

HIBRIDNI FUNKCIONALNI PANI/TiO₂ NANOKOMPOZITI ZA TRETMAN DEGRADACIJE ORGANSKIH BOJA

HYBRID FUNCTIONAL PANI/TiO₂ NANOCOMPOSITES FOR DYES DEGRADATION TREATMENT

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Aktuelna potreba za zaštitom životne sredine ne jenjava i s tim u vezi postavljeni su visoki zahtevi vezani za tematiku primenjenih tehnologija za uklanjanje organskih zagađujućih supstanci. Ispostavlja se da napredni procesi oksidacije (engl. Advanced oxidation processes, AOPs) predstavljaju jedan od najefikasnijih procesa, među kojima heterogena fotokataliza, bazirana na upotrebi nanokristala TiO₂ aktiviranih UV zračenjem, nesumnjivo predstavlja jedan od najčešće korišćenih tretmana za degradaciju organskih boja. Problem ograničene fotokatalitičke efikasnosti TiO₂ pod dejstvom sunčevog zračenja može se prevazići formiranjem kompozita sa polianilinom (PANI), čija se uloga bazira na smanjenju rekombinativnih procesa e^-/h^+ , kao i sposobnosti PANI-a da optički aktivira nanokristale TiO₂, što je bila osnova za formiranje novih funkcionalnih PANI/TiO₂ nanokompozita. Takvi hibridni nanomaterijali bazirani na provodnom polimeru i nanokristalima različitih oblika pokazuju jedinstvena svojstva koja najčešće nisu karakteristika pojedinačnih komponenti, već njihovog sinergističkog dejstva. Efikasnim i ekološki prihvatljivim sintezama razvijena je serija funkcionalnih nanokompozita na bazi PANI-a i koloidnih TiO₂ nanočestica (NPs) (TP), karbonizovanog PANI-a i koloidnih TiO₂ NPs (TPC) i karbonizovanog PANI-a i TiO₂ nanotuba (NTs) (TTPC). Nanokristali TiO₂ različitog oblika pažljivo su sintetisani sol-gel i hidrotermalnom metodom i procenjen je uticaj njihove veličine i oblika na fotokatalitičku efikasnost hibridnih nanokompozita. Nekarbonizovani PANI/TiO₂ nanokompoziti sintetisani su hemijskom oksidativnom polimerizacijom anilina sa amonijum peroksidisulfatom, u prisustvu odabranih nanokristala TiO₂, dok je karbonizovana serija uzoraka dobijena naknadnim procesom karbonizacije, prateći polimerizaciju, u inertnoj atmosferi na 650 °C. Morfologija i struktura sintetisanih fotokatalitički aktivnih sistema ispitana je TEM analizom i Ramanskom spektroskopijom. Funkcionalnost nanokompozita je procenjena prateći procese fotokatalitičke degradacije model-jedinjenja Methylene blue i Rhodamine B i primećena je povećana efikasnost degradacije testiranih organskih boja.

Ključne reči: nanokompoziti; PANI; TiO₂; karbonizacija; životna sredina

A calling need for environmental protection is not abating and high demands have been set for the current topic that deals with applied technologies for removal of organic pollutants. The AOPs appear to be one of the most effective processes, where heterogeneous photocatalysis using efficient UV light-harvesting TiO₂ nanocrystals has unquestionably become one of the most commonly used process for dyes degradation treatment. Limited photocatalytic efficiency of TiO₂ under sunlight illumination was overcome by coupling with polyaniline (PANI) as notably investigated conductive polymer. Reducing the level of e^-/h^+ recombination in TiO₂ and photosensitized properties of PANI was the basis for creation of new functional PANI/TiO₂ nanocomposites. Such hybrid

