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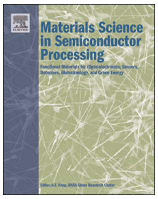

Photosensitization of titanium dioxide with 4′-dimethylaminoflavonol

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ABSTRACT

The paper focuses on spectral properties of 4′-dimethylaminoflavonol (DMAF) in the presence of colloidal titanium dioxide (q-TiO_2). The influence of q-TiO_2 on absorption and fluorescence properties of DMAF (spectral changes, fluorescence quenching, increase of the fluorescence lifetimes) confirms the photosensitization effect, observed also as visible light induced photocurrents. Interestingly, an efficient photosensitization of titanium dioxide was observed also in TiO_2-based systems with the surface modified with hydrophobic silyl groups or fluoride anions. Quenching of fluorescence of DMAF and DMAF@TiO_2 by oxygen points at the generation of reactive oxygen species, indispensable in the process of organic pollutants degradation.

1. Introduction

Photosensitization of wide band-gap semiconductors is still in focus of research in the field of photocatalysis and photovoltaics. Various approaches to extend the spectral response of semiconducting photomaterials are under a continuous development. One of them involves doping wide band-gap semiconductors (*e.g.* titanium dioxide) with various metal ions or non-metal dopants [1–4]. Another way of titanium dioxide sensitization encompasses application of dyes [5–8], including the systems photosensitized according to the photoinduced electron transfer (PET) and optical electron transfer (OET) mechanisms [9]. In the PET mechanism the photon absorption by the adsorbed dye generates its excited state capable of an electron injection into the conduction band (or, alternatively, a hole injection into the valence band). The OET process is a single step mechanism involving the ligand to metal charge transfer from the ligand coordinated to TiO_2 surface to titanium(IV) center. Formed titanium(III) is equipollent to the electron in the conduction band.

Photochemistry of organic dyes adsorbed or chemisorbed at the surface of wide band-gap semiconductors is determined by several possible pathways of excited states deactivation. The electron transfer from the excited dye to the conduction band of TiO_2 is a desirable key step of a semiconductor photosensitization which opens a possibility to use such hybrid systems as photocatalytic, photovoltaic or optoelectronic materials. The goal of this research was to search for hybrid photomaterials based on organic dyes chemisorbed at the surface of TiO_2 which could offer a visible light induced catalytic activity and/or visible light induced generation of current. Flavonols (3-hydroxy-2-phenylchromen-4-ones; Fig. 1) can be considered as possible sensitizers of titanium dioxide due to their visible light absorption and two neighboring oxygen atoms enabling coordination of the molecule to TiO_2. Flavonols are also used as fluorescent probes [10–12], photoprotective agents [13,14] and antioxidants [15]. The 3-hydroxy-2-phenylchromen-4-one derivatives exhibit the excited state intramolecular proton transfer (ESIPT) phenomenon [12,16–22], based on the intramolecular proton transfer from a proton donor (–OH) to a proton acceptor (=O) group. The proton transfer results in a zwitterion formation, possessing different spectral properties than the neutral form [12,16–22].

The studies on flavonoids as sensitizers of TiO_2 are limited to a few papers, dealing with applications of these systems in dye-sensitized solar cells [23] and photoinduced inhibition of the growth of fungi (*Helminthosporium maydis*) by the quercetin-sensitized TiO_2 film [24]. In this work we study the sensitization of TiO_2 by a representative of flavonols, 4′-dimethylaminoflavonol (DMAF). Photoelectrochemical measurements confirm the

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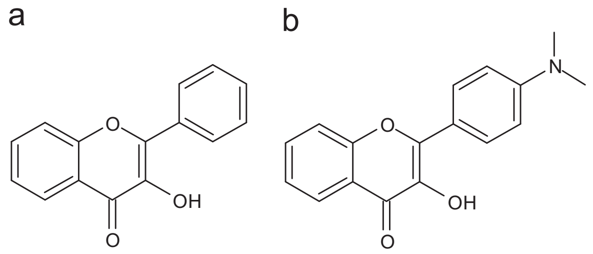

Fig. 1. (a) Flavonols (neutral form) and (b) 4′-dimethylaminoflavonol.

photoactivity of DMAF as the titanium dioxide photosensitizer, while spectroscopic studies reveal the details on the photosensitization process.

2. Experimental section

The synthesis of the 4′-dimethylaminoflavonol, based on the reaction of Algar, Flinn, and Oyamada [12,25], was performed according to the procedure described elsewhere [20].

DMAF was adsorbed at the surface of various TiO_2 materials: P25 (anatase/rutile, 50 $m^2\,g^{-1}$, Evonik), UV-100 (anatase, 300 $m^2\,g^{-1}$, Hombikat), T-805 (silylated P25; Degussa), fluorinated TiO_2 (F-TiO_2; prepared by impregnation of TH-0 (anatase, 330 $m^2\,g^{-1}$, Kerr–McGee), with an aqueous solution of KF, as described elsewhere [26]). The dye adsorption was realized in the agate mortar by impregnation of the corresponding titanium dioxide material (20 mg) with the methanolic solution of DMAF (*ca.* 2 mM, 0.2 mL). The mixture was ground and dried in the air at room temperature.

