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# Modulation of Layered Double Hydroxides for photocatalytic air purification

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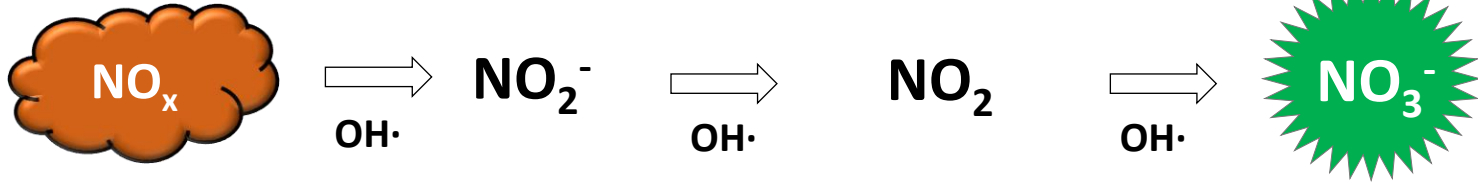
WORKSHOP  
PHOTOCATALYSIS FOR  
ENERGY AND CLEAN  
ENVIRONMENT



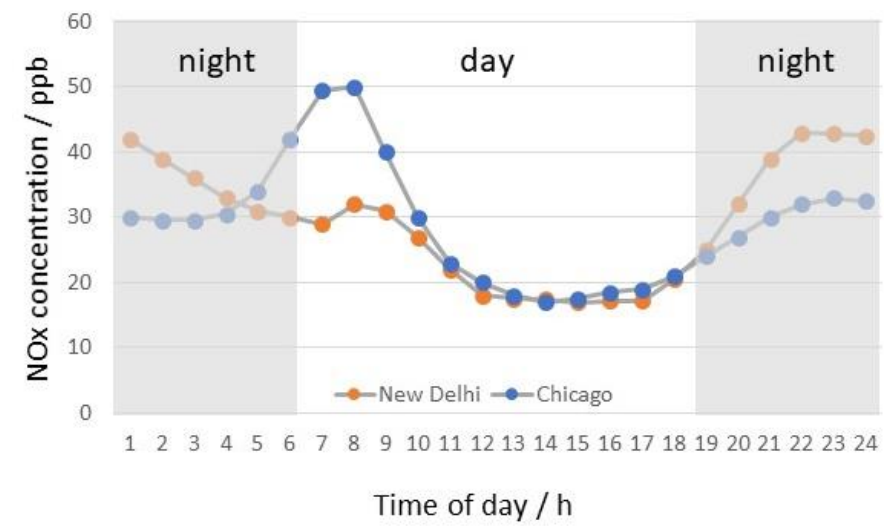
MÁLAGA, OCTOBER 18<sup>TH</sup>  
2022

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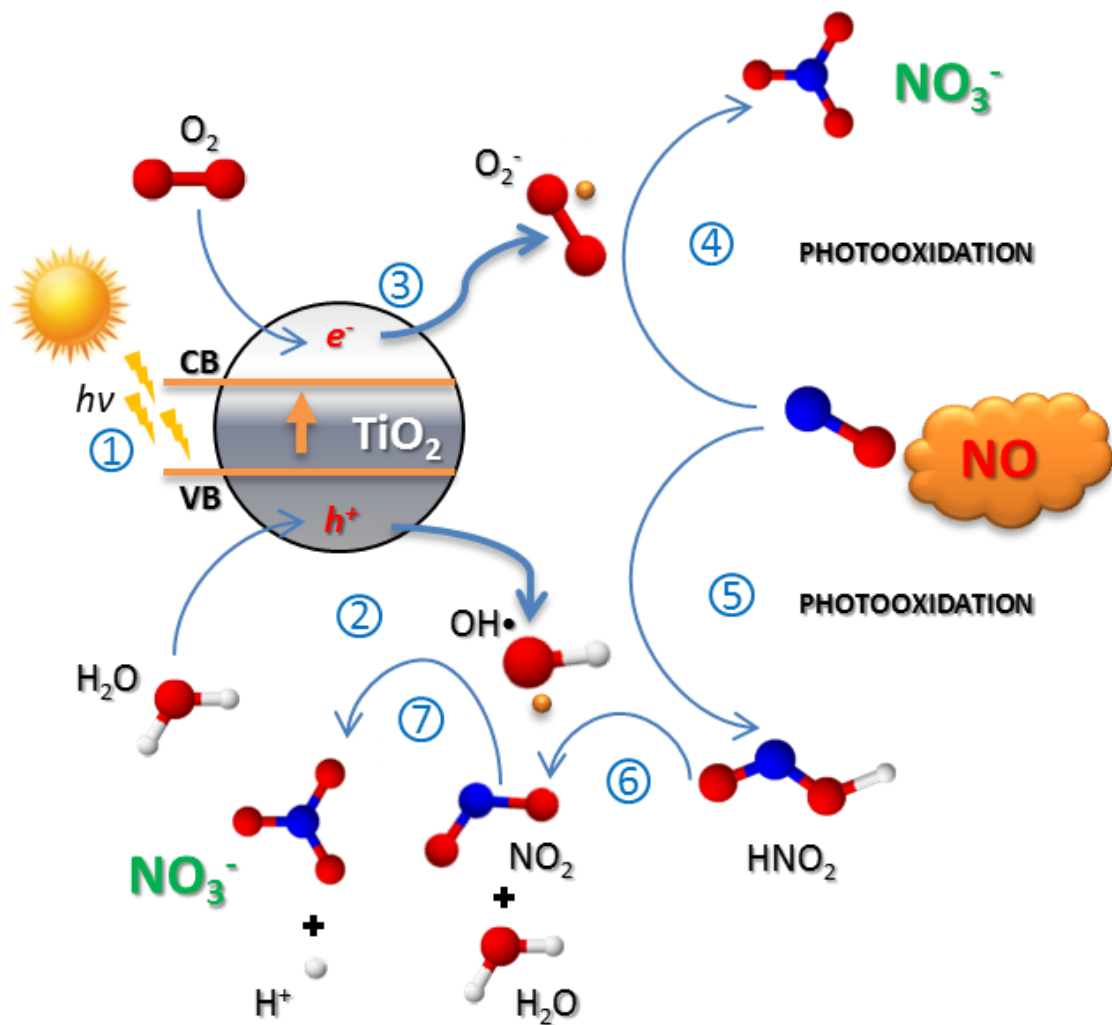




**Figure 1:** Diurnal profiles of NOx concentrations at urban centers



# Photochemical De-NO<sub>x</sub> mechanism



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Review

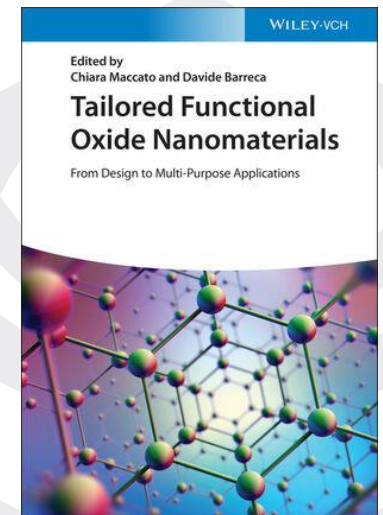
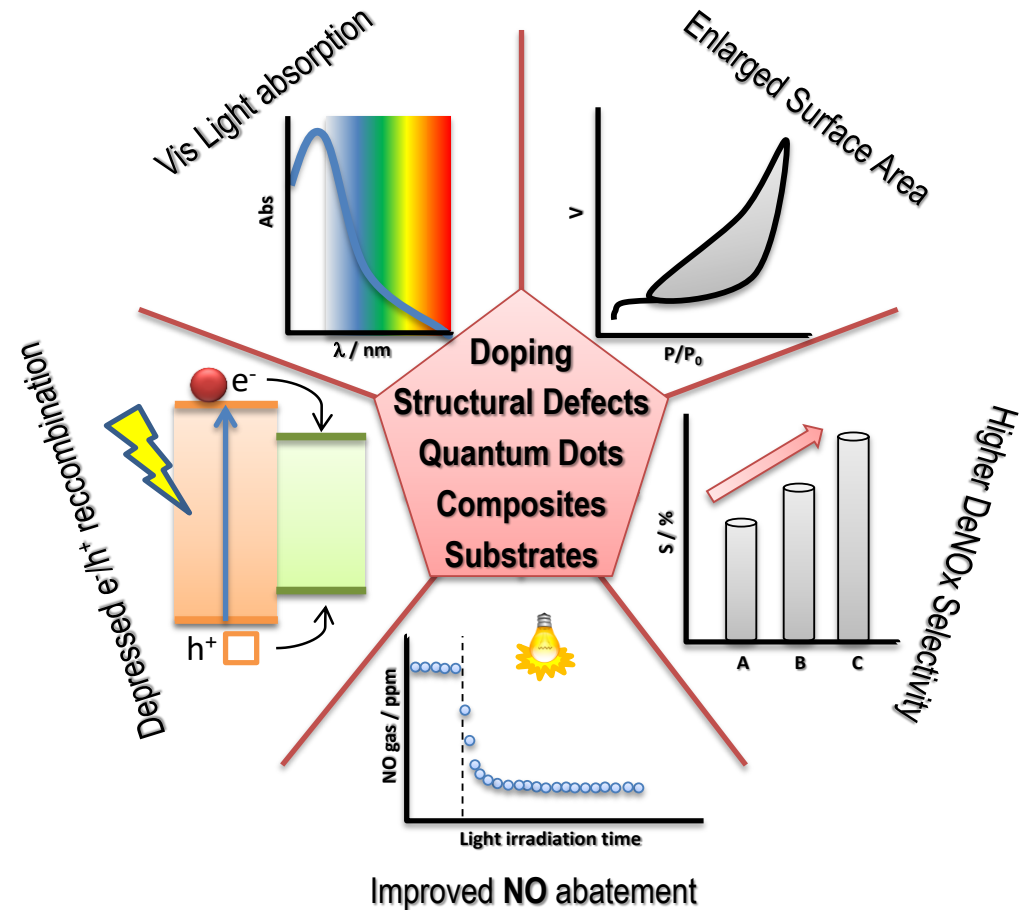
Journal of  
*Nanoscience and Nanotechnology*  
Vol. 15, 6373–6385, 2015  
[www.aspbs.com/jnn](http://www.aspbs.com/jnn)

