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Photocatalytic degradation of acetic acid in the presence of visible light-active TiO₂-reduced graphene oxide photocatalysts

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ABSTRACT

Visible light-active TiO₂-reduced graphene oxide photocatalysts were prepared using simple mechanical mixing of titanium dioxide with different amounts of rGO (0.1, 0.5, 1.0 and 2.0 wt.%) in the presence of 1-butyl alcohol. Structures and morphologies of the samples were examined by means of FTIR/DRS, UV-vis/DR, XRD, SEM, TEM and Raman spectroscopy. The photocatalytic properties were checked on the basis of acetic acid photooxidation (the steady rate of linear increase of the CO₂ yield was used for the estimation of photocatalytic activity). The maximum photodegradation rate was observed for TiO₂ decorated with 0.5 wt.% of rGO. The enhancement of photodegradation efficiency should be related to π -conjugation system, two-dimensional planar structure and efficient charge separation of reduced graphene oxide nanosheets.

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1. Introduction

In recent years, graphene, a two-dimensional novel carbon nanomaterial with zero band gap, large specific surface area, excellent mechanical, electrical, optical and thermal properties and its applications in sensors and biosensors, electronic devices, liquid crystalline displays, capacitors solar cells, H₂ production, energy storage and nanocomposites including TiO₂/graphene materials, has been intensively studied [1–10]. Graphene is composed of single or less than 10 planar sheets of sp²-bonded carbon atoms forming six-membered rings [11]. Singh et al. [5] described in detail the most common methods of graphene preparation: exfoliation and cleavage, chemical vapour deposition CVD, graphene oxide reduction, total organic synthesis or unzipping carbon nanotubes.

Recently, the combination of graphene and semiconductors, especially titanium dioxide, as a promising route to obtain new graphene-TiO₂ nanocomposites with enhanced charge separation in electron-transfer, has been intensively studied. Incorporation of graphene or graphene oxide into TiO₂ provides large specific surface area and high charge carrier mobility due to the moving of TiO₂

generated electrons across the graphene 2D-sheets, which minimizes the electron-hole recombination and enhances the oxidative reactivity [11–13]. Huang et al. [13] explained the enhancement of TiO₂-graphene nanocomposites photocatalytic activity by interfacial charge transfer through a C-Ti bond, which increased the number of holes participating in the photocatalytic process due to markedly decreasing recombination of electron-hole pairs. The formation of Ti-O-C bonds results expanding the light absorption to longer wavelengths and the possibility of TiO₂ excitation with visible or solar light.

Wang et al. [11] proposed the graphitization of melamine used as carbon source dispersed in methanol and mixed with P25 TiO₂ and then homogenized in ultrasonic bath. The significant enhancement of photocatalytic activity of new hybrid TiO₂-graphene materials, calculated on the basis of Methylene Blue (MB) decomposition under UV light source, was caused by a rapid photoinduced charge separation and the inhibition of recombination for electron-hole pairs. This results in the increase of number of holes participating in the photooxidation process of used thiazine dye. Thus the synergetic effect between graphene-like carbon and titanium dioxide was also proved. Ni et al. [14] discussed new photocatalytic mechanisms of MB degradation under visible light in the presence of graphene supported TiO₂ and graphene strongly wrapped-TiO₂ nanocomposites. Firstly, the higher photoactivity of

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graphene-modified TiO₂ samples was found in comparison with bare TiO₂ and commercial P25 due to enhanced light absorption, separation of photogenerated carriers, and improved dye adsorption. Secondly, it was found that in the case of graphene supported TiO₂ nanocomposites the photogenerated electrons from excited MB adsorbed on graphene can flow on the graphene surface freely, but these electrons cannot inject into the titania conduction band due to the slightly lower graphene energy level in comparison with TiO₂. Hence, the electrons rapidly recombined to the MB ground state. The excitation of graphene strongly wrapped-TiO₂ nanocomposites and MB molecules allowed the electrons from the excited MB be transferred to the TiO₂ conduction band via graphene. Most of the electrons will be trapped to form reactive oxygen species (ROS), which can easily oxidize MB, causing degradation of organic contamination.

Furthermore, Meng et al. [15] prepared graphene-based TiO₂ nanocomposites by atomic layer deposition and Peining et al. [7] proposed a very simple method of TiO₂-graphene nanomaterials fabrication by electrospinning. However, modified Hummer's method is the preparation method most frequently used for TiO₂-graphene nanocomposites [16–18].

In this paper, the study on the photocatalytic performance of TiO₂-graphene nanocomposites activated by visible light is reported. A large number of already published articles describe the activity of TiO₂-graphene photocatalysts usually under UV light. According to the facts that graphene is a carbonaceous material and carbon doping of titania generally contributes to bathochromic shift of absorption band, the investigation of TiO₂-rGO photoactivity under visible light seems to be crucial. In our case the photocatalytic activity of prepared nanomaterials was calculated on the basis of acetic acid decomposition. Additionally, TiO₂-graphene nanocomposites were obtained in different TiO₂-to-graphene mass ratio by mechanical mixing of starting TiO₂ supplied by sulfate technology and reduced graphene oxide (rGO) in the form of flakes synthesized according to modified Hummer's method.

