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Effect of silver nanoparticles on TiO_2-mediated photodegradation of Alizarin Red S

Michele L. de Souza, Paola Corio*

Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo–PO Box 26.077, 05513-970 São Paulo/SP, Brazil

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ABSTRACT

Titanium oxide (TiO_2) is widely employed in photocatalysis and in organic solar cells despite certain efficiency shortcomings regarding the high e^-/h^+ pair recombination rate and wide E_{gap}. Wet chemistry immobilization of plasmonic Ag NPs onto commercial TiO_2 (P25) through a bifunctional linker molecule (3-mercaptopropionic acid) was employed as a strategy to overcome such shortcomings. This paper proposes the main photodegradation excitation mechanisms according to the irradiation energy source. The photodegradation of the textile dye Alizarin Red S (ARS) catalyzed by bare P25 and a P25-Ag composite was studied applying UV/visible and visible radiation. Under UV/visible radiation, the P25-Ag composite showed a 40% improvement in the photodegradation rate constant in comparison to the bare P25, a phenomenon assigned to the charge separation due to the Schottky barrier. After 180 min under visible radiation the ARS degradation was 80%, i.e. low P25 photosensitization, while the P25-Ag composite showed a 7% increase in the percentage degradation of the unsaturated compounds, which was attributed to the plasmonic local field enhancement at the TiO_2 surface.

1. Introduction

Titanium dioxide (TiO_2) has been largely employed as a photocatalyst in advanced oxidative processes (AOPs) due to its favorable environmental and economic properties (low toxicity, relatively high photocatalytic efficiency and low cost). Recent studies have revealed that the pure forms of the most common polymorphs of TiO_2 (anatase and rutile) exhibit lower photocatalytic activity than their mixtures. A mixture of approximately 80% anatase and 20% rutile has presented the best photoactivity in comparison with other fractions [1–3]. In this context, commercial TiO_2 sold as Degussa P25 (P25) presents properties which fulfill the requirements of AOPs in terms of its morphology, polymorphous fraction and surface area, and thus P25 has become a standard material in this field [1].

Semiconductor materials employed in photoconversion systems present a moderately wide energy gap between the conduction band (CB) and the valence band (VB), this separation being known as the band-gap energy (E_{gap}). The absorption of irradiation energy of certain wavelengths by a semiconductor (semiconductor excitation process) promotes electron transfer from the VB to the CB, leaving vacancies in the VB called holes. The photogenerated electron/hole (e^-/h^+) pair promotes the reduction and oxidation of species adsorbed at the surface of the semiconductor and induces oxidative degradation of species in solution through radical reactions [4]. TiO_2 is widely employed in wastewater treatment and in dye sensitized solar cells, although TiO_2 has some shortcomings such as a wide E_{gap} (approximately 3.2 eV) and high number of e^-/h^+ pair recombination events [5–7].

Only a small fraction of the sunlight that reaches the troposphere is UV radiation (3–5%), while visible radiation corresponds to approximately 40% of solar light [4]. Thus, employing TiO_2 as a photocatalyst requires the use of artificial UV sources, which increases the process costs. In addition, recombination events decrease the photocatalysis and photoconversion quantum efficiencies. In this regard, some important strategies to improve the TiO_2 efficiency must be considered: (i) extending or intensifying the TiO_2 excitation under visible irradiation; (ii) decreasing the e^-/h^+ pair recombination events [8–10].

Hybrid materials are commonly employed to extend the excitation of semiconductors toward the visible range. The photosensitization mechanism occurs through the indirect excitation under low energy radiation of colored compounds adsorbed at the surface of the semiconductor, such as dyes (Methylene Blue, Acid Orange 7), organic compounds (fullerene), and metallic complexes (ruthenium trisbipyridyl complex), [7,11,12] and the injection of electrons into the semiconductor CB [4,7,11]. If the oxidation of the adsorbed compound occurs irreversibly after the electron injection into the semiconductor CB, the radical cations generated induce further oxidation reactions with species in solution triggering their degradation [4,7,12]. In dye-sensitized solar cells, the charge of the

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* Corresponding author. Tel.: +55 11 3091 3853; fax: +55 11 3091 3890.
E-mail address: paola@iq.usp.br (P. Corio).

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absorbed compound is restored by a reversible redox pair, regenerating the hybrid material.

A semiconductor-metal nanoparticle catalyst (composite) is employed in order to promote charge separation after the direct excitation of the semiconductor under UV irradiation [9,13,14] and consequently increase the oxidation events at the TiO_2 surface positively affecting the photoinduced reactions such as photocatalysis [15,16]. At the semiconductor/metal interface a significant redistribution of charge occurs due to the overlap of the wave functions from the two sides, depending on the metal work function and semiconductor electron affinity. The formation of a depletion zone causes the bending of semiconductor VB and CB which, in an n-type semiconductor, are shifted downward in relation to the Fermi level. The transfer of the photoexcited electrons from the CB to the metal is facilitated, but the opposite scenario is prevented, forming the so-called Schottky barrier [17].

Noble metal nanoparticles (Ag, Au and Cu NPs) have distinct optical and catalytic properties which are not usually observed in the bulk metal. One of these distinct properties, the interaction of the conduction electrons at the NPs with the electromagnetic field at specific wavelengths, causes coherent electron cloud oscillations increasing the energy density at the NP surface; this phenomenon has being known as localized surface plasmon resonance (LSPR) [18]. LSPR causes the extinction of light (scattering and absorption) in the visible range, and concentrates energy at the NP surface. Thus, noble metal NPs immobilized on the semiconductor surface can either concentrate the local field energy under visible excitation through the LSPR effect or withdraw electrons from the TiO_2 CB under UV excitation due to the Schottky barrier, thereby enhancing photocatalytic or energy conversion efficiencies [10,19,20].

