BUT

Iranica Journal of Energy & Environment

Journal Homepage: www.ijee.net

IJEE an official peer review journal of Babol Noshirvani University of Technology, ISSN:2079-2115

Photocatalytic Degradation of Anti-inflammatory Drug on Ti Doped $BaBiO_3$ Nanocatalyst under Visible Light Irradiation

S. Jain*, K. Sharma, U. Chandrawat

Ekpoma, Nigeria Department of Chemistry, Govt. P.G. College, Kota 324001, India

P A P E R I N F O

Paper history:
Received 20 July 2015
Accepted in revised form 31 August 2015

Keywords:
Pechini synthesis
$BaBiO_3$
$BaBi_4Ti_4O_{15}$
Photodegradation
Ibuprofen

A B S T R A C T

Nanosized perovskites $BaBiO_3$ and $BaBi_4Ti_4O_{15}$ were prepared using Pechini method. These structures were confirmed through thermogravimetric analysis (TGA), X-ray diffraction (XRD), UV-Vis diffusion reflection spectroscopy (UV-Vis DRS), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The XRD patterns suggest that $BaBiO_3$ is crystalized in the monoclinic structure while a member of aurivillius family, bismuth-based layer-structured $BaBi_4Ti_4O_{15}$ is crystalized in tetragonal structure. The band gap is calculated from the UV-Vis DRS and is found to be 2.07 eV and 1.80 eV for $BaBiO_3$ and $BaBi_4Ti_4O_{15}$, respectively. The low band gap and the UV-Vis DRS of $BaBi_4Ti_4O_{15}$ showed a clear improvement in reflectance under visible light irradiation, indicating a new Ti doped nano $BaBiO_3$ catalyst. Furthermore, the prepared nanosized perovskites were applied in the degradation of ibuprofen, one kind of non- steroidal anti-inflammatory drug, via photocatalytic processes. It is shown that $BaBi_4Ti_4O_{15}$ exhibited drastic enhancement on degradation of drug under visible light irradiation compared to $BaBiO_3$. The drug was also more efficiently mineralized in the $BaBi_4Ti_4O_{15}$ photocatalytic process. The degradation pathway can be described as an interconnected successive principal decaroxylation, hydroxylation and demethylation steps.

***doi**: 10.5829/idosi.ijee.2016.07.01.10*

INTRODUCTION

Recently, semiconductor photocatalysts have attracted extensive attention because of their potential application in decomposing all kinds of pollutants [1-3]. Photocatalytic degradation of harmful drugs shows a good performance and could be used in the wastewater treatment domain. TiO_2 was considered to be the best semiconductor photocatalyst because of its non-toxicity, low cost, long-term stability, high photocatalytic activity and environmental friendly [4-6]. However, TiO_2 is a wide band gap semiconductor and can only absorb about 4% of sunlight, so its reaction is inefficient and scope of application is limited. Therefore, a significant amount of research is being conducted on visible-light-sensitive photocatalysts that can respond to sunlight and illumination from an indoor lamp. There have been two approaches to realize a visible –light sensitive photocatalyst. One approach is doping cation or anion using TiO_2 [7-10]. Another approach to some visible-light sensitive photocatalysts has been developed, such as $LaNiO_3$, $GdCoO_3$, $CeVO_3$, $NdVO_3$ and $SrTiO_3$ [11-15].

Recently, Tang et al. [16] prepared novel perovskite $BaBiO_3$, where Bi^{+3} and Bi^{+5} ions coexist. The material can absorb a wide range of light irradiation, which almost covers the region from UV through all strong visible light in the sunlight and an indoor lamp's illumination. The theoretical calculation shows that the material is an indirect semiconductor. In the present work $BaBiO_3$was used in photocatalytic degradation of ibuprofen drug at first. All experiments indicate that the $BaBiO_3$ is not efficiently active for degradation of ibuprofen drug in aqueous solutions under visible- light irradiation. Hence, further efforts were carried out to increase the activity of the material for ibuprofen drug degradation. We succeeded in synthesizing Ti doped $BaBiO_3$ ($BaBi_4Ti_4O_{15}$) which proved its potential for active decomposition of ibuprofen drug in aqueous solution

* Corresponding author: S. Jain
E-mail: jay4seema@yahoo.co.in
Tel: +919413514369

Please cite this article as: S. Jain, K. Sharma, U. Chandrawat, 2016. Photocatalytic Degradation of Anti-inflammatory Drug on Ti Doped $BaBiO_3$ Nanocatalyst under Visible Light Irradiation, Iranica Journal of Energy and Environment 7 (1): 64-71.

under visible-light irradiation. $BaBi_4Ti_4O_{15}$ as the n=4 member of the aurivillius family has Bi^{+3} and Ba^{+2} ions at the A-sites and Ti^{+4} ions at the B-sites of the perovskite block $[(Bi_2O_2)^{2+}(BaBi_2)Ti_4O_{13})^{2-}]$ [17]. Recently, barium bismuth titanate, $BaBi_4Ti_4O_{15}$ has been extensively studied for its ferroelectric and other excellent properties [18-21]. For synthesis, Pechini method [22] 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 the doped and undoped catalysts were examined by different analytical techniques. According to UV-DRS, $BaTi_4Bi_4O_{15}$ can absorb light stronger in comparison to the pure $BaBiO_3$ in the visible region.

