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ORIGINAL ARTICLE

Photocatalytic deposition of Ag nanoparticles on TiO_2: Metal precursor effect on the structural and photoactivity properties

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Abstract A series of 1 wt.% Ag–TiO_2 photocatalysts were obtained by photodeposition using different organic (acetylacetonate, Ag-A) and inorganic (nitrate, Ag-N, and perchlorate, Ag-C) silver precursors in order to determinate the influence of the silver precursor on final properties of the photocatalysts. The resulting photocatalytic materials were characterized by different techniques (UV–Vis DRS, TEM/HRTEM and XPS) and their photocatalytic activity was evaluated in the degradation of rhodamine B (used as model pollutant) in aqueous solution under simulated solar light. The photocatalytic reduction of Ag species to Ag^0 on TiO_2 was higher with silver nitrate as precursor compared to acetylacetonate or perchlorate. All the Ag-modified TiO_2 photocatalysts exhibited a surface plasmon resonance effect in the visible region (400–530 nm) indicating different metal particle sizes depending on the Ag precursor used in their synthesis. A higher photocatalytic activity was obtained with all the Ag/TiO_2 samples compared with non-modified TiO_2. The descending order of photocatalytic activity was as follows: Ag-A/TiO_2 ≈ Ag-N/TiO_2 > Ag-C/TiO_2 > TiO_2-P25. The enhanced photoactivity was attributed to the presence of different amounts Ag^0 nanoparticles homogeneously distributed on Ag_2O and TiO_2, trapping the photogenerated electrons and avoiding charge recombination.

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1. Introduction

In recent years, noble metal nanoparticles (e.g. Ag, Au, Cu) have received much attention for new applications in biotechnology, catalysis, electronics, environmental and optics [1–9]. For instance, silver nanoparticles have been investigated in fields such as high-density information storage, photoluminescence and electroluminescence devices, surface-enhanced Raman scattering, heterogeneous catalysis, photocatalysis and disinfection [10–14]. In heterogeneous catalysis, supported silver catalysts have been successfully used at industrial scale for the oxidation of methanol to formaldehyde and ethylene to ethylene oxide [15].

Lately, Ag-doped semiconductor nanoparticles have had much interest in photocatalysis (i.e. degradation of organic pollutants, hydrogen production, CO_2 photoreduction, disinfection), in order to improve the photoconversion yield and allow the extension of the light absorption of wide band gap semiconductors to the visible light [4,11,16–19]. As it is well-known, Ag nanoparticles can trap the excited electrons from titanium dioxide and leave the holes for the degradation reaction of organic pollutants, improving the charge carrier separation [20]. On the other hand, silver nanoparticles can absorb visible light due to localized surface plasmon resonance [21], extending their wavelength response toward the visible region, leading to new applications such as antibacterial textiles, engineering materials, medical devices, food preparation surfaces, air conditioning filters and coated sanitary wares [22].

Concerning the photoactivity of Ag^0/Ag_2O deposited on TiO_2, it has been proposed that the photoexcitation of Ag_2O rather than Ag^0 acts as active sites responsible for the enhanced photocatalytic activity, whereas Ag^0 might contribute to the stability [23]. Also worth mentioning is that the p-Ag_2O/n-TiO_2 nanoheterojunction has shown a significant improved photocatalytic activity under UV–Vis irradiation explained in terms of a better charge separation [24]. Recently, it has been shown that a heterostructure type Ag–Ag_2O/TiO_2, synthesized by a simple electrochemical method, resulted in a high active and stable photocatalyst under visible light, following a Z-scheme charge transfer mechanism [25].

The investigation of the relationship between the synthesis process parameters on the size and morphology of the nanoparticles, which is connected to its optical and electronic properties, has led to a large number of preparation methods [10,11]. In a recent review concerning the synthesis and applications of silver nanoparticles, it has been reported that most synthesis processes produce spherical Ag nanoparticles with less than 20 nm of diameter; they are often synthesized via reduction of $AgNO_3$ dissolved in water and using reducing agents such as $NaBH_4$, among other compounds [26].

