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Enhanced photocatalytic properties of CdS nanoparticles decorated α-Fe_2O_3 nanopillar arrays under visible light

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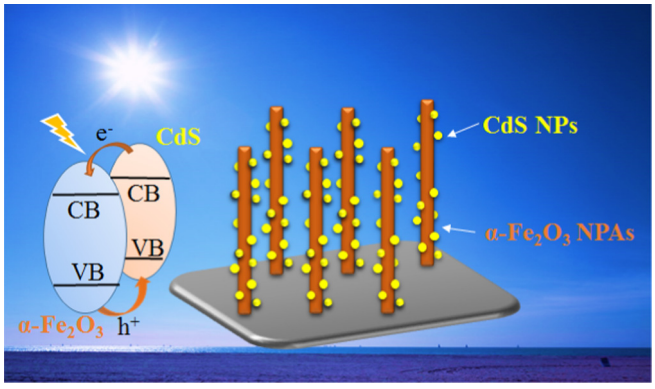
GRAPHICAL ABSTRACT



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ABSTRACT

CdS nanoparticles (NPs) decorated α-Fe_2O_3 nanopillar arrays (NPAs) were fabricated through several steps. Fe NPAs were firstly fabricated by glancing angle deposition technique and oxidized in air to gain α-Fe_2O_3 NPAs. Then these NPAs were decorated by CdS NPs through successive ion layer adsorption and reaction (SILAR). Here we have tested photodegredation of methylene blue (MB) and photoelectrochemical properties under visible light. Especially, when SILAR cycle number reaches to 10, it shows the highest degradation efficiency (94% in 75 min on MB) which improves 72% comparing with pure one and the highest photocurrent density (2.0 mA cm^{-2} at 0.4 V vs Ag/AgCl electrode). α-Fe_2O_3/CdS hetero-junctions could greatly enhance photocatalytic performance, which can help to accomplish sufficient usage of solar energy and be exploited on pollution abatement in future.

1. Introduction

Fujishima and Honda first observed photoelectrochemical (PEC) splitting of water over TiO_2 electrodes in 1972 [1], which made semiconductors as good photocatalyst candidates. Due to its

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property of conversion solar energy into electrical and chemical energy efficiently, which can be applied into many fields, especially decomposing organic pollutants, hydrogen and oxygen generation, etc. [2]. Because of ~3.0 eV wide bang gap, TiO_2 makes it be active just under UV region which accounts only ~4% in solar energy [3]. Thus broadening lights activation range has been highly demanded to a great photocatalyst. However, since researches began, there still remain various big challenges on optimizing physical and chemical properties of catalysts. Thus it's worth noting that besides exploiting new type materials, traditional materials can be skillfully modified through different methods as well to make them be more active under visible light wavelength range eventually.

Hematite (α-Fe_2O_3) is a kind of typical *n*-type traditional semiconductor, which has been found usable in many application as catalysts [4], pigment [5], and gas sensors [6]. Due to its narrow band gap (~2.1 eV), highly stability against photocorrosion and high theoretical solar-to-hydrogen efficiency (~17%), α-Fe_2O_3 could work effectively under visible light range [7]. Therefore, it can be found that many research work have been focus on α-Fe_2O_3 during these twenty years [8–19]. However, there is also some drawback hindering the wide usage of α-Fe_2O_3 such as poor minority charge carrier mobility (0.2 $cm^2\ V^{-1}\ s^{-1}$) and short hole diffusion length (2–4 nm). These special material properties eventually cause a high electrons and holes recombination rate, a quite short excited state lifetime (~10 ps), and poor electrical conductivity [20,21]. To enhance advantage and avoid disadvantage, a large amount of efforts and tries have been made, like constructing α-Fe_2O_3 as nanotubes, nanoparticles, nanocubes, nanowires, nanofibers, nanorods, and hierarchical structures [8–19,22]. Or fabricating heterojunctions, doping and so on, have been taken into optimization of photocatalytic performance [9,23–26].

