

Low-Temperature Synthesis, Characterization and Photocatalytic Activity of Nanorods BaBiO₃ Perovskite under Visible Light Irradiation

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ABSTRACT: Perovskite structured BaBiO₃ was prepared at low temperature by polymeric precursor method (Pechini method). In this approach, metal nitrate, citric acid, and ethylene glycol were used as the source of metal, chelating agent and connecting agent respectively. The raw photocatalyst was activated at different temperatures. The structure and morphology of annealed samples were characterized by Thermo Gravimetric Analysis (TGA), Powder X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and UV-Visible Diffuse Reflectance Spectroscopy (UV-DRS). The XRD patterns suggested that pure crystalline powder was obtained at 800 °C. The SEM images revealed the nano size and rod-like shape of BaBiO₃ particles. The band gap energy was calculated from the UV-DRS and it was found to be 2.07 eV. The band gap and the crystal structure data suggest that this material can be used as photocatalyst in visible region. The photocatalytic activity of BaBiO₃ was evaluated for the degradation of diclofenac drug (DCF) under indoor lamp illumination and solar radiation. The obtained results were also compared with Degussa P-25 TiO₂ and comparison showed that BaBiO₃ catalyst was more efficient in visible region. Additionally, the recycling experiments confirmed the attractive stability of the catalyst.

KEYWORDS: BaBiO₃, Perovskite, Pechini methods, Low temperature synthesis, Diclofenac drug, Photocatalysis.

I. INRODUCTION

Photocatalysis using solar energy is highly expected to be an ideal “green” technology for sustainable development of human beings, where an active photocatalytic material is definitely an important key. To date, TiO₂ is considered to be the best photocatalytic material because of its non-toxicity, low cost, long-term stability, high photocatalytic activity and environmental friendly nature [1]. Owing to wide band gap energy (3.2 eV) TiO₂ can only absorb ultraviolet light (UV) which is merely 4% of entire solar energy, so its scope of application is limited [2,3]. Therefore, a significant amount of research is being done on visible light sensitive photocatalysts that can respond to sunlight and illumination from an indoor lamp. Numerous attempts have been made to improve the low efficiency of TiO₂ in the visible region by cation or anion doping [4, 5]. But its activity is not high enough for practical application due to low stability of doped ions. Many studies are devoted to develop new photocatalytic material which, independent of TiO₂, can efficiently utilize solar light. Among all the visible light activated photocatalysts, perovskite –type transition metal oxides have attracted considerable attention due to their stable crystal structure, low band gap and high catalytic activity [6-8]. The properties of perovskite type oxides, of general formula ABO₃, depend tightly on the nature of A and B ions and on the valence state of A and B. The A site ions are in general catalytically inactive and influence thermal stability of perovskite, while the transition metal ions at B position are active components. Many researchers have developed visible- light-sensitive perovskite such as LaNiO₃, GdCoO₃, CeVO₃, NdVO₃ and SrTiO₃ [9-13]. Very recently, a family of Bi based oxides has been found to be very active under visible light irradiation such as BiVO₄, BiWO₆, CaBi₂O₄, BiMoO₆, BiTaO₄, KBiO₃ and LiBiO₃ [14-19]. Recently formed perovskite, NaBiO₃ [20] exhibits much higher activity for the decomposition of methylene blue dye under visible light. The attractive performance of NaBiO₃ is ascribed to its band structure where the conduction band (CB) consists of hybridized Na (3s) and O (2p) orbitals that exhibit large dispersion with high mobility for photo-excited electrons.

In the present paper, Bi containing perovskite BaBiO₃ was synthesized by the pechini method [21] at different calcinations temperatures. For synthesis, pechini method was adopted as it has many advantages such as good homogeneity, good stoichiometric control and good control of the particle morphology. The structure and morphology of BaBiO₃ were examined by different analytical techniques. According to UV-DRS, the oxide can absorb light with wavelength smaller than 600 nm, which almost covers the region from UV through all strong visible light, in the

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sunlight and an indoor lamp illumination. Furthermore, the photocatalytic activity of the prepared perovskite has been evaluated via degradation of diclofenac drug in aqueous solution under visible light irradiation.

