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# SPR enhanced photocatalytic properties of Au-dispersed amorphous $BaTiO_3$ nanocomposite thin films

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## ABSTRACT

$Au_x/BaTiO_3$ ($x = 0$, 5, 10, 15, 25, 35, and 45, where $x$ is mol% of Au) composite thin films dispersed by Au nanoparticles (NPs) were prepared by a sol–gel spin-coating approach. The crystal structure, optical and photocatalytic properties of the films were investigated with a special emphasis on the influences of $x$. The approximately spherical Au NPs with 20–45 nm in diameter are embedded uniformly in the amorphous $BaTiO_3$ matrix. The absorption peaks appeared at the wavelength from 580 to 620 nm are due to the surface plasmon resonance (SPR) effect of Au NPs, and the SPR peaks generally manifest a red-shift with increasing $x$ from 5 to 45. The $Au_x/BaTiO_3$ composite film with the optimal SPR effect ($x = 35$) exhibits the highest photocatalytic activity for the degradation of Rhodamine B (RhB) aqueous solution among all films under whole spectrum sunlight irradiation.

## 1. Introduction

In recent years, semiconductor photocatalysts have been attracting increasing attentions in anticipation of employing them as a green and sustainable technology to solve the energy and environmental issues such as the generation of hydrogen [1] as well as the degradation of organic dyes [2]. However, most of the current studied photocatalytic materials are suffered by their poor photo-absorption capability in visible light range and high recombination rate of photogenerated electron–hole pairs [3]. Aiming at solving these problems, several strategies have been developed in the past decades, including doping with metal ions [4], combining with semiconductor of narrow bandgap [5–7] and dispersing noble metal nanoparticles (NPs) [8–12]. In particular, previous works have demonstrated that the absorption ability can be effectively tuned by dispersing noble metal NPs such as Au [8,9], Ag [10,11] and Cu [12], originating from their surface plasmon resonance (SPR) effect [13,14]. On the other hand, the metal NPs can behave as an electron sink to facilitate exciton separation, and thus improve the photocatalytic activity in such metal/semiconductor heterojunction systems [15,16]. In addition, it has also been discovered very recently that Au NPs could inject electrons into the semiconductor and also serve as catalytic sites for gas generation [17–19].

Metal NPs dispersed composite films with expected composition, structure and feature, which can be fabricated by dispersing metal NPs into suitable dielectric matrixes (e.g. $Cu/SiO_2$ [12], $Ag/TiO_2$ [20]), are significant because of their potential application in the field of photocatalysis. Among all metal NPs, gold is considered as one of the most effective dispersing elements for enhancing the photocatalytic property since it has a remarkable SPR effect and chemical stability [8]. On the other hand, $BaTiO_3$ with high dielectric constant and refractive index [21] has attracted much attention because of its excellent optical property [22], and the $BaTiO_3$ thin films can be incorporated with noble metal NPs such as Au. The relevant studies [21–25] about $BaTiO_3$ films dispersed by Au NPs have been reported, demonstrating an absorption peak due to the SPR effect of Au NPs. In addition, the absorption peaks manifest a red shift and intensify with the increase of Au addition within certain limits, which can broaden the absorption range and thus make efficient use of the sunlight. However, almost all of the published works have been only focused on the optical properties of various $Au/BaTiO_3$ composite films, whose photocatalytic properties have not been reported so far. The exploration of the relationship between the SPR effect and the photoactivity of the composite system would provide useful insight for designing efficient thin film based plasmonic photocatalyst.

In the present study, $Au/BaTiO_3$ thin films were prepared by a sol–gel spin-coating method in expect that these films could be a

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potential photocatalyst. The optical absorption properties and photocatalytic activities, along with the microstructure of the thin films were investigated on the effect of Au loading content. An enhanced nonlinear optical absorption property and a good photocatalytic activity were obtained in the Au/$BaTiO_3$ thin films, whereby they would have potential applications in nonlinear optical and photocatalysis fields.

## 2. Experimental

The $Au_x/BaTiO_3$ thin films with different Au/(Au + $BaTiO_3$) molar ratios $x$ ($x = 0, 5, 10, 15, 25, 35$ and 45 mol% of Au) were prepared by a sol–gel spin-coating method. First, 1 mol of $Ba(CH_3COO)_2$ was dissolved in a mixed solution of $CH_3COOH$ (10 ml), $H_2O$ (10 ml) and $C_3H_8O_3$ (5 ml), and then stirred for 2 h. Subsequently, 1 mol of $Ti(C_4H_9O_4)_4$ was added to the solution, followed by stirring for another 2 h. Several drops of nitric acid were added to adjust the pH value of the solution between 2 and 3. Then, $HAuCl_4{\cdot}4H_2O$ was added into the above mentioned precursor solution with desired chemical composition of the $Au_x/BaTiO_3$. To form the $Au_x/BaTiO_3$ films, the ultimate solution was spin coated onto a glass substrate with a dimension of 2 × 2 cm at 500 rpm for 5 s, and successively 3000 rpm for 15 s. Finally the films were dried at 150 °C for 30 s and then heated to 500 °C for 1 h.

