

Interfacial electron transfer at TiO₂ nanostructured electrodes modified with capped gold nanoparticles: The photoelectrochemistry of water oxidation

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Abstract

We have studied the photoelectrochemical behavior of nanostructured anatase electrodes modified with gold nanoparticles stabilized either with citrate (Au_{cit}) or with tetraoctylammonium bromide (Au_{TOAB}). An increase both in photocurrent and in photopotential was observed in 0.05 M NaOH upon modification with Au_{TOAB}. This behavior is attributed to an efficient hole consumption at the gold nanoparticles, which implies an effective hole transport to them from the TiO₂ nanostructure, probably facilitated by the capping agent. Once in the Au particles, the holes would promote an oxidation process (O₂ generation), which requires that the Au nanoparticles attain a high enough local electrode potential. This is possible as long as the Au_{TOAB} nanoparticles may behave as nanocapacitors with a very low capacity (ca. 1 aF) and thus the accumulation of a few holes may induce important changes in their potential. In acidic medium or in the presence of 0.1 M CH₃OH no enhancement was detected. In the case of TiO₂ modified with Au_{cit}, no increase of the photoelectrochemical response was observed in any case. It is suggested that a proper design of the metal/semiconductor nanojunctions may lead to an enhanced charge separation and to the eventual development of photoinduced metal electrocatalysis.

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1. Introduction

Heterogeneous photocatalysis based on TiO₂ particles is one of the most promising advanced oxidation processes for environmental applications [1,2]. However, it is noteworthy that the efficiency of the photooxidation process is limited by several factors, such as a low electron transfer rate to oxygen or a high electron-hole recombination rate [1]. In a number of reports, the deposition of small amounts of metal at the semiconductor (SC) surface has been proposed as an effective method to increase the quantum yield [3–10]. The deposited metal islands may act as

catalysts for either cathodic [5,11,12] or anodic processes [6,7], or both. Photoelectrochemical experiments can be advantageously applied to elucidate the role of metal nanoparticles in the electrode/solution interfacial charge transfer because they provide direct information on the photoinduced charge separation and the subsequent reaction rates.

The modification of TiO₂ nanostructured electrodes with gold nanoparticles has been reported previously. Kamat and co-workers [16–19] observed an increase in the photocurrent and a shift in the apparent flat band potential for TiO₂ electrodes upon deposition of tetraoctylammonium bromide (TOAB) capped gold nanoparticles (Au_{TOAB}). Nevertheless, only a 10–15% increase in the photocatalytic oxidation of Acid Orange 7 was obtained with these films [14]. Similarly, Currao et al. [15] reported

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a very stable enhanced photocurrent, when AgCl electrodes were modified with Au colloids.

Kamat and co-workers [16–19] also studied the behavior of the Au/TiO₂ nanojunctions in the form of suspensions. They observed that electrons accumulate in the metal nanoparticles under illumination of a deaerated dispersion in 50:50 (v/v%) ethanol–toluene [16,18]. Such charge accumulation led to a shift of the Fermi level (E_F), which could be measured.

This work aims at unraveling the different photoinduced charge transfer processes occurring at metal/SC nanocomposite electrodes. Naked and gold-modified nanostructured anatase electrodes have been tested in different electrolytes to acquire information on such charge separation processes. A kinetic model is proposed to understand the different roles that metal nanoparticles can play in the photoelectrochemical behavior of nanostructured SC matrices.

2. Experimental

All chemicals: HClO₄, NaOH, methanol and toluene from Merck, HAuCl₄ (Alfa Aesar) and TOAB (Fluka), were used as received. All solutions were prepared using Millipore Elix3 water.

Nanoporous thin film electrodes were prepared from an aqueous slurry (0.6 g ml⁻¹) of commercial anatase nanoparticles (Alfa Aesar; APS 32 nm). A volume of 10 μl of this slurry was spread (doctor-blade) over 1.5 cm² of a F:SnO₂ transparent conducting glass plate (U-type Asahi Glass Co). The TiO₂ films, 2.5–3-μm thick, were annealed in air at 450 °C for 1 h.