II. MATERIALS AND METHODS

2.1. Chemicals and reagents: Barium nitrate $\text{Ba}(\text{NO}_3)_2$, Bismuth nitrate, $\text{Bi}(\text{NO}_3)_3$, Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) were purchased from Merck (India). Diclofenac (DCF) sodium salt was purchased from Sigma-Aldrich. The Degussa P-25 TiO_2 was purchased from Degussa Chemical, Germany. Deionized water was used in all the experiments.

2.2. Preparation of BaBiO_3 Perovskite: BaBiO_3 perovskite was prepared from highly pure polymeric precursors using the method proposed by Pechini. Barium nitrate and Bismuth nitrate (1.0 M) solutions were prepared using deionized water. These solutions were mixed and heated up to 90°C . At this stage, citric acid (CA) was added in a ratio of 4:1 with respect to metal ion. After 15 minutes stirring, ethylene glycol (EG) was added in the EG:CA ratio of 40:60 (w/w). Now, this solution was homogenized by stirring at room temperature for 1 h followed by heating on hot plate until a brown gas was released and the solution became a dark brown resin. The obtained resin was polymerized at 300°C for 2 h. The resulting black sponge polymer was calcined in air at different temperature 600°C and 800°C , for 12 h. A brown crystalline ceramic powder was obtained thereafter.

2.3. Characterization: Several techniques were used for characterization of the powders. Thermal gravimetric analyses were carried out in a TGA-7 Perkin-Elmer balance under an air flow of 50 ml min^{-1} . The maximum temperature was set to 900°C and the heating rate to 5°C min^{-1} . Powder X-ray diffraction (Siemens D5000 diffractometer) analyses were carried out using Cu K α radiation at 2θ angles from 0° to 80° with scan speed of 5°min^{-1} . Ultraviolet and visible diffuse reflection spectra (Shimadzu Lambda 900 spectrophotometer) were measured at 240-800 nm wavelengths. The morphology of the sample was observed with a scanning electron microscope (SEM) (Hitachi X650, Japan).

2.4. Catalytic activity: Photodegradation experiments were performed with a photocatalytic reactor system. This bench-scale system consisted of a cylindrical Pyrex-glass cell with 1.5 L capacity (12 cm inside diameter and 15 cm height and a reflective interior surface). A 500 W halogen lamp was placed in a 5 cm diameter quartz tube with one end tightly sealed by a Teflon stopper. The lamp and the tube were then immersed in the photoreactor cell. The photoreactor was filled with 1L aqueous crystal violet dye solution with BaBiO_3 perovskite. The whole reactor was cooled with a water cooled jacket on its outside and the temperature was kept at 25°C . Magnetic stirrer was also used to keep the solution chemically uniform. A 1mL sample was drawn and make up upto 10 mL. The residual concentrations of diclofenac drug were observed from its characteristic absorption at 276 nm using a UV-Visible spectrophotometer. All experiments were carried out at pH 6.0 (natural). Finally, the photocatalytic activities were determined using the following formula:

$$\text{Drug removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where, C_0 and C_t are the initial concentration of solution and the concentration after photocatalytic degradation by BaBiO_3 photocatalyst, respectively.

3.1. Characterization of BaBiO₃

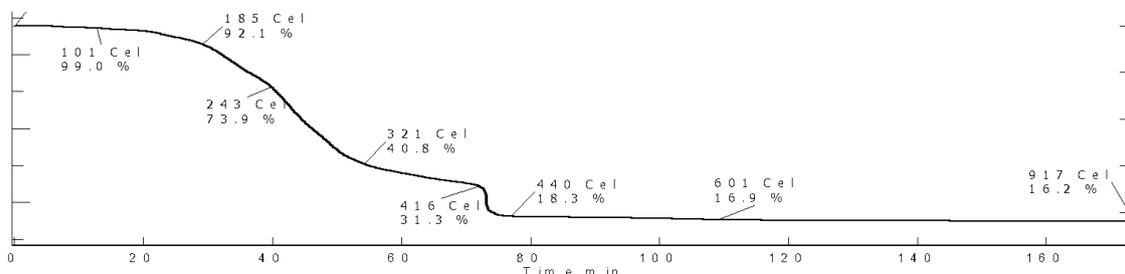


Fig.1. TGA analysis of the thermal decomposition of BaBiO₃ precursor resin in air and heated at 25 °-900 °C at 5 °C min⁻¹.