## Nanomaterials to Combat NO<sub>x</sub> Pollution

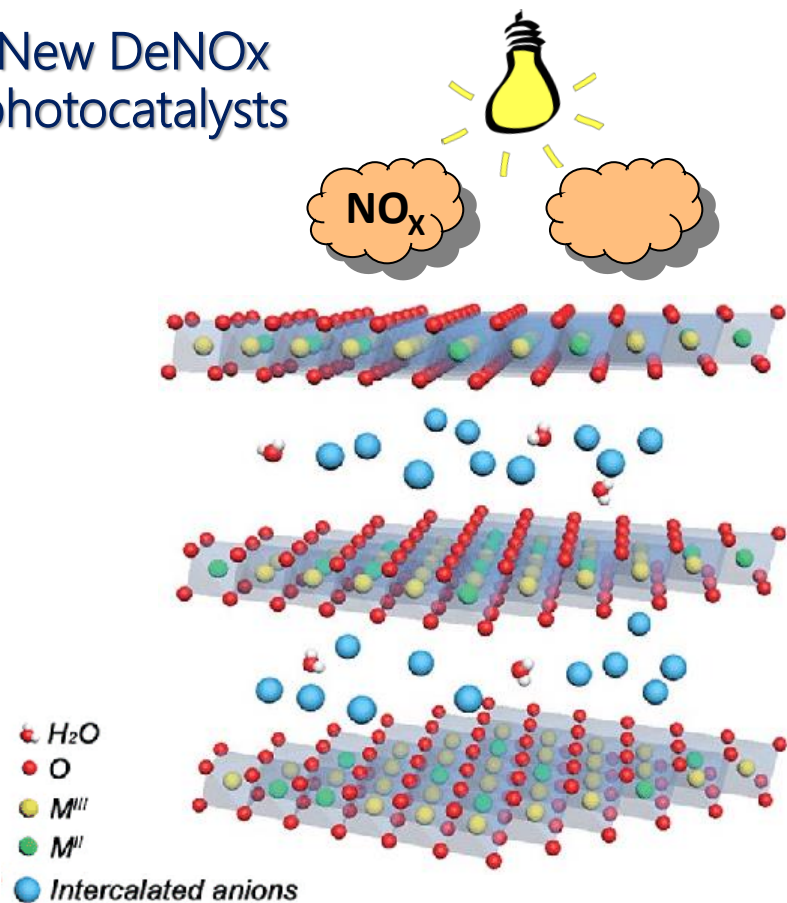
J. Balbuena, M. Cruz-Yusta, and L. Sánchez\*

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Campus de Rabanales, Edificio Marie Curie, 14071–Córdoba, Spain

# New materials to combat NO<sub>x</sub> gases

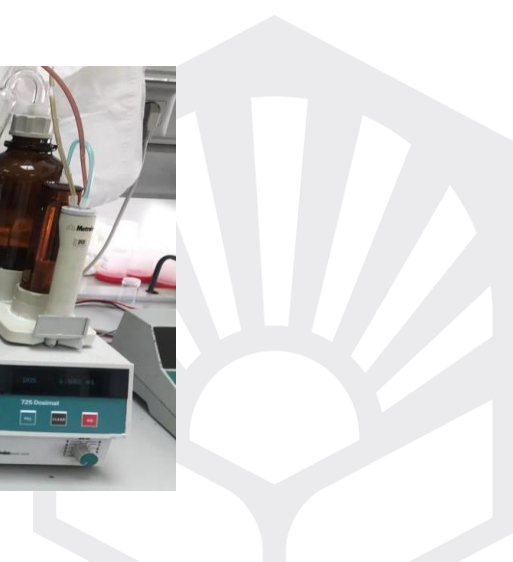
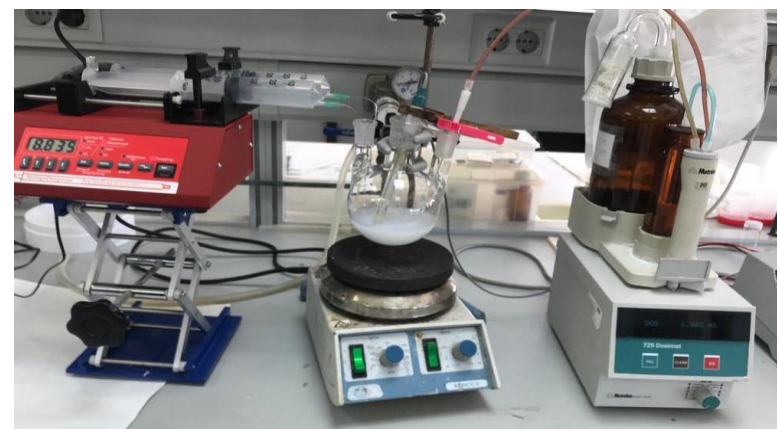


## New DeNO<sub>x</sub> photocatalysts



## LDHs (Hidrotalcites)

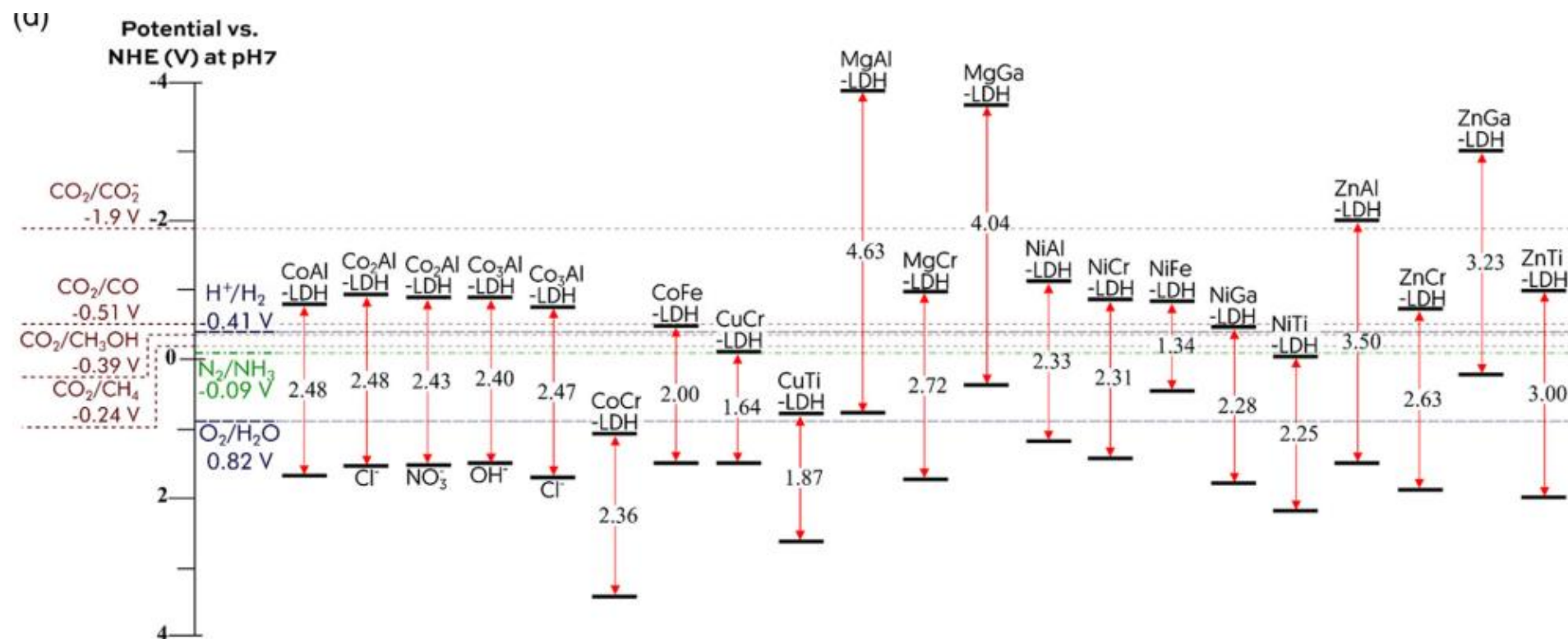
- Based  $\text{Mg}(\text{OH})_2$  structure
- A versatile chemical fórmula :
$$[\text{M}_{1-x}^{\text{II}}\text{M}_x^{\text{III}}(\text{OH})_2]^{x+} \text{X}_{x/n}^{n-} \cdot m\text{H}_2\text{O}$$
- An important group of photocatalysts
- Simple, low-cost and scalable synthesis.



