Plasmonic Bi nanoparticle decorated BiVO₄/rGO as an efficient photoanode for photoelectrochemical water splitting

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abstract

We report the application of plasmonic Bi nanoparticles supported rGO/BiVO₄ anode for photoelectrochemical (PEC) water splitting. Nearly, 2.5 times higher activity was observed for Bi-rGO/BiVO₄ composite than pristine BiVO₄. Typical results indicated that Bi-rGO/BiVO₄ exhibited the highest current density of 6.05 mA/cm² at 1.23 V, whereas Bi–BiVO₄ showed the current density of only 3.56 mA/cm². This enhancement in PEC activity on introduction of Bi-rGO is due to the surface plasmonic behavior of BiNPs, which improves the absorption of radiation thereby reduces the charge recombination. Further, the composite electrode showed good solar to hydrogen conversion efficiency, appreciable incident photon-to-current efficiency and low charge transfer resistance. Hence, Bi-rGO/BiVO₄ provides an opportunity to realize PEC water splitting.

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Semiconductor based photoelectrochemical cells have been receiving great attention for water splitting due to their ability to absorb photons and generate voltage [1]. Alongside, the efficiency of photoelectrochemical (PEC) cells strongly depend on the generation of charge carriers, and their separation and mobility [2]. In order to display high PEC activity, the generation of charge carriers must be high and their recombination must be minimal [3]. The monoclinic BiVO₄ is one such visible light active photoanodes for water oxidation whose bandgap lies between 2.4 and 2.5 eV, with suitably positioned valence band edge for oxygen evolution [4–6] and its superior chemical stability under light illumination [7]. Unfortunately, the reported conversion efficiencies are poor due to its low carrier mobility and fast recombination. To improve the mobility and minimize the recombination, BiVO₄ has been modified by various techniques such as formation of heterojunction with other semiconductors [8,9], metal doping [10,11], loading co-catalyst [12] etc. For example, in heterojunction systems like TiO₂/BiVO₄ [8] and WO₃/BiVO₄ [9] excellent PEC activity are reported. Metal doping such as Mo, W [10,11] is known to enhance the charge carrier concentration and electronic conductivity of BiVO₄. Furthermore, introduction of a co-catalyst on BiVO₄ also lead to significant improvement in PEC water oxidation due to its enhanced photostability [12].

Among the numerous modification methods, introduction of plasmonic metal nanoparticles gained sufficient attention owing to their ability to improve the visible-light absorption and prevent charge recombination due to the surface plasmon resonance (SPR) effect [13]. As a result, good photochemical energy conversion efficiency, photostability and interfacial charge transfer kinetics are observed [14]. Noble metals like Au [15,16] and Ag [14] have displayed surface plasmon resonance (SPR) property when combined with semiconductors [17]. For example, Jeong et al. fabricated BiVO₄ electrode decorated with Ag nanoparticles that showed ~3.3 times higher current than BiVO₄ film [18]. Kim et al. reported Au/BiVO₄/ZnO heterojunction to obtain ~4.5 times higher photocurrent than pristine BiVO₄ photoelectrode [19]. Interestingly, bismuth nanoparticles (BiNPs) exhibit unique electronic properties such as SPR, high electron mean free path [20], high anisotropic fermi surface and small bandgap energy, etc [21,22]. Moreover, optical response of Bi nanostructures can be tuned between UV to IR region [23–26]. Toudert et al. reported that BiNPs exhibit tunable SPR phenomenon in near-UV to near-IR range region [27]. The heterojunction of Bi and BiVO₄ as reported by Wulan et al. shows two-fold increment in photocurrent density (1.96 mA/cm² at 1.23 V vs RHE) [28]. However, BiNPs have low chemical stability and poor SPR property. In order to showcase its SPR property, a support system is needed. With this background, we have used rGO as the support to improve charge transfer from BiNPs and thereby improving the overall PEC activity [14,29,30].

