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High photocatalytic activity of hydrogen production from water over Fe doped and Ag deposited anatase TiO_2 catalyst synthesized by solvothermal method

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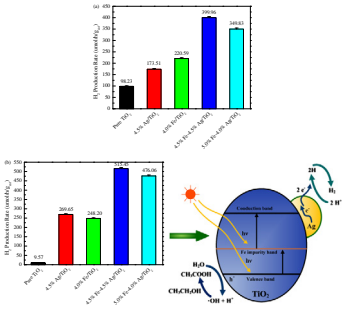
HIGHLIGHTS

- Fe^{3+} doped and Ag deposited TiO_2 was prepared by one-step solvothermal method.
- TiO_2 showed well optical property of light absorption by introducing of Fe and Ag.
- Fe doped and Ag deposited TiO_2 was applied to H_2 production from water.
- Recombination rate of electron–hole pairs was effectively reduced by this method.
- The mechanism of H_2 production through water splitting was also proposed.

GRAPHICAL ABSTRACT

H_2 production rate from water over TiO_2 catalysts: (a) UV light irradiation; and (b) visible light irradiation ($\lambda > 400$ nm) and the mechanism of H_2 production by water splitting over Fe–Ag/TiO_2.



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ABSTRACT

Metallic Ag deposited and Fe^{3+} ions doped anatase TiO_2 nanoparticles were successfully synthesized by one-step solvothermal method with using tetrabutyl titanate as precursor and ethanol as solvent. All prepared TiO_2 samples were single anatase phase through XRD and Raman spectroscopy analysis. Compared with pure TiO_2, Fe doped and Ag deposited TiO_2 showed higher visible light absorption activity and lower electron–hole pair recombination rate. In all TiO_2 samples, 4.5% Fe–4.5% Ag/TiO_2 displayed the highest absorption intensity of visible light and lowest recombination rate of electron–hole pairs, its absorption wavelength edge moved remarkably with a red shift to 610 nm. Based on XPS and TEM analysis, Fe^{3+} located in the TiO_2 lattice and metallic Ag particles deposited on the surface of it were detected, the particle sizes of Ag were about 2–3 nm. Average maximum H_2 production rate through water splitting was 515.45 μmol h^{-1} g_{cat}^{-1} with using 4.5% Fe–4.5% Ag/TiO_2 as catalyst (a measured time of 6 h, visible light irradiation, $\lambda > 400$ nm). At last, the mechanism of H_2 production by water splitting under visible light irradiation was also proposed.

1. Introduction

Because of increasing energy needs, decreasing fossil fuel resources, and serious environmental problems, modern society has been seeking for a new technology to effectively address these issues. Due to solar energy is endless and clean, and hydrogen

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energy is also environmentally friendly, utilization of solar energy to generate hydrogen gas (H_2) through water splitting has been regarded as a promising solution [1–5], since the first report in 1972 that TiO_2 could act as a catalyst to generate hydrogen and oxygen from water [6]. Water splitting into H_2 and O_2 needs the standard Gibbs free energy change ΔG° of 237 kJ/mol or 1.23 eV [2], as shown in the following equation:

$$H_2O \rightarrow \frac{1}{2}O_2 + H_2 \quad (1)$$

Therefore, to drive this reaction with the use of light, the photocatalytic materials should absorb radiant light with photon energies of >1.23 eV (equal to wavelengths of ~1000 nm and shorter) to convert solar energy into H_2 and O_2.

Nowadays, over 130 inorganic materials and their derivatives have been applied to generate hydrogen gas through water splitting [7]. Titanium dioxide (TiO_2) has been regarded as a strong candidate for photocatalytic hydrogen production [8–10], which results from its efficient photocatalytic activity, excellent stability, low cost and environmental friendly. However, TiO_2 belongs to a wide band gap n-type semiconductor material (anatase for E_g = 3.2 eV) which can only harvest UV light [9–11]. What's more, the high recombination rate of electron–hole pairs will also lead to its low photocatalytic efficiency [5,9]. Because of the above two main problems, the applications of it are greatly restricted. An optimal material of water splitting should remain stable in contact with water and have a proper band gap that can absorb much more solar radiation energy [1]. Hence, extending the photo-response of TiO_2 to visible light range, and improving the separation efficiency of photo-induced electrons and holes are the two big challenges for utilization of light to photo-generate H_2 from water [5,10,12–14].

Generally, noble metals, such as Pt, Au, Ag, Pd, Rh and Ru [4,8,10,13,15–18], are often applied to modify TiO_2 for enhancing its H_2 production activity. TiO_2 doped with other lower cost 3d transition metals, such as Fe, Cr, and Ni [5,14,19], can also extend its light absorption to the visible spectrum and improve the separation efficiency of photo-induced electrons and holes. Just due to the above two main reasons, TiO_2 doped with these low cost metals can also display higher photocatalytic activity of H_2 production than that of un-doped [5,14]. Furthermore, it should be noted that TiO_2 doped with Fe indicates higher photocatalytic activity in the experiments than that of other 3d transition metals doping [5,20–22]. And this point that Fe is a good dopant for improving photocatalytic activity of TiO_2 has been demonstrated in the references through theoretical calculations [23,24]. Up to now, lots of literatures about Fe doped TiO_2 applied in decomposing organic substances have been reported [25–32]. However, there are few reports about that TiO_2 doped with 3d low cost transition metals are used in the application of H_2 production from water.

