ENHANCED DECOLORIZATION OF METHYLENE BLUE IN AQUEOUS SOLUTION OVER COMPOSITE PHOTOSENSITIZED TiO₂ CATALYST BY VISIBLE LIGHT

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ABSTRACT

The synergistic effect of coupling a squaraine dye (SQ) as a photosensitizer with a composite catalyst containing TiO₂ and reduced graphene oxide (TiO₂/rGO) has been investigated. A three-component TiO₂/rGO/SQ catalyst was synthesized and its ability to improve the decoloration of Methylene Blue (MB) in aqueous solution under irradiation of visible light has been tested. XRD, SEM, TEM and VIS spectroscopy were employed to characterize the samples. Squaraine dye being excited by visible light is capable of transferring electrons to TiO₂/rGO material which contributes to increasing the apparent decolorization rate constant up to 0.028 mol/l.s. that is 18 times higher than that of the bare titania.

Keywords: photocatalysis, squaraine, photosensitizer, TiO₂, graphene.

INTRODUCTION

Water pollution due to the textile industry is a matter of great concern these days. The dye effluent contains given substances which could be toxic, carcinogenic or mutagenic to living organisms [1]. Treatment of dye effluent is a significant challenge because wastewater can be complex containing different types of chemicals. The use of semiconductor photocatalyzed degradation of organics in the wastewater pollutants is a promising method [2, 3]. Several semiconductors such as TiO₂, ZnO, Fe₃O₄,WO₃, SnO₂, ZrO₂, CdS, SrTiO₃, ZnS have band gap energies sufficient for catalyzing a wide range of chemical reactions [4, 5]. Considerable efforts have been devoted to the design of long-term operating photocatalytic systems exhibiting a high efficiency and stability for transforming light into chemical energy. Fenton and photo-Fenton catalytic processes, where Fe³⁺ cations have a beneficial effect because of the ability of Fenton reactants to consume H₂O₂ in the aqueous phase [6 - 9] have been studied under various experimental conditions for organic pollutions removal from waste waters. The overall efficiency of the photocatalysts strongly depends on the life time of the separated electron-hole charge carriers generated under UV light irradiation. In chemically effective semiconductor photocatalysts the recombination of the electron-hole pairs could be suppressed by trapping the photogeated electron, hole or both of them near the surface. Further these charges are transferred across the inter-phase boundary and upon reaching the adsorbed substances they can become involved in oxidation-reduction reactions [10]. Heterogeneous photocatalysis using TiO₂ as photo-catalyst appears to be the most widely deployed purification approach because of the strong oxidizing potential of the TiO₂ positively charged holes providing the best combination between catalytic performance and stability in aqueous media [11, 12]. Doping the TiO₂ nanoparticles with noble metals has been proven to be efficient approach for increasing its photocatalytic
activity. The photogenerated electrons, being injected in the conduction band of the titania, might be transferred to the lowest unoccupied molecular orbital (LUMO) of the dopant and subsequently further to the absorbed species, which are being reduced. Coupling the titania with gold, platinum, palladium and silver have been widely applied for improving the destructive power of the photocatalysts acting as traps of electrons by transferring them to the outer system [13 - 15]. These photocatalysts can be activated only under ultraviolet light (UV) irradiation, under which they work efficiently. However, their activity is limited as UV light is absorbed by the ozone in the stratosphere and only 4 - 6 % can reach the earth surface. In order to overcome this disadvantage and to extend the efficiency of photocatalysts to the visible area, TiO₂ is being doped with metal ions, including Fe, Au, Gd, and Ag, or non-metallic ions such as C, N, and S [16 - 18].

