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Solar photocatalytic disinfection of water using titanium dioxide graphene composites

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HIGHLIGHTS

- TiO_2–RGO composites formed by photocatalytic reduction of graphene oxide.
- TiO_2–RGO composites used for photocatalytic disinfection of water under real sun.
- Rapid solar photocatalytic inactivation of *E. coli* and *Fusarium solani* spores was observed.
- The TiO_2–RGO composites form singlet oxygen under visible irradiation.
- Evidence of enhanced disinfection of *E. coli* under solar irradiation.

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ABSTRACT

Interest has grown in the modification of titanium dioxide with graphene to improve the photocatalytic behaviour. In this work, titanium dioxide–reduced graphene oxide (TiO_2–RGO) composites were synthesised by the photocatalytic reduction of exfoliated graphene oxide (GO) by TiO_2 (Evonik P25) under UV irradiation in the presence of methanol as a hole acceptor. The composite materials were characterised using high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Raman and XPS analysis provided evidence that GO was converted to RGO by photocatalytic reduction. The TiO_2–RGO composites were compared to TiO_2 in suspension reactors for the disinfection of water contaminated with *Escherichia coli* and *Fusarium solani* spores under real sunlight. Very rapid water disinfection was observed with both *E. coli* and *F. solani* spores. An enhancement in the rate of inactivation of *E. coli* was observed with the TiO_2–RGO composite compared to P25 alone. The rate of inactivation of *F. solani* spores was similar for both the TiO_2–RGO and P25. When the major part of the solar UVA was cut-off ($\lambda > 380$ nm) using a methacrylate screen, there was a marked increase in the time required for inactivation of *E. coli* with P25 but no change in the inactivation rate for the TiO_2–RGO. There is evidence of singlet oxygen production with visible light excitation of the TiO_2–RGO composites which would lead to *E. coli* inactivation.

1. Introduction

The availability of safe drinking water is a high priority issue for human existence and quality of life. It is estimated that around 780 million people are without access to an improved drinking water source and many more are forced to rely on sources that are microbiologically unsafe [1]. Furthermore, water recycling and reuse is becoming very important in several regions throughout the world and a sustainable method for the disinfection of water for reuse is needed. Irradiating water with solar light can improve the safety of the water by reducing the pathogen loading. This process is referred to as solar disinfection or SODIS [2–4]. One potential method for enhancing the efficiency of solar disinfection is by the addition of a photocatalyst, such as titanium dioxide (TiO_2) [2]. Heterogeneous photocatalysis utilises light along with a semi-

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conductor to produce reactive oxygen species (ROS) which can inactivate bacteria and degrade a wide range of chemical contaminants in water [5]. UV excitation of TiO_2 results in the formation of charge carriers, conduction band electrons (e^-_{CB}) and valence band holes (h^+_{VB}). The conduction band has a negative electrochemical reduction potential relative to normal hydrogen electrode (NHE) and is able to reduce dissolved oxygen to form superoxide radical anions, hydroperoxyl radicals, and through subsequent reduction reactions, hydrogen peroxide and hydroxyl radicals. The valence band hole has a very positive electrochemical reduction potential and is able to oxidise water to form hydroxyl radicals. These reactive oxygen species can attack and inactivate microorganisms in water [6]. TiO_2 has a wide band gap (anatase E_{bg} = 3.2 eV or λ < 387 nm) and requires UV excitation. Only ca. 5% of the solar radiation at sea level is in the UV domain. Different approaches have been utilised to improve the solar efficiency for TiO_2 including metal doping (or metal loading of the surface) [7] and non-metal doping [8]. An interesting approach to improving photocatalytic efficiency is to create TiO_2 composite materials with graphene.

The preparation of graphene, a one-atom-thick sheet of sp^2-bonded carbon atoms in a hexagonal two-dimensional lattice, was first reported in 2004 [9]. The properties of graphene include very high surface area (2600 m^2/g), ballistic electronic conduction, exceptional thermal conduction, and good chemical and thermal stability. The utilization of graphene as a two-dimensional support to anchor catalyst nanoparticles (NPs) and facilitate electron transport opens up new possibilities for designing the next generation catalysts. Graphene oxide (GO) is most commonly prepared by the oxidation of graphitic carbon using Hummers' method [10] along with an exfoliating step, e.g. high intensity ultrasound. The GO can then be reduced back towards single or multilayer graphene using thermal or chemical reduction [11]. As complete removal of oxygen functionalities may not be achieved in the reduction stage, the reduced form is referred to as reduced graphene oxide (RGO). In 2008 Williams, Seger and Kamat reported that GO undergoes photocatalytic reduction to RGO as it accepts electrons from UV-irradiated TiO_2 suspensions (in the presence of a hole scavenger) [12]. The direct interaction between TiO_2 particles and graphene sheets hinders the collapse/re-stacking of exfoliated sheets of graphene. Therefore, the photocatalytic reduction of GO by TiO_2 presents a clean and safe route to the formation of TiO_2–RGO composites.