Human pharmaceutical and their metabolites are discharged by sewage treatment plants to river, lake, and seawater. Numerous studies have shown that the pharmaceutical residues are widespread in the aquatic environment. Ibuprofen (IBF) is a kind of the pharmaceutical drug used for its analgesic, antipyretic and anti-inflammatory properties. They have been frequently detected in surface waters and urban wastewater [23]. Their molecular structures are shown below. Degradation of ibuprofen by advanced oxidation processes such as ozonation [24] and UV/H_2O_2 [25] has been investigated. In the present work, ibuprofen is selected as target compound and was degraded by the prepared $BaBiO_3$ and $BaBi_4Ti_4O_{15}$ pervoskite. The obtained results indicate that the $BaBi_4Ti_4O_{15}$ pervoskite showed good photocatalytic activities towards degradation of ibuprofen under visible light irradiation. The degradation intermediates were also identified.

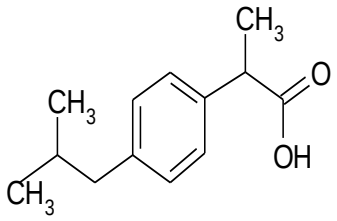


Figure 1. Molecular structures of Ibuprofen drug

MATERIAL AND METHODS

Materials

Barium nitrate $Ba(NO_3)_2$, bismuth nitrate $Bi(NO_3)_3$, titanium chloride $TiCl_4$, citric acid ($C_6H_8O_7$) and ethylene glycol ($C_2H_6O_2$) were purchased from Merck (India). Ibuprofen was purchased from Sigma-Aldrich. Deionized water was used in all the experiments.

Preparation of BaBiO3Perovskite

$BaBiO_3$ perovskite was prepared from highly pure polymeric precursors using the method proposed by Pechini. A stoichiometric amount of barium nitrate was dissolved in the distilled water and bismuth nitrate dissolved in minimum amount of dilute HNO_3 to avoid precipitation of Bi ions. These solutions were mixed and heated up to 90 ^oC. 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 ^oC for 2 h. The resulting black sponge polymer was calcined in air at 800 ^oC, for 12 h. A brown crystalline ceramic powder was obtained thereafter.

Preparation of BaBi4Ti4O15 Perovskite

Barium nitrate and Bismuth nitrate and titanium chloride were used as starting materials. A stoichiometric amount of barium nitrate was dissolved in the distilled water, bismuth nitrate dissolved in minimum amount of dilute HNO_3 to avoid precipitation of Bi ions and titanium chloride $TiCl_4$ dissolved in the ice cold distilled water were mixed together. The above mixture is mixed with citric acid to get the ratio of the citric acid to total metal cations as 4:1. After 15 minutes stirring, ethylene glycol (EG) was added in the EG:CA ratio of 40:60 (w/w). Since there was no precipitation during mixing, the pH of the solution was not varied. Heating on hot plate, a yellowish resin was formed after evaporation of water. The obtained resin was polymerized at 300 ^oC for 2 h. The resulting black sponge polymer was calcined in air at 800 ^oC, for 4 h. A yellowish crystalline ceramic powder was obtained thereafter.

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 ^oC and the heating rate to 5 ^oC min^{-1}. Powder X-ray diffraction (Siemens D5000 diffractometer) analyses were carried out using Cu Kα radiation at 2θ angles from 0^o to 80^o with scan speed of $5^o min^{-1}$. Ultraviolet and visible diffuse reflection spectra (Shimadzu Lambda 900 spectrophotometer) were measured at 240-800 nm wavelengths. The morphology of the samples was observed with a scanning electron microscope (SEM) (Hitachi X650, Japan).

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 Xe arc lamp (intensity 137mWcm^{-2}) 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 containing the prepared pervoskite was filled with 1L aqueous ibuprofen drug solution. The whole reactor was cooled with a water cooled jacket on its outside and the temperature was kept at 25 ºC. Magnetic stirrer was also used to keep the solution chemically uniform. During ibuprofen treatment, an aliquot of solution samples was collected from the reactor at definite time intervals. The concentration of ibuprofen was measured using an HPLC-UV with a C-18 column and diode array detector. The mobile phase was 75% of methanol and 25% of water at a flow rate of 1.0 $mLmin^{-1}$. The dectection wavelength was set at 220 nm. Finally, the photocatalytic activities were determined using the following formula:

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

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

Total organic carbon (TOC) was measured using a multi N/C 3000 TOC analyzer (Analytik Jena AG, Germany) to evaluate the mineralization of ibuprofen. Identification of IBF degradation products was achieved with the aid of LC-MS (ThermoQuest LCQ DUO, USA) with a C-18 HPLC column.

RESULTS AND DISCUSSION

Characterization of the provskites

Fig. 2 shows TGA and DTG analysis of the thermal decomposition of $BaBiO_3$ and $BaBi_4Ti_4O_{15}$ precursor resin in air and heated at 25º – 900ºC at 5ºCmin^{-1}.

