



## Visible light photocatalysis over solid acid: Enhanced by gold plasmonic effect



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### ABSTRACT

Solar driven catalysis by semiconductors is considered as a promising route to mitigate environmental problems caused by the combustion of fossil fuels and water pollution. Surface plasmon resonance (SPR) has offered a new opportunity to overcome the limited efficiency of photocatalysts. Herein we report that the SPR-mediated visible-light-responsive photocatalyst, 0.5 wt.% Au/SO<sub>4</sub><sup>2-</sup>-TiO<sub>2</sub>, can achieve over 99% conversion of pollutants (thiophene, thiol, rhodamine B, and phenol) during photocatalytic oxidation with oxygen or air as oxidant under visible light irradiation. The considerable enhancement of photocatalytic activity can be attributed to the synergistic effect of Au SPR and Lewis acidic SO<sub>4</sub><sup>2-</sup>-TiO<sub>2</sub> which are beneficial for the efficient separation and transfer of the photo-generated electrons and holes. Such a strategy would be important to the design and preparation of highly photocatalytic active semiconductor catalysts.

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### 1. Introduction

Solar driven catalysis on semiconductors is widely considered as a promising route to mitigate environmental problems caused by the combustion of fossil fuels and water pollution [1,2]. SO<sub>x</sub> produced from the automobile exhaust gas *via* the burning of sulfur-containing components present in fuels results in serious air pollution. Thiophene and thiol are the typical representatives among the sulfur-containing components. Thiophene with the aro-

maticity and the low electron density on sulfur atom is the most difficult to oxidize with conventional oxidative desulfurization processes [3]. Several effective photocatalysts are reported for the photocatalytic desulfurization [4–7]. Besides, polluted wastewater from industry is a globally environmental problem. The mitigation of azo dyes rhodamine B (RhB) and toxic chemicals (e.g. phenol) induced by the industry is necessary for the environmental pollution control. Consequently, several materials that enable the cleanup of polluted water *via* a far less aggressive approach are developed [8,9].

Titania-based catalyst as one of the most photoactive semiconductor catalysts has been extensively investigated. TiO<sub>2</sub> exhibits high activity and stability, and has proven to be an excellent photocatalyst material under UV light exposure [10,11]. The photocatalytic activity of TiO<sub>2</sub> varies significantly with its phase structure, crystallinity and particle size [12–14]. Various methods have been employed to control the crystal phases of TiO<sub>2</sub> [15–19]. Li et al. [20] investigated the photocatalytic reforming of methanol on Pt/TiO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup> as a model reaction of biomass reforming. TiO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup> with a tunable surface phase was prepared by

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calcining commercially available TiO<sub>2</sub> with deposited sodium sulfate Na<sub>2</sub>SO<sub>4</sub> as a modifier. Colon et al. [21] used a sol-gel method to synthesize the sulfated TiO<sub>2</sub>. They found that SO<sub>4</sub><sup>2-</sup> could maintain the anatase phase of TiO<sub>2</sub>. However, the sulfated TiO<sub>2</sub> was mainly used in the photocatalytic esterification reaction and oxidation of alcohols/pollutants [22–24].

On the other hand, it was reported that the deposition of noble metal such as Pt, Ag, and RuO<sub>2</sub> as cocatalysts on TiO<sub>2</sub> [25,26] greatly improved the activity of the photocatalysts [27,28]. Very recently, we found that photocatalyst RuO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-TiO<sub>2</sub> could display the excellent photocatalytic activity in thiophene oxidation [29,30]. The synergistic effect of RuO<sub>2</sub> as an oxidation cocatalyst and Lewis acidic SO<sub>4</sub><sup>2-</sup>-TiO<sub>2</sub> which capture superoxide species/activate thiophene molecules is beneficial for the efficient photocatalytic oxidation of thiophene. The co-existing oxidation cocatalyst and Lewis acid site offer a more promising approach for the photocatalytic oxidation of pollutants. The recent development of surface plasmon resonance (SPR) has offered a new opportunity to overcome the limited efficiency of photocatalysts. SPR improves the solar-energy-conversion efficiency by (i) expanding light absorption to longer wavelengths, (ii) increasing light scattering, and (iii) exciting electron-hole pairs in the semiconductor by transferring the plasmonic energy from the metal to the semiconductor [31,32]. The deposition of plasmonic metal nanoparticles (NPs) on semiconductors can enhance photocatalytic activity toward water splitting and organic compound degradation [33–41].

In process (iii), the concentrated energy contained in localized plasmonic oscillations is transferred to the semiconductor, inducing charge separation in the semiconductor. So far, the SPR-induced charge separation mechanism remains unclear. It is reported as the direct electron transfer (DET), SPR-mediated local electromagnetic field (LEMF) and resonant energy transfer (RET) process. DET depends on the alignment of the band levels of the semiconductor and Fermi level of the plasmonic metal. DET occurs after the excitation and subsequent decoherence of the SPR, which leaves a population of hot electrons that are able to transfer to the semiconductor. LEMF and RET process lead to the charge separation and create carriers in the semiconductor which is in favor of high photocatalytic activity [31,32].

Herein we report the photocatalytic oxidation of thiol, thiophene, RhB, and phenol by a SPR-mediated visible-light responsive photocatalyst Au/SO<sub>4</sub><sup>2-</sup>-TiO<sub>2</sub> (Au/ST). An extraordinary photocatalytic activity (over 99% conversions of pollutants) can be achieved under visible light irradiation ( $\lambda \geq 420$  nm). We find the synergistic effect of Au SPR and Lewis acidic SO<sub>4</sub><sup>2-</sup>-TiO<sub>2</sub> is beneficial for the highly efficient photocatalytic oxidation of pollutants.