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functional nanomaterials consisting of conductive polymers and dissimilar nanocrystals manifest the unique properties, usually not characteristic of independent components but their synergistic effect. Series of developed functional nanocomposites based on PANI and colloidal TiO₂ nanoparticles (NPs) (TP), carbonized PANI and colloidal TiO₂ NPs (TPC) and carbonized PANI and TiO₂ nanotubes (NTs) (TTPC) by the efficient and harmless synthesis pathways are presented. Differently shaped TiO₂ nanocrystals are carefully prepared via sol-gel and hydrothermal synthesis and the influence of their size and shape on the photocatalytic efficiency of hybrid nanocomposites was evaluated. The non-carbonized PANI/TiO₂ nanocomposites were synthesized by the chemical oxidative polymerization of aniline with ammonium peroxydisulfate, in the presence of selected TiO₂ nanocrystals, while the carbonized class was obtained in the subsequent carbonization process, following the polymerization, in an inert atmosphere at 650 °C. The morphology and structure of these nano-based photocatalysts was determined by TEM analysis and Raman spectroscopy. Functionality of nanocomposites was evaluated following the photocatalytic degradation processes of model compounds Methylene blue and Rhodamine B and enhanced degradation efficiencies in the used dyes were observed.

Key words: nanocomposites; PANI; TiO₂; carbonization; environment

1 Introduction

Widespread application of an efficient UV light-harvesting TiO₂ nanocrystals, considering various crystalline structures and shapes, is gaining momentum for photocatalytic removal of organic pollutants taking into account its simple synthesis, low cost and the ability to resist photocorrosion [1]. However, limited use of only ~5% of solar radiation of TiO₂ crystals leads to the constant development of new strategies for tuning optical response of TiO₂ in visible region with an aim to increase its photoactivity [2]. An approach that meets both demands, including visible light absorption and non-hindered charge separation in TiO₂, is based on the synthesis of nanocomposite systems consisting of electronically coupled conductive polymers (*e.g.*, polyaniline (PANI), polythiophene, polypyrrole, and their derivatives) and TiO₂ [3], [4]. Actually, such extended π -conjugated electron systems, as conducting polymers electronically coupled to TiO₂, possess moderate-to-high mobility of charge carriers, enabling better separation of photoinduced e^-/h^+ in TiO₂ nanocrystals. Generally, hybrid functional materials consisting of conductive polymers and dissimilar nanocrystals exhibit some unique properties which are usually not a property of individual components [5], [6].

Excluding formerly mentioned aspects of N-containing conductive polymers (PANI or polypyrrole) in photoinduced charge-transfer processes, these materials are also used in the obtaining of new N-containing 1-D nanostructured carbon materials during the carbonization process at high temperature (500-1050 °C) and in an inert atmosphere [7-9]. Nanocomposites based on such N-containing carbonaceous materials and dissimilar inorganic components (metals, oxides) provide supplemental properties/improvements in various applications [10]. Therefore, the possibility to design the photocatalysts with tailored and unique properties is open by the evolution of carbon-nanostructure-based-titania nanocomposites [11].

Conventional photoactive nanocomposites based on neat and carbonaceous materials and TiO₂ nanocrystals are ordinarily synthesized by challenging routes using costly equipment or at high temperatures. In contrast, this research offers a simplified approach for the synthesis of multiple classes of these functional nanocomposites.

Concerning the examination of the influence of carbonization process of PANI, as well as the influence of shape of TiO₂ nanocrystals on the photocatalytic efficiency of the developed classes of nanocomposites, the degradation processes of model molecules (*Methylene blue, MB* and *Rhodamine B, RB*) is followed within this research. The morphological properties of designed nanocomposites are investigated by TEM analysis, while the molecular properties of individual components are studied by Raman spectroscopy. Photocatalytic activity of carbonized PANI/TiO₂ nanocomposites, synthesized in the presence of either colloidal or tubular TiO₂ nanocrystals, are compared to non-carbonized nanocomposites examined in our previous work [7].

2 Experimental part

2.1 Synthesis of TiO₂ nanoparticles

The colloidal solution of TiO₂ nanoparticles (NPs) was prepared in a manner analogous to the procedure proposed by Rajh *et al.* [12]. The concentration of TiO₂ was determined from the concentration of the peroxide complex obtained after dissolving the particles in concentrated H₂SO₄ [13].

2.2 Synthesis of TiO₂ nanotubes

TiO₂ nanotubes (NTs) were synthesized in alkaline conditions by hydrothermal treatment in accordance with procedure of Vranješ *et al.* [14]. Calcined TiO₂ NTs (carbonized tubes) were synthesized in an argon atmosphere, starting from the described TiO₂ NTs powder, which was subsequently heated from room temperature to 650 °C, kept at that temperature for 15 min and cooled down to room temperature in an inert atmosphere.