Successful improvements in TiO_2 photoactivity have been made regarding processes such as redox reactions, [9] water splitting [21,22] and energy conversion [23] employing such composites. Smith and Zhao studied the effect of Ag loading in TiO_2 nanorods on the photocatalytic effect of Methylene Blue under UV radiation by the charge separation effect and found the optimal concentration of 0.25 wt.% Ag. However, a low concentration, such as 0.09 wt.% Ag, presented improvement in the photocatalysis under UV radiation [24] and 0.05 wt.% Au presented good results for photoinduced hydrogen gas evolution catalyzed by Au-TiO_2 composites [10].

The most common procedures employed to immobilize metal NPs on the TiO_2 surface involve chemical reduction and photoreduction at the semiconductor surface under UV radiation [8]. Wet chemistry immobilization of CdSe nanoparticles by a bifunctional linker has shown good stability in studies on organic solar cells [25] and this approach was employed in this study to immobilize plasmonic Ag NPs on the TiO_2 surface.

The aim of this study was to develop a stable plasmonic P25-Ag composite by means of the wet chemistry immobilization of Ag NPs on the P25 surface employing a bifunctional linker, and to evaluate the plasmonic effect on its photocatalytic efficiency along with the charge separation and the P25 photosensitization. The catalytic efficiency of the P25-Ag composite is discussed in comparison to bare P25 in relation to the photocatalytic degradation of the textile dye Alizarin Red S (ARS) under UV/visible and visible radiation. ARS was employed as a proof-of-principle molecule and its degradation through the P25 photosensitization under visible excitation was also considered.

2. Experimental methods

2.1. Materials

Silver nitrate (purity >99%), 3-mercaptopropionic acid (MPA), sodium borohydride and ARS were purchased from Sigma–Aldrich, and TiO_2 P25 Aeroxide® from Degussa-Evonik. All chemicals were used without further purification. A high pressure Hg lamp 125 W Phillips HPL-N without the glass bulb was employed as the UV/visible radiation source. Museum Glass® (True Vue™) was placed between the lamp and the reaction vessel as a UV cut-off filter.

A Shimadzu UV-3101 PC spectrophotometer was used to monitor the decay in the ARS absorbance bands (260 nm and 422 nm) and to characterize the photocatalysts through Diffuse Reflectance (DR) spectroscopy using integrating sphere. Raman analysis was performed on a Renishaw InVia Reflex, coupled to a Leica DM 2500 M microscope, with 632.8 nm laser He/Ne excitation and a CCD detector. Infrared spectra were obtained on an FTIR Bomem MB-100 coupled with ATR. The emission lines spectrum was acquired on a Jobin Yvon U1000 Raman spectrometer coupled to a PMT detector.

The pore volume, pore diameter and surface area of the catalysts were determined from Brunauer–Emmet–Teller (BET) adsorption isotherms obtained on a Quantachrome Instruments analyzer, model NOVA 1200e, at liquid N_2 temperature. The amount of Ag in the composite was investigated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and measurements were obtained with a Spectro Ciros CCD. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) were performed on a Philips CM 200 microscope operating at 200 kV and high-resolution TEM (HRTEM) images and EDX spectroscopy were performed on a TECNAI F20 X-Twin operating at 200 kV in order to confirm the morphology, dimensions and composition of Ag NPs in the composites. The light intensity was measured on Instruterm MRUR-202, MRUR-203 and LD-200 instruments to detect UVA, UVC and visible radiation, respectively.

2.2. Synthesis of Ag nanoparticles (Ag NPs)

The procedure applied to obtain Ag NPs was that described by Creighton et al. [26]. The reaction was carried out by the reduction of 1.0×10^{-3} mol L^{-1} aqueous $AgNO_3$ with an excess of an ice-cold aqueous solution of 2.0×10^{-3} mol L^{-1} $NaBH_4$ (1:3 v/v). The solutions were rapidly mixed with vigorous shaking in a sonicator to aid monodispersity. The Ag nanoparticle final suspension was yellow and a single sharp visible extinction band near 400 nm was observed.

2.3. P25-Ag composite synthesis (immobilization of Ag NPs on P25)

In this procedure, 87.5 mL of deionized water, 12.5 mL of Ag NPs suspension and 200 μL of 0.1 mol L^{-1} MPA/acetonitrile solution were kept under stirring in the dark for 10 h to yield MPA-capped Ag nanoparticles. Deionized water (12.5 mL) containing 0.5 g P25 was then added to this MPA-capped Ag suspension and kept under stirring for 24 h at room temperature. The resulting suspension was filtered, rinsed abundantly with deionized water to remove unbounded NPs, and dried under vacuum overnight. Finally, the orange solid (P25-Ag composite) obtained was ground in an agate mortar. The catalyst was characterized by BET, ICP-AES, TEM, and Raman and DR spectroscopies.

2.4. ARS adsorption isotherms and photocatalytic degradation measurements

Analysis to obtain the adsorption isotherms for the adsorption of ARS by P25 and P25-Ag composite, and the ARS photocatalytic degradation data was performed in an open-air glass cell connected to a thermostatic bath at $20.0 \pm 0.2\,^{\circ}C$ under vigorous stirring. Adsorption measurements were taken during 60 min of interaction with the catalysts in the dark. The ARS