

Fabrication of Fe₃O₄@NiAl-LDH Core-shell Structure Demonstrating the Dual Catalytic Photo-Fenton Activity

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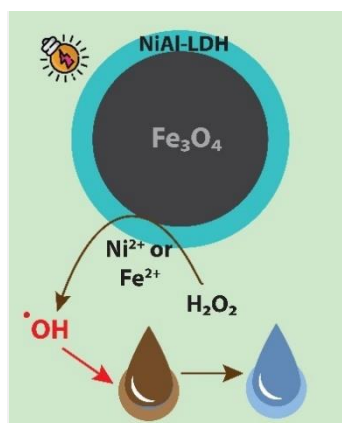
Journal: YES (JECE)

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Heterogeneous Fenton catalysts are emerging materials for water purification applications due to their reusability and enhanced degradation efficiency. This study examines the enhanced photo-Fenton (PF) activity of Fe₃O₄@NiAl-LDH core-shell type catalyst towards the degradation of contaminants of emerging concern (CEC). The TEM images show the presence of NiAl-LDH covered on the surface of Fe₃O₄. The PF degradation experiments using acetaminophen (ACT) reveal improved degradation efficiency for Fe₃O₄@NiAl-LDH compared to Fe₃O₄ and NiAl-LDH. The improved catalytic efficiency of Fe₃O₄@NiAl-LDH was attributed to the reduced rate of electron-hole pair recombination. The study emphasises the potential of core-shell structured catalysts for efficient pollutant degradation applications.

Introduction

The photo-Fenton (PF) technique is a promising method for the degradation of contaminants of emerging concern (CEC) owing to its excellent capacity to produce highly oxidising hydroxyl radicals. Iron-based catalysts are capable of performing PF reactions in the presence of H₂O₂. Different heterogeneous catalysts, such as ferrites, magnetite, pillared clays, layered double hydroxides (LDH), and metal-organic frameworks (MOFs), have been reported for PF-related applications. [1]

Among the various PF catalysts, magnetites are of particular interest due to their magnetic properties and photophysical characteristics. However, their PF activity is limited by the fast recombination rate of electron-hole pairs[2]. LDH materials are interesting due to their higher surface area and tunable chemical composition. The core-shell structured catalysts are receiving increased attention because of the combination of properties of a magnetic core and a reactive outer shell, as well as the potential for synergistic effects between them[3]. Herein, we report the synthesis of a Fe₃O₄@NiAl-LDH core-shell structured catalyst through a co-precipitation strategy and demonstrate enhanced PF activity compared to Fe₃O₄ and NiAl-LDH.

Material and Methods

The Fe₃O₄ nanoparticles were prepared through an ethylene glycol-based solvothermal reaction[3]. The NiAl-LDH was subsequently coated on the surface of Fe₃O₄ via a co-precipitation strategy, and the resulting catalyst was named Fe₃O₄@NiAl-LDH. The

sample was characterised using XRD, FTIR, Raman, XPS, photoluminescence (PL), and BET measurements. The morphology of the catalysts was observed through the SEM and TEM images. The PF degradation of ACT, a contaminant of emerging concern, was performed using a 10 mg/L concentration of ACT, 0.5 g/L of the catalyst, and 1.5 mM H₂O₂. The PF tests were conducted under simulated solar light in a Q-SUN Xenon test chamber for 3 hours.

Results and Discussion

XRD was utilised to analyse the crystallinity and phase of the prepared samples. The peaks at 2θ values of 30.5°, 35.6°, 43.3°, 53.6°, 57.1°, and 62.7° were attributed to the (220), (311), (400), (422), (511), and (440) crystal planes of Fe₃O₄, respectively. Similarly, the peaks at 2θ values of 11.4°, 23.2°, 35.0°, and 39.6° corresponded to the crystal planes (003), (006), (012) and (015) of NiAl LDH, respectively. The peaks corresponding to both Fe₃O₄ and NiAl-LDH were observed in the Fe₃O₄@NiAl-LDH catalyst [4].

