



## Research Paper

Cocatalyst free Z-schematic enhanced H<sub>2</sub> evolution over LaVO<sub>4</sub>/BiVO<sub>4</sub> composite photocatalyst using Ag as an electron mediatorNaveen Kumar Veldurthi<sup>a,\*</sup>, Neerugatti KrishnaRao Eswar<sup>b</sup>, Satyapaul A. Singh<sup>a</sup>, Giridhar Madras<sup>a</sup><sup>a</sup> Department of Chemical Engineering, Indian Institute of Science, Bangalore, India<sup>b</sup> Centre for Nanoscience and Engineering, Indian Institute of Science, Bangalore, India

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## ABSTRACT

A novel cocatalyst free Z-schematic photocatalytic system of Ag/LaVO<sub>4</sub>/BiVO<sub>4</sub> was successfully fabricated for clean hydrogen fuel evolution. The spherical nanoparticles of LaVO<sub>4</sub> were prepared in solution combustion method for the first time using glycine as a fuel, BiVO<sub>4</sub> was deposited onto LaVO<sub>4</sub> through a deposition–precipitation method and Ag was loaded on the surface of LaVO<sub>4</sub>/BiVO<sub>4</sub> composite by photoreduction method. The composites were characterized by XRD, UV–vis DRS, SEM, TEM, EDS and XPS to ensure the successful integration of Ag or (and) BiVO<sub>4</sub> with LaVO<sub>4</sub>. A series of photocatalytic H<sub>2</sub> evolution experiments, employing Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> as hole scavengers, showed that the Ag/LaVO<sub>4</sub>/BiVO<sub>4</sub> composite exhibited a superior photocatalytic performance compared to single LaVO<sub>4</sub> or BiVO<sub>4</sub>. Although BiVO<sub>4</sub> cannot be used for H<sub>2</sub> evolution, it can significantly enhance the H<sub>2</sub> evolution performance of LaVO<sub>4</sub> through a Z-scheme mechanism with Ag as an electron mediator. Moreover, investigations on photoluminescence and fluorescence lifetime measurements demonstrated the greater separation efficacy of photoinduced excitons in the Z-scheme Ag/LaVO<sub>4</sub>/BiVO<sub>4</sub> photocatalytic system. This newly constructed LaVO<sub>4</sub> based Z-scheme system exhibits promising photocatalytic H<sub>2</sub> evolution activity with significant longevity and will be useful for potential applications in energy driven technologies.

## 1. Introduction

Hydrogen has been heralded as a clean and sustainable fuel with zero carbon emission and high energy yield (141.9 MJ/kg) than conventional fuels [1]. Solar light driven photocatalytic water splitting to produce hydrogen has become a promising solution to the tapering resources of fossil fuels and detrimental effects of greenhouse gases produced due to their combustion. Strenuous attempts have been carried out to enhance the visible light absorption of the conventional photocatalysts such as TiO<sub>2</sub>, ZnO etc. which are just active under UV-light irradiation [2–4]. However, it is obvious that mere visible light absorption will not guarantee higher photocatalytic efficacy. Typically, the performance of photocatalysts is significantly favored by three conditions: (i) a narrow band gap that can facilitate the efficient utilization of sunlight (ii) a more negative conduction band (CB) potential and a more positive valence band (VB) potential for the reduction and oxidation reactions, respectively (iii) reducing the rate of recombination of photogenerated charge carriers [5]. However, condition (ii) will widen the band gap of a photocatalyst, resulting poor sunlight

absorption i.e., incongruity of condition (i). Therefore, it is difficult for a single semiconductor photocatalyst to simultaneously possess broad solar light-absorption, enhanced separation of charge carriers and strong redox ability.

In addition, most semiconductors cannot produce H<sub>2</sub> without a cocatalyst (often Pt), even by using sacrificial electron donor [6]. The indispensable need of expensive noble metal cocatalyst, to localize the protons for the formation of hydrogen gas, is another factor that makes the photocatalytic water splitting a rather unfeasible proposition [7]. In this context, there is an urgent quest for designing cocatalyst free composite photocatalytic systems, without compromising with the efficiency, by prudently choosing the relative band positions of the two photocatalysts for efficient utilization of solar energy and limiting the rate of recombination of photogenerated charge carriers.

