Photocatalytic degradation of MB as an organic dye over a novel MOF/$BiFeO_3$ composite

Hamed Ramezanalizadeh[a] **and Faranak Manteghi**[a,*]

[a] Department of chemistry , Iran university of Science and Technology, Narmak, Tehran, 16846-13114, Iran.

(e-mail: f_manteghi@iust.ac.ir)

Abstract

In this study, a novel visible light-induced MOF/$BiFeO_3$ composite was successfully synthesized by introducing $BiFeO_3$ into a metal-organic framework (MOF). The prepared composite was characterized by means of scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). The photocatalytic activity of prepared photocatalyst was evaluated for the degradation of methylene blue (MB), as an organic dye under visible LED light irradiation. According to obtained results MOF/$BiFeO_3$ composite showed better photodegradating behavior for methylene blue (MB) compared to pure MOF and $BiFeO_3$. The enhanced photocatalytic performance could be due to the high separation efficiency of the photogenerated electron-hole pairs.

Keywords: MOF, $BiFeO_3$, photocatalyst, degradation

1. Introduction

Pigments are one of the most common pollutants in waste water of many industries such as textiles, chemicals, etc [1]. One of these hazardous pigments is methylene blue, a cationic pigment being a mutagen, carcinogen and resistant to biological decomposition [2]. There are various techniques to eliminate this pollutant, for example, chemical oxidation [3], floatation and coagulation [4], electrochemical treatment [5], liquid-liquid extraction [6], membrane filtration [7], ozonation [8] and surface adsorption [9]. Another way of eliminating this pollutant is photocatalytic analysis. Among these treatment methods, photocatalysis is a green and suitable technology to decrease organic pollutants in wastewater which has considered as a promising approach for pollution abatement and recovering of wastewaters [10]. Many studies have been reported that numerous organic pollutants can be decomposed completely through photocatalysis using metal oxide semiconductor nanostructure under UV irradiation [11]. Due to this reason that only about 4% of the solar spectrum occupies with the UV region, various high performance visible light photocatalysts have been developed [12].

2. Experimental

2.1. Materials

In this study, $Ni(NO_3)_2\cdot6H_2O$, $Co(NO_3)_2\cdot6H_2O$, $Bi(NO_3)\cdot5H_2O$, $Fe(NO_3)\cdot9H_2O$, terephthalic acid, pyrazine, H_2O, DMF, Ethanol, 2-methoxyethanol and acetic acid were purchased from Merck Co. and used to prepare the samples.

2.2. Preparation of $BiFeO_3$

For synthesis of $BiFeO_3$, a hydrothermal method was used in this work using a stoichiometric mixture of $Bi(NO_3)_3\cdot5H_2O$ and $Fe(NO_3)_3\cdot9H_2O$ in a KOH solution. In a typical procedure, equal molar ratio of $Bi(NO_3)_3\cdot5H_2O$ and $Fe(NO_3)_3\cdot9H_2O$ were introduced directly into the 50 ml of KOH solution (4 M) under ultrasound irradiation. After ultrasound irradiation for 15 min, a brown precipitate was formed and then transferred into a stainless Teflon-lined autoclave for hydrothermal treatment. Certain amounts of KNO_3 were added to the autoclave as the mineralizer. The autoclave was sealed, heated up to 200 °C and held for 6 h, and then cooled to room temperature, gradually. The final products were gathered using a centrifuge and then washed with distilled water and absolute ethanol several times, and then dried in vacuum oven at 70 °C.

2.3. Preparation of MOF/$BiFeO_3$

$[CoNi(\mu_3\text{-tp})_2(\mu_2\text{-pyz})_2]$ was synthesized using a recently reported procedure which was slightly modified [13]. To prepare MOF/$BiFeO_3$ composite a solid mixture of $Co(NO_3)_2\cdot6H_2O$ (1 mmol), $Ni(NO_3)_2\cdot6H_2O$ (1 mmol), terephthalic acid (2 mmol) and pyrazine (2 mmol) was dissolved in H_2O (14 ml). Then a calculated weight percent of prepared $BiFeO_3$ powder was added to the mixture. Then the mixture was heated to 80 °C in 30 minutes, kept at 80 °C for one day and then slightly cooled to RT with the rate of 5 °C/h. The synthesized powder was washed by ethanol and collected by centrifuging.