# Engineering Layered Double Hydroxide–Based Photocatalysts Toward Artificial Photosynthesis: State-of-the-Art Progress and Prospects

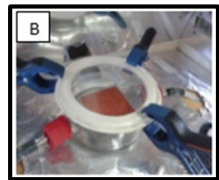
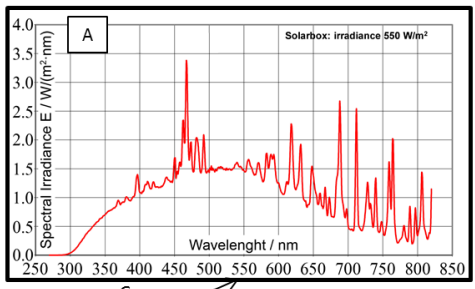
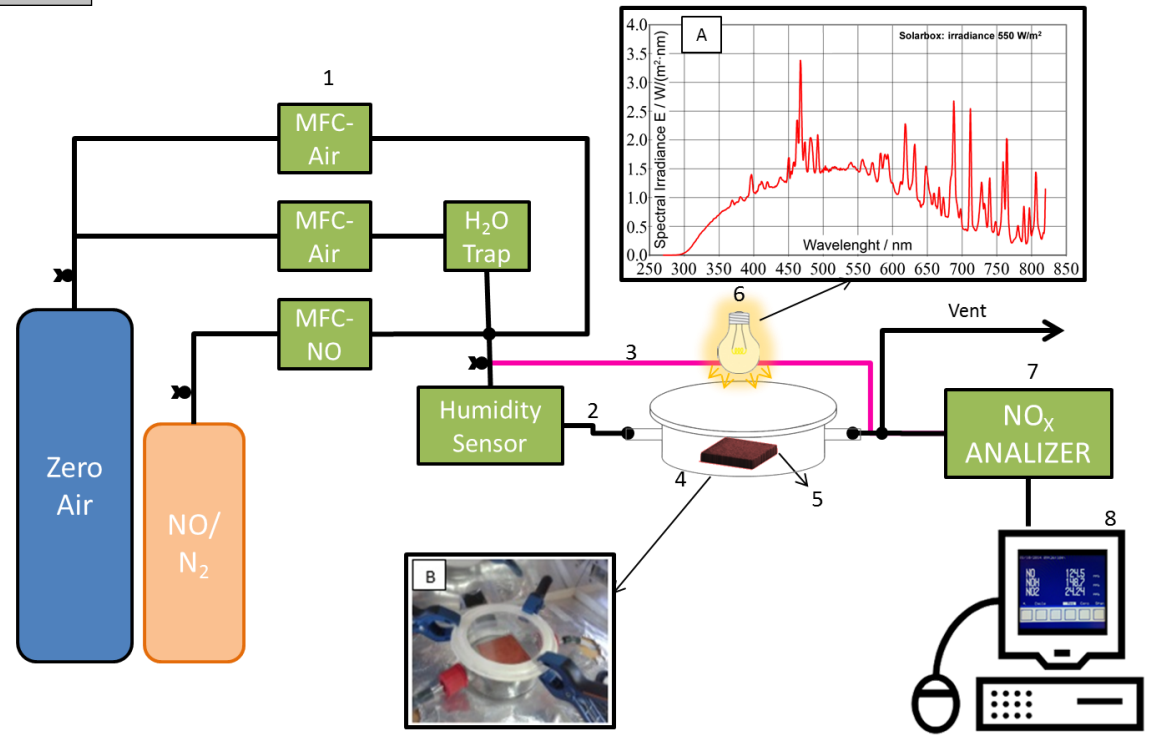
*Sol. RRL* 2021, 5, 2000535  
DOI: 10.1002/solr.202000535

Sue-Faye Ng, Michelle Yu Ling Lau, and Wee-Jun Ong\*

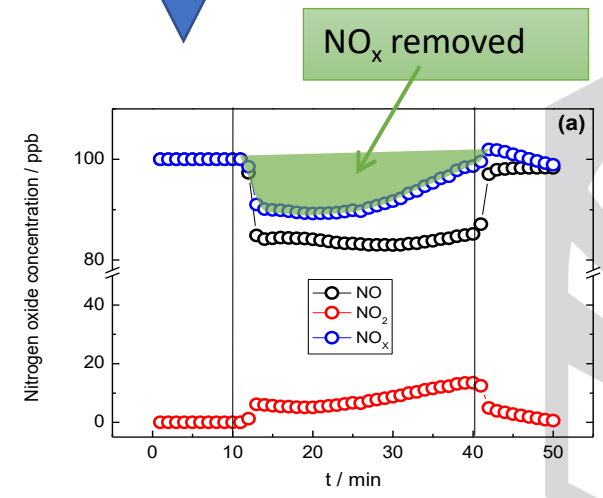


**Figure 1.** a) Divalent and trivalent metal cations in the periodic table which have been studied as the constituents of LDH. b) Number of yearly publications and c) citations from the year 2000–2020 with the topic keywords of “LDH & photocatal\*” in the ISI Web of Knowledge database, dated 24th August 2020. d) Band positions of different LDH photocatalysts with respect to selected redox potentials of H<sub>2</sub>O splitting, CO<sub>2</sub> reduction, and N<sub>2</sub> fixation.

# De-NO<sub>x</sub> test



Standar:  
**Evonik TiO<sub>2</sub>-P25**  
 (75 % anatase + 25 % rutile)





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Contents lists available at ScienceDirect

# Chemical Engineering Journal

journal homepage: [www.elsevier.com/locate/cej](http://www.elsevier.com/locate/cej)



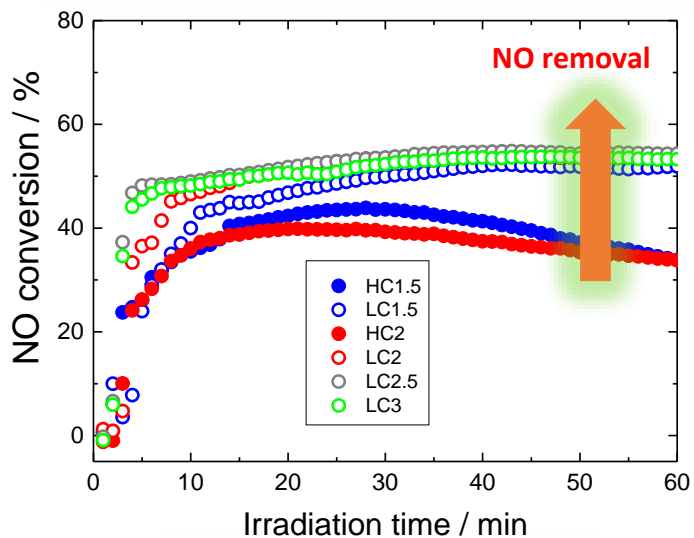
## Zn-Al layered double hydroxides as efficient photocatalysts for NO<sub>x</sub> abatement

Fredy Rodriguez-Rivas<sup>1</sup>, Adrián Pastor, Cristobalina Barriga, Manuel Cruz-Yusta, Luis Sánchez\*, Ivana Pavlovic\*

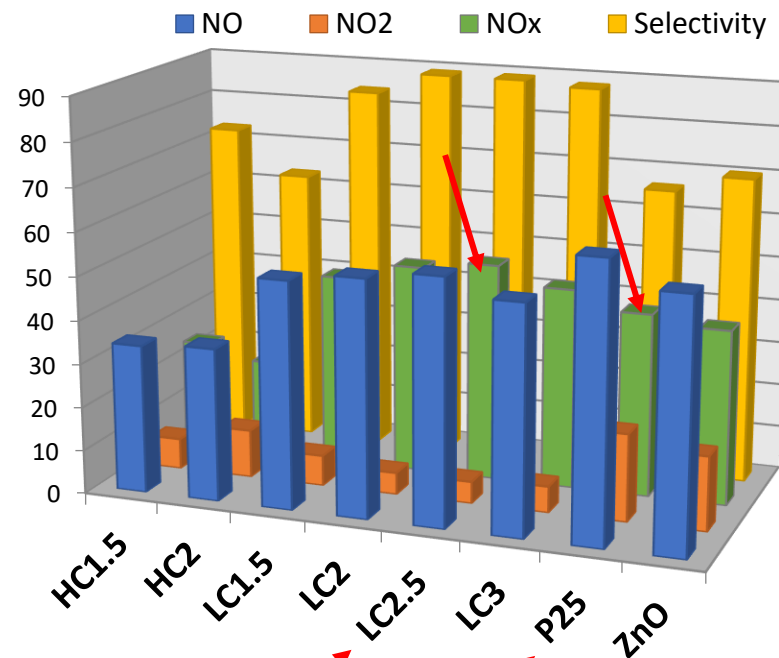
Systems: Zn<sub>x</sub>Al-CO<sub>3</sub> (x : 1.5 – 3.0)