Good electron-hole separation efficiency can greatly help to improve the photocatalytic property [27]. PbS [28], CdSe [29], ZnS [30], and CdS [31,32] all belong to narrow band gap semiconductors, which have been already regarded as nanostructured TiO_2 sensitizers showing greatly enhanced visible light response. Among them CdS (band gap ~2.4 eV), with high absorption coefficient, is a good candidate in photocatalytic material. After irradiation, electrons generated from CdS nanoparticles (NPs) transfer into α-Fe_2O_3 quickly to reach efficiently separation of induced electrons and holes. Thus it is suitable to combine CdS with α-Fe_2O_3 and can be greatly developed into photoelectrochemisty and photocatalytic applications [33]. CdS NPs have superiority such as high extinction coefficient, spectral tunability by size, and good stability [34]. The fabrication methods of CdS NPs had been exploited through electrodeposition [30], chemical bath deposition (CBD) [35], and successive ion layer adsorption and reaction (SILAR) [36,37]. And among them, SILAR methods could be easily controlled by just changing the cycle number.

Traditional photocatalysts are mostly powders, and they are hard to be collected and recycled. Here the fabrication of vertically aligned α-Fe_2O_3 nanopillar arrays (NPAs) on different substrates are introduced. These kind of materials are more convenient to recycle. When CdS NPs are decorated on α-Fe_2O_3 NPAs with the incensement of SILAR cycle numbers, the photocatalytic performance gets better first and then worse. Thus the decoration of CdS is an efficient method to enhance degradation efficiency only when appropriate loading quantity.

2. Methods

2.1. Fabrication of α-Fe_2O_3 NPAs

Fe NPAs were firstly deposited vertically by the e-beam glancing angle deposition technique respectively on three substrates: (1) quartz substrates for degradation dye test, (2) F-doped SnO_2 (FTO) substrates (20 Ω per square) for PEC curve characteristic, and (3) (001) planar silicon substrates for sample characterization. Substrates before deposition were ultrasonically cleaned in acetone, ethanol and deionized water baths each for 7 min, consequently. Deposition chamber was firstly evacuated to a vacuum level above 1×10^{-8} Torr. After deposition process, the samples were oxidized in a quartz tube furnace at temperatures of 400 °C for 1 h at a ramp of 2 °C min^{-1} in air to obtain α-Fe_2O_3 NPAs.

2.2. CdS NPs deposition on α-Fe_2O_3 NPAs

SILAR method of CdS NPs decoration with slight modification is adopted, as previously reported [32]. α-Fe_2O_3 NPAs substrates were dipped in $Cd(Ac)_2$ and Na_2S solutions alternatively each for several seconds and then got the CdS nanocrystallites eventually. The substrates were immersed into Na_2S (0.05 M) for 30 s, then cleaned in deionized water for 30 s and then turned to $Cd(Ac)_2$ (0.05 M) for another 30 s. Later substrates were cleaned by deionized water again. This whole cycle was regarded as one single SILAR cycle and it was repeated until desired CdS NPs decoration quality.

2.3. Materials characterization

The structure and morphology of the α-Fe_2O_3 NPAs/CdS NPs were examined by field-emission scanning electron microscope (FESEM, JEOL-7001F), Raman spectroscopy (LABRAM HR800, excitation wavelength set at 633 nm) and high-resolution transmission electron microscope (HRTEM, JEOL-2011), respectively. The special element analysis of the samples was analyzed by X-ray photon electron spectrometer (XPS, Perkin Elmer PHI 5300), and the binding energy was calibrated with the reference to the C 1s peak centered at 284.6 eV.

2.4. Property measurement

The steady sate current densities (*j*–*V*) test was characterized by an electrochemistry workstation (CHI 660D, Chenhua instrument). The products were regarded as the working electrode. And a Pt and Ag/AgCl electrode (saturated KCl) sheet were used as the counter electrode and reference electrode, respectively. The working electrode was illuminated by a 300 W Xe lamp. And between the light source and the quartz cell there is an ultraviolet filter placed to cut off the UV light in wavelength <420 nm. Photocurrent densities were tested in the light on-off process with a pulse of 30 s at 0.4 V bias vs Ag/AgCl electrode under visible light (200 mW cm^{-2}).

The photocatalytic performance was studied by the photodegradation of methylene blue (MB) dye with Xe lamp exposure. The sample deposited on quartz substrate was immersed into beaker containing 5 mL of MB (5 μM) under fixed time. At different time point during whole photodegradation, the UV–vis absorbance spectra of the MB solution were also measured.

3. Results and discussions

3.1. Characterization of photocatalysts

Top-view SEM images of samples fabricated at different steps are shown in Fig. 1. And from Fig. 1(a), we can find that vertically aligned Fe NPAs with the diameter of ~40 nm and length of ~200 nm are quite uniform. And it can be seen that after annealing