



Photocatalytic Degradation of Anti-inflammatory Drug on Ti Doped BaBiO₃ Nanocatalyst under Visible Light Irradiation

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ABSTRACT

Nanosized perovskites BaBiO₃ and BaBi₄Ti₄O₁₅ 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 BaBiO₃ is crystallized in the monoclinic structure while a member of aurivillius family, bismuth-based layer-structured BaBi₄Ti₄O₁₅ is crystallized 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 BaBiO₃ and BaBi₄Ti₄O₁₅, respectively. The low band gap and the UV-Vis DRS of BaBi₄Ti₄O₁₅ showed a clear improvement in reflectance under visible light irradiation, indicating a new Ti doped nano BaBiO₃ 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 BaBi₄Ti₄O₁₅ exhibited drastic enhancement on degradation of drug under visible light irradiation compared to BaBiO₃. The drug was also more efficiently mineralized in the BaBi₄Ti₄O₁₅ photocatalytic process. The degradation pathway can be described as an interconnected successive principal decarboxylation, hydroxylation and demethylation steps.

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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. TiO₂ 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, TiO₂ 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 TiO₂ [7-10]. Another approach to some visible-light sensitive photocatalysts has been developed, such as LaNiO₃, GdCoO₃, CeVO₃, NdVO₃ and SrTiO₃ [11-15].

Recently, Tang et al. [16] prepared novel perovskite BaBiO₃, 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 BaBiO₃ was used in photocatalytic degradation of ibuprofen drug at first. All experiments indicate that the BaBiO₃ 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 BaBiO₃ (BaBi₄Ti₄O₁₅) which proved its potential for active decomposition of ibuprofen drug in aqueous solution

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under visible-light irradiation. $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ 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 $[(\text{Bi}_2\text{O}_2)^{2+}(\text{BaBi}_2)\text{Ti}_4\text{O}_{13}]^{2-}$ [17]. Recently, barium bismuth titanate, $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ 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, $\text{BaTi}_4\text{Bi}_4\text{O}_{15}$ 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 $\text{UV}/\text{H}_2\text{O}_2$ [25] has been investigated. In the present work, ibuprofen is selected as target compound and was degraded by the prepared BaBiO_3 and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ perovskite. The obtained results indicate that the $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ perovskite showed good photocatalytic activities towards degradation of ibuprofen under visible light irradiation. The degradation intermediates were also identified.

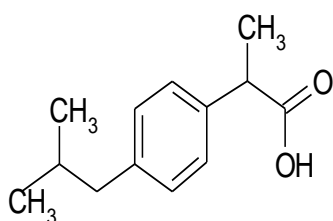


Figure 1. Molecular structures of Ibuprofen drug

MATERIAL AND METHODS

Materials

Barium nitrate $\text{Ba}(\text{NO}_3)_2$, bismuth nitrate $\text{Bi}(\text{NO}_3)_3$, titanium chloride TiCl_4 , 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). Ibuprofen was purchased from Sigma-Aldrich. Deionized water was used in all the experiments.

Preparation of BaBiO_3 Perovskite

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°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 800°C , for 12 h. A brown crystalline ceramic powder was obtained thereafter.

Preparation of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ 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°C for 2 h. The resulting black sponge polymer was calcined in air at 800°C , 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°C and the heating rate to 5°C min^{-1} . Powder X-ray diffraction (Siemens D5000 diffractometer) analyses were carried out using $\text{Cu K}\alpha$ 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 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 perovskite 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 °C. 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 detection wavelength was set at 220 nm. 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 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 BaBiO₃ and BaBi₄Ti₄O₁₅ precursor resin in air and heated at 25° – 900°C at 5°Cmin⁻¹.

The thermal decomposition and crystallization behaviour of both the BaBiO₃ and BaBi₄Ti₄O₁₅precursors are 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 °C, respectively. At temperature below 130.59°C, 14.9% weight-loss was assigned to dehydration and depolymerisation of the polymeric residual in the precursor. Apparently, the endothermic peak at 263.12 °C 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 °C, 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 CO₂. In the last stage above 600 °C, small weight change occurs due to the crystallization of the sample and subsequent conversion to the perovskite phase.

