



# Photocatalytic performance of plasmonic Au/Ag-TiO<sub>2</sub> aerogel nanocomposites

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## ABSTRACT

Porous nanocomposites of Au/Ag-TiO<sub>2</sub> aerogels benefit from unique morphological characteristics of aerogels, intrinsic physical, chemical and also photocatalytic required properties of TiO<sub>2</sub> and strong plasmonic effects of metal nanoparticles, i.e., Au and Ag. Therefore, they are able to be applied as an ideal photocatalyst overcoming the intrinsic weak points of conventional TiO<sub>2</sub>. In this research, several composites of TiO<sub>2</sub> aerogel modified with Au, Ag and mixture of Au-Ag nanoparticles were prepared by applying two different methods of synthesis. The photocatalytic efficiency of the samples was established by using salicylic acid (SA) as a standard pollutant molecule. The photodegradation rate of SA under irradiation was investigated by the decrease in its concentration in time, and found to depend on specific surface area and type of metal nanoparticles trapped into the TiO<sub>2</sub> network. The larger surface area and the presence of the two metal nanoparticles lead to the best results. Furthermore, the morphological characterizations and physical properties of the nanocomposites were investigated through BET results, FESEM and TEM images.

## 1. Introduction

Photocatalysis, a recently common word, is a process in which the clean “inexhaustibly” safe energy of the sun is harnessed and converted to chemical energy in the presence of a catalyst [1–6]. Photocatalysis is a useful and efficient process for producing solar fuels [4], water splitting [1,7–9] and chemical decontamination of air, water and soil due to the ability of destroying organic compounds, such as alcohols, carboxylic acids, amines, herbicides, aldehydes, etc. ... In the case of chemical decontamination unlike the conventional two-step treatment methods, i.e., concentration of the chemical and then its disposal, photocatalysts directly convert the chemicals into non-toxic wastes [6,10–16]. Among different promising photocatalytic metal oxides (e.g., TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, PbO) [4], TiO<sub>2</sub> due to its highly photoactivity, chemical stability, nontoxicity and low price is almost an ideal photocatalyst and the best candidate for industrial use at present and also probably in the future [1,2,6,10,12,17,18].

One of the most important properties of an efficient photocatalyst is its effectiveness of solar energy conversion which depends on four factors: light absorption, charge separation, charge migration, and charge recombination [3,19,20]. Considering these factors, TiO<sub>2</sub> has two main drawbacks: (1) relatively large band gap energy of 3–3.2 eV necessitating UV-excitation, which comprises only ~5% of solar radiation and (2) small lifetime of charge carriers

[3,7,10,12,15,17,21–25]. To overcome these intrinsic limitations, different methods have been used, i.e., doping TiO<sub>2</sub> with metallic or inorganic species, applying organic dyes as photosensitizers, hybrid photocatalysts (TiO<sub>2</sub> and other semiconductors, carbon nanotubes and etc.) and incorporating plasmonic metal nanoparticles into the structure of TiO<sub>2</sub> [3,15,25–28].

Rapid development of surface plasmon resonance (SPR) has brought up a new and more efficient method to enhance the limited efficiency of photocatalysts and even photovoltaic devices [3,22,29–33]. SPRs enhance the photocatalytic activity by increasing the efficiency of solar energy conversion through three processes: (1) extending the light absorption wavelength to visible and infrared (IR) ranges, (2) increasing light scattering cross section which is associated with SPR and (3) increasing the induced charge separation by transferring the metal plasmonic energy to the semiconductor via Schottky junction [3,14,22]. These enhancement processes strongly depend on the size, shape and concentration of the nanoparticles and also the way they are located in the structure of the semiconductor and performing as an efficient trap for the charge carriers (Schottky junction) [3,7,12,34]. Among different plasmonic metals gold (Au) and silver (Ag) in accordance with their size, have local surface plasmon resonances (LSPRs) covering most of the visible and near infrared wavelength range and therefore are the best candidates in photocatalytic activities. Also, they are more stable in the air and in aqueous environments [14,15,18,25,35,36].

