**Keywords**

Water Treatment; photoelectrocatalysis; Contaminants of emerging concern

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## O92 2D/2D Heterojunction of NiFe-LDH/$MnO_2$ with promoted visible-light-driven photocatalytic performance for NOx removal

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**Extended Abstract**

**Summary**

In the present study, 2D/2D heterojunctions between ultrathin NiFe-$CO_3$ layered double hydroxide (LDH) and birnessite (d-$MnO_2$) were prepared by a self-assembly strategy. The close interface contact between each semiconductor in the NiFe/$MnO_2$ composite enhanced the photocatalytic performance compared to individual semiconductors. The influence of the atomic ratios on photocatalytic behaviour has been demonstrated, highlighting a 10:1 ratio of NiFe:$MnO_2$ as the most optimal proportion for a better response. These heterojunctions effectively controlled NOx emissions, being their photooxidative mechanism under visible light here described.

**Background**

The rapid development of contemporary society has caused a deterioration of air quality [1]. Over the last decades, it has been crucial to devise new remediation strategies to eliminate these pollutants from the atmosphere. In this context, this study proposes the development of the NiFe/$MnO_2$ composite as a new advanced photocatalyst towards NOx gas removal with enhanced properties, especially strengthening its absorption in the region of the visible light spectrum [2].

**Methodology**

Given its laminar structure rich in negative charges, birnessite (δ-$MnO_2$) [3] represents an ideal structural phase for self-assembly with NiFe-LDH nanosheets [4], endowed with positive charges. The structural complementary between delaminated layers of opposite charge facilitates the electrostatic interaction resulting in stable and well-organized composite structures. Finally, several composites were obtained by varying $MnO_2$ proportions (0, 10, 33 and 66%).

**Results and Discussion**

Comprehensive characterisation confirmed the successful formation of 2D/2D NiFe/$MnO_2$ composites by a simple self-assembly method through the pure phases of precursors. Figure 1 shows that incorporating a higher $MnO_2$ content in the LDH sample affects textural parameters, reducing specific surface area and pore volume. This decrease limits the number of active centres for anchoring NO gas molecules. Band gap values were determined for NiFe-LDH (2.5 eV) and NiFe/$MnO_2$ composites (1.9 – 2.4 eV range), all able to be activated by visible light. In contrast, the $MnO_2$ (1.7 eV) narrow band gap causes greater light harvesting but supposes higher recombination of charge carriers ($e^-/h^+$).

Photocatalytic DeNOx test demonstrated enhanced performance in NiFe-LDH/$MnO_2$ heterojunctions under visible light, resulting in a notable increase in $E_{NO}$ values and exceptional selectivity for all samples (S = 100%), Figure 2A. The high $e^-/h^+$ recombination experienced by $MnO_2$ is reduced in NiFe/$MnO_2$ composites, correlating with superior DeNOx activity

results for NiFe/$MnO_2$-0.1 with $E_{NO}$ = 41 %, against 7% and 23% for $MnO_2$ and NiFe-LDH, respectively. Figure 2B illustrates a proposed photooxidative mechanism inferred from XPS, EPR and scavenger data. Activated under visible light (λ = 427 nm), the heterojunction promotes the movement of photogenerated electrons to the conduction band (CB) and the creation of holes in the valence band (VB), with an electron flow from NiFe-LDH to $MnO_2$ CB facilitated by their intimate electronic contact and their edge band position. Additionally, experimental results emphasise the crucial role of superoxide radicals ($\cdot O_2^-$) in the reaction. The generated radicals subsequently react with environmental molecules, particularly NOx gases, effectively transforming them into nitrate and nitrite species.

