



# Mesoporous plasmonic Au-loaded Ta<sub>2</sub>O<sub>5</sub> nanocomposites for efficient visible light photocatalysis



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## ABSTRACT

Au-loaded mesoporous Ta<sub>2</sub>O<sub>5</sub> (Au/m-Ta<sub>2</sub>O<sub>5</sub>) with high visible light photocatalytic activities were successfully prepared via a facile photodeposition methodology. The photocatalytic activities of Au/m-Ta<sub>2</sub>O<sub>5</sub> were then evaluated by photocatalytic hydrogen production from a methanol aqueous solution as well as photodegradation of Rhodamine B in aqueous solution under visible light irradiation ( $\lambda > 400$  nm). The photocatalytic experimental results showed that Au/m-Ta<sub>2</sub>O<sub>5</sub> exhibited enhanced visible light photocatalytic activities than those of Au-loaded commercial bulk Ta<sub>2</sub>O<sub>5</sub> (Au/b-Ta<sub>2</sub>O<sub>5</sub>). This was mainly due to its large specific surface area and mesoporous structure. The possible visible-light-driven photocatalytic mechanism of Au/Ta<sub>2</sub>O<sub>5</sub> was also proposed.

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## 1. Introduction

Noble metal nanoparticles (NPs), typically Au or Ag, have attracted great attention because they exhibit a surface plasmon resonance (SPR) band in the visible light region originating from the collective oscillations of the electrons on the surface of NPs. The unique plasmon absorbance features of these noble metal NPs have been used for a variety of applications including use in colorimetric sensors [1], photovoltaic devices [2], photochromic devices [3] and photocatalysis [4–9]. Recently, it has been particularly reported that many semiconductors modified by nanosized noble metals like Au and Ag showed excellent photocatalytic activities, e.g., in photocatalytic water splitting into hydrogen and photodegradation of organic pollutants. Garcia and co-workers [10] loaded TiO<sub>2</sub> with plasmonic Au NPs to enhance the photocatalytic activity of TiO<sub>2</sub> for hydrogen production under visible light irradiation ( $\lambda > 400$  nm) or a monochromatic 532 nm laser excitation. The appropriate loading and smaller size of Au NPs are key factors for the further enhancement of photocatalytic activity. Awazu et al. [11] developed a novel method to prepare a plasmonic Ag@SiO<sub>2</sub>@TiO<sub>2</sub> photocatalyst by depositing TiO<sub>2</sub> on a core-shell Ag@SiO<sub>2</sub> NP in which the SiO<sub>2</sub> shell

then prevented the oxidation of Ag by direct contact with TiO<sub>2</sub>. This plasmonic photocatalyst exhibited enhanced catalytic activity for decomposition of methylene blue as compared with pure TiO<sub>2</sub>. Huang and co-workers [12–15] have systematically investigated the visible light photocatalytic activities of Ag@AgX (X = Cl, Br and I) plasmonic photocatalysts. These photocatalysts showed excellent photocatalytic activities and stabilities for the decomposition of organic pollutants under visible light illumination.

Although many reports have demonstrated that the SPR effect of noble metal NPs can contribute to the enhancement of the visible light photocatalytic activity of semiconductors, especially UV-light responsive wide bandgap semiconductors, such as TiO<sub>2</sub>, uncertainties still remain in the understanding of the enhanced visible light photocatalytic activity. For example, Au NPs loaded TiO<sub>2</sub> showed enhanced photocatalytic activity for hydrogen production from water splitting under visible light irradiation produced from a Xenon lamp equipped with an ultraviolet cut-off 420 nm filter. However, the pristine TiO<sub>2</sub> can also split water into hydrogen under the same irradiation condition, although the hydrogen production efficiency is low [16]. There are two reasons for it: one is, for a commercialized ultraviolet cut-off 420 nm filter, its optical transmittance usually starts at 400 nm; the other, the absorption tail of TiO<sub>2</sub> can extend to 425 nm or even longer wavelength due to the existence of mid-gap states related to defects and impurity [17]. Consequently, the enhanced photocatalytic activity of Au