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Furthermore, increasing the solar conversion efficiency, improving the photocatalytic activity also depends on the morphological properties of the photocatalyst, such as: specific surface area, pore volume, pore structure, crystalline phase, exposed surface facets crystalline phase and particle size [2,12,13,17,19,24,34,37–43]. Recently, there has been a great interest in constructing an appropriate nano- or micro-structures of TiO<sub>2</sub> to improve the efficiency of this intrinsic suitable photocatalyst. Among different structures that have been fabricated, such as: spheres, nanorods, fibers, tubes and interconnected networks, it has been noticed that a three dimensional (3D) porous interconnected network can best adjust to the photocatalytic requirements [2,10,24,25,37,41,44]. These structures have potentially large surface areas and because of their porous interconnected structure, they not only provide efficient pathways for the carriers (pollutants) mobility but also support their purification, separation, and storage [2].

Considering these two important factors, i.e., plasmonic effects and structural properties, modifying TiO<sub>2</sub> 3D porous structure with metal nanoparticles can be an effective choice to improve the photocatalytic properties of TiO<sub>2</sub>. This matrix can also prevent the entrapped metal nanoparticles from aggregation and make them much more stable in time in different environments [10].

In this paper as a 3D structure TiO<sub>2</sub> aerogel, i.e., an interconnected mesoporous network with very high specific surface area and extremely porous structure, was modified with Au/Ag nanoparticles. Here, different composites were prepared using Au, Ag and mixture of Au-Ag nanoparticles with different sizes and concentrations, applying two different methods of synthesis: (1) introducing the Au/Ag colloidal solution directly into the TiO<sub>2</sub> sol during the sol-gel process and (2) impregnating the TiO<sub>2</sub> gel with Au/Ag nanoparticles. Applying these two methods makes the nanoparticles diffuse and be trapped into the gel network [7,12,34,40]. The Au/Ag/TiO<sub>2</sub> aerogel composites were obtained after supercritically drying the modified gels. The samples were analyzed from a morphological and structural point of view after being dried. All the samples were used in photocatalytic activity and their efficiency was investigated by monitoring the decrease in the absorption intensity of the salicylic acid (SA) band located around 297 nm applying UV-vis spectroscopy.

As it will be seen in the following sections, in the first method (referred to as *method A*) there is a limitation in the amount of the nanoparticles that can be introduced into the gel structure which is either 900 or 1800  $\mu\text{L}$  although the morphological properties of the aerogels are better, i.e., specific surface area is higher. On the other hand as the gel time is very short, there is not enough time for the nanoparticles to be stirred well in the solution and thus there is no control on their homogeneous distribution throughout the gel.

## 2. Experimental methods

### 2.1. Sample preparation

#### 2.1.1. Preparation of gold nanoparticles (AuNPs)

**2.1.1.1. Type 1.** A 20 mL aqueous solution containing  $5 \times 10^{-4}$  M HAuCl<sub>4</sub>·3H<sub>2</sub>O (99.5% MERCK) and  $5 \times 10^{-4}$  M Na<sub>3</sub>C<sub>3</sub>H<sub>5</sub>O(COO)<sub>3</sub>·2H<sub>2</sub>O (trisodium citrate/Na<sub>3</sub>citrate) (MERCK) was prepared in an Erlenmeyer flask. Next, 0.6 mL of ice-cold, freshly prepared 0.2 M NaBH<sub>4</sub> (MERCK) solution was added all at once to the solution while stirring. The solution turned pink immediately after adding NaBH<sub>4</sub>, indicating the Au nanoparticles' formation [45] The AuNPs obtaining from this method have a maximum UV-visible absorption ( $\lambda_{\text{max}}$ ) at about 513 nm.

**2.1.1.2. Type 2.** In a 50 mL Erlenmeyer flask, 20 mL of 2 mM HAuCl<sub>4</sub>·3H<sub>2</sub>O (99.5% MERCK) aqueous solution was brought to boil, under vigorous stirring. 2 mL of 77.6 mM ( $2 \times 38.8$  mM) Na<sub>3</sub>citrate (MERCK) was added to the solution all at once while vigorously stirring on the magnetic hot-plate. Within a few minutes the yellow solution

turned clear, dark blue and then a deep red burgundy color. After the burgundy color was observed stirring and boiling was continued for 10–15 min. Then the solution was removed from heat while stirring for 15 more minutes. After the solution was reached at room temperature, the volume was adjusted to 20 mL adding Milli-Q water (BioIdea) [46]. The AuNPs obtaining from this method have a maximum UV-visible absorption ( $\lambda_{\text{max}}$ ) at about 522 nm.

