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Serbian Chemical Society



Klub Mladih hemičara Srbije
Serbian Young Chemists' Club



**54. SAVETOVANJE
SRPSKOG HEMIJSKOG DRUŠTVA**

**5. KONFERENCIJA
MLADIH HEMIČARA SRBIJA**

**KRATKI IZVODI
i
KNJIGA RADOVA**

**54th MEETING OF
THE SERBIAN CHEMICAL SOCIETY**

**5th Conference of
Young Chemists of Serbia**

**Book of Abstracts
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54. SAVETOVANJE SRPSKOG HEMIJSKOG DRUŠTVA I

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KRATKI IZVODI I KNJIGA RADOVA

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TI 01

Photocatalytic activity of PET fabric modified with polypyrrole and TiO₂ nanoparticles

Darka Marković, Marija Radoičić*, Željko Radovanović, Zoran Šaponjić*, Maja. Radetić**

Innovation Center of the Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia

**Institute of Nuclear Sciences "Vinča", University of Belgrade, P.O. Box 522, Belgrade, Serbia*

***Faculty Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia*

Introduction

Nanoscale titanium dioxide (TiO₂) has been widely exploited as a photocatalyst due to its nontoxicity, good stability, low cost, simple preparation method and high photoactivity¹⁻³. However, TiO₂ nanoparticles (TiO₂ NPs) have a wide band gap (3.2 eV) indicating that they are photoactive only under the UV light. Taking into account that the UV light makes up only about 4-6% of the sunlight it could be concluded that TiO₂ NPs cannot be efficiently activated only by sunlight². The high recombination rate of photogenerated electrons and holes in TiO₂ NPs additionally decreases its photocatalytic activity². In order to overcome these drawbacks many methods have been developed to enhance the TiO₂ NPs photoactivity under sunlight. It was reported that the doping of TiO₂ NPs with noble metals, transition metal ions and rare earth metal ions have positive affect on TiO₂ photoactivity under the sunlight¹⁻⁴. On the other hand, the photosensitization with organic dyes and conductive polymers seems to be a promising method for TiO₂ modification in order to improve the visible light utilization¹⁻⁴. Conductive polymers with extended π -conjugates electron systems (e.g. polyaniline, polypyrrole, polythiophene etc.) have remarkable electronic, optical and magnetic properties⁵. Owing to their high absorption coefficients in the visible region, efficient electron donating, high mobility of charge carriers and excellent stability conductive polymers are increasingly used as a photosensitizers for modification of inorganic semiconductors with a wide band gap such as TiO₂^{2,5}.

Simple preparation method and excellent conductivity have been the main reasons for the selection of polypyrrole (PPy) as a photosensitizer for TiO₂ NPs in this study. *In situ* synthesis of PPy and TiO₂ NPs on polyethylene terephthalate (PET) fabric was performed. The photocatalytic activity of this nanocomposite was compared with the PET fabric loaded with TiO₂ NPs by testing it in aqueous solution of the dye C.I. Acid Orange 7 in three repeated photodegradation cycles.

Experimental

All chemicals used in the synthesis were of analytical grade and used as received without any further purification. Milli-Q deionized water was used as a solvent. Colloidal TiO₂ NPs were synthesized by acidic hydrolysis of TiCl₄⁶. The solution of TiCl₄ (Fluka) cooled down to -20 °C was added dropwise to cooled water (at 4 °C) under vigorous stirring and kept at this temperature in the next 30 min. The pH of the solution ranged between 0 and 1, depending on the concentration of TiCl₄. Slow growth of the particles was achieved by dialysis against water at 4 °C until the pH of the solution reached 3.5. The concentration of TiO₂ colloid was determined from the concentration of the peroxide complex obtained after dissolving the particles in concentrated H₂SO₄⁷. In order to improve the crystallinity and overall photocatalytic efficiency of generated TiO₂ NPs, the colloid was thermally treated in reflux at 60 °C for 16 h⁸. Mostly single crystalline, irregularly shaped TiO₂ NPs with average dimensions of 6 nm were observed by HREM⁸. The electron diffraction pattern and Raman spectroscopy measurements confirmed the formation of anatase crystal structure⁹. Obtained TiO₂ NPs were used for synthesis of PPy/TiO₂ coating on PET fabric.

