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Gallium Oxide Nanostructures for Wastewater Treatment: Photocatalytic Degradation of Methyl Orange

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Abstract: In recent years, various fabrication methods of photocatalytic materials have been developed for photo degradation of organic and inorganic pollutants from consumable resources. Particularly, inorganic semiconductor nanomaterials have been considered as most promising agents for photocatalytic applications due to their remarkable physical and chemical properties with large effective surface area, and a variety of morphologies, such as nanorods, cubes, spheres and flowers, synthesized by cost effective chemical route.

This work is directed towards the development of group III metal oxide nanostructures of Ga_2O_3 which have been recognized as an important material for several applications including catalysts, gas sensors, solar cells, and photodetectors. Typically, the Ga_2O_3 nanostructures were obtained by calcination of gallium oxide hydroxide (GaOOH) synthesized via a chemical bath method. Then, as-prepared GaOOH nanostructures were calcined at different temperatures of 500–1000°C for obtaining Ga_2O_3 nanostructures. This system was characterized by traditional tools like XRD, FESEM, EDX, UV-Vis to investigate the phase information, morphological features, composition and the information about band gap of the same. Also, the photocatalytic performance of Ga_2O_3 nanostructures was studied by time evolved UV-vis absorption spectrum of degradation of Methyl Orange (MO) solution. Under UV irradiation for 120 min, the Ga_2O_3 nanorods exhibited a high photodegradation efficiency of (98%). This work proposes a simple cost-effective eco-friendly route for synthesis of Ga based oxide photocatalysts for wastewater treatment.

Keywords: Ga_2O_3 nanorods, XRD, FESEM, EDX, UV-Vis, wastewater treatment, Photocatalytic Degradation.

I. INTRODUCTION

With faster technological development, industrial wastewater is threatening us with their increasing pollution due to rapid development of polymer, photographic, textile, dyeing industries. Different types of organic pollutants such as dyes, phenol and its derivatives are the most potential contaminations liberated from various productions due to printing and dyeing in paper, textile, paints, leathers; oil refining; polymeric resin production; coal gasification; coking plants etc. [1] Nowadays removal of wastes from water is really a big challenge as some conventional methods like activated carbon adsorption, solvent extraction and common chemical oxidation frequently suffer from significant drawbacks including high cost or generation of hazardous by products. For example, more toxic chlorinated compounds may form during water purification by chlorination method [2].

In the past decades various metal oxide nano particles such as TiO_2, ZnO, WO_3 have drawn considerable attention as a promising candidate for photocatalysis due to exhibiting their high efficiency in decomposition of a wide range of stubborn organic pollutants into carbon dioxide and water under UV irradiation [3-6]. However, it is necessary to investigate new strategies to enhance the photocatalytic activity that is by reducing the size of a metal oxide and improving its surface-to-volume ratio, porosity, structural uniformity, stability etc. Five different polymorphisms exist in Ga_2O_3 like α, β, γ, δ, ϵ-gallia. Among these crystalline phases, β-Ga_2O_3 having monoclinic crystal structure possess excellent thermal and chemical stability. Being a wide band gap semiconductor β- Ga_2O_3 (Eg = 4.9 eV) [7] is UV transparent and displays a promising prospect in the fields of photocatalysis, including the degradation of organic pollutants [8], Hydrogen evolution [9], CO2 reduction [10] etc. Ga_2O_3 has been considered as a cost-effective material for water decontamination because of its superior charge separation, favourable mobility of the photo-generated electrons and its capability for converting light energy into chemical energy. Here we have attempted to prepare the porous gallium oxide nanostructures with large surface to volume ratio via a relatively simple, cost effective, environmental friendly wet chemical bath method followed by calcination. In our work, β-phase Ga_2O_3 was prepared via a facile chemical bath method and proper calcination.

Then to get the information about crystallinity, phase, morphology, composition etc, we have characterized our sample by conventional tools like X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray analysis (EDX) etc. The as-synthesized materials displayed exceptional photocatalytic performance under UV irradiation for the decomposition of organic pollutant Methyl orange (MO) to get the pure water under ambient conditions. The efficiency of degradation was correlated with the porous feature of the nanostructures.

