



Photocatalytic activity enhancement of anatase–graphene nanocomposite for methylene removal: Degradation and kinetics



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ABSTRACT

In the present research, the TiO₂–graphene nanocomposite was synthesized by an eco-friendly method. The blackberry juice was introduced to graphene oxide (GO) as a reducing agent to produce the graphene nanosheets. The nanocomposite of anatase–graphene was developed as a photocatalyst for the degradation of methylene blue, owing to the larger specific surface area and synergistic effect of reduced graphene oxide (RGO). The UV spectroscopy measurements showed that the prepared nanocomposite exhibited an excellent photocatalytic activity toward the methylene blue degradation. The rate of electron transfer of redox sheets is much higher than that observed on GO, indicating the applicability of proposed method for the production of anatase–RGO nanocomposite for treatment of water contaminated by cationic dye. The prepared materials were characterized with Fourier transform infrared spectroscopy, X-ray diffraction, Brunauer–Emmett–Teller surface area measurement, scanning electron microscopy and transmission electron microscopy. A facile and rapid route was applied for the uniform deposition of anatase nanoparticles on the sheets. The resulting nanocomposite contained nanoparticles with a mean diameter of 10 nm. A mechanism for the photocatalytic activity of nanocomposite was suggested and the degradation reaction obeyed the second-order kinetics. It was concluded that the degradation kinetics is changed due to the reduction of GO in the presence of blackberry juice.

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1. Introduction

The tremendous increase in the use of dyes over the past few decades has eventually resulted in the flux of organic substances into the environment which are mostly non-degradable in natural condition. Many industries such as paint, textile, plastic, tannery, paper and rubber discharge wastewaters containing anionic and cationic dyes which in turn contaminate the natural water and soil. Different techniques are applied for the water and wastewater treatments to remove these hazardous materials. These processes can be performed physically as adsorption [1,2] and/or chemically as photocatalytic reactions [3]. The TiO₂ based composites show interesting photocatalytic properties and anatase is renowned as a great of importance photocatalyst with the high degradation capacity for degradation of dyes [4]. The evolution of hydrogen and oxygen in the presence of TiO₂ particles under the sunlight irradiation causes the formation of OH radicals as a result promotes the photocatalytic activity [5]. Therefore, the techniques for production nano-sized TiO₂ were developed as effective ways to overcome these environmental problems [6].

The photocatalytic efficiency of single phase anatase was seriously limited due to the rapid recombination of photo-generated electrons

(e⁻) and holes (h⁺) pairs [7]. In order to enhance the photocatalytic activity, many efforts were presented for coupling anatase with other semiconductors to form nanocomposite. The strategy of coupled nanocomposites has been proved to prevent the rapid recombination of photo-generated electrons and holes pairs. The appropriate matching in the photocatalytic systems drives the electrons from one particle to neighbors as a result, electrons and holes separation occurs, steadily. Thus, the interaction between components in the nanocomposite plays an important role in the photocatalytic activity.

Graphene is a flat monolayer of carbon atoms packed into a two-dimensional honeycomb lattice [8]. Graphene oxide (GO) and reduced graphene oxide (RGO) are interesting materials for production of TiO₂–graphene based photocatalysts [9,10]. Recently, these materials have found a great of attention in the synthesis of photocatalysts due to superior electrical conductivity, high specific surface area and chemical stability. GO has been mainly considered as a precursor for cost-effective, large-scale production of TiO₂-based photocatalysts. The layers of GO contain large amounts of oxygen functional groups, decorating the basal plane and edges of a typical graphene sheet [11]. These functional groups are responsible for insulating behavior of GO. The incremental removal of oxygen can move the material to a semiconductor and ultimately to a graphene-like material. Although a lot of methods have been developed for the preparation of graphene sheets, the most suitable and efficient approach was the solution based chemical

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reduction of GO to RGO due to low cost and feasibility of production in a controllable condition [12,13]. For example, hydrazine was used to reduce graphene oxide by stirring in hot water under acidic condition [14]. GO and RGO can be readily dispersed in water to yield the stable dispersions by simple sonication. Furthermore, the active sites cause the limitation of nanoparticle growth and improvement in the stability and dispersion of nanoparticles on GO or RGO. The attached nanoparticles are also helpful for electrons and holes separation, maintaining the excellent properties of photocatalyst [15].

From the engineering point of view, a fine control of TiO₂–graphene structure is required because the performance of system depends on the reduction state of graphene oxide and TiO₂ particle morphology which can be strongly affected by material interfaces and interactions [16]. Various techniques have been developed for fabricating the high reactive TiO₂–graphene nanocomposite, which include the hydrothermal [17,18], direct redox reaction [19], sol–gel [20], solvo-thermal treatment [21], spark plasma [22], ultrasonic spray pyrolysis [23], chemical exfoliation [24], graphitization [25], hydrogels [26] and spin-coating [27]. These approaches have generally produced TiO₂–graphene composites with weak interactions among TiO₂ and graphene or are more complex to apply in practice. In fact, the formation of chemical bonds between TiO₂ and graphene is the critical point in the performance of photocatalyst. Therefore, the new strategy is urgently required to develop advanced TiO₂–graphene nanocomposite. On the other hands for improvement of TiO₂–graphene nanostructure, it is preferable to use nontoxic reagents.

