A SHORT REVIEW OF TITANIA – GRAPHENE OXIDE BASED COMPOSITES AS A PHOTOCATALYSTS

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New and effective methods of water purification are necessary to minimize pollution. Many methods have been used in wastewater treatment, but sorption is considered as an easy and economic process. The efficiency of any sorption process mainly depends on the physicochemical properties of the used adsorbent. Since photocatalysts can initiate reactions of decomposition organic contaminants under ultraviolet or sunlight irradiation without using chemicals or producing chemical wastes, photocatalytic reactions are considered a sustainable way to remove a variety of environmental pollutants. Ultraviolet water purification became the most effective method of water disinfection and purification. Heterogeneous semiconductor photocatalysts have recently emerged as an efficient material for purifying water. The crystal structure is crucial for photocatalytic activity and efficiency of semiconductors, thus optimal parameters must be provided during the preparation of photocatalysts. To overcome problems with semiconductors usage, the use of co-catalysts and photocatalyst carriers is one of the solutions. Recently, much emphasis has been placed on using graphene oxide (GO) supported semiconductor photocatalysts. In this paper, a short review of composites of titanium dioxide and graphene oxide-based materials is given.

Keywords: Graphene oxide, Titanium dioxide, Titania/Graphene oxide composite, Photocatalysts, Water pollution, UV water treatment

Introduction

Nowadays, water pollution is a major global problem that is causing serious and irreparable damage to the natural world and human society. Therefore, new and effective methods of water purification are necessary to minimize pollution. The dyes (colors), dyes intermediates and non-biodegradable organic compounds, which have a central part in textile and dyeing businesses, are some of the most dangerous pollutants of clean water (ranked as number two pollutant, after agriculture) [1]. The dyes in wastewater are a serious problem not only because of their harmful effects on the environment, but also on humans [2] and it is necessary to remove the dyes before disposal. Many methods have been used in wastewater treatment, such as ultrafiltration [3], oxidation [4], biodegradation [5], photocatalytic degradation [6] and adsorption [7]. Among these approaches, sorption is considered as an easy and economic process. The efficiency of any sorption process mainly depends on the physicochemical properties of the used adsorbent [8]. Important properties that a good adsorbent should have are high adsorption capacity, fast adsorption rate, large specific surface area and special surface reactivity [9]. Various materials, such as commercial active carbon, bioadsorbents, natural materials and wastes from agriculture, have been used for adsorption processes [10]. The fast development in the

technology of nanomaterials is important for wastewater treatment. Nanomaterials are well-known for the adsorption of metal ions [11], antibiotics [12] and dyes [13]. Graphene and its derivatives have recently been used in environmental applications. Graphene oxide (GO) and its composites could be used for phenolic [14], heavy metal [15], arsenic [16] and dye removal [17] from wastewater. An important discovery is that GO can be directly used as an effective absorbent for the decoloration of methylene blue (frequently used dye for cotton, wood and silk) [18].

Nowadays, ultraviolet water purification has become the most effective method for water disinfection with an efficiency of about 99.99%. Also, heterogeneous photocatalysis has been proven to be an efficient wastewater treatment method. Since photocatalysts can initiate reactions of decomposition organic contaminants under ultraviolet (UV) or solar radiation without using chemicals or producing chemical wastes, photocatalytic reactions are considered a sustainable methods for the removal of a variety of environmental pollutants [19].

Photocatalytic processes for water purification have numerous advantages over traditional purification methods. The main advantage is that in photocatalytic treatment organic compounds can be completely mineralized with CO₂, H₂O and some mineral acids as final products.

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This is very significant because no waste is produced or additional treatment is needed. Thus, photocatalytic treatments are cheaper and more effective, and more eco-friendly processes for water purification.

The main limiting factors for the use of photocatalysts are their wide band gap, fast electron/hole recombination, low adsorption rate, and cost. In order to increase the photocatalytic efficiency, photocatalytic material has been improved by modifying the surface properties. Most of the photocatalysts are wide band gap semiconductors and it is important to find new photocatalyst materials due to their huge impact on the environmental issues [20].