Reduced graphene oxide (rGO) can be easily mixed with different polymers and other materials, thereby improving the mechanical and electromagnetic properties [19, 20]. Moreover, the surface properties of the graphene make it suitable for the production of composite material in combination with TiO₂ having excellent adsorption which can facilitate efficacy in photodegradation of pollutants. Thanks to the unique properties of graphene, the composite simultaneously combines three excellent properties, i.e., increasing the adsorption of pollutants, expanding the absorption range of light and separation of charges by efficiently transferring electrons from TiO₂ to the graphene (rGO). On the other hand, some transition metal based dyes can be used as sensitizers of TiO₂ in the visible spectrum because of their high molar absorption coefficient as well as a broad absorption band [21 - 24]. Due to the exceptionally rigid, planar and zwitterionic structures, squaraines have strong absorption [molar absorptivity (ε) equal or more than 10⁴ L mol⁻¹ cm⁻¹] in the visible to the near-IR region. The intense absorption properties of squaraines are suitable for applications related to the photosensitization phenomenon [25]. Sensitizing TiO₂ semiconductor with squarine may produce a highly effective photocatalytic system due to the electron transfer from the excited dye to the CB of TiO₂ or pre-adsorbed molecular oxygen. The effective photocatalytic decomposition of different types of pollutants through dye-sensitized TiO₂ systems is due to the simultaneous effect of both semiconductor and dye where the critical factor in this cooperation is the charge transfer (e⁻ - h⁺) between them as the mechanism of the charge transfer and the type of active oxidizers produced are affected by the nature of the irradiation source. Typically, these photocatalysts are activated by irradiation with visible or sunlight, but the best efficiency for contaminant degradation is generally obtained under solar light [26].

The purpose of this work is to investigate the synergistic effect resulting from the combination of a squaraine dye (SQ) acting as a photosensitizer on the one hand and a TiO₂/rGO composite on the other hand. To accomplish this, a TiO₂ / rGO / SQ catalyst was synthesized at a concentration of 5% rGO to TiO₂ and a 1: 3 ratio between TiO₂ / rGO and SQ, which according to the discovery of Z. Li et al. [27]. The GrO concentration was selected from literature data as optimal for the operation of TiO₂/rGO mixed catalysts [28]. The selected ratio shows the highest rate constant of the oxidation reaction and the highest degree of destruction of the studied dye. The photocatalytic experiments were carried out under visible light irradiation in order to examine the ability of squaraine dye for enhancing the photoactivity of the TiO₂/rGO nanocomposite in decolorization of Methylene Blue (MB).

**EXPERIMENTAL**

**Preparation of the photocatalyst**

Graphite powder (≥150 μm, ≥ 99.99 % trace metals basis; Sigma-Aldrich) sulphuric acid (98 %, Merk), sodium nitrate, potassium permanganate, hydrogen peroxide solution (30 wt. % in H₂O), were used for the synthesis of graphite oxide. TiO₂ (Degussa, P25) and Methylene blue (MB) were employed as an ingredient for preparation of the catalyst and as substrate, respectively. The following Sigma-Aldrich chemicals were used as commercial products of analytical grade, without further purification for the synthesis of squaraine dye: 1,3,3-trimethyl-2-methyleneindoline, squaric and ethyl l-lactate.

Graphene oxide was synthesized using Modified Hamer’s method. It can be divided into three stages. “Cold stage” - 5 gr of graphite, 115 ml sulfuric acid and 2.5 g of sodium nitrate were mixed in an ice bath for 30 minutes. Then 15 g of KMnO₄ was slowly added while stirring over two hours keeping the temperature below 5°C since upon the reaction KMnO₄ + H₂SO₄ = K₂SO₄ + MnO₂ + H₂O; the resulting MnO₂ decomposes explosively at a temperature about 50°C. During the second
“mid-stage” the temperature was raised to 45°C under stirring for one hour. Finally, 230 ml distilled water was added, and the temperature was raised to 95°C while stirring for 30 min. The “high-temperature stage” - Reducing the residual permanganate and manganese dioxide to colorless soluble manganese sulfate was achieved by adding 600 mL distilled water and 150 mL H₂O₂ (9 %) to the mixture. The suspension was filtered, washed in 5 % HCL then distilled water to reach neutral pH and dried at 60°C. The dried cake was added to 50 mL of water under stirring then sonicated for 6 hours. The dry form of graphene oxide was obtained by centrifugation, followed by drying at 60°C [29].

The TiO₂/rGO composite containing 5 wt. % rGO was prepared by dissolving ten milliliters of concentrated GO solution (∼150 mg GO) in 500 mL DI water and then put under ultrasonic dispersion for about 5 h. Then into the solution was gradually added 0.5 g of TiO₂ powder to anchor the TiO₂ particles onto the surfaces of GO. In order to turn GO into graphene 3 g of sodium hydroxide was then added as well. After 10 h of vigorous stirring the resulting solution was transferred into Teflon-sealed autoclave and kept under 120°C for 24 h then the resulting suspension was washed with DI water, filtered and dried at 60°C. The reference rGO sample was prepared similarly without adding TiO₂ into the hydrothermal vessel.