In recent years, plant-mediated biological synthesis of nanoparticles is gaining importance due to simplicity and eco-friendliness. Blackberry is a fruit of interest because of its high content of anthocyanins and ellagitannins as well as other phenolic compounds which contribute to its high antioxidant capacity. The high antioxidant activity of blackberries is based on their oxygen radical absorbance capacity compared to other fruits [28]. Worldwide commercial production of blackberry is estimated to be approximately 155 thousands tons. Blackberries are mostly consumed fresh but can be processed as juice. North America, Europe, Asia, South America, Oceania Central America and Africa are the main regions for blackberry production.

According to the presented introduction, this investigation attempted to synthesize the TiO₂–RGO nanocomposite for the photocatalytic degradation of methylene blue under sunlight irradiation. Recently, the authors have determined the optimal content of GO in a sol–gel route to fabricate the TiO₂–GO nanocomposite as a photocatalyst with high uniformity [29]. The average size and content of TiO₂ nanoparticles could be easily controlled by adjusting the appropriate content of GO. It was shown that the formation of TiO₂ nanoparticles favors the enhancement of photocatalytic activity. However, it is well known that the reduced graphene oxide usually exhibit the higher photocatalytic activity. Therefore, in this study smaller anatase nanoparticles were uniformly deposited on RGO by modifying the reduction condition of GO in the presence of blackberry juice. This method environmentally features the reduction of GO and attachment of TiO₂ by eco-friendly technique. The aim of the present work is to increase the knowledge on the degradation mechanism of MB by TiO₂, TiO₂–GO and TiO₂–RGO. Finally, a detailed study was presented for MB degradation mechanism by kinetic model.

2. Materials and Methods

2.1. Materials

Graphite powder was obtained from Merck Company (104206, purity > 99 wt%, Germany). Potassium manganite (223468, purity > 98 wt%) and titanium butoxide (24412, purity > 97 wt%) were purchased from Sigma Aldrich (USA). Sulfuric acid (98 wt%), hydrochloric acid (37 wt%) and ethanol were supplied by Merck Company. Hydrogen peroxide was a product of Sigma Aldrich. The blackberry juice used for

the reduction process was prepared by taking local blackberry (Urmia, Iran). Methylene blue (C₁₆H₁₈ClN₃S, 115943) corresponding to molecular weight of 319.85 g·mol⁻¹ was obtained from Merck. All chemicals were of guaranteed or analytical grade reagents, commercially available and used without further purification. The water used throughout this work was the deionized grade.

2.2. GO and RGO Preparations

Graphene oxide was prepared from purified natural graphite by a modified Hummers method [30]. The graphite powder (10.0 g) was added to the concentrated H₂SO₄ (230 ml) in an ice bath. KMnO₄ (30.0 g) was gradually blended under stirring with the obtained suspension. The mixture was stirred at 35 °C for 2 h and then deionized water (150 ml) was slowly added to the mixture, followed by rapid stirring the mixture at 98 °C. The suspension was further diluted with deionized water and the reaction was terminated by blending H₂O₂ (35 ml) under stirring at room temperature, followed by washing with deionized water several times.

The aqueous colloid of GO was prepared by dispersing 0.2 g graphene oxide into 40 ml of blackberry juice, resulting in an inhomogeneous dispersion. The suspension was then stirred for 6 h followed by ultra-sonication and centrifugation for 2 h. The obtained material was washed for several times with deionized water and dried in oven for 24 h at 65 °C.

2.3. Synthesis of TiO₂–Graphene Nanocomposites

TiO₂–graphene oxide (TGO) and TiO₂–reduced graphene oxide (TRGO) nanocomposites were synthesized by a facile, rapid and green process. Firstly, 60 mg of GO or RGO was dispersed in 60 ml of ethanol by ultra-sonication to form a stable colloids over 3 h at 37 °C, and then mixed with 0.67 ml of titanium butoxide. The pH of suspensions was adjusted at level of 7 by dropwise adding appropriate amounts of hydrochloric acid and ammonia solutions. The products were collected by centrifugation, washed several times with deionized water and then dried in a laboratory oven at 80 °C. The samples were achieved after calcination at 400 °C over 2 h (TiO₂/GO ratio is about 2.6). Following above procedures the pure anatase nanoparticles was synthesized in the absence of GO and RGO.

2.4. Photocatalytic Degradation Performance

For studying the photocatalytic degradation performance of TGO and TRGO under sunlight irradiation, the MB solution was prepared by mixing dye with deionized water (3.0 mg l⁻¹) then the photocatalysts (12.0 mg) were added to prepared solution (25 ml). Prior to sunlight degradation, the suspensions were stirred for 30 min in the dark space for adsorption–desorption equilibrium. The bright blue color of the solutions was gradually vanished, indicating the degradation of cationic dye. The variation of MB concentration with time, 5–90 min, was monitored spectrophotometrically (UV–vis spectrophotometer, T80, PG, Ltd., UK) at a wavelength range of 400–700 nm. The dye degradation is presented as a conversion, $1 - (C/C_0)$, where C₀ and C are the concentration of MB at dark condition after adsorption–desorption equilibrium and the concentration of dye at different irradiation times, respectively. Each set of photocatalytic measurements was repeated three times, and the experimental error was found to be within the error bar of ± 5%.

2.5. Characterizations

Fourier transform infrared spectroscopy (FTIR, Nexus 670, Thermo Nicolet, Germany) was used at room temperature in the range of 400–4000 cm⁻¹ to identify the chemical bands in the prepared samples.

The crystalline structures were characterized by X-ray diffraction (XRD) analysis on a Bruker X-ray diffractometer (Model D8-Advance,

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