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Reduced graphene oxide/bismuth vanadate composite as an efficient piezocatalyst for degradation of organic dye

Manish Kumar¹, Gurpreet Singh¹, Rahul Vaish*

School of Engineering, Indian Institute of Technology Mandi, Mandi, Himachal Pradesh 175005

*Corresponding author E-mail address: rahul@iitmandi.ac.in

¹Both authors have equally contributed.
Abstract

Reduced graphene oxide (rGO)/bismuth vanadate (BiVO₄) composites with varying rGO content (0, 1, 2, 3, and 5 wt%) were synthesized and explored for their piezocatalytic dye degradation performance. X-ray diffraction (XRD) and Raman spectroscopy evidenced the co-existence of BiVO₄ and rGO phases in all composite samples. The interfacial coupling between BiVO₄ and rGO phases in a typical rGO/BiVO₄ composite was confirmed using transmission electron microscopy (TEM). Elemental oxidation states in a typical rGO/BiVO₄ composite were identified using X-ray photoelectron spectroscopy (XPS). The piezocatalytic activity of all samples was analyzed by the use of a model dye named methylene blue (MB) using an ultrasonicator. Results demonstrate that the piezocatalytic activity greatly depends upon its rGO content of composite. Piezocatalytic dye degradation performance of composites showed an initial increase with increment in rGO content up to 2 wt% followed by a decrease with further increment in rGO content. The best piezocatalytic active composite sample (2wt% rGO/BiVO₄) showed ~81% of MB dye degradation as compared to pure BiVO₄ (~19 %) under 180 min of ultrasonication. Thus, the 2 wt% rGO/BiVO₄ composite has promising piezocatalytic capability to be used for water remediation.

Keywords: rGO; BiVO₄; piezocatalysis; dye; interfacial coupling; ultrasonication.
1. Introduction

The water pollution crisis is a prevailing concern these days due to the rapid development of mankind and industries [1]. The discharge of colored organic dyes from textile industries into natural water sources is one of the main sources causing water pollution [2]. This problem has attracted the focus of many researchers. Recently, the piezocatalysis process has emerged as a promising technology for water remediation, which has been related to piezoelectric materials [3]. The presence of polarization field inside the piezoelectric materials under the stimulation of mechanical strain retard recombination of free charge carriers (electrons; e\(^-\)-holes; h\(^+\)) [3]. These generated free charge carriers further participate in the surface redox reactions generating reactive oxygen species (ROS) such as ‘OH, ‘O\(_2^\cdot\), etc. ROS further decomposes dye molecules into simpler products [4–6]. Piezocatalysis has been mainly reported for organic pollutant degradation [7]. ZnO [8], MoS\(_2\) [9], NaNbO\(_3\) [10], and PbTiO\(_3\) [11], BaTiO\(_3\) [12] etc., have already been reported for piezocatalytic applications. In the piezocatalysis field, much attention has given to piezocatalysis using BaTiO\(_3\) catalyst. BaTiO\(_3\) crystals in the form of nanowires, nano-dendrites, and nanoparticles exhibited promising piezocatalytic dye degradation [13,14] and water-splitting [14]. Various composites/heterostructures of BaTiO\(_3\) such as BiOX/BaTiO\(_3\) (X=Cl, Br, and Cl\(_{0.166}\)Br\(_{0.834}\)) [13], BaTiO\(_3\)/graphene [15], iodide-doped BiVO\(_4\)/BaTiO\(_3\) [16] have also been reported to show superior piezocatalysis over bare BaTiO\(_3\). The dye degradation can further be enhanced using combined photo-piezocatalysis. In this direction, Zhou et al. achieved 97% RB dye degradation within 30 min during combined photo-piezocatalysis using ZnO/BaTiO\(_3\) heterostructures, which was higher than dye degradation achieved using only light source and only sonication [17]. However, this new field still needs identification and exploration of new piezocatalytic active materials with promising performance [6,18].
Monoclinic bismuth vanadate (m-BiVO₄) exhibits excellent technological properties such as solar energy absorption, ionic conductivity, ferroelasticity, less toxicity, coloristic [19], eco-friendly, high chemical stability, and is cost-effective [20,21]. It has been widely reported for its photocatalytic application under visible light stimulation. Though BiVO₄ has a centro-symmetric structure, however, it has been reported to be piezo-responsive due to the flexoelectric effect [22]. Recently, in our previous published work, BiVO₄ ceramics pellets demonstrated enhanced piezocatalytic dye degradation capability in addition to photocatalytic activity [23]. However, the piezocatalytic performance of BiVO₄ should be further improved.