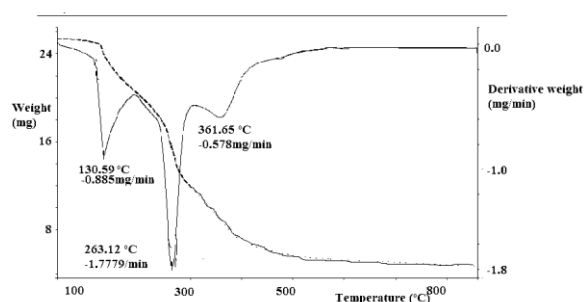


Figure 2. TGA and DTG analysis of the thermal decomposition of BaBiO₃ and BaBi₄Ti₄O₁₅ precursor resin in air and heated at 25° – 900°C at 5°Cmin⁻¹

Fig. 3 shows the XRD pattern of the prepared undoped and Ti doped BaBiO₃ ceramic powders indicating that both the materials are well crystallized. The parent sample, BaBiO₃ 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 BaBiO₃ were $a=6.183\text{Å}$, $b=6.13\text{Å}$, $c=8.666\text{Å}$, $\beta=90.16^\circ$. 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 $c=41.851\text{Å}$) [27]. It should be noted that the diffraction peak, which are not present in BaBiO₃, are clearly observed in BaBi₄Ti₄O₁₅ indicating that Ti ions are well aligned in the proper site of the perovskite structure. In the XRD of BBT, diffraction peak at 2 θ angles of 21.2°, 23.1°, 30.0°, 32.7°, 39.3°, 44.8°, 46.0°, 51.5°, 56.8° 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 2 θ 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].

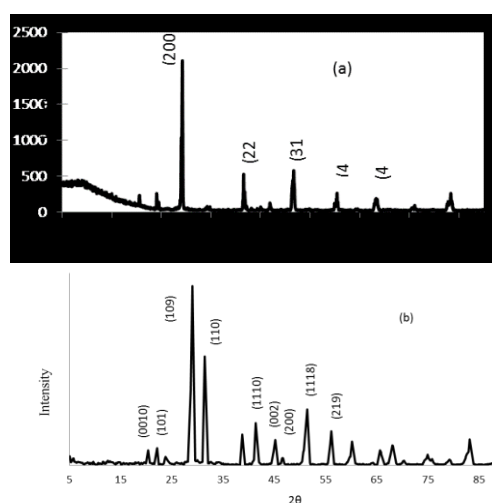


Figure 3. XRD pattern of (a) BaBiO₃ and (b) BaBi₄Ti₄O₁₅ perovskite

SEM was used to study the surface morphology for the prepared powders. Fig. 4 shows the SEM image for the BaBiO_3 and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ at different magnification. It can be clearly seen from the micrographs that the Ti ion doping has a strong 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 $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ is decreased upto 203 nm from 520 nm of BaBiO_3 . The particles in the $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ tend to scattered in cluster due to its small size. The density of the $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ 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 $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ are shown in the Fig. 5. The spectra were obtained by scanning of the samples in the range of 200-800 nm. The reflectance edge of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ has a red shift and also shows a strong reflectance as compared to the pure BaBiO_3 in the visible region. The band gaps (E_g) were found to be 2.07 eV and 1.8 eV for BaBiO_3 and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$, respectively using UV-vis diffused reflectance spectra [29]. The higher photo catalytic activity is expected for $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ perovskite as it can reflect light in a wider range of visible region owing to its lower band gap in comparison to pure BaBiO_3 .

