



The influence of alizarin and fluorescein on the photoactivity of Ni, Pt and Ru-doped TiO₂ layers

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ARTICLE INFO

Article history:

Received 6 June 2012

Received in revised form 3 December 2012

Accepted 6 January 2013

Available online 19 January 2013

Keywords:

Titanium dioxide

Metal dopants

Alizarin

Fluorescein

ABSTRACT

The doping with different metal ions and sensitization with organic compounds are two well known methods used to improve the photoactivity of TiO₂. In this respect, the metallic ions-doped TiO₂ samples were prepared by embedding Ni, Pt and Ru ions into TiO₂ crystalline network and then, each sample was sensitized with alizarin and fluorescein dyes. The qualitative evaluation of prepared TiO₂-based materials was made by: UV-vis spectroscopy, spectrofluorimetry, FT/IR spectroscopy and microscopy, X-ray diffraction and N₂ physisorption measurements. The optoelectronic properties investigated by UV-vis spectroscopy show that the optical response of Ni-doped TiO₂ layer shifts to visible. The X-ray spectra do not show peaks of nickel, platinum and ruthenium oxide crystals or pure metals. The FT/IR spectra proved the presence of dye molecules adsorbed on titania nanoparticles surface. These results demonstrated that the studied dopants and dyes have potential to promote modified TiO₂-based materials as good candidates to be used in photoelectrocatalytic processes.

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1. Introduction

Titania (TiO₂) is a semiconductor material that can be activated only in UV field of solar spectrum; this process is dictated by the energy width of the band gap (3.00–3.2 eV) [1–4].

In the last decades, many scientific studies were focused on the extending of titanium dioxide spectral response in visible region. Thus, different strategies were developed in order to enhance the TiO₂ photoactivity. One of them refers to doping with various metals (Pt, Ag, Au, Gd, Fe, Zn, Zr, Nd, Co, Ni, Cu, Cr, Ru, W, Sn, Eu) [5–10] or non metals (N, S, C, P, B, Cl, Br) [4,5,7,8]. Another efficient method to improve the spectral response of titania is the surface sensitization with various organic compounds having photocatalytic potential, such as porphyrins [11,12], phthalocyanines, coordination compounds of transitional metals (*ruthenium polypyridil complexes*, Ru(bpy)₃²⁺), dyes based on cyanine, xanthenes, cumarines [10,13], natural dyes extracted from fruits, flowers or leaves (cyanine, anthocyanins, tannin, chlorophyll) [14,15] or from insects (carminic acid) [16]. The association of TiO₂ with other semiconductors (CdS, SnO₂, WO₃, ZnO, Nb₂O₅, Fe₂O₃, SnO₂, CeO₂, Cr₂O₃, WO₃, V₂O₅, MoO₃ etc.) is also, considered a good way to increase its photoactivity [17–20].

In this experimental research, the contribution of Ni, Pt and Ru dopant ions as well as the influence of alizarin and fluorescein

as sensitizers on TiO₂-based layers were evaluated. In the TiO₂ host network, Ti ions are substituted by Ni ions, these ones being considered as acceptors of electrons in the TiO₂ layer [21–23]. The platinum ions produce the highest Schottky barrier among the metals, and thus facilitate the capture of photoexcited electrons. They migrate to metal and, by blocking them, the separation of charges has a longer lifetime and probability of electron-hole recombination is suppressed [6,8,24]. The ruthenium ions can introduce intermediate energy levels into TiO₂ band gap [8]. Supplementary, the role of alizarin and fluorescein as sensitizer of TiO₂-based materials doped with Ni, Pt and Ru was investigated. Alizarin (1,2-dihydroxy-9,10-anthraquinone) (Fig. 1a) is a natural dye with a distinctive red colour; it is a polyphenolic compound originally extracted from the madder root (*Rubia tinctorum*), herb of the spontaneous flora, found mainly on the hills vineyard. This natural pigment belongs to anthraquinones class involved in pharmacology, biochemistry, textiles and dyes industries. Fluorescein or resorcinolphthalein (Fig. 1b) is a poly-functional heterocycle, an orange-red organic compound that exhibits intense fluorescence. It has applications in biomedical field as a marker, oceanography as a tracer, and textiles as a dye.