The thermal decomposition behaviour of the BaBiO₃ precursor resin was characterized by TGA. The thermal decomposition could be divided into four stages according to Fig.1. In the TGA curve, first stage happens below 185 °C temperature and accompanied by 8.9% weight-loss which was assigned to dehydration and depolymerisation of the polymeric residual in the precursor. The second stage occurs at the temperature range of 185 °C- 416 °C with a weight loss of 60.80% which was explained by the complex decomposition and combustion of the polymeric resin. In the third stage, temperature range of 416 °C- 440 °C, 13.0% weight loss was observed. This weight loss could be due to the decomposition of the nitrates or nitrites and residual carbonate intermediate and the evolved product was mainly NO and CO₂ [21]. In the last stage above 850 °C small weight change occurs due to the crystallization of the sample and subsequent conversion to the perovskite phase which is in accordance with the XRD results shown in Fig.2.

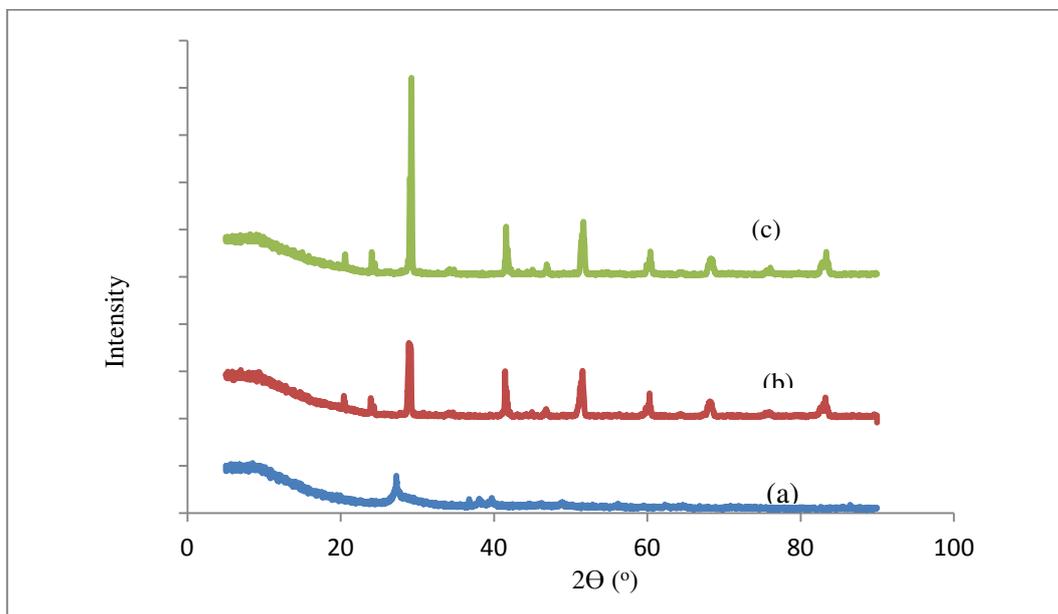


Fig.2. X-ray diffraction pattern of BaBiO₃ at different temperature (a) 300 °C (b) 600 °C and (c) 800 °C

Fig.2 shows XRD patterns of the samples which were calcined at different temperature 300 °C (a), 600 °C (b) and 800 °C (c). The XRD pattern (a) revealed the amorphous nature of sample after calcinations at 300 °C as no sharp peaks appeared here. When the sample was calcined at 600 °C, the peaks became broader and less intense in the XRD pattern (b) which showed it is poorly crystalline nature. Well resolved X-ray pattern were obtained from the sample calcinated at 800 °C (c) clearly suggesting the formation of a highly crystallized powder. The XRD patterns clearly showed that degree of crystallization increase on increasing the annealing temperature. The strongest diffraction peaks at 2θ were observed to be 29.23°, 45.00°, 51.67° and 59.90° here. The peaks are related to the BaBiO₃ perovskite as reported elsewhere [22].