Key factors:

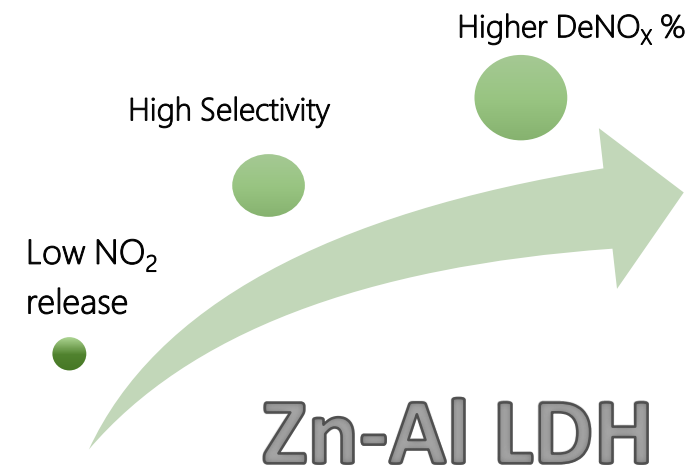
Specific surface area  
Zn/Al ratio



NO conversion efficiencies

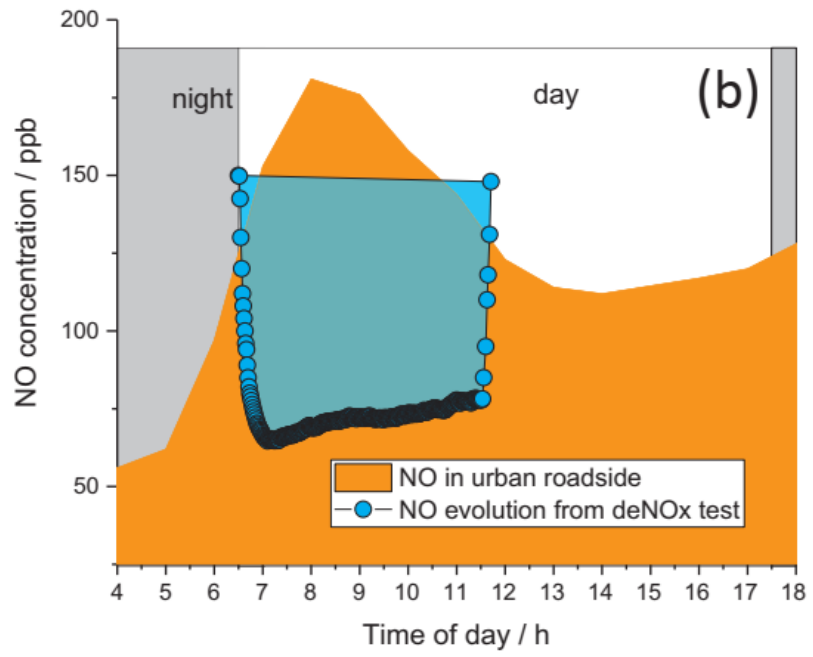


NO and NO<sub>x</sub> conversion, NO<sub>2</sub> released and selectivity values.

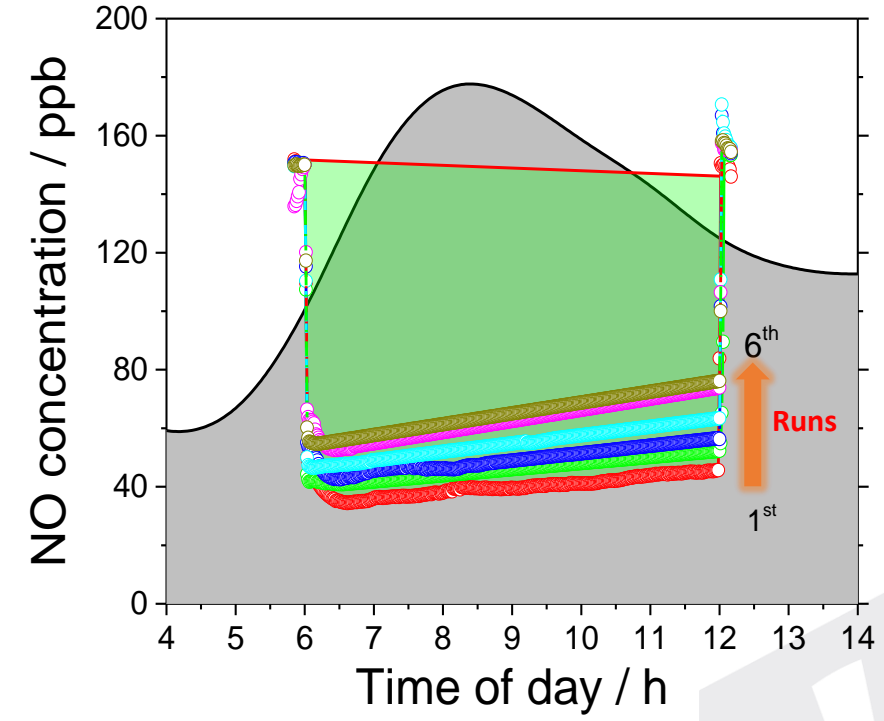




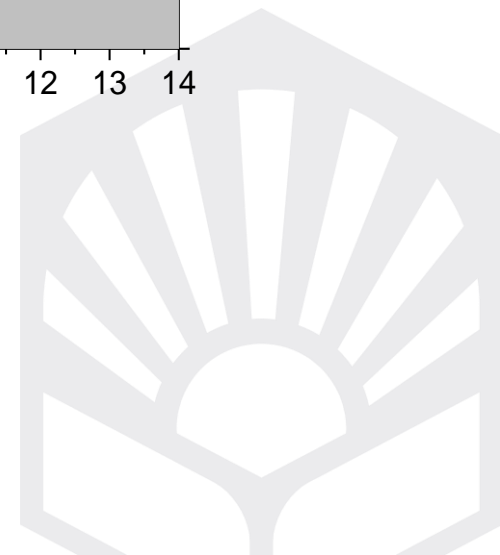
# Photocatalytic De-NOx test ZnAl systems



Good reusability



*!! Potential application to remove NOx gases from road traffic!!*





Contents lists available at [ScienceDirect](#)

## Chemical Engineering Journal

journal homepage: [www.elsevier.com/locate/cej](http://www.elsevier.com/locate/cej)



Chemosphere 275 (2021) 130030

### Effects of Fe<sup>3+</sup> substitution on Zn-Al layered double hydroxides for enhanced NO photochemical abatement

Adrián Pastor<sup>a</sup>, Fredy Rodriguez-Rivas<sup>a,b</sup>, Gustavo de Miguel<sup>c</sup>, Manuel Cruz-Yusta<sup>a</sup>, Francisco Martín<sup>d</sup>, Ivana Pavlovic<sup>a,\*</sup>, Luis Sánchez<sup>a,\*</sup>

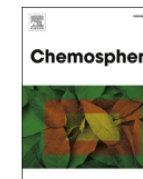
Science of the Total Environment 706 (2020) 136009



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## Chemosphere

journal homepage: [www.elsevier.com/locate/chemosphere](http://www.elsevier.com/locate/chemosphere)



### Insight into the role of copper in the promoted photocatalytic removal of NO using Zn<sub>2-x</sub>Cu<sub>x</sub>Cr-CO<sub>3</sub> layered double hydroxide

J. Fragoso<sup>a</sup>, M.A. Oliva<sup>a</sup>, L. Camacho<sup>b</sup>, M. Cruz-Yusta<sup>a</sup>, G. de Miguel<sup>b</sup>, F. Martín<sup>c</sup>, A. Pastor<sup>a</sup>, I. Pavlovic<sup>a,\*</sup>, L. Sánchez<sup>a,\*\*</sup>



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## Science of the Total Environment

journal homepage: [www.elsevier.com/locate/scitotenv](http://www.elsevier.com/locate/scitotenv)



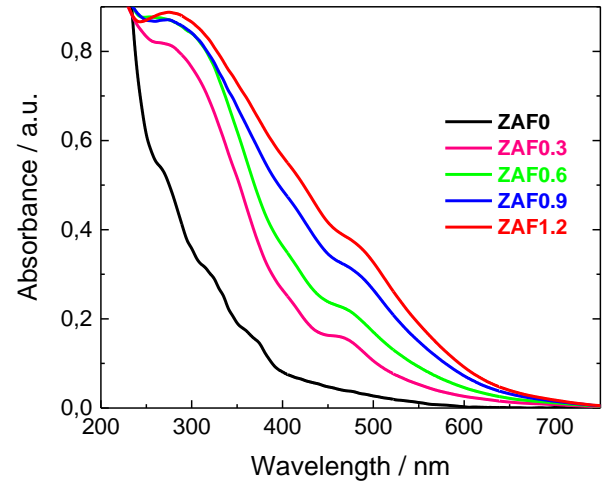
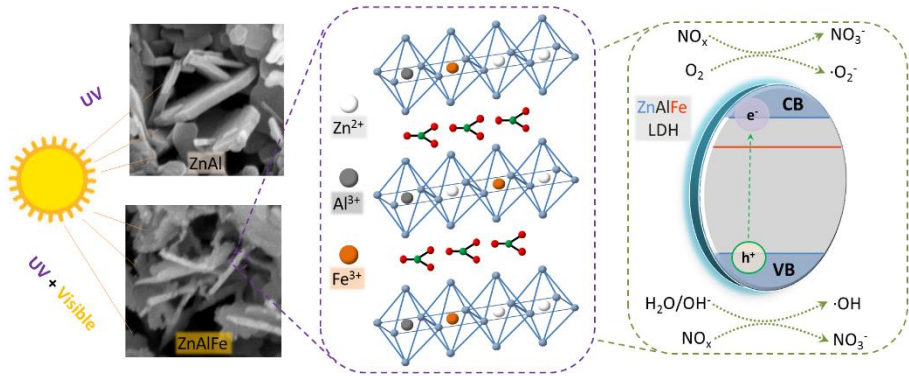
### Cr<sup>3+</sup> substituted Zn-Al layered double hydroxides as UV-Vis light photocatalysts for NO gas removal from the urban environment