II. EXPERIMENTAL

All the reagents used in the synthesis procedure were analytical pure grade chemicals. Bar-like Ga_2O_3 were prepared by a simple chemical bath method followed by calcination. To prepare the growth solution initially the mixture of hydrated Gallium nitrate $(Ga(NO_3)_3.nH_2O)$ (0.1 M) and ammonium hydroxide (NH_4OH) was stirred and heated at 105°C maintaining pH 9 to produce white precipitate of Gallium Oxide hydroxide bars. Further the as-synthesized GaOOH samples were calcined in an oven at a heating rate of 10°C per min for 2 hours, then that temperature was maintained for 3 hours to obtain gallium oxide structures of β phase.

Traditional characterizations with X-ray diffractometer (Bruker D8 Advanced), field emission scanning electronmicroscopy (FESEM, Hitachi S-4800), EDX spectrophotometer attached with FESEM (EDS, Thermo Scientific attached with Hitachi S-4800) were carried out to analyze crystal structure, morphology and chemical composition of the synthesized Ga_2O_3 nanostructure. For photocatalytic experiment, 40 ml of 10-5 M methyl orange dye and 0.03 g of the as-prepared Ga_2O_3 powder sample were taken as pollutant and catalyst. The dye-catalyst solution was stirred in dark condition for 30 mins before UV exposure. Afterwards the solutions containing the powder sample was subjected to UV irradiation using two 40W UV tube (Phillips) emitting wavelength of 254.6 nm (UVC). The time evolved absorption spectra were recorded with the solutions collected in different time intervals using UV-Vis spectrophotometer.
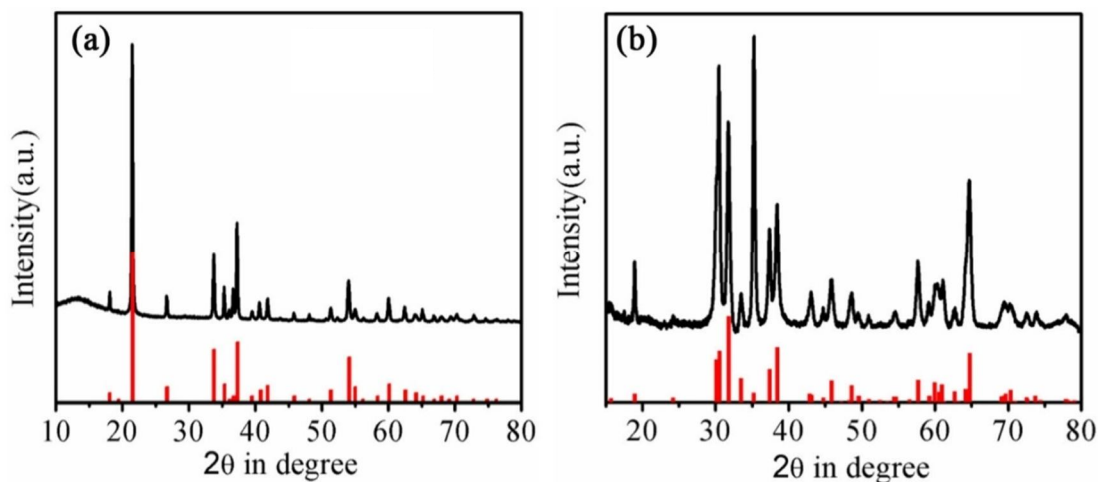
III.RESULTS AND DISCUSSION

Fig. 1. XRD patterns of (a) as-prepared GaOOH; (b) β- Ga_2O_3 microbars

The XRD pattern of the as prepared samples can be found in fig. 1. It can be clearly seen that the GaOOH microbars and Ga_2O_3 microbars exhibit good crystallinity with the later following β phase. The lattice planes for the GaOOH and β-Ga_2O_3 samples were correlated with JCPDS card no: 06-0180 and 76-0573 respectively. The intense lattice peaks indicate the proper crystallinity of Ga_2O_3 samples.