Alizarin molecules are attached to TiO₂ surface through the interaction of oxygen electron pair from –OH groups with *d* orbitals of the Ti atoms (Fig. 2a). The stable geometry, corresponding to a bidentate structure, forms two chemical bonds with the same titanium atom by loss of a H₂O molecule from TiO₂ saturated surface [25–27]. Fluorescein molecules are chemical adsorbed onto TiO₂ surface either through their –COOH group [26] forming the ester,

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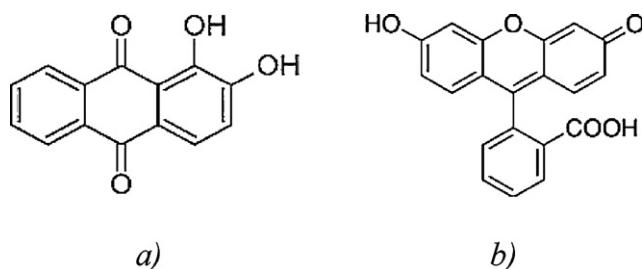


Fig. 1. Structural formula of: (a) alizarin, and respectively (b) fluorescein.

in bridge or chelating type bonds [28] (Fig. 2b), or through their functional hydroxyl groups.

As modifying methods of semiconductors surface using photoactive compounds (e.g. dyes), the sensitizing processes are based on interfacial electronic transfer from the dye molecule to the semiconductor oxide. Under the solar radiation action, the photons can cause the electrons transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the dye molecule, and thus electron-hole pairs were generated. The ground energy level is located into the semiconductor band gap and the resulting electronic excited state is resonant with the conduction band of the semiconductor. The more negative potential of sensitizers in excited state compared to the potential of semiconductor conduction band enables the ultrafast electron transfer (of femtoseconds order). As a result of electron transfer process, the dye cations appear. All the engendered active species induce a photocatalytic activity under light irradiation [25,26,29,30].

2. Experimental details

The TiO₂-based materials were produced by wet chemical route. As starting chemicals were used: P25 TiO₂ commercial powder (Degussa AG, Germany), methylcellulose (Serva, Germany), acetylacetone (Merck, Germany) and Triton X-100 (Fluka, Switzerland). Titania powder (5 g) was dispersed into 4 ml bi-distilled water, adding then 1.2 ml mixture of acetylacetone:Triton X-100 (1:2, volumetric ratio). Later, 20 ml methylcellulose 0.01% was introduced in colloidal suspension in order to obtain a better dispersion and uniformity of TiO₂ nanoparticles and to enhance the adherence onto substrates [31].

The preparation of Ni, Pt and Ru-doped TiO₂ materials required the utilization of their corresponding metal ion salt precursors, namely nickel (II) chloride hexahydrate, NiCl₂·6H₂O (Reactivul București, Romania); hexachloroplatinic acid, 8%, H₂PtCl₆ (Sigma-Aldrich, Germany) and ruthenium (III) chloride, RuCl₃ (Merck, Germany). The dopant ions concentration was 0.5 wt% Ni, Pt, Ru. The homogeneous pastes obtained by mixing the reagents with a magnetic stirrer were applied by spin-coating on ITO glass supports (sheet resistance ≤20 Ω/square). The samples were dried by lyophilization method and annealed in normal conditions at

500 °C, 2 h, with a temperature ramp of 5 °C/min in order to modify some physical, mechanical and chemical properties of materials. Finally, four TiO₂-based samples were obtained. The doping metal ion determines a specific colour of TiO₂ samples, namely: Ni²⁺ – green colour, Pt²⁺ – brown colour and Ru³⁺ – dark brown colour (TiO₂ layers have a white colour).