## 2. Experimental

### 2.1. Catalyst preparation

All chemicals used in these experiments were of analytical reagent grade. The solid acid SO<sub>4</sub><sup>2-</sup>-TiO<sub>2</sub> catalysts were prepared by incipient wetness method [7]. TiO<sub>2</sub> (Degussa P25) was submerged in a nM H<sub>2</sub>SO<sub>4</sub> solution (n=0.5, 1–3). The mixture was heated at 50 °C to evaporate water and then calcined at 450 °C for 3 h to obtain the solid acid SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>. Solid-acid SO<sub>4</sub><sup>2-</sup>-TiO<sub>2</sub> catalysts were denoted as n ST (n = 0.5, 1–3 M H<sub>2</sub>SO<sub>4</sub>, ST = SO<sub>4</sub><sup>2-</sup>-TiO<sub>2</sub>).

The deposition of Au NPs on solid acid ST was prepared as follows. A certain amount of polyvinyl alcohol (PVA) aqueous solution was added to an aqueous solution of HAuCl<sub>4</sub> under vigorous stirring. Then an excessive NaBH<sub>4</sub> was rapidly added (NaBH<sub>4</sub>/Au (mol/mol) = 5), resulting in the chemical reduction of Au<sup>3+</sup> cations. The color of the solution immediately changed from light yellow to

dark red, indicating the formation of Au sol. After stirring for 1 h, the required amount of the solid acid ST was added to Au sol in order to obtain an i wt.% Au loaded ST catalyst (i = 0.1, 0.5, 1.0, 2.0). The pH value of solution was 1–2 after the addition of solid acid ST. After the vigorous stirring for 2 h, the catalyst was filtrated, washed thoroughly with distilled water and dried at 80 °C under vacuum for 24 h. The as prepared i wt.% Au/SO<sub>4</sub><sup>2-</sup>-TiO<sub>2</sub> was denoted as i Au/ST. In some cases, i Au/ST was further calcined at 300 °C in air to remove PVA.

### 2.2. Catalyst characterization

The prepared samples were characterized by X-ray powder diffraction (XRD) on a Rigaku D/Max-2500/PC powder diffractometer. Each sample was scanned using Cu-K $\alpha$  radiation with an operating voltage of 40 kV and an operating current of 200 mA. The scan rate of 5° min<sup>-1</sup> was applied to record the patterns in the range of 10–80° at a step of 0.02°. UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded on a UV-vis spectrophotometer (PerkinElmer Lambda 750) equipped with an integrating sphere. Transmission Electron Microscopy (TEM) was used to examine the size of Au NPs. The TEM images were obtained on a Quanta 200F microscope (FEI Company) with the accelerating voltage of 0.5–30 kV and a Tecnai G2 Spirit microscopy (FEI Company) with the accelerating voltage of 120 kV. A FEI Tecnai G2 F20 transmission electron microscope (TEM) equipped with a high-angle annular dark field scanning TEM (HAADF-STEM) detector operated at 200 kV was utilized to observe Au NPs. Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out on a 7300 DV (Perkin Elmer) ICP OES spectrophotometer. X-ray photoelectron spectroscopy (XPS) was acquired on Thermo ESCALAB 250Xi with an Al K $\alpha$  X-ray ( $h\nu = 1486.6$  eV).

Mott-Schottky (MS) analysis was carried out at a DC potential range 0–1 V vs. RHE with an AC potential frequency of 1 kHz under dark condition. The fabricated electrode, a platinum electrode, and saturated calomel electrode (RHE) were used as working, counter and reference electrodes, respectively. If there is no special mention, 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH 6.8) was used as an electrolyte after saturation with Ar gas for 30 min.

The nitrogen adsorption-desorption isotherms were obtained at –196 °C with a micromeritics ASAP 2020 apparatus. Prior to the measurement the samples were outgassed at 250 °C for 6 h. Specific surface area determination was based on BET formalism. The mesopore size distributions were calculated from the desorption branch.

ESR signals of radicals trapped by DMPO were recorded at ambient temperature on a Bruker ESR A200 spectrometer. After bubbling O<sub>2</sub> for 10 min, the samples were introduced into the homemade quartz cup inside the microwave cavity and illuminated with a 300 W Xe lamp (CERAMAX LX-300). The settings for the ESR spectrometer were as follows: center field, 3486.7 G; sweep width, 100 G; microwave frequency, 9.8 GHz; modulation frequency, 200 kHz; power, 10.0 mW. Magnetic parameters of the radicals detected were obtained from direct measurements of magnetic field and microwave frequency.

### 2.3. Photocatalytic reaction

The photocatalytic reactions of thiophene and thiol were carried out in a Pyrex reaction cell with O<sub>2</sub> or air bubbling at a constant flow rate. Photocatalyst (1 g L<sup>-1</sup>) was dispersed in an acetonitrile solution containing given amounts of thiophene ([sulfur content]<sub>initial</sub> = 600 ppm). The suspension was irradiated by a 300 W Xe lamp (CERAMAX LX-300), which is equipped with an optical filter ( $\lambda \geq 420$  nm) to cut off the light in the ultraviolet region. The temperature of the reaction solution was maintained at 10 ± 2 °C

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