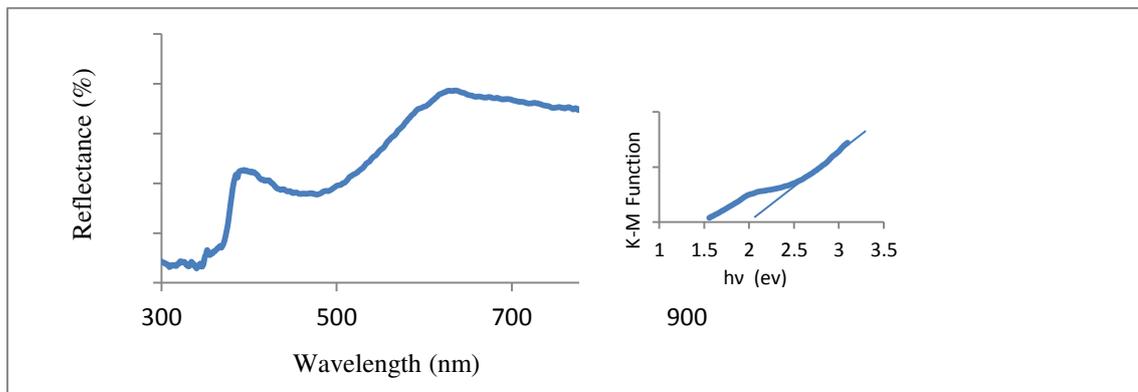


Fig.3. UV-Vis diffuses reflectance spectra of BaBiO₃ pervoskite

In order to investigate the band gap of the prepared BaBiO₃ sample the UV-Vis. DRS was measured in range of 300-800 nm. Fig.3. shows that the prepared BaBiO₃ sample was sensitive to visible region. Further; for the determination of band gap from obtained UV DRS, we used the Tauc plot, which obeys the following equation:

$$(h\nu\alpha)^{1/n} \propto (h\nu - E_g) \dots\dots\dots(1)$$

Where h,ν, E_g,α are the planck’s constant, vibrational frequency, band gap and absorption coefficient respectively. Typically n depends upon the nature of transition in a semiconductor; here it was determined as 2 because of indirectly allowed transition [23]. The value of band gap for the photo catalyst was calculated as 2.07 eV by plotting KM function with respect to photon energy (eV). The KM function was obtained by the conversion of acquired DRS [24]. The band value of BaBiO₃ was consistent with the previous results measured by momentum transfer resolved electron energy loss spectroscopy [25]. The UV- Visible DRS spectrum was also consistent with the colour of the compound; BaBiO₃ is brown indicating considerable visible light absorption by this oxide.

