Graphene wrapped BiVO₄ photocatalyst and its enhanced performance under visible light irradiation

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Abstract

Graphene wrapped BiVO₄ (GW-BiVO₄) photocatalyst is successfully synthesized via facile sol–gel method and characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and transmission electron microscopy techniques. The morphology of GW-BiVO₄ looks like a human embryo embedded inside the amniotic sac. The photocatalytic performance of GW-BiVO₄ for the decolorization of methylene blue is investigated. GW-BiVO₄ system reveals enhanced photocatalytic activity for degradation of methylene blue in water under visible light irradiation as compare to pure BiVO₄ catalyst and BiVO₄ decorated on graphene sheet (GD-BiVO₄). The experimental result shows that the wrapping of the graphene sheets in this composite catalyst enhances the photocatalytic performance under visible light. This enhance activity is mainly attributed to the effective quenching of the photogenerated electron–hole pairs which confirmed by photoluminescence spectra. Trapping experiments of radicals and holes were performed to detect the reactive species generated in the photocatalytic system, experimental results found that the direct hole oxidation reaction is obviously dominant during the photocatalytic reactions on the GW-BiVO₄ system.

Keywords: Graphene oxide, GW-BiVO₄ composite, Methylene blue, Photocatalysis

Background

The development of semiconductor photocatalysts for degradation of organic pollutant and water splitting under solar-light is a challenging and indispensable topic. TiO₂, the widely used photocatalyst, is only active under UV light irradiation due to its wide bandgap (3.20 eV) [1-4]. It is well known that the UV region occupies only about 4% of the entire solar spectrum, while 45% of the energy belongs to visible light. Therefore, the development of visible-light responsive photocatalysts for environmental remediation has become an active research area in recent years. To resolve this problem, the doping of TiO₂ by metal and non metal has received a lot of attention. However, these dopant works as recombination center between photogenerated carriers which make them unsuitable for commercial application. Apart from TiO₂, many single-phase multicomponent oxides such as BiVO₄ [5], BaCrO₄ [6], silver containing metal vanadate, tungstate, niobate, chromate, and tantalate [7-11] are found to be active for degradation of organic pollutants or water splitting under visible light irradiation.

Among these works, due to low bandgap (2.4 eV) and easy-to-synthesize monoclinic bismuth vanadate, BiVO₄ has attracted considerable attention for its photocatalytic activity under visible-light irradiation [5]. However, its poor adsorptive performance and difficulty of migrating photogenerated electron–hole pairs of pure BiVO₄ restrict its wide application in the photocatalytic degradation of organic contaminants. To enhance the photocatalytic effect, few reports were proposed on the development of doping BiVO₄, such as Eu/BiVO₄ [12], Ag/BiVO₄ [13], Fe/BiVO₄ Co/BiVO₄, Cu/BiVO₄ [14], AgO/BiVO₄ [15], WO₃/BiVO₄ [16], and V₂O₅/BiVO₄ [17].

As a two-dimensional crystalline material, graphene possesses a number of excellent intrinsic properties and can be utilized as a supporting material to disperse and...
stabilize nanocrystals for potential applications in catalysis [18-20]. Considering the large specific surface area, which is desirable to disperse and stabilize the inorganic nanoparticles, the combination of BiVO₄ and graphene may effectively inhibit the aggregation of these nanoparticles and consequently give a higher photocatalytic performance. Recently, Ng et al. prepared a graphene decorated BiVO₄ through a facile photocatalytic reaction to improve its photo-response in visible light and found remarkable enhancement in photoelectrochemical water splitting compared to pure BiVO₄ under visible illumination. This enhancement is due to the longer electron lifetime of excited BiVO₄ as the electrons are injected to graphene instantly at the site of generation, leading to a minimized charge recombination [20]. It is well documented that the photocatalyst which was better for water splitting may or may not be good for degradation of organic pollutants. Herein, a facile and straightforward strategy is designed to prepare a graphene wrapped BiVO₄ (GW-BiVO₄) molecules by simple sol–gel method and its effects on the photocatalytic performance on the degradation of methylene blue as a representative of dye.