For squaraine dye synthesis (Fig. 1) 1,3,3-trimethyl-2-methyleneindoline (10 mmol, 1.73 g ~ 1.77 mL), squaric acid (5 mmol, 0.57 g) and ethyl L-lactate (10 mL), were poured into a 100-mL Erlenmeyer flask. The reaction mixture was then heated in a microwave oven at 450 W to 140°C. After 1 min, the reagents were dissolved, and the liquid turned blue. The reaction was maintained at 140°C for 4 min. The mixture was allowed to cool down to room temperature then diluted with ethanol (10 mL) and poured in water (200 mL) with ice (50 g). The resulting precipitate was filtered off, washed with 200 mL hot water until the filtrate is colorless and air dried.

The ternary composite catalyst TiO₂/rGO/SQ was prepared by adding 20 mg of SQ into 70 ml water suspension containing 60 mg TiO₂/rGO. After continuously ultrasonication for 3 h, and subsequent stirring for 2 h the resulting product was filtered and dried at 60°C till the constant mass was reached.

Methods and Experimental setup

X-ray diffraction (XRD) measurements were carried out at room temperature using a Bruker D8 Advance powder diffractometer with Cu Kα radiation source and SolIX detector. The samples were scanned at 20 angles ranging from 10° to 80° at a scanning rate of 0.04° s⁻¹. The X-ray power was operated with a current intensity of 40 mA applying a voltage of 45 kV. Morphologies of the photocatalyst were examined with a transmission electron microscope (JEOL 2100). VIS spectra of the samples were recorded by a Vis-scanning spectrophotometer Shimadzu UV-2700.

Studies on photocatalytic decolorization of MB were performed in a self-constructed cylindrical reactor (150 mm outer diameter, 130 mm high) at 25°C, maintained by recirculating water through the reactor jacket. Photocatalytic efficiency of the catalyst was evaluated based on the degradation rate of MB (10 mg/l) in water under visible light irradiation employing halogen lamp. The reaction suspension of 400 ml containing 10 mg L⁻¹ MB and 0.1 g L⁻¹ catalyst was stirred for 30 minutes in dark to achieve a possible adsorption-desorption equilibrium on the catalyst surface. Samples were collected at every 20 min and filtered (Whatman, Grade 42) prior to measuring its absorption in the visible spectrum.

RESULTS AND DISCUSSION

Catalysts characterization

Crystalline phase composition of prepared catalytic samples were analyzed by XRD. Fig. 1 shows the XRD patterns of samples used in our study. The main peaks in the spectrum of the TiO₂/rGO/SQ composite catalyst correspond to a tetragonal TiO₂ – anatase, whose content dominates over that of the rutile (73:23 %, respectively),

![Fig. 1. Preparation of squaraine dye.](image-url)
which is also represented in the spectrum. By comparing the XRD spectra of the individual samples presented on Fig. 2, we can see that, during the hydrothermal treatment as a stage of the synthesis, GO has successfully turned into rGO. Proof of this is the disappearing of the diffraction peak at $2\theta = 10.18^\circ$ on the TiO$_2$/rGO/SQ spectrum which is indicative for GO and its shift to $2\theta = 25^\circ$ characteristic for rGO [30].

Peaks characteristic for graphene are not visible on the composite catalyst spectrum since the rGO main peak at about $2\theta = 25^\circ$ overlaps with that of the anatase $2\theta = 25.54^\circ$, even more so it is in low concentration and possibly not detectable by XRD. Those ones visible on the SQ and TiO$_2$/rGO/SQ spectra at $2\theta = 11.5^\circ$ and $14.2^\circ$ confirm successful SQ attachment to the TiO$_2$/rGO support during the catalyst synthesis. The morphology of the sample prior attaching the SQ was studied by high resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM). Figs. 3 and 4 represent the SEM and TEM images of a TiO$_2$/rGO sample, respectively. One can be seen from the pictures that the titania clusters are distributed on rGO sheets. The size of the individual TiO$_2$ particles measured from TEM images were in range 15 - 20 nm.