3. Results and Discussion

SEM images of pure MOF, $BiFeO_3$ and MOF/$BiFeO_3$ are presented in Fig. 1 .The SEM images of MOF in Fig. 1.a shows that a 3D rod-like (Co/Ni)-MOF was prepared through hydrothermal process. Furthermore, no other morphologies can be detected, indicating a high uniformity of the product with the 3D hierarchical rod-like morphology. A typical SEM image of pure $BiFeO_3$ is shown in Fig. 1.b, which shows that the samples have wafer-like morphology with highly porous structure. The SEM images of MOF/$BiFeO_3$ composite of Fig. 1 c show that $BiFeO_3$ particles are well dispersed on the MOF surface.

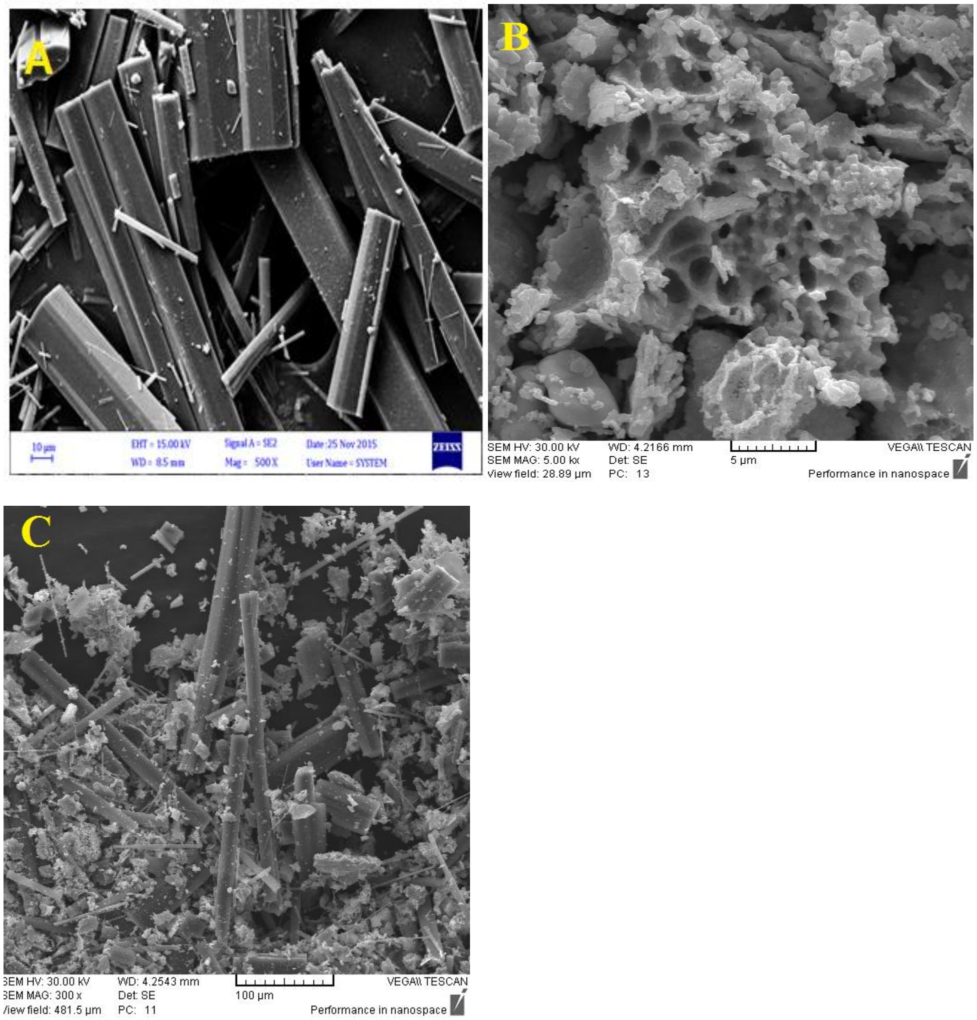

Fig. 1. The SEM images of (A) MOF, (B) $BiFeO_3$ and (C) MOF/$BiFeO_3$ composite.

In Fig. 2, FT-IR spectra of MOF, $BiFeO_3$ and MOF/$BiFeO_3$ composite have been investigated. In the spectra of MOF, the peaks appeared in the finger print region assign to the metal-ligand bond formation. The peaks appeared at 1577 and 1627 cm^{-1} are related to the asymmetric stretching vibrations of carboxylate groups. Absence of the bands for protonated carboxylate groups at 1690-1730 cm^{-1} confirms the complete deprotonation of the terephthalic acid in the role of ligand. In the FT-IR spectrum of $BiFeO_3$ the broad band around 3448.49 cm^{-1} arises from the antisymmetric and symmetric stretching of bond H_2O and OH^- groups. Two strong absorptive peaks around 545.82 and 441.67 cm^{-1} are attributed to the Fe—O stretching and O—Fe—O bending vibrations. According to metal-Oxygen band, formation of perovskite structure can be confirmed. In the FT-IR spectrum, with the formation of MOF/$BiFeO_3$ composite, intensity of the MOF carbonyl peaks has been decreased due to the MOF and $BiFeO_3$ strong interaction.

