



Gadolinium oxide decorated multiwalled carbon nanotube/tridoped titania nanocomposites for improved dye degradation under simulated solar light irradiation



Gcina Mamba^{a,b}, Xavier Yangkou Mbianda^a, Ajay Kumar Mishra^{b,*}

^a Department of Applied Chemistry, University of Johannesburg, Faculty of Science, P.O. Box 17011, Doornfontein 2028, South Africa

^b Nanotechnology and Water Sustainability Research Unit, College of Engineering, Science and Technology, University of South Africa Florida Science Campus, 1709 Florida, South Africa

ARTICLE INFO

Article history:

Received 8 August 2015

Received in revised form 13 November 2015

Accepted 18 November 2015

Available online 22 November 2015

Keywords:

A. semiconductors

A. nanostructures

A. sol-gel chemistry

B. optical properties

D.

ABSTRACT

Neodymium/gadolinium/europium, nitrogen and sulphur tridoped titania (Nd/Gd/Eu, N,S-TiO₂) was hybridised with pre-synthesised gadolinium oxide decorated multiwalled carbon nanotubes (MWCNT-Gd) using a sol-gel method. Subsequent to drying and calcination, composite photocatalysts: MWCNT-Gd/Nd,N,S-TiO₂, MWCNT-Gd/Gd,N,S-TiO₂ and MWCNT-Gd/Eu,N,S-TiO₂, were obtained and characterised using TEM, SEM-EDX, UV-vis, XPS, XRD and FT-IR. Acid blue 74 (AB74) was used as a model dye to investigate the photocatalytic degradation properties of the prepared materials under simulated solar light irradiation. Coupling the different tridoped titania with MWCNT-Gd enhanced their activity compared to MWCNT/TiO₂, MWCNT-Gd/TiO₂ and MWCNT/Gd,N,S-TiO₂. MWCNT-Gd/Gd,N,S-TiO₂ showed the highest activity towards AB74 degradation reaching 100% decolourisation after 150 min of irradiation. Total organic carbon analysis revealed that over 50% of the AB74 molecules were completely mineralised after 180 min of irradiation in the presence of MWCNT-Gd/Gd,N,S-TiO₂.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Photocatalysis has been identified as a potential solution towards treatment of industrial effluents laden with organic compounds and the general decontamination of the environment. The release of industrial compounds such as dyestuffs into the environment leads to undesirable health, aesthetic and environmental effects [1]. Semiconductor photocatalysis presents a number of advantages over the conventional tools for organic pollution remediation. Such merits include its versatility in terms of application i.e. photocatalysis can be used for inactivation of micro-organisms such as bacteria [2], oxidation/reduction of inorganic species [3,4], organic compounds [5] and can be utilised in the treatment of the pollutants both in aqueous and gaseous form [6,7]. Moreover, photocatalysis has the potential to completely mineralize organic pollutants into carbon dioxide, water and inorganic ions, thereby minimizing sludge formation which often poses further disposal challenges in processes such as adsorption and coagulation [8]. The immunity of photocatalysis towards the toxic nature of some of the organic compounds and

the absence of fouling are other advantages of the process over biological and membrane processes [9].

However, the search for an energy efficient photocatalyst with high photocatalytic activity remains a research challenge. Titania, which is regarded as the benchmark for semiconductor photocatalysis suffer from the inability to absorb visible light which rules out the possibility of utilizing sunlight as a source of energy and curb on the expensive energy requirements of the process [10]. In addition to the energy problems, pure titania suffer from a high recombination rate of the photogenerated electron/hole pairs which significantly lower its photocatalytic activity [11]. Coupling titania with carbon nanomaterials such as CNTs, GO and rGO has been highlighted as a promising method to improve the photocatalytic activity of titania by improving visible light absorption, surface area and charge separation and transportation [12,13]. Strong and intimate interface between the carbon nanomaterial and titania is a prerequisite to ensure the exploitation of the combined properties of the materials [13]. Previous work by Mamba et al. [14] showed that decorating MWCNTs with gadolinium oxide nanoparticles prior to incorporation into titania matrix significantly improved the photocatalytic activity of the nanocomposite compared to MWCNT/TiO₂ nanocomposite. This was mainly credited to improved charge separation by the gadolinium oxide nanoparticles at the interface of the two