In recent years, many researchers mainly focus on using of Ag to modify TiO_2 which is applied to many kinds of photocatalytic field [8,10,33,34,3,35–38], which results from the high-efficiency of electron–hole separation by forming a Schottky barrier at the Ag–TiO_2, thus improving its photocatalytic activity [33,34]. Therefore, metal Ag, less expensive than other precious noble metals, such as Pt, Au and Pd, has more significant practical value to modify TiO_2. Qiu et al. [37] have demonstrated that Ag/TiO_2 displayed the highest photocatalytic efficiency of decomposing methylene blue (MB) under visible light irradiation in 10 types of doped catalysts. Alenzi and his colleagues [8] have synthesized Ag/TiO_2 nanocomposite thin films, which displayed higher water splitting activity than that of pure TiO_2, and average hydrogen production rate could reach up to 182.5 μmol h^{-1} g_{cat}^{-1}. Mazheika et al. [39] have reported that Ag could affect the anatase surface of TiO_2 through the density functional theory, and some defects on anatase surface were generated by introducing Ag. O vacancies, a kind of defects, are very close with the charge transfer in TiO_2 [40,41], which can create a transport channel for high conductivity [41], thus leading to effective separation of electrons and holes.

Compared with TiO_2 prepared by sol–gel method, solvothermal method has been used well to synthesize of TiO_2 with small particle sizes, large surface area and well-crystalline phase [42,43], these characteristics would affect its photocatalytic activity [44]. Recently, our teams used solvothermal method to successfully synthesize single anatase phase of doped TiO_2 nanoparticles, and found that Fe doped TiO_2 displayed a higher visible light absorption activity, better ability of separating photo-induced hole-electron pairs, smaller particle sizes and higher crystallinity than that of Ni doping [45]. Because of the above these reasons, TiO_2 doped with Fe showed the higher H_2 production activity of water splitting than that of Ni doping. Aim of the present study is to obtain TiO_2 photocatalyst with good performance of H_2 production. Several kinds of a single anatase phase of TiO_2 photocatalysts were successfully prepared by solvothermal method with using tetrabutyl titanate as precursor and ethanol as solvent. Their properties of TiO_2, Fe/TiO_2, Ag/TiO_2 and Fe–Ag/TiO_2 were investigated in detail. TiO_2 photocatalysts were applied to generate H_2 by water splitting to evaluate their photoactivity. At last, the mechanism of H_2 production by water splitting under visible light irradiation was also proposed by us.

2. Experimental

2.1. Preparation of TiO_2 photocatalysts

All the reagents used in this study were analytical grade without further purification. The route of solvothermal method to prepare TiO_2 was same with our previous article [45]. Obtained samples were referred to as *x*% A/TiO_2 with x representing the molar A/Ti ratio (A = Fe or Ag) in the starting materials. Mixed solution of $Fe(NO_3)_3{\cdot}9H_2O$ (or $AgNO_3$), CH_3CH_2OH, CH_3COOH and H_2O was dropped into the mixture of CH_3CH_2OH and tetrabutyl titanate. Then final solution was magnetic stirred for 0.5 h before introduced into a 100 ml Teflon-lined stainless steel autoclave, and it was maintained at 180 °C for 24 h. TiO_2 powder was obtained through filtrating, washing and drying. Finally, the powder was calcined at 500 °C for 0.5 h, and denoted as TiO_2, *x*% Fe/TiO_2, *x*% Ag/TiO_2 and *x*% Fe–*x*% Ag/TiO_2, respectively.

2.2. Characterization

The crystalline phase was identified by X-ray diffraction using a Shimadzu XRD 6000 powder diffractometer (Cu Kα as radiation source, 40 kV, 30 mA). Raman spectra were examined by a Laser Raman spectrophotometer (Renishaw, Invia Reflex). UV–vis absorption spectra were carried out on a Shimadzu UV-3600. Photoluminescence spectra and phosphorescence spectra of samples were performed on a Fluorescence spectrophotometer (Hitachi F-7000). Thermal behavior of the prepared dried TiO_2 samples was investigated by using a simultaneous thermal analyzer (USA, TA, SDT Q2000) with a heating rate of 10 °C min^{-1}. X-ray photoelectron spectroscopy data was obtained with Phobios 100 electron analyzer (SPECS GmbH) using an unmonochromated Mg Kα X-ray source (1253.6 eV). Its morphology of TiO_2 was measured by Field emission scanning electron microscope (Hitachi S-4800) and Transmission electron microscopy (FEI, Tecnai G2 F20 S-TWIN).

2.3. Photocatalytic reaction tests

The apparatus used for photocatalytic reaction tests has been described in detail in our previous article [45]. It consisted of a