We fabricated Bi–rGO/BiVO₄ photoanode, where BiNPs were synthesized by chemical reduction method while rGO by Hummer’s method. The fabrication of photoelectrodes was done by drop-casting. A systematic study was carried out to propose and understand the role of Bi-nanoparticles and rGO in improving the PEC performance of BiVO₄.

### Materials

Bismuth acetate (Bi(CH₃COO)₃), bismuth nitrate trihydrate (Bi(NO₃)₃·5H₂O), acetic acid (CH₃COOH), sodium borohydride (NaBH₄), ethanol (C₂H₅OH), concentrated sulphuric acid (H₂SO₄), graphite powder, sodium nitrate (NaNO₃), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂), acetylacetone, vanadyl acetylacetonate, hydrochloric acid (HCl). FTO glass used for fabrication of electrode has a sheet resistance of 13 Ω/cm² and is purchased from Aldrich. All the FTO glass plates are pre-cleaned with HCl solution. All the FTO glass were cleaned with deionized water followed by ethanol via centrifugation. The obtained precipitate was dried at 60 °C.

### Fabrication of BiVO₄ and Bi–BiVO₄ photoanodes

Firstly, BiVO₄ photoanode was prepared by organic decomposition method followed by drop casting. The photoanode was fabricated as follows: 173 mg of Bi(NO₃)₃·5H₂O was dissolved in glacial acetic acid (0.4 ml) and sonicated to form a clear solution A. On the other hand, 95 mg of vanadyl acetylacetone was taken in 4.6 ml of acetylacetone solution, dissolved in glacial acetic acid (0.4 ml) and sonicated to form a clear solution B. To this solution, sodium borohydride was added drop-wise under stirring. A brownish-black precipitate formed was washed with deionized water followed by ethanol via centrifugation. The obtained precipitate was dried at 70 °C.

### Synthesis of BiNPs

The synthesis of BiNPs was carried out by chemical reduction method. Briefly, ~193 mg of bismuth acetate was taken in 10 ml acetic acid, sonicated for 10 min to obtain a clear solution. To this solution, sodium borohydride was added drop-wise under stirring. A brownish-black precipitate formed was washed with deionized water followed by ethanol via centrifugation. The obtained precipitate was dried at 60 °C.

### Fabrication of Bi-rGO and Bi–rGO/BiVO₄ photoanodes

GO and rGO were prepared by modified Hummer’s method (provided in S1). The prepared BiNPs and GO are dissolved in ethanol and sonicated for 30 min. The resulting solution contains BiNPs decorated on the surface of rGO.

The Bi–rGO/BiVO₄ electrode was fabricated by drop-casting Bi–rGO (0.5 ml) solution on BiVO₄ electrode and dried at 70 °C for 30 min. The deposition scheme of Bi–rGO/BiVO₄ photoanode as presented in Scheme 1.

### Characterizations

Shimadzu UV-3600 instrument was used for collecting UV–Vis spectra for synthesized photoanodes, whereas the phase purity and presence of constituent materials was confirmed by powder X-ray diffraction (XRD) recorded by...
using a PANalytical XpertPRO diffractometer. Surface morphologies of the samples were measured using a FESEM (Zeiss supra 40), whereas, TECNAI G-2 FEI (300 kV) was used to collect HR-TEM images.

**Photoelectrochemical measurements**

Linear sweep voltammetric (I–V) studies were performed on LOT-Oriel with a 150 W Xe with a power density of ~100 mW cm$^{-2}$, which is measured by Newport Oriel instrument (Optical power/Energy meter-model 842.FE). Chronoamperometric (I-t) studies, electrochemical impedance spectroscopic (EIS) and cyclic voltammograms (CV) studies were performed on an Autolab PGSTAT 302 N using NOVA 2.1 software. Incident photon-to-current conversion efficiency (IPCE) data was performed by Oriel IQE-200 instrument with a 250 W quartz tungsten halogen lamp as a light source. A Trace-1310 GC equipped with a TCD was used to quantify hydrogen gas. The PEC measurements consist of a three electrode system, where the fabricated electrodes act as the working electrode (WE), Ag/AgCl, platinum (Pt) wire as the reference electrode (RE) and the counter electrode (CE) respectively. The fabricated electrodes were tested in 0.1 M Na$_2$SO$_4$ solution.