The thermal decomposition and crystallization behaviour of both the $BaBiO_3$ and $BaBi_4Ti_4O_{15}$precursorsare found to be almost the same and represented by Fig. 2 through Thermogravimetric (TG) and differential thermogravimetric (DTG) curves. The DTG curve reveals three main endothermic events at 130.59, 263.12 and 361.65 ºC, respectively. At temperature below 130.59ºC, 14.9% weight-loss was assigned to dehydration and depolymerisation of the polymeric residual in the precursor. Apparently, the endothermic peak at 263.12 ºC with a weight loss of 60.80% was explained by the complex decomposition and combustion of the polymeric resin. In the third endothermic peak at 361.65 ºC, 7.9 % weight loss was observed which could be due to the decomposition of the nitrates or nitrites and residual carbonate intermediate and the evolved products were mainly NO and CO_2. In the last stage above 600 ºC, small weight change occurs due to the crystallization of the sample and subsequent conversion to the perovskite phase.

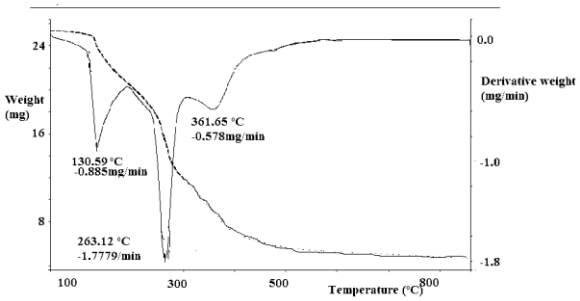


Figure 2. TGA and DTG analysis of the thermal decomposition of $BaBiO_3$ and $BaBi_4Ti_4O_{15}$ precursor resin in air and heated at 25º – 900ºC at 5ºCmin^{-1}

Fig. 3 shows the XRD pattern of the prepared undoped and Ti doped $BaBiO_3$ceramic powders indicating that both the materials are well crystallized. The parent sample, $BaBiO_3$ was found to be in the monoclinic structure (JCPDS35-1020) which is in good agreement with the earlier reported results [26]. The lattice constants of $BaBiO_3$ were a=6.183Aº, b=6.13 Aº, c=8.666 Aº, β=90.16º. The sample doped with titanium was found to be in the tetragonal structure of an aurivillius phase Bi layered oxide and all the peaks match with the standard JCPDS card data (JCPDS35-0757, a= 3.8624 and c= 41.851 Aº) [27] . It should be noted that the diffraction peak, which are not present in $BaBiO_3$, are clearly observed in $BaBi_4Ti_4O_{15}$indicating that Ti ions are well aligned in the proper site of the perovskite structure. In the XRD of BBT, diffraction peak at 2Θ angles of 21.2º, 23.1º, 30.0º, 32.7º, 39.3º,44.8º, 46.0º,51.5º,56.8º are established. They correspond to BBT (0010), (101), (109), (110), (1110), (002), (200),(1118) and (219) planes, respectively. Analysis of the peak (002) (200) (tetragonal) in the 2Θ range 44-46 degree is important and shown in Fig. 3. The splitting of (002 and 200) peaks clearly indicate the presence of tetragonal phase [28].

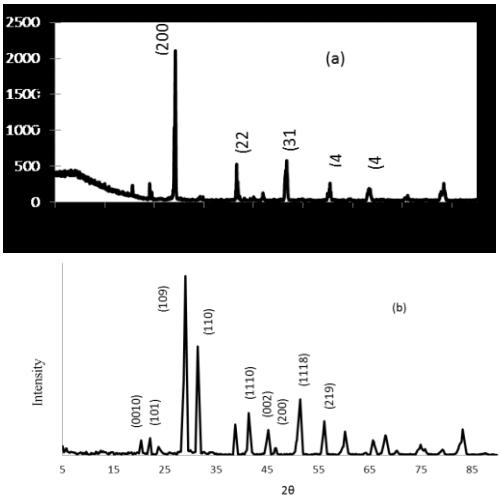
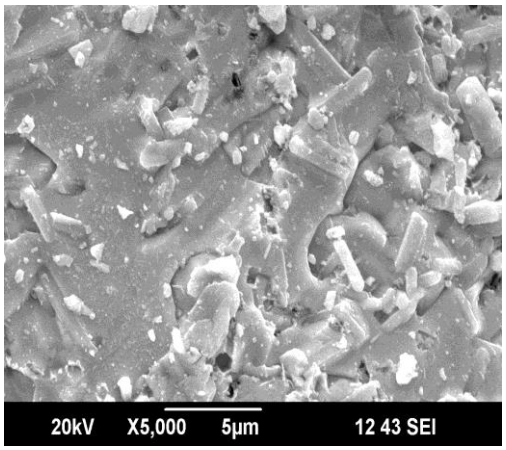


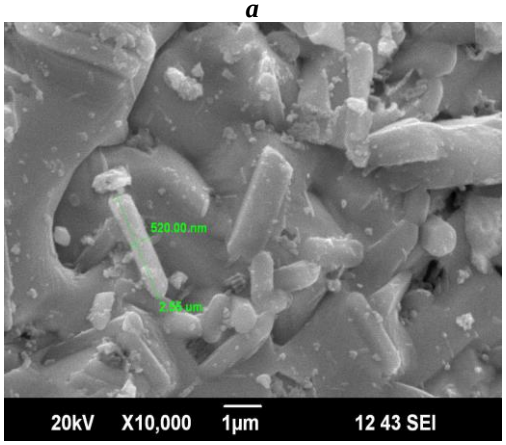
Figure 3. XRD pattern of (a) $BaBiO_3$ and (b) $BaBi_4Ti_4O_{15}$ perovskite