Heterogeneous semiconductor photocatalysts (TiO_2 , ZnO , SnO_2 , ZrO_2) have recently emerged as an efficient material for purifying water and air and they have exhibited effectiveness for the degradation into less toxic organic compounds of a wide range of organic pollutants [21]. Crystal structure is crucial for the photocatalytic activity of semiconductors, so it is necessary to apply the right optimal method of synthesis and modification. High-temperature synthesis is necessary to obtain highly crystalline photocatalysts, but these processes may also lead to specific surface reduction [22]. Therefore, optimal parameters must be provided during the preparation of photocatalysts. Photocatalytic usage of semiconductors is followed by quick recombination of photoexcited electron/hole pairs, resulting in low quantum efficiency and low photocatalytic activity. Precisely for these reasons, the use of cocatalysts and photocatalyst carriers is becoming more frequent [23]. Recently, much emphasis has been placed on using graphene oxide (GO) supported semiconductor photocatalysts for photodegradation of organic dyes, water splitting of hydrogen evolution and CO_2 photoreduction into hydrocarbon fuel, thanks to the favorable characteristics of the material itself [24].

Graphene oxide

Graphene oxide (GO) hydrophilic sheets have tunable properties and many functions and they show remarkable performance as photocatalysts in water splitting [25]. Also, this material shows fine biocompatibility in comparison with the potential hazard of carbon nanotubes (CNTs) to human health [26]. GO is characterized as a layered solid and has a strong covalent bond along the basal planes with weak hydrogen-bonded intercalated water molecules in the interlayer spacing; its chemical composition is generally written as $\text{C}_x^+(\text{OH})_y^-(\text{H}_2\text{O})^2$ [27]. GO nanosheets, which contain a single atomic layer, provide mechanical support and electric charge carrier transport for photocatalysts [28]. GO is known to intercalate a different species (alcohol, ammonium ion, amine and some polymers) in the interlayer area, where a large number of oxygen-containing functional groups is known to stabilize the colloidal form of GO material [29]. Consequently, GO is a p-doped material because oxygen atoms are more electronegative than carbon atoms [30]. The affinity of graphene oxide can be mainly attributed to the aromatic matrix and it tends to hydrophobic organics by π - π stacking or hydrophobic in-

teractions [31]. Some other favorable characteristics are control of fast electron/hole pairs, tunable band gap, high thermal conductivity, easy processability, a planar structure and low cost as metal-free cocatalyst (replacement for expensive platinum metal) [24].

Preparation of graphene oxide

The most common methods for obtaining graphene oxide are Brodie [32], Staudenmaier [33] and Hummers-Offeman methods [34]. The principle of all three methods is the oxidation of graphite with strong oxidizing agents to exfoliate graphite. The oxygen-containing functional groups and the associated charge on exfoliated graphite oxide may assist in the selective adsorption of compounds and be very useful [29].

Hummers and Offeman [34] prepared GO from graphite flakes using chemical oxidation with potassium permanganate (KMnO_4). The chemical reaction was performed by mixing natural graphite powder (usually fine grade), sodium nitrate (NaNO_3) and concentrated sulphuric acid (H_2SO_4) in an ice bath (mixture had been cooled to 0°C). After mixing the suspension for 30 minutes, KMnO_4 was added in small portions to keep the temperature in the reactor lower than 20°C . After KMnO_4 was added, the reactor was heated to $35\pm3^\circ\text{C}$ and kept at this temperature for additional 30 minutes. As the reaction progressed, the suspension became pasty and the color was brownish grey. At the end of 30 minutes period, water was slowly stirred into the paste to prevent violent effervescence and the temperature was increased to $95\text{--}98^\circ\text{C}$. The diluted brown suspension was mixed at this temperature for 15 minutes. After that period, hydrogen peroxide (H_2O_2) and more water were added to reduce the residual permanganate and manganese dioxide (MnO_2) to colorless soluble manganese sulfate (MnSO_4) and the color of suspension turned bright yellow. The warm suspension was filtered and the filter cake was washed with distilled water, 30% hydrochloric acid (HCl) and ethanol. The dry form of graphene oxide was obtained by centrifugation and dried at 60°C for 24 hours.

