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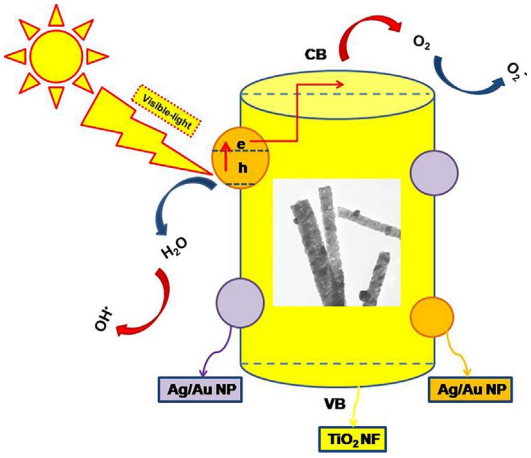
Research paper

Immobilization of plasmonic Ag-Au NPs on the TiO_2 nanofibers as an efficient visible-light photocatalyst

Pegah Shahini, Ali Akbar Ashkarran*

Department of Physics, Faculty of Basic Sciences, University of Mazandaran, Babolsar, Iran

GRAPHICAL ABSTRACT



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ABSTRACT

A heterostructure photocatalyst including metallic silver (Ag), gold (Au) in the form of nanoparticles (NPs) and titanium oxide (TiO_2) nanofibers were fabricated using a combination of photodeposition and electrospinning techniques. In this procedure, electrospun TiO_2 nanofibers were decorated by plasmonic Ag and Au NPs on the surface of nanofibers which were generated via photochemical reduction process. The synthesized Ag-Au/TiO_2 nanocomposites which were considered as a favorable candidate for enabling the more access to visible-light in photocatalytic performance were subsequently characterized by field emission scanning electron spectroscopy (FESEM), transmission electron spectroscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and ultra-violet-visible (UV–vis) spectroscopy. UV–vis studies indicate the extension in the absorption region of composite toward the visible-light range have been occurred through the loading metallic nanoparticles into the TiO_2 structure. Microscopic assessments in addition to EDS revealed that metallic NPs deposited on the surface of the fibers through photochemical reduction process. It was found that, the ratio of utilized Ag/Au in the final composite can significantly enhance the photocatalytic efficiency. It was suggested that introduction of the proper amount of noble metal NPs into the TiO_2 matrix leads to the notable enhancement of visible-light decomposition of rhodamine B (Rh. B) as a model dye.

* Corresponding author.
E-mail address: ashkarran@umz.ac.ir (A.A. Ashkarran).

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1. Introduction

Recently, due to the growing threat about environmental pollution specially water pollution and its terrible effects on human life, the severe need for the efficient purification system to remove the harmful products from water has been strongly appeared [1,2]. Therefore, the application of composites containing semiconductors in removal of toxic materials from wastewater have been widely received interest [3–5]. Among the large number of semiconductors, TiO_2 has attracted much attention as a pivotal material in water and air purification because of its non-toxicity, stability, accessibility, high activity and low-cost [6,7]. But, the main shortcoming is that these kinds of photocatalysts displayed the high photocatalytic activity for degradation of pollutants only under UV light irradiation. Compared with the visible-light region, UV region just owns a small part of the solar light. This restriction in photocatalytic performance of TiO_2 is attributed to its wide band gap (3.2 eV), so that only the UV irradiation can activate it. Moreover, the photocatalytic activity of pristine TiO_2 has been diminished by high rate of recombination of electron-hole pairs [8,9]. Hence, to overcome these impediments concluding the improvement in photocatalytic performance of TiO_2 for decomposition of organic pollutants by the photoactivation process of TiO_2 under sunlight, numerous strategies have been utilized. These efforts include the introduction of some materials such as metal and non-metal elements into the TiO_2 matrix [10–12]. Recent investigations revealed that modification of TiO_2 by noble metals can enhance the photocatalytic activities [13]. Indeed, doping with noble metal not only can shift the absorption region of TiO_2 from UV to visible-light region, but also can prevent the recombination of charge carries (electron-hole pairs) [14,15]. The enhancement in photoctalytic performance of TiO_2 modified by noble metals is assigned to the surface plasmon resonance (SPR) effect of noble metals such as Ag, Au and Cu which can absorb different frequency of incident solar light. In fact, the resonant frequency (SPR band) of these elements can be adjusted from visible-light to near-infrared by changing their size, shape and surrounding dielectric environment [16–19]. By considering the effective role of noble metals in the enhancement of photocatalytic activity, it is expected that integration of two noble metals can be a promising approach for maximization of visible-light harvest in photocatalytic reaction. In fact, many studies have been done to prepare the suitable heterostructures including two different noble metals and investigation of their applications in catalysis field. Among them, Ag and Au due to owing SPR wavelength in visible-light region (410–420 nm and 525–550 nm for small spherical Ag and Au NPs, respectively) and similar lattice constant (2.3/2.4 A for Ag (111)/Au (111)) are attractive candidates for production of multiple composites. Based on the previous reports, TiO_2 in any forms such as nanoparticle, nanofiber and nanosheet exhibited good photocatalytic activity, nevertheless NPs are the most common form of TiO_2 in fabrication of photocatalyst composite [20,21]. Compared with NPs, nanofibers because of possessing relatively large surface to volume ratio can increase the photocatalytic efficiency of the nanocomposite. In this regard, a large number of procedures are proposed for synthesis of TiO_2 nanofibers, but electrospinning technique due to the simplicity and cheapness has been considered as a novel and suitable method for preparation of nanofibers [22,23].