The photoactivity of the DMAF@TiO_2 systems was monitored through photocurrent measurements as a function of the electrode potential and incident light wavelength. Photocurrents were measured in a ternary electrode system consisting of the ITO working electrode with deposited DMAF@q-TiO_2 material. A platinum wire and Ag/AgCl, placed in 0.1 M KNO_3 electrolyte, served as counter and reference electrodes, respectively. The working electrode was irradiated with a monochromatic light supported by 150 W xenon lamp (XBO-150) equipped with a monochromator and a shutter (Instytut Fotonowy, Poland). The measurements were controlled by Autolab PGSTAT302N potentiostat.

Absorption spectra were recorded using UV–vis Perkin Elmer Lambda 950 spectrophotometer. Spectral properties of DMAF were studied in methanol. To study the influence of nanoparticles on spectral properties of DMAF, 2–20 μL of aqueous q-TiO_2 solution (anatase, 15 wt%, the average particle size 15 nm, Nanostructured and Amorphous Materials) were added to 5.2×10^{-3} mM methanolic solution of the dye (3 mL). Emission spectra and lifetimes of fluorescence were measured using Horiba Jobin Yvon Fluorolog-3 system. Prior to the measurement the samples were saturated with argon, oxygen or air (the appropriate gas was bubbled through the solution for 10 min).

3. Results and discussion

Synthesis of DMAF yielded a yellow, crystalline powder, well soluble both in polar and in nonpolar solvents. Due to two neighboring oxygen atoms DMAF coordinates efficiently to the surface of titanium dioxide. Absorption spectra of 4′-dimethylaminoflavonol solution recorded in methanol prior to and after the addition of q-TiO_2 are presented in Fig. 2. A significant bathochromic shift of the absorption band (from 403 to 465 nm) is observed upon addition of TiO_2. This observation points at a strong interaction between DMAF and TiO_2 lowering the excitation energy of the dye. The spectral characteristics of DMAF in methanol in the absence and presence of TiO_2 is presented in Table 1.

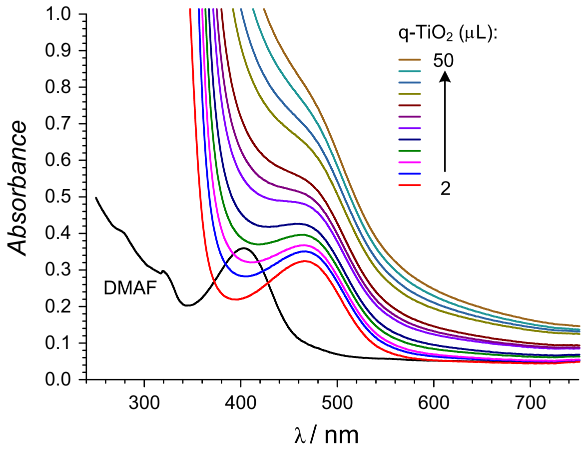

Fig. 2. DMAF spectra in methanol upon addition of aqueous solutions of q-TiO_2.

Table 1
Spectral characteristics of 4′-dimethylaminoflavonol.

Studied system	λ_{abs}		λ_{em}		Stokes shift	
	nm	eV	nm	eV	nm	eV
DMAF in CH_3OH	403	3.08	531	2.33	128	0.75
DMAF@q-TiO_2 (aq) in CH_3OH	465	2.67	544	2.28	79	0.39

λ_{abs}, λ_{em} – positions of long wavelength absorption and emission maxima.

The steady-state fluorescence spectra of DMAF were also recorded in neat methanol and upon addition of aqueous, colloidal solution of q-TiO_2 (Fig. 3). Positions of emission maxima are listed in Table 1. The fluorescence intensity of 4′-dimethylaminoflavonol is strongly quenched by q-TiO_2, while the maximum is shifted from 531 to 544 nm. Similar shifts of absorption and emission maxima of DMAF in methanol were reported by Moroz et al. [20]. The changes were attributed to complexation of the neutral form of DMAF with lithium ions. Upon addition of colloidal TiO_2 the dye adsorbs strongly at the oxide surface. The fluorescence quenching results from an efficient electron transfer from the excited dye to the conduction band of titanium dioxide. This is a fundamental step in the process of TiO_2 photosensitization. Photocurrents generated at electrodes covered with TiO_2 materials and DMAF@TiO_2 composites revealed an efficient photosensitization

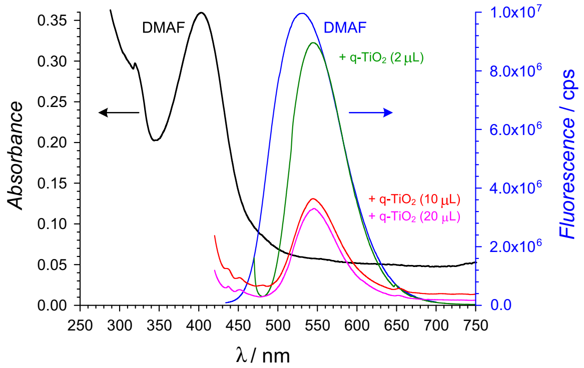

Fig. 3. Absorption (black) and fluorescence spectra of 4′-dimethylaminoflavonol in methanol (blue) and after addition of an aqueous solution of q-TiO_2 (green, red, and pink). Fluorescence spectra recorded upon excitation at 403 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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