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NPs loaded  $\text{TiO}_2$  under visible light irradiation can not completely ascribe to the SPR effect of Au NPs, because  $\text{TiO}_2$  can also be photoexcited by visible light in the region about from 410 to 425 nm or even broader, moreover Au NPs can act as electron buffer and active sites for further enhanced  $\text{H}_2$  generation. Besides visible light photocatalytic hydrogen production,  $\text{TiO}_2$  based plasmonic photocatalysts, but not restricted to, meet the similar problem in visible light photodecomposition of organic dyes. The weak visible light excitation of semiconductors such as  $\text{TiO}_2$  in the region near 420 nm can be avoided by using wider bandgap semiconductors without any visible light response. Therefore, further studies are still necessary not only to develop novel visible-light-driven photocatalysts based on SPR effect, but also to clarify the SPR effect on the improved visible light activity of semiconductor photocatalysts.

Mesoporous semiconductors with tunable pore structure and tailored framework composition are of great interest for heterogeneous catalysis application [18–21]. In particular, mesoporous structures have proved to be excellent for photocatalysis due to their considerable surface areas and multiple scattering of light, thereby enabling more light to be harvested. In addition, the presence of a great number of continuous channels facilitates the transfer of reactants and products [22–24]. Among those materials, mesoporous  $\text{Ta}_2\text{O}_5$  (m- $\text{Ta}_2\text{O}_5$ ) has been widely used for highly efficient photocatalytic hydrogen under UV-light irradiation. Domen et al. [25–27] have reported that m- $\text{Ta}_2\text{O}_5$  prepared by the ligand-assisted templating method showed much higher photocatalytic activity for the overall water splitting as compared with bulk  $\text{Ta}_2\text{O}_5$  (b- $\text{Ta}_2\text{O}_5$ ). However, due to the wide bandgap ( $E_g = 4.0$  eV),  $\text{Ta}_2\text{O}_5$  photocatalyst can only absorb UV light which accounts for only 4% of the total sunlight, thereby greatly restricting their practical applications.

Although numerous works have reported on extending the light absorbance of  $\text{Ta}_2\text{O}_5$  into visible light region to improve its visible light photocatalytic activity with various modifications, such as nitrogenization [28–31], doping [32] and composites [33,34], reports on the development of  $\text{Ta}_2\text{O}_5$  based visible-light-driven plasmonic photocatalysts are still at present scarce. Moreover, compared with the 3.0–3.2 eV bandgap of  $\text{TiO}_2$ , the wider 4.0 eV bandgap of  $\text{Ta}_2\text{O}_5$  can guarantee that  $\text{Ta}_2\text{O}_5$  has no visible light response and thus the visible light activity of  $\text{Ta}_2\text{O}_5$  based plasmonic photocatalysts can fully ascribe to the SPR effect of metal NPs. In this work, Au NPs loaded mesoporous  $\text{Ta}_2\text{O}_5$  (Au/m- $\text{Ta}_2\text{O}_5$ ) visible-light-driven plasmonic photocatalyst was successfully synthesized by loading Au NPs onto m- $\text{Ta}_2\text{O}_5$ . The visible light photocatalytic activity of Au/m- $\text{Ta}_2\text{O}_5$ , including photocatalytic hydrogen production from methanol aqueous solution and photodecomposition of Rhodamine B (RhB) in aqueous solution, was evaluated as compared with that of Au NPs loaded commercial bulk  $\text{Ta}_2\text{O}_5$  powder (Au/b- $\text{Ta}_2\text{O}_5$ ).

## 2. Experimental

### 2.1. Preparation of m- $\text{Ta}_2\text{O}_5$

All chemicals in the experiments were analytical grade and were used without further purification. m- $\text{Ta}_2\text{O}_5$  was prepared according to the method reported by Kondo and co-workers [35]. Typically, 1.0 g of triblock copolymer P123 ( $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{OH}$ ) was dissolved in 10 g of ethanol with constant stirring for 10 min. Subsequently, 2.15 g of  $\text{TaCl}_5$  was added under vigorous stirring. After 10 min, 0.108 g of deionized water was added and the solution was stirred for 2 h to promote hydrolysis. The resulting sol solution was transferred to a Petri dish for aging at 40 °C for 7 d

to obtain a gel precursor. The gel was then calcined at 500 °C for 5 h to remove the polymer template.