In this study, we have reported the fabrication of a heterogeneous composite containing Ag and Au NPs which deposited on the surface of electrospun TiO_2 nanofibers. To obtain this heterogeneous catalyst, composition of Ag and Au NPs which has been produced through the photo-reduction process deposited on the surface of TiO_2 nanofibers which were first generated by electrospinning method. Previous studies have shown that photocatalytic activities of such nanocomposites strongly depend on the content of noble metal in the final composite [20]. Indeed, we can tune the photoctalytic performance by controlling the amount of Ag to Au value. In this regard, composites with various Ag an Au contents have been synthesized and their visible-light photocatalytic activity for removal of Rh. B as a model pollutant under low-power 40 W LED lamp has been studied.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$) and gold chloride trihydrate ($HAuCl_4{\cdot}3H_2O$) were provided from Sigma. Titanium isopropoxide (TIP), ethanol (purity 99.8%) and acetic acid (purity 99.8%) were obtained from Merck and Polyvinyl pyrrolidone (PVP) with molar mass = 1,300,000 g/mol were purchased from Sigma.

2.2. Sample preparation

Ag-Au/TiO_2 nanofibers have been prepared through electrospinning method which followed by photochemical reduction process. Firstly, TiO_2 nanofibers were generated via a facile electrospinning technique at ambient conditions as we have reported in our previous work [24]. In our home-made set up which was placed vertically, electrospinning solution involving 0.45 g PVP, 10 ml ethanol, 3 ml acetic acid and 1.5 ml TIP which were magnetically stirred at room temperature has been transferred to a syringe pump (Ascor AP 22) followed by spinning and calcination at 500 °C for 2 h. In order to incorporate Ag and Au into the TiO_2 matrix and fabrication of Ag-Au/TiO_2 composites, a given contents of silver precursor (aqueous solution of $AgNO_3$ with concentration of 100 mg/l) added to the solution containing 100 mg powder of electrospun TiO_2 nanofibers which were dissolved in 15 ml ethanol and then irradiated by UV lamp for 1 h. This procedure was followed by introduction of gold precursor (aqueous solution of $HAuCl_4{\cdot}3H_2O$ with concentration of 100 mg/l) to the mixture under UV illumination for another 1 h. Different Ag-Au/TiO_2 heterostructures with various Ag and Au contents were synthesized by controlling the molar ratio of total (Ag + Au) to the TiO_2 in the final solution.Whereas in all samples the mentioned molar ratio was fixed to 1%, the various Ag-Au/TiO_2 composites were obtained through adjusting the utilized portion of $AgNO_3$ to $HAuCl_4$ in the resulting composites. Accordingly, samples with varied Ag/Au ratio of 1:4, 2:3, 3:2 and 4:1 were prepared which named S1,S2, S3 and S4, respectively (the pristine TiO_2 was named S0). Subsequently, the composite mixture was centrifuged with ethanol for more than 2 times and dried at 60 °C in air. The whole procedure for fabrication of Ag-Au/TiO_2 composite is illustrated in Fig. 1.

2.3. Characterization

The fabricated nanostructures have been characterized by various techniques. FESEM and EDS analysis were done using a MIRA3TESCAN-XMU instrument at 5–20 kV accelerating voltage by fixing the powder on the Al substrate. TEM analysis was performed by a Philips EM208 instrument at 50–200 kV accelerating energy by deposition of the obtained Ag-Au/TiO_2 nanofibers on a copper grid at room temperature. Crystalline phase and structure of the samples were obtained by XRD diffractometer (Advance Bruker 8D) with wavelength of Cu K_α radiation in 2θ range from 10° to 80° by 0.04° s^{-1} steps. FTIR analysis was performed through a Thermo Nicolet IS 10 spectroscope in the range of 500–4000 cm^{-1} using KBr powder. UV–vis spectroscopy of the samples was taken out by a double beam Optizen POP spectrophotometer (Mecasys Company, Korea) from 200 nm to 1000 nm with a step of 1 nm. Deionized water (DI water) was obtained by New Human Power I water purification system with 18.3 MΩ-cm (0.055 mS) resistivity.

2.4. Photocatalytic test

In order to evaluate the efficiency of visible-light induced