Fredy Rodriguez-Rivas<sup>a,b</sup>, Adrián Pastor<sup>a</sup>, Gustavo de Miguel<sup>c</sup>, Manuel Cruz-Yusta<sup>a</sup>, Ivana Pavlovic<sup>a</sup>, Luis Sánchez<sup>a,\*</sup>

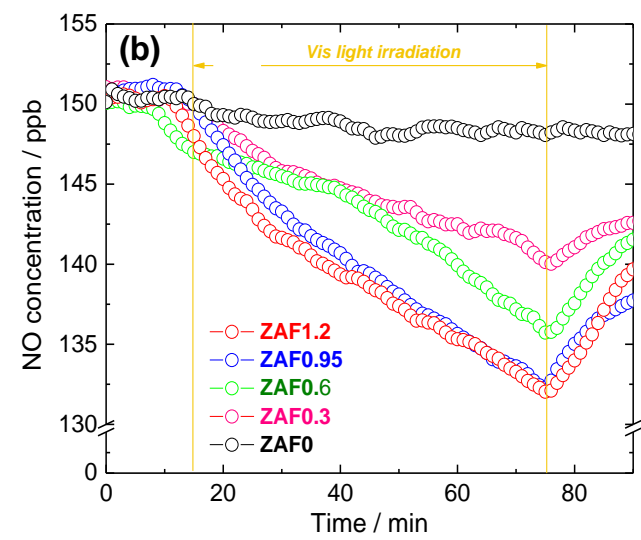


# Systems: $Zn_3Al_{1-x}Fe_x-CO_3$ ( $x : 1.5 - 3.0$ )

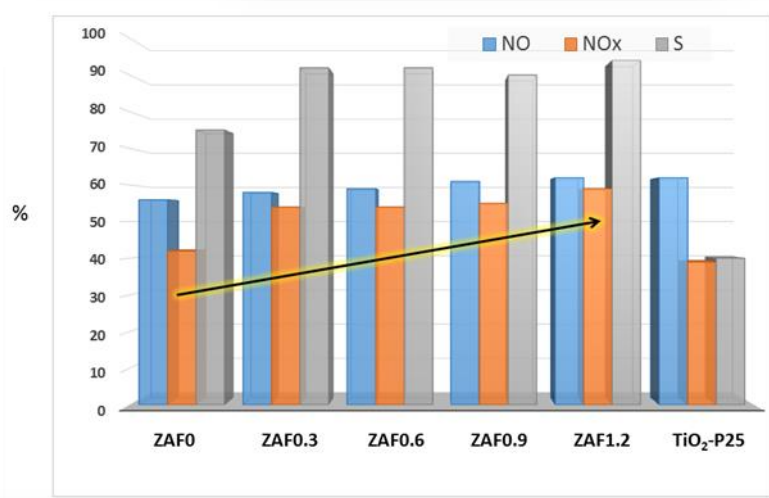
# Visible light De-NO<sub>x</sub> photocatalysis



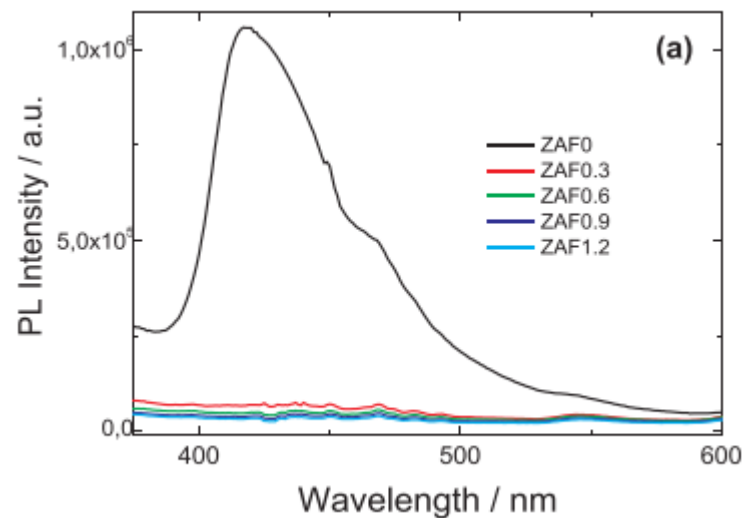
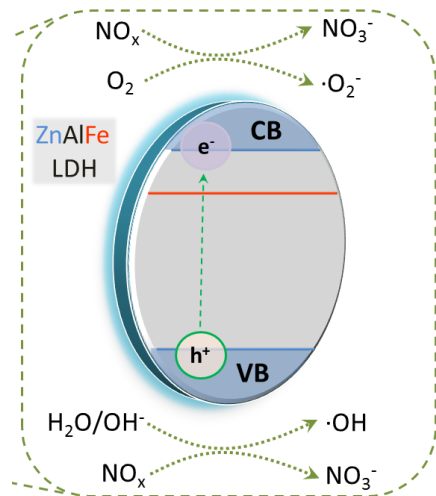
The UV-Vis absorption spectra



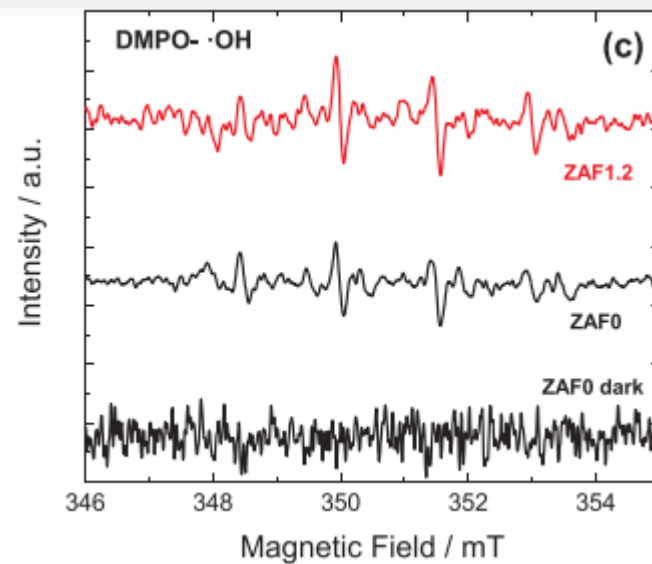
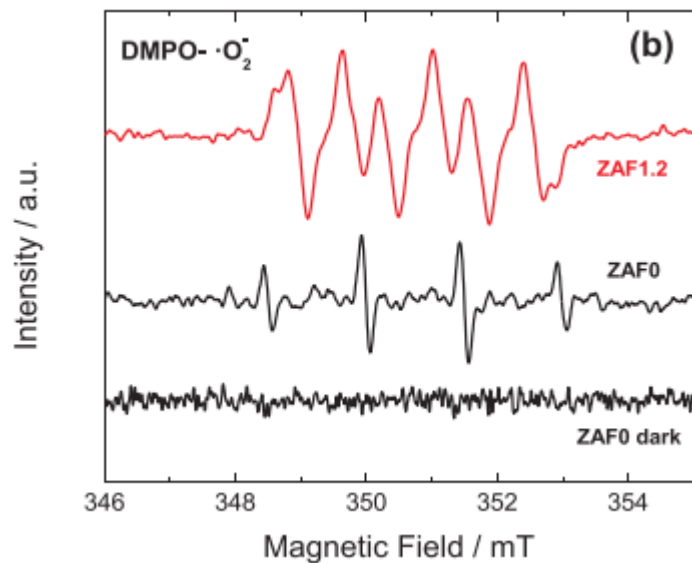
Nitrogen oxides concentration profiles



NO conversion, NO<sub>x</sub> conversion and Selectivity values (%)



Photoluminescence (PL) spectra (excitation wavelength = 300 nm)