Titanium dioxide

Titanium dioxide (TiO_2) is most commonly used photocatalyst in many areas of application and plays a significant role in the remediation of ecological pollutants. The most important properties for which TiO_2 is often used are: high removal efficiency [19], chemical stability (stable in acidic and alkaline aqueous solution) [35], cost-effectiveness (low cost), easy availability [19] and non-toxicity [36].

However, numerous difficulties hinder the maximization of photocatalytic activity in these materials: low adsorption ability [37], wide band gap (3.2 eV), ability to absorb only UV light [38] and fast recombination of photo-induced electron-hole [39].

To solve these problems, a number of strategies have been used such as doping with metallic or non-metallic elements and compounds [40] and hybridization with carbon materials [41]. Recently, hybridization with carbon

nanomaterials has been increasingly used. In particular, hybridization with graphene oxide has received considerable attention as a successful method for charge separation efficiency and increasing substrate adsorption [42]. In TiO_2/GO composite, the photogenerated electrons in TiO_2 can easily transfer from the conduction band to graphene because the two-dimensional π -conjugated structure of graphene sheet and the composite effectively suppresses the charge carrier recombination [17]. GO can be an electron acceptor/transporter for TiO_2 nanoparticles and can significantly improve the life time of electron/hole pairs. Therefore, the TiO_2/GO nanocomposites have a wider light-response area, leading to an improved ability of photocatalysis under UV and visible light [43]. Potential macromolecular photosensitizer GO may also transform wide band-gap semiconductors (like TiO_2) into visible light photocatalysts [44].

Preparation of TiO_2/GO

Different chemical methods have been used for the synthesis of TiO_2/GO materials: sol-gel [45], electro-spinning [42], hydrothermal [46], spin coating [47], liquid phase deposition [36] and electrophoretic deposition method [48]. This paper will discuss liquid phase deposition and sol-gel and hydrothermal techniques, which are also the most common methods in the preparation of these materials.

Jiang et al. [36] prepared TiO_2/GO composites in situ depositing TiO_2 nanoparticles on graphene oxide nanosheets by a liquid phase deposition. Graphene oxide was added to distilled water and ultrasonically exfoliated in a bath sonicator for 30 minutes to reach a light-brown color of graphene oxide dispersion. Ammonium hexafluorotitanate ($(\text{NH}_4)_2\text{TiF}_6$) and boric acid (H_3BO_3) were added into the dispersion and the mixture was vigorously stirred. The prepared solution was sealed and heated at 60 °C for 2 hours in a water bath. Solid material was cooled and separated by filtration, washed and dried in a vacuum. After that, the material was calcinated in a furnace at 200 °C for 1 hour. The resulting product was TiO_2/GO composite.

Atout et al. [45] used a modified sol-gel method to prepare TiO_2/GO composite. First, GO was dispersed in deionized water and stirred for 1 hour, and then stirred with ultrasonication for 1 hour more. The pH of the dispersion was adjusted to 1.5 with nitric acid (HNO_3). Solution of tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$) in ethanol was prepared and stirred for 1 hour. Then, required amounts of GO dispersion were added drop wise to the $\text{Ti}(\text{OC}_4\text{H}_9)_4$ solution under ultrasonication. The obtained solutions were transferred into a Teflon-sealed autoclave and kept at 120 °C for 5 hours. After that, the obtained product was filtered and washed with deionized water and ethanol, dried at 60 °C for 15 hours and calcinated under flowing argon (50 mL/min) at 500 °C for 5 hours with a ramp of 2 °C/min.