In particular, the photochemical and photocatalytic reductions have been studied extensively since the decade of the 80s, and they are considered as efficient ways to synthesize nanoparticles directly on semiconductor supports [27]. The photocatalytic deposition is carried out in the presence of metal ions, semiconductor support and hole scavengers. After irradiation, the photogenerated electrons reduce the surface-adsorbed metal ions forming metal clusters, and then, Ag nanoparticles via a repeated reduction process [27]. We recently synthesized Ag/TiO_2 composites by photocatalytic deposition that exhibit strong absorption centered at 420 nm with Ag nanoparticles (around 6–20 nm) uniformly deposited on the semiconductor [10]. As mentioned above, $AgNO_3$ dissolved in water is the most common salt precursor used in the synthesis of Ag/TiO_2 composites, even in the photochemical routes. Therefore, the present research was focused to the synthesis of Ag/TiO_2 composites by photocatalytic deposition employing different organic (acetylacetonate) and inorganic (nitrate and perchlorate) silver precursors. The effect of silver precursor on structural characteristics and photoactivity under simulated solar light was mainly studied.

2. Experimental section

Silver nitrate (Ag-N Fermont 99%), silver perchlorate (Ag-C, Sigma–Aldrich 97%) and silver acetylacetonate (Ag-A, Sigma Aldrich, 98%) were used as silver precursors. Ethanol (absolute, Fermont) was used as solvent and commercial TiO_2 (TiO_2-P25, Evonik) was used as support. The supported Ag nanoparticles were obtained using the photocatalytic route as follows: an ethanolic solution of Ag precursor (0.5 mM) was mixed with TiO_2-P25 in a 100 mL batch reactor and it was dispersed with ultrasonic irradiation. Then a nitrogen flow of 50 mL min^{-1} was bubbled through the slurry to purge dissolved oxygen and to achieve an inert reaction atmosphere. The batch reactor was irradiated for 4 h using a LuzChem photoreactor (model LZC-4) equipped with 14 low pressure mercury lamps (8 W, λ_{max} = 360 nm). After the irradiation time, the obtained material was washed with ethanol, separated by centrifugation and it was dried at 50 °C in a convection oven.

The characterization was carried out by UV–Vis diffuse reflectance (GBC Cintra 20), X-ray photoelectron spectroscopy (XPS, ThermoScientific K-Alpha) and structural characterization was achieved from conventional TEM and HRTEM by means of a JEOL FEG 2010 FasTem electron microscope with 1.9 Å of resolution (point to point). For TEM and HRTEM studies, the samples were suspended in ethanol in order to disperse the powders then a drop of the sample was deposited on a lacey carbon copper grid as a TEM support.

The composites were tested in a model reaction such as Rhodamine B (RhB) degradation in aqueous solutions. Typically, powdered photocatalyst in the amount of 0.1 g L^{-1} was suspended in aqueous solution of 9.6 ppm of RhB. The suspension was magnetically stirred in the dark during 30 min to achieve a complete adsorption/desorption equilibrium and then it was irradiated for 60 min with a solar light simulator (Newport model 67005) equipped with a 150 W Xe lamp and a power source which allows to change the light intensity of the lamp. The light intensity was measured using a digital light meter (A.W. Sperry SLM-110) and the measured light intensity was 1.5 mW cm^{-2} (I_0) at 20 cm from the source. The reaction temperature was kept constant at 25 °C during all the experiments and aliquots of the reaction medium were periodically sampled and filtered using a PTFE membrane filter (Millipore, 0.45 μm) prior to analysis. The RhB concentration was measured employing a spectrophotometric method by using a GBC Cintra 20 spectrophotometer and following the decrease in the absorbance of RhB at 550 nm.