Besides tuning the photocatalyst itself, the coupling of two semiconductors in staggered alignment of band structures provides more separation of photogenerated excitons. As a result of irradiation, the two conjoint semiconductors in a heterojunction composite photocatalyst are activated simultaneously. The photogenerated electrons are

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transferred from a higher conduction band to a lower conduction band, whereas the holes transport to a higher valence band from a lower valence band. Thus designing heterojunction photocatalysts has emerged as the inevitable route to achieve efficient charge separation [8]. However, increment in the separation of charge carriers occurs while dampening the redox ability, due to the photogenerated electrons and holes are accumulated on the band with lower redox potentials [9]. It is difficult to achieve strong redox ability and higher electron–hole separation simultaneously by the heterojunction composite photocatalysts.

Z-scheme water splitting mimicking photosynthesis of green plants was first introduced by Bard in 1979 [10]. Since then many efforts have been made to construct Z-scheme photocatalytic systems without redox mediators (i.e., liquid ionic pairs such as  $\text{IO}_3^-/\text{I}^-$ ,  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{Co}(\text{bpy})_3^{3+}/\text{Fe}^{2+}$ ) causing backward reactions [11,12]. In 2006, an all solid state Z-scheme system of  $\text{CdS-Au-TiO}_2$  was reported for the first time, using Au as an electron mediator between two photocatalysts [13]. As no redox couples were used, the stability and the charge transfer was simultaneously improved. In direct Z-scheme system of two narrow band gap photocatalysts, photogenerated electrons of one semiconductor with a lower conduction band and holes of other semiconductor with a higher valence band are recombined. Therefore, Z-scheme photocatalyst (with or without electron mediator) not only boosts the separation efficiency of photogenerated electron-hole pairs, but also preserves excellent redox ability.

More recently, significant attention has been paid to the monoclinic lanthanum vanadate ( $\text{m-LaVO}_4$ ) owing to its notable properties such as light absorption in the visible region and surface catalytic ability [14,15]. However, its utilization in the photocatalytic hydrogen generation has not been reported so far.  $\text{LaVO}_4$ -based photocatalysts suffer from certain limitations such as lower surface area and the quick recombination of photogenerated excitons. Based on the above considerations,  $\text{BiVO}_4$  has been chosen to couple with  $\text{LaVO}_4$  to remedy the defect of faster recombination of charge carriers thereby improving the photocatalytic efficiency.  $\text{BiVO}_4$  has several merits such as visible light absorption, chemical stability, low cost and non-toxic properties [16].  $\text{BiVO}_4$  alone is unable to produce hydrogen through water splitting because its conduction band is located at a more positive potential than the potential of water reduction [0 eV Vs NHE;  $\text{H}^+/\text{H}_2$ ]. However, considering the composite of  $\text{LaVO}_4/\text{BiVO}_4$ , it is expected to enhance the rate of  $\text{H}_2$  evolution through the Z-scheme mechanism. Furthermore, previous reports suggest that  $\text{LaVO}_4$  has suitable band edges ( $E_{\text{CB}} = -0.06$  eV,  $E_{\text{VB}} = 2.01$  eV), that match well with  $\text{BiVO}_4$  band edge positions ( $E_{\text{CB}} = 0.46$  eV,  $E_{\text{VB}} = 2.86$  eV) to probably form a direct Z-scheme photocatalytic system [17,18].

The poor interfacial charge transfer efficiency has a negative influence on the electron–hole separation ability. In particular,  $\text{BiVO}_4$  is known for poor electron conductivity [19]. Therefore, an effective conductive charge mediator is essential at the interface of  $\text{LaVO}_4\text{-BiVO}_4$  for attaining high efficiency. For instance, Ag has been used as such electron mediator in many Z-scheme systems because of its excellent electron conductivity [20–22]. Ag has been chosen as an electron mediator as it is cheaper than other electron mediators such as Au, Ru, Pd, Ir and Pt. Further, the Fermi level of metallic Ag is more negative than the valence band of  $\text{LaVO}_4$ , more positive than conduction band of  $\text{BiVO}_4$ . Thus, Ag makes a good charge transfer bridge between  $\text{LaVO}_4$  and  $\text{BiVO}_4$ . Therefore, in the current work,  $\text{LaVO}_4$  and  $\text{BiVO}_4$  was combined with and without Ag to construct a novel solid-state Z-scheme photocatalytic system for  $\text{H}_2$  evolution from water using  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_3$  solution as a sacrificial agent. Moreover, the present Z-scheme photocatalytic system avoids the inherent requirement of the expensive noble metal cocatalyst to generate hydrogen. The essence of the thermodynamic relationship between  $\text{LaVO}_4$  and  $\text{BiVO}_4$  is explained and the mechanism of effective charge separation based on the Z-scheme fashion is also studied in detail.

