



Rapid degradation of naproxen by AgBr- α -NiMoO₄ composite photocatalyst in visible light: Mechanism and pathways

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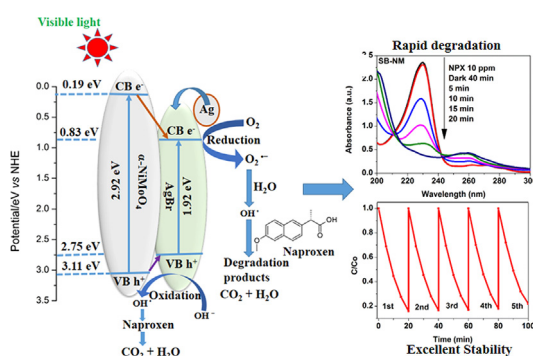
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HIGHLIGHTS

- Rapid degradation of naproxen by AgBr- α -NiMoO₄ in visible light within 20 min.
- Excellent photochemical stability of composite up to 5th cycle.
- Identification of nineteen degraded naproxen fragments by HR-QTOF ESI/MS.
- Proposed five different pathways for naproxen degradation.
- Complete mineralization of naproxen within 100 min.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel strategy for fabrication of visible light driven AgBr- α -NiMoO₄ composite photocatalyst has been developed, including microwave hydrothermal and precipitation-deposition method. The fabrication of heterojunction photocatalyst was proved by XRD, FESEM mapping, HRTEM, SAED, EDS, and XPS techniques. The composite photocatalyst degraded naproxen drug around 84% within 20 min under visible light irradiation. The active species trapping experiment confirmed that OH[•], O₂⁻, and h⁺ play a crucial role for naproxen degradation. Due to efficient charge separation, well matched energy band of AgBr and α -NiMoO₄ as well as surface plasmon resonance of silver particles, the composite revealed the high photocatalytic performance with excellent stability up to fifth cycle. In addition, the composite is photochemical stable. Furthermore, the five degradation pathways were proposed on the basis of retention time and theoretical/observed molecular masses of 19 degraded organic fragments that was confirmed by high-performance liquid chromatography-photodiode array (HPLC-PDA) and high resolution-quadrupole time of flight electrospray ionization mass spectroscopy (HR-QTOF ESI/MS) techniques. The different reactions (methylation, demethylation, decarboxylation, hydroxylation, oxidation, and coupling) were observed during NPX degradation by photocatalyst. TOC (total organic carbon) analysis revealed that naproxen drug was completely mineralized by composite photocatalyst within 100 min. So, this work represents the fabrication of visible light induced novel composite photocatalyst for rapid degradation of pharmaceutical pollutant with detailed mechanism and pathways.

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1. Introduction

In the past few years, the introduction of pharmaceutical pollutants in environmental sources including surface water, groundwater, sediments, soil, and even drinking water causes serious hazard to humans as well as freshwater and marine ecosystem [1,2]. The pharmaceutical industries, inappropriate disposal of unused or expired drugs, hospitals, and farms are the major sources of pharmaceutical pollutants. Among pharmaceutical pollutants, naproxen (NPX) is a nonsteroidal anti-inflammatory drugs (NSAID) with analgesic and antipyretic properties that has been applied in treatment of rheumatoid arthritis [3,4]. In addition, it is also used as veterinary medicine. It has been detected in different environment at concentration (ng mL^{-1} to $\mu\text{g mL}^{-1}$) because of incomplete degradation [2,5]. Several techniques have been applied for removing the pharmaceutical pollutants from waste water [6]. Among them, advanced oxidation process (AOP) is effective technique in which semiconductor photocatalyst can degrade the pharmaceutical pollutants by utilizing the natural energy of sun light [6–8].

NiMoO_4 photocatalyst consists of low temperature α -phase that has monoclinic structure and $\text{C}_{2/m}$ space group with stable at room temperature. In addition, it has an octahedral co-ordination of Mo^{6+} and Ni^{2+} ions and edge shared oxygen atoms. It consists of low cost and environmentally friendly features. The photocatalytic activity of α - NiMoO_4 is very low due to rapid recombination of electron and hole. Although, it has an appropriate band gap (2.8 eV) with utilizing visible light from solar spectrum [8–10]. Recently, several approaches have been applied to overcome the lower photocatalytic performance of α - NiMoO_4 [8–11]. Among them, the designation of heterojunction photocatalyst is an effective architecture for improving the photocatalytic activity. The advantage of heterojunction photocatalytic systems consists of effective charge separation, fast charge transfer to the surface, higher lifetime of the charge carriers, separation of locally adverse oxidation/reduction reactions in nanospace, and formation of small barrier [12]. The silver bromide (AgBr) is efficient co-catalyst for making heterojunction photocatalyst [13]. The narrow band gap (2.5 eV) of AgBr has strong absorption in visible light region. However, it is an unstable photocatalyst due to formation of cluster of silver atoms in AgBr by absorbing photons via interaction of the photoinduced electrons with interstitial Ag^+ [14]. In addition, the compounding of AgBr with other semiconductor materials improve the photocatalytic stability of AgBr. To date, various heterojunction semiconductors have been designed by coupling with AgBr photocatalyst for improving the photocatalyst stability of AgBr as well as the life time of charge carriers [13–15]. Also, visible light induced α - NiMoO_4 and AgBr photocatalyst have matching energy level structure that can prevent the electrons and holes recombination for photocatalytic enhancement [10,11,16]. Moreover, the intermediate organic fragments, mechanism, and pathways are necessary for systematic investigation of photocatalytic degradation of pharmaceutical pollutants. So, the fabrication of AgBr- α - NiMoO_4 stable composite photocatalyst is perfect option for the rapid degradation of drugs with identification of intermediate products, degradation pathways, and mechanism.