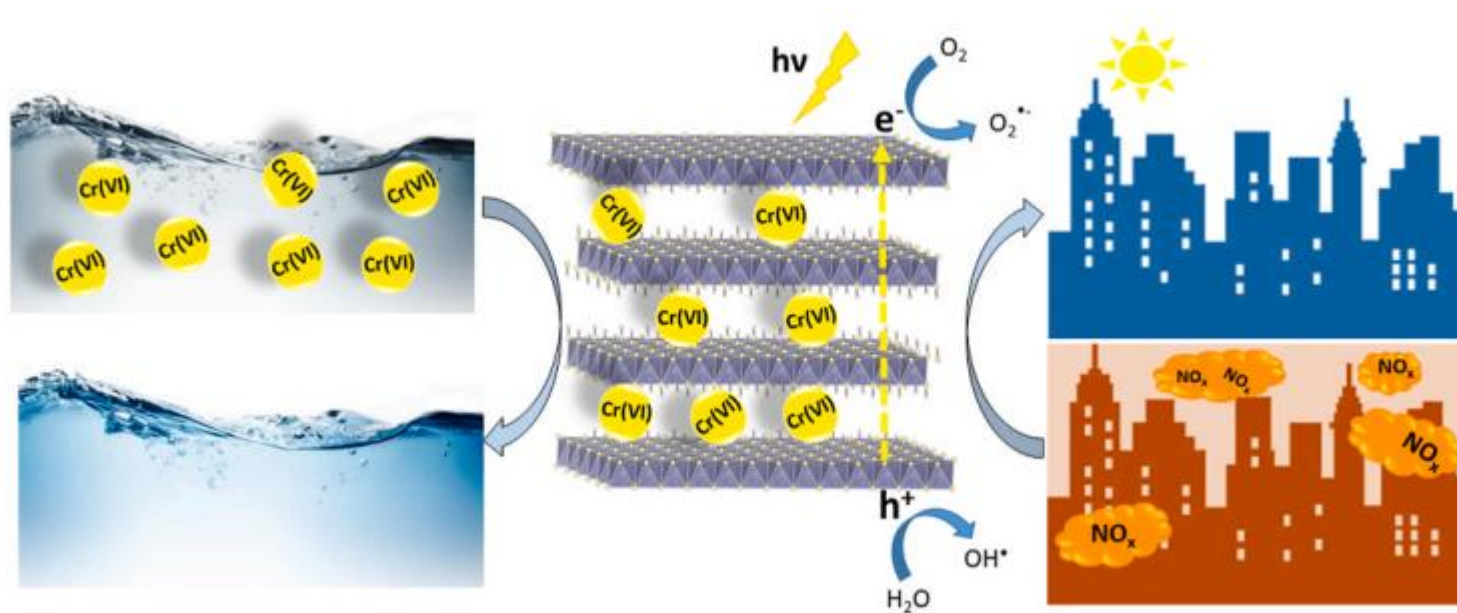
DMPO spin-trapping EPR spectra



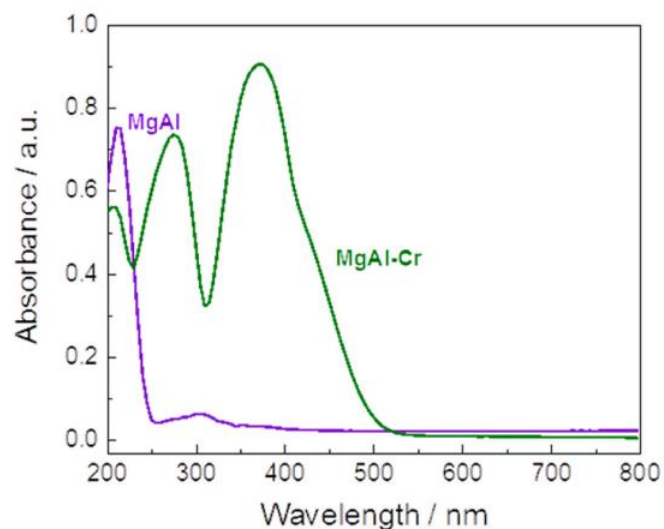


## Use of LDH- chromate adsorption co-product as an air purification photocatalyst

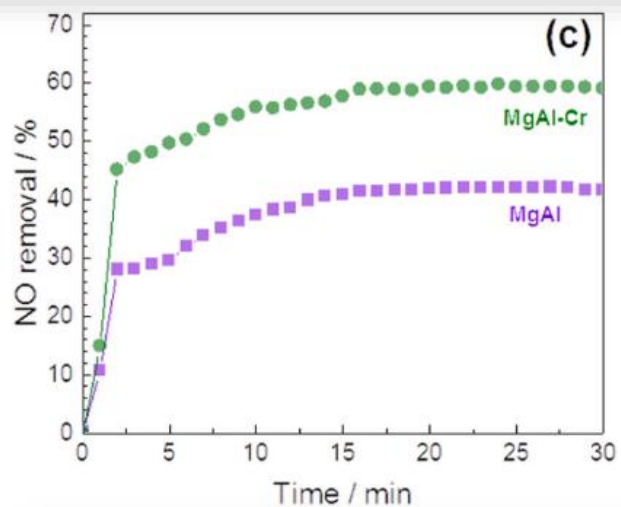
A. Nehdi<sup>a</sup>, N. Frini-Srasra<sup>a,b</sup>, G. de Miguel<sup>c</sup>, I. Pavlovic<sup>d,\*</sup>, L. Sánchez<sup>d</sup>, J.Fragoso<sup>d,\*\*</sup>



# System: $\text{Mg}_3\text{Al-CrO}_4$

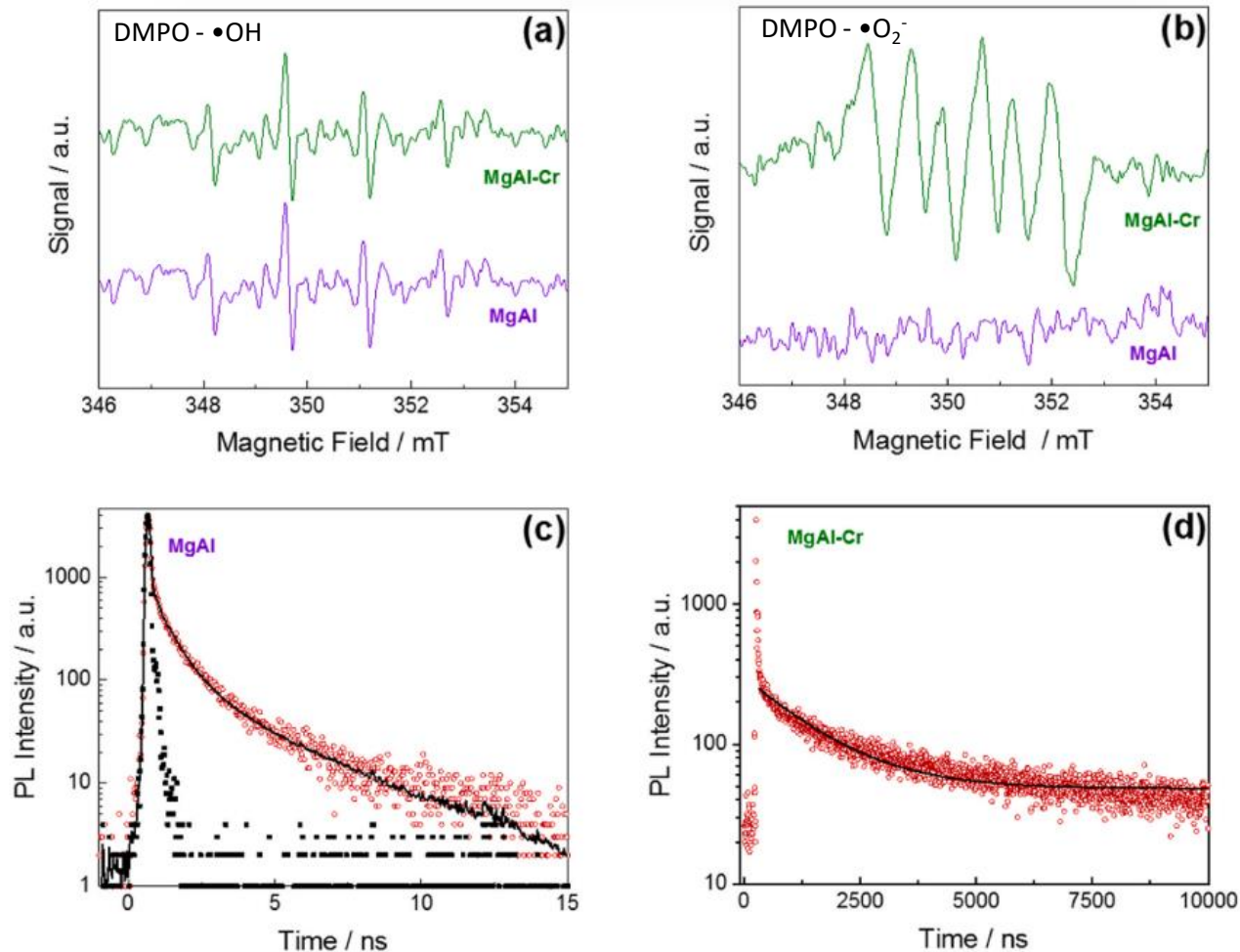


UV-Vis absorption spectra of the MgAl and MgAl-Cr samples.



NO removal efficiency for both LDH samples.

DMPO spin-trapping EPR spectra of the MgAl and MgAl-Cr samples



Decay times of the (c) MgAl and (d) MgAl-Cr samples.



