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Visible active reduced graphene oxide-$BiVO_4$-ZnO ternary photocatalyst for efficient removal of ciprofloxacin

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ABSTRACT

A highly effective rGO-$BiVO_4$-ZnO photocatalyst was synthesized by hydrothermal method and characterized by XRD, FE-SEM, HR-TEM, XPS, Photoluminescence, FT-Raman, FT-IR and Diffuse reflectance spectroscopy. The narrow peaks of rGO-$BiVO_4$-ZnO reveal good crystallinity and strong diffraction peaks of GO at 11.30° and 42.43° correspond to the layered structure of GO. Average crystalline size of the rGO-$BiVO_4$-ZnO was 35 nm. TEM images reveal the presence of nanorods of ZnO and pristine structure of $BiVO_4$ on the rGO sheet. The band gap energy for rGO-$BiVO_4$-ZnO is 2.35 eV. The reduced PL emission at 524.6 nm by rGO-$BiVO_4$-ZnO relative to the synthesized ZnO, reveal a decrease of recombination of the photon-induced electron-hole pair by loading of $BiVO_4$ on ZnO. Ternary nanocomposite rGO-$BiVO_4$-ZnO exhibits highest photodecomposition activity, achieving 98.4% decomposition efficiency for ciprofloxacin in 60 min under visible light irradiation. Photogenerated holes play a major role in the photocatalytic decomposition of ciprofloxacin (CIP), Low cost rGO-$BiVO_4$-ZnO is stable and recyclable for effective decomposition of ciprofloxacin. Based on the GC-MS analysis, the CIP decomposition pathway as well as decomposition mechanism of piperazine ring oxidation are proposed. The photo-decomposition efficiency is mainly due to charge transfer and excellent electron hole separation by doping of rGO.

1. Introduction

The widespread use of antibiotics in human medicine has resulted in frequent findings on the surface water, ground water, soil and sediment. The traditional method of water treatment is difficult to remove the antibiotics from aqueous water system [1–4]. The CIP, a second generation of fluoroquinolone, is more active than the first and third generation CIP. Currently, heterogeneous catalysts are excellent in the decomposition of the second and third generation fluoroquinolone [5–7]. As ZnO has the intrinsic drawbacks such as more electron-holes recombination and UV light active, it is very much important to improve its characterisitics. Elemental doping and coupling of ZnO with other semiconductor is an effective way to adjust the band gap structure to make visible active [8–10]. The $BiVO_4$ has large attention due to low band gap (2.4 eV) good stability and excellent efficiency for decomposition of organic pollutants.

Nowadays, reduced graphene oxide (rGO) based nanocomposite materials are used to improve the photocatalytic efficiency. Structurally similar Graphene oxide (GO) and rGO differ in surface area and in rGO, edges of the GO are modified by oxygen-containing functional groups like −OH, C−O−C, COOH, CO−. Reduced graphene oxide has attracted more attention by its features like extremely high mobility, electronics transport, high elasticity and electromechanical properties [11–14]. Binary semiconducting materials with rGO may have low band gap energy level, higher electron-hole separation and visible light absorption [15]. Reduced graphene oxide loaded TiO_2 composite material also exhibits synergistic effect. It was reported that rGO-TiO_2 composite effectively decomposed ciprofloxacin, compared with pure TiO_2 [16,17]. Hence loading of rGO with a coupled semiconductor oxide materials forming a ternary composite may have improved

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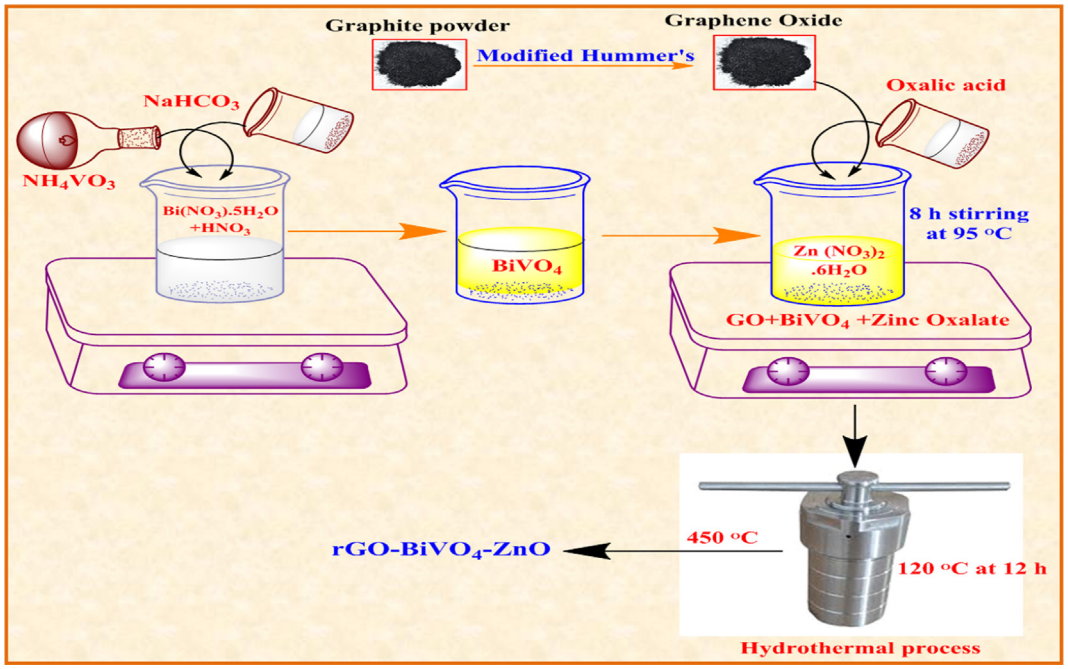

Scheme 1. Synthesis of rGO-$BiVO_4$-ZnO nanocomposite.

