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One-step synthesis of mulberry-shaped TiO_2-Au nanocomposite and its H_2 evolution property under visible light

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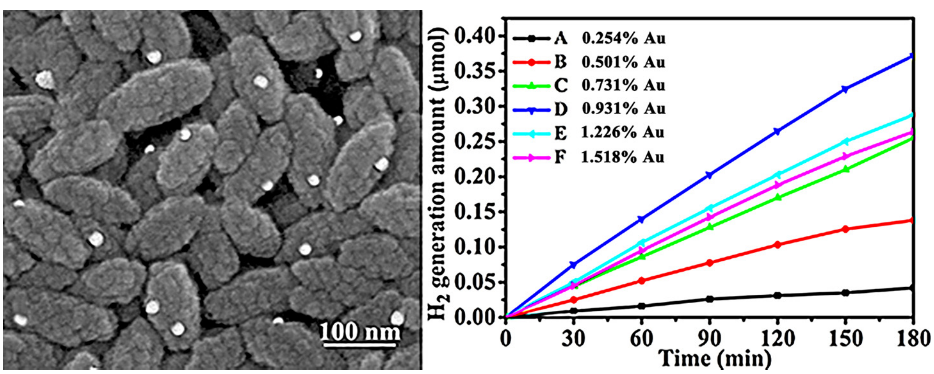
GRAPHICAL ABSTRACT



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ABSTRACT

In this work, mulberry shaped TiO_2-Au nanocomposite has been successfully prepared by a one-step hydrothermal method relying on the redox reaction between Au (III) and Ti (III) with polyvinyl pyrrolidone (PVP) as protective agent for the first time. PVP plays an important role on monodisperse and homogeneity of mulberry shaped TiO_2-Au. The TiO_2-Au nanocomposite shows excellent stability towards the catalytic reduction of water under visible light. Based on characterization and testing, we propose the photocatalytic process for efficient H_2 generation. Uniformly dispersed Au NPs enhance visible light absorption on account of the LSPR, leading to the H_2 evolution increased.

1. Introduction

In the quest to solve environmental remediation and solar energy conversion issues, photocatalysis that based on electron/hole pair production in semiconductors has been attracting significant attention in recent years [1–3]. Among various photocatalysts developed to date, TiO_2 is highlighted due to its high stability and abundant reserves. However, bulk TiO_2 has relatively large band gap (3.2 eV for anatase TiO_2) that limits its light absorption spectral range within the ultraviolet (UV) region of solar radiation [4]. Over the years, significant efforts have been made in developing visible light-absorbing TiO_2-based photocatalysts [5–16]. One of these promising strategies in improving the visible light photoactivity of TiO_2 is surface modification by noble metal nanoparticles (NPs) that have unique localized surface plasmon resonance (LSPR) properties [17–23]. Among various plasmonic metals, Au is the most widely studied metal due to its high stability and strong visible-light absorption over a wide range as we reported before [24–26]. TiO_2 could act as a support to avoid the

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agglomeration of noble metal NPs so as to make a better use of their active sites. Moreover, many studies have indicated that the synergistic interaction between the supported metal NPs and the metal oxide support plays important roles in the catalytic activity of the catalysts [27–30]. As a consequence, a series of TiO_2-Au catalysts have been developed for solar water splitting and photocatalytic degradation of organic compounds [31,32]. To improve the photocatalytic activity of TiO_2-Au catalysts, most of works mainly focus on improving the dispersion of Au NPs and the surface area of TiO_2 [33–35].

In previous studies, most of metal oxide-noble metal nanocomposites are prepared by two-step methods, which are fairly complicated and time-consuming. We have done some research, but it needs to continue to improve the preparation process [36,37]. Although there are some works using one-step strategy to fabricate TiO_2/Au composites, the reaction conditions are relatively rigorous [38]. Therefore, it remains a great challenge to prepare well-defined TiO_2-Au nanostructures through a simple method.