PPy coated PET fabrics were fabricated by in situ polymerization of Py (Acros Organic) in the presence of colloidal TiO₂ NPs with APS in acidic (HCl) medium, at room temperature. An initial mole ratio of [APS] and [Py] was 1.25. 1.00 g of PET fabric was immersed in 80mL of 0.1M TiO₂ colloid and stirred for 10 min. Afterwards, 10mL of 1.2 M HCl solution containing Py (6 μL) was poured into TiO₂ colloidal solution and stirred for further 10 min. Finally, 10 mL of 1.2 M HCl solution containing APS drop by drop was added into reaction mixture. The PPy/TiO₂ nanocomposite prepared at initial [TiO₂]/[Py]=100:1 mole ratio was labeled as PET+PPy/TiO₂. The reaction mixture was stirred for 3 days. In order to remove residual monomer, oxidant and low-molecular weight fractions, the samples were rinsed in 0.01 M HCl. Finally, the nanocomposites were dried at room temperature until the constant mass was reached.

As a reference sample, TiO₂ treated PET fabric was used. PET sample was immersed in TiO₂ NPs colloidal solution (0.1 M) for 10 min at liquor-to-fabric ratio of 25:1, squeezed out through laboratory pad (2 kg/cm²) and dried at room temperature. After 5 min long curing at 100 °C the sample was rinsed twice (5 min) with deionized water and dried at room temperature. This sample was marked as PET+TiO₂ in the following text.

The photocatalytic activity of TiO₂ NPs deposited on PET samples was examined in aqueous solution of acid dye C.I. Acid Orange 7 (AO7, Cassella). The chemical structure of AO7 is shown in Fig. 1.

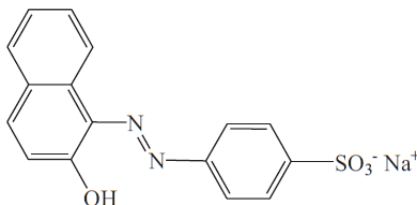


Figure 1. Chemical structure of dye AO7

The morphology of the fibers was analyzed by field emission scanning electron microscopy (FESEM, Tescan

Mira3 FEG). The samples were coated with a thin layer of Au prior to analysis. Energy-dispersive X-Ray spectroscopy (EDS) of the fibers was performed using a JEOL JSM 5800 SEM with a SiLi X-Ray detector (Oxford Link Isis series 300, UK).

Photocatalytic degradation experiments were performed in accordance with a following procedure: 0.50 g of PET+TiO₂ and PET+PPy/TiO₂ samples were put into 25 mL of AO7 solution (10 mg/L). The beaker with a sample was placed in the water bath (with shaking) and it was illuminated by ULTRA-VITALUX lamp (300 W, Osram). The applied lamp provides sun-like irradiation. The distance between the lamp and the sample was set to 35 cm. Optical power was measured using R-752 Universal Radiometer Readout with sensor model PH-30, DIGIRAD and it was 30 mW·cm². The concentration of AO7 solution after 30, 60, 90, 120, 180, 240, 300 and 1440 min of illumination was determined by measuring absorption intensity of AO7 dye at λ_{max}=484 nm using an UV-VIS spectrophotometer Cary 100 Scan (Varian). The percentage of dye removal was calculated according to the following expression:

$$\text{Dye removal, \%} = \frac{(C_0 - C)}{C_0} \times 100 \quad (1)$$

where: C_0 is the initial concentration of dye solution and C is the concentration of dye solution at investigated time.