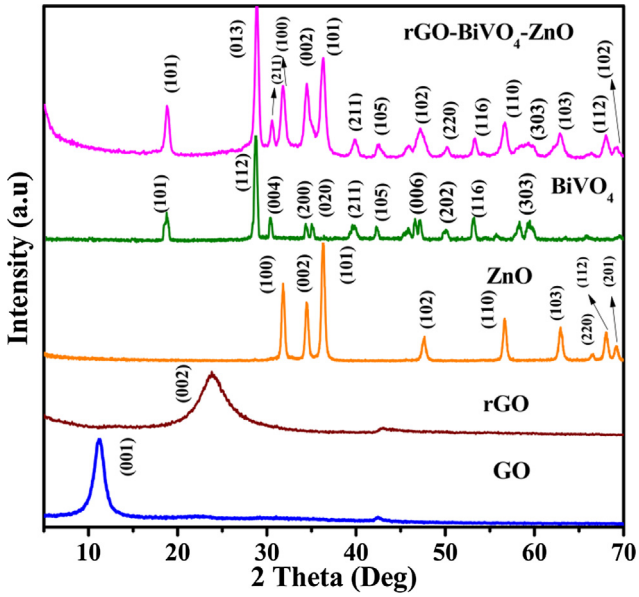

Fig. 1. X-ray diffraction patterns of prepared GO, rGO, $BiVO_4$ and rGO-$BiVO_4$-ZnO.

photodecomposition efficiency through higher electron-hole pair separation, and light absorption. CIP, being stable and easily soluble in water, induces chronic health effect and hence the removal of CIP from the environment becomes an important issue [18]. CIP decomposition has been studied previously using $BiVO_4$, TiO_2, ZnO and rGO-$BiVO_4$ photocatalysts under visible light irradiation [19,20]. These reported catalysts are limited by long time reaction and low reusability. The Binary or ternary semiconductor with different band potentials can increase the electron-hole pair and interfacial charge transfer efficiency [21–23]. Coupling of semiconducting oxides, having different energy levels, improves electron-hole pair separation [24]. Hence the ternary nanocomposite material rGO-$BiVO_4$-ZnO catalyst may overcome these shortcomings. In continuation of our work on modification of ZnO [25,26], we report the fabrication of rGO loaded coupled $BiVO_4$-ZnO by a simple hydrothermal method for the degradation of CIP.

2. Methodology

2.1. Materials and methods

The commercially available chemicals such as bismuth nitrate pentahydrate, zinc nitrate hexahydrate, ammonium metavanadate, oxalic acid, isopropyl alcohol, Graphite powder, ethanol, hydrochloric acid, ciprofloxacin, sulphuric acid, Potassium permanganate, hydrogen peroxide were obtained from Merck chemicals. The XRD patterns were recorded at room temperature by a Rigaku X-ray diffractometer under the range of 2θ from 2° to70° with the scanning rate of 2°/min. The morphological structures of rGO-$BiVO_4$-ZnO were analyzed using FE-SEM model ULTRA-55. Transmission Electron Microscopy investigation was done with JEOL 2100X model with an operating voltage of 200 kV. XPS spectra of Photocatalysts were measured by ESCA-3 model. The oxygen and carbon content in the GO and rGO were obtained from EDS and elemental mapping by JEOL JXA 8530F model. FT-Raman spectral analysis was done by BRUKER, Model RFS 27 in the wavenumber range between 3500 and -400 cm^{-1}. FT-IR spectra were taken in the wavenumber range from 4000 to 400 cm^{-1} using a Nicolet model spectrometer. UV–Visible diffused reflectance spectra were recorded by Shimadzu UV-2450 UV–Visible spectrophotometer. Photoluminescence spectra (PL) were recorded by Perkin Elmer LS 55 fluorescence spectrometer. The gas chromatography were recorded at GC-MS, TSQ Quantum XLS model and the column temperature was increased from 70 °C to 220 °C over 79 min. The organic pollutant concentrations were obtained using Shimadzu UV-1800 UV–visible spectrophotometer.

2.2. Synthesis of GO and rGO-$BiVO_4$-ZnO

GO was prepared by Modified Hummer's method. GO, obtained, was filtered and dried at 40 °C under vacuum condition for 24 h [27,28]. The $BiVO_4$ was prepared by mixing of 0.02 M $Bi(NO_3).5H_2O$ (0.980 g) in 20 mL of 0.1 M HNO_3 in 100 mL double distilled water with 0.02 M NH_4VO_3 of 0.468 g in 100 mL of sodium bicarbonate solution in double distilled water. The yellow precipitate $BiVO_4$ was mixed with 8 g of $Zn(NO_3).6H_2O$ (0.4 M) solution of 100 mL and 0.6 M oxalic acid