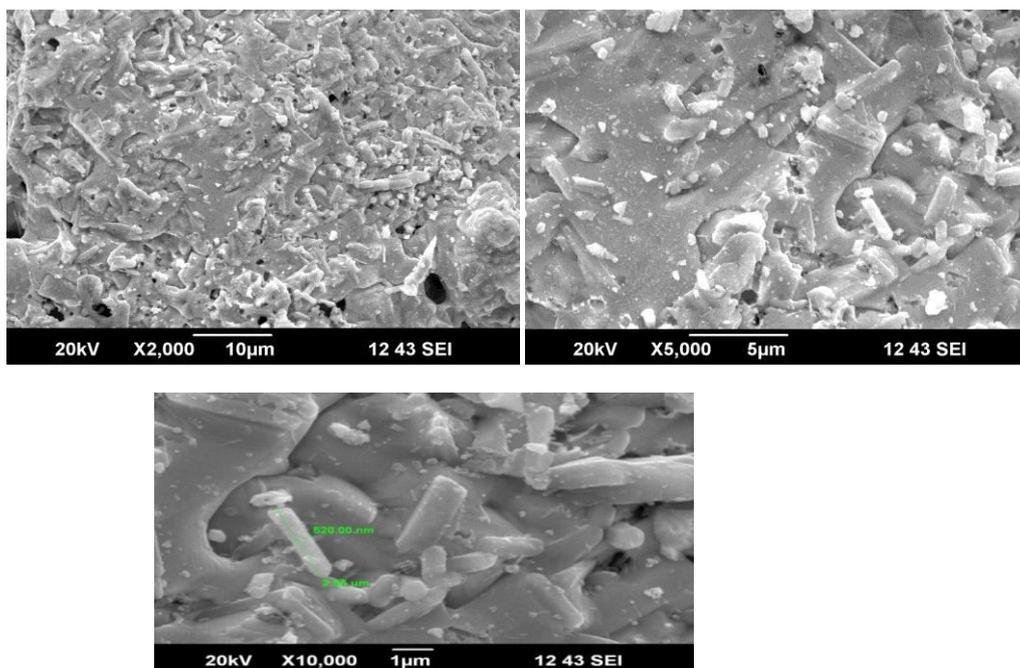


Fig.4. SEM images of BaBiO₃ pervoskite at different magnificence

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The scanning electron micrograph of BaBiO₃ sample was taken at different magnifications and shown in Fig. 4. As seen in the micrographs, morphology of the BaBiO₃ particles were road likes with average width 520 nm and length up to 2.55µm.

3.2. Photocatalytic activity: We conducted experiments to evaluate the photocatalytic activity of BaBiO₃ oxide in degradation of diclofenac drug under visible light irradiation. For degradation study, we used diclofenac drug as probe molecule because it is one of the most frequently detected pharmaceuticals in river and surface waters and also considerably stable under normal environmental conditions [28]. Thermal treatment was an important step to prepare BaBiO₃ oxide, during which different annealing temperature may deeply influence the materials performance. Thus in this work, the influence of calcinations temperature on BaBiO₃ for photocatalytic degradation of diclofenac drug under visible irradiation was examined. As exhibited in Fig.5. the diclofenac drug was almost degraded (96.17 %) by the sample calcined at 800 °C in 240 min., while for the samples calcined at 300° and 600 °C, 64.33% and 17.12% degradation was found after 240 min. respectively. The best photocatalytic activity of the BaBiO₃ perovskite calcined at 800 °C was because of its high degree of crystallinity as evidenced from our XRD results (Fig.2.)

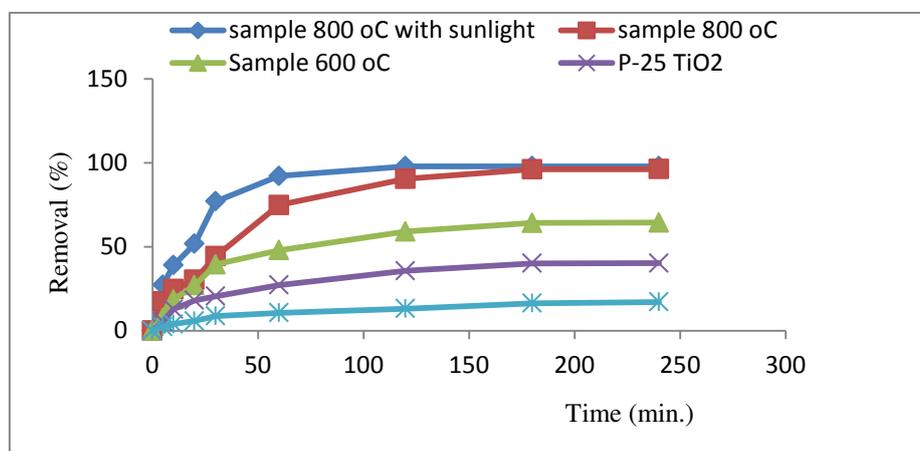


Fig.5. photodegradation curves of diclofenac drug using BaBiO₃ oxide obtained at different calcinations temperature, P-25 TiO₂ and solar light (Drug concentration= 40 ppm; catalyst amount 1g/1000 mL; solution pH=6)

We also carried out the following controlling experiments: (i) With P-25; Degussa TiO₂ (ii) In sunlight; use of solar light instead of artificial light is important for the industrial point of view.