**Results and discussion**

The formation of BiVO$_4$, BiNPs and GO was confirmed by XRD patterns as displayed in Fig. 1a. As noticed in Fig. 1a, BiVO$_4$ has monoclinic crystal lattice with (110), (121), (040), (002), (112) and (031) crystal planes (JCPDS NO-140688) at 2$\theta$ values = 19.1, 28.91, 30.05, 34.79, 35.42, 40.07 and 42.6$^\circ$ respectively. BiNPs have rhombohedral crystal lattice with (003), (012), (104), (110), (015), (006), (202), (024), (116) and (122) planes (JCPDS NO-851331). For GO, a characteristic (002) plane of graphene oxide was confirmed from the peak at 2$\theta$ = 10.28$^\circ$ while, the Bi-rGO showed similar peaks as BiNPs, however, no rGO peak due to its low concentration (Fig. S1). Raman spectral analysis of synthesized samples BiNPs, Bi-rGO and Bi-rGO/BiVO$_4$ are displayed in Fig. 1b, which shows two characteristic vibrational bands at 280 and 320 nm for rGO respectively. The absorption spectra of BiNPs, Bi-rGO, BiVO$_4$, Bi–BiVO$_4$ and Bi-rGO/BiVO$_4$ composites are shown in Fig. 2. The Bi nanoparticles displayed a sharp surface plasmon resonance peak centered at 320 nm that extended to near IR region. Further, BiNPs supported on rGO show improvement in the absorption intensity as shown in Fig. 2b, where absorption peaks are observed at 280 and 320 nm for rGO and SPR effect of BiNPs respectively. The absorption spectra of BiVO$_4$ reveal that they exhibit a narrow absorption with an absorption edge at 580 nm corresponding to the bandgap of 2.15 eV. BiNPs in combination with BiVO$_4$ lead to enhanced absorption. The absorption for Bi–BiVO$_4$ and Bi-rGO/BiVO$_4$ composites are shown in Fig. 2d.

The morphology of the samples was analyzed by FE-SEM and are displayed in Fig. 3. The synthesized Bi nanoparticles have a flower like morphology (Fig. 3a), whereas, rGO has a sheet like morphology (Fig. 3b). The surface morphologies of BiVO$_4$ appear to be porous with an average diameter of 300–350 nm as shown in Fig. 3c. Fig. 3d indicates the presence of BiNPs on BiVO$_4$. The composite Bi–BiGO/BiVO$_4$ shows similar morphology like Bi–BiVO$_4$ and randomly aggregated with no specific shape but high surface roughness. The morphology of the composite is shown in Fig. 3e and the EDAX shown in Fig. 3f reveals the presence of BiNPs and the relative atomic percentages.

The HR-TEM images of BiNPs, Bi-rGO and Bi-rGO/BiVO$_4$ composite are shown in Fig. 4. The high resolution image of Bi-rGO and the composite are shown (Fig. 4b and d). The lattice spacing of 0.24 nm of BiNPs matches with the d-spacing calculated from (012) plane in XRD (JCPDS-851331) (Fig. 4a and c). Similarly, the lattice spacing of 0.31 nm matches with (121) plane for monoclinic BiVO$_4$ (JCPDS NO-140688) (Fig. 4e). SAED pattern of Bi-rGO/BiVO$_4$ composite is shown in Fig. 4f along with the planes.

![Scheme 1](image-url)  
**Scheme 1** – The deposition scheme of Bi-rGO/BiVO$_4$ photoanode.
Fig. 1 — (a) X-ray diffraction patterns of pristine BiVO$_4$, BiNPs and GO films (b) Raman spectra of BiNPs, Bi-rGO and Bi-rGO/BiVO$_4$ nanocomposite.