The detail analysis of morphology has been depicted in fig. 2. It can be clearly seen from fig. 2(a) that the GaOOH samples are adequately uniform in size and shape with compact surface structure. Whereas fig. 2(b) shows that the Ga_2O_3 samples are almost same in shape, with only difference of surface porosity. The pore distribution was found to be uniform. The occurrence of pores is directly correlated to the temperature effect. As the GaOOH microbars are subjected to high temperature annealing, the internal water molecules vaporized leaving appreciable vacant space within the structure.
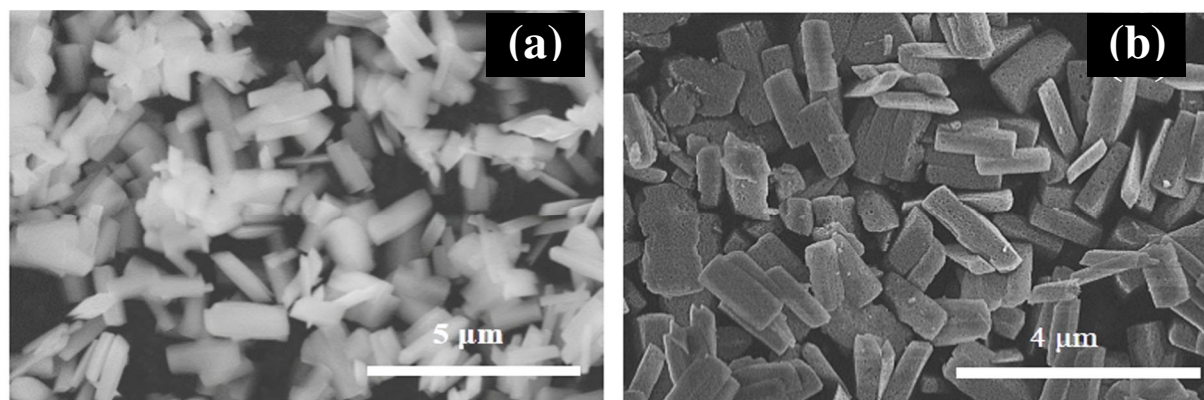
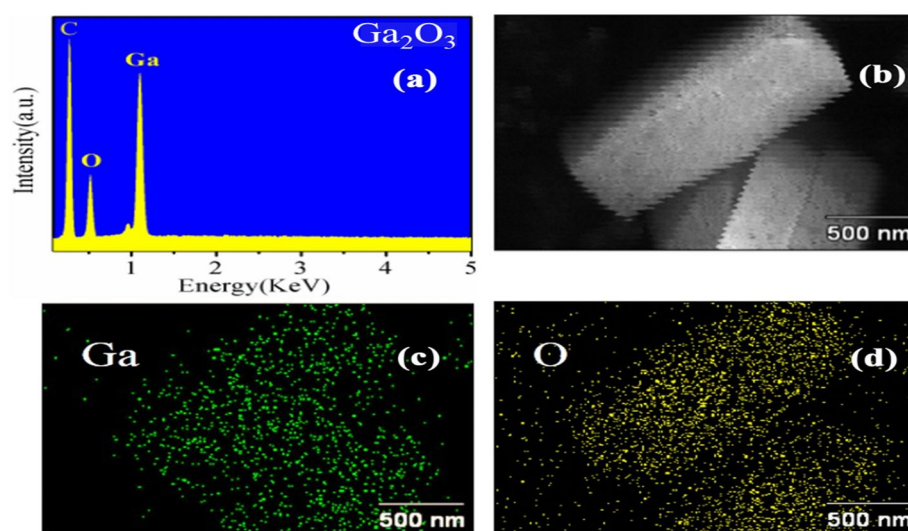Fig. 2. FESEM images of as-prepared GaOOH (a) and β-Ga2O3samples (b)

Fig. 3. EDX spectrum of β-Ga$_2$O$_3$ (a), with morphology (b), and their corresponding elemental mapping represents the distribution of Ga and O (c-d), respectively.

