BiOI/MWCNT COMPOSITES FOR PHENOL DEGRADATION UNDER VISIBLE LIGHT

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Abstract
In the present work, composites of BiOI with multi-walled carbon nanotubes (MWCNTs) of different compositions (0.5%, 1%, and 2% in weight percentage) were synthesized via hydrothermal synthesis at different time and temperature conditions (4:30 and 6:30 hours at 120°C and 150°C each). The composites were characterized by X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Diffuse Reflectance Spectroscopy (DRS) for their structural, morphological and optical properties. The morphology of the composites varied with different temperature conditions. The nano-plates/sheets-like structure was observed at 120°C while microflowers were observed at 150°C. However, no significant results were observed in overall photocatalytic efficiency of the composites with change in morphology. BiOI/MWCNT showed enhanced photocatalytic degradation of phenol under visible light as compared to BiOI.

Introduction
In recent past, enormous energy crises and water pollution instances have risen and has threatened the sustainable development of human beings. Wastewaters containing organic pollutants are of major environmental concern. Apart from being toxic and carcinogenic in nature, they persist in the environment for a long time and therefore, adversely affects the human health. Heterogeneous photocatalysis have now emerged as one of the most effective and "greener" technique to eliminate such organic pollutants by complete mineralization [1-2]. Bismuth oxyhalides (BiOX) are among one of the efficient photocatalysts in addition to TiO_2, to decompose pollutants into non-toxic molecules for environmental remediation [3-4]. Several classes of visible light photocatalyst are being investigated and modified, but bismuth oxyhalides, (BiOX, X= Cl, Br, I), due to their unique layered structure, suitable band gap values, and stability has shown promising visible light response. They have relative stability under UV/visible light irradiation, show visible light active response and superior performance compared to Evonik Aeroxide P25 (titania) under UV irradiation [5-6].
Among BiOX, BiOI is known to have narrow band gap (1.72-1.9 eV), therefore shows a high rate of utilization of visible light. However, BiOI suffers from drawbacks such as easy recombination of e^-/h^+ pairs, weak photo-oxidation ability and low quantum yield. Different methodologies have been adopted to improve the photocatalytic response: building a hierarchal structure, composite formation, heterojunctions, dye sensitization etc. In the past BiOI/carbon composites (BiOI/g-C3N4, BiOI/activated carbon, BiOI/graphene) have been reported to show enhanced photocatalytic response [7-8]. Carbon nanotubes composites due

to their hollow structure, excellent electronic properties and good adsorbent properties, are one of the promising nanomaterials effective in improving the charge transfer between the nanostructure interfaces and they also exhibit high catalytic activity.

Experimental

Materials

Bismuth nitrate pentahydrate [Bi $(NO_3)_3 \cdot 5H_2O$] purchased from Sigma–Aldrich, 98.0%, glacial acetic acid, 100% purchased from Molar Chemicals Kft. and potassium bromide [KBr], 99.0 % purchased from Reanal, Phenol (VWR extra pure, 100%) was purchased from VWR. Deionized water was used for the entire study. All the reagents were of analytical grade and were used without further purification.

Synthesis of BiOI

For the synthesis of BiOI, bismuth nitrate pentahydrate (1 mM in the final synthesis mixture, 3.0 g) was dissolved in 3 mL glacial acetic acid with slight heating (40 - 45 ºC) to decrease the dissolution time. This solution was added to 25 mL deionized water (marked as solution A) and was stirred until it was well dispersed. For solution B, potassium iodide (1 mM in in the final synthesis mixture, 0.78 g) was dissolved in 25 mL deionized water under magnetic stirring until it was completely dissolved. Further, solution A was added to solution B dropwise and the mixture was stirred for 20 minutes to ensure completion of the reaction. A yellow precipitate appeared which was transferred to a stainless-steel, Teflon lined autoclave and subsequently heated at two different time and temperature conditions (120 ºC & 150 ºC for 4:30 hours and 6:30 hours each.). It was then cooled down to room temperature (naturally) and the product was collected and washed with ethanol and deionized water three times each using centrifugation at 4400 rpm for 5 minutes. The final product was dried at 60-80 ºC in a vacuum furnace overnight.

Synthesis of BiOI/MWCNT composite

BiOI/MWCNTs composites were prepared in a similar manner, except the MWCNTs were added to solution A prior mixing of the two solutions (A and B). Therefore, after adding desired % content of MWCNTs (0.5%, 1%, 2% - values in weight percentage), solution A was sonicated for 2 hours, during which a black colored suspension was formed. This was now solution A with MWCNTs, while solution B was prepared similarly as mentioned before and the same procedure follows.

Results and discussion

X-Ray diffraction: The composites were characterized by X-Ray diffractometer for their structural analysis. All the peaks corresponds to the tetragonal phase (JCPDS Card No. 10-0445) and no additional characteristic peaks were observed which implies pure BiOI. The diffraction peaks for MWCNTs were not visible due to their low content. Fig. 1 shows the X-Ray diffraction of composites prepared at different time and temperature conditions with 0.5% and 1% MWCNTs content (by weight). In some of the cases, diffraction peaks of (001) and (101) facets were appearing. This suggests some structural changes have occurred.