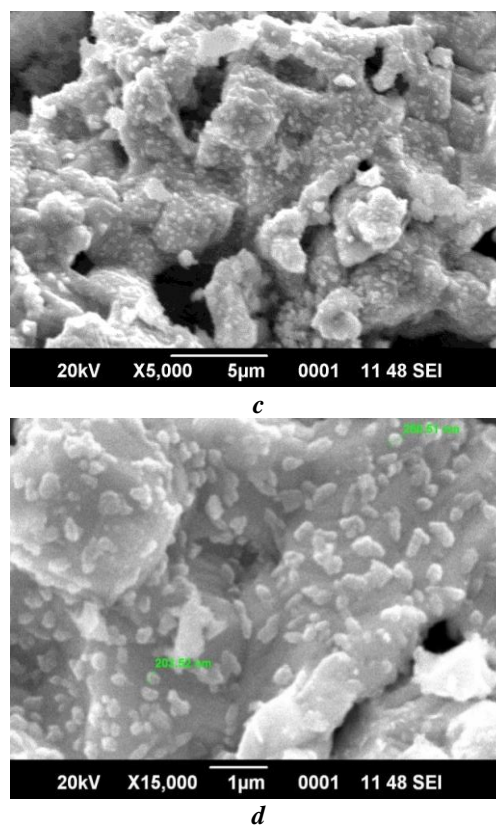
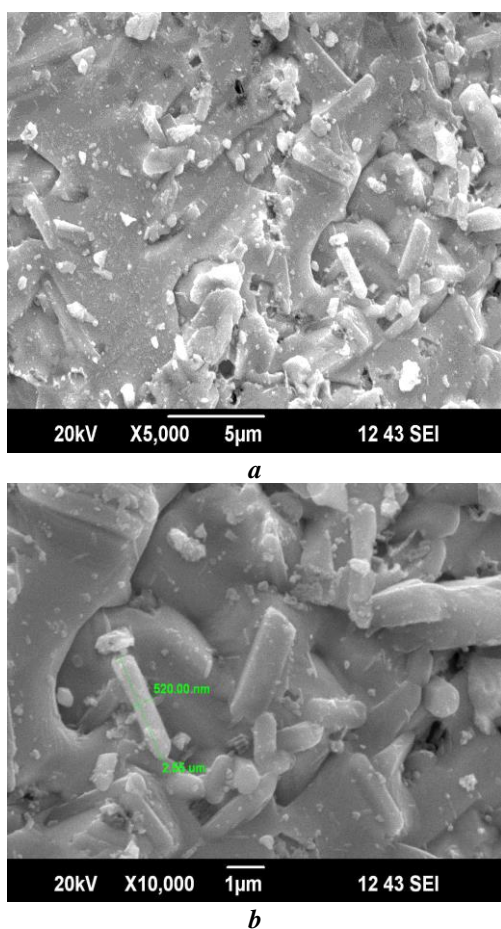


Figure 4. SEM images for BaBiO_3 (a) & (b) and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ perovskite (c) & (d)

Figure 5. UV-Vis DRS patterns of perovskite (a) BaBiO_3 and (b) $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$

Fig. 6 shows the FTIR spectra of nanostructured pure BaBiO_3 and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ in the range $4000-400\text{ cm}^{-1}$. 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. Additionally, the absorption band at 1420 cm^{-1} was observed in the both spectra revealing 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 absorptiopr wave number of Bi-O bond gets shifted to lower side i.e from around 486 cm^{-1} to 428 cm^{-1} and a newpeak appears at 494 cm^{-1} due to Ti-O bond [31].

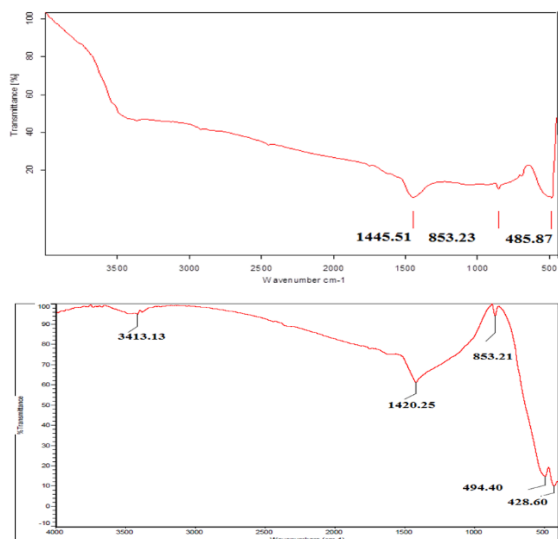


Figure 6. FTIR spectra of (a) BaBiO_3 and (b) $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ perovskite