* Corresponding author. Fax: +27124713434

E-mail address: mishrak@unisa.ac.za (A.K. Mishra).

materials which functioned as a charge transfer channel. Furthermore, it was shown that incorporating MWCNTs, SWCNTs and rGO in lanthanide, nitrogen and sulphur tridoped titania significantly enhance the photocatalytic activity of the nanocomposite compared to MWCNT/TiO₂, commercial TiO₂ and the tridoped titania [15–17]. This enhancement was credited to improved visible light absorption as observed from UV-vis, charge separation and transportation.

In this work Gd,N,S-TiO₂, Nd,N,S-TiO₂ and Eu,N,S-TiO₂ were coupled with gadolinium oxide nanoparticle decorated MWCNTs to form MWCNT-Gd/Gd,N,S-TiO₂, MWCNT-Gd/Nd,N,S-TiO₂ and MWCNT-Gd/Eu,N,S-TiO₂, respectively. This innovation aims at fabrication of materials with multichannel electron conduction system to ensure efficient charge separation, good visible light absorption and high photocatalytic activity. Decoration of Gd³⁺ on the MWCNT promotes electron scavenging and transfer from TiO₂ to MWCNT at the MWCNT/TiO₂ interface and improves charge separation. The rare earth metals doped in TiO₂ ensure adequate electron scavenging on the outer surface of TiO₂ nanoparticle through formation of a Schottky barrier at the metal/titania interface. Tridoping titania with the rare earth ions, nitrogen and sulphur is expected to significantly improve its visible light absorption which will be further enhanced by incorporation of the decorated MWCNTs. Photocatalytic properties of the prepared materials were evaluated for the degradation of acid blue 74 (AB74) in aqueous solutions under simulated solar irradiation. The effect of the different rare earth metal ions incorporated in the tridoped titania was investigated in terms of the overall photocatalytic activity of the nanocomposites.

2. Experimental

2.1. Preparation of MWCNT-Gd

Decoration of MWCNTs with gadolinium oxide nanoparticles proceeded as outlined in our previous work [14]. The loading of gadolinium ion nanoparticles was about 3.0% relative to the MWCNTs. There was no reduction step in this procedure.

2.2. Preparation of MWCNT-Gd/Rare earth, N,S-TiO₂ nanocomposites

The procedure employed during preparation of the nanocomposite photocatalysts was adopted from our previous work [16]. The amount of MWCNT-Gd was kept at 0.5% relative to TiO₂ by weighing 0.0117 g into the TiO₂ precursor followed by addition of appropriate amounts of gadolinium nitrate hexahydrate, Neodymium nitrate hexahydrate and europium nitrate hydrate as Gd³⁺, Nd³⁺ and Eu³⁺ sources, respectively. The amount of the rare earth ions was kept at 0.6% relative to TiO₂. Subsequently, the mixture was sonicated and thiourea (N and S source) solution in formic acid was added drop wise to form a precipitate which was then dried and calcined in an oven. MWCNT/TiO₂, MWCNT/Gd,N,S-TiO₂ and MWCNT-Gd/TiO₂ were prepared from the corresponding starting materials following the same procedure and used as controls.