There are a number of potential advantages for utilising TiO_2–RGO composites for photocatalysis. For example, conduction band electrons may be rapidly transferred to the RGO therefore inhibiting charge carrier recombination, behaving similar to metal clusters on the surface of the photocatalyst [13]. Graphene (RGO) may act as an electrocatalyst for the oxygen reduction reaction [14,15]. RGO should present a high surface area for adsorption of pollutants, possibly yielding a synergistic effect for pollutant removal. In addition, visible light activity might be enhanced due to the GO/RGO absorbing UV/Vis and producing reactive oxygen species. UV or visible irradiation of GO can lead to the expulsion of oxygen as reactive oxygen species [16,17]. Graphene based photocatalytic composites have been reviewed by An and Yu in 2011 [18]. Others have previously reported on the formation of superoxide and singlet oxygen through visible light excitation of fullerenes [19].

Akhavan and GhaderiIt reported that such TiO_2–RGO nanocomposites could improve the efficiency for the killing of *Escherichia coli* bacteria under solar irradiation [20]. They reported that the optical absorption was not significantly different following the deposition of the RGO and they used the 'so-called' anti-bacterial drop test in their experiments. They suggested that the enhanced solar activity was due to the reduced graphene oxide platelets acting as electron sinks, accepting conduction band electrons from the UV excited TiO_2 and effectively decreasing the rate of recombination of charge carriers. In 2011, Liu et al. reported on simple two-phase assembling method to produce graphene oxide–TiO_2 nanorod composites [21]. After combining with graphene oxide (GO), the TiO_2–GO composites showed higher photocatalytic activities than that of TiO_2 nanorods alone for the inactivation of *E. coli* under solar simulated light. The enhanced effect of graphene oxide nano-sheets on the photocatalytic properties of TiO_2 was attributed to a thin two dimensional sheet support, a large surface area and much increased adsorption capacity, and the strong electron transfer ability of the thermally reduced graphene oxide in the composite. In 2013, Gao et al. reported on the inactivation of *E. coli* under visible light irradiation of TiO_2–GO composites [22]. The GO was produced using Hummers' method and the TiO_2–GO composites were formed by reacting partially hydrolysed $TiCl_3$ with sonicated GO. Antibacterial tests were carried out by dispersing the TiO_2–GO composite directly to an agar plate seeded with *E. coli* followed by illumination from an indoor light (400–700 nm). They reported an increase in the percentage inactivation for the TiO_2–GO composites as compared to TiO_2 alone. Although TiO_2–RGO and TiO_2–GO composites have been previously reported to improve the inactivation efficiency for *E. coli*, none of the previously published work has utilised a common protocol for the assessment of water disinfection and none has compared the efficiency against a well known material e.g. *Evonik Aeroxide P25*.

In this work we modified P25 to form TiO_2–RGO composites using the photocatalytic reduction of exfoliated GO in the presence of a hole scavenger. The materials were then tested for the disinfection of water under real sun conditions using two different microorganisms, using P25 as a test standard. We also investigated the contribution of visible light activity to the disinfection mechanism.

2. Materials and methods

2.1. Synthesis of TiO_2–RGO

Graphene oxide (GO) (Nanoinnova) and TiO_2·P25 particles (2% w/v) were suspended separately each in 100 mL absolute methanol and sonicated using a tip sonication for 10 min. The two suspensions were mixed to obtain 5% w/v GO concentration with respect to TiO_2. The suspension was ultrasonicated for about 1 h to obtain grey-blue suspension. The suspension obtained was irradiated with UV-B light source for 6 h with constant stirring with oxygen free nitrogen (OFN) sparging (flow rate 200 mL min^{-1}). The product was dried off in air to obtain a dry powder.

2.2. Characterisation of the TiO_2–RGO

The TiO_2–RGO/GO composites were characterised by HR-TEM using a Joel 2100F with a 200 kV field emission source. Raman spectra were recorded using an ISA instruments Labram 300 spectrometer with 514 nm argon and 633 nm helium neon laser sources. Chemical composition analysis was undertaken by X-ray photoelectron spectroscopy (XPS) with a Kratos Axis Ultra employing an Al Kα source. The binding energy of the samples were calibrated relative to the C 1s peak at 284 eV. Linear background subtraction and Gaussian–Lorentzian curves were used for peak fitting.

2.3. Solar photocatalytic disinfection

2.3.1. Bacterial strain enumeration and quantification

E. coli K-12 (ATCC 23631) was used as the model bacterium for assessing the disinfection kinetics under real sun conditions. It was