

Synthesis of Nitrogen-doped RGO/BaWO₄ Nanocomposites with Highly Enhanced Photocatalytic Activity

Mohamed Jaffer Sadiq*, Paruthimal Kalaiganan

Department of Industrial Chemistry, Alagappa University, Karaikudi, India

Email address:

sadiqmsc@gmail.com (M. J. Sadiq)

*Corresponding author

To cite this article:

Mohamed Jaffer Sadiq, Paruthimal Kalaiganan. Synthesis of Nitrogen-doped RGO/BaWO₄ Nanocomposites with Highly Enhanced Photocatalytic Activity. *International Journal of Photochemistry and Photobiology*. Special Issue: *Synthesis of Advanced Nanocomposites for Environmental Applications*. Vol. 3, No. 1, 2019, pp. 10-14. doi: 10.11648/j.ijpp.20190301.12

Received: June 13, 2019; Accepted: July 27, 2019; Published: September 2, 2019

Abstract: A series of nitrogen-doped reduced graphene oxide/barium tungstate (NRGO/BaWO₄) nanocomposites has been synthesized by microwave method and it was examined by the photocatalytic studies for the degradation of methylene blue (MB) dye under visible light irradiation. The as-synthesized catalysts were confirmed by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Photoluminescence Spectroscopy (PL) and Diffuse Reflectance Spectroscopy (DRS) techniques. The prepared nanocomposites are tested for its performance to the photodegradation of MB dye via illumination of 120 minutes under visible light source. Significantly, the 2.5%-NRGO-BaWO₄ nanocomposite indicated that the highest photocatalytic activity under visible light source. The observed photocatalytic performances were ascribed to the synergetic effects of NRGO and BaWO₄ and improved photogenerated electron-hole pairs charge separation efficiency. On the basis of the experimental results, we concluded that the new strategy of these types of photocatalytic property of NRGO/BaWO₄ based binary nanocomposites materials can be a suitable candidate for the various environmental applications.

Keywords: NRGO/BaWO₄ Nanocomposites, Microwave Irradiation, Photocatalyst, Degradation

1. Introduction

Semiconductor photocatalysis has attracted interest of research community as it can solve environmental problems [1]. A good photocatalyst should have an extended excitation wavelength, the low recombination rate of charge carriers and active sites on the surface to facilitate adsorption and reaction. Several strategies have been developed to achieve the above said properties like doping, coupling with semiconductors and compositing with layered materials to improve the surface area [2]. Despite these efforts commercialization of these materials is yet to be realized. Hence designing materials with catalytic activity such as, high performance towards photodegradation would help in solving the environmental problems must be thoroughly considered. Such catalysts will provide an economical way to serve several applications.

Semiconducting materials with narrow band gap have been used as photocatalysts. Since the band gap energy lies in the energy range of the UV or visible light [3]. Tungsten

oxides, hydrates, and metal tungstates have been studied for their photocatalytic capabilities [4]. In particular, ZnWO₄, CoWO₄, FeWO₄, NiWO₄ have been extensively used for the preparation of composites for water splitting [5-6]. On the other hand, BaWO₄ which has a wide variety of applications has been studied meagerly in the field of photocatalysis due to its instability and slow electron transfer rate. To extend the absorption of BaWO₄ from UV region to visible region of solar spectrum the band gap has to be decreased. For visible light absorption, the band gap has to be small which leads to higher recombination rate, the transport property is tuned by doping carbon containing species to improve the photocatalytic efficiency [7].

Graphene based architectures not only provide support to other materials but also have the potential to harness the electrical and redox properties [8]. The electronic property and the chemical reactivity of graphene can be tailored by doping nitrogen. In N doped graphene ~0.5 electron per N atom is provided to carbon π conjugated system thus enhancing the photocatalytic efficiency. When composited

with semiconductors, NRGO increases the rate of transfer of electrons from the conduction band of semiconductors in comparison with graphene [9].

Based on the above facts, we report the synthesis of NRGO/BaWO₄ nanocomposites via microwave method. To the best of our knowledge, this is the first report on such kind of binary nanocomposite with catalytic activity. The as-synthesized material is thoroughly characterized using various advanced techniques. The reported material is highly efficient in photocatalytic degradation of MB dye under visible light irradiation.

2. Experimental

2.1. Materials

All the reagents and chemicals procured were of analytical grade and utilized without further purification. Deionized water was utilized for all the study.