2. Experimental

2.1. Materials and reagents

A crude titanium dioxide slurry supplied by sulfate technology in Grupa Azoty Zakłady Chemiczne "POLICE" S.A. (Poland) containing post-production residues of sulfuric acid (2.1 wt.%) was rinsed with aqueous solution of ammonia water (solution 25%, CAS: 1336-21-6, Avantor Performance Materials Poland S.A.) and further with distilled water to pH = 6.8. The solution of ammonia water was used in order to remove the residues of sulphuric acid through formation of ammonium sulfate, which is easily dissolved in water. The prepared material was dried at 105 °C for 24 h in a muffle furnace to remove water molecules adsorbed on the surface of starting TiO₂. 1-butyl alcohol (purity 99.5%, CAS: 71-36-3) was purchased from Avantor Performance Materials (Poland). Natural graphite (Asbury Carbons, USA) was a starting material in a process of graphene preparation. All the chemicals were used as received without further purification. The ultrapure water from Millipore ultrafiltration system was used in all the experiments. Commercial titanium dioxide KRONOClean 7000 (Kronos International, Inc., Germany) was used as the reference carbon-modified TiO₂ photocatalyst.

2.2. Preparation of reduced graphene oxide (rGO)

Graphene oxide (GO) was obtained by modified Hummer's method [19] as follows. The starting material was the flake graphite (Asbury Carbons, USA) intercalated with mineral acids, which

has been expanded at a temperature of about 1000 °C. Next the appropriate amounts of NaNO₃ (pure p.a., CAS: 7631-99-4) and concentrated H₂SO₄ (pure p.a., CAS: 7664-93-9) were added to sample of expanded graphite. The KMnO₄ (pure p.a., CAS: 7722-64-7) used as the oxidant, was gradually added into the mixture maintaining the reaction temperature below 5 °C. The process was conducted with continuous stirring the reactants. In the next step the mixture was heated to 35 °C and left at this temperature for 3 h. Then, the reaction mixture was heated to 95 °C. To complete the reaction, deionized water was added and a small amount of hydrogen peroxide. The product was washed with 3% HCl (pure p.a., CAS: 7647-01-0) solution to remove of sulfate ions and finally with deionized water. The purified product was subjected to exfoliation using ultrasonic processor. Such obtained GO sample was dried under vacuum and then thermally reduced. Used reagents of analytical grade were purchased from Avantor Performance Materials Poland S.A., Poland.

2.3. Preparation of TiO₂/rGO nanocomposites

A 5 g of titanium dioxide (named as starting TiO₂) and appropriate mass ratio (0.1, 0.5, 1.0 and 2.0 wt.%) of reduced graphene oxide-to-titania were mechanically mixed in the presence of 100 mL 1-butyl alcohol and then ultrasonicated for 30 min. After sonication step, a slurry of TiO₂, 1-butanol and rGO was partially evaporated in order to remove the excess of primary aliphatic alcohol. Then, each sample was dried at 100 °C for 24 h in a muffle furnace to remove water and residues of 1-butyl alcohol from the obtained photocatalysts surface. The final products are denoted as TiO₂-rGO(x), where x is appropriate mass ratio of added rGO. The TiO₂-rGO nanocomposites were prepared without calcination process.

2.4. Photocatalysts characterization

The surface properties of tested materials were examined using a FTIR/DRS spectrophotometer FTIR 4200 (Jasco, Japan) equipped with a diffuse reflectance accessory (Harrick, USA). The FTIR band under examination covered wave numbers ranging from 400 to 4000 cm⁻¹, and each spectrum was collected with 4 cm⁻¹ resolution.

The light reflectance abilities of the samples were obtained by UV-vis/DR spectrometry using a V-650 UV-vis spectrophotometer (Jasco, Japan) equipped with an integrating sphere accessory for studying DR spectra. BaSO₄ (purity 98%, CAS: 7727-43-7, Avantor Performance Materials, Poland) was used as a reference material. Crystal structures and relative phase compositions of obtained photocatalysts were analyzed using X-ray powder diffraction analysis (X'PRO Philips diffractometer) with Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$). Titania anatase-over-rutile ratio was calculated in a way described previously [20,21]. The standard uncertainties were estimated from fivefold XRD measurements of the same sample. Subsequently, phase content and crystallite sizes were evaluated. For obtained values the average and standard deviation was calculated. The surface morphologies of obtained materials was checked via transmission electron microscopy (TEM) on an electron microscope (FEI Tecnai F30, Frequency Electronics Inc., Mitchel Field, NY, USA) operated at an acceleration voltage of 200 kV. Additionally, scanning electron microscopy (SEM) Hitachi SU8020 Ultra-High Resolution Field Emission Scanning Electron Microscope (Japan) was used. The 5 kV electrons energy was applied for the excitation of studied samples. Raman spectrum was recorded on a Renishaw Micro Raman spectrometer ($\lambda = 785 \text{ nm}$). The N₂-BET specific surface area measurements of the photocatalysts were carried out based on N₂ adsorption isotherms at 77 K using the Quadrasorb Si analyzer (Quantachrome, USA). Prior to analyses,

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