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 10 mg/L) was irradiated for 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 photocatalysis experiment with BaBiO_3

As shown in Fig. 7, adsorption and photocatalytic degradation was performed using BaBiO_3 with 10 mg/L concentration of ibuprofen solution. Firstly, fixed amount of BaBiO_3 was mixed in 30 mL vials at free pH condition ($\text{pH } 6.25 \pm 0.25$), constant controlled temperature ($30\text{ }^\circ\text{C}$) and continuous dark stirring during 24 h. After 24 h stirring in darkness, 22% removal of ibuprofen was observed along with decrease 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 along with OH^\cdot from BaBiO_3 particles. These active radicals are responsible for ibuprofen degradation.

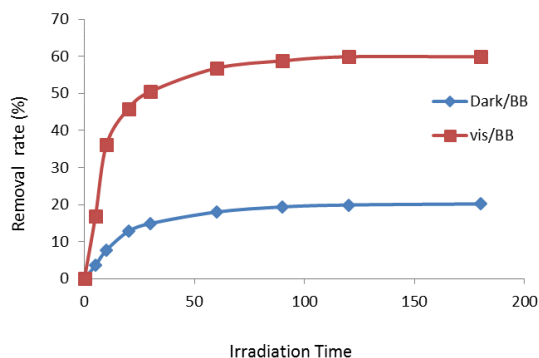


Figure 7. Variation of ibuprofen concentration in the adsorption and photocatalysis using BaBiO_3 (IBF conc. 10 mg/L , BaBiO_3 dose 1 g/L)

Adsorption and photocatalysis experiment with $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$

As indicating by Fig. 8, under similar experimental conditions, 26% removal was observed for ibuprofen with $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ after 24 h darkness due to adsorption. Owing to the lower band gap value (1.8 eV) of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ promising results were obtained in photocatalytic experiments. More than 80% removal of drug was achieved after 2 h. 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 .

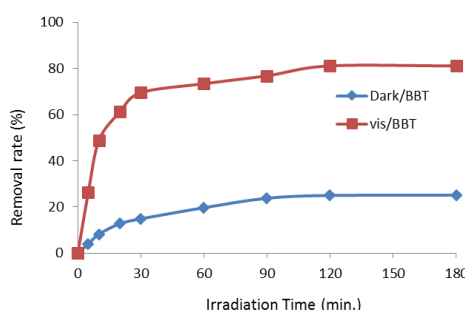


Figure 8. Variation of ibuprofen concentration in the adsorption and photocatalysis using $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ (IBF conc. 10 mg/L , $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ dose 1 g/L)

Fig. 9 depicts degradation pathways of the ibuprofen on BaBiO_3 and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ perovskite under visible light irradiation.

Intermediate analysis and degradation pathways of ibuprofen

During photocatalytic treatment of ibuprofen, many intermediates were formed and then destructed in the solution simultaneously. A total of 9 aromatic intermediates were tentatively identified in the $\text{BaBiO}_3/\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ solution by an LC/ESI-TOF-MS. In addition, a variety of aliphatic carboxylic acid