2.2. Synthesis of Graphene Oxide (GO)

GO was synthesized through chemical exfoliation of natural graphite powder by using modified Hummers' method previously reported [10]. 2.5 g of graphite flakes and 1.25 g of NaNO₃ was added in 75 mL of concentrated H₂SO₄ under constant stirring. Then, 7.5 g of KMnO₄ was added slowly and the mixture was further stirred for 12 hours. Finally, the reaction mixture was diluted with distilled water and 5 mL of H₂O₂ was subsequently added. The GO obtained was separated from the yellow solution by centrifugation, washed with dilute HCl and water until the pH was 7. Later it was exfoliated by sonication.

2.3. Synthesis of BaWO₄

The BaWO₄ nanoparticles were prepared by microwave method. In a typical synthesis, solutions of barium chloride, ammonium tungstate and cetyl trimethyl ammonium bromide (CTAB) in H₂O/ethanol were prepared with desired molar ratio and mixed together using ultrasonication for about 30 minutes. The resulting mixture was treated with microwave irradiation at 350 W for 10 minutes and then allowed to cool to room temperature. The obtained precipitate of BaWO₄ was filtered and washed thoroughly with 10% ethanol several times to remove the impurities. Finally, the precipitate was dried at 60 °C overnight.

2.4. Synthesis of NRGO/BaWO₄ Nanocomposites

The NRGO/BaWO₄ nanocomposites were prepared using microwave method. In a typical synthesis, a calculated amount of GO (0.5 to 5.0%) was dispersed in the water. Then solutions of barium chloride, ammonium tungstate, CTAB and urea in H₂O/ethanol with desired molar ratios were added. The pH of the reaction mixture was maintained at 9 using ammonia. After 30 minutes of ultrasonication, the resulting mixture was treated with microwave irradiation at 350 W for 10 minutes and then allowed to cool to room

temperature. The obtained precipitate of NRGO/BaWO₄ nanocomposite was filtered and washed thoroughly with 10% ethanol several times and finally dried at 60 °C overnight. The prepared samples were denoted as 0.5%-NRGO/BaWO₄, 1.0%-NRGO/BaWO₄, 2.5%-NRGO/BaWO₄ and 5.0%-NRGO/BaWO₄, respectively, with the number referring to the weight ratios of NRGO to BaWO₄.

2.5. Characterization

The powder X-ray diffraction (XRD) patterns were determined by X-ray diffractometer (Rigaku, Japan) with the Cu-K_α target ($\lambda=0.154$ nm). The surface morphology were obtained using scanning electron microscopy (SEM, JEOL). DRS of the composites were recorded by utilizing UV-visible spectrometer (Analytik Jena). Photoluminescence (PL) spectra were obtained using Horiba Jobin Yvon spectrometer with an excitation wavelength of 380 nm.

2.6. Photocatalytic Measurements

The photocatalytic activity of NRGO/BaWO₄ nanocomposites in the degradation of MB was evaluated as follows. Firstly, 0.02 g of NRGO/BaWO₄ nanocomposite was dispersed into a 200 mL MB (10 mg/L) aqueous solution in a Pyrex glass photocatalytic reactor furnished with water cooled immersion tube and then the dispersion was kept in the dark for 30 minutes at room temperature to establish the adsorption equilibrium. The solution was irradiated using a 250 W Hg lamp (cutoff filter of wavelength 400 nm). During the irradiation, samples were taken out at given time intervals, filtered and then the concentration of MB was determined at 664 nm using a UV-Visible spectrophotometer (Analytik Jena) from which percentage degradation was calculated. The percentage degradation of MB dye was calculated by using the following equation.

$$\% \text{ Degradation of the MB dye} = [(C_0 - C) / C_0] \times 100 \quad (1)$$

where, C_0 is the initial concentration and C is the concentration at a given interval time, of the MB dye solution, respectively.

3. Results and Discussion

3.1. X-ray Diffraction Studies

The XRD patterns of NRGO, BaWO₄, and NRGO/BaWO₄ nanocomposite are shown in Figure 1. The diffraction peak at $2\theta = 24.4^\circ$ corresponds to the (002) reflection plane of the reduced phase of NRGO. The diffraction peaks corresponding to NRGO/BaWO₄ nanocomposite can be indexed to scheelite type tetragonal crystal of BaWO₄ (JCPDS No. 43-0646) with space group I41/a indicating that incorporation of BaWO₄ into NRGO matrix does not change the orientation and crystal structure of Scheelite BaWO₄ [11]. The peaks found at 2θ values 17.3° , 26.5° , 28.1° , 31.9° , 43.0° , 45.7° , 48.7° , 53.6° , 54.5° , 66.6° , 67.7° , and 69.4° can be ascribed to the (101), (112), (004), (200), (204), (220),

(116), (312), (224), (400), (208) and (411) planes of BaWO₄, respectively.

