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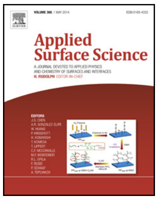

Exfoliated graphite/titanium dioxide nanocomposites for photodegradation of eosin yellow

Thabile Ndlovu[b], Alex T. Kuvarega[a], Omotayo A. Arotiba[a], Srinivasan Sampath[d], Rui W. Krause[c], Bhekie B. Mamba[a,*]

[a] University of Johannesburg, Department of Applied Chemistry, P.O. Box 17011, Doornfontein 2028, Johannesburg, South Africa
[b] University of Swaziland, Department of Chemistry, Private Bag 4, Kwaluseni, Swaziland
[c] Rhodes University, Department of Chemistry, P.O. Box 94, Grahamstown 6140 South Africa
[d] Indian Institute of Science, Department of Inorganic and Physical Chemistry, Bangalore 560012, India

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ABSTRACT

An improved photocatalyst consisting of a nanocomposite of exfoliated graphite and titanium dioxide (EG-TiO_2) was prepared. SEM and TEM micrographs showed that the spherical TiO_2 nanoparticles were evenly distributed on the surface of the EG sheets. A four times photocatalytic enhancement was observed for this floating nanocomposite compared to TiO_2 and EG alone for the degradation of eosin yellow. For all the materials, the reactions followed first order kinetics where for EG-TiO_2, the rate constant was much higher than for EG and TiO_2 under visible light irradiation. The enhanced photocatalytic activity of EG-TiO_2 was ascribed to the capability of graphitic layers to accept and transport electrons from the excited TiO_2, promoting charge separation. This indicates that carbon, a cheap and abundant material, can be a good candidate as an electron attracting reservoir for photocatalytic organic pollutant degradation.

1. Introduction

Due to the limited amount of potable water, polluted water must be remediated for re-use or before being re-introduced into the environment. The main aim of treating drinking water is to produce water that is safe (without pathogenic microbes and toxins), attractive (free from colour, taste and odour) and to avoid accumulation of solids, corrosion and after-growth of bacteria in the distribution and transport pipeline [1]. Industrial or agricultural wastewaters, rich in organic chemicals, are potential sources of pollution of natural water bodies. They contain a wide range of toxic compounds, hazardous to the environment as well as to human health, which need special treatment procedures for their removal [2]. Due to the rising demand for synthetic organic substances, their massive production brought about an inevitable increase in the occurrence and concentration of organic contaminants in effluents, sewage and sewage sludge [3], which has led to the drastic deterioration of the water quality in the world, South Africa included [4]. In order to protect the environment from pollution by various chemical materials, adsorption/absorption and decomposition are pointed out to be important in the remediation of water. For the former function, activated carbons have played a great role and for the latter titanium dioxide (TiO_2) with anatase-type structure which has marked photocatalytic activity has widely been studied [5].

Photocatalysis has been gaining popularity as a remediation method for organic contaminants, primarily with the goal of complete mineralization of the contaminants to carbon dioxide and water [6]. These photocatalytic reactions are initiated by the excitation of a semiconductor catalyst with energy greater than its band gap, resulting in the promotion of electrons from the valence band to the conduction band, thus producing electron/hole pairs [6]. The holes are highly oxidising and can scavenge water or hydroxyl ions to produce hydroxyl radicals whilst the electrons are highly reducing, converting oxygen molecules to superoxide radicals.

Titanium dioxide is one of the most investigated oxide materials owing to its technological importance for application in areas such as water purification, photocatalysis or gas sensing [7]. It has high photocatalytic activity and presents stability in aqueous media making it an optimal catalyst for advanced photodegradation of water contaminants [8]. Earlier studies reported the use of TiO_2 in its powder form which results in high efficiencies in the photodegradation of organics [7]. It however, suffers from the high rate

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* Corresponding author. Tel.: +27 11 559 6152; fax: +27 11 559 6425.
E-mail addresses: atkuvarega@gmail.com (T. Ndlovu), bmamba@uj.ac.za (B.B. Mamba).

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of recombination of the photogenerated electron/holes besides the technical problems that may arise from post treatment of treated water such as catalyst recycling as well as obtaining powder-free water. Hence the use of TiO_2 embedded onto large surface area supports constitutes an alternative option to avoid material recovery problems.

Carbon–carbon composite materials are considered indispensable for use in advanced technologies due to the combination of their low density and the unique thermal, mechanical and biomedical properties [9]. Exfoliated graphite (EG) is a low-density material which has excellent properties such as compressibility, resilience, thermal stability and corrosion resistance [10]. It is obtained by subjecting the bisulphate ion intercalated graphite to thermal shock [11]. The process results in a rapid phase transition of the material resulting in puffed up, very low density graphite [11–14].

Exfoliated graphite has been mainly used as a raw material for making flexible graphite sheets. Recently, EG has attracted research attention because of its high sorption capacity [15] and Kang et al., reported EG as a good absorbent especially for materials with large molecular size and weak polarity [10]. Several studies have suggested that the space among the worm-like particles of EG plays the most important role in the sorption of heavy oil [16–19]. Dyes are common in the textile and paper manufacturing industrial effluent but they are difficult to degrade biologically. If these are not removed from the treated wastewater, they cause formidable contamination of the water, as colour tends to persist even after conventional treatment [20].