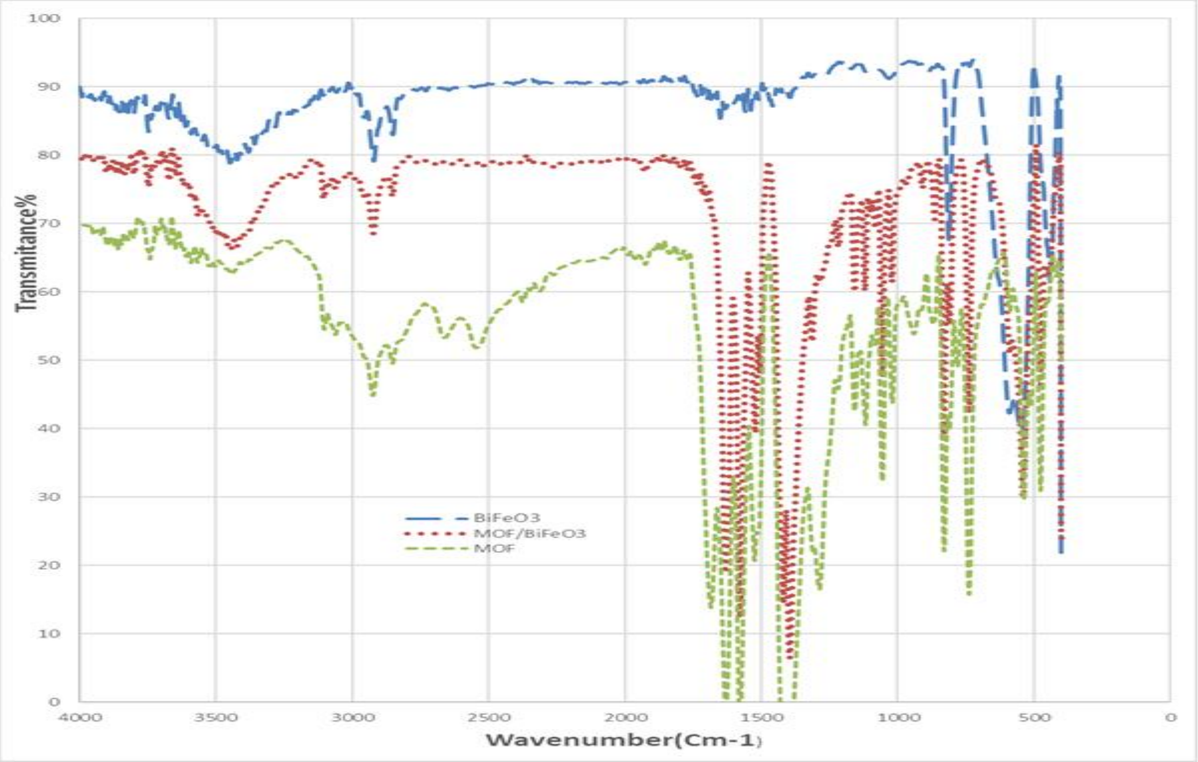

Fig. 2. FT-IR spectra of MOF, $BiFeO_3$ and MOF/$BiFeO_3$.

The photocatalytic activity of pure MOF, pure $BiFeO_3$ and MOF/$BiFeO_3$ photocatalysts under visible LED light irradiation was defined by measuring the photodegradation of MB aqueous solutions. Methylene blue is a cationic dye with a methyl nitride group $[(CH_3)_2N^+]$. Fig .3 Exhibits time dependent UV-Vis spectrum of MB degradation catalyzed by MOF/$BiFeO_3$ under visible light irradiation. The absorption peaks corresponding to MB diminished gradually as the exposure time was extended. By monitoring the MB absorption peak at 665 nm, the plots of the percentage degree of degradation vs. reaction time were obtained for the samples. The percentage degree of MB degradation was calculated by the following equation:

$$\% \text{ degradation} = \frac{C0 - C}{C} \times 100$$

Where C_0 and C are the initial and final concentrations of MB, respectively.

