

Sensitization of TiO₂ nanostructures with Coumarin 343S. Palmas^{a,*}, A. Da Pozzo^a, M. Mascia^a, A. Vacca^a, P.C. Ricci^b^a Dipartimento di Ingegneria Meccanica Chimica e dei Materiali, Università di Cagliari, Via Marengo 2, 09123 Cagliari, Italy^b Dipartimento di Fisica, Università di Cagliari, s.p. n 8 Km 0.700, 09042 Monserrato, Cagliari, Italy

H I G H L I G H T S

- ▶ TiO₂ nanotubes electrochemically functionalized with diazonium salt are investigated.
- ▶ Subsequent sensitization with Coumarin is proposed.
- ▶ Photocatalytic properties of the obtained samples, used as photoanodes, are compared.
- ▶ Functionalization with diazonium allows itself an enhancement of the current yield.
- ▶ The presence of the adsorbed dye further increases the performance of the sample.

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In this work the synthesis of hybrid electrodes obtained by electrochemical functionalization of nanotubular TiO₂ arrays with diazonium salt and subsequent sensitization with Coumarin is proposed. Nanotubes are grown by electrochemical anodization of Ti foils. Anodization is performed at 35 V in ethylene glycol solution and in the presence of fluoride ions. The results obtained in the present study indicate that the functionalization with diazonium allows itself an enhancement of the current yield of the water electrosplitting process. Photocurrents further increased after the sensitization of the samples with Coumarin dye, so indicating good chances for possible applications of the electrodes in DSSC.

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1. Introduction

Due to their useful semiconducting and photo-catalytic properties, TiO₂ nanostructures can be exploited in several technological fields as sensors, membranes, photocatalysis and solar cells. Such characteristics as cheapness, nontoxicity and great availability, make TiO₂ one of the most investigated compounds in semiconductor material science. In this work we present the results of an experimental study devoted to the preparation of nanostructured electrodes based on TiO₂ efficient in the near-Vis range of wavelengths, which may be exploited in a photo-electrochemical cell (PEC) for the water electrosplitting process. It is also in the aim of the work to derive useful information for a possible use of the electrodes as anodes in a dye-sensitized solar cell (DSSC) for energy production from solar light radiation. Actually, photocatalytic water splitting and DSSC definitely benefit from titania processed at the nanometer scale [1]. The large surface area provided by nanostructured morphology is necessary to assure an optimal light

harvesting that is one of the critical factors determining the efficiency of the photocatalytic processes [2]. Moreover, high surface area is needed to guarantee a high dye loading, when possible applications in the field of DSSCs are considered. In a conventional particulated photoanode based on nanostructured TiO₂ the considerably large surface area of nanoparticles ensures a high dye loading for light harvesting, but the injected photoelectrons in TiO₂ proceed via a random walk which can lead to a reduction in electron collection efficiency [2–5]. To overcome this issue one-dimensional nanostructures, such as those of nanotubes (NTs) may be used: a good electron transfer in the electrode structure, favours a rapid collection of the charges, keeps the electrons away from the solution interface so avoiding their recombination with the excited dye [6–8]. However, depending on the operative conditions adopted in the NT synthesis, the morphology of the resulting nanostructure may be more or less favourable to light scattering, so that further modifications could be needed to increase the light harvesting efficiency [2,9].

Among the possible routes to synthesize nanotubular structures, electrochemical oxidation presents some advantages, mainly connected to the possibility of a direct growing of nanotubes on

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