Methods

Synthesis of GW-BiVO₄ composite

Graphene oxide (GO) was synthesized according to the method reported by Hummers and Offeman from purified natural graphite [21]. We prepared the composite as reported by Ng et al. but with slight variations in experimental conditions. A typical experiment for the synthesis of GW-BiVO₄ oxide composite is as follows: 30 mg of GO and 0.485 g of Bi (NO₃)₃·5H₂O were dispersed into 100 mL of 0.75 M HNO₃ solution with stirring for 1 h. Then, 0.0584 g of NH₄VO₃ was separately added into the above solution and stirred for 24 h at room temperature, yielding stable bottle-green slurry, centrifuge and isolate with acetone, and dry at 80°C. For comparison, the same method was used to synthesize the pure BiVO₄ without GO and BiVO₄ decorated on graphene sheet by the method reported by Ng et al. To prepare GW-BiVO₄ composite, reductions GO was carried out under visible light in ethanol as reported [20].

Characterization

The X-ray diffraction (XRD) measurements were carried out by a polycrystalline X-ray diffractometer (XPERT-PRO, PANalytical B.V., The Netherlands) under room temperature with Cu Kα radiation, and the scanning angle ranged from 5° to 90° of 2θ. Fourier transform infrared (FTIR) spectra were recorded on a FTIR spectrophotometer (BRUKER Model-Alpha, BrukerOptikGmbH, Ettlingen, Germany) with ATR Technique. The transmission electron microscopy (TEM) images were taken using a transmission electron microscope (Philips-CM200 TEM, Chalmers, Gothenburg, Sweden). Scanning electron microscope images and energy dispersive X-ray spectroscopy (EDS) were taken with a JEOL-JSM-5200 microscope (JEOL Ltd., Akishima, Tokyo, Japan). The UV-visible absorption spectra were recorded with an UV–vis spectrophotometer (ShimadzuUV-1800, Shimadzu, Kyoto, Japan). Photoluminescence (PL) spectra were recorded on a Shimadzu RF-5301 PC spectrofurophometer, and a 450 W Xe-lamp was used as the excitation source.

Photocatalytic activity measurement

The badgap of GW-BiVO₄ is demonstrated to be 2.48 eV, thus the photocatalytic activity measurement should be carried out in visible spectrum instead of the full-spectrum. Photocatalytic activity of the samples was determined by the degradation of methylene blue (MB), under visible-light irradiation. Photo-irradiation was carried out using a Philips lamp (40 W/230 V) and was placed 10 cm away from the reaction vessel, which was used to provide a full-spectrum emission without any filter to simulate the sunlight source. Experiments were conducted at the ambient temperatures in the following manner: 0.2 g of GW-BiVO₄ composite photocatalyst was added to 100 mL of 2 ppm MB aqueous solution. Before starting the illumination, the reaction mixture was stirred for 30 min in the dark in order to reach the adsorption-desorption equilibrium between the dye and the catalyst. At regular time interval of irradiation, 3 mL aliquots were withdrawn, and then centrifuged to remove essentially all the catalyst. The concentration of the remnant dye was spectrophotometrically monitored by measuring the absorbance of solutions at 663 nm during the photodegradation process.

Results and discussion

Characterization

GW-BiVO₄ composites were characterized by XRD, FTIR, TEM, EDS, DRS, and PL techniques. The XRD patterns of the pure BiVO₄ and GW-BiVO₄ are shown in Figure 1. From the Figure 1, it is confirmed that all the diffraction peaks of monoclinic scheelite type BiVO₄ (JCPDS 14–0688), which exhibits the most active photocatalysis under visible-light irradiation [22]. The present XRD pattern for GW-BiVO₄ does not show any diffraction peak of GO (001) which is may be due to the crystal growth of BiVO₄ between the layers of GO. This crystal formation between the layers might leads to exfoliation and wrapping of graphene.