The gold nanoparticles were prepared as an aqueous colloidal gold dispersion stabilized with citrate (denoted as Au “Seed Colloid” solution in [20]), or as a toluene colloidal dispersion stabilized with TOAB [21].

TiO₂ modification with Au_{TOAB} was achieved through immersion of the sintered anatase films in the gold dispersion for 20 min. The films were then allowed to dry in air. The deposition of citrate-stabilized Au particles (Au_{cit}) was performed in a three-electrode conventional electrochemical setup. A potential of 2.5 V (vs. Au electrode in the same Au_{cit} dispersion) was applied for 1 h to an anatase electrode immersed in the Au_{cit} dispersion, using a platinum wire as counterelectrode.

The photoelectrochemical measurements were performed in a 3-electrode cell, equipped with a fused silica window using a Wenking POS2 potentiostat. The illumination was performed from the electrolyte-side with the full output of a Xe arc lamp (Bausch & Lomb 150 W). Light intensity was measured with an optical power meter (Oriol model 70310) equipped with a thermopile head (Ophir Optronics 71964).

UV–Vis absorption spectroscopy experiments were performed using a spectrophotometer (UV-2401 PC Shimadzu) equipped with an integrating sphere (ISR-240A, Shimadzu). Transmission electron microscope (TEM)

images were taken using a Jeol microscope model JEM 2010.

3. Results

Fig. 1 shows absorbance spectra recorded for TiO₂ nanostructured films modified with Au nanoparticles from both colloidal dispersions. For the TiO₂ sample modified with Au_{TOAB} (Fig. 1(a)), an absorption peak can be observed at around 527 nm, corresponding to the surface plasmon band of gold [13,22]. As expected, increasing the adsorption time leads to a progressively growing absorption in the visible as more gold gets deposited. In the case of Au_{cit}-modified TiO₂ thin films (Fig. 1(b)), upon gold adsorption, the spectrum is characterized by a featureless increase of the absorbance in the whole visible region. This broadness can be attributed to the fact that the Au_{cit} nanoparticles are embedded in the SC matrix. Incidentally, Lee et al. [23] have observed that a strong interaction between the gold nanoparticles and the surrounding TiO₂ induces broader absorption peaks. However, this broadening can also be associated to aggregation processes during nanoparticle electrodeposition [22]. In the case of Au_{TOAB}, the

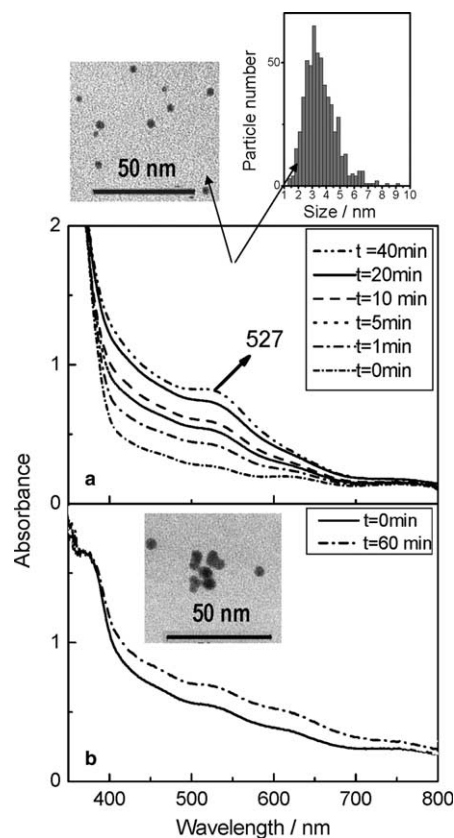


Fig. 1. Absorption spectra for : (a) a TiO₂ film after immersion in a Au_{TOAB} colloidal dispersion for different times; (b) a TiO₂ film before and after 1 h electrodeposition in a Au_{cit} dispersion. Insets: TEM images for Au_{TOAB} and Au_{cit}. The Au_{TOAB} size distribution histogram is also shown ($N = 568$ particles).

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