In this paper, we demonstrate the synthesis of AgBr- α - NiMoO_4 composite photocatalyst by two step (microwave hydrothermal and precipitation-deposition) process. The morphologies and optical properties were investigated. The photocatalytic degradation of NPX was analyzed under visible light illumination. The photochemical stability of composite was evaluated. HR-QTOF ESI/MS and HPLC-PDA techniques were carried out for determination of NPX intermediate products to find out the degradation pathways and mechanism. Furthermore, the mineralization of NPX by samples was investigated by TOC (total organic carbon) analysis.

2. Materials and methods

2.1. Synthesis of AgBr- α - NiMoO_4 composite photocatalyst

The chemicals (Sigma Aldrich) were purchased from of analytical grade and used without any further purification. In experimental procedure, aqueous solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (2×10^{-2} mol/40 mL) and aqueous solution of H_2MoO_4 (2×10^{-2} mol/40 mL) were prepared in the separate beaker. The solutions were mixed drop wise by the continuous magnetic stirring for 3 h to form greenish yellow precipitate. The aqueous ammonia (30%) was used to maintain the pH 7 of the solution. The resulting precursor suspension was placed in microwave reactor (Eyla MWO-1000 wave Magic) for the microwave hydrothermal process ($150^\circ\text{C}/1\text{h}/200\text{ W}$). The obtained precipitate was washed with water/ethanol at various times. Then, it was dried (70°C) and calcined in air ($500^\circ\text{C}/5\text{h}$). In this way, the α - NiMoO_4 sample was synthesized. The AgBr- α - NiMoO_4 composite photocatalyst was synthesized by precipitation-deposition method. First, the CH_3COOAg (0.83 g/40 mL water/30 mL ethanol) and NaBr (0.51 g/40 mL) were mixed/stirred to form brown precipitate. At the same time α - NiMoO_4 (2 g) powder was placed in the precipitated solution. The solution was continuous magnetic stirring for 7 h. The obtained precipitate was washed with water/ethanol several times. Finally, it was dried in air (70°C). The composite photocatalyst consists of 1 g AgBr and 2 g α - NiMoO_4 powder. The AgBr sample was also synthesized by same procedure (precipitation-deposition). The sample were coded as NM (α - NiMoO_4), SB (AgBr), and SB-NM (AgBr- α - NiMoO_4).

2.2. Characterization

The powder X-ray diffraction (XRD) patterns are used to investigate the crystal structure and phases of sample by using Rigaku, D/MAX 2200HR diffractometer at scan rate of 4°min^{-1} in the range of 10 – 80° . The morphologies of samples were analyzed by field emission scanning electron microscopy (FESEM) and high resolution transmission electron micrograph (HRTEM)/Energy-dispersive X-ray spectroscopy (EDS)/selected area electron diffraction (SAED) by using JSM-6700F and FEI Titan (TM) 80–300, respectively. The chemical states of different elements in the samples were identified in multilab system with Al K α source at 15 kV/200 W. The UV–Vis diffuse reflectance spectra (DRS) of samples were measured by V 570, Jasco International Co. Ltd. The photocatalytic degradation of naproxen by samples was carried out by using solar simulator (portable solar simulator PEC-L01, 150 W short-arc Xe lamp, $100 \text{ mW}/\text{cm}^2$, Pecell, Am 1.5G) as a light source. For visible light source, UV cut-off filter ($\lambda < 420 \text{ nm}$) was inserted in solar simulator. The UV–Vis spectrophotometer (MECASYS, Optizen2120) was used to obtain the absorption spectra of degraded NPX liquid by photocatalyst.

2.3. Photocatalytic activity and radical trapping experiment

The photocatalyst powder sample (0.1 g) was placed in a Pyrex glass that consists of 70 mL of aqueous solution of NPX with concentration 10 ppm. The mixture was placed in dark (40 min with constant stirring) for obtaining the adsorption-desorption equilibrium. Then, the drug suspension with sample was constantly stirred (magnetic stirrer) in visible light. The nearly 12 cm was adjusted between the distance between lamp and Pyrex glass during degradation process. During degradation of NPX in visible light, approximately 1.5 mL of aliquot was collected in Eppendorf Tube by using syringe at every 5 min intervals and centrifuged (10000 rpm/5 min). Then, the suspension was passed through a filter (DISMIC-25 HP/pore size: $0.20 \mu\text{m}$) to obtain the supernatant liquid. The photocatalytic degradation rates of NPX was analyzed by using UV–Vis spectrophotometer at their maximum absorption wavelength (230 nm). Then, the supernatant liquid was again placed into Pyrex glass and there was no change in the solid

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