EDX elemental mapping of Ga$_2$O$_3$sample can be seen in fig. 3. Presence of all atomic constituents was detected in the result and also in the spectrum. The elemental distribution was also found to be appropriate indicating proper stoichiometry of the sample.
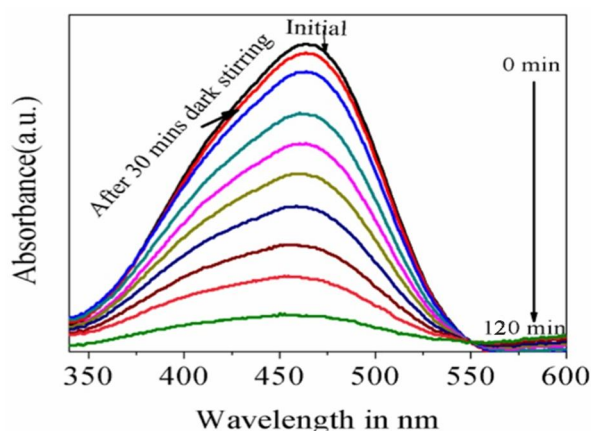

Fig.4. UV-Vis spectra of photocatalytic degradation of Methyl Orange dye.

The major thrust of this work, i.e. photocatalytic activity analysis is presented in fig. 4. The time evolution of the absorbance curve corresponding to MO indicates that the presence of MO in solution is gradually decreasing with time. The amount of MO in the solution after 2h treatment with Ga_2O_3 samples became almost undetectable. The photocatalytic dye degradation parameters are shown in fig.5. It can be seen that the Ga_2O_3 can efficiently remove hazardous dyes from consumable water. The degradation rate constant was determined using the following equation [11]

$$r = \frac{-dc}{dt}$$
$$= \frac{k_r k_a C}{1 + k_a C} \ldots\ldots(1)$$

where, k_r and k_a represent rate constant and adsorption constant respectively. The same equation can be further simplified to the following form

$$ln\frac{C_0}{C} = k_r k_a t = kt \ldots\ldots\ldots(2)$$

here C and C_0 are the concentration of the dye at time (t) and k is the degradation rate constant.

From fig 5.(a) it is shown that after 120 minutes of constant stirring in presence of continuous UV light irradiation, C/C_0 became 0.2; the photodegradation efficiency became 98% (fig 5.(b)).

The efficiency of dye degradation by Ga_2O_3 can be explained in terms of morphology of the same. The presence of multiple pores in the structure of Ga_2O_3, enable high effective surface area. The dye molecules are therefore allowed to the contact of the catalyst in a high extent. This higher degree of sample contact to the dye under UV exposure cause efficient degradation of MO.
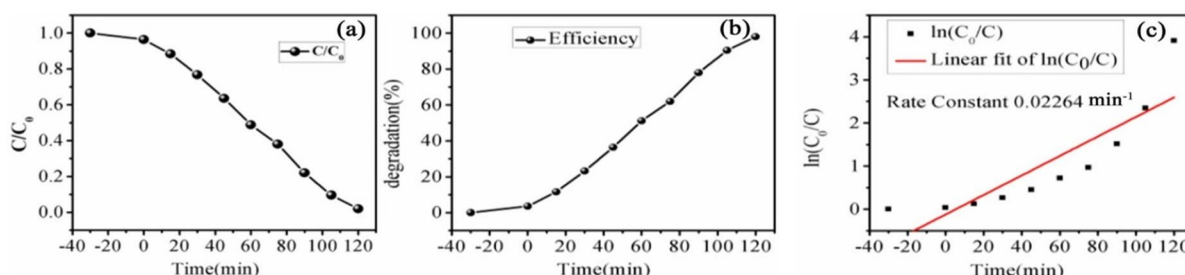

Fig. 5. C/C_0 vs. irradiation time plot (a); percentage of degradation vs. irradiation time plot (b); Kinetic fit plot of $ln(C_0/C)$ vs. irradiation time of β-Ga_2O_3 microbars.

IV. CONCLUSIONS

Porous β-Ga_2O_3 microbars were synthesized via cost effective chemical route. Traditional characterizations were performed to investigate structural morphological and compositional properties. The synthesized sample was subjected to photocatalysis experiment to check its ability in degrading methyl orange. The sample showed efficient dye degradation performance with degradation rate constant of 0.02264. This work therefore establishes porous β-Ga_2O_3 samples as efficient material for wastewater treatment remediation.

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