2.3 Synthesis of non-carbonized and carbonized PANI/TiO₂ nanocomposites

Non-carbonized PANI/TiO₂ nanocomposites were synthesized by chemical oxidative polymerization of aniline (ANI) by oxidant (ammonium peroxydisulfate, APS) in the presence of colloidal TiO₂ NPs at room temperature. The first set of the samples was prepared in the presence of colloidal TiO₂ NPs, with TiO₂:ANI molar ratio of 50, 100 and 150, and denoted as TP-50, TP-100 and TP-150.

Carbonized TPC nanocomposite samples were prepared in the two-step procedure. The first step of synthesis included chemical oxidative polymerization (previously described). The second step was based on the carbonization process, considering heating of the samples from room temperature to 650 °C, keeping at this temperature for 15 min, and cooling to room temperature. Whole process was conducted in an inert atmosphere. The second set of the samples was prepared in the presence of colloidal TiO₂ NPs, with TiO₂:ANI molar ratio of 20, 50 and 80, and denoted as TPC-20, TPC-50 and TPC-80.

The third set of the samples was prepared in the same manner as TPC nanocomposites, where TiO₂ NTs were used instead of colloidal TiO₂ NPs. Initial molar ratios of TiO₂ NTs and ANI were 50, 100 and 150, and samples were denoted as TTPC-50, TTPC-100 and TTPC-150.

All chemicals used for the synthesis were commercial analytical quality products (*Aldrich*, *Fluka*, *Centrohem*) used as-received except ANI. ANI (*Centrohem*, Serbia, p.a. > 99.5%) was distilled under the reduced pressure and stored at room temperature, under argon, prior to use. *Milli-Q* deionized water was used as a solvent.

3 Methods

3.1 TEM analysis

The shape and size of synthesized nanocomposites (TP-50, TPC-50, TTPC-50) were determined by Transmission Electron Microscopy (TEM) using a *JEOL 100CX* device operating at 100 kV.

3.2 Raman analysis

Raman spectra of TP-50, TPC-50, TTPC-50 nanocomposite samples, excited by a HeNe gas laser (excitation wavelength: 633 nm), were collected on a *Thermo Scientific DXR* Raman microscope equipped with a research optical microscope and a CCD detector. The scattered light was analyzed by the spectrograph with a 600 lines-per-mm grating. Laser power at the sample was 0.5 mW.

3.3 Photocatalytic performances

The photocatalytic performances of all samples were investigated by monitoring the degradation processes of the test dye molecules, MB and RB, under simulated solar light. A 1 gL⁻¹ of the photocatalyst was mixed with the 50 mL of 1 × 10⁻⁵ molL⁻¹ of aqueous dye solution, continuously

stirred in an air atmosphere and illuminated by a lamp that simulates solar irradiation (*Osram Vitalux* lamp, 300 W). Before illumination, the system was stirred in the dark for 30 min to achieve adsorption-desorption equilibrium. The aliquots were taken every 1h for TP, 5 min for TPC and 2 min for TTPC samples. Changes in the absorbance of dye molecules (MB or RB) in supernatant were measured on *Thermo Scientific Evolution 600* UV/Vis spectrophotometer λ (MR) = 664 nm and λ (RB) = 554 nm.

4 Results and discussion

4.1 Morphological properties – TEM analysis

The shape and size of synthesized nanocomposites, TP-50, TPC-50 and TTPC-50 are presented in *Fig. 1*. On the TEM micrograph of non-carbonized nanocomposite prepared in the presence of colloidal TiO₂ NPs (TP-50) thin PANI layer on anatase TiO₂ NPs was observed. According to the distance between crystal planes and thickness of the carbonized PANI (CPANI) cover onto NPs in TPC-50 sample, it can be observed that carbonization process caused change in the crystal phase of TiO₂ NPs (appearance of the rutile phase), as well as decreasing of the thickness of the carbonized polymer layer. Nanocomposites prepared in the presence of TiO₂ NTs and carbonized thereupon showed completely change of morphological structure (TTPC-50, *Fig. 1*). Namely, process of carbonization completely destroyed tubular structure of TiO₂ NTs and formation of granular structure occurs. In addition, the CPANI layer still exist after thermal process in an inert atmosphere and it can be clearly observed at *Fig. 1*. (TTPC-50).