Thermogravimertry (TG: HCT-1, Beijing Optical Instrument Inc., China) and differential thermal analysis (DTA: HCT-1, Beijing Optical Instrument Inc., China) were carried out for the precursor powder which was dried at 60 °C for a week and heated in air with a constant heating rate of 10 °C/min. The crystal structure of all samples were investigated by X-ray diffraction (XRD: DMAX-RB, Rigaku Inc., Japan) with Cu K$\alpha$ radiation ($\lambda$ = 1.5406 Å) filtered through a Ni foil. The microstructure was observed by transmission electron microscopy (TEM: JEM-100CXΠ, JEOL, Japan). The chemical binding state of the constitute elements of the prepared films was characterized by X-ray photoelectron spectroscopy (XPS: PHI-5300, PHI, USA) using Al K$\alpha$ radiation (1486.6 eV) as an X-ray source. The energies of all spectra were calibrated by normalizing with respect to the C 1s peak at 284.8 eV, giving binding energy values within an accuracy of ±0.1 eV. The XPS spectra were obtained by deconvolution using the program of XPS Peak 4.0. The absorption spectra were measured by UV–vis spectrophotometer (UV-2800, UNICO Instruments Co., Ltd., China). Steady state photoluminescence (PL) spectra of thin films were measured using F-4500 FL spectrophotometer with an excitation wavelength of 335 nm at room temperature.

The photocatalytic activities of the films were evaluated by the degradation of Rhodamine B (RhB) under UV–vis light irradiation using a 500 W Xe lamp (Beijing institute of electrical light sources, China). The RhB solution (20 mM) was spin coated onto the surface of the thin films. The reaction temperature was kept at room temperature to prevent any thermal catalytic effect. The films with RhB layer were statically placed in the dark for 30 min to reach the adsorption/desorption equilibrium between photocatalysts and RhB before illumination. The degradation of RhB was monitored from the intensity of absorption peak at 580 nm relative to its initial intensity using the spectrophotometer under different illumination time.

## 3. Results and discussions

Fig. 1 shows the TG-DTA curves of the precursor powers (choosing $Au_{35}/BaTiO_3$ as a representational sample) dried at 60 °C for a week. Weight loss in the TG trace shows five well-defined steps to generate the Au/$BaTiO_3$ composite film from room temperature to ca. 600 °C, corresponding to two endothermic and three exothermic peaks in the DTA curve. The first weight loss ca. 3% below 165 °C, along with a very weak endothermic peak near 103 °C, is due to the evaporation of low-boiling point solvent [26]. The second weight loss (7%) with a small endothermic peak at around 197 °C could be attributed to the decomposition of organic species [26]. The third weight loss (ca. 11% with an exothermic peak around 333 °C) can be ascribed to the disintegration of $HAuCl_4$ [27]. As the temperature increased from 333 to 525 °C, a very weak exothermic peak appeared at 435 °C with ca. 5% weight loss could result from the burning of some organic compounds and disintegration of acetate [24]. The strongest exothermic peak at ca. 525 °C accompanied with a weight loss of ca. 9% should be due to the formation of dielectric matrix [26]. No further weight loss was detectable above 600 °C, demonstrating that the beginning crystallization temperature of the matrix is ca. or higher than 600 °C. A previous study on the thermal behavior of $BaTiO_3$ thin films with 10 vol% of Au by Otsuki et al. [23] demonstrated that the matrix is still amorphous up to 600 °C and crystallizes above 650 °C. Another work by Kineri et al. [24] showed that the matrix of the Au/$BaTiO_3$ film begins to crystallize at temperature over 600 °C. Our result accords with these reports.

Fig. 2 exhibits the XRD patterns of the $Au_x/BaTiO_3$ thin films after

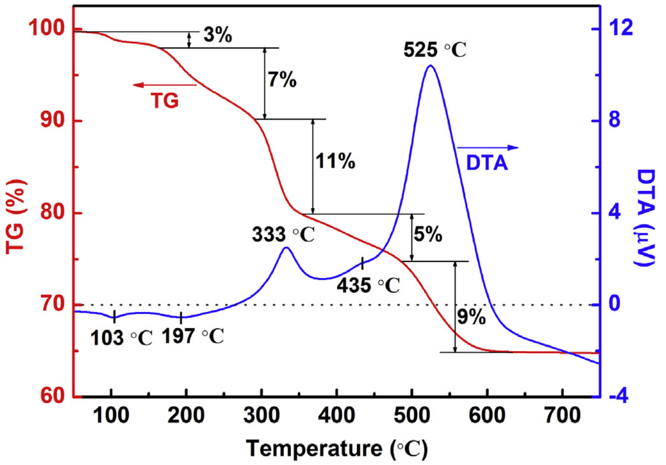

**Fig. 1.** TG-DTA curves of the $Au_{35}/BaTiO_3$ precursor powders.

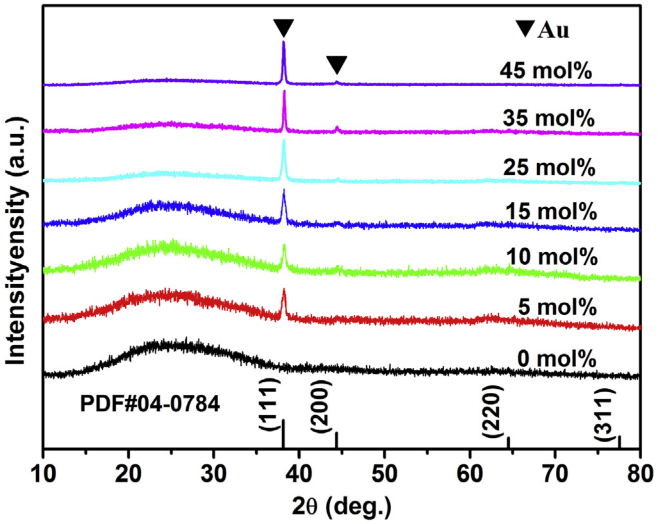

**Fig. 2.** XRD patterns of the $Au_x/BaTiO_3$ thin films.