Reduced graphene oxide (rGO) has a 2-D conjugated structure with a very high surface area along with high electrical conductivity and carrier mobility [24]. The formation of composite between BiVO₄ and rGO showed enhanced photocatalytic activity over pristine BiVO₄ through enhancement of free charge carriers separation [25,26]. Likewise, it is expected that rGO/BiVO₄ composite will also provide enhancement in piezocatalytic performance as well. So, in this present study, the rGO/BiVO₄ composites (varying in rGO content) are investigated for their piezocatalytic performance.

2. Materials and methods

2.1 Synthesis of BiVO₄ ceramic powder

Firstly, BiVO₄ ceramic powder was synthesized using Bi₂O₃ and V₂O₅ oxides as starting powders, taken in accordance with their stoichiometric molar ratios, which were manually mixed and grounded for about 30 min. The procured homogenous and fine powdered mixture was subjected to calcination at 700 °C for the duration of 8 h for the formation of the BiVO₄ phase. The obtained BiVO₄ powder was ball milled for 12 hours at 250 rpm.
Scheme 1. Synthesis process of rG-BV composite

2.2 Synthesis of rGO/BiVO$_4$ composites
To synthesize rGO/BiVO$_4$ composites, the calculated amount of 1 wt%, 2 wt%, 3 wt%, and 5 wt% of rGO were initially dispersed in 25 ml ethanol solution in separate vials followed by adding the remaining wt% of BiVO$_4$ sample to it. Further, ultrasonication was carried out for 45 min at 30 °C till the homogenous solution was obtained. The solution was then irradiated by 3 Havells LED bulbs of power 15W each for a duration of 48 h with stirring in order to achieve more reduction of rGO using BiVO$_4$ photocatalytic activity. The procured sample was transferred to 100 ml capacity, Teflon lined stainless steel autoclave for hydrothermal treatment for forming a better connection between rGO and BiVO$_4$. Filling 40% volume with solution, the autoclave was sealed and kept at a temperature of 200 °C for 8 h and then further cooled till room temperature. The precipitates procured were washed thoroughly with ethanol and distilled water 3 times. The obtained products were dried in the oven at 70°C for 4 hours duration. The total synthesis process has been schematically shown in scheme 1.

2.3 Characterization

Structural phases of all the synthesized samples were identified through an X-ray diffractometer (XRD) using Rigaku diffractometer, Japan (9 kW Cu-K$_\alpha$ anode). Sample scan was carried over the scan range of 10-90 with a scan rate of 3°/min. Raman spectroscopy was used to find the bonding and structure that exists in all samples. The Raman spectra were acquired using HORIBA (Japan-made, Model-LabRAM HR Evolution) where 10% power and 532 nm laser excitation wavelength along with 600 gratings were used to scan the samples. A scan range of 100-2000 cm$^{-1}$ was provided. Nova Nano SEM-450 (JFEI, USA) field emission scanning electron microscope (FE-SEM) was used to analyze the microstructures and morphology of the sample. UV–Visible spectrophotometer (Shimadzu-2600 was used for recording the absorbance spectra of the samples. The interfacial coupling between rGO and BiVO$_4$ in one composition was
confirmed through a transmission electron microscope (TEM) with the use of FP-Tecnai G2 S-TWIN TEM instrument (FEI made in USA). To analyze the compositional chemical state of elements, X-ray photoelectron spectroscopy (XPS) was used. Nexsa X-ray photoelectron spectrophotometer possessing Al-Kα source was used to obtain XPS spectrum.

