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Polymer dye-containing nanocomposites as photocatalysts

Oksana Linnik^a and Oksana Nadtoka^b

^aChuiko Institute of Surface Chemistry, National Academy of Science of Ukraine, Kyiv, Ukraine; ^bTaras Shevchenko National University of Kyiv, Kyiv, Ukraine

ABSTRACT

A significant improvement of photocatalytic efficiency is achieved by the synthesis of TiO_2/SiO_2 nanocomposites where silica matrix provides the transport of reagents to TiO_2 nanoparticles via porous structure, generation of the new active sites and thermal stability. The semiconductive films contained 10 or 30% of TiO_2 in silica matrix are synthesized by sol-gel method using concentrated anatase titania colloid. The complex composites consisted of i) the Acridine Yellow dye molecules and the polyepoxypropyl carbazole; ii) the azobenzene containing polymer covered onto the titania/silica films are obtained as photocatalytic materials. Photocatalytic activity of the composites is tested via the reduction of dichromate ions. **KEYWORDS**

photocatalysis; semiconductivity; polyepoxypropyl carbazole; azopolymer; dyes

1. Introduction

The significance of the wastewater treatment, management and its disposal gradually increases in the modern times and it becomes a major concern for public health scientific interest. The low-cost and non-toxic semiconductor composites based on titania are perspective materials for solar energy utilization in the processes of soil and water purification as well as photovoltaic materials. Titanium dioxide (TiO₂), as an important semiconductor, has been widely investigated in the photocatalytic field, due to its abnormal chemical and physical behavior. Interaction of the semiconductor particles with quantum of light leads to the appearance of the active radicals that are able to the simultaneous oxidation and reduction reactions. In our previously works we have showed the high catalytic activity of synthesized mesoporous titania thin films in various redox processes [1]. Titania possesses optical properties at UV light trapping which are corresponded to its band energy. A significant improvement of photocatalytic efficiency is achieved by the synthesis of TiO₂/SiO₂ nanocomposites where silica matrix provides the transport of reagents to TiO₂ nanoparticles via porous structure, generation of the new active sites and improved mechanical strength, thermal stability and surface area of titania [2]. On the other hand, the high charge recombination rate in TiO_2 considerably limits its photocatalytic application [3].

In recent times, some studies have been published on the combination of conductive polymers and TiO_2 to get better performance of UV light and sunlight activities [4–7]. Among the conducting polymers polycarbazole (PCz) is attributed with good electroactivity, thermal,

CONTACT Oksana Nadtoka 🖾 oksananadtoka@ukr.net

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Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl. © 2017 Taylor & Francis Group, LLC electrical and photophysical properties [8]. The increasing interest in PCz is determined by its role as a hole-transport material and an efficient photoluminescence unit upon visible light excitation. Therefore, conjugated polymer PCz with large band gap inorganic semiconductors is used for optical, electronic, photocatalytic and photoelectric conversion applications.

Different derivatives of azobenzene show the best advantage as photoactive fragments [9]. Illumination of these materials with exciting light stimulates reversible or irreversible *transcis* isomerization of azochromophores. The role of the various excited states of azobenzene in photoisomerization reaction has attached close attention. Excitation of the *n*- π^* bands of *cis*- and *trans*- azobenzene resulted in isomerization with quantum yields of 0.70 and 0.20, respectively. However, π - π^* excitation is also accompanied by isomerization, and this state could be also involved. In the latter case, quantum yields of 0.44 and 0.10 are observed for the cis- and trans-isomers respectively [10]. To create photocatalytic semiconductor dye-polymer films the methacrylic azobenzene containing polymers were used too.

2. Experimental section

2.1. Synthesis and characterization of materials

Unless otherwise specified the reagents were obtained from Aldrich and used as received without further treatment. Carbazole (analytical grade) was used after recrystallization. Poly-(N-epoxypropyl carbazole) was synthesized by the reaction N-epoxypropyl carbazole with anhydrous N, N-dimethylformamide and further anion polymerization according to the literature [11]. Methacrylic azopolymer were synthesized by free-radical copolymerization of methacrylic azomonomer and methyl methacrylate.