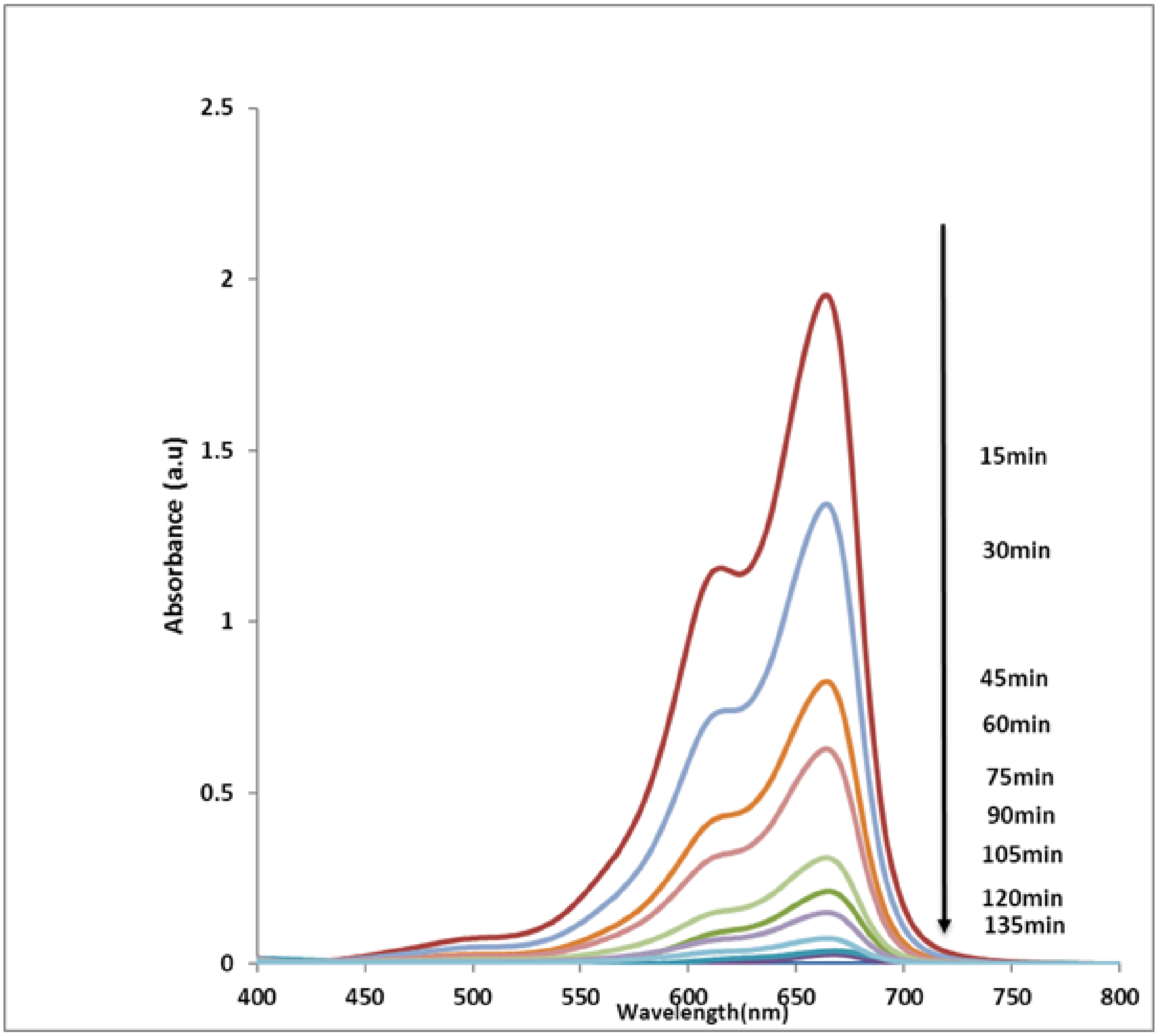

Fig. 3. Time dependent UV-vis spectrum changes of MB catalyzed by MOF/$BiFeO_3$ (initial concentration: 10 mgL^{-1}, 50 ml, 0.02 g of catalyst, under LED visible light irradiation).

4. Conclusion

In this work, MOF composite with $BiFeO_3$ was successfully fabricated and studied systematically for the photodegradation of MB under visible light irradiation. In order to investigate the effect of $BiFeO_3$ content on the photocatalytic activity, a series of the MOF/$BiFeO_3$ composite with different weight ratios and also pure MOF and $BiFeO_3$ were prepared. The composite with 1:1 molar ratio has superior activity in the degradation of MB under visible light irradiation. After visible light irradiation for 150 min, about 98% of MB molecules were degraded on MOF/$BiFeO_3$ (with 1:1 molar ratio) composite that is better than the other samples. This work provides a novel approach with the aid of MOF/$BiFeO_3$ for visible light-induced photodegradation of organic contaminants for environmental remediation.

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Graphical Abstract