2.4 Piezocatalytic experiments

Piezocatalytic performances of all the rGO/BiVO₄ samples were analyzed using piezocatalytic experiment under ultrasonication. 0.05 g of each sample was utilized. Before starting the piezocatalytic experiment, complete adsorption of all the samples in connection with the dye solution was achieved in dark with continuous stirring at the rate of 500 rpm. Once adsorption saturation was achieved, the previously used dye was being replaced with a fresh 10 ml dye of initial dye concentration~5 mg/L. The dye solution along with the sample in it was subjected to ultra-sonication. For providing the ultrasonic vibrations, an ultrasonicator with 70W power and 40 kHz frequency with water acting as a medium was used. Absorbance spectra measurement was done with 1 mL of MB dye solution after every 30 min of ultrasonication and the constant volume was maintained by recovering back the dye to the beaker. Water is used as an ultrasonication medium and was replaced after at most 15 min duration to avoid the dye solution heating. To determine MB dye percentage removal from aqueous solution, the formula in Eq. 1 was taken in use[27].

\[
\text{% removal of MB dye} = \frac{C_o - C}{C_o} \times 100
\]

(1)

Where the symbol \(C_o\) and \(C\) denote the MB dye solution concentration initially and at a time‘t’ respectively.

3. Results and discussion
Fig. 1. XRD patterns of BV, rGO, 1rG-BV, 2rG-BV, 3rG-BV, and 5rG-BV powders.

Fig. 1 shows XRD patterns of BV, rGO, 1rG-BV, 2rG-BV, 3rG-BV, and 5rG-BV powders. The obtained sharp XRD peaks in pure BV and all rG-BV samples evidenced high crystallinity. All XRD peaks in the BV sample showed a good match with that of peaks reported in standard JCPDS 01-075-1866 for pure monoclinic phase of BiVO$_4$. Peaks of rG-BV composites are similar to that of BV except for an extra peak at ~27.2°, confirming the monoclinic phase of BiVO$_4$ in all rG-BV composites [28]. The extra peak at ~27.2°, associated to the (002) plane of the rGO phase. Generally, the (002) plane of graphite showed a peak at 26.5° [29]. In most of the literature, the (002) peak of rGO has been reported at 2θ angle which is less than that was found
in the case of graphite (26.5°). But in the present case, the rGO peak was found at the same 2θ angle of 26.5°. The peak of rGO at 26.5° is similar to that of graphite which is due to restacking of the rGO layers. There is slight shift in the peaks from 26.5° to 27.2° in rG-BV composites which may be due to enhanced restacking of rGO layers and/or further reduction of rGO during synthesis through ultrasonication, photocatalytic induced reduction and hydrothermal treatment [29–31]. Thus, XRD peaks affirm the presence of both rGO and BiVO₄ in the prepared composites with high crystallinity. The as-prepared powdered samples are shown along with their respective XRD patterns.

![Raman spectra](image)

**Fig. 2.** Raman spectra of BV, rGO, 1rG-BV, 2rG-BV, 3rG-BV, and 5rG-BV.

Raman spectra of BV and all rG-BV composites have been shown in Fig. 2. Raman bands at around 118, 204, 324, 360, 818 cm⁻¹ in both BV and all rG-BV composites correspond to the
BiVO₄ phase [32]. The strongest band at 818 cm⁻¹ results due to symmetric stretching of V-O in the crystal structure. Two other Raman modes at 324 and 360 cm⁻¹ were viewed because of the symmetric and antisymmetric bending of V-O bonds, respectively [33]. The observed external modes at 118 and 204 cm⁻¹ were evidenced because of translation and rotation of the BiVO₄ crystal lattice structural units. In addition to these bands, two additional Raman bands at 1356 and 1594 cm⁻¹ were viewed in case of all rG-BV composites are associated with rGO carbon, which has been claimed in the literature as G and D bands, respectively [19]. G band represents in-planar stretching of symmetric sp² C-C bonds, while D band represents the interruption that occurred in symmetric hexagonal graphitic lattice [34]. Additionally, there was observed a little shift in the D and G bands of 1rG-BV, 2rG-BV, 3rG-BV, and 5rG-BV sample as compared to rGO which might have resulted from the changed surface strain during the interaction of rGO with BiVO₄ in composites [35].
SEM micrographs of (a) rGO, (b) BV, (c) 2rG-BV and (d) 5rG-BV.