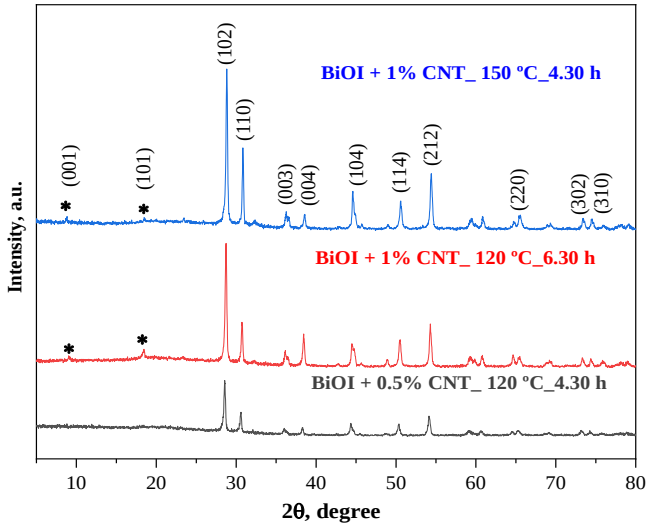

Figure 1. XRD patterns of BiOI/MWCNT composites with different amount of CNTs, prepared at different hydrothermal time and temperature conditions

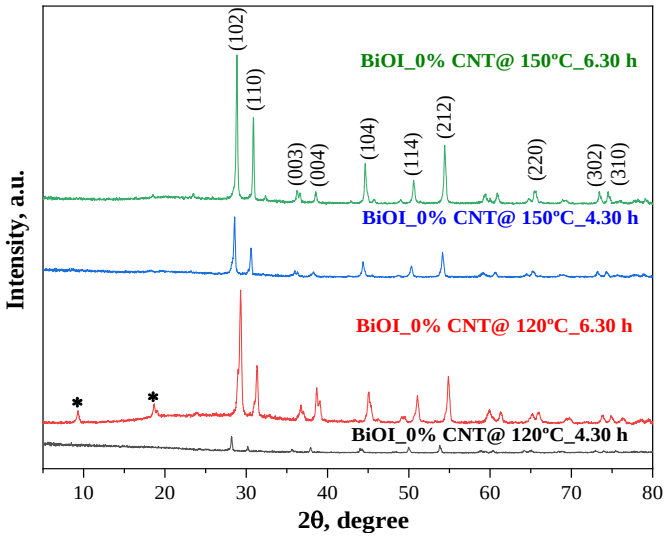

Figure 2. XRD patterns of BiOI prepared at 120°C and 150°C at 4:30 and 6:30 hours

N_2 adsorption: The BET calculated specific surface areas of the samples varied with changes in hydrothermal synthesis parameters (time and temperature). These measurements confirmed that all the samples have low surface area in agreement with the higher crystallite size as calculated from XRD data. The specific surface area ranges from 2.6 m^2/g to 9.2 m^2/g.

Scanning Electron Microscopy (SEM): The morphology of the composites varied with different hydrothermal temperature conditions. The nano-plates/sheets-like structure was observed in case of 120°C (Fig. 3 (a),(b)) while microflowers in case of 150°C as shown in Fig. 3 (c), (d).

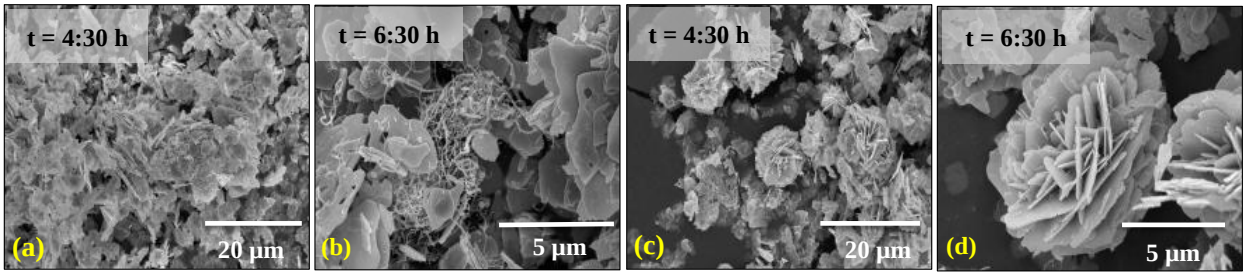

Figure 3. SEM micrographs of samples prepared at two different hydrothermal temperature conditions (120C and 150C) depicting two different morphologies

Diffuse Reflectance Spectroscopy (DRS): The optical properties of the prepared samples were studied via UV-vis absorption spectra in the wavelength range of 200-800 nm. The band gap energy value of the BiOI/CNT composites fall in the range 1.62-1.89 eV. The color of the samples gradually changed from red to brick-red to brown with the increasing carbon content. The darker the sample is, the more light it will absorb. Therefore, the BiOI/CNT composites may exhibit enhancement in absorbing visible light compared to pure BiOI.
Photocatalytic Test: Photocatalytic activity of BiOI and BiOI/CNT were evaluated by photodegradation of phenol under visible light. The experimental results were shown in Fig. 4. BiOI/CNT composites showed enhanced photocatalytic activity as compared to pure BiOI.

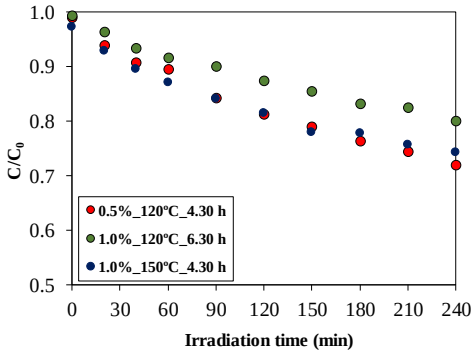

Figure 4. Photocatalytic degradation of phenol under visible light by BiOI/CNT composite

Conclusion

Composites of BiOI/CNTs were prepared at various hydrothermal time and temperature conditions. Different morphologies were observed. Nanoplates were derived at 120°C and microflowers were obtained at 150°C. However, no significant effects were observed on the overall photocatalytic efficiency of the composites. BiOI/CNT composites resulted in the photodegradation of phenol under visible light. Pure BiOI showed the least photocatalytic activity. Therefore, to some extent CNTs played a role of charge separation in the photocatalytic process.

Acknowledgement

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