Synthesis of *N*-epoxypropyl carbazole (EPC) Carbazole (0.167 g, 1 mmol), sodium methoxide (0.16 g, 3 mmol) and 23 mL of anhydrous N, N-dimethylformamide were added to a three necked flask. The solution was heated to 40°C and dropwise added epichlorohydrin (1.28 g, 13 mmol), then stirred for 1 h and was allowed to cool to room temperature. After removal of the solvent, the remaining crude product was isolated by flash chromatography (silica gel, hexane/dichloromethane: 5/1) to isolate 1 as a white solid in 53% yield. ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 8.12 (d, 2H); 7.48 (d, 4H); 7.24 (t, 2H); 4.66 (d, 1H); 4.40 (d, 1H); 3.35 (d, 1H); 2.81 (d, J = 4.0 Hz, 1H); 2.58 (t, J = 4.8 Hz, 1H).

Synthesis of poly-(N-epoxypropyl carbazole) (PEPC). Potassium hydroxide (0.0176 g, 0.3 mmol), 18-crown-6 (0.1170 g, 0.4 mmol) and 8 mL methanol were added to a flask. When the solid dissolved, 8 mL toluene was added. The mixture was heated in vacuo until the volume of the distillate became half that of the volume of the original solution. Then a new portion of toluene was added and distilled again. This procedure was repeated five times. The solution was then cooled down to room temperature and filtered. Polymerization of EPC was carried out in a flask equipped with nitrogen purge. 8 mL of the mentioned solution and EPC (0.8741 g) were added to the flask. The solution was heated at 90°C for 12 h. The resulting polymers were isolated by precipitation in hexane or in methanol and dried in vacuo at ambient temperature.

Synthesis of methacrylic azopolymer (AzoP). Copolymers of 4⁻⁻methacryloxyhexyloxy-4nitroazobenzene and methyl methacrylate were synthesized by free-radical polymerization in toluene. The polymerization was carried out in 10 wt.% toluene solution of monomer with AIBN as free radical initiator (10 wt.% of monomer) at 80°C over more than 30 hours. Polymers were isolated from the reaction solution by precipitation into excess of methanol followed by reprecipitation from toluene into methanol and then dried at 20°C overnight. The



Figure 1. Structural formulas of dye (AY), semiconductor polymer (PEPC) and Azopolymer (AzoP).

synthetic work is described in more details in a separate paper [12]. The synthesized azopolymers were characterized by ¹H NMR spectroscopy. The obtained results were in agreement with the proposed structures.

Tetraethoxysilane Si(OC₂H₅)₄, aqueous solution of hydrochloric acid, de-ionized water, Pluronic P123 (BASF) were used to prepare silica sols. To control hydrolysis-condensation reaction rates and to prevent oxides precipitation, acetylacetone was used as the complexing agent. Silica-titania films (10 and 30 wt% TiO₂) were obtained via addition of TiO₂ in anatase crystalline form (6–7 nm) [13] to SiO₂ sol. Dip-coating procedure was used for film-forming (withdrawal rate was 1.5 mm/s). The clean and dried glass substrates were used for this target. Thermal treatment of films was performed at 350°C.

Acridine Yellow (AY) $(1 \times 10-6 \text{ mol/L})$ was applied onto the films for 24 hours for adsorption. After film drying on the air, the polyepoxypropylcarbazole (PEPC) (5% PEPC in benzene) was twice covered onto adsorbed AY. The composites were left for 48 hours at the room temperature. The obtained composites are signed as x%TiO₂/SiO₂//AY//PEPC. They consist of 10 or 30 wt% of titania in silica mesoporous thin films, AY dye and PEPC layers.

Methacrylic azopolymer (AzoP) was dissolved in dichloroethane up to the final concentration of 1.5 w/w %. Obtained solution was used for dip-coating onto freshly synthesized films. The systems were dried on the air for 48 hours. The synthesized composites are signed as x%TiO₂/SiO₂//AzoP where x means the amount of titania in the silica matrix (10 or 30%). The chemical structure of used substances is presented on Figure 1.