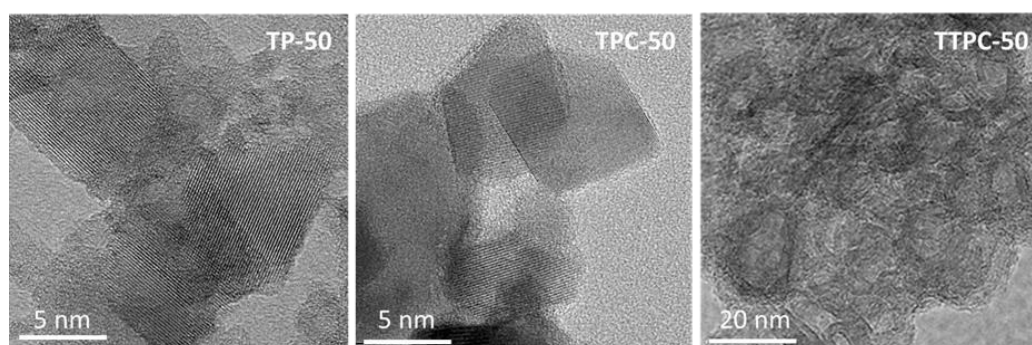


Fig. 1. TEM micrographs of TP-50, TPC-50 and TTPC-50 nanocomposite samples.

4.2 Raman analysis

A molecular structure of TP-50, TPC-50 and TTPC-50 was provided by Raman spectroscopy analysis and shown in *Fig. 2*. Vibrational bands positioned at 1598, 1513, 1345 and 1172 cm⁻¹ corresponds to the C=C and C~C stretching vibrations of the quinonoid (*Q*) and/or semiquinonoid (*SQ*) rings, respectively (~ denotes the bond intermediate between the single and double bond), the N-H bending vibration of protonated amine, the C~N⁺ stretching vibration of polaronic structures and the C-H bending in-plane vibration of *SQ* rings in polaronic structures, respectively. Also, the bands which have been associated with the substituted phenazine units of ordinary PANI, were also observed at 1633, 1569 and 1410 cm⁻¹ for the TP-50 sample.

Carbonization process had a strong influence on both components of composite. Namely, appearance of *G* (1584 cm⁻¹) and *D* (1350 cm⁻¹) bands in treated samples (TPC-50 and TTPC-50) confirmed formation of carbonaceous material and completely destruction of PANI emeraldine salt form. In the course of the carbonization of PANI/TiO₂ at 650 °C, some changes in the crystalline structures of TiO₂ NPs are observed. To be precise, in the Raman spectrum of TPC-50 and TTPC-50 nanocomposite sample, the appearance of the bands at 147 cm⁻¹ (*E_g* phonon mode) and 382 (400) cm⁻¹ (*B_{1g}* mode) confirmed the presence of anatase crystalline phase [1]. Also, the new bands that appeared at 613(605), 447(479), 245 and 147 cm⁻¹ can be assigned to *A_{1g}*, *E_g*, second-order scattering and *B_{1g}* modes of rutile crystalline phase, respectively, formed by the temperature induced phase transformation in TiO₂ component of the nanocomposite [1]. The band at 147 cm⁻¹ is formed by mixed contributions of rutile *B_{1g}* mode and anatase *E_g* mode.

