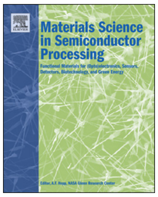
Materials Science in Semiconductor Processing 16 (2013) 1551–1557

Contents lists available at SciVerse ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp



Physical–chemical characterization of titanium dioxide layers sensitized with the natural dyes carmine and morin

Marcela-Corina Rosu*, Ramona-Crina Suciu, Maria Mihet, Ioan Bratu

National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath Street,
400293 Cluj-Napoca, Romania

ARTICLE INFO

Keywords:
Titanium dioxide
Photoactivity
Carmine
Morin
Photosensitizers

ABSTRACT

The titanium dioxide (TiO_2)-based layers sensitized with carmine and morin dyes were prepared using commercial P25 TiO_2 powder as starting material. The influence of natural colorants as natural photosensitizers on TiO_2 photoactivity was discussed from the point of view of UV–VIS and Fourier transform infra-red (FTIR) spectroscopy, fluorescence analysis, microscopy, X-ray diffraction and nitrogen adsorption-desorption isotherms determination. A shift to visible region of the sensitized TiO_2 layers is observed. The decrease of sensitized TiO_2 band gap improves its photoactivity in the visible domain. The fluorescence quenching of TiO_2 sensitized with carmine is correlated with better adsorption of the dye molecules to the TiO_2 surface and with electron injection process, also. The FTIR absorption spectra of samples proved the presence of dye molecules on TiO_2 nanoparticles surface. Thus, the investigated sensitized TiO_2-based layers could have potential in photoelectrochemical applications.

1. Introduction

Titanium dioxide (TiO_2) is a metal oxide semiconductors used in paints, plastics, textiles, foods, pharmaceuticals and cosmetics industries due to its well-known physical and chemical characteristics [1–3]. Also, TiO_2 is employed in other numerous and various applications in the field of electronics (diodes or transistors) [4], optical devices (light-emitting diodes [5,6], photodetectors [7,8], solar cells [9]), biomedical sensors [10,11], cancer cells inactivation [12,13], antimicrobial activity [14–17], orthopaedic and dental implants [18,19]), water/air purification (photo-catalytic degradation of organic dyes [20], asphalt pavements [21], construction materials [22], self-cleaning materials [23], decontamination and disinfection materials [24]), gas sensors (H_2 [25], O_2 [26], CO [27], NO_2 [28], NH_3 [29]), hydrogen storage [30,31] etc.

TiO_2 is an n-type semiconductor due to oxygen vacancies [1], with a wide band gap (3.0–3.2 eV), thus it becomes active only under UV irradiation [1,32]. In order to improve the absorption efficiency of titania in the visible region of solar spectrum, several aspects of the solid-state structure must be modified. However, these TiO_2 modification processes impact properties (crystal structure, particle size and shape, surface morphology and chemistry) that are in a strong correlation with TiO_2 photocatalytic activity [2]. To this end, a number of methods have been developed such as coupling with other semiconductors, embedding of metals/nonmetals ions in TiO_2 lattice, or surface sensitization of nanoparticles with photosensitive organic compounds [1,33,34]. Dye sensitization involves the adsorption of dye molecules onto TiO_2 particles surface through physical or chemical interactions [35,36]. The interfacial electron transfer at dye-TiO_2 interface takes place and leads to free-charge carriers due to the absorption of a photon. As a result of photoinduced processes an enhanced photoactivity of semiconductor can occur [1,9,37].

---

* Corresponding author. Tel.: +40 264 584037; fax: +40 264 420042.
E-mail address: marcela.rosu@itim-cj.ro (M.-C. Rosu).

1369-8001/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.mssp.2013.05.020

Carmine is a red pigment, a complex of aluminium and natural dye cochineal (carminic acid) [38] extracted from a parasitic plant belonging to the family *Coccidea* or from tropical insects body (*Dactylopius coccus*) native to Central and South America [39]. Carminic acid (7-α-D-glucopyranosyl–9,10-dihydro–3,5,6,8-tetrahydroxy–1-methyl–9,10-dioxo-anthracene carboxylic acid) is a hydroxyl anthraquinone compound with a side-chain of a glucose sugar unit attached (Fig. 1a). It is used in textiles and foods industries as a colorant and also in medicine as antiviral and antitumoral agent [39–42].

Morin (3,5,7,2′,4′-pentahydroxyflavone) is a polyphenolic compound derived from flavones (Fig. 1b). It is a yellow pigment that can be extracted from mulberry, fig and other Oriental medicinal plants belongi to *Moracee* family and also from almond hulls and old fustic (*Chlorophora tinctoria*) [43–46]. Morin is a flavonoid that possesses a wide range of bioactivities and is often employed as anti-inflammatory, antioxidant, anti-neoplasic and cardiovascular protector agent [43,44,47].