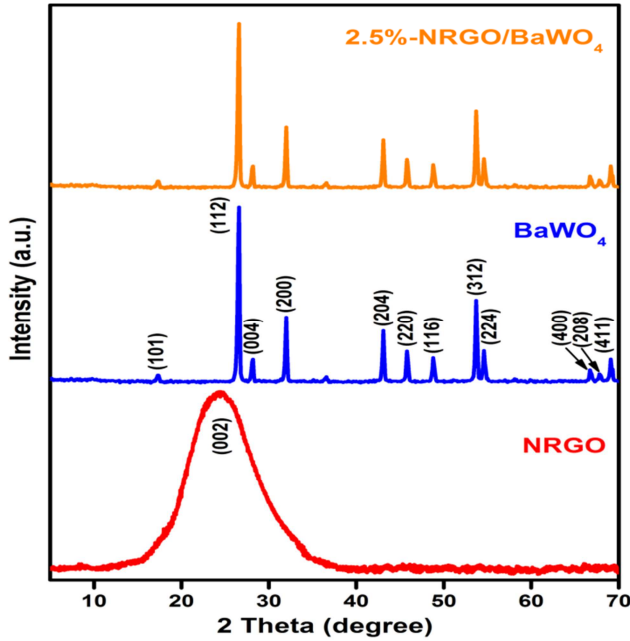


Figure 1. XRD patterns of the NRGO, BaWO₄, and NRGO/BaWO₄ nanocomposite.

3.2. Surface Morphology Studies

The morphologies of the NRGO/BaWO₄ nanocomposite were studied using SEM (Figure 2). The SEM image reveals narrow elliptical BaWO₄ particles wrapped in NRGO sheets.

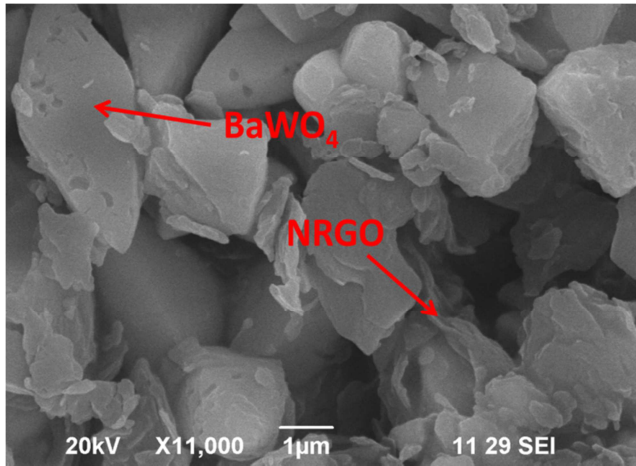


Figure 2. SEM image of the NRGO/BaWO₄ nanocomposite.

3.3. Optical Studies

The optical properties of NRGO, BaWO₄, and NRGO/BaWO₄ nanocomposite were studied using UV-Visible DRS technique (Figure 3). As shown in Figure 3, the NRGO absorbs in the whole visible region. BaWO₄ absorbs in the UV region while the absorption edge of the NRGO/BaWO₄ composites shifts towards the visible region with an increase in the intensity of absorption. Thus, the observation suggests that the NRGO/BaWO₄ nanocomposite

can efficiently utilize visible-light and generate more electron-hole pairs under visible light irradiation.

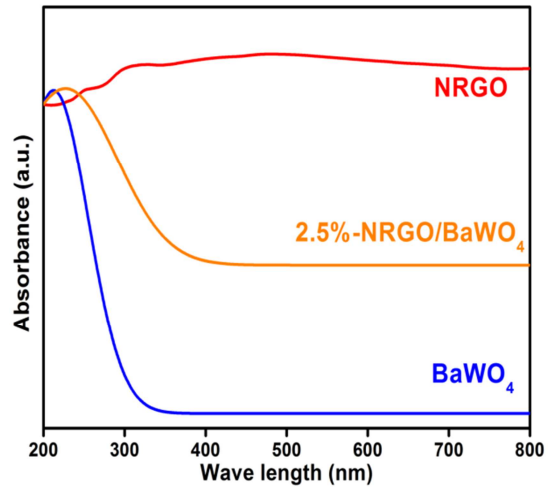


Figure 3. DRS spectrum of the NRGO, BaWO₄ and NRGO/BaWO₄ nanocomposite.