In order to evaluate a possible reusability of samples impregnated with TiO₂ and PPy/TiO₂ described procedure was repeated two more times.

Results and Discussion

The morphology of the surface of PET and PET+PPy/TiO₂ fibers was evaluated by FE-SEM analysis (Fig. 2). Fig 2a revealed the smooth surface of PET fiber. Unevenly distributed PPy/TiO₂ layers are visible on the surface of PET+PPy/TiO₂ fiber (Fig 2b). The formation of similar PPy layers after coating of cotton fiber with PPy can be found in ^{10,11}.

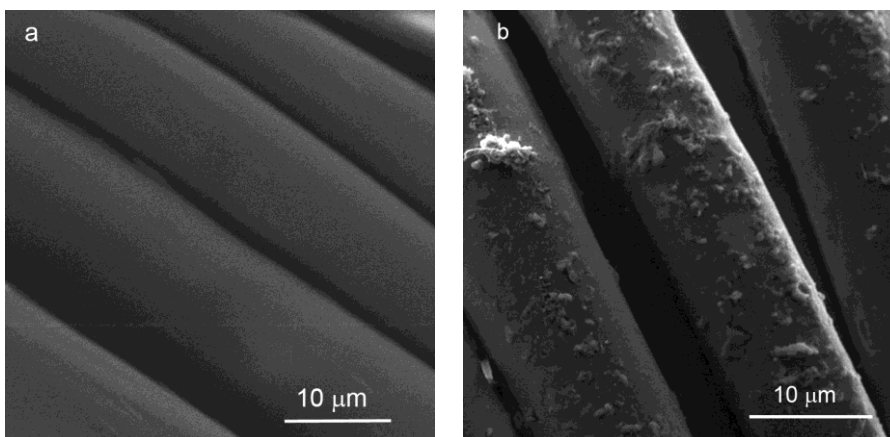


Figure 2. FE-SEM images of the (a) untreated PET fiber, (b) PET+PPy/TiO₂ fiber

In addition, EDS was applied for the elemental composition analysis. EDS spectrum (Fig 3) revealed the presence of titanium and nitrogen on the PET+PPy/TiO₂ surface originating from TiO₂ NPs and PPy, respectively.

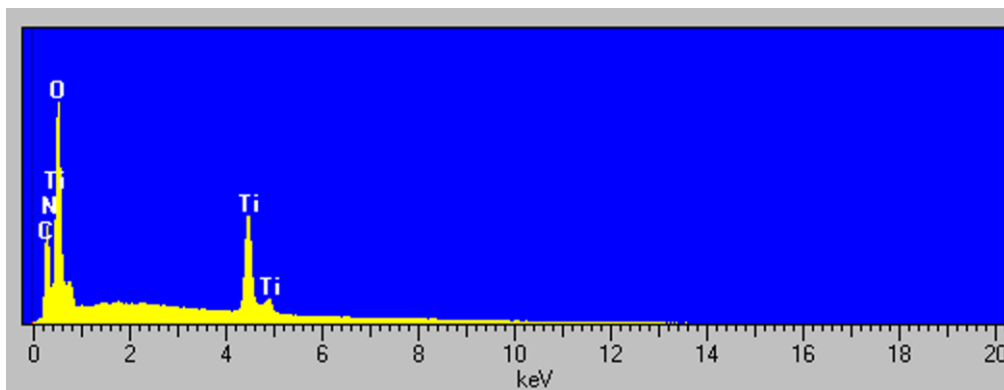


Figure 3. EDS spectrum of the PET+PPy/TiO₂ sample

The photocatalytic activity of the PET+TiO₂ and PET+PPy/TiO₂ samples was assessed by following the degradation of AO7 in aqueous solution under sun-like illumination. In order to exclude the contribution of possible photolysis of dye AO7 the dye solution was exposed to sun-like illumination for 24 h. It was shown that this dye was not prone to photolysis as the change in dye concentration could not be detected.

