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Enhanced photocatalytic activity of a novel $NiO/Bi_2O_3/Bi_3ClO_4$ nanocomposite for the degradation of azo dye pollutants under visible light irradiation

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ABSTRACT

In this work, a novel $NiO/Bi_2O_3/Bi_3ClO_4$ heterojunction nanocomposite with high visible-light-driven photocatalytic performance has been fabricated via an improved Pechini sol-gel method. The results exhibited that by controlling the process parameters such as kind of carboxylic acids, gelling agents and molar ratio of carboxylic acid to metals, the $NiO/Bi_2O_3/Bi_3ClO_4$ nanocomposites with various morphologies were synthesized. Furthermore, compared to pure NiO/Bi_2O_3 and other nanocomposites, $NiO/Bi_2O_3/Bi_3ClO_4$ demonstrated more photodegradation efficiency with 89% removal of acid red 88 azo dye in 120 min under visible light irradiation after four times cycles. The enhanced photocatalytic performance can be attributed to the effective separation and transfer of the photoexcited electron-hole pairs, fine particle size distribution and favorable absorption capability of $NiO/Bi_2O_3/Bi_3ClO_4$ ternary nanocomposite. In addition, the reliable photocatalytic mechanism was explained on the basis of the radical trapping experiment, which revealed the photoinduced active species superoxide radicals and holes were the prevailing active species in the photocatalytic process.

1. Introduction

In recent years, photocatalysis process as a green technique, has become a most effective and economical technology for the destruction of organic dye pollutants from wastewaters, because this process can utilize of solar energy to perform photochemical degradation [1,2]. Semiconductor-based photocatalytic degradation has exhibited the promising potential to eliminate the organic pollutants from aqueous solutions, because it is a solar-driven, environment friendly, cost effective and repeatable process [3,4]. Nevertheless, effective utilization of the traditional catalysts for dye decomposition is limited due to their broad band gaps which only excited under ultraviolet illumination [5]. Besides, visible light constitutes about 44% of the total sunlight, thus fabrication of efficient visible-light-driven photocatalysts with favorable energy gaps for effective removal of organic pollutants is essential [6].

Nickel oxide (NiO) structures have received considerable attention for their numerous chemical and physical applications in catalysis, gas sensing, energy conversion, smart windows, anti-ferromagnetic film, dye-sensitized photocathodes, anti-microbialactivity and photocatalysis [7–13]. It is reported that the NiO nanostructures have been synthesized by various methods including combustion, hydrothermal, thermal decomposition, precipitation, microemulsion, solid-state and sol-gel approaches [8,13–17]. Nickel oxide as a p-type semiconductor has an indirect band gap of about 3.55 eV, which is specifically suitable for photocatalysis process [18].

Bismuth-oxide materials, notably Bi_2O_3, possess several desirable features including unique catalytic, electrical, high refractive index, photoluminescence and conducting properties [19–23], and wide applications in solid oxide fuel cells, high temperature superconductors, ceramic materials, catalysis and photocatalysis processes [23–25]. Heretofore, different approaches have been employed to synthesize Bi_2O_3 structures such as hydrothermal, sonochemical, laser ablation, solid-state reaction, precipitation, electrodeposition and sol-gel [23–27]. Bi_2O_3 as p-type semiconductor has a direct band gap in visible range (about 2.8 eV), which exhibits excellent photocatalytic performance under visible light irradiation [28,29].

Bismuth oxyhalides are an important category of bismuth compounds that exhibit unique layered structures composed of $[Bi_2O_2]^{2+}$ layers stacked between two slabs of halogen ions. Bismuth oxychloride

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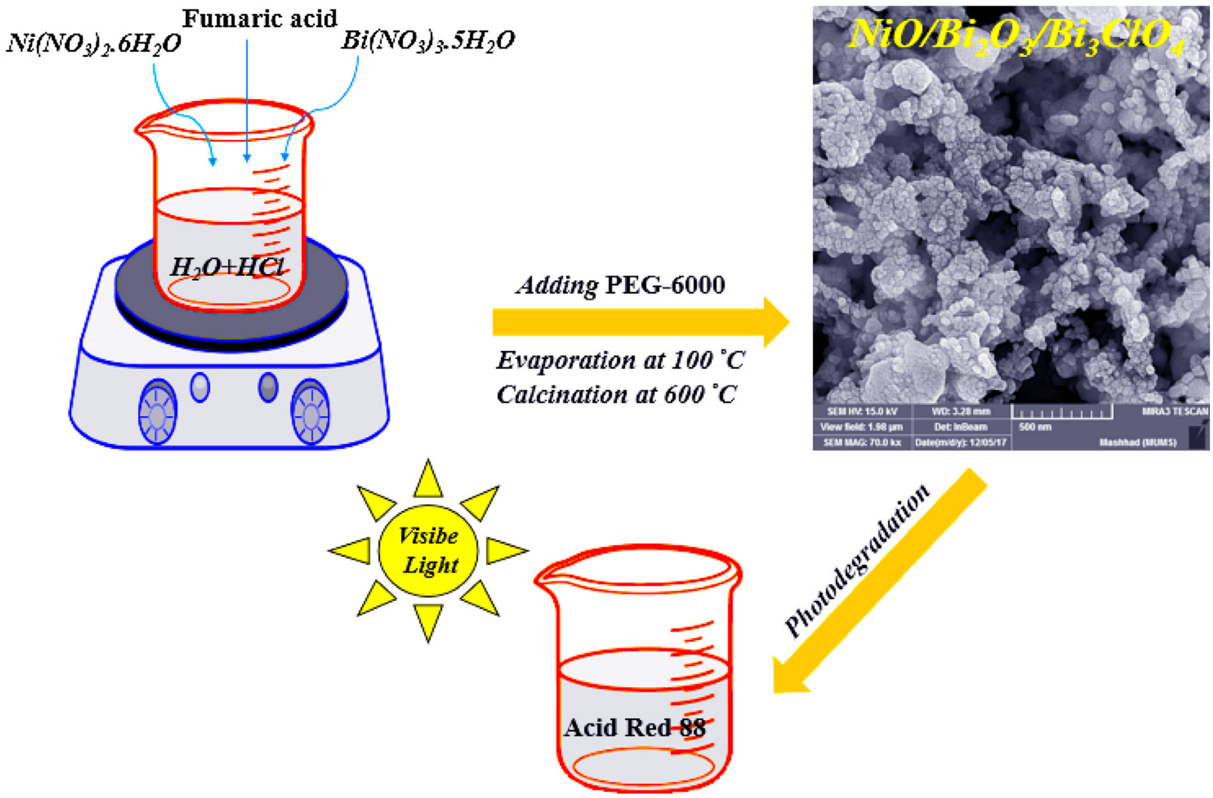