SEM micrographs showing the morphology of BV, rGO, 1rG-BV, and 5rG-BV are presented in Figs. 3(a-d). In the BV sample, the irregular morphology of BiVO$_4$ particles was visualized as shown in Fig. 3(a). The rGO layered structure can be viewed in Fig. 3(b). The accumulation of rGO layers on BiVO$_4$ particles in the case of 2rG-BV and 5rG-BV can be seen in Figs. 3(c-d), which reveals an adequate contact and interfacial interaction among BiVO$_4$ and rGO phases.

TEM micrographs of a typical composite sample (2rG-BV) are viewed in Figs. 4(a-b). Fig. 4(a) shows the presence of rGO layers and BiVO$_4$ crystals in the 2rG-BV composite. Fig. 4(b) shows the well-defined and tight interfacial coupling formed between rGO and BiVO$_4$ phases in the 2rG-BV composite. The observed fringe spacing of $d = 4.67\text{Å}$ corresponds to the BiVO$_4$ (011) crystallographic plane [23]. The right side shows multiple rGO layers. Thus, TEM evidenced the existence of proper interfacial coupling between rGO and BiVO$_4$ phases in rG-BV composites.
This interface formed will support the transport of electrons from BiVO$_4$ to the rGO phase and thus will assist in effective charge separation within the composite during the dye degradation.

The XPS spectra of a typical composite sample (2rG-BV) showing V2p, Bi4f, C1s, and O1s scans are presented in Figs. 5(a-d). In the case of Bi4f spectrum, the peaks displayed Bi4f$_{7/2}$ and Bi4f$_{5/2}$ components which further deconvoluted into the components Bi$^{3+}$ and Bi$^{2+}$ [36]. Bi$^{3+}$ oxidation state presence in the sample can be confirmed by the high peaks positioned at 159.2 and 165 eV while the weaker peaks at 157 and 163 eV confirm Bi$^{2+}$ oxidation state in the sample. For the V2p scan, the split peaks displayed V2p$_{1/2}$ and V2p$_{3/2}$ peaks which further deconvoluted into components and V$^{4+}$ and V$^{5+}$ [37]. The V$^{5+}$ oxidation state presence in the sample can be confirmed by the peaks positioned at 159.2 and 165 eV while the high peaks at 157 and 163 eV confirm the existence of some V$^{4+}$ oxidation state in the sample. For O1s scan spectra, there exist an asymmetric component O1s which is further deconvoluted into O$_{L}$ and O$_{A}$ components. The O$_{L}$ component positioned at 530.01 eV corresponds to the lattice oxygen (O$^{2-}$) while the O$_{A}$ component positioned at 531.20 eV corresponds to oxygen vacancies along with many other adsorbed oxygen species [36,38]. The intrinsic defects formed during thermal treatment (i.e.,
localized oxygen vacancies) trap the charge in excess as electron pairs which results in the reduction of $V^{5+}$ to $V^{4+}$ and $Bi^{3+}$ to $Bi^{2+}$. This leads to signal peak observance of $Bi^{2+}$ and $V^{4+}$ along with that of $Bi^{3+}$ and $V^{5+}$ in the XPS spectra. For rGO confirmation in the 2rG-BV sample, C species can be detected [39]. For this C1s scan was performed and deconvoluted into 3 peaks as viewed in Fig. 5(c). The deconvoluted peak at $\sim 284.6$ eV, $\sim 286.4$ and $\sim 288.6$ eV demonstrate sp$^2$ hybridized carbon (C-C) species, the oxygen-containing functional groups (C-O, epoxy, and hydroxyl) species and (C = C, carboxyl) species, respectively [25].