#### 2.1.2. Preparation of silver nanoparticles (AgNPs)

**2.1.2.1. Type 1.** 20 mL of 2 mM AgNO<sub>3</sub> (MERCK) was added dropwise (about 1 drop a second) to an Erlenmeyer flask located in an ice bath, containing 30 mL of 4 mM NaBH<sub>4</sub> (MERCK) solution stirring vigorously. The solution turned light yellow after the addition of 2 mL of AgNO<sub>3</sub> and then turned to brighter yellow when all of the AgNO<sub>3</sub> solution was added. It took about 3 min. to add all the solution. Then the Erlenmeyer flask was removed from the ice bath but kept stirring until the solution reached at room temperature in order to avoid the aggregation of the AgNPs [47]. The AgNPs obtaining from this method have a maximum UV-visible absorption ( $\lambda_{\text{max}}$ ) at about 392 nm.

**2.1.2.2. Type 2.** 18 mg of AgNO<sub>3</sub> (MERCK) was dissolved in 100 mL of Milli-Q water (BioIdea) and brought to boiling while stirring. 2 mL solution of 38.8 mM Na<sub>3</sub>citrate (MERCK) was added all at once to the aqueous solution of silver. The solution was kept on boiling and stirring for about 45 to 60 min while its color changed from almost clear to greenish yellow [48]. The AgNPs obtaining from this method have a maximum UV-visible absorption ( $\lambda_{\text{max}}$ ) at about 442 nm.

#### 2.1.3. Preparation of Au/Ag/TiO<sub>2</sub> aerogels composites

TiO<sub>2</sub> gels were prepared through sol-gel process using titanium isopropoxide (TIP) (97% Sigma-Aldrich), ethanol (MERCK), nitric acid (65% Merck) and deionized water (deionized water system in the lab) at molar ratio 1: 21: 0.08: 7.35, as our previously reported results [49]. The gels were aged in ethanol bath at room temperature for 60 days in order to stiffen their structures, then after 3 times of solvent exchange with acetone for every 24 h in order to remove reaction byproducts and replace the pore liquid with acetone, which is miscible with liquid CO<sub>2</sub>, the solvent was extracted supercritically with CO<sub>2</sub> (65 °C, 220 atm).

Three different groups of composites were prepared according to the type of applied nanoparticles: (1) Au-TiO<sub>2</sub>: applying AuNPs, (2) Ag-TiO<sub>2</sub>: applying AgNPs and (3) Au/Ag-TiO<sub>2</sub>: applying both AuNPs and AgNPs. These composites were synthesized by two different methods:

**2.1.3.1. Method A.** The nanocomposite was prepared by adding the intended nanoparticle colloidal solution instead of the deionized water directly to the TiO<sub>2</sub> sol during the sol-gel process. After the gelation occurred, the modified gel was aged for about 60 days and after 3 times of solvent exchange with acetone for every 24 h, was dried supercritically with CO<sub>2</sub>. The color of the prepared gels was pink, deep red, bright yellow or greenish yellow according to the type of nanoparticle that was used.

**2.1.3.2. Method B.** After the aging period and 3 times of solvent exchange, TiO<sub>2</sub> gel was immersed in the intended nanoparticle colloidal solution. Being maintained in the colloidal solution for at least three days, the gel was impregnated with nanoparticles which was obvious by the color change of the gels from translucent to pink, deep red, bright yellow or greenish yellow according to the type of nanoparticle that was used. Then after the second cycle of 3 times of solvent exchange with acetone for every 24 h, the impregnated gel was dried supercritically with CO<sub>2</sub>.

The Ag-TiO<sub>2</sub> nanocomposites applying AgNPs type 1 were prepared by using the diluted nanoparticles colloidal solution. In order to dilute the nanoparticle colloidal solution, first the needed volume of the solution for the synthesis of the composite is evaluated. Then the evaluated amount of solution is prepared by using equal volumes of

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