Herein we for the first time propose a facile method to fabricate mulberry-shaped TiO_2-Au nanocomposite by combining the facile hydrothermal technique with the redox reaction between Au (III) and Ti (III) in the presence of PVP. PVP is a polymer that can combine with Ti^{3+} to slow its release, which has a big influence on the morphology of the final TiO_2. The obtained TiO_2 NPs show high homogeneity in size and morphology, and the loaded Au NPs with a diameter of about 20 nm could enhance the visible light harvest due to LSPR. The catalytic performance towards the hydrogen production under visible light based on LSPR as a model reaction was also investigated. Interestingly, it was found that the mulberry-shaped TiO_2-Au nanocomposite shows good catalytic stability, which allows it to be reused over multiple cycles while maintaining its catalytic activity.

2. Experimental

2.1. Reagents

Polyvinylpyrrolidone-k30 was bought from Aldrich. Titanium (III) chloride (15% in 3% hydrochloric acid) was purchased from sinopharm reagents Co (China). HAuCl4·3H2O (≥49.0% Au basis) was obtained from Sigma Aldrich and used as-received without further purification. Water used for preparation of aqueous solutions was purified using a Millipore-Q water purification system.

2.2. Synthesis of TiO_2-Au

The TiO_2-Au nanocomposite was synthesized by combining hydrothermal reaction technique with a redox reaction between Au (III) and titanium (III) with PVP-K30 protection. PVP-K30 4.5 g was dissolved in 100 mL deionized water, and the mixture was stirred using a Teflon-coated magnetic stirrer. 200 μL titanium (III) chloride (15% in 3% hydrochloric acid) was added into 15 mL above PVP-K30 solution and the colour changed obviously to light brown which means that there is coordination occurs between $TiCl_3$ and PVP-K30. A certain amount of $HAuCl_4$ aqueous solution (1 mM) *via* 0.4–2.4 mL was added into above mixture with stirring to give a homogeneous solution. These solutions were adjusted to the same volume before being transferred to hydrothermal reactor for 16 h at 180 °C. After the reaction, a light red suspension indicated the occurrence of the redox reaction of Au (III) with titanium (III) to Au NPs and TiO_2 with PVP-K30 protection. After cooling to room temperature, the light red precipitate was collected by centrifugation (8000 rpm, 20 min), washed with ethanol and deionized water three times before dried at 80 °C.

2.3. Apparatus

UV–vis detection was carried out on a Shimadzu UV–vis spectrophotometer (UV-2600). SEM, TEM and HRTEM images were observed by scanning electron microscopy (SEM, JEOL S-4800) and transmission electron microscopy (TEM, JEOL JEM-2010). Scanning transmission electron microscope (STEM) images were taken on a JEOL ARM 200 F HAADF operating at 200 kV accelerating voltage. The composition and phase purity of all samples were analyzed by a Shimadzu XRD-6000 X-ray diffractometer using Cu-Kα (λ = 1.54178 Å) irradiation with a scan rate of 6° per minute, operated at 40 kV voltage and 50 mA current. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250 spectrometer (Perkin-Elmer) to characterize the surface composition. Gas chromatography-mass spectrometry (GC–MS) analyses were performed using an Agilent 7890b-5977 A.

2.4. Photocatalytic H_2 production by visible light

The temperature was controlled to about 5 °C by a cooling fan. A solar simulator (CEL-HXF300, Jin Yuan) equipped with a 300 W Xe arc lamp was used as light source (1 cm between the housing box and the reactor). In a typical photocatalytic experiment, the TiO_2-Au photocatalyst (10 mg) was dispersed in 20 mL of aqueous solution of v/v 20% methanol by sonicating for 10 min. Prior to irradiation using a 420 nm long pass filter, the reactor with a catalyst suspension was bubbled with Ar for 30 min to completely remove the dissolved O_2 to assure the anaerobic condition. Magnetic stirring (500–800 rpm) was applied in order to keep the photocatalyst particles suspended in the solution throughout the experiment. The reaction process was monitored by measuring the H_2 concentration with a gas chromatograph (N2000 Zhejiang University, equipped with TCD detector, Ar carrier gas). Sampling was processed with 0.1 mL gas intermittently through the septum. All glassware was rinsed thoroughly with Milli-Q water prior to use.

3. Results and discussion

The preparation process of mulberry-shaped TiO_2-Au nanostructure is illustrated in Scheme 1 (for detailed experimental steps, please see ESI). Briefly, PVP-K30 and $TiCl_3$ were first mixed to form a transparent

Scheme 1. Preparation of mulberry-shaped TiO_2-Au nanocomposite.