SEM was used to study the surface morphology for the prepared powders. Fig. 4shows the SEM image for the $BaBiO_3$ and $BaBi_4Ti_4O_{15}$at different magnificance. It can be clearly seen from the micrographs that the Ti ion doping has a stronge effect on the grain size. In other words the grain size of the sample reduces with introduction of titanium content and the average grain size of $BaBi_4Ti_4O_{15}$ is decreased upto 203 nm from 520 nm of $BaBiO_3$. The particles in the $BaBi_4Ti_4O_{15}$ tend to scattered in cluster due to its small size. The density of the $BaBi_4Ti_4O_{15}$ also increase with Ti doping and increase in the photocatalytic activity due to increase the reactive particles in per unit volume.

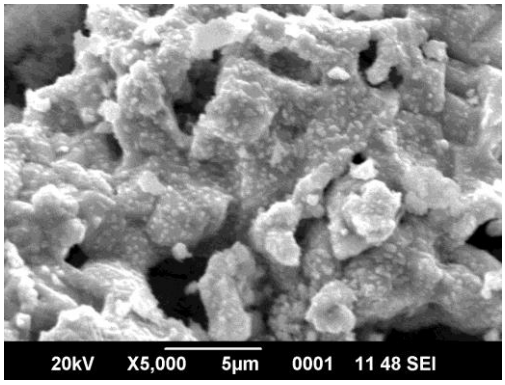
The UV-visible reflectance spectra pattern of $BaBiO_3$ and $BaBi_4Ti_4O_{15}$ are shown in the Fig. 5. The spectra wereobtained by scanning of the samples in the range of 200-800 nm. The reflectance edgeof $BaBi_4Ti_4O_{15}$ has a red shift and also shows a strong reflectance as compared to the pure $BaBiO_3$ in the visible region. The band gaps (Eg) were found to be 2.07 eV and 1.8 eV for $BaBiO_3$ and $BaBi_4Ti_4O_{15}$, respectively using UV-vis diffused reflectance spectra [29]. The higher photo catalytic activity is expected for $BaBi_4Ti_4O_{15}$ perovskite as itcan reflect light in a wider range of visible region owing to its lower band gap in comparison to pure $BaBiO_3$.



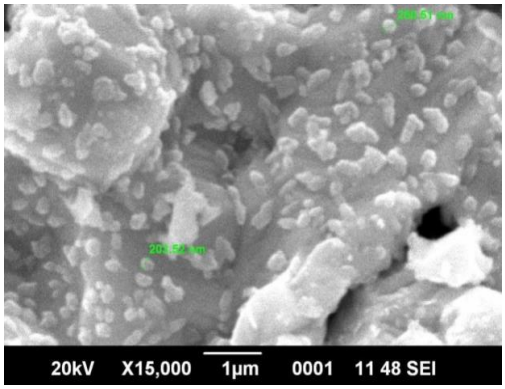
a



b



c



d

Figure 4. SEM images for $BaBiO_3$ (a) & (b) and $BaBi_4Ti_4O_{15}$ perovskite (c) & (d)

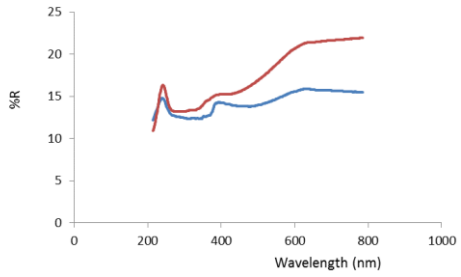


Figure 5. UV-Vis DRS patterns of perovskite (a) $BaBiO_3$and (b) $BaBi_4Ti_4O_{15}$

Fig. 6 shows the FTIR spectra of nanostructured pure $BaBiO_3$ and $BaBi_4Ti_4O_{15}$ in the range 4000-400 cm^{-1}. A broad absorption band around 3413 cm^{-1} appearing in the both FTIR spectra has been assigned to O-H stretching modes of surface adsorbed water.Additionaly, the absorption band at 1420 cm^{-1} was observed in the both spectrarevealing the existence of carbonate, which is possibly due to absorption of atmospheric CO_2 during drying process. The FTIR spectrum of pure $BaBiO_3$ also shows two more bands at 853 cm^{-1} and 485 cm^{-1} which are considered to be a characteristic feature of the sample and are attributed to the vibration of Ba-O and Bi-O bond

respectively [27],[30]. When Ti is introduced into $BaBiO_3$, the absorptiopn wave number of Bi-O bond gets shifted to lower side i.e from around 486 cm^{-1} to 428 cm^{-} and a newpeak appears at 494 cm^{-1} due to Ti-O bond [31].