The dependence of percent of dye removal versus time of sun-like illumination is presented in Fig 4. Fig 4a shows that the PET+TiO₂ sample provided complete dye removal from the solution after 24 h of illumination. Fig 4a also revealed that complete dye removal from the solution in the presence of the PET+TiO₂ sample was obtained in repeated photodegradation cycles. It should be noticed that the rate of dye degradation was significantly slower during the third photodegradation cycle compared to the first and the second cycle. However, the overall photodegradation efficiency

after 24 h was still comparable with the first and the second cycle. Observed decrease in photodegradation rate was probably due to some desorption of TiO_2 NPs from the surface of the $\text{PET}+\text{TiO}_2$ fabrics during the repeated photodegradation cycles. Fig 4b shows that the $\text{PET}+\text{PPy}/\text{TiO}_2$ sample ensured complete removal of dye from the solution already after 120 min of sun-like illumination. It is also clear that excellent photodegradation efficiency was preserved during the second and the third photodegradation cycle. Slight drop of photodegradation rate can be observed during the third photodegradation cycle.

(a) (b)

Figure 4. The percent of AO7 dye removal during repeated photodegradation processes in presence of the: (a) $\text{PET}+\text{TiO}_2$ and (b) $\text{PET}+\text{PPy}/\text{TiO}_2$ samples

The results presented in Fig 4 pointed out that the $\text{PET}+\text{PPy}/\text{TiO}_2$ sample exhibited significantly higher photocatalytic activity than the $\text{PET}+\text{TiO}_2$ sample. When $\text{PET}+\text{PPy}/\text{TiO}_2$ sample is illuminated with sunlight, the electrons in PPy (e^-) are excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (Fig 5)^{1, 4-5}. The excited electrons are injected in the conduction band of the TiO_2 leading to a creation of positive holes (h^+) in the HOMO of PPy.

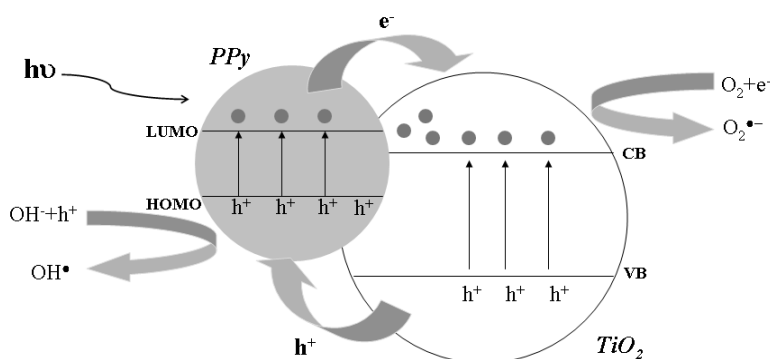


Figure 5. Schematic illustration of the processes that occur on PPy/TiO_2 composites under sunlight

At the same time TiO_2 absorbs the light (UV part of the sunlight), electron-hole pairs are produced and excited electrons in TiO_2 migrate from the valence band to the conduction band. The excited electrons from the PPy molecules can be injected into the conduction band of TiO_2 and finally react with oxygen at the surface. This results in the formation of highly reactive particles such as

superoxide radical ion $O_2^{\cdot-}$ and consequently the hydroxyl radical OH^{\cdot} . The latter is responsible for the degradation of organic compounds¹². In this case PPy also have photosensitizing function. The photogenerated holes in the HOMO-orbital of PPy can migrate to the interface and react with water to yield hydroxyl radicals. Moreover, photoproduced holes from valence band of TiO_2 can migrate to HOMO-orbital of PPy and additionally contribute to efficient photocatalytic process. Therefore, the higher photocatalytic activity of this system compared to bare TiO_2 NPs is due to rapid charge separation and slow charge recombination¹².