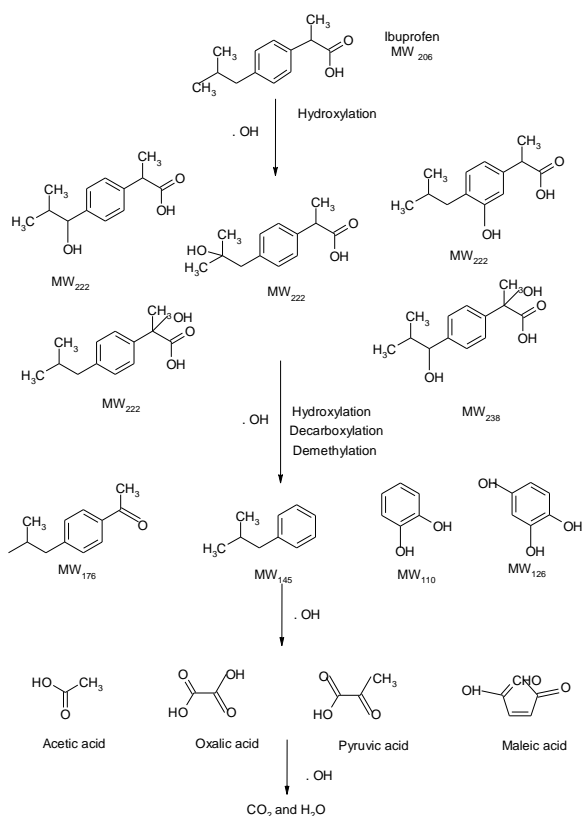


Figure 9. Degradation pathways of the ibuprofen on BaBiO₃ and BaBi₄Ti₄O₁₅ perovskite under visible light irradiation

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 show that the aromatic intermediates including hydroxylated ibuprofens and their decarboxylated and demethylated derivatives were rapidly formed and then destructed during BaBiO₃/BaBi₄Ti₄O₁₅ photocatalytic treatment. Simple phenols were also rapidly formed and then degraded with the photocatalytic treatment. The initial reaction step in ibuprofen degradation by BaBiO₃/BaBi₄Ti₄O₁₅ can thus be mainly attributed to the ·OH attack on ibuprofen. In the present 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 cleavage of benzene ring that leads to the formation of a variety of linear carboxylic acids. These acids are then oxidized by ·OH to CO₂ and H₂O 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 BaBi₄Ti₄O₁₅ solution.

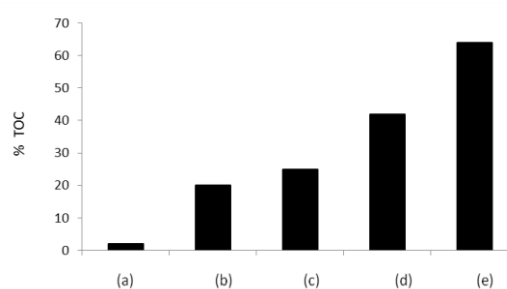


Figure 10. TOC removal in ibuprofen solution (10mg/L initial concentration) obtained by photolysis (a) adsorption on BaBiO₃ (b) adsorption on BaBi₄Ti₄O₁₅ (c) photocatalysis in the presence of BaBiO₃ (d) photocatalysis in the presence of BaBi₄Ti₄O₁₅ (e).

CONCLUSION

The ceramic powders BaBiO₃ and Bi-layered BaBi₄Ti₄O₁₅ were prepared by the Pechini method. X-ray diffraction pattern show that synthesized BaBiO₃ has monoclinic structure while BaBi₄Ti₄O₁₅ 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 BaBiO₃. From the detailed analysis of FTIR spectra, the new absorption peak was observed at 494 cm⁻¹ due to Ti-O bond. Low band gap and higher reflectance of the nanosized BaBi₄Ti₄O₁₅ 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 CO₂ and H₂O.

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Persian Abstract

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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 $BaBi_4Ti_4O_{15}$ بهبود واضحی در بازتاب، تحت تابش نور مرئی نشان می دهد که دلالت بر کاتالیست جدید Ti دوپ شده با نانو $BaBiO_3$ 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 $BaBiO_3$ به نمایش گذاشت. این دارو همچنین در روند فوتوکاتالیستی $BaBi_4Ti_4O_{15}$ کار آمد بود و مسیر تخریب در ارتباط تنگاتنگ با *demethylation* و *decarboxylation* مراحل پی در پی است.