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GO/$BiVO_4$ NANOCOMPOSITES FOR *Escherichia coli K12* PHOTOCATALYTIC INACTIVATION

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***Abstract*— Graphene oxide, a carbon-based nanomaterial has gained a wide attraction in the antibacterial field due to its large surface area, surface charge density, and various physicochemical properties. In this work, water disinfection using Graphene oxide/Bismuth vanadate (GO/$BiVO_4$) composite was studied against *Escherichia coli K12 (E. coli K12),* where the composite was developed through a facile and simple blending method at room temperature. Bismuth vanadate ($BiVO_4$) nanoparticles synthesized through the sol-gel method having a particle size of 21.3 nm was used to decorate over graphene oxide (GO) sheets. The composites whereof five different combinations namely, 0.5 %, 1 %, 1.5 %, 2 % and 2.5 % of GO/$BiVO_4$ (wt.% of GO). The as-synthesized composites were characterized by X-ray diffraction (XRD) for the crystal structure, Raman spectroscopy for the structural analysis, and UV-Vis diffuse reflectance (DR) to determine the bandgap of GO/$BiVO_4$ semiconducting composites. The antibacterial ability of all the synthesized five different composites was tested under a visible-light-driven home-made photoreactor. The results revealed the efficiency of 1.5% GO/$BiVO_4$ nanocomposite in 0.1 g/L was giving 90% disinfection in 30 mins under visible light irradiation.**

Keywords*— Graphene oxide, Bismuth vanadate nanoparticles, nanocomposite, Escherichia coli K12, photocatalysis, disinfection

I. INTRODUCTION

Water is a vital part of living beings and therefore, the availability of clean drinking water is one of the rights belonging to the human and animal world. When the conventional and traditional techniques were not able to provide complete assurance for the quality of the water due to the generation of disinfection by-products (DBPs) during the disinfection process, photocatalysis has gained major attention for eradicating the water pollution. Visible light photocatalyst has prior importance due to its efficiency for absorbing visible light for photocatalysis thereby reducing the energy crisis by utilizing solar light. The photocatalyst, $BiVO_4$ in its monoclinic scheelite phase has good activity in the visible light region but, due to its fast electron-hole pair recombination and low absorption capability, the photocatalytic performance of $BiVO_4$ is limited [1]–[4]. Therefore, incorporating GO, which is an excellent electrical conductive and has got high carrier mobility can diminish the disadvantage of $BiVO_4$ by acting as an attractive medium for electron transfer [5]. This work is based on the synthesis and characterization of $BiVO_4$ nanoparticles and GO/$BiVO_4$ nanocomposites (0.5, 1.0, 1.5, 2.0, and 2.5 wt.% GO) and the preliminary studies on the photocatalytic disinfection.

II. EXPERIMENTAL

A. Materials

Graphene oxide (GO) was purchased from Graphenemex, Mexico, and was maintained in an appropriate conditions. For the synthesis of $BiVO_4$, we have used Bismuth nitrate ($(Bi(NO_3)_2.5H_2O$), Ammonium meta-vanadate (NH_4VO_3), and Citric acid ($C_6H_8O_7$). Ammonium hydroxide (NH_4OH) has been used for adjusting the pH. All the chemical reagents were of analytical grade and used without any purification. The deionized (DI) water was generated from a Millipore Milli-Q water purification system.

B. Bacterial culture preparation

The bacterial strain, *Escherichia coli K12 (E.coli K12)* (CBDB-11-1538) was obtained from Colección Nacional de Cepas Microbianas Celulares (CDBB) of CINVESTAV, Mexico and was maintained at 37°C. For the preparation of the bacterial stock suspension, 3 µl of *E. coli K12* suspension was added into 200 mL of Luria Bertani (LB) liquid medium and incubated for 16 hours at 37˚C under shaking. The initial concentration of bacterial suspension was around 10^9 CFU/mL. Then bacterial cells were collected by centrifugation at 4000 rpm for 20 min. The pellets were resuspended and washed with sterile phosphate buffer saline (PBS) three times and the final pellet were stored in PBS.