Štengl et al. [46] synthesized TiO_2/GO material via a typical hydrothermal process. Titanium oxo-sulfate (TiOSO_4) was hydrolyzed by slow addition of ammonium hydroxide (10% solution NH_4OH) and constant stirring at a

temperature of 0 °C in an ice bath. The reaction mixture was stirred until it reached pH 8.0. The obtained white precipitate was separated using filtration. Depuration of sulfate ions from precipitate with distilled water was confirmed by the BaCl_2 . The wet precipitate was mixed with hydrogen peroxide (15% solution H_2O_2) and a yellow solution of titania peroxo-complex was obtained. GO nanosheets were dispersed using ultrasound in water, added to the yellow precursor of titania peroxo-complex and tempered at a heated mantle in a round-bottom flask with a reflux condensator at 100 °C for 48 hours. The obtained blue TiO_2/GO nanocomposite was filtered off and dried at 105 °C.

Characterization of GO and TiO_2/GO composite materials

Numerous characterization techniques have been used to analyze morphological, physical, photochemical and crystallo-chemical properties of GO and TiO_2/GO composites: X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Raman spectroscopy, Brunauer-Emmett-Teller (BET) surface area, Thermogravimetric Analysis (TGA) and UV-vis Diffuse Reflectance Spectroscopy (DRS). In this paper TEM, SEM, XRD and DRS will be discussed.

TEM and SEM provide microstructures and morphological information for materials. Yang et al. [18] reported the morphology of GO using TEM and the GO sheets were mainly in a single-layer state.

Khan et al. [21] reported the SEM micrograph of TiO_2 , GO and TiO_2/GO (8%) nanocomposites. Their results showed that the TiO_2 nanostructures were uniformly distributed and had a spherical shape, but in an agglomerated form, while GO was in a single-layer formation. The results also showed that the TiO_2/GO composite had uniform distribution of TiO_2 deposited over the GO sheets. The SEM image showed that the lattice in TiO_2/GO (8%) nanocomposites were not visible because of the high concentration of TiO_2 compared to carbon sheets.

Štengl et al. [46] reported the TEM micrograph of graphene oxide and TiO_2/GO nanocomposite. Figure 1 [46] shows that it was also confirmed that TiO_2 nanoparticles were dispersed uniformly on the graphene plane in TiO_2/GO composite using TEM analysis.

Figure 1 TEM Images of a) graphene oxide and b) TiO_2/GO nanocomposite [46]

Figure 2 SEM images of: (a) starting TiO_2 , (b) graphene oxide, (c) TiO_2/rGO (0.5) and TEM image of: (d) TiO_2/rGO (0.5) nanocomposite [49]

Figure 2 [49] shows SEM images of titania and reduced graphene oxide-titania composites synthesized by Morawski et al. titania particles form agglomerates even as free forms (Fig. 2a), even on rGO surface (Fig. 2c).

In fig, 2b thin rGO flakes with up to 5 layers can be seen. Figures 2c and 2d confirm that titania particles cover the rGO flakes, and TiO_2 -decorated rGO hybrid materials are obtained.

XRD was used to achieve structural and crystallographic information. XRD analysis was carried out to confirm the crystalline phases of TiO_2 and TiO_2/GO .

Atout et al. [45] reported that XRD results showed that all samples reveal peaks that can be assigned mainly to TiO_2 in anatase form and a small percent in rutile form in TiO_2/GO composite prepared by hydrothermal route. Rutile phase formation is inhibited when TiO_2 is formed by the sol-gel method in the presence of GO during the synthesis of the TiO_2/GO nanocomposites. Characteristic peaks of GO or reduced GO were not found in any of the composite XRD patterns, which exhibit the reduction of GO during hydrothermal treatment. These results showed a clear influence of the preparation method and the TiO_2/GO weight ratio on the structural characteristics of the prepared composites.

Using XRD patterns, Min et al. [50] also showed that all the peaks for the TiO_2/GO composites were Using XRD patterns, Min et al. [50] also showed that all the peaks for the TiO_2/GO composites were indexed to the anatase phase of TiO_2 , without peaks of layered GO and these results demonstrate that the GO was considerably reduced to graphene sheet during the solvothermal reaction.