Under identical experimental conditions, the total photodegradation of the diclofenac drug reached only 40.19% in 240 min. with widely used and very versatile P-25TiO₂ which justifies the use of our synthesized BaBiO₃. In the next experiment, the aqueous solution of diclofenac drug and BaBiO₃ oxide were exposed to sunlight. It was found that the degradation of drug proceeds much more rapidly in the presence of solar light (97.88%) confirming the higher potential of the catalyst under sunlight.

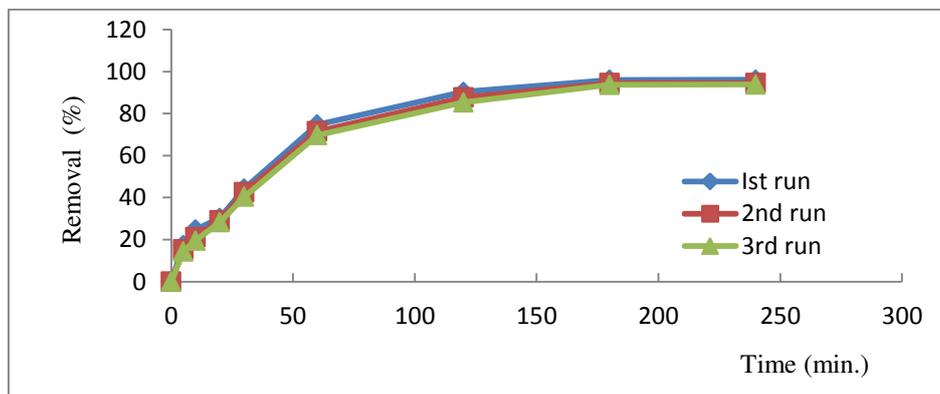


Fig.6. Evaluation of durability of BaBiO₃ perovskite (Drug concentration= 40 ppm; catalyst amount 1g/1000 mL; solution pH=6)

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In our work, we also recycled the used BaBiO₃ perovskite by sedimentation within 10 min. Then, the long-term stability of the BaBiO₃ oxide was tested by contacting fresh diclofenac drug solutions with used catalyst for the degradation of DCF drug under identical reaction condition at same pH. As observed in Fig.6. about 96.17% degradation efficiency of DCF drug was achieved within 240 min of irradiation in the first run. In the second run, 94.53% degradation of DCF drug was achieved and the third run shows almost the same degradation rate. The results indicate that BaBiO₃ nanorods retain most of its catalytic activity for long time.

IV.CONCLUSION

Pure nanorod structured BaBiO₃ perovskite photocatalyst was prepared when the sample was calcined at 800 °C for 12 h through pechini method. The prepared catalyst was characterized by TGA, XRD, SEM and UV-DRS. TGA result shows that total mass loss in the precursor powder was 83.10 % and it occurred in four steps between 30 to 900 °C. The TGA and XRD analysis also indicated the formation of the oxide phase at 800 °C. The SEM images show the shape of particles were rods like and size was in the nanoscale range. The diffusion reflectance spectroscopy showed that the catalyst has a broad absorbance around 600 nm with band gap of 2.07 eV. Due to the low band gap the catalyst can be used for the photocatalytic activity under solar light and indoor lamps illuminations. The photocatalytic study was carried out for the degradation of diclofenac drug. The results show that the highest degradation of diclofenac was achieved with sample annealed at 800 °C using solar light. The BaBiO₃ perovskite skeleton structure was stable and can be reused in recycled drug degradation reactions. The use of low temperature synthesized and biologically inactive catalyst offers an economical and feasible solution for the processing of liquid waste especially in regions of abundant sunlight.

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