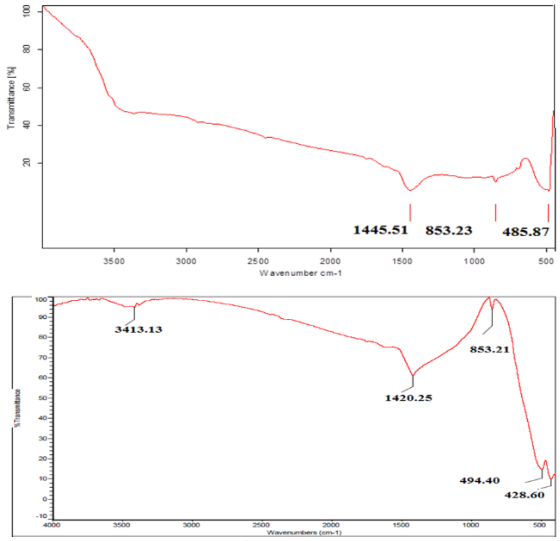


Figure 6. FTIR spectra of (a) $BaBiO_3$ and (b) $BaBi_4Ti_4O_{15}$ perovskite

Photocatalytic degradation of ibuprofen

Photolysis

Non-photocatalytic assay was undertaken to evaluate its isolated influence on the degradation of ibuprofen. For the photolysis experiment, the solution of ibuprofen (initial concentration 10mg/L) was irradiatedfor 2 h in the photoreactor. Photolysis of ibuprofen shows that concentration and TOC of ibuprofen remains unchanged. The negligible degradation attained by photolysis was expected due to the low IBP molar absorption coefficient above 300 nm [32].

Adsorption and photolcatalysis experiment with$BaBiO_3$

As shown in Fig. 7, adsorption and photocatalytic degradation was performed using $BaBiO_3$with 10 mg/L concentration ofibuprofen solution. Firstly,fixed amount of $BaBiO_3$ was mixed in 30 mL vials at free pH condition (pH 6.25 ± 0.25), constant controlled temperature (30 ºC) and continuous dark stirring during 24 h. After 24 h stirring in darkness, 22% removal of ibuprofen was observed alongwith adecrease in TOC due to its adsorption by $BaBiO_3$.Thenafter, photocatalysis process was carried out irradiating a solution of ibuprofen for 2 h.In contrast to the dark experiment, photocatalysis showed 60% of degradation of the drug.Under visible light irradiation , the photogenerated electrons and holes are produced alongwith ·OH from $BaBiO_3$particles. These active radicals are responsible for ibuprofen degradation.

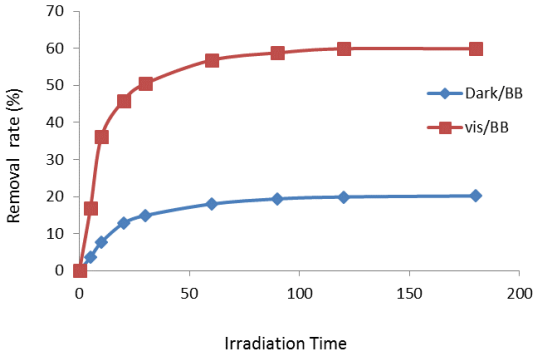


Figure 7. Variation of ibuprofen concentration in the adsorption and photocatalysis using $BaBiO_3$ (IBF conc. 10 mg/L, $BaBiO_3$ dose 1g/L)

Adsorptionand photocatalysis experiment with $BaBi_4Ti_4O_{15}$

As indicating by Fig. 8, under similar experimental conditions, 26% removal was observed for ibuprofen with $BaBi_4Ti_4O_{15}$ after 24 h darkness due to adsorption. Owing to the lower band gap value (1.8 eV) of $BaBi_4Ti_4O_{15}$ promising results were obtained in photocatalytic experiments. More than 80% removal of drugwas achieved after 2h . It can be observed that the degradation rate of ibuprofen is faster reaching more than 60% removal in initial 20 min.These values are 20 % higher than those observed with $BaBiO_3$.

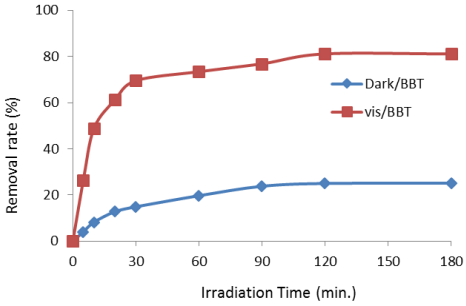


Figure 8. Variation of ibuprofen concentration in the adsorption and photocatalysis using $BaBi_4Ti_4O_{15}$ (IBF conc. 10 mg/L, $BaBi_4Ti_4O_{15}$ dose 1g/L)

Fig. 9 depicts degradation pathways of the ibuprofen on $BaBiO_3$ and $BaBi_4Ti_4O_{15}$ perovskite under visible light irradiation.

Intermediate analysis and degradation pathways of ibuprofen

During photocatalytic treatmant of ibuprofen, many intermediates were formed and then destructed in the solution simultaneaously. A total of 9 aromatic intermediates were tentatively identified in the $BaBiO_3$/$BaBi_4Ti_4O_{15}$ solution by an LC/ESI-TOF-MS. In addition, a variety of aliphatic carboxylic acid