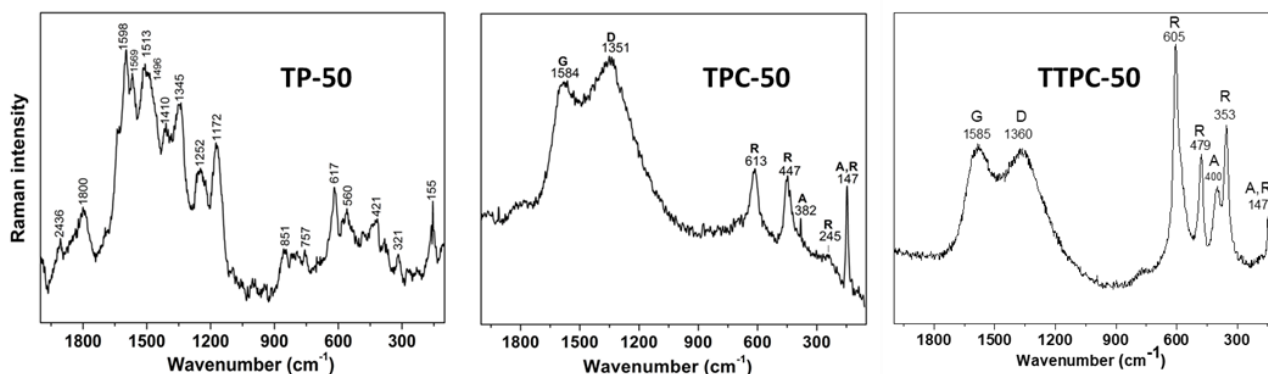


Fig. 2. Raman spectra of synthesized nanocomposites: TP-50, TPC-50 and TTPC-50.

4.3 Photocatalytic activity test

The photocatalytic degradation of organic dyes, MB and RB, was studied in the presence of three different PANI/TiO₂ nanocomposite sets, under white light irradiation in an oxygen atmosphere. The photodegradation of both dyes was monitored by concentration changes (C/C_0) as a function of illumination time (Fig. 3).

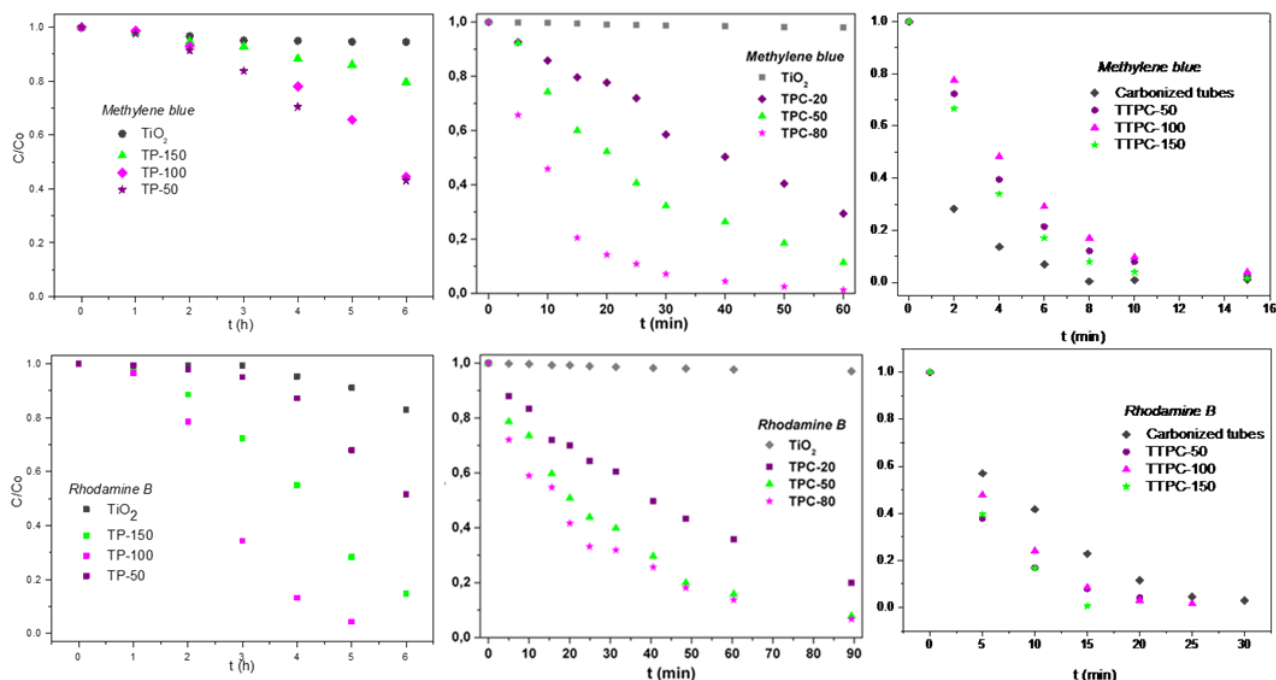


Fig. 3. Photocatalytic properties of TP, TPC and TTPC sets of nanocomposite photocatalysts.