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C. *Synthesis of $BiVO_4$ nanoparticles*

The nanoparticles of $BiVO_4$ were synthesized by sol-gel methodology. $Bi(NO_3)_2.5H_2O$ has been dissolved in 50ml of HNO_3 and $C_6H_8O_7$. NH_4VO_3 was dissolved in hot water at 60°C. To this, the solution of $C_6H_8O_7$ is added and mixed under stirring and the process temperature was kept under 80°C. The pH of the solution was kept between 6.5 to 7 and the heating continued until it forms the gel. The formed gel has dried and calcinated at 500°C for 2 hours [6].

D. *Synthesis of GO/$BiVO_4$ nanocomposites*

The synthesis of *x*GO/$BiVO_4$ nanocomposites (herein denoted as *x*GOB), where "*x*" is GO content (0.5,1, 1.5, 2, 2.5 wt.%) were done by one-step mixing with synthesized $BiVO_4$ nanoparticles, GO, and deionized water. In 200 ml of deionized water, the desired amount of GO was dissolved to obtain an aqueous dispersion. In the same way, $BiVO_4$ nanoparticles were also dispersed in deionized water and added to GO dispersion. The whole mixture was sonicated for 1.5 hrs. and then magnetically stirred at room temperature for 12 hrs. so that a homogeneous solution is obtained. The product after filtration was further dried in an oven at 50˚C for 4 hrs. [7].

III. CHARACTERIZATION

The structure and phase composition of the samples were analyzed by Bruker D2 Phaser X-ray Diffractometer (XRD) with Cu K_α radiation at a wavelength of 0.15406 nm and 2θ range from 10˚ to 80˚ for GO, 20˚ to 80˚ for $BiVO_4$ nanoparticles, and 10˚ to 80˚ for *x*GO/$BiVO_4$ composites with a scan rate of 0.02˚. The crystalline size for all the samples was carried out by the Scherrer equation. Raman analysis was recorded in the range 0 cm^{-1} to 2000 cm^{-1} at ambient temperature by Horiba-Jobin-Yvon spectrometer (Lab RAM HR800) with a helium-neon laser of wavelength 632.8 nm as the excitation source. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) of all the powder samples was performed with an Agilent-carry-5000 spectrophotometer.

IV. ANTIBACTERIAL TEST

3 µl of *E. coli K12* was added into 3 mL LB liquid medium, which was then transferred into a 37˚C incubator with gentle shaking. After 16 hr. incubation, the cell counts approximated 10^9 CFU/mL. Then bacterial cells were collected by centrifugation at 4000 rpm for 20 min, followed by washing with PBS buffer (pH=7.4) 3 times to remove the supernatant; and then resuspended in PBS buffer (pH=7.4). Nanoparticle suspensions were freshly prepared in ultrapure water and were both sonicated for 30–35 mins to ensure good dispersion before each experiment. Disinfection studies were performed under simulated solar radiation by halogen lamp with a light intensity of 500 W/m^2. Photocatalytic disinfection was carried out in a 100 mL glass beaker kept over a magnetic stirrer to ensure proper homogenization. The bacterial suspension was diluted to 10^7 CFU/mL. The studies were performed to identify the best nanocomposite (0.5GOB, 1.0GOB, 1.5GOB, 2.0GOB and 2.5GOB and dosage (0.1 g/L, 0.575 g/L, 1.05 g/L, 1.525 g/L, and 2 g/L). The suspension (50 mL) containing the respective amount of photocatalyst and *E. coli K12* (10^7 CFU/mL) was stirred. The set up was kept in dark condition for 30 min to attain equilibrium. In the process of sampling,100 µl of bacterial suspension was taken out. Samples were serially diluted in sterile water and plated on Eosin-Methylene blue (EMB) agar. Inoculated samples were incubated at 37˚C for 24 hrs. before counting. A controlled study using no photocatalyst was also carried out under the same conditions. The percentage of inactivation was calculated by the equation:

$$Percentage\ of\ inactivation\ = \frac{N(control)-N(time)}{N(control)} \times 100\%$$

where, *N (control)* and *N (time)* is the number of viable cells calculated from control and at time t, respectively.