2.3. Characterisation techniques

TEM analyses were done on a Jeol JEM 2100 transmission electron microscope (Japan) and SEM studies were done on a ZEISS AURIGA focussed ion beam-scanning electron microscope (FIB-SEM) (Germany) coupled with an energy dispersive X-ray analyser (EDS). FTIR spectra of the photocatalysts were obtained from a PerkinElmer Spectrum 100 FT-IR spectrophotometer (USA) and samples were analysed as KBr discs. XPS analyses were done on a Kratos Axis Ultra DLD spectrometer (UK) with

an aluminium monochromatic anode. The instrument was equipped with a charge neutraliser and the operating pressure was kept below 5×10^{-9} Torr. For the survey scan, the emission current was maintained at 5 mA, the anode voltage (HT) at 15 kV and the resolution at 160 eV pass energy using a hybrid lens in the slot mode. A step size of 1 eV was used with dwell times kept at 300 ms. High resolution spectra were obtained using a pass energy of 40 eV in slot mode and a step size of 0.1 eV. UV-vis diffuse reflectance spectra of the photocatalysts were collected on a Shimadzu UV-2450 UV-vis spectrophotometer (Japan) using barium sulphate as a reference. X-ray diffraction patterns of the photocatalysts were obtained from a Philips PANanalytical X'pert diffractometer (Netherlands) operated at 40 kV and 40 mA. A Cu α radiation beam with an excitation wavelength (λ) of 0.15406 nm was used as an X-ray source. A nickel filter (0.02 mm) was fitted on the diffracted beam optics to filter off X-rays from tungsten. A beam knife, beam mask (20 mm), solar slits (0.04 rad), anti-scatter slit (4°) were used. Powdered samples were loaded into the XRD sample holders and measurements were done from 5° to 90° (2 θ values). Crystallite size (D) calculations were performed using Scherrer equation (Eq. (1)) for a specific angle (θ) and FWHM (full width at half maximum for the (101) anatase peak, β).

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

2.4. Evaluation of the photocatalytic properties of the nanocomposites

In all the photocatalytic degradation experiments the photocatalysts (0.10 g) was mixed with AB74 solution (20 ppm, 100 mL) and the mixture was stirred in the dark for 1 h to establish adsorption equilibrium. A sample was drawn from the solution using a syringe fitted with a PVDF, 0.45 μ m syringe membrane filter and that was taken as the initial concentration (C_0). The solar simulator Oriel Newport (USA) was equipped with an Oriel 500 W xenon lamp, set at an input power of 400 W and kept at a fixed position to deliver an irradiation of about 1 sun to the sample. The solar simulator was fitted with a dichroic UV filter ($\lambda > 420$ nm). Samples were drawn from the solution at 30 min intervals, filtered and analysed using a Shimadzu UV-2450 UV-vis spectrophotometer. The experiments were run for a period of 3 hrs. UV-vis photometric measurements of standards and samples were done at 608 nm (λ_{\max} for AB74) to obtain the concentration of AB74 after the elapsed time interval (C_t). A calibration curve was obtained from the standards and the percentage AB74 degraded was calculated using Eq. (2):

$$\% \text{AB74 degraded} = \frac{C_0}{C_t} \times 100 \quad (2)$$

The UV-vis absorption spectra of AB74 were also recorded to monitor any changes with increasing irradiation time.

2.4.1. Hydroxyl radical detection

Terephthalic acid solution (6 mM) was used as a diagnostic tool to probe the production of the hydroxyl radicals during photocatalytic degradation of AB74. The terephthalic acid solution (instead of AB74 solution) was mixed with MWCNT-Gd/Gd,N,S-TiO₂ (0.10 g) and treated in a similar manner as the dye solution. Aliquots were drawn at 30 min intervals and the reaction was run for 1.5 h. Samples were analysed in a quartz cuvette using a PerkinElmer LS 45 fluorescence spectrometer with a xenon flash lamp. The samples were excited at 315 nm and the emission was measured from 200 to 600 nm.

Download English Version:

<https://daneshyari.com/en/article/1487475>

Download Persian Version:

<https://daneshyari.com/article/1487475>

[Daneshyari.com](https://daneshyari.com)