![Figure 5](image)

**Fig. 5.** The XPS spectra of 2rG-BV sample (a) V2p (b) Bi4f (c) C 1s (d) O 1s.
To investigate the piezocatalytic performance of rGO-BiVO₄ composite samples, piezocatalytic degradation of MB dye was done and the acquired results are shown in Figs. 6(a-c). It is to be taken into account that here adsorption saturation was achieved cautiously prior to the commencement of the piezocatalytic test using ultrasonicator. The concentration of MB dye during the piezocatalytic experiment was calculated by recording an absorbance peak at 664 nm. The absorbance spectra obtained during the piezocatalytic experiment with the use of 2rG-BV composite are displayed in Fig. 6(a). The absorbance peak intensity was observed to continuously decrease with vibration time, which indicates a decrease in MB dye concentration in the dye solution. Fig. 6(b) displays the $\frac{C}{C_0}$ vs vibration time plots for piezocatalytic experiments without and with the use of samples. Under ultrasonication, only $\sim$15% dye degradation was obtained with no sample. During the ultrasonication process, the constant formation, growth, and collapse of water bubbles take place, which gives rise to local hot spots formation with localized temperature commence near 4000-5000K [40]. Since there is an occurrence of localized hot spots, •OH radical forms from the thermolytic decomposition of water. The generated •OH radicals are further used for MB dye degradation [40]. This overall process has been referred to as sonolysis in literature [41]. With the use of BV, rGO, 1rG-BV, 2rG-BV, 3rG-BV, and 5rG-BV sample, the dye degradation was achieved as 19%, 29%, 72%, 81%, 31%, and 30%, respectively within the 180 min of ultrasonication. Results show that the piezocatalytic activity greatly depends upon its rGO content of composite. Piezocatalytic dye degradation performance of composites showed an initial increase with increment in rGO content up to 2 wt% followed by a decrease with further increment in rGO content. The best piezocatalytic active composite sample (2wt%- rGO/BiVO₄) showed $\sim$81% of MB dye degradation as compared to pure BiVO₄ ($\sim$19%) under 180 min of ultrasonication. Scavengers
such as p-benzoquinone (p-BQ), ethylenediaminetetraactic acid (EDTA), and isopropanol (IPA) were added separately in the dye solution during piezocatalytic experiments in view to trap the active species like superoxide radical (\(\bullet O_2^-\)), holes (h\(^+\)), and hydroxyl radical (\(\bullet OH\)) respectively. With the capture of main active species there incurs a reduction of piezocatalytic performance [4,42,43]. Fig. 6(c) clearly shows that BQ scavenger drastically put an impact on the piezocatalytic activity, which scavenge superoxide (\(\bullet O_2^-\)) radicals. This specifies that \(\bullet O_2^-\) radicals acted as main active radical species behind piezocatalytic dye degradation [44]. The 2rG-BV sample showed the best piezocatalytic activity among all the synthesized samples. This might be due to the fact that at higher wt% of reduced graphene oxide, most of the surface of BiVO\(_4\) gets covered with rGO layers, which reduces the piezocatalytic performance. 2rG-BV is an optimum composite for best piezocatalytic performance under study.

![Absorption spectra acquired during piezocatalytic experiment with the use of 2rG-BV sample, (b) \(\frac{C}{C_0}\) vs time plots acquired during the piezocatalysis with sample and without sample, (c) scavengers’ effect on the percentage MB dye degradation acquired during the piezocatalysis experiment with the use of 2rG-BV sample.](image)