Figure 3 a) The XRD pattern of graphene oxide, b) The XRD of TiO_2/GO nanocomposites, diffraction line a - TiGO_001 , b - TiGO_005 , c - TiGO_010 , d - TiGO_050 , e - TiGO_075 , f - TiGO_100 , g - TiGO_200 , h - TiGO_300 , i - TiGO_400 and j - TiGO_500 [46]

Figure 3 [46] shows the XRD diffractograms obtained by Štengl et al for pure GO (a) and TiO_2 -GO composites (b). Diffractograms of TiO_2 -GO composites shows only the anatase phase. It can be seen that as the peak of

GO content increases to 26.50° (arrow G in the figure) characteristic of graphene begins to appear, which can be explained by possible partial reduction of GO. Between 10° and 12° (GO arrow), there is a hint of GO peak, but low intensity is a consequence of small particle size and low concentrations.

Khan et al. [21] showed that characteristic peaks at $2\theta = 25.3^\circ$ and 47.9° are for the anatase phase of TiO_2 which has a more open structure and large surface area for high photocatalytic activity. 2θ peak at 11.97° by GO corresponds to d-spacing of 7.40 nm larger than d-spacing of natural graphite at 0.33 nm and this large spacing provided the information that graphite is oxidized. XRD analysis of TiO_2/GO composite showed an almost similar diffraction pattern as pure TiO_2 . Lower content of GO showed no separate peak, while higher content of GO exhibited a higher amount of anatase phase, which was attributed to GO larger surface area. The average crystallite size of TiO_2 and TiO_2/GO (8%) nanocomposites calculated by the Debye-Scherrer formula was 12.42 nm and 12.50 nm respectively.

XRD patterns of starting TiO_2 , TiO_2 -rGO composites and reference KRONOClean 7000 obtained by Morawski et al. are shown in Figure 4 [49]. It can be seen that starting and modified samples consist of the anatase phase with a small rutile content. Reference sample consists of 100% anatase crystalline phase of TiO_2 . Diffractograms showed that no phase transition occurred after graphene modification which is in accordance with thermal treatment.

Figure 4 XRD patterns of: (1) KRONOClean 7000, (2) Starting TiO_2 , (3) TiO_2/rGO (0.1), (4) TiO_2/rGO (0.5), (5) TiO_2/rGO (1.0), (6) TiO_2/rGO (2.0) [49]

Optical properties of light absorption and the influence of graphene oxide on the band energy on TiO_2 can be detected using UV-vis Diffuse Reflectance Spectroscopy.

Khan et al. [21] reported that TiO_2 absorbs only UV light (≤ 300 nm) because of its wide band gap and rapid recombination of the photogenerated electron-hole pairs, while TiO_2/GO composite could be active photo-catalytically under visible light (400-700 nm).

Štengl et al. [46] showed that different amounts of GO had significant influences on the optical properties of light absorption. With the increasing quantity of GO in the TiO_2/GO nanocomposite, light absorption intensity in the UV region grew and a red shift to a higher wavelength in the absorption edge at about 400 nm was also observed. The band gap of the TiO_2/GO nanocomposite was also reduced depending on the amount of GO (the larger percent of GO, the reduction is bigger).

Atout et al. [45] reported that the band gap values decreased when TiO_2 doped with GO: 3.26 eV for TiO_2 nanoparticles shifting to 3.10 eV in the TiO_2/GO composites. Authors showed that this band gap reduction was produced by the interaction between C and Ti atoms, which reduced the recombination of photo-generated electron-hole pairs.

BET method is an important analysis technique for the measurement of the specific surface area of materials. This method was carried out to measure the specific surface area and determine characteristics of this surface area of GO, TiO_2 and TiO_2/GO .

Wang et al. [50] found that BET surface areas of TiO_2/GO composites are larger than pure TiO_2 . This can be explained by the presence of GO in the composite. Graphene oxide has an extremely high surface area and also prevents the agglomeration of TiO_2 nanoparticles.

Tri et al. [51] found that their TiGO material exhibits higher specific surface area and pore volume than pure TiO_2 . This can be due to the distribution of TiO_2 particles onto sheets of graphene oxides. High surface area and pore volume can provide a more active site for interaction with molecules of pollutants.

