## Solar light driven ternary AgI/rGO/BiVO<sub>4</sub> photocatalyst for efficient degradation of Rhodamine B and Tetracycline

Sandeep K. Lakhera<sup>1</sup>, Heechul. Choi<sup>2</sup>, Bernaurdshaw Neppolian<sup>3\*</sup>

<sup>1</sup>Department of Physics and Nanotechnology, SRM University, Kattankulathur, Chennai, 603203, Tamilnadu, India

<sup>2</sup> Gwangju Institutes of Science and Technology (GIST), Gwangju, South Korea

<sup>3</sup>SRM Research Institute, SRM University, Kattankulathur, Chennai, 603203, Tamilnadu, India <u>neppolian.b@res.srmuniv.ac.in</u>

#### Abstract

A solar light responsive Z-scheme AgI/rGO/BiVO<sub>4</sub> ternary nanocomposite was designed by ultrasonic assisted hydrothermal and wet impregnation methods. Photocurrent measurements indicated the presence of significantly high surface charge trap states in bare BiVO<sub>4</sub>. However, the detrapping process was not observed suggesting fast recombination of trapped charges on the surface of bare BiVO<sub>4</sub>. The photocatalytic performance of the nanocomposites was tested with Tetracycline (TC), a common antibiotic and RhB dye, as model pollutants. The AgI/rGO/BiVO<sub>4</sub> nanocomposite displayed nearly 84% and 99% photocatalytic degradation for TC and RhB, respectively under direct solar light irradiation in 25 min. The Total Organic Carbon (TOC) analysis revealed more than 35% and 25% mineralization efficiency for both TC and RhB under 2 h of reaction. Based on XPS, Mott-Schottky, and reactive radical trapping experiments, a Z-scheme charge carrier separation and migration pathway in the nanocomposite is proposed.

*Keywords:* AgI/rGO/BiVO<sub>4</sub>, Tetracycline, Z-scheme, Surface trap states, Reduced graphene oxide, Visible light photocatalysts

#### Introduction

Wide band gap semiconductors, such as TiO<sub>2</sub>, SnO<sub>2</sub>, ZnO are extensively used for the degradation of organic pollutants. However, owing to their wide band gap, they respond to only UV illumination. In the solar spectrum, UV comprises of only 3 - 5%, while visible light consists of nearly 43%. For efficient and cost effective applications, it is necessary to have a visible light absorbing semiconductor. In recent years, nontitania based visible lights semiconducting metal oxides, halides, sulfides, oxychloride and carbonitride have been designed for photocatalytic applications.

Bismuth vanadate (BiVO<sub>4</sub>) has attracted considerable attention as a photocatalyst, due to its visible light absorption, non-toxicity, and chemical stability in aqueous solution under irradiation. It has a narrow band gap of  $\sim 2.4$  eV and shows high photocatalytic activity. However, the photocatalytic efficiency of BiVO<sub>4</sub> is limited by the rate of recombination of photoexcited charge carriers, poor electrical conductivity, and adsorptive performance, thus limiting the wide application of BiVO<sub>4</sub> in the field of solar conversion and pollutant degradation. By doping BiVO<sub>4</sub> with a co-catalyst and selecting an appropriate band potential, the photocatalytic efficiency can be enhanced.

Herein, we report the preparation of an efficient AgI/rGO/BiVO<sub>4</sub> photocatalyst for Rhodamine B and Tetracycline degradation under solar irradiation. Reduced graphene oxide, was used to enhance the charge separation efficiency, owing to its large surface area and high electron mobility. AgI is a p-type semiconductor having a band gap in the visible region (2.8 eV) and, the band edge positions favorable for the formation of a p-n heterojunction between AgI and BiVO<sub>4</sub>. Therefore, a heterojunction formation between BiVO<sub>4</sub>, AgI, and rGO leads to an enhanced photocatalytic degradation activity.

#### Materials and Methods

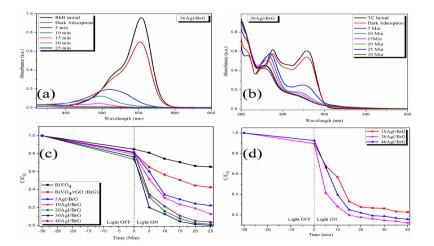
Graphene oxide (GO) was prepared from graphite powder by modified Hummers' method. A combination of hydrothermal, photoreduction and ultrasound assisted wet impregnation method was adopted for the synthesis of AgI/rGO/BiVO<sub>4</sub>. GO solution and BiVO<sub>4</sub> powder were mixed together and ultrasonicated (20 kHz ultrasonicator) for 1h, followed by wet impregnation and photoreduction. The prepared rGO/BiVO<sub>4</sub> (BrG) sample was dispersed in water and an appropriate amount of aqueous solution of KI and Ag(NO<sub>3</sub>) added in it under vigorous stirring in dark. The turbid solution was pre-dried using a hot plate and washed several times using deionized water. The resultant sample was dried in a hot air oven at 80 °C for 12 h and named as (5,10, 20, 30, 40 wt%) AgI/BrG.

#### **Results and Discussion**

The photocatalytic degradation efficiency of the prepared catalyst (AgI/rGO/BiVO<sub>4</sub>) was investigated under the solar irradiation using Rhodamine-B dye and antibiotic Tetracycline. As shown in Fig. 1(a), the absorption peak of RhB at 553 nm decreases and also shows a blue shift with respect to irradiation time, indicating the formation of intermediate products. Similarly, the absorption peak of Tetracycline at 358 nm also decreases with increasing the irradiation time, Fig. 1(b). The rate of RhB and Tetracycline degradation using AgI/rGO/BiVO<sub>4</sub> photocatalyst with different wt% of AgI is shown in Fig. 1 (c & d). It is observed that BiVO<sub>4</sub> exhibits superior performance when loaded with 1wt% rGO and 30 wt% AgI. Compared to bare BiVO<sub>4</sub> and rGO/BiVO<sub>4</sub>, 30wt% AgI loaded rGO/BiVO<sub>4</sub> shows a 65% and 42% enhancement in photocatalytic degradation activity for RhB dye, respectively. The optimized catalyst degrades 100% of the RhB dye in 25 min and 88% of the antibiotic Tetracycline in 40 min. The % mineralization for RhB and Tetracycline was found to be 25 and 35%, respectively. The photocatalytic degradation pathway of AgI/rGO/BiVO<sub>4</sub> was investigated with the scavenger trapping experiments.

### Conclusions

In summary, a visible light driven AgI/rGO/BiVO<sub>4</sub> heterojunction photocatalyst was prepared by a combination of hydrothermal, photoreduction and ultrasonic assisted wet impregnation method. The photocatalytic activity of BiVO<sub>4</sub> under solar light for RhB dye and antibiotic Tetracycline significantly increased after loading of rGO and AgI. This may have resulted due to the formation of an effective p-n heterojunction between BiVO<sub>4</sub>, rGO and AgI particles. The photocatalyst exhibits stability and recyclability without any significant loss of photocatalytic activity and may be a promising catalyst for wastewater remediation.



# Fig. 1 UV-vis absorbance spectra of photodegradation of (a) RhB, (b) Tetracycline and comparison of photodegradation activity of (c) RhB and (d) Tetracycline using different wt% of AgI/rGO/BiVO<sub>4</sub> photocatalyst.

### References

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