Each one of Ni, Pt and Ru-doped TiO₂ layers were sensitized with alizarin (A) and fluorescein (F) by dipping the layers in 2 × 10⁻⁴ M dye solutions (as solvent was used a mixture of ethanol:bi-distilled water = 1:4, volumetric ratio). The samples were held for 72 h in dye solutions, and then were dried at 28 °C. A TiO₂ undoped and non-sensitized layer was used as standard. The samples were noted as function of Ni, Pt, Ru dopants (T–Ni, T–Pt, T–Ru) and dyes: alizarin (TNi–A, TPt–A, TRu–A) and fluorescein (T–Ni–F, T–Pt–F, T–Ru–F) content.

The samples were prepared and investigated in triplicate. Due to many factors which can be involved in materials preparation, in this work we chose to study the following variables: dispersion of TiO₂ nanoparticles in colloidal suspension, uniformity of TiO₂ layer and heat treatment conditions.

All samples (TiO₂, raw dyes and doped/sensitized TiO₂-based materials) were characterized following the same experimental procedure corresponding to each method. Optoelectronic properties of all TiO₂-based layers were investigated by UV–vis spectroscopy and spectrofluorimetry. UV–vis spectroscopy was performed on a JASCO V-550 instrument. In order to obtain the spectral response of the investigated materials a corresponding reference TiO₂ layer was used. The ABL&E JASCO V 6500 with xenon lamp was used for recording spectrofluorimetry spectra. The X-ray diffraction patterns were obtained using a standard BRUKER D8 Advance X-ray powder diffractometer, in a step-scanning mode, working at 40 kV and 40 mA. The CuK_α radiation was monochromatized with a germanium monochromator placed in the incident X-ray beam. FT/IR spectra were measured on JASCO FTIR-6100 using the KBr pellet technique (1 mg sample, sample:KBr = 1:300 mass ratio). Morphological investigation of all TiO₂-based samples surface was recorded by FT/IR microscopy using JASCO IRT-3000 Irtron, in reflexion mode by scanning a large area (150 × 150 μm). Surface area and porosity data were obtained from N₂ adsorption–desorption isotherms (measured at –196 °C), using the BET model for surface determination, and Dollimore–Heal method for porosity. The isotherms were recorded using a Sorptomatic 1990 apparatus (Thermo Electron Corporation). The samples (approximately 400 mg) were degassed at 200 °C for 3 h at a pressure of 1 Pa prior determination.

3. Results and discussion

3.1. UV–vis results

Fig. 3 presents UV–vis absorption spectra of Ni, Pt and Ru-doped TiO₂ layers in comparison with the undoped TiO₂ layer spectrum, recorded in the field of 240–900 nm.

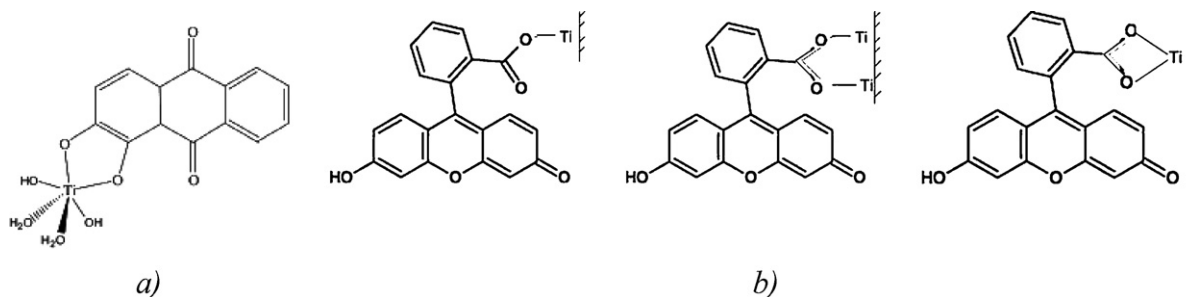


Fig. 2. Possible binding types of dye molecules onto the TiO₂ particle surface: (a) alizarin-TiO₂ [25], and respectively (b) fluorescein-TiO₂.

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