Fig 6 shows the photographs of the samples after repeated photodegradation cycles. It should be noted that the PET+ TiO_2 sample remained white after repeated photodegradation cycles. In addition, pale gray color of native PET+PPy/ TiO_2 sample was kept after each photodegradation cycle implying that dye was removed from both the solution and the samples.

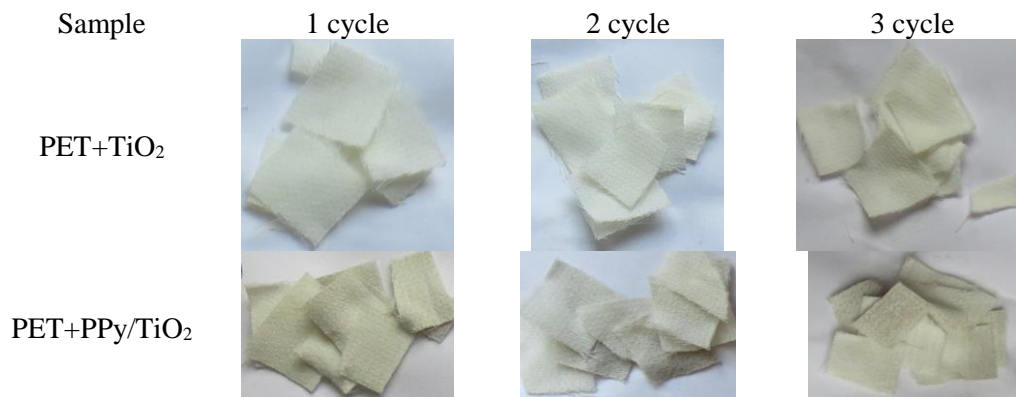


Figure 6. The photographs of the samples after repeated photodegradation cycles

Conclusions

Composite textile material based on PET fabric, PPy and TiO_2 NPs was successfully prepared by *in situ* synthesis. FE-SEM analysis confirmed the presence of unevenly distributed PPy/ TiO_2 layer on the PET fiber. The results of photocatalytic activity of the PET+ TiO_2 sample as a referent sample showed that complete photodegradation of dye AO7 was achieved after 24 h long exposure to sun-like illumination. The PET+PPy/ TiO_2 sample provided complete photodegradation of dye already after 120 min of sun-like illumination. It is assumed that the presence of PPy on the PET+PPy/ TiO_2 samples enhanced the photocatalytic activity of TiO_2 NPs by reducing the recombination rate of electrons and holes in TiO_2 NPs. It was also shown that the photocatalytic efficiency was preserved after three repeated cycles.

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Fotokatalitička aktivnost PET tkanine modifikovane polipirolom i nanočesticama TiO_2

U ovom radu je ispitana mogućnost dobijanja kompozitnog tekstilnog materijala na bazi PET tkanine, polipirola i nanočestica TiO_2 sa efikasnom fotokatalitičkom aktivnošću. Prisustvo PPy/ TiO_2 kompozitnog sloja na površini vlakana je potvrđeno FE-SEM i EDS analizom. Fotokatalitička aktivnost PET tkanine obrađene polipirolom i nanočesticama TiO_2 kao i PET tkanine obrađene samo nanočesticama TiO_2 ispitana je u vodenom rastvoru boje C.I. Acid Orange 7. Rezultati ispitivanja fotokatalitičke aktivnosti su pokazali da uzorak modifikovan polipirolom i nanočesticama

TiO_2 potpuno degradira boju za samo 120 minuta osvetljavanja lampom koja simulira sunčevo zračenje dok je uzorku modifikovanom nanočesticama TiO_2 za to potrebno 24 h. Takođe je utvrđeno da kompozitni uzorak PET+PPy/ TiO_2 pokazuje odlična fotokatalitička svojstva u drugom i trećem ciklusu fotodegradacije. Znatno bolja fotokatalitička aktivnost kompozitnog uzorka u odnosu na PET tkaninu modifikovanu nanočesticama TiO_2 je upravo posledica prisustva polipirola.

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