**Photocatalytic activity testing**

Titanium dioxide supported on rGO sensitized by SQ was tested in photocatalytic decolorization of MB in aqueous solution. The batch reactor experimental results were assessed in terms of maximum of absorption for

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**Fig. 2.** The XRD patterns of TiO$_2$ GO, SQ, rGO and TiO$_2$/rGO/SQ samples. ( ▼ - anatase, • - rutile, ♦ - SQ).

**Fig. 3.** SEM micrograph of TiO$_2$/rGO/SQ sample.

**Fig. 4.** TEM image of TiO$_2$/rGO/SQ sample.
The blank experiment to assess the self-destruction of MB was done. The concentration of MB was calculated at equal intervals according to the absorption spectra during the process applying Beer-Lambert law. The result showed that the self-conversion was in frames of 4% for 120 min of irradiation. Higher degradation efficiency in terms of MB was observed using pure TiO$_2$ reaching around 16% conversion under the same conditions. Fig. 5 represents the visible absorption of the reaction solution in the course of the experiment in the presence of the TiO$_2$/rGO/SQ sample under visible light.

The percent decolourization efficiency ($D$) was evaluated after analysis by the eq. (1) using the data from Fig. 5 that represents the MB decay in the course of illumination.

$$ D = \frac{C_0-C_t}{C_0} \times 100 $$

where $C_o$ is the initial concentration of dye solution in ppm and $C_i$ is the concentration of dye solution after irradiation in selected time interval in mol L$^{-1}$.

It was found that the nanocomposite showed much higher degradation rate than the pure TiO$_2$, reaching above 90% conversion that indicates that the TiO$_2$/rGO/SQ nanocomposite possessed remarkable photocatalytic activity under visible light.

A plot of ln[MB] versus $t$ gives a straight line with 0.996 coefficient of determination. So, the reaction can be considered as first order in MB. Further using the first order kinetics we were able to calculate the apparent rate constants of the destruction of MB according to eq. (2).

$$ \ln\left(\frac{C_0}{C}\right) = k_{app} t \quad \text{or} $$

$$ C_t = C_0 e^{-k_{app} t} $$

where $C_0$ is the concentration of MB at the moment of turning on the VIS lamp and $C$ is its concentration at time $t$.

The corresponding apparent rate constants were calculated according to the plot of ln(Co/C) versus time (Fig. 7). Calculated statistics for all scatter plots showed strong positive correlation coefficients and lines passing across the points fit reasonably well. The coefficients are as follows: self destruction, $r = 0.984$; bare TiO$_2$, $r = 0.966$; TiO$_2$/rGO/SQ, $r = 0.993$. The highest rate constant reaching 0.028 mol L$^{-1}$ s$^{-1}$ exhibited the reaction in the presence of composite catalyst TiO$_2$/rGO/SQ that is 18 times higher than that in the presence of the bare titania. As TiO$_2$ has a wide energy band gap of 3.2 eV and remains transparent to the visible light its photonic efficiency is close to zero because of the insufficient photon energy needed for excitation of the electrons from the valence to the conduction band. The photodegradation of the dye, in this case, is realized by the photosensitization procedure as the light is almost exclusively absorbed by the dye with subsequent transfer of the excited electron into the conduction band of the semiconductor leaving behind a hole localized on the dye. Then the atmospheric molecular oxygen acts as a scavenger for the separated electron so that the recomb-
Combining the rGO and SQ together with TiO₂ is found to be the most effective MB destroyer, having apparent rate constant 0.028 mol L⁻¹ s⁻¹, as mentioned above. This result was achieved as each of these three components gives its contribution to the overall decomposition process shown in Fig. 8.

CONCLUSIONS
A ternary squaraine photosensitized titania catalyst containing 5 wt. % reduced graphene oxide was synthesized. The novel catalyst TiO₂/rGO/SQ exhibited remarkable activity with respect to photo-decolorization of MB in aqueous solution under visible light irradiation leading to increasing the apparent rate constant of the process 18 times compared to that of the bare titania.

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Fig. 7. Apparent rate constants of MB degradation under Vis-light.

Fig. 8. Schematic illustration of the MB destruction mechanism.
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