For a given semiconductor, its band gap energy (E_g) was calculated employing the Tauc relation [7] given below in equation (2) and are shown in Figure 4.

$$\alpha h\nu = k(h\nu - E_g)^{n/2} \quad (2)$$

where α , h , ν , E_g and k are the absorption coefficient, Plank constant, frequency of light, band gap energy and constant, respectively. The “ n ” value of 1 corresponds to direct and 4 corresponds to an indirect transition in the semiconductor material. According to equation 2, the intercept of the tangents to the plots of $(\alpha h\nu)^2$ vs photon energy could be employed to determine the band gaps of the given materials, due to their direct electronic transitions.

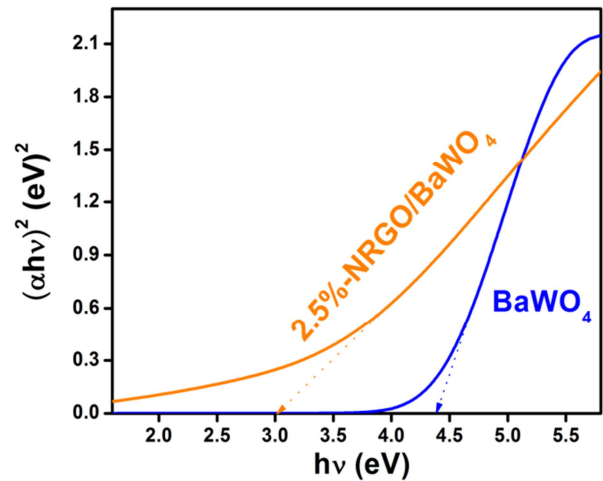


Figure 4. Band gap plots of the BaWO₄ and NRGO/BaWO₄ nanocomposite.

The band gaps of pure BaWO₄, and NRGO/BaWO₄ nanocomposite are 4.43 eV, and 3.04 eV, respectively (Figure 4). The band gaps of NRGO/BaWO₄ nanocomposite are reduced compared to its pure components. Such a reduction in the band gap of the materials is beneficial for

enhancing both visible light absorption and photocatalytic activity.

3.4. PL Studies

PL analysis can be used to determine the effectiveness of the charge separation and recombination rate of the photogenerated electron-hole pairs. If the intensity of PL peak is lower it means the recombination rate is lower [12]. The nature of charge carrier recombination in BaWO₄, and NRGO/BaWO₄ nanocomposites were investigated by PL analysis (Figure 5). The excitation wavelength corresponds to 400 nm while the emission peak is exhibited around 545 nm (green emission). BaWO₄ shows highly intense peak indicating high recombination rate. After NRGO was introduced, the composites exhibit lower intensity than pure BaWO₄. The PL Peak of NRGO/BaWO₄ shows very less intensity indicating the low recombination rate of the electron-hole pairs generated by the visible light irradiation.

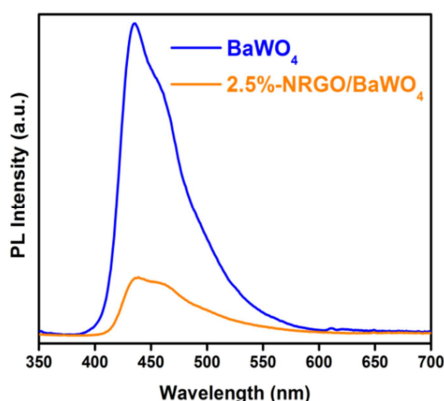


Figure 5. PL spectrum of the BaWO₄ and NRGO/BaWO₄ nanocomposite.

3.5. Photocatalytic Studies

The photocatalytic degradation of MB was studied in the presence of NRGO/BaWO₄ nanocomposites in aqueous solution using visible light source. First, in the absence of the catalyst, the degradation was negligible. As shown in Figure 6, the photodegradation efficiencies of various catalyst compositions were compared and it was found that the MB dye degradation 2.5%-NRGO/BaWO₄ nanocomposite showed maximum efficiency for 120 minutes under visible light irradiation, respectively.