The composite film was immersed in 40 ml of an aqueous solution of potassium dichromate (the initial concentration of dichromate ions was 2×10^{-4} M). The reducing agent (disodium salt of ethylenediaminetetraacetic acid (Na₂EDTA)) in the molar ratio 1:1 was adjusted to

2.2. Observation and measurements

 $pH \ge 2$ by perchloric acid.

The XRD spectrum of TiO₂ sol was recorded with DRON-4-07 diffractometer (CuK_{α} radiation). Calculation of apparent crystallite size for titania has been performed by Debye-Scherrer formula β (2 θ) = 0.94 $\lambda/(D\cos\theta)$, using (1 0 1) reflections employing the FWHM procedure.

Optical spectra of the composites were recorded with a double beam spectrophotometer (Lambda 35, PerkinElmer) within the wavelength range of (190–1200) nm.

The Cr(VI) ions concentration change was monitored by a Lambda 35 UV-Vis spectrophotometer (Lambda 35, PerkinElmer) every 20 min at $\lambda = 350$ nm.



Figure 2. Absorption spectra of 10% TiO₃/SiO₃//PEPC (1) and 10% TiO₃/SiO₃//AY//PEPC (2) composites.

The Brunauer–Emmett–Teller (BET) surface area and pore size distribution of the thin films were measured from hexane adsorption–desorption isotherms. Hydrophilic properties of films were estimated by measurements of water contact angle using the sessile drop method with a MIR-1 microscope (LOMO, St. Peterburg, Russia). Measurements were carried out at room temperature ($20 \pm 2^{\circ}$ C).

3. Results and discussion

In **the** applied science, the photocatalysts in the film form are more convenient (suitable) comparing to the powders due to the avoidance of the technical stage such as the sedimentation and/or ultrafiltration of the solid form from liquid phase.

Analyzing FTIR and XPS data of TiO₂, SiO₂ and TiO₂/SiO₂ we have concluded [14] that molecular scale mixing for sol–gel derived titanosilicates with formation of Ti–O–Si bonds is a key factor affecting surface properties such as level of surface hydroxylation and surface acidity as well as the catalytic function of silica–titania. Freshly prepared TiO₂/SiO₂ films showed high hydrophylic properties with the water contact angles being ca. 12 before and 5° after UV irradiation. In addition, the enhanced adsorption of AY on SiO₂/TiO₂ film (1.5–2 time higher) in comparison with that on the parent oxide: SiO₂ or TiO₂ film surfaces, coincides with high acidity, surface area and hydrophilicity of synthesized films. Thus, strong adsorption of AY on specific surface sites of SiO₂/TiO₂ films is responsible for its high efficiency of light absorption and its stability.

The semiconductor//dye//polymer composites were tested for the stability in several solvents (water, ethanol/water mixtures and pure ethanol). No penetration of AY molecules through PEPC layer in aqueous media was noted for the films with the amount of adsorbed AY. The appeared maximum at 435 nm is signed to the adsorbed AY molecules onto TiO_2/SiO_2 surface (Fig. 2).

AzoP covered onto TiO2/SiO2 films influences on the red shift in the absorption region of the composites (Fig. 3.) where two-layered films exhibit an optimum absorption shift (all reported results are related to two-layered systems only). At the same time as shown on Figure 3, no significant change in the absorption spectra is observed for the systems contained 10 and 30% of titania.

Photocatalytic activity of the films was assessed via tetracycline hydrochloride (TC) degradation and dichromate ions reduction. TC is one of the most frequently prescribed groups of antibiotics. Residues of TC and their metabolites were detected in eggs, meat and animals based on different exposure methods [15]. Their accumulation in human organism



Figure 3. Absorption spectra of cut-off-filter (bold curve), 10% TiO_2/SiO_2 (1), 30% TiO_2/SiO_2 (2), 10% $TiO_2/SiO_2//AzoP$ (3) and 30% $TiO_2/SiO_2//AzoP$ (4) films.

can produce arthropathy, nephropathy, central nervous system alterations, spermatogenesis anomalies, possible mutagenesis and photosensitivity in human beings. In turn, chromium containing ions are recognized as a pollutant derived from the chrome-plating and electronic industries.