V. RESULTS AND DISCUSSION

A. *XRD analysis*

Fig: 1 represents the XRD pattern of $BiVO_4$ which was synthesized by the sol-gel route shows the monoclinic tetragonal scheelite phase of $BiVO_4$ nanoparticles with high crystallinity. The characteristic peak of GO at any position was not observed, which may be due to the intensity of peaks of $BiVO_4$ nanoparticles covering the peaks of GO or due to the low detection limit of the diffractometer. From Fig: 2, the shift of peaks is observed when the GO content is increased [1], [4]. Crystallite size, 2θ values, and FWHM parameters which was calculated from the XRD spectra are displayed in Table 1. Using Scherrer's equation, average crystallite size was calculated, which was found to be 20 nm.

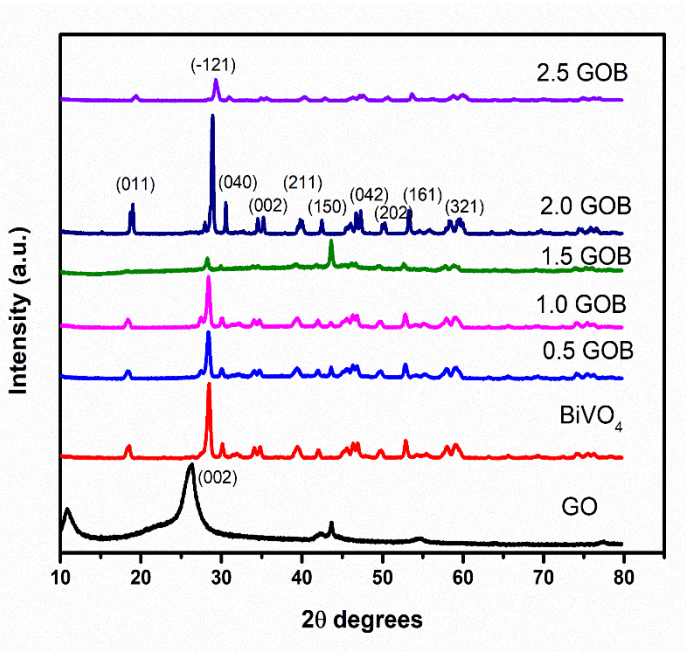


Fig 1: XRD spectra of GO, $BiVO_4$, and five different nanocomposites

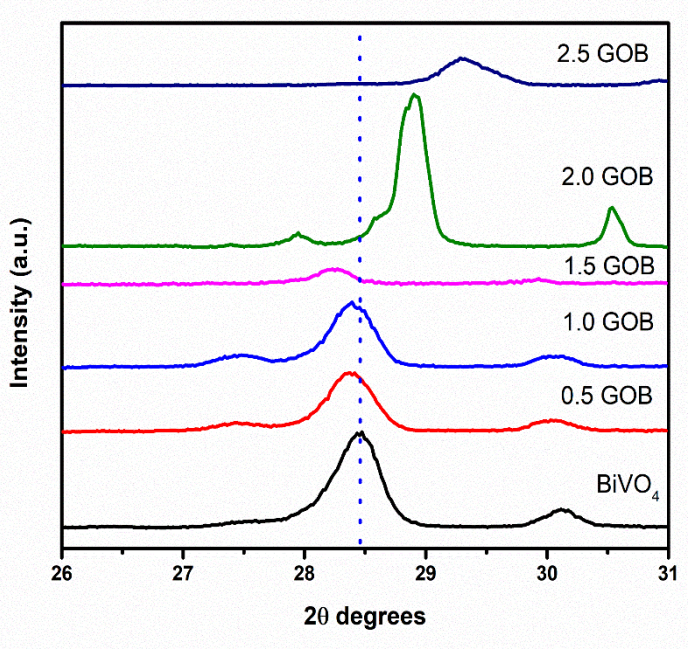


Fig 2: Enlarged view of XRD pattern showing the shift

TABLE I. XRD PARAMETERS

Sample	XRD analysis		
	FWHM	*2θ*	*Crystallite size (nm)*
GO	1.58	26.16	5.72
BiVO4	0.426	28.45	21.3
0.5GOB	0.425	28.37	21.4
1.0GOB	0.402	28.39	22.6
1.5GOB	0.335	28.42	27.1
2.0GOB	0.259	28.89	35.2
2.5GOB	0.442	29.31	20.6

B. *Raman analysis*

From Fig 3, Raman spectra modes reveal the monoclinic phase of the $BiVO_4$ nanoparticles, where the stretching and bending vibrations modes are the result of the VO_4^{3-} tetrahedron. The presence of D and G band of GO in the Raman spectra of nanocomposites confirms the presence of GO which was not observed in the XRD pattern. A shift is observed at the positions of D and G bands in the composites when GO content is increased (Fig: 4) [8].