The aim of this experimental research is to evaluate the influence of carmine or morin dyes on the optical, morphological and structural characteristics of TiO_2 in order to improve the titanium dioxide photoactivity required in photoelectrochemical applications.

2. Experimental details

2.1. Preparation of TiO_2-based layers

The titanium dioxide powder (anatase/rutile mass ratio of 4:1) was supplied from Degussa AG. Methylcellulose (Serva, Germany), acetylacetone (Merck, Germany) and Triton X-100 (Fluka, Switzerland) were used as additives. A specific amount of TiO_2 (6 g) was dispersed in a mixture of acetylacetone:Triton X-100 (2:1 volumetric ratio) and then 20 ml 0.05 wt% methylcellulose were added. The chemicals were stirred on magnetic device for several hours; the homogenous paste was deposited on conductive ITO glass supports (sheet resistance $\leq 20\ \Omega$/square) by spin-coating technique. The samples were dried by lyophilisation and then heat treated at 450 °C for 1 h. The samples have been dipped in the 2×10^{-4} M carmine (Sensient) and morin (Difco) solutions and also in a mixture of 1:1volumetric ratio of dyes solution. Methanol (Fluka, Switzerland) and double distilled H_2O (4:1 volumetric ratio) were used as solvents for dyes. The samples were kept in dye solutions for 72 h, and then were dried at 28 °C. Four samples were obtained and they are noted according to the used sensitizer, namely TC (carmine-sensitized TiO_2 layer), TM (morin-sensitized TiO_2 layer) and TCM (carmine/morin-sensitized TiO_2 layer). An unsensitized TiO_2 sample (noted T) was used as standard.

2.2. Characterization of TiO_2-based layers

The optoelectronic properties of TiO_2-based samples and dyes were performed by UV–VIS spectroscopy (JASCO V-550) and spectrofluorimetry (ABLE&JASCO V 6500). The morpho-structural TiO_2-based materials were investigated FTIR microscopy (JASCO IRT-3000 Irtron) and spectroscopy (JASCO FT/IR-6100). The physical properties of the prepared TiO_2-based materials were compared with that of the commercial P25 titanium dioxide by recording the nitrogen adsorption-desorption isotherms at −196 °C with a Sorptomatic 1990 apparatus (Thermo Electron).

3. Results and discussion

3.1. UV–VIS results

The UV–VIS spectra of dye solutions in methanol are presented in Fig. 2. The absorption spectrum of carmine shows characteristic peaks at 281 nm, 332 nm, 515 nm and 553 nm due to π–π^* electronic transitions that can be attributed to conjugated double bonds, with a shift to longer wavelengths, similar with those of carminic acid [39,41]. The coexistence of four different geometric states of carminic acid determines the presence of the same number of absorption peaks. Carminic acid is a polyprotic acid due to carboxyl group (–COOH) and also, the hydroxyl groups (–OH) from 3, 5, 6 and 8 positions of antraquinone rings that are susceptible to the loss of proton. So, carminic acid is expected to appear in the methanol/H_2O solution, both in the protonated state (CA) and in the deprotonated states (CA^-, CA^{2-} and CA^{3-}); water forms strong H bonds with oxo and hydroxyl groups from carminic acid molecule [48–50].

The UV–VIS spectrum of morin in methanol is mainly formed by two absorption peaks due to π–π^* electronic transitions: band I (275 nm) attributed to light absorption

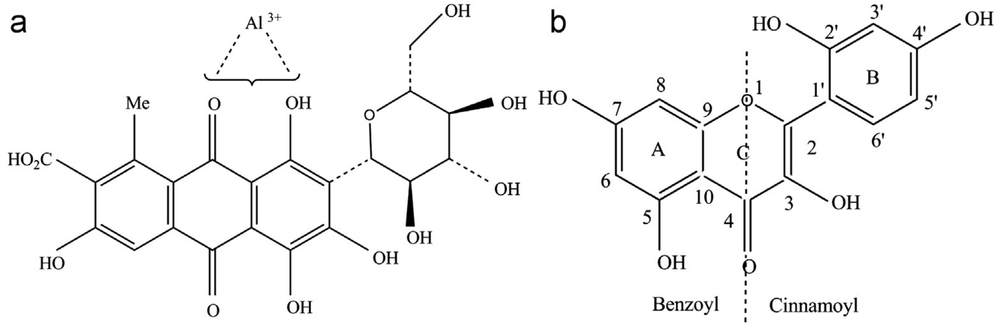


Fig. 1. Structural formula of dyes: (a) carmine [39] and (b) morin [43].