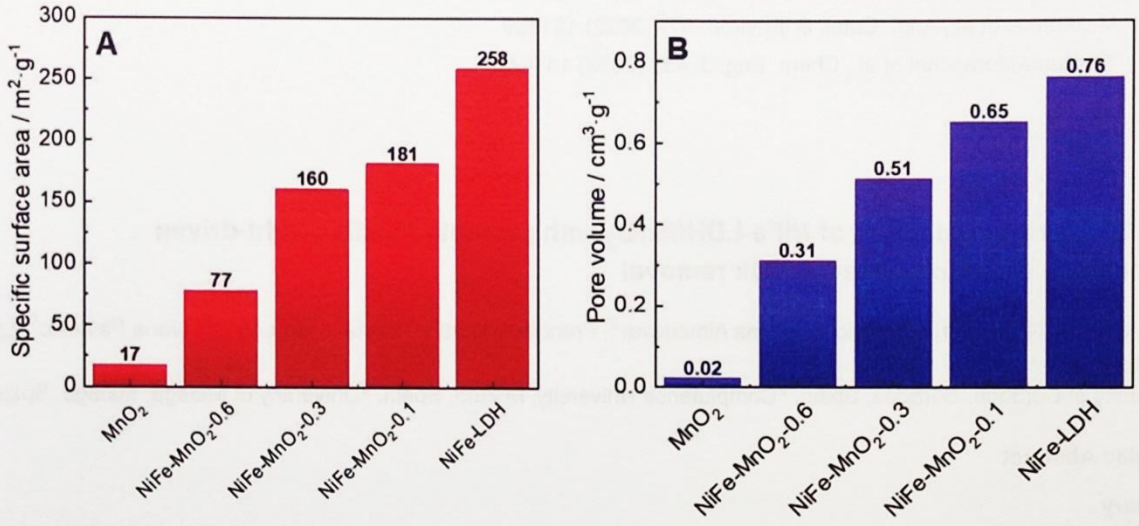


Figure 1. Histogram of the (A) specific surface area and (B) pore volume for the NiFe/$MnO_2$ system.

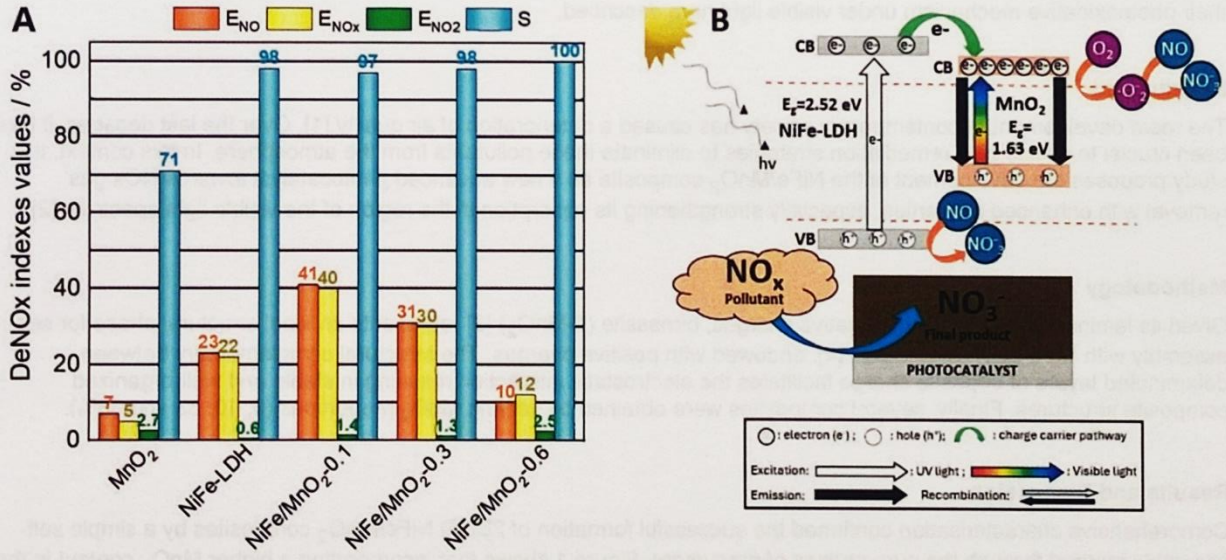


Figure 2. (A) DeNOx indexes of the photocatalytic test under visible light (λ= 427 nm) and (B) schematic diagram for the photodegradation of NOx over NiFe/$MnO_2$ photocatalysts.

**Conclusions**

The present study has demonstrated a perfect electronic interaction of a type-I heterostructure. By identifying the optimal ratio of $MnO_2$ and NiFe-LDH, a favourable band alignment, and establishing correlations in their electronic and physical properties, the recombination of charge carriers was reduced. Furthermore, it optimized the specific surface area and the

formation of reactive oxygen species (ROS). Consequently, these improvements led to a superior photocatalytic performance.

**Keywords**

LDH; Birnessite; Heterojunction; Photocatalysis; Nitrogen Oxides.

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