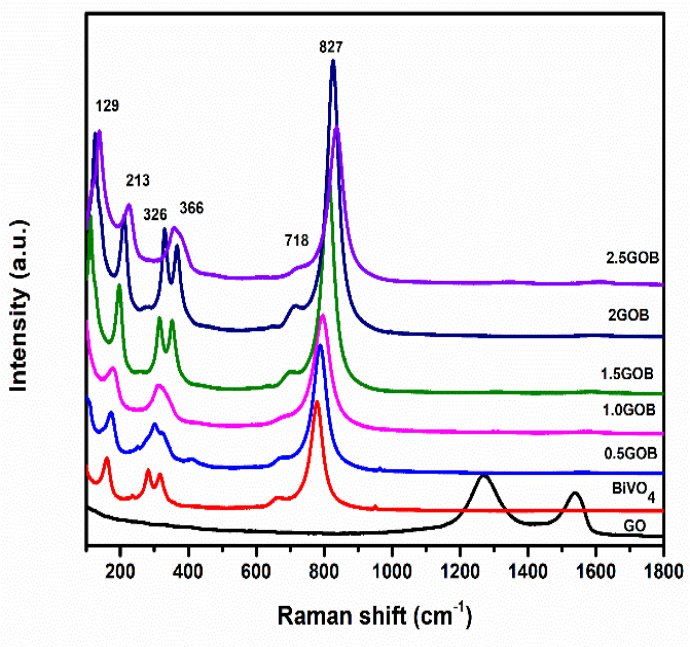


Fig 3: Raman spectra of GO, $BiVO_4$, and xGOB

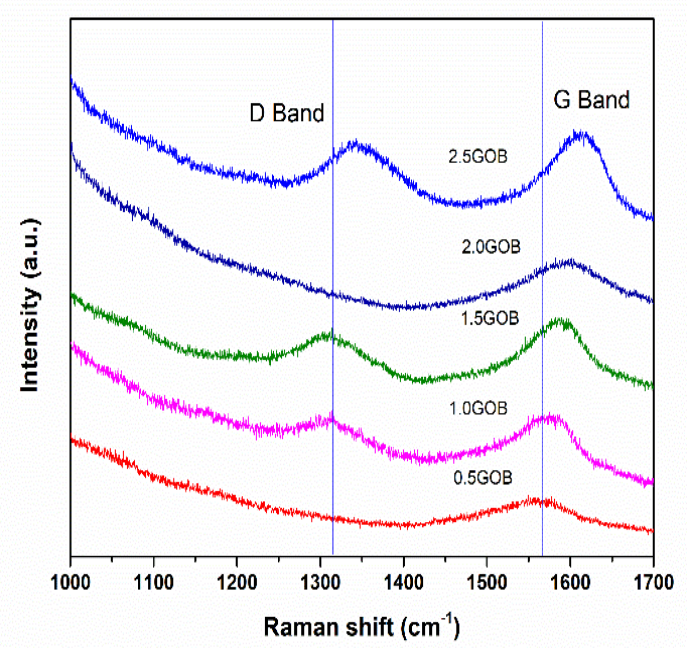
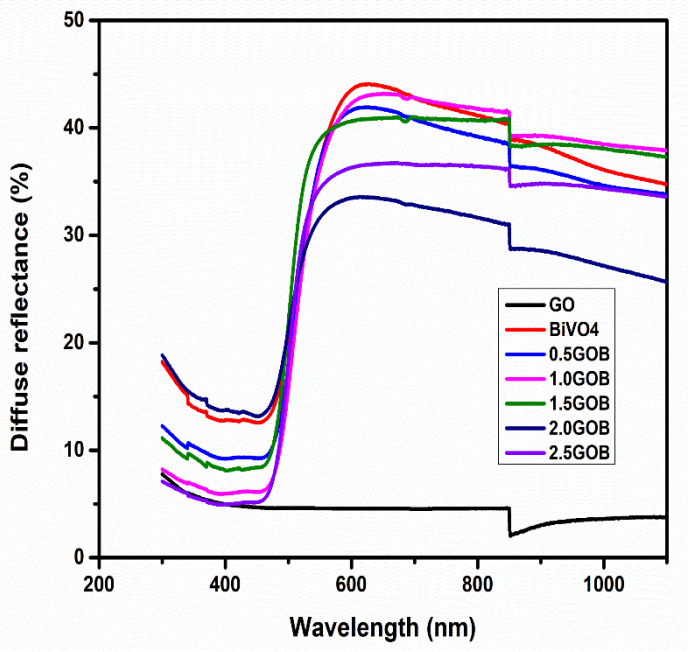


Fig 4: Shift at D and G band positions in Raman spectra

C. *UV-Visible spectroscopy*

The optical spectra (Fig 5) of the synthesized $BiVO_4$ nanoparticles and five different nanocomposites were performed. The visible light response of $BiVO_4$ nanoparticles can be observed through the absorption around 500 nm. The redshift is observed in the bandgap analysis of nanocomposites confirming the increase of light absorption ability.