The efficiency of photodegradation of the NRGO/BaWO₄ nanocomposites increased with increasing the NRGO contents from 0.5 to 5.0 wt%. With the increase in the NRGO content, initially the efficiency of photocatalytic activity increases up to 2.5%. At 2.5% NRGO content, the nanocomposite showed higher efficiency compared to other samples. This may be ascribed to the higher surface area available for charge separation which in turn enhances the catalytic efficiency. The decrease in the activity above 2.5% NRGO content may be ascribed to the coverage of NRGO on the semiconductor material and hence preventing the latter from effective absorption of incident light radiation and

causing low activity. Overall, the results indicate that the synergistic effect makes NRGO/BaWO₄ nanocomposites as an excellent photocatalytic material under visible light irradiation.

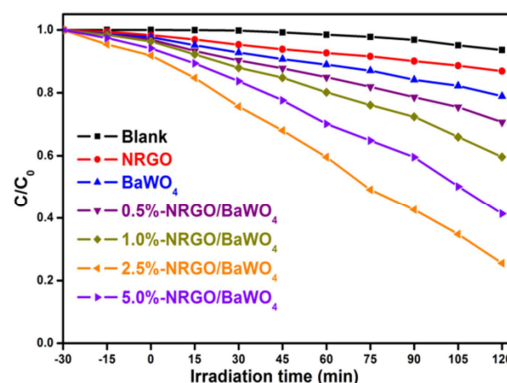


Figure 6. Degradation plots of MB over Blank, NRGO, BaWO₄ and NRGO/BaWO₄ nanocomposites under visible light irradiation.

The possible schematic scheme for photocatalytic degradation was given in Figure 7. NRGO/BaWO₄ nanocomposite absorbs the visible light and electron-hole pairs are created in BaWO₄. NRGO due to its high charge carrier mobility can act as an electron acceptor and transporter and delay the recombination of photogenerated electron-hole pair. The negatively charged electrons react with dissolved oxygen to produce the superoxide anion radicals (O₂^{•-}). The holes react with the water molecules to form hydroxyl radicals (OH[•]).

The proposed reactions are shown in equations (3-7),

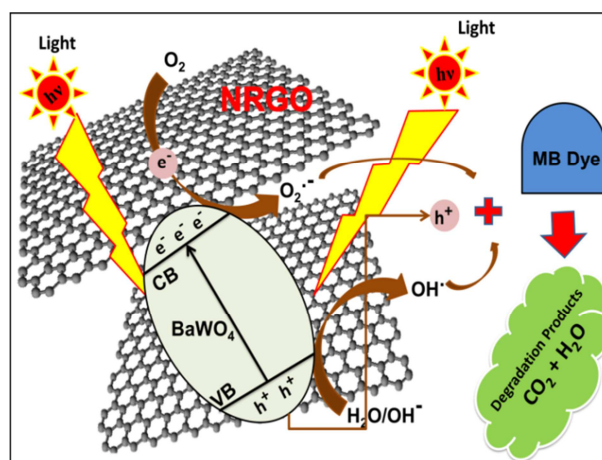
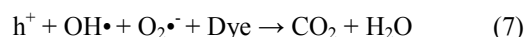


Figure 7. Proposed mechanism for the photocatalytic degradation of dye by NRGO/BaWO₄ nanocomposite under visible light irradiation.

4. Conclusions

In this work, a series of NRGO/BaWO₄ nanocomposites were successfully synthesized by microwave method and characterized by different analytical techniques. The photocatalytic activities of the NRGO/BaWO₄ nanocomposites have been studied using MB dye under visible light irradiation. We observed that the NRGO/BaWO₄ nanocomposite with the optimal NRGO content of 2.5 wt% show the maximum photocatalytic performance of dye degradation in comparison to the other ratios studied. The improved photocatalytic performance of the BaWO₄ is due to the increase in visible light absorption range and the reduction in recombination rate of photogenerated electron-hole pair due to the composited NRGO. Hence, the above results indicate that the synergistic effect makes NRGO/BaWO₄ nanocomposites can be a potential eco-friendly photocatalytic material under visible light irradiation.

Acknowledgements

The author M. J. S acknowledges the financial support from the Alagappa University, Karaikudi, in the form of research fellowship under RUSA 2.0 Scheme.

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