading to high operational costs [12,18].

Ag-based photocatalysts, such as Ag_3PO_4 [19], Ag_2CO_3 [20], and Ag_2CrO_4 [21], have become a hot research topic owing to their great potential for visible light adsorption. Lou et al. [22] recently synthetized a highly efficient silicate-derived photocatalyst ($Ag_6Si_2O_7$). This material possessed an internal electric field along the *b*-direction and three different AgO_n (n = 2, 3, and 4) polyhedral coordination structures. Photogenerated electron–holes (e^-–h^+) can be effectively separated under the application of the internal electric field produced by the $Ag_6Si_2O_7$ crystal structure and by electron transfer among the different coordinations. As a result, $Ag_6Si_2O_7$ presents a quite narrow band gap (1.58 eV) and is active over almost the entire visible light region (<740 nm). Nevertheless, $Ag_6Si_2O_7$ is easily reduced and decomposed to Ag by the photogenerated electrons produced during the photocatalytic process, which prevents its wide use in environmental applications. Recent reports have pointed out that the combination of TiO_2 and Ag_3PO_4 could enhance the chemical stability and activity of Ag_3PO_4 as their appropriate energy band structure [23]. Moreover, construction of heterojunctions by combining two types of semiconductors having well-matched band potentials has turned out to improve the photocatalytic performance to some degree [24,25]. Thus, the combination of TiO_2 and $Ag_6Si_2O_7$ may be a promising method to improve the stability and photocatalytic activity of $Ag_6Si_2O_7$.

In order to solve the issue of difficult separation and recovery of powdered photocatalysts, some researchers have immobilized catalysts on different supports such as activated carbon [26], glass [27], and Al fiber [28]. Superparamagnetic Fe_3O_4 has a cubic inverse spinel structure and non-equivalent cations with two valence states (Fe^{2+}, Fe^{3+}), leading to the formation of a unique magnetic structure [29,30]. Photocatalysts supported on Fe_3O_4 have been proved to be effectively separated and recycled from the treating solution in a rapid, simple, and low-cost manner [31–33]. Moreover, the excellent conductivity of Fe_3O_4 can also act as an electron–transfer channel and acceptor, thereby suppressing the photogenerated carrier recombination and enhancing the photocatalytic activity [33,34] .

We hypothesized that the $Fe_3O_4/TiO_2/Ag_6Si_2O_7$ composites containing three raw materials would provide three advantages: excellent photocatalytic activity under visible light, good stability after multiple cycles, and good separation and recovery performance under an external magnetic field. The main objectives of the present study were: (1) to prepare a novel magnetic separable $Fe_3O_4/TiO_2/Ag_6Si_2O_7$ composite; (2) to evaluate the photocatalytic activity and stability of the $Fe_3O_4/TiO_2/Ag_6Si_2O_7$ composite under simulated visible light; (3) to analyze the properties of the material (i.e., morphology, chemical composition, spectroscopic/magnetic properties) via a series of characterization techniques; and (4) to study the mechanism of the photocatalytic reaction. This work offers a systematic approach including catalyst preparation, characterization, photocatalytic tests, and mechanism research. The as-synthesized photocatalyst is expected to be used in practical engineering applications.

2. Materials and methods

2.1. Material and chemicals

Ferric chloride ($FeCl_3{\cdot}6H_2O$), sodium acetate trihydrate ($NaAC{\cdot}3H_2O$), ethylene glycol (EG, $(CH_2OH)_2$), sodium silicate ($Na_2SiO_3{\cdot}9H_2O$), tetrabutyl titanate (TBT, $C_{16}H_{36}O_4Ti$), and dichloromethane (CH_2Cl_2) were purchased from Sinopharm Chemical Reagent Co., Ltd., while silver nitrate ($AgNO_3$), concentrated nitric acid (HNO_3), acetic acid glacial (AG, CH_3COOH), ethyl alcohol (CH_3CH_2OH), isopropanol (IPA, $(CH_3)_2CHOH$) and methylene blue (MB) were obtained from Beijing Chemical Works. Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, $C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$) and p-benzoquinone (BQ, $C_6H_4O_2$) were obtained from the Tianjin Guangfu Technology Development Co., Ltd. All the materials were of analytical grade and used without further purification.

2.2. Synthesis of $Fe_3O_4/TiO_2/Ag_6Si_2O_7$

Fe_3O_4 nanoparticles were prepared by solvothermal method [31]. Typically, 2.70 g of $FeCl_3{\cdot}6H_2O$ and 4.10 g of $NaAC{\cdot}3H_2O$ were mixed in 80 mL of EG. The mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. After cooling down to room temperature, the resulting black Fe_3O_4 particles were separated by application of an external magnetic field and washed five times with ethyl alcohol and distilled water. Finally, the black product was dried at 60 °C for 12 h.

TiO_2-capped Fe_3O_4 nanoparticles were synthesized via a sol–gel method. In a typical process, 0.43 mL of TBT, 0.10 mL of HNO_3, and 0.50 g of Fe_3O_4 were added into 20 mL of ethyl alcohol to prepare a solution A. The solution A was ultrasonically treated for 30 min. Meanwhile, 3.0 mL of H_2O and 1.0 mL of AG were added into 10 mL ethyl alcohol to obtain a solution B, which was subsequently added dropwise to the solution A under mechanical stirring. The resulting solution was stirred for 20 min, and subsequently placed to form a gel. The gel was subsequently dried at 60 °C and calcined at 450 °C for 2 h. The resulting product was finally crushed into uniform powders.

$Ag_6Si_2O_7$ was deposited on the surface of Fe_3O_4/TiO_2 via ion exchange and hydrolysis processes. 0.24 g of Fe_3O_4/TiO_2 and 0.85 g of $AgNO_3$ were dispersed into 60 mL of deionized water. A Na_2SiO_3 aqueous solution (30 mL, 0.06 M) was subsequently added dropwise to the above solution under continuous mechanical stirring. In a subsequent step, the obtained products were separated by an external magnetic field and washed five times with ethyl alcohol and distilled water. The samples were finally dried at 60 °C for 12 h.

2.3. Photocatalytic tests

The photocatalytic tests were performed by degrading MB solution under simulated visible light (40 mW/cm^2, CEL-HXF300, China). In the photocatalytic system, a 250 mL beaker provided with a magnetic stirrer was used as the reactor. 0.1 g of photocatalyst and 100 mL of MB (10 mg/L) solution were mixed in dark to