The FT-IR spectra of GW-BiVO₄ composites, pure BiVO₄ and graphene oxide are described in Figure 2. Figure 2a shows that in this process, all the representative peaks for GO, such as peak near 1,710 cm⁻¹ representative of the C=O stretching of carboxylic groups and
a broad peak at 3,400 cm$^{-1}$ (here we want cm inverse please keep as it is.) representative of O-H stretch, disappeared indicating the reduction of exfoliated wrapped graphene layer. The presence of the absorption with very small peaks at 1,625 cm$^{-1}$ is due to aromatic C=C stretching (skeletal ring vibration) in Figure 2b [23]. Similar behaviors were observed for bands at 1,410 and 1,285 cm$^{-1}$ attributed to carboxyl C-O and tertiary C-OH groups, respectively. The broad absorption peaks at low frequency (below 1,000 cm$^{-1}$) are attributed to 1(VO$_4$) and 3(VO$_4$) and were reported for pure BiVO$_4$ in Figure 2c [24]; these peaks matches with the GW-BiVO$_4$.
composite in Figure 2b which confirmed the formation of BiVO$_4$.

TEM images of the prepared GW-BiVO$_4$ composites are shown in Figure 3. From the figure, it can be clearly seen that the almost transparent graphene sheets are wrapped over the BiVO$_4$ crystals with an average particles size of 88 nm and a thickness of about 25 nm. It is observed that the graphene forms a sac-like structure, in that BiVO$_4$ is embedded inside, and the resultant morphology looks like an embryo of a human inside the amniotic sac (Figure 3a). TEM images of the GW-BiVO$_4$ composite and pure BiVO$_4$ (in Additional file 1 Figure S1a-b) clearly shows distinct surface morphology and crystal growth.

The experimental finding in the present context shows how the small change in the preparative strategy changes the resultant product. In Ng et al., all three materials such as GO, V$_2$O$_5$, and Bi(NO$_3$)$_3$ are mixed simultaneously, and the resultant product which is graphene-decorated BiVO$_4$ was obtained. In our experiment, GO and Bi(NO$_3$)$_3$ were mixed first and allowed to interact for 1 h followed by the addition of NH$_4$VO$_3$. This gives us graphene wrapped BiVO$_4$. On the basis of data, we assume that the Bi(NO$_3$)$_3$ was hydrolyzed in water, and that it interacted with the graphene with electrostatic attraction which gives the wrapping of graphene sheet which further converted to GW-BiVO$_4$ composites in addition of NH$_4$VO$_3$. Well-wrapped graphene layer is transparent enough to allow light rays to reach to BiVO$_4$ and excite electrons, which could be easily transferred to graphene template results inhibiting quick recombination. Wrapping by graphene layer offers quick shuttling of the excited electron, and therefore, it shows expected enhanced photocatalytic activity.

From the EDS elemental analysis shown in electronic supplementary information (Additional file 1 Figure S2), we can easily predict that the sample is composed of Bi, V, O, and C. These four elements in the product (the Al signals come from the Aluminum mesh) having the Bi/V atomic ratio of 1.08 is close to the theoretical value for BiVO$_4$.

The UV–vis diffuse reflectance spectra of GW-BiVO$_4$ composite is shown in Additional file 1 Figure S3. We observed the bandgap of 2.48 eV corresponding to significant absorption in the region below 550 nm for pure GW-BiVO$_4$, calculated from Kubelka-munk equation. Also, it is found that the wrapping of graphene does not affect the absorption since graphene layer is transparent enough to pass light through it. For the GW-BiVO$_4$, the energy can be estimated to be according to the absorption band edge in Additional file 1 Figure S3.