Non-carbonized TP nanocomposites with a colloidal TiO₂/ANI molar ratio ranging from 50 to 150 removed only 20-60% of MB within 6 h of white-light illumination, while the degradation efficiency of RB was in the range of 50-100% for the same period [7]. New sets of nanocomposites (TPC and TTPC) were formed through the carbonization process, with a significant improvement in photocatalytic properties. Compared to non-carbonized samples, the complete decomposition of the investigated dye molecules occurred after 60 (for MB) – 90 (for RB) min with TPC *i.e.* after 15 (for MB) – 30 (for RB) min with TTPC nanocomposite samples [1]. In the investigated photocatalytic processes for the reference samples, neat colloidal TiO₂ NPs and TiO₂ NTs showed a noticeably lower photocatalytic ability to degrade molecules of MB and RB organic dyes. It can be observed that the presence of PANI and CPANI layer on TiO₂ nanocrystals (NPs and NTs) caused a successful hindrance of the e^-/h^+ recombination processes in TiO₂, as well as a photosensitizing effect for efficient use of sunlight irradiation.

In accordance with the obtained results, it can be noticed that both variables, the carbonization process, as well as the shape of TiO₂ nanocrystals have a huge and positive influence on the photocatalytic activity of the synthesized nanocomposites during the degradation/decomposition of organic pollutants.

5 Conclusion

With the aim to improve the photocatalytic properties of TiO₂, PANI/TiO₂ nanocomposites were synthesized and three different sets of samples were prepared: 1) non-carbonized TP nanocomposites and 2) carbonized TPC nanocomposites, which are synthesized in the presence of colloidal TiO₂ NPs and 3) carbonized TTPC nanocomposites synthesized in the presence of TiO₂ NTs. The carbonization process was carried out in an inert atmosphere by heating the samples from room temperature to 650 °C, kept at this temperature for 15 min, and cooled down to room temperature. The synthesized nanocomposites were further characterized by TEM measurements and Raman spectroscopy. TEM micrographs showed changes in the crystal structure and shape of TiO₂ nanocrystals, as well as the formation of a thin PANI or CPANI layer onto TiO₂. Raman spectroscopy confirmed the presence of emeraldine form of PANI in TP nanocomposites, the presence of *D* and *G* bands in carbonized TPC and TTPC nanocomposites. The temperature treatment caused changes in the crystalline phases of TiO₂, in addition to anatase, rutile crystal structure was obtained in the carbonized TPC and TTPC samples. The synthesized samples showed an improved ability to photodegrade the tested dyes, compared to untreated TiO₂ nanocrystals. The photocatalytic activity of nanocomposites is strongly influenced by the initial molar ratio of TiO₂:ANI, the carbonization process, the crystal and molecular structures of individual components, as well as the molecular structures of the used organic dyes.

6 Nomenclature

ANI – Aniline

AOPs – Advanced oxidation processes

APS – Ammonium peroxydisulfate

CPANI – Carbonized polyaniline

e⁻ – Electrons

h⁺ – Holes

MB – Methylene blue

NPs – Nanoparticles

NTs – Nanotubes

PANI – Polyaniline

RB – Rhodamine B

TEM – Transmission Electron Microscopy

TP – Non-carbonized nanocomposites based on PANI and colloidal TiO₂ NPs

TP-50, TP-100, TP-150 – TP nanocomposites with TiO₂:ANI molar ratio of 50, 100 and 150, respectively

TPC – Carbonized nanocomposites based on PANI and colloidal TiO₂ NPs

TPC-20, TPC-50 and TPC-80 – TPC nanocomposites with TiO₂:ANI molar ratio of 20, 50 and 80, respectively

TTPC – Carbonized nanocomposites based on PANI and TiO₂ NTs

TTPC-50, TTPC-100 and TTPC-150 – TTPC nanocomposites with TiO₂:ANI molar ratio of 50, 100 and 150, respectively

7 References

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