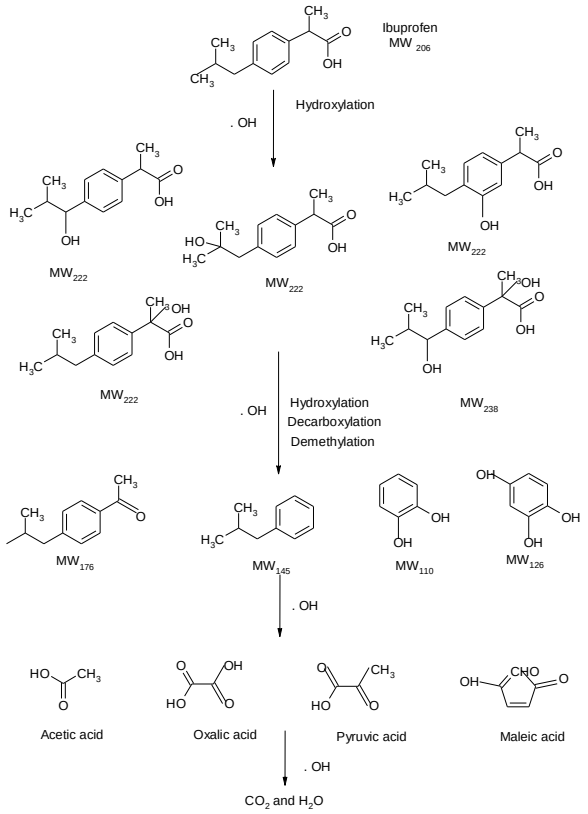


Figure 9. Degradation pathways of the ibuprofen on $BaBiO_3$ and $BaBi_4Ti_4O_{15}$ perovskite under visible light irradiation

intermediates were identified by comparing their retention time with analytical standard using HPLC-UV. Most of these intermediates have been reported in many other ·OH induced advanced oxidative degradation process of ibuprofen [33]. This similarity suggests that ·OH also plays an important role in ibuprofen mineralization throughout the photocatalytic degradation.

The LC-MS results showthat the aromatic intermediates including hydroxylated ibuprofens and their decarboxylated and demethylated derivatives were rapidly formed and then destructed during $BaBiO_3$/$BaBi_4Ti_4O_{15}$ photocatalytic treatment.Simple phenols were also rapidly formed and then degraded with the photocataltic treatment. The initial reaction step in ibuprofen degradation by $BaBiO_3$/$BaBi_4Ti_4O_{15}$ can thus be mainly attributed to the ·OH attack on ibuprofen. In the prsent study, four isomers of mono hydroxylated ibuprofen (MW= 222) were detected in the solution. In addition, derivative of multi-hydroxylated ibuprofen with MW=238 was also detected. This result is consistent with the previous reports [34] that ·OH attack can occur at various position of ibuprofen to yield a variety of hydroxylated ibuprofen. Further ·OH attack on the hydroxylated species of ibuprofen result in decarboxylation and demethylation at the ibuprofen side chains which yields smaller aromatic intermediates such as 1-[4-(2-Methylpropyl)phenyl]ethanone (MW = 176), 2-Methyl-1-phenylpropane (MW = 134) and phenols. The phenols are probably the final aromatic intermediates before the cleavge of benzene ring that leads to the formation of a variety of linear carboxilic acids. These acids are then oxidized by ·OH to CO_2 and H_2O accomplishing the mineralization of ibuprofen.

The removal of the initial compound does not indicate that the total mineralization was achieved therefore, a study of the total organic carbon (TOC) quantification was also necessary. As shown in Fig.10 TOC removal was negligible in photolysis experiment i.e. in absence of photocatalyst while under visible light irradiation this rate is highest with $BaBi_4Ti_4O_{15}$ solution.

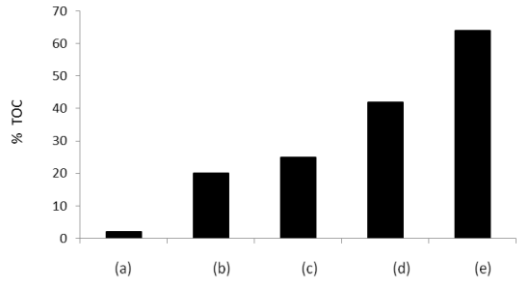


Figure 10. TOC removal in ibuprofen solution (10mg/L initial concentration) obtained by photolysis (a) adsorption on $BaBiO_3$ (b) adsorption on $BaBi_4Ti_4O_{15}$(c) photocatalysis in the presence of $BaBiO_3$ (d) photocatalysis in the presence of $BaBi_4Ti_4O_{15}$ (e).

CONCLUSION

The ceramic powders $BaBiO_3$ and Bi–layered $BaBi_4Ti_4O_{15}$ were prepared by the Pechini method. X-ray diffraction pattern show that synthesized $BaBiO_3$ has monoclinic structurewhile $BaBi_4Ti_4O_{15}$ ceramic can be well fitted to a tetragonal structure and indexed to an aurivillius phase Bi-layered oxide structure with n=4. SEM results revealed that Ti ion doping has suppressed the grain size of the $BaBiO_3$. From the detailed analysis of FTIR spectra, the new absorption peak was observed at 494 cm^- due to Ti-O bond. Low band gap and higher reflectance of the nanosized $BaBi_4Ti_4O_{15}$ obtained from UV-DRS contribute to its higher photocatalytic activities under visible light irradiation in the degradation of ibuprofen. The degradation proceeded by opening of phenyl ring to CO_2 and H_2O.

Acknowledgements

The authors are thankful to University Grant Commission (UGC), New Delhi, India for the financial support in the form of Women Scientist postdoctoral fellowship. We would also like to thank STIC (Sophisticated Test and Instrumentation Centre), Cochin

University of Science & Technology for providing experimental support.