### 2.2. Preparation of Au/m- $\text{Ta}_2\text{O}_5$

Au/m- $\text{Ta}_2\text{O}_5$  was prepared by a facile photodeposition method. 200 mg of m- $\text{Ta}_2\text{O}_5$  powder was suspended in a 50 mL quartz tube with 20 mL 20 vol% methanol aqueous solution. Then, various amounts of  $\text{HAuCl}_4$  solution (10 mmol/L) were added. The weight ratio of Au to  $\text{Ta}_2\text{O}_5$  was 0.1%, 0.5%, 1.0% and 3.0% in that order. Next, the quartz tube was purged with  $\text{N}_2$  for at least 30 min to remove air and then sealed with a rubber septum. The suspension was irradiated with a 500 W high-pressure mercury lamp for 3 h under magnetic stirring (XPA-7 photochemical reactor, Nanjing Xujiang Machine-electronic Plant). The temperature of the suspension during irradiation was maintained at 298 K using a thermostatically controlled water bath. The resultant Au/m- $\text{Ta}_2\text{O}_5$  was centrifuged, washed with distilled water three times, and dried at 60 °C under vacuum for 6 h. The Au/m- $\text{Ta}_2\text{O}_5$  with different sizes of Au NPs were obtained by adjusting the photodeposition time from 10 min to 3 h. For comparison, Au/b- $\text{Ta}_2\text{O}_5$  was also prepared by the same procedure.

### 2.3. Characterization

The powder X-ray diffractometer (XRD) patterns of the samples were performed on a Bruker D8 Focus X-ray diffractometer with monochromated  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15418$  nm). Transmission electron microscopic (TEM) and high resolution TEM (HRTEM) images were obtained using a JEOL-2011F microscope equipped with an energy dispersive spectrometer (EDS) with an accelerating voltage of 200 kV. UV–vis diffuse reflection spectra of the samples were recorded using a Varian spectrophotometer (Cary 5000) with an integrating sphere. The decrease in total organic carbon (TOC) was determined using a TOC analyzer (Multi N/C 2100, Jena).  $\text{N}_2$  adsorption-desorption isotherms and pore-size distributions were obtained on a Quadrasorb SI MP apparatus at 77 K. Prior to the experiments, the samples were degassed in vacuum at 200 °C for 12 h. The total specific surface area of samples was calculated using the Brunauer–Emmett–Teller (BET) method.

### 2.4. Photocatalytic activities

The photocatalytic hydrogen evolution from methanol aqueous solution was conducted in a 50 mL quartz tube with a rubber septum. The obtained photocatalyst powders (50 mg) were dispersed in a water/methanol solution (20 mL, v/v = 4:1) in a quartz tube using a magnetic stirrer. The solution was then purged with  $\text{N}_2$  for at least 30 min to remove  $\text{O}_2$  and then sealed with a rubber septum. The light source was a 300 W Xenon lamp (CEL-HXF 300, Beijing CEL Tech. Co., Ltd) equipped with an ultraviolet cut-off filter ( $\lambda > 400$  nm). The amount of evolved hydrogen was determined by a Shimadzu GC-2014 gas chromatography ( $\text{N}_2$  carrier gas, molecular sieve 5 Å TCD detector).

The photocatalytic activities of the as-obtained samples were also evaluated by the decomposition of RhB in aqueous solution under visible light irradiation. A 300 W Xenon lamp equipped with an ultraviolet cut-off filter ( $\lambda > 400$  nm) was used as the light source. Aqueous suspensions of RhB (30 mL, 10 mg/L) and 30 mg of photocatalyst powders were placed in a quartz tube. Prior to irradiation, the suspensions were first ultrasonicated for 10 min and then magnetically stirred in the dark for 30 min to ensure adsorption equilibrium. At given time intervals, 0.2 mL aliquots were sampled and centrifugated to remove the photocatalyst particles. The filtrates were analyzed by recording the variations of the absorption band maximum at  $\lambda = 553$  nm on a Hitachi UV-3900 spectrometer.

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