Photocatalytic efficiency of the catalysts
The photodegradation rates of GW-BiVO$_4$ composite, pure BiVO$_4$, and without photocatalyst under visible-
light irradiation are shown in Figure 4. Comparative degradation efficiency of the prepared samples GW-BiVO₄, pure BiVO₄, and without photocatalyst was monitored on the UV–vis spectrophotometer under visible light irradiation. From the results, it is found that in the case of GW-BiVO₄, composite degradation reach up to 89% within 150 min which will reach up to 95% after the irradiation for 210 min which is found nearly twofold than that of the pure BiVO₄, since MB itself is photocatalytically active during the blank experiment, without the catalyst, it shows some decolorization. The GW-BiVO₄ composite photocatalyst shows enhance catalytic activity than the pure BiVO₄, but it is slightly less than the pristine CdS, a well-known visible light active catalyst.

The enhanced photocatalytic efficiency of the composite over the pure BiVO₄ is attributed to the obviously low recombination rate of photogenerated hole–electron pairs due to the presence of graphene layer. Previous results demonstrate that anchoring of semiconductors over graphene layer decreases the recombination rate of the photogenerated electrons. However, simply anchoring renders nearly 75% surface of the semiconductor naked due to which most of the photogenerated electrons and holes away from the graphene layer are unable to percolate over the layer, and in most of the cases, expected enhancement in the properties does not obtained. Instead, if the same graphene layer wrapped completely over the semiconductor, it would provide expected enhancement in properties as graphene layer is transparent enough to pass the light through it.

Experimental finding demonstrates enhanced photocatalytic activity from the results; it is found that it is achieved due to the effective combination of BiVO₄ and graphene. The possible major reaction steps in this photocatalytic degradation mechanism under visible light irradiation are summarized by the following equations:

\[
\begin{align*}
\text{BiVO}_{4} + \text{hv} & \rightarrow \text{BiVO}_{4}(h^+ + e^-) \quad (1) \\
\text{BiVO}_{4}(e^-) + \text{graphene} & \rightarrow \text{BiVO}_{4} + \text{graphene} \quad (2) \\
\text{graphene}(e^-) + O_2 & \rightarrow O_2^{*-} + \text{graphene} \quad (3) \\
\text{BiVO}_{4}(h^+) + \text{OH}^- & \rightarrow \text{BiVO}_{4} + \cdot \text{OH} \quad (4) \\
\text{BiVO}_{4}(h^+) + \cdot \text{OH} + O_2^{*-} + \text{dyes} & \rightarrow \text{Degradation products} \quad (5)
\end{align*}
\]

Enhancement in photoactivity under light irradiation depends upon the efficient separation of photogenerated electrons inhibiting recombination. In case of this, composite wrapped graphene layer effectively captured photogenerated electrons from BiVO₄ due to effective contact (1). The electron–hole pairs are generated on the BiVO₄ surface upon visible-light excitation, followed by instant transfer of photo generated electrons to graphene sheets via a percolation mechanism (2), and then, the negatively charged graphene sheets can activate the dissolved oxygen to produce superoxide anion radical (3), while the holes can react with the adsorbed water to form hydroxyl radical (4). Finally, the active species (holes, superoxide anion radical and hydroxyl radical) oxidize the dye molecules adsorbed on the active sites of the GW-BiVO₄ nano composite photocatalyst (5) [25].

To examine the efficiency of charge carrier trapping, immigration, and transfer, as well as to understand the
fate of e−/h+ pairs in semiconductor particles, PL spectra are frequently used. The room temperature PL emission spectra of pure BiVO4, GD-BiVO4, and GW-BiVO4 monitored at an excitation wavelength of 254 nm are shown in Additional file 1 Figure S4. Significant fluorescence signals do not observed for GW-BiVO4, implying that the recombination of photogenerated electrons and holes is inhibited greatly. Instant shuttling of photogenerated electrons to the graphene layer minimizes the charge recombination and offers enhanced photocatalytic efficiency, even though quenching of the single observer in GD-BiVO4 but wrapped graphene shows slightly more quenching than GD-BiVO4.