The development of carbon nanostructure composites is another emerging area that has led to the design of photocatalysts with tailored properties [21]. The superior physical, mechanical and multifunctional properties of EG including its ability to capture and shuttle electrons, provides a unique opportunity to develop catalyst with multifunctional characteristics. This has prompted an investigation into its application in photocatalytic pollutant removal from water. Currently, there are few reports on the synthesis of EG/TiO_2 nanocomposites and their applications in visible light driven photodegradation of pollutants. Optimisation of EG usage in various applications including water purification requires assembling of nanostructures such as semiconductor photocatalysts onto their surfaces. A combination of EG and TiO_2 is expected to deliver exceptional performances in removal of organic pollutants from water. In this study EG/TiO_2 nanocomposites were prepared with the aim to utilise the excellent electron conductivity of EG to lengthen the lifetime of photogenerated charge carriers in the semiconductor and hence improve the photoactivity.

2. Experimental

2.1. Materials

Natural graphite (NG) flakes were purchased from Sigma Aldrich while sulphuric acid, nitric acid, 2-isopropanol, titanium (IV) isopropoxide, eosin yellow and formic acid were obtained from Merck Chemicals. All chemicals were used as received.

2.2. Preparation of exfoliated graphite exfoliated graphite/TiO_2 nanocomposite

Natural graphite was soaked in H_2SO_4:HNO_3 (3:1) acid mixture overnight and washed several times with deionised water until the water had no sulphate ions and the pH was neutral. The product, graphite intercalated compound (GIC), was dried in an oven (100 °C). The GIC was subjected to thermal shock at 800 °C for about 30 s forcing the intercalated material out of the graphite lattice, thereby rupturing the layers. This procedure resulted in the puffed material called exfoliated graphite (EG) that is characterised by a very low density of 0.0068 g/ml.

2.3. Preparation of exfoliated graphite/TiO_2 nanocomposite

The preparation of TiO_2 supported on EG was as follows; EG (1 g) was sonicated in 2-isopropanol (50 ml) for 15 min. Titanium (IV) isopropoxide (10 ml) was then added and the mixture was left to stir for 30 min. Formic acid (13 ml) was gradually added while stirring and this was left to stir for two and a half hours. The mixture was then allowed to age for two hours after which it was washed with 2-propanol and then distilled water repeatedly. After filtration, the residue was dried at 100 °C overnight. This product was named EG/TiO_2. This material was used for the photodegradation of eosin yellow under visible light after calcining at 400 °C.

2.4. Characterisation

Raman spectra, excited by a red diode laser (785 nm), were recorded on a Czerny-Turner micro-Raman spectrometer (Perkin Elmer Raman microscope). X-ray diffraction (XRD) measurements were performed using on a Philips PANanalytical X'pert X-ray diffractometer operated at 40 kV and 40 mA, using Cu Kα radiation ($\lambda = 0.15406$ nm) as the source. Scanning electron microscopy (SEM) images were obtained on a NOVA FEI/FIB Instrument and transmission electron microscopy, (TEM) analysis was performed under bright field on a Tecnai G^2 Spirit. BET surface area measurements were performed on a Micromeritics TriStar II apparatus. Prior to the analysis the samples were degassed in a vacuum at 150 °C for an hour reaching a final pressure of 1 mm Hg.

2.5. Evaluation of photocatalytic activity

The photocatalytic performances of commercial TiO_2, EG and EG-TiO_2 were quantified by measuring the rate of degradation of eosin yellow under simulated solar irradiation. The material (0.1 g) was suspended in 100 ml of eosin yellow solution of concentration 200 ppm. A solar simulator (Oriel, Newport), with an Oriel Xenon lamp (500 W) was employed as a radiation source. The power output was set to 300 W in order to give an irradiance of 1000 Wm^{-2} at 25 °C, using an Air Mass1.5 Global Spectral Filter. An Oriel PV reference cell system equipped with a 2 cm × 2 cm monocrystalline silicon photovoltaic cell and a Type K thermocouple was used to set the simulator irradiance to 1 sun under normal laboratory temperature. The suspensions were ultra sonicated for about 10 min and then magnetically stirred in the dark for an hour to allow for adsorption equilibrium to be reached before illumination. Aliquots (2 ml) of the suspension were withdrawn at 15 min intervals using a 5 ml Neomedic disposable syringe and filtered through a 0.22 μm PVDF syringe filter for 180 min. Changes in the concentration of eosin yellow were monitored on a Shimadzu UV-2450 UV–Vis spectrophotometer (Japan) at $\lambda = 515$ nm.

3. Results and discussion

3.1. Characterisation of EG and EG-TiO_2

The preparation of EG-TiO_2 was followed by characterisation using SEM, TEM, XRD and Raman spectroscopy. SEM micrographs show that the TiO_2 particles had a spherical morphology and they were evenly distributed on the EG layers as shown in Fig. 1.

Fig. 2a presents a typical TEM image of EG/TiO_2 sample clearly indicating many small TiO_2 clusters uniformly deposited on the surface of EG with little agglomeration. The TiO_2 nanoparticles attached onto the surface of EG were less than 10 nm as shown in Fig. 2b.