A proposed piezocatalytic reaction mechanism for the BiVO\(_4\), rGO, and rGO/ BiVO\(_4\) composite for MB dye degradation is schematically shown in Fig. 7. As per literature, BiVO\(_4\) is known to
possess localized surface piezoelectricity [22]. Due to local surface piezoelectricity, the polarization charges (internal electric field) are induced in BiVO$_4$, when mechanical stress in the form of ultrasonication vibration is provided [45]. The free electrons and holes within BiVO$_4$ get attracted, move in opposite direction towards the opposite polarity of the internal electric field. In this way, the recombination of free electrons and holes are inhibited, which results in more transportation of these free charge carriers to the BiVO$_4$ surface [46–48], which further participate in piezocatalytic surface reactions. Moreover, the piezoelectric polarization field also provides further band bending, which further assists in the easy transfer of free carriers to adsorbed pollutants undergoing piezocatalytic reactions [4,46,49]. It is suggested in many literatures that the origin of free charge carriers inside the piezoelectric materials is due to the existence of defects in them at room temperature [4,50]. Also, temperature rise due to hot spot results in thermal emission of electrons from the valence band to conduction band of semiconductor [50,51]. In the present work, rGO also shows some amount of dye degradation. It is suggested in the literature that the rGO edges contain unsaturated carbon and the presence of other defects on rGO may serve as catalytic active centers for catalytic activity [52]. Moreover, it is also suggested in the literature that the adsorption of organic dye also increases under ultrasonication, which may have some contribution here [53]. In case of rGO/BiVO$_4$ composite, the mechanism is slightly different. Infact in this case, the free electrons in BiVO$_4$ surface readily transfer from BiVO$_4$ to rGO due to multiple favorable conditions. Bai et al. reported that, when n-type BiVO$_4$ and rGO come in contact with each other through the formation of heterojunction/composite, the flow of electrons from BiVO$_4$ to rGO takes place until the fermi level of the system reaches a balance (otherwise before contact, the fermi level of rGO is higher than that of BiVO$_4$ and the work function of rGO (4.75 eV) is smaller than that of BiVO$_4$ (5.27
eV). As a result, the band bending occurs at the interface of BiVO$_4$ and rGO, which favors the transfer of electrons from BiVO$_4$ to rGO [54]. In addition to this, electron transportation is also favored due to the possession of delocalized electrons on the π-π graphitic carbon network and higher conductivity of rGO [55]. In addition to these factors, it is also reported that the piezoelectric polarization field also provides further band bending [4,46]. All these factors favor the migration of free electrons from BiVO$_4$ to rGO, hence increase the lifetime of free charge carriers. Thus, these free charge carriers have more time to participate in the piezocatalytic surface reactions. During piezocatalytic surface reactions, the free electrons on the rGO surface get captured by adsorbed oxygen (O$_2$) to generate superoxide radicals (O$_2^\cdot$). While the holes in the VB of BiVO$_4$ oxidize hydroxide ions (OH$^-$) to generate hydroxyl (·OH) radicals. These generated O$_2^\cdot$ and ·OH radicals degrade MB dye into harmless degradation products such as CO$_2$ and H$_2$O [56,57]. The piezocatalytic reactions can be summarized in the form of Eqs. 2–6 provided as follows:

\[
\text{BiVO}_4 + \text{sonication} \rightarrow \text{BiVO}_4 (e^- + h^+) \quad (2)
\]

\[
\text{BiVO}_4 (e^-) + \text{rGO} \rightarrow \text{BiVO}_4 + \text{rGO} (e^-) \quad (3)
\]

\[
\text{rGO} (e^-) + \text{O}_2 \rightarrow \cdot\text{O}_2^- \quad (4)
\]

\[
\text{BiVO}_4(h^+) + \text{OH}^- \rightarrow \cdot\text{OH} \quad (5)
\]

\[
\cdot\text{OH}/\cdot\text{O}_2^- + \text{MB dye} \rightarrow \text{Degradation products} \quad (6)
\]
4. Conclusions

Composites of rGO-BiVO₄ were synthesized for piezocatalytic MB dye degradation. Piezocatalytic dye degradation performance increased initially with increment in rGO content up to 2 wt% followed by a decrease with further increment in rGO content. The synthesized 2 wt% rGO-BiVO₄ composite demonstrated superior piezocatalytic performance as compared to other BiVO₄ composites which can be ascribed to the presence of interfacial coupling established between rGO and BiVO₄, which causes elevated charge separation ability and enhanced carrier mobility. Thus, rGO-BiVO₄ composites can be considered as a novel method to ensure effective dye degradation through piezocatalysis.

Conflict of interest
The authors declare not having any conflicts of interest.

**Data Availability**

All data are included within this manuscript.

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