The TEM images of Fe₃O₄@NiAl-LDH (Figure 1) reveal the presence of Fe₃O₄ at the core of the catalyst, with a layer of NiAl-LDH on the surface of Fe₃O₄.

The surface elemental composition and chemical state of the catalysts were analysed using XPS analysis. The predominant existence of the elements Ni, Al, Fe, O and C was observed in the XPS survey

spectra of $\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$. The high-resolution Ni2p spectra indicated the presence of Ni in two different oxidation states, Ni^{2+} and Ni^{3+} , in the $\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$ catalyst. By comparing the XPS spectra of $\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$ before and after the PF reaction, the variations in the $\text{Ni}^{2+}/\text{Ni}^{3+}$ ratio on the surface of the catalyst were assessed. This suggests the possibility of electron transfer between Ni and Fe and the potential for dual catalytic PF action exhibited by $\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$ catalyst.

The PF degradation studies in the presence of NiAl-LDH and Fe_3O_4 resulted in 31.3% and 56.8% degradation of ACT, respectively. Subsequently, the PF degradation using the $\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$ resulted in 95.8% degradation of ACT. It was observed that all three catalysts followed a pseudo-first-order kinetic reaction. The calculated kinetic rate constant values for the $\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$ were six times greater than those observed for NiAl-LDH.

The BET specific surface area (SSA) measurements were conducted (Table 1) in order to determine the potential connection between SSA and PF activity. The SSA value observed for the Fe_3O_4 catalyst was $17.4 \pm 1.6 \text{ m}^2/\text{g}$, while coating Fe_3O_4 with NiAl-LDH ($\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$) resulted in a SSA value of $157.7 \pm 2.1 \text{ m}^2/\text{g}$. The increased SSA value observed for the $\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$ compared to Fe_3O_4 suggests that there are more catalytic sites available for the

PF degradation reaction, which leads to improved catalytic efficiency.

Higher intensity of the PL spectra is typically associated with a more rapid recombination rate of electron-hole pairs[5]. Here, in the case of $\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$, a lower emission intensity was observed, compared to NiAl-LDH. This indicates that a slower rate of electron-hole pair recombination could be the reason for the improved PF activity of $\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$ [4].

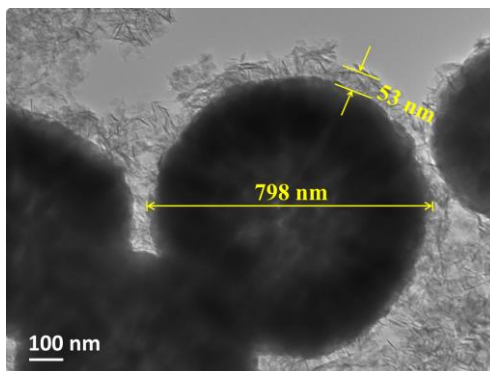


Figure 1. TEM image of the $\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$ catalyst

Table 1. BET specific surface area of the catalysts.

Catalysts	BET surface area (m^2/g)
NiAl-LDH	159.0 ± 2.2
Fe_3O_4	17.4 ± 1.6
$\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$	157.7 ± 2.1

Conclusions

This study demonstrates the preparation of $\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$ core-shell type catalyst. The efficiency of the $\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$ in degrading ACT was found to be 95.8%, which is significantly higher than that of NiAl-LDH (31.3%) and Fe_3O_4 (56.8%). The observed increase in the catalytic performance of $\text{Fe}_3\text{O}_4@\text{NiAl-LDH}$ was attributed to the slower electron-hole pair recombination and the potential dual catalytic action involving Ni and Fe.

Acknowledgements

The authors acknowledge the financial support from the European Union's Horizon 2020 research and innovation programme for the PANIWATER project (GA 820718), funded jointly by the European Commission and the Department of Science and Technology (DST), India.

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