REFERENCES

1. Bahnemann, W., M. Muneer and M. Haque, 2007. Titanium dioxide-mediated photocatalysed degradation of few selected organic pollutants in aqueous suspensions. Catalysis Today, 124(3): 133-148.
2. Benhebal, H., M. Chaib, T. Salmon, J. Geens, A. Léonard, S.D. Lambert, M. Crine and B. Heinrichs, 2013. Photocatalytic degradation of phenol and benzoic acid using zinc oxide powders prepared by the sol–gel process. Alexandria Engineering Journal, 52(3): 517-523.
3. Khan, M.M., S.F. Adil and A.A. Mayouf, 2015. Metal oxide as photocatalysts. Journal of Saudi chemical society, 19(5): 462-464.
4. Mills, A. and R. Davies, 1995. Activation energies in semiconductor photocatalysis for water purification: the 4-chlorophenol-TiO 2 O 2 photosystem. Journal of Photochemistry and Photobiology A: Chemistry, 85(1): 173-178.
5. Wang, M., J. Ioccozia, L. Sun, C. Lin and Z. Lin, 2014. Inorganic-modified semiconductor TiO 2 nanotube arrays for photocatalysis. Energy & Environmental Science, 7(7): 2182-2202.
6. Akpan, U. and B. Hameed, 2009. Parameters affecting the photocatalytic degradation of dyes using TiO 2-based photocatalysts: a review. Journal of hazardous materials, 170(2): 520-529.
7. Gharagozlou, M. and R. Bayati, 2014. Photocatalytic activity and formation of oxygen vacancies in cation doped anatase TiO 2 nanoparticles. Ceramics International, 40(7): 10247-10253.
8. Ma, D., Y.Xin, M. Gao and J. Wu, 2014. Fabrication and photocatalytic properties of cations and anions S-doped TiO2 nanofibers by electrospinning. Applied Catalysis B: Environmental, 147(1): 49-57.
9. Li, G., L. Chen, N.M. Dimitrijevic and K.A. Gray, 2008. Visible light photocatalytic properties of anion-doped TiO 2 materials prepared from a molecular titanium precursor. Chemical Physics Letters, 451(1): 75-79.
10. Likodimos, V., C. Han, M. Pelaez, A.G. Kontos, G. Liu, D. Zhu, S. Liao, A.A. de la Cruz, K. O'Shea and P.S. Dunlop, 2013. Anion-doped TiO2 nanocatalysts for water purification under visible light. Industrial & Engineering Chemistry Research, 52(39): 13957-13964.
11. Li, Y., S. Yao, W. Wen, L. Xue and Y. Yan, 2010. Sol–gel combustion synthesis and visible-light-driven photocatalytic property of perovskite LaNiO 3. Journal of Alloys and Compounds, 491(1): 560-564.
12. Mahata, P., T. Aarthi, G. Madras and S. Natarajan, 2007. Photocatalytic degradation of dyes and organics with nanosized GdCoO3. The Journal of Physical Chemistry C, 111(4): 1665-1674.
13. Saha, D., S. Mahapatra, T.G. Row and G. Madras, 2009. Synthesis, Structure, and Photocatalytic Activity in Orthorhombic Perovskites LnVO3 and Ln1− x Ti x VO3 (Ln= Ce, Pr, and Nd). Industrial & Engineering Chemistry Research, 48(16): 7489-7497.
14. Sulaeman, U., S. Yin and T. Sato, 2011. Visible light photocatalytic activity induced by the carboxyl group chemically bonded on the surface of SrTiO 3. Applied Catalysis B: Environmental, 102(1): 286-290.
15. Anandan, S., Y. Ikuma and V. Murugesan, 2011. Highly active rare-earth-metal La-doped photocatalysts: fabrication, characterization, and their photocatalytic activity. International Journal of Photoenergy, 2012.
16. Tang, J., Z. Zou and J. Ye, 2007. Efficient photocatalysis on BaBiO3 driven by visible light. The Journal of Physical Chemistry C, 111(34): 12779-12785.
17. Bobić, J.D., M.M. Vijatović, T. Rojac and B.D. Stojanović, 2009. Characterization and properties of barium bismuth titanate. Processing and Application of Ceramics, 3(1-2): 9-12.
18. Bobić, J., M.V. Petrović, J. Banys and B. Stojanović, 2012. Electrical properties of niobium doped barium bismuth-titanate ceramics. Materials Research Bulletin, 47(8): 1874-1880.
19. Rosyidah, A., D. Onggo, K. Khairurrijal and I. Ismunandar, 2010. FERROELECTRIC PROPERTIES OF BaBi 4 T i4 O 15 DOPED WITH Pb 2+, Al 3+, Ga 3+, In 3+, Ta 5+ AURIVILLIUS PHASES. Indonesian Journal of Chemistry, 9(3): 398-403.
20. Nalini, G. and T. Guru Row, 2002. Structure determination at room temperature and phase transition studies above T c in ABi 4 Ti 4 O 15 (A= Ba, Sr or Pb). Bulletin of Materials Science, 25(4): 275-281.
21. Kumar, S. and K. Varma, 2014. Relaxor behaviour in BaBi4Ti4O15 ceramics fabricated using the powders obtained by mechanochemically assisted synthesis route. Bulletin of Materials Science, 37(6): 1233-1241.
22. Razavia, R.S., M.R.L. Estarkib and M.F. Khouzani, 2012. Synthesis and Charaterization of ZnO nanostructures by Polmeric Precursor Route. Acta Physica Polonica A, 121(1): 98-100.
23. Santos, J., I. Aparicio and E. Alonso, 2007. Occurrence and risk assessment of pharmaceutically active compounds in wastewater treatment plants. A case study: Seville city (Spain). Environment International, 33(4): 596-601.
24. Quero-Pastor, M., M. Garrido-Perez, A. Acevedo and J. Quiroga, 2014. Ozonation of ibuprofen: a degradation and toxicity study. Science of the Total Environment, 466: 957-964.
25. Kwon, M., S. Kim, Y. Yoon, Y. Jung, T.-M. Hwang, J. Lee and J.-W. Kang, 2015. Comparative evaluation of ibuprofen removal by UV/H 2 O 2 and UV/S 2 O 8 2− processes for wastewater treatment. Chemical Engineering Journal, 269: 379-390.
26. Sunarso, J., S. Liu, Y. Lin and J.D. da Costa, 2009. Oxygen permeation performance of BaBiO 3− δ ceramic membranes. Journal of membrane science, 344(1): 281-287.
27. LAZAREVIĆ, Z., N. ROMČEVIĆ and J. BOBIĆ, Study of ferroelectric BaBi4Ti4O15 obtained via mechanochemical synthesis.
28. Sreenu, K., T. Bhargavi and K.L. Kabeta, 2014. Characterization and Phase Transitions of Bi Doped BaTiO 3 Ceramics Prepared through Chemical Route. Science, Technology and Arts Research Journal, 3(1): 39-43.
29. Dharma, J., A. Pisal and C. Shelton, 2009. Simple method of measuring the band gap energy value of TiO2 in the powder form using a UV/Vis/NIR spectrometer. Application Note Shelton, CT: PerkinElmer.
30. Lee, C., K.Y. Song and R. Sperline, 1996. Molecular Dyamics Simulation and Far Infrared Measurements of $ Ba_ {0.6} K_ {0.4} BiO_3$. Korean Journal of Materials Research, 6(6): 555-560.
31. Vasconcelos, D.C.L., E.H.M. Nunes, M. Gasparon and W.L. Vasconcelos, 2011. Infrared spectroscopy of titania sol-gel coatings on 316L stainless steel. Materials Sciences and Applications, 2(10): 1375.
32. Zhao, X., J. Qu, H. Liu, Z. Qiang, R. Liu and C. Hu, 2009. Photoelectrochemical degradation of anti-inflammatory pharmaceuticals at Bi 2 MoO 6–boron-doped diamond hybrid electrode under visible light irradiation. Applied Catalysis B: Environmental, 91(1): 539-545.
33. Mendez-Arriaga, F., S. Esplugas and J. Gimenez, 2010. Degradation of the emerging contaminant ibuprofen in water by photo-Fenton. water research, 44(2): 589-595.
34. Li, X., Y. Wang, S. Yuan, Z. Li, B. Wang, J. Huang, S. Deng and G. Yu, 2014. Degradation of the anti-inflammatory drug ibuprofen by electro-peroxone process. Water research, 63: 81-93.