Photocatalytic activity of nanocomposite materials based on metal oxides are in function of their physical characteristics as surface area, functional groups and surface defects. Khan et al. [21] synthesized series of $\text{TiO}_2/\text{graphene oxide}$ nanocomposites with 2% to 8% and demonstrated that nanocomposites have a greater surface area (64-91 m^2/g) than pure TiO_2 (56 m^2/g). Also, their results show that pore size distribution decreases with graphene oxide content increase from about 21 nm for pure TiO_2 to 16-4 nm for nanocomposites.

Štengl et al. [46] found that their TiO_2 -graphene oxide composites have a surface area in interval 800-200 m^2/g . These results are relatively low compared to the theoretical values for graphene oxide, but significantly larger than pure TiO_2 catalysts. As can be seen, specific surface decreases with the increase of graphene oxide content, which can be explained by the agglomeration of GO particles. Since TiO_2 particles coat GO nanosheets, the specific surface of TiO_2 -GO nanocomposites is mostly determined by anatase nanoparticles.

Natarajan et al. [52] confirmed that photocatalytic activity of $\text{TiO}_2/\text{graphene oxide}$ nanocomposites is strongly affected by surface area, which is correlated with GO content. Surface area increases with GO content increase and reaches a maximum of 7% GO. Better surface area, pore size and pore volume had a great impact on photocatalytic activity.

Table 1. BET method: Summarizing results of the specific surface area and pore volume for GO, TiO₂ and TiO₂/GO

Catalysts	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Reference
TiO ₂	45.20		
TiGO-10%	79.20		[50]
TiGO-20%	83.60		
TiO ₂		40.10	
TiGO	25.00	68.90	[51]
TiO ₂	55.93	0.55	
TiO ₂ /GO (2%)	63.70	0.43	
TiO ₂ /GO (4%)	72.40	0.33	[21]
TiO ₂ /GO (6%)	81.10	0.21	
TiO ₂ /GO (8%)	91.25	0.12	
TiGO_001	100.20	0.6530	
TiGO_005	151.40	0.7846	
TiGO_010	195.70	1.4668	
TiGO_050	185.70	0.6230	
TiGO_075	119.20	0.6501	
TiGO_100	168.40	0.6687	[46]
TiGO_200	178.00	0.6247	
TiGO_300	78.90	0.6180	
TiGO_400	68.60	0.5545	
TiGO_500	78.10	0.6089	
TiO ₂	1.06	2.40	
GO	2011.00	0.02	
TiO ₂ /GO 0.5%	63.58	0.11	
TiO ₂ /GO 1%	35.57	0.29	
TiO ₂ /GO 2%	73.57	0.12	[52]
TiO ₂ /GO 5%	80.56	0.25	
TiO ₂ /GO 7%	97.08	0.26	
TiO ₂ /GO 10%	92.55	0.16	

Results of numerous studies presented in Table 1. show that the presence of graphene oxide in composites with TiO₂ strongly affects specific surface areas. Mostly, the GO component leads to an increase in specific surface area which later leads to better in general activity. Greater surface area means more active sites on catalyst surface so this leads to the improvement of TiO₂ as photocatalyst. As can be seen, TiO₂/GO composites have better surface characteristics than pure TiO₂.

Application of GO and TiO₂/GO composite

Min et al. [53] synthesized chemical-linked graphene/TiO₂ composites. These prepared composites are employed as photocatalysts to decolorize methylene blue solution under UV and visible light irradiation. 30 mg of powdered composites were dispersed in 100 mL of MB solution concentration 2x10⁻⁵ M. The results showed a remarkable enhancement in visible light-induced decolorization. Graphene/TiO₂ composites were compared to P25 and pure TiO₂, and photocatalytic activity of composites was higher than P25 and pure TiO₂ under UV irradiation. The enhancement factor of graphene/TiO₂ composites was 2.55 and 2.78 than P25 under UV and visible light irradiation, respectively. The presence of gra-

phene in composites improved the photocatalytic activity of TiO₂ by effective charge transfer.