## 2. Experimental

### 2.1. Synthesis

Monoclinic  $\text{LaVO}_4$  was prepared by solution combustion method for the first time using glycine as a fuel. Solution combustion is a one step self-propagating synthesis method. In this method, reactant mixture is ignited to a temperature that is considerably lower than the actual phase formation temperature in a short time and it is considered as one of the energy efficient preparative methods [23–25]. The precursor solution was made by dissolving stoichiometric amounts of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (1.705 g) and  $\text{NH}_4\text{VO}_3$  (0.46 g) in 15 mL of water and 5 mL of 3 M nitric acid, respectively. Both were mixed in a combustion petri dish and stirred with magnetic stirrer. Stoichiometric amount of glycine (0.55 g) was dissolved in 10 mL of water and added to the above mixture. This solution mixture was placed into a muffle furnace held at 400 °C for 20 min. The obtained product was heated in furnace at 500 °C for 2 h to obtain pure lanthanum vanadate powders. The product yield is approximately 1 g.

The  $\text{LaVO}_4/\text{BiVO}_4$  composite photocatalysts were prepared by a facile deposition-precipitation method [26]. Typically, 0.2 g of  $\text{LaVO}_4$  was dispersed in 30 mL of deionized water using ultrasonication. Subsequently,  $\text{Bi}(\text{NO}_3)_3$  and  $\text{NH}_4\text{VO}_3$  were precisely weighed with the molar ratio of 1:1 and were individually dissolved in a 3 M nitric acid solution. Then, the two solutions were mixed well and the pH was adjusted to 9 by slowly adding NaOH solution. An orange yellow precipitate was obtained and then it was blended with the  $\text{LaVO}_4$  suspension under vigorous stirring for 12 h. The final product was obtained by filtering the precipitate followed by sintering at 500 °C for 5 h. The composites with different weight ratios of  $\text{LaVO}_4$  to  $\text{BiVO}_4$  were  $\text{LaVO}_4/\text{BiVO}_4$  (10 wt%),  $\text{LaVO}_4/\text{BiVO}_4$  (20 wt%),  $\text{LaVO}_4/\text{BiVO}_4$  (30 wt%) and  $\text{LaVO}_4/\text{BiVO}_4$  (50 wt%), which are labeled as LV/BV10, LV/BV20, LV/BV30 and LV/BV50, respectively. The bare monoclinic  $\text{BiVO}_4$  sample was also synthesized under the same conditions without adding  $\text{LaVO}_4$ .

In addition, Ag deposited  $\text{LaVO}_4/\text{BiVO}_4$  composite was prepared by photodeposition method. The previously prepared LV/BV20 was added into 50 mL of 10 vol% methanol solution. After that, calculated amount of  $\text{AgNO}_3$  was added, and the suspension was irradiated with a 400 W metal halide lamp for 60 min. The product was washed with ethanol and water for three times, and dried at 60 °C.  $\text{Ag/LaVO}_4$  was also prepared by the same procedure by depositing 10 wt% of Ag on  $\text{LaVO}_4$ .

### 2.2. Characterizations

X-ray diffraction patterns were recorded on a Bruker D8 diffractometer using  $\text{Cu-K}\alpha$  radiation at a scan rate of 2°/min in the 20°–80° scan range. Diffuse reflectance spectral studies were performed using solid state UV–vis spectrophotometer (PerkinElmer, Lambda 35). ULTRA55 FESEM, Carl Zeiss was used to obtain SEM images. Prior to taking images, the samples drop-casted on silicon wafers, they were dispersed in absolute ethanol and ultrasonicated for 5 min. The drop-casted samples were gold sputtered using Quorum sputtering before imaging in order to restrict charging of the sample. TEM images were captured using FEI Tecnai T-20 operated at 180 kV. TEM samples were dispersed in absolute ethanol and drop-casted onto copper grids. X-ray photoelectron spectra were obtained using ESCA+, (omicron nanotechnology, Oxford Instrument Germany). Powder samples were deposited on Cu tape and degassed for overnight in XPS FEL chamber to avoid the air contamination on sample surface. A charge neutralizer of 2 keV is applied to overcome the charging problem and binding energy of C1 s core at 284.6 eV was considered as reference. Photoluminescence spectra were obtained using a PerkinElmer LS 55 Luminescence spectrophotometer. Time-resolved fluorescence emission decay measurements of the samples were collected on a FL980 Fluorescence Spectrometer (Edinburgh Instruments) and the excitation

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