Persian Abstract

DOI: 10.5829/idosi.ijee.2016.07.01.10

چکیده

پروسکایت های $BaBiO_3$ و $BaBi_4Ti_4O_{15}$ در ابعاد نانو با استفاده از روش pechini آماده شدند. این ساختار ها از طریق آنالیزهای حرارتی (TGA، XRD، UV-Vis DRS)، (FT-IR) و (SEM) تایید شدند. الگوهای XRD نشان می دهد که $BaBiO_3$ در میکروسکوپ الکترونی روبشی (SEM) بلوری شده است. الگوهای XRD نشان می دهد که $BaBiO_3$ در ساختار مونوکلینیک متبلور است در حالی که یک عضو از خانواده aurivillius، بر مبنای بیسموت و ساختار لایه ای $BaBi_4Ti_4O_{15}$ در ابعاد نانو به صورت چهار وجهی بلوری شده است. شکاف باند با UV-Vis DRS محاسبه شد و برای $BaBiO_3$ و $BaBi_4Ti_4O_{15}$ به ترتیب ۲,۰۷ و ۱,۸۰ الکترون ولت بود. شکاف کم باند و UV-Vis DRS از BaBi4Ti4O15 بهبود واضحی در بازتاب ، تحت تابش نور مرئی نشان می دهد که دلالت بر کاتالیست جدید Ti دوپ شده با نانو babio3 دارد. علاوه بر این، پروسکایت های آماده شده در ابعاد نانو در تخریب ایبوپروفن، یک نوع از داروی ضد التهابی غیر استروئیدی، از طریق فرآیندهای فوتوکاتالیستی استفاده شد. همچنین نشان داده شد که $BaBi_4Ti_4O_{15}$ بهبودی بنیادی بر روی تخریب مواد مخدر، تحت تابش نور مرئی در مقایسه با BaBiO3 به نمایش گذاشت. این دارو همچنین در روند فوتوکاتالیستی $BaBi_4Ti_4O_{15}$ کار آمدبود و مسیر تخریب در ارتباط تنگاتنگ با decarboxylation و demethylation مراحل پی در پی است.