When visible light was applied, the conversion percentage was increased slightly for 10% $TiO_2/SiO_2//AY//PEPC$ and doubled for 30% $TiO_2/SiO_2//AY//PEPC$ comparing with the AY free composites in dichromate reduction process (Fig. 4 A). The efficiency of the photocatalysts was enhanced in 2 and 4 times for 10% and 30% in $TiO_2/SiO_2//AY//PEPC$, respectively during TC destruction (Fig. 4 B). It must be noted that the AY free composites were completely



Figure 4. Photocatalytic activity of the composites tested in the reduction of dichromate ions (A and C) and degradation of TC (B and D): $1 - 10\% \text{ TiO}_2/\text{SiO}_2//\text{PEPC}$, $2 - 10\% \text{ TiO}_2/\text{SiO}_2//\text{AY}//\text{PEPC}$, $3 - 30\% \text{ TiO}_2/\text{SiO}_2//\text{PEPC}$, $4 - 30\% \text{ TiO}_2/\text{SiO}_2//\text{AY}//\text{PEPC}$.



Figure 5. The proposed mechanism of dichromate reduction (pathways 1.2, 2.1, 1.5 and 2.2) and TC destruction (pathways 1.4, 2.3, 1.3 and 2.4) under visible (blue) and UV (red) light over TiO₂/SiO₂//AY//PEPC composite.

inert under visible light (Fig. 4 A and B, columns 1 and 3). Upon visible light, the exciting of AY molecule takes place with the following charge carrier transfer from the excited (AY*) molecules to the CB of TiO₂ known as dye-sensitization process (Eq. 1, 2 and Fig. 5, pathway 1.1). Further steps should implicate the reduction of the oxidized species (AY⁺⁺) by electron donor such as EDTA or TC (Eq. 3; Fig. 5, pathways 1.3 and 1.5) and processes involving electrons from the CB as namely dichromate or oxygen reduction (Eq. 5 and 7; Fig. 5, pathways 1.2 and 1.4).

When light with energy higher than 3.2 eV interacts with titania particles, an electron transition from the valence band (VB) of semiconductor to the conduction band (CB) occurs (Eq. 4). As the photocatalytic actyvity of AY free TiO₂/SiO₂//PEPC enhances comparing with the blank experiment and depends on TiO₂ amount for both processes (Fig. 4 C, D columns 1, 3), it leads to the conclusion that the photogenerated electrons became to be trapped and/or directly move through PEPC layer to the redox couple.

Dye – sensitization process

$$AY + h\nu (\leq 3.2eV) \rightarrow AY^* + e^- \rightarrow AY^{\bullet +}$$
(1)

$$\mathrm{TiO}_{2} + \mathrm{e}^{-} \to \mathrm{Ti}^{\mathrm{IV}}\mathrm{O}_{2}/\mathrm{Ti}^{3+}\left(\mathrm{e}^{-}_{\mathrm{CB}}\right)$$

$$\tag{2}$$

$$AY^{\bullet+} + TC/EDTA \to AY + TC^{\bullet+}/EDTA^{\bullet+}$$
(3)

Direct photocatalysis

$$\operatorname{TiO}_{2} + h\nu (\geq 3.2 \mathrm{eV}) \to \operatorname{TiO}_{2} \left(\mathrm{e}_{\mathrm{CB}}^{-} + \mathrm{h}_{\mathrm{VB}}^{+} \right)$$

$$\tag{4}$$

Photocatalytic reduction of dichromateions

$$Cr_2O_7^{2-} + 14H^+ + 6e^-_{CB/trapped} \rightarrow 2Cr^{3+} + 7H_2O$$
 (5)

$$\text{RCOOH}(\text{EDTA}) + h^+_{\text{VB/trapped}} \to \text{RCOO}^{\bullet} + H^+(H_2\text{O}) \to \text{CO}_2 + R^{\bullet}$$
(6)