Yang et al. [18] reported that GO can be used as an effective adsorbent for MB removal. GO has a great adsorption capacity, which is comparable with other good adsorbents. The advantage of GO over other adsorbents is a very fast process. The maximum adsorption of GO for MB removal is 714 mg/g. For the initial concentration of MB lower than 250 mg/L, removal efficiency is higher than 99%.

Zhang and Pan [54] prepared TiO₂(P25)/graphene composite by thermal reduction of graphene oxide in order to improve visible light photocatalytic activity. The photocatalytic activity was tested by decolorization of 12 mg/L MB solution using 100 mg of photocatalysts. They found that decolorization of MB was about 70% for P25/graphene composite after 5 h, in contrast, the efficiency of pure P25 was only 10. The presence of graphene oxide leads to an increase the specific surface area of the composite which contributed to more MB molecules being adsorbed on the composite surface and reacting with photocarrier. Štengl et al. [46] prepared TiO₂/graphene oxide nanocomposite by thermal hydrolysis of graphene oxide and titania peroxo-complex suspension. Photocatalytic

activity of TiO_2/GO nanocomposite in poly(hydroxyethyl methacrylate) was determined from the kinetics of the photocatalytic degradation of butane in the oxygen atmosphere under UV and visible light, with a measuring time of 2 hours. The results showed that the best photocatalytic activity under UV and visible light have samples with graphene oxide content 100 mg denoted TiGO_100 ($k = 0.03012 \text{ h}^{-1}$) and with graphene oxide content 75 mg denoted TiGO_075 ($k = 0.00774 \text{ h}^{-1}$). The presence of graphene oxide provides very good support for TiO_2 deposition and enhances the adsorption ability of the TiO_2/GO nanocomposite and butane photodegradation as an acceptor and photosensitizer.

Nguyen-Phan et al. [55] presented a one-step colloidal blending method for the preparation of $\text{TiO}_2/\text{graphene}$ oxide composites and these prepared composites were

employed for methylene blue photodegradation. The dye uptake capacity strongly increased in the presence of the composites compared to pure TiO_2 . The quantity of methylene blue was directly proportional to graphene oxide content and the sample with 10% GO exhibited the best adsorptivity (37.3 mg/gcatalyst), along with the lowest kads (0.00005 g/mg min), compared to lower proportions of GO. In other experiments, the photocatalytic activities of pure TiO_2 and TiO_2/GO composites were detected under UV and visible light after dark adsorption. They found that decolorization of MB was more than 90% for $\text{TiO}_2/\text{graphene}$ composite, compared to the 50% efficiency of pure TiO_2 . 10GO/Ti sample (with 10% graphene oxide) eliminated all of the dye after 1 h under UV irradiation and approximately 95% dye under visible light.

Krishnamoorthy et al. [20] reported photocatalytic

Table 2. Summarizing photocatalytic activity for GO and TiO_2/GO

Catalysts	Pollutant	Activity	Reference
Graphene oxide	Phenoxazin-3-one	35-44% reduction in 40 min	[20]
Graphene oxide - TiO_2 composite	Methylene blue	Over 90% degradation under UV light, 30-50% degradation over visible light	[53]
$\text{TiO}_2(\text{P25})/\text{graphene}$ composite	Methylene blue	70% decolorization after 5 h of irradiation in visible light	[54]
$\text{TiO}_2/\text{graphene}$ oxide composite	Methylene blue	More than 90% in UV light	[55]
TiO_2/GO composite	Methylene blue	Adsorption rate after 35 min 5-93%; UV irradiation (140 min) after adsorption (35 min) – degradation rate 28-97%	[50]
TiO_2 nanoparticles modified with GO and rGO	Remazol black B	Maximum degradation 99.9% at pH 6-7 after 60-75 min irradiation	[56]
TiO_2/GO nanocomposite	Methylene blue and ciprofloxacin	Up to 99% degradation of MB after 45 min with TiO_2/GO against 52% degradation with TiO_2 after 120 min; 97% degradation of ciprofloxacin with TiO_2/GO after 60 min, while only 65% was degraded with TiO_2	[21]
$\text{TiO}_2\text{-GO}$	Methyl orange	87% degradation after 15 min for $\text{TiO}_2\text{-GO}$, while Degussa P25 shows 38% degradation for the same period	[57]
TiO_2/GO nanocomposite	2,4-dichlorophenoxyacetic acid	Up to 100% degradation after 240 min of UV irradiation for TiO_2/GO nanocomposites against 62% with pure TiO_2	[52]
TiO_2/GO nanocomposites	Reactive brilliant red X-3B	Up to 98% degradation after 40 min of UV irradiation	[58]