Trapping experiments of radicals and holes were performed to detect the reactive species generated in the photocatalytic system. Figure 5 shows the time profile of C/C0 (photodegradation rate) using GW-BiVO4 + EDTA-Na, GW-BiVO4 + t-BuOH, and GW-BiVO4 under visible-light irradiation at 25°C, where C is the concentration of MB at the irradiation time t, and C0 is the concentration of the adsorption-desorption equilibrium solution of MB. It can be clearly seen that the photodegradation rate of MB on GW-BiVO4 was decreased markedly by the addition of EDTA-Na. Upon visible-light excitation, the electron–hole pairs (Figure 5). Photocatalytic degradation rates of MB under visible light irradiation with GW-BiVO4+ EDTA-Na, GW-BiVO4+ t-BuOH, and GW-BiVO4 are generated on the BiVO4 surface; the holes can been captured instantly at the site of generation by EDTA-Na in the photocatalytic system, inhibiting greatly the formation of hydroxyl radical, and therefore, the photocatalytic activity is significantly decreased. In contrast, no significant changes were observed for the photodegradation rate of MB through adding the scavenger of hydroxyl radicals (t-BuOH). Therefore, we can summarize that the direct hole oxidation reaction is obviously dominant during the photocatalytic reactions on the GW-BiVO4 system.

Conclusions

GW-BiVO4 photocatalyst with an excellent performance has been successfully prepared via a one-step sol–gel method. TEM observations indicate that the graphene sheets are fully exfoliated and wrapped over BiVO4 because the graphene sheets play the role of template to allow two-dimensional planar growth. The photocatalytic activity measurements demonstrate that the GW-BiVO4 photocatalysts show superior photoactivity in degradation of MB under visible-light irradiation. The significant enhancement in photoactivity can be ascribed to the efficient separation of photogenerated electrons in the BiVO4 and graphene coupling system and the concerted effects of individual components or their integrated properties.

Additional file

Additional file 1: Title: TEM images, EDS spectra, UV–vis spectra, DRS, photoluminescence, and photocatalytic activity of pure BiVO4. Description: Figure S1: TEM images of the pure BiVO4. The TEM images of the pure BiVO4 samples are given above; if we compare these images with the GW-BiVO4 composite material, we find that the growth of the particles, in case of composite material, is very unique and wrapped by graphene layer uniformly. Figure S2: Energy-dispersive X-ray spectroscopy spectra of GW-BiVO4. Figure S3: The UV–vis diffuse reflectance spectra of GW-BiVO4 composite. Figure S4: Photoluminescence spectra of pure BiVO4 and graphene decorated BiVO4 (GD-BiVO4), graphene Wrapped BiVO4 (GW-BiVO4). Figure S5: Photocatalytic activity of GW-BiVO4 (100 mg) catalyst in the degradation of MB in four cycles under visible light. XRD of the GW-BiVO4 (100 mg) catalyst before (a) and after (b) the four cycles under visible light.
Competing interests
Both authors declare that they have no competing interest.

Authors’ contributions
SBG and SRT contributed equally to the manuscript. All authors read and approved the final manuscript.

Authors’ information
SBG is a research student working on major research project sanctioned by UGC New Delhi (India). He has a 3-year research experience. He is pursuing his Ph.D. degree at RTM Nagpur University, India. He is presently working on the development of nanoscale materials and their applications as an environmental photocatalyst. SRT is an associate professor of chemistry at the Government Institute of Science, Nagpur (India). He is also a visiting professor at the Nanotechnology Department, Science College, Nagpur (India). He had his Ph.D. from the Department of Chemistry, RTM Nagpur University, Nagpur, India. His main research activity includes the synthesis of advanced materials in different morphologies at nanoscale and studies their impact on physical properties. He has published more than 15 research papers at international level.

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