Photocatalytic destruction of TC

 $O_2 + e^-_{CB/trapped} \rightarrow O_2^{\bullet -} \rightarrow H_2O_2 + H^+$ (7)

$$TC + h^+_{VB/trapped} \rightarrow TC^{\bullet +} \rightarrow CO_2 + NH_3 + H_2O$$
 (8)



Figure 6. Absorption spectra of $30\% \text{ TiO}_2/\text{SiO}_2//\text{AY}/\text{PEPC}$ composites: 1 - before irradiation; 2 - after 90 min of visible light exposure; 3 - after 90 min of full light irradiation.

Almost no influence on the photocatalytic performance under *UV light* was observed for $TiO_2/SiO_2//AY//PEPC$. Even the decrease in conversion percentage of dichromate reduction is noted (Fig. 4 C, column 4). While the TC conversion is slightly raised or unchanged for $TiO_2/SiO_2//AY//PEPC$ (Fig. 4 D, columns 2 and 4).

Figure 6 shows the change in the absorption spectra of 30% TiO₂/SiO₂//AY//PEPC composites after light exposure. The intensity of adsorbed AY molecules is obviously lowered as a result of AY destruction by UV light. It is assumed that the photoformed electrons in CB of semiconductor are involved in the reaction with new formed AY residues making the pathways 2.1 impossible. However, the destruction process with the holes participation follows



Figure 7. Photocatalytic activity of the composites tested in the reduction of dichromate ions: $\mathbf{a} - 10\%$ TiO₂/SiO₂//PEPC (1), 10% TiO₂/SiO₂//AY//PEPC (2), 30% TiO₂/SiO₂//PEPC (3), 30% TiO₂/SiO₂//AY//PEPC (4); $\mathbf{b} - 10\%$ TiO₂/SiO₂ (1), 10% TiO₂/SiO₂//AzoP (2), 30% TiO₂/SiO₂ (3), 30% TiO₂/SiO₂//AzoP (4).

freely (Fig. 4 D columns 2 and 4; Fig. 5, pathways 2.2). Based on this, we assumed the fate of the pathways 2.2 and 2.3 (Fig. 5).

The $TiO_2/SiO_2//AzoP$ composites possessed much lower photocatalytic activity than TiO_2/SiO_2 systems. It can be caused by insufficient electron transferring from the semiconductor through the polymer layer to the liquid phase when UV or visible light is applied (Fig. 7b). The azobenzene fragments broaden the absorption region of the photocatalytic systems, however they may be subject to photodegradation [16] and perform as electron-traps. In this case the photocatalysts should be modified by semiconducting polymers such as PCz or others. So the regularities established may be used for formulation of the general rules, which could allow predict and improve the photocatalytic activity of TiO_2/SiO_2 composites.

Conclusions

Hence, the complex composites based on the mesoporous TiO_2/SiO_2 thin films with adsorbed AY dye and PEPC as well as azopolymer are designed. The double PEPC covering prevents the penetration of AY molecules to the liquid phase when aqueous solution is applied.

The presence of acidic surface sites in TiO_2/SiO_2 thin films, amount of adsorbed AY as well the number of PEPC layers have different influence on the stability of the composites. The $TiO_2/SiO_2//AY//PEPC$ films can be used as the new type of photocatalytic systems in Ecological Photocatalysis as the significant increase in the photoactivity under visible light for reduction process is reported.

It was shown that $TiO_2/SiO_2//AzoP$ composites possess much lower photocatalytic activity comparing with $TiO_2/SiO_2//AY//PEPC$. However, the further investigation has to be done to find out the appropriate synthesis conditions to improve their photocatalytic activity and stability to the more aggressive media as well as to find out the new opportunities for the photochromic materials with azobenzene moieties.

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