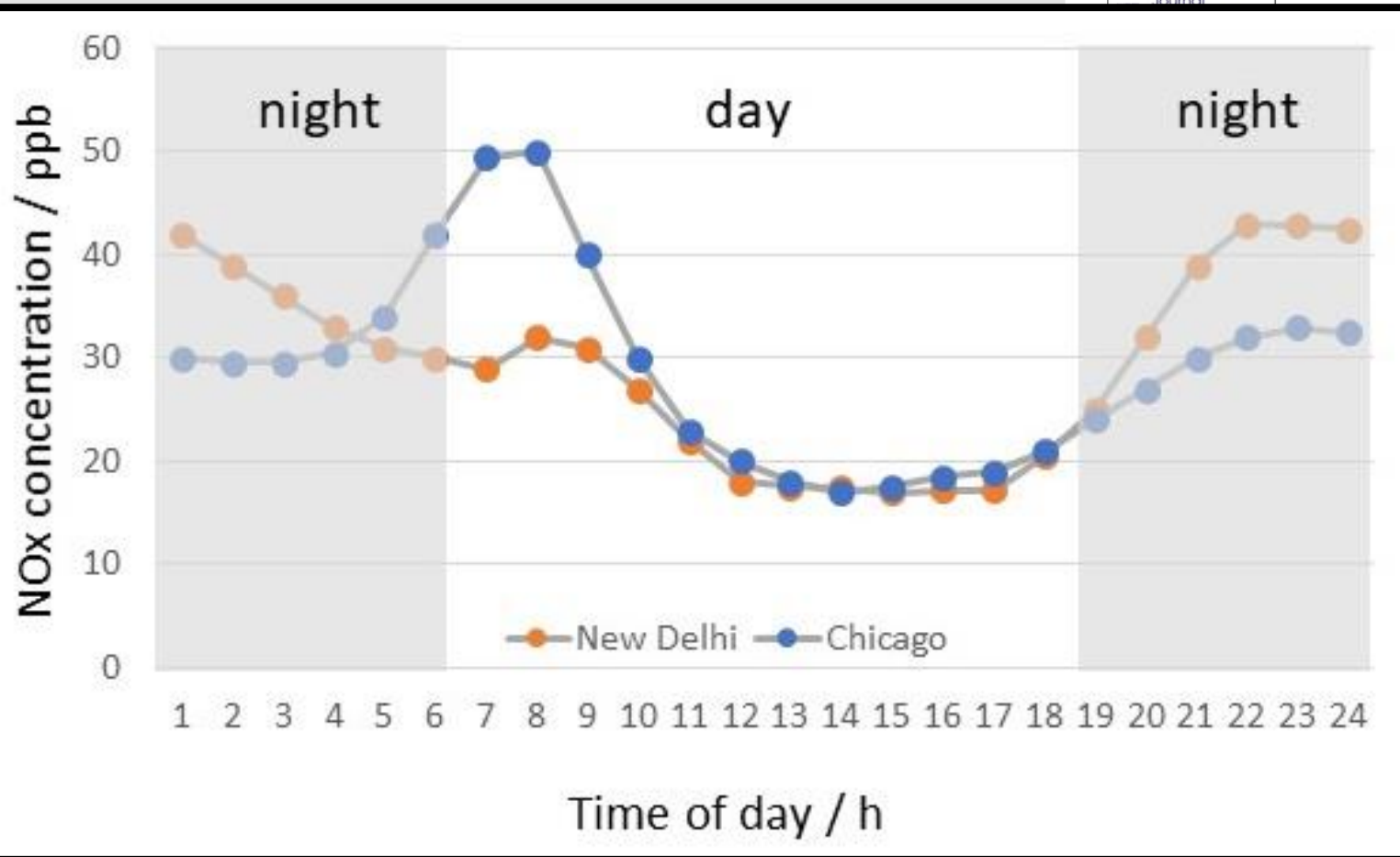
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Aqueous misci  
De-NO<sub>x</sub> photo

Adrián Pastor<sup>a</sup>, Ch  
Jean-Charles Buffe

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Chemical  
Engineering  
Journal

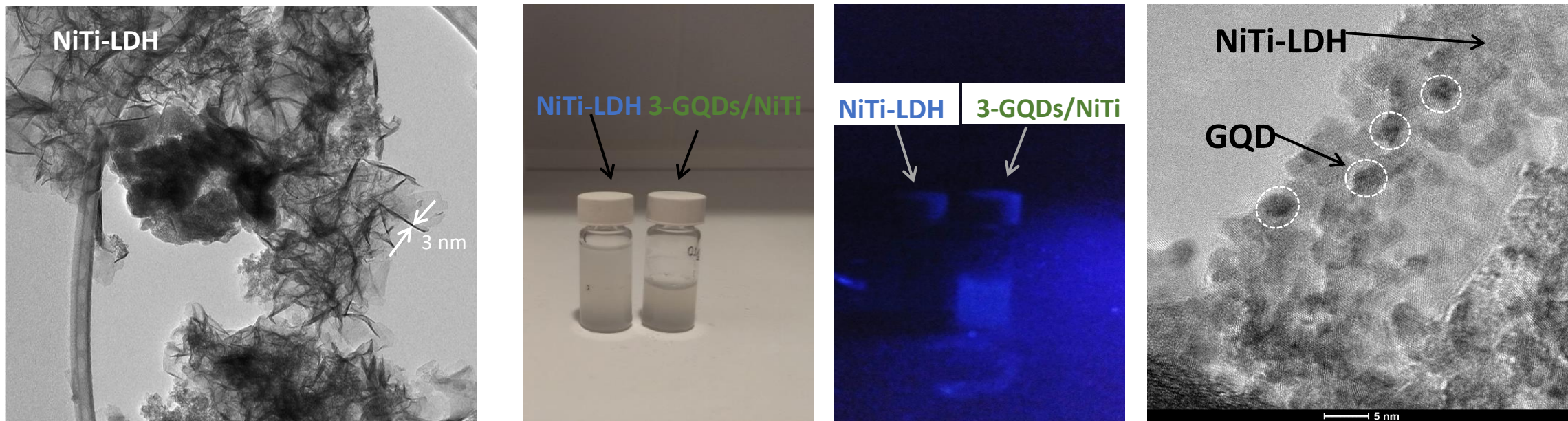


a highly efficient De-



Graphene quantum dots/NiTi layered double hydroxide heterojunction as a highly efficient De-NO<sub>x</sub> photocatalyst with long persistent post-illumination action.

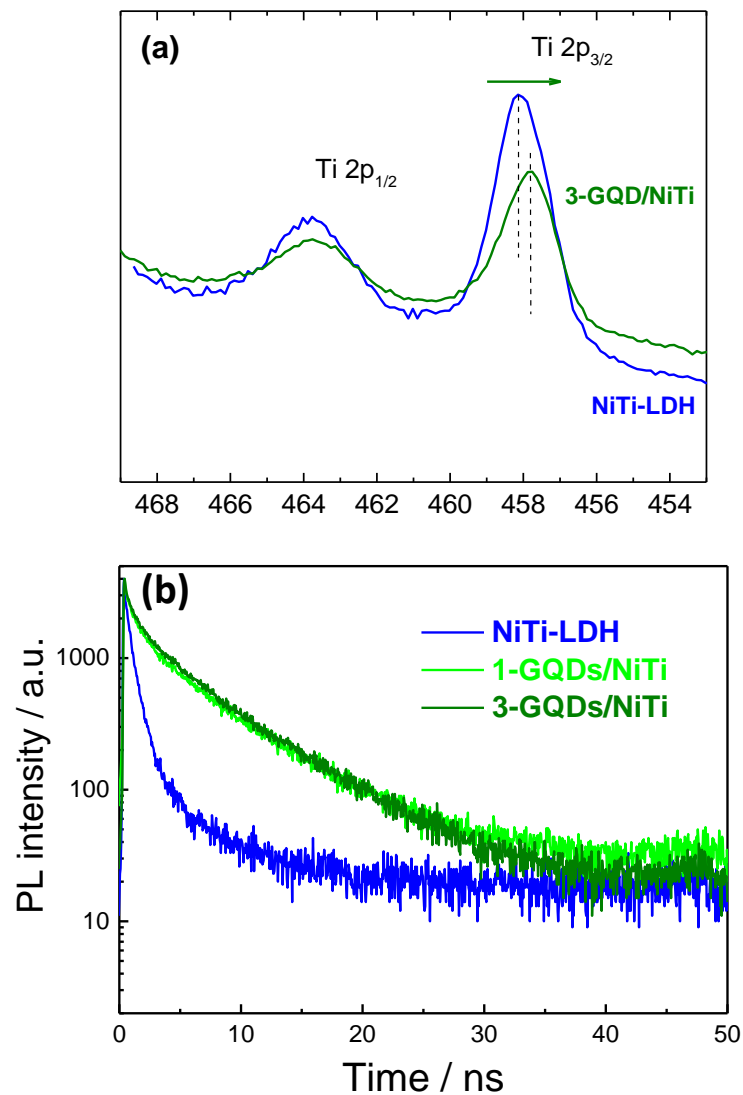
*(Appl. Cat B: Environmental – revision submitted)*