Scheme 1. Schematic design of the synthesis of $NiO/Bi_2O_3/Bi_3ClO_4$ nanocomposite (sample 1) and its photodegradation evaluation.

Table 1
The preparation conditions of the $NiO/Bi_2O_3/Bi_3ClO_4$ and NiO/Bi_2O_3 samples synthesized in this work.

Sample No.	Carboxylic acid type	Gelling agent type	Molar ratio of carboxylic acid to total metals	Figure of FESEM images
1	Fumaric acid	PEG-6000	10:1	4a
2	Maleic acid	PEG-6000	10:1	4b
3	Citric acid	PEG-6000	10:1	4c
4	Fumaric acid	EG	10:1	5a
5	Fumaric acid	Glycerol	10:1	5b
6	Fumaric acid	PEG-6000	5:1	6a
7	Fumaric acid	PEG-6000	1:1	6b
8[a]	Fumaric acid	PEG-6000	10:1	7

[a] NiO/Bi_2O_3 sample.

(BiOCl) structures demonstrate superior optical, electrical, catalytic and photoluminescent properties, and especially excellent photocatalysis performance [30–32]. BiOCl semiconductors have been used for industry-wide applications including oxidative cracking and coupling reactions, cosmetics, pharmaceuticals, jewellery, battery cathodes, photoelectrochemical devices and particularly in the photocatalytic reactions [33–36]. Recently, different routes have been used to fabricate BiOCl structures such as sonochemical, microemulsion, hydrolysis, hydrothermal, and chemical vapor deposition [36–40]. Bismuth oxychlorides (BiOCl), with a wide band gap of about 3.6 eV, have been widely employed for environmental pollutants removal due to the intrinsic defect of oxygen vacancy, open crystal structure, hybridized valence band and indirect optical transition [36,41,42].

In recent years, semiconductor nanocomposites as compounds consisting of heterogeneous phases, have been extensively considered from the scientific and practical points of view. It has been reported that the junction between semiconductors with various band gap energies, can enhance the separation and lifetime of the charge carriers, and thus improve the photocatalytic performances. Since pure NiO,

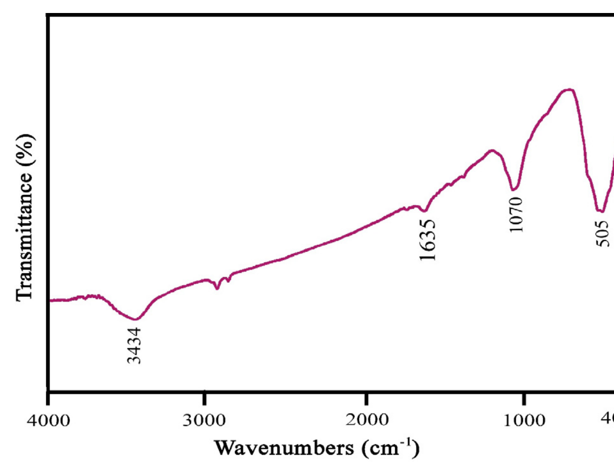

Fig. 1. FT-IR spectra of the sample 1.

Bi_2O_3 and Bi_3ClO_4 structures have relatively poor photocatalytic activity under sun-light irradiation, therefore, heterojunction modification can promote the photocatalytic efficiency of $NiO/Bi_2O_3/Bi_3ClO_4$ photocatalyst. So far, a lot of the NiO, Bi_2O_3 and Bi_3ClO_4-based heterojunction photocatalysts have been reported, including NiO/Bi_2O_3, NiO/Bi_2O_3, $BiOCl/Bi_2O_3$, Bi_2O_3/BiOCl and NiO/BiOCl. For example, Fornasiero et al. reported that NiO/Bi_2O_3 nanocomposites exhibited significantly higher photocatalytic activity compared to its components in the pure phase for the decolorization of methylene blue and methyl orange. According to Li et al., the presence of NiO in the NiO/Bi_2O_3 heterojuctions increases the absorbance in the visible light region, the separation rate of the photogenerated electron-hole pairs and the formation of superoxide radicals in the photocatalytic discoloration of methyl orange aqueous solutions. Lee and his co-workers fabricated heterojunctioned $BiOCl/Bi_2O_3$ photocatalyst, which exhibited superior