**On the role of Au nanoparticles in hybrid TiO2 structures for photoelectrocatalytic processes**

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**Highlights**

* Photoelectrocatalytic performances of hybrid TiO2/Au structures are tested
* Different distribution of Au clusters is performed at the TiO2 interface
* The role of Au NP in the working mechanism of the whole structure is investigated

**1. Introduction**

The paper examines and discusses the behavior of hybrid 3D TiO2 electrodes, modified with Au nanoparticles (NP), useful as photoanodes for the oxidation of organic compounds from aqueous solution. In such a process H2 evolution is always the concomitant cathodic reaction, while photogenerated holes are responsible for the oxidation of the organic compound, which may occur either by direct reaction at the active sites of the photoanode, or mediated by OH radicals, generated by the water splitting. In this context, high surface to volume ratios are generally mandatory, being the reactions involved heterogeneous: nano or meso porous structures are commonly used to this aim [1,2]. However, increase of the surface area may not be sufficient to obtain effective catalysts. Actually, the intrinsic characteristics of the semiconductor (SC) cannot be neglected: the structure crystallinity (anatase, rutile or amorphous), as well as the possible presence of defects, which may constitute recombination centers for the photogenerated charges, are of crucial importance to determine the real effectiveness of the SC.

Further considerations are needed when the SC has to be used with solar light. Due to the large band gap, TiO2 is not suitable in all the wavelength range. In this case, the presence of dopant, or the use of hybrid structures, in combination with another SC with narrow band gap, can allow exploiting the low energetic wavelengths.

Finally, the inclusion of noble metal NPs, such as Ag, Au, Pt, single or alloyed, represents a possible way to enhance the ability of TiO2 to absorb light in a wider range of wavelength [1, 2] via plasmonic effects, or to favor charge carrier separation to inhibit recombination, directly contributing to the production of long-lived charges, owing to the resulting low Fermi level [3, 4, 5].

In this work the performances of samples of TiO2 with a hierarchical nanostructure, modified by Au NP, are investigated for the oxidation of bisphenol A, used as model molecule, representative of a class of organic compounds of particular concern for the human health.

**2. Methods**

Vapor phase Pulsed Laser Deposition (PLD) was used to produce nanostructured TiO2 photoanode films, while Au NP were produced by PLD or thermal evaporation. By varying the process parameters and exploiting annealing treatments, we tune Au NP size distribution and the hierarchical TiO2 nanoscale morphology. Optimized Au NPs are coupled with TiO2, involving deposition of NPs at the bottom or at the top of the TiO2 as well as co-deposition of integrated TiO2/Au-NPs assemblies [6]. Photoelectrochemical characterization of the samples was done by direct and alternate current tests: cyclic and linear sweep voltammetry, and photocurrent tests were used in d.c.; electrochemical impedance spectroscopy was used to investigate the response to a.c. signal. A 300 W xenon lamp equipped with air mass (AM) 0 and 1.5 D filters was used to simulate the solar radiation.

**3. Results and discussion**

The performances of the different samples are investigated, in terms of voltammetric behavior, photocurrent transients, impedance spectroscopy (EIS) responses, in order to understand the working mechanism of the hybrid structures, during electrolysis carried out in supporting electrolyte or in the presence of organic compound, in the dark or under simulated solar light irradiation.

In these conditions the different active centers of the structure play different roles: TiO2, which always represents the majority component of the hybrid structure, is active for the narrow range of UV light, while Au NP, which constitute the minority component, is fundamental to exploit the Vis range where TiO2 cannot act. The right combination of the two components is crucial to achieve good performance, in the examined conditions.

**4. Conclusions**

The results demonstrated that the effectiveness of the samples is connected to both the load and the dispersion of the Au NP with respect to TiO2. An optimal metal loading has to be individuated in order to guarantee that the Au nanoclusters do not cover all the TiO2 interface, so that the charge transfer between electrode and electrolyte is not hindered.

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