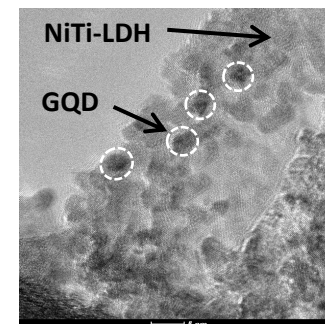
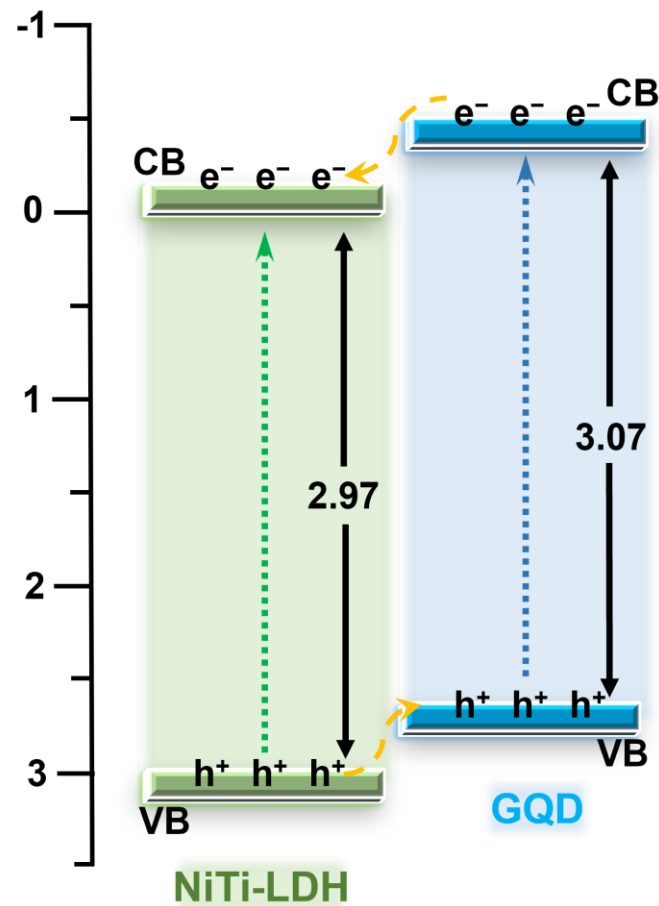
**Figure 2:** NiTi-LDH nanosheets (left). NiTi-LDH and GQDS/NiTi dispersions in light and dark conditions (center). HRTEM image for 3-GQD/NiTi sample (right) .





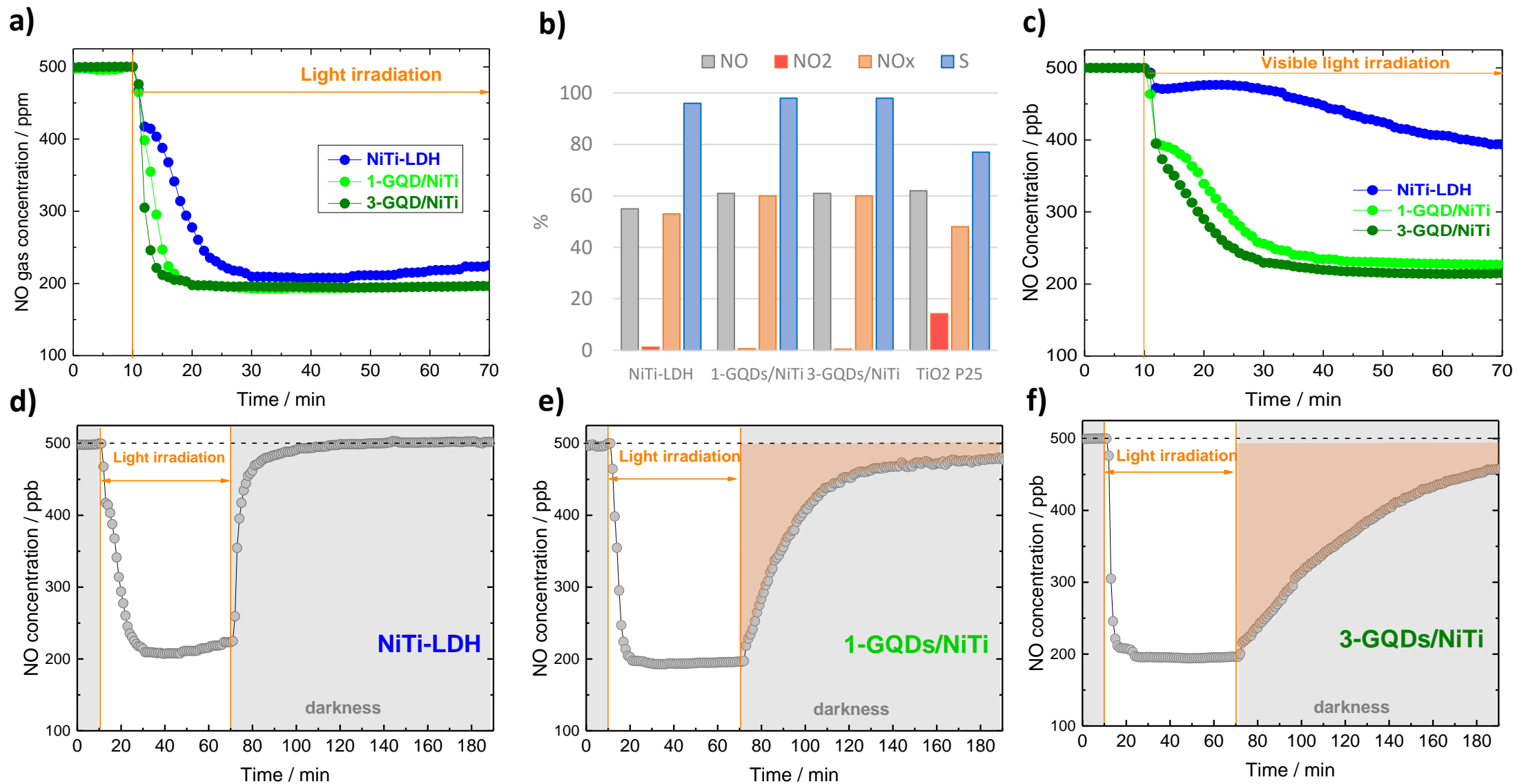


Potential vs. NHE (V)

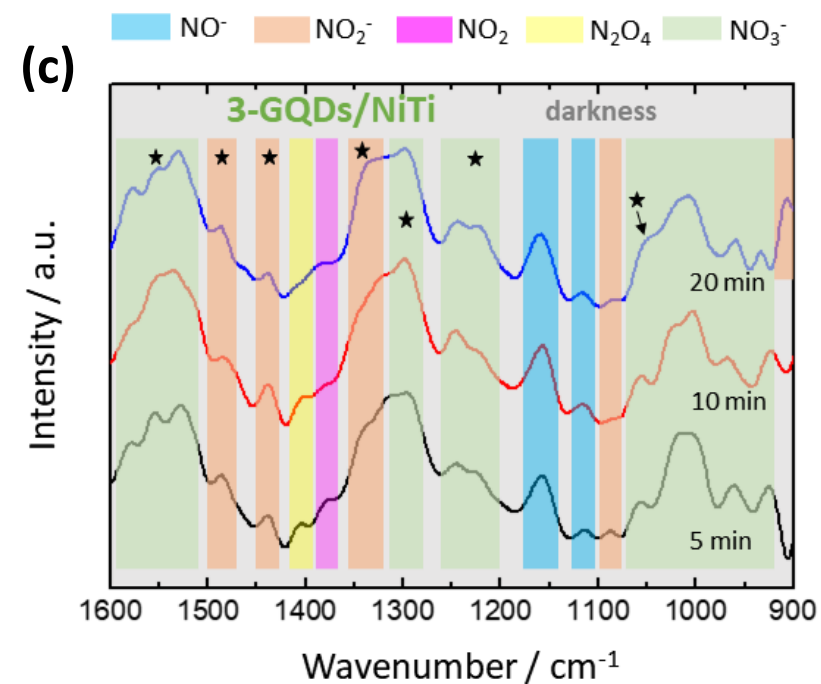
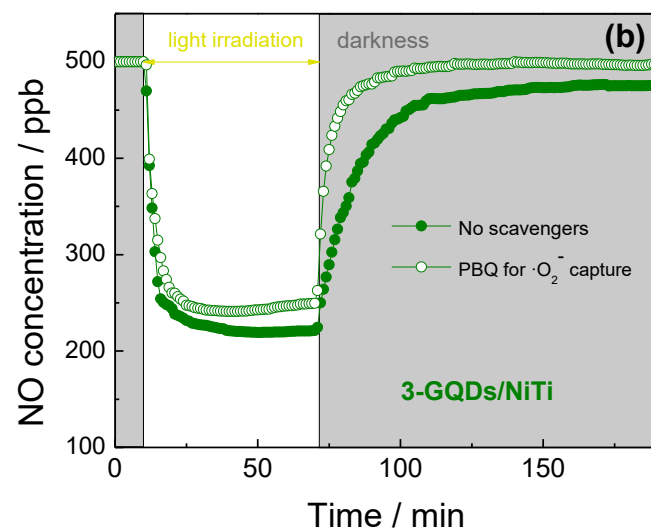