properties of graphene oxide nanostructures by assessing the reduction in resazurin (RZ) into resorufin (RS) under UV irradiation. RZ is a redox indicator (phenoxazin-3-one), blue color, used in many biological assays. After 40 min of irradiation, the photocatalytic reduction percentage of RZ was estimated as 34.93%, 39.09% and 44.10% for 0.5 mg, 0.75 mg and 1 mg amount of GO, respectively.

As can be seen from Table 2. TiO_2 /graphene oxide-based materials have very good photocatalytic activity for the degradation of various organic pollutants. Degradation percents are very high after relatively short irradiation time. Also, it is obvious that composites are significantly more active than unmodified TiO_2 photocatalysts. The improvement of photocatalytic activity of TiO_2 after modification or combination with graphene or graphene oxide can be observed by the fact that TiO_2 /GO nano-composite can be photocatalytic active even in visible light irradiation, while pure TiO_2 is active only under UV irradiation. These results show that TiO_2 /GO composite materials have great potential for photocatalytic usage in wastewater treatment or other degradation processes.

Conclusion

Graphene oxide-based materials can be used as support or modifier of titanium dioxide-based photocatalysts. Graphene oxide significantly improves efficiency by shifting band gap to visible light region. Also, the graphene oxide component improves sorption characteristics of composites, so pollutant molecules become closer to photoactive centers on the surface of the catalysts. Composites of graphene oxide and photocatalytic semiconductors have a future and represents a topic for further research.

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Izvod

KRATAK PREGLED PRIMENE KOMPOZITA NA BAZI TITANIJA-GRAFEN OKSID KAO FOTOKATALIZATORA

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Nove i efikasne metode prečišćavanja vode su neophodne kako bi se zagađenje svelo na minimum. Mnogo metoda se koristi za prečišćavanje otpadnih voda, ali se adsorpcija smatra jednostavnim i ekonomičnim procesom. Efikasnost bilo kog procesa sorpcije uglavnom zavisi od fizičko-hemijskih svojstava upotrebljenog sorbenta. Budući da fotokatalizatori mogu pod dejstvom ultraljubičastog zračenja ili zračenja sunčeve svetlosti pokrenuti reakcije razgradnje organskih zagađivača bez upotrebe hemikalija ili stvaranja hemijskog otpada, fotokatalitičke reakcije se smatraju održivim načinom za uklanjanje različitih zagađivača životne sredine. Tretmani vode ultraljubičastim zračenjem postali su najefikasniji postupci za dezinfekciju i prečišćavanje vode. Heterogeni poluprovodnički fotokatalizatori nedavno su privukli pažnju kao potencijalno efikasni materijali za prečišćavanje vode. Kristalna struktura je presudna za fotokatalitičku aktivnost i efikasnost poluprovodnika, tako da tokom pripreme fotokatalizatora moraju biti obezbeđeni optimalni parametri. Kako bi se prevazišli problemi sa upotrebom poluprovodnika, jedno od rešenja je upotreba fotokatalizatora i nosača fotokatalizatora. U poslednje vreme je stavljen veliki naglasak na upotrebu poluprovodničkih fotokatalizatora na nosačima od grafen oksida. U ovom radu je dat kratak pregled kompozitnih materijala na bazi titan-dioksida i grafen oksida.

Ključne reči: Grafen oksid, Titanijum dioksid, Titanija/Grafen oksid kompozit, Fotokatalizatori, Zagađenje vode, UV tretman vode