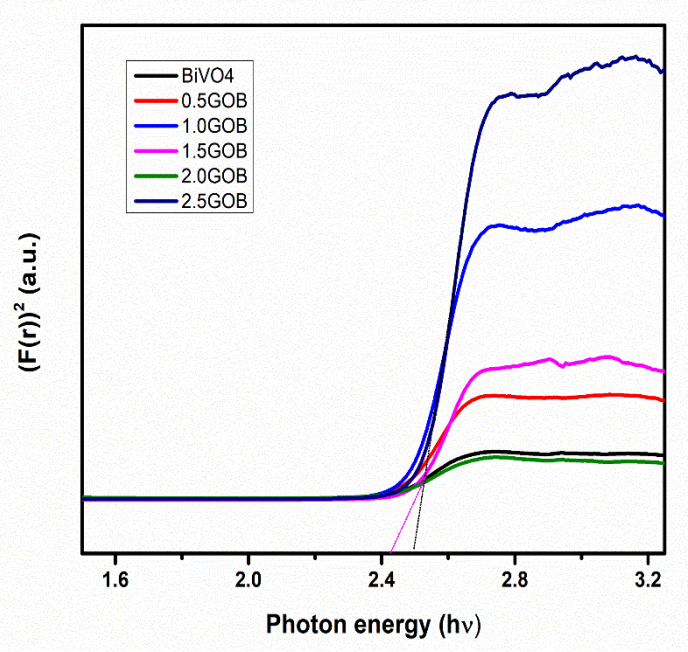


Fig 5: Reflectance and bandgap analysis of GO, BiVO4, and nanocomposites

D. Photocatalytic disinfection

The synthesized nanocomposites were used to study the photocatalytic activity against *Escherichia coli K12*. To find out the suitable nanocomposite, the dosage was fixed as 1.05 g/L for all the nanocomposites and photocatalytic test was performed for 90 mins. The dosage study was carried out with five dosages for light irradiation of 120 mins. From the results, it was found that 1.5GOB as the best nanocomposite (Table II) showing 90 % disinfection in 30 mins (Fig: 6) under visible light irradiation using very low dosage of 0.1 g/L for a bacterial concentration of 10^7 CFU/mL (Fig: 7). The activity was reduced when the time duration was increased more than 30 mins which may be due to the increased content of GO sheets [9].

Fig 6: The disinfection activity after 30 mins (control and 30 mins)

TABLE II. PERCENTAGE OF INACTIAVTION CALCULATED FOR FIVE DIFFERENT GOB NANOCOMPOSITE

Nanocomposite	Percentage of inactivation			
	0 min	*30 mins*	*60 mins*	*90 mins*
0.5GOB	0 %	77 %	80 %	50 %
1.0GOB	0 %	79.3 %	73 %	60.3 %
1.5GOB	0 %	99.3 %	90 %	86 %
2.0GOB	0 %	68 %	33.3 %	0 %
2.5GOB	0 %	75.3 %	69 %	0 %

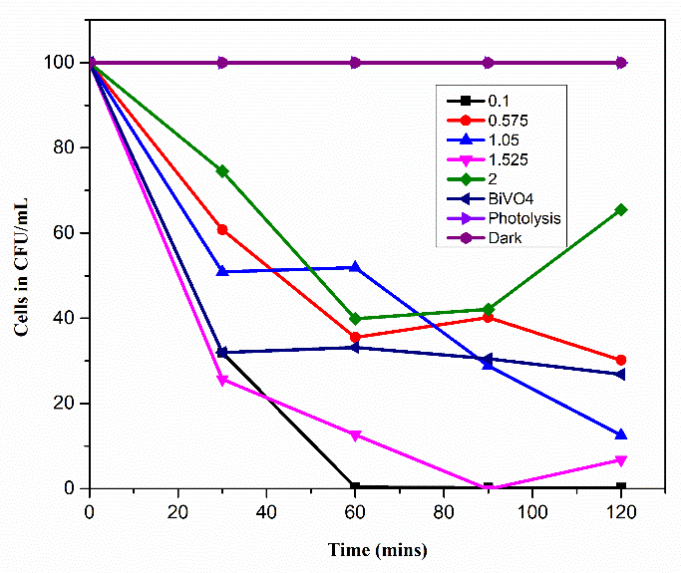


Fig 7: Relative density of cells after the disinfection study based on dosage

VI. CONCLUSION

Through the sol-gel route, $BiVO_4$ nanoparticles of 21.3 nm were synthesized. The formed BiVO4 nanoparticles were incorporated into GO sheets using a simple blending process and thereby synthesizing five different ratios of GO/$BiVO_4$ nanocomposites varying the weight percentage of GO. The basic characterizations were performed for $BiVO_4$ nanoparticles and the nanocomposites. The formation of monoclinic $BiVO_4$ nanoparticles was confirmed with XRD spectra. The peaks for the GO was not observed in the nanocomposites due to the low detection limit of the diffractometer, even though the composites formed were of high crystalline quality with no impurities. Raman spectra also confirmed the formation of monoclinic $BiVO_4$ nanoparticles and the presence of GO in the composites was confirmed by positioning D and G bands. The bandgap analysis proved the shift towards the visible light region through bandgap engineering. The as-synthesized nanocomposites were used to perform a photocatalytic disinfection study using *Escherichia coli K12* giving 90 % antibacterial activity by 1.5GOB in 30 mins under visible light irradiation using a dosage of 0.1 g/L.

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