Fig. 2 — Absorption spectra of (a) BiNPs (b) Bi-rGO (c) pristine BiVO$_4$ and (d) Bi–BiVO$_4$ and Bi-rGO/BiVO$_4$ nanocomposite.
Photoelectrochemical studies

The PEC studies were performed under visible light illumination. The LSV plots or current versus potential (I vs V) curves are displayed in Fig. 5a. The electrolyte used for the experiment is 0.1 M of Na₂SO₄. The potential was measured with respect to Ag/AgCl reference electrode and converted to RHE as shown in supporting information (SI). All the studied photoelectrodes show no photocurrent under dark conditions.

Upon light on and off mode (chopped illumination), the observed photocurrent density for BiVO₄, Bi–BiVO₄ and Bi-rGO/BiVO₄ nanocomposite is 2.39, 3.56 and 6.05 mA/cm² at 1.23 V, respectively. Bi-rGO/BiVO₄ composite produced the highest photocurrent density, which is two-times and nearly three-times higher than Bi–BiVO₄ and BiVO₄, respectively. The Bi-rGO/BiVO₄ has the onset potential of 0.15 V, which is lower than pristine BiVO₄ (0.26 V). The decrease in the onset potential for Bi-rGO/BiVO₄ can be due to increase in charge carrier separation and facile transfer due to incorporation of Bi and rGO. Among Bi–BiVO₄ and Bi-rGO/BiVO₄, the latter has higher photocurrent density due to conductive nature of rGO. Solar-to-hydrogen conversion (STH) for BiVO₄, Bi–BiVO₄ and Bi-rGO/BiVO₄ nanocomposite has been calculated by using equation (2) (SI), which are 0.82, 1.35 and 2.34% at 0.61 V respectively (Fig. 5b). This improved activity of Bi-rGO/BiVO₄ suggests that rGO stabilize BiNPs and improves the activity. The HER is shown in photograph (Fig. S3), which demonstrates
The stability of the photoanodes is examined by chronoamperometric studies. The photocurrent for BiVO₄, Bi–BiVO₄ and Bi-rGO/BiVO₄ electrodes at 0.6 V vs RHE as a function of time is shown in Fig. 6a. It is worth mentioning that Bi-rGO/BiVO₄ nanocomposite exhibits long term stability up to 5000 s. The current density value obtained in LSV and chronoamperometry is consistent and in both studies, Bi-rGO/BiVO₄ composite showed higher current than pristine BiVO₄ and Bi–BiVO₄. The H₂ evolution, quantified by gas chromatography is plotted as a function of time. As shown in Fig. 6b, the Bi-rGO/BiVO₄ photoanode showed the maximum H₂ evolution of 2466 µmol at 2 h as compared to BiVO₄ (1071 µmol) and Bi–BiVO₄ (1941 µmol). Impressively, the composite exhibited nearly 2.5 times increment in H₂ evolution than pure BiVO₄ electrode. Thus, the quantification studies feature that Bi-rGO/BiVO₄ is a promising photoanode for PEC water splitting. The IPCE response of the all photoelectrodes is shown in Fig. 6c, Bi–BiVO₄ and Bi-rGO/BiVO₄ exhibit 34 and 41% conversion, respectively at 310 nm as compared to only 27% for pure BiVO₄. The IPCE expression is given in SI. The best performance is shown by Bi-rGO/BiVO₄ due to the formation of energetic hot electrons by plasmonic excitation of BiNPs. This evolution of H₂ bubbles at the Pt CE during the PEC measurement.

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is also supported by the maximum photocurrent at around 310 nm. Impressively, the composite exhibited higher IPCE than other electrodes. This concludes that BiNPs on rGO suppresses the charge recombination and also facilitates higher charge injection transfer to the composite. BiNPs chemical stability and plasmon-induced hot electrons injection are complemented by the conductive nature of rGO. In addition, the high surface area and electrical conductivity of rGO improves the interfacial active sites in BiVO4 which were unavailable in pure BiVO4 thereby improving the dynamics of BiVO4 for OER reaction.

In order to validate the ease of charge transfer at the electrode-electrolyte interface, EIS experiments were performed. The Nyquist plots obtained for BiVO4, Bi–BiVO4 and Bi-rGO/BiVO4 photoanodes over the frequency range (1 kHz-1 Hz) under light irradiation are shown in Fig. 6d. All the electrodes have a solution resistance ~41 Ω. High Rct value of 1.46 kΩ for BiVO4 is due to low charge separation and weak carrier mobility which are the main reasons for its poor water oxidation performance. However, BiNPs loading on the surface of BiVO4 enhanced the charge carrier density since BiNPs acts as active sites for the PEC reaction which is evident from the Rct value of 0.80 kΩ as shown in Fig. 6d. Further, the rGO supported BiNPs on BiVO4 significantly lower charge resistance (Rct value of 0.61 kΩ) which is attributed to the nature of rGO acting as a medium of transportation. In typical, the diameter of the semicircle represents charge transfer resistance (Rct) in the Nyquist plot. Lower the Rct, better the charge transfer process at the electrode-electrolyte interface [32–34]. Lowest Rct is observed for Bi-rGO/BiVO4 composite over the fabricated photoanodes (BiVO4 and Bi–BiVO4). In simple terms, it could be explained as photogenerated electrons from BiVO4 can be effectively collected with the help of Bi-rGO and consolidated electrons are transferred to counter electrode. Therefore, Bi-rGO/BiVO4 exhibit dominated PEC response.

The mechanistic details of the electron transfer process in Bi-rGO/BiVO4 composite photoelectrodes are shown in the schematic representation in Fig. 7c. The Fermi level of BiNPs, VB and CB positions of BiVO4 are obtained from cyclic voltammetry (Fig. 7a and b). The procedure for calculation of band positions in the energy level diagram is presented in (SI). Due to absorption of solar radiation, excitons are generated. The surface plasmons are facilitated by BiNPs and electrons from Bi-rGO are injected into the CB of BiVO4. Since, Bi-rGO facilitates quick charge injection, the generated charge carriers are efficiently transferred to FTO. Therefore, the presence of rGO accelerates the overall charge transport and hence better electron injection and enhanced PEC activity.

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**Fig. 6** (a) Stability of pure BiVO4, Bi–BiVO4 and Bi-rGO/BiVO4 nanocomposite photoelectrodes at 1.23 V vs RHE during 5000 s. (b) H2 evolution of Bi-rGO/BiVO4 under light illumination under 2 h in comparison with pure BiVO4 and Bi–BiVO4. (c) IPCE of pristine BiVO4, Bi–BiVO4 and Bi-rGO/BiVO4 photoelectrodes under monochromatic light radiation. (d) Nyquist plots for BiVO4, Bi–BiVO4 and Bi-rGO/BiVO4 photoelectrodes.
Briefly, the PEC activity could be explained by the light-driven holes in the VB of BiVO₄ that react with electrolyte to evolve oxygen and release protons. On the other side, the electrons are transferred through external circuit to counter electrode which favor HER. The whole movement of photogenerated carriers effectively takes place due to the conducting nature of Bi-rGO, which improves the charge transfer thereby improving the over all PEC performance for hydrogen production.

Conclusions

A promising photoanode Bi-rGO/BiVO₄ was fabricated and used for photoelectrochemical water splitting reaction. This ternary photoanode displayed the best photocurrent density of 6.05 mA/cm² at 1.23 V over BiVO₄ and Bi–BiVO₄ with STH efficiency of 2.34% at 0.61 V. The best IPCE and less charge transfer resistance for Bi-rGO/BiVO₄ facilitates the charge separation and improves the charge carrier mobility. Chronoamperometric results revealed the stability of the photoanode over 5000 s. The SPR property of BiNPs is enhanced by rGO and efficient PEC activity of Bi-rGO/BiVO₄ is due to combined action of BiNPs in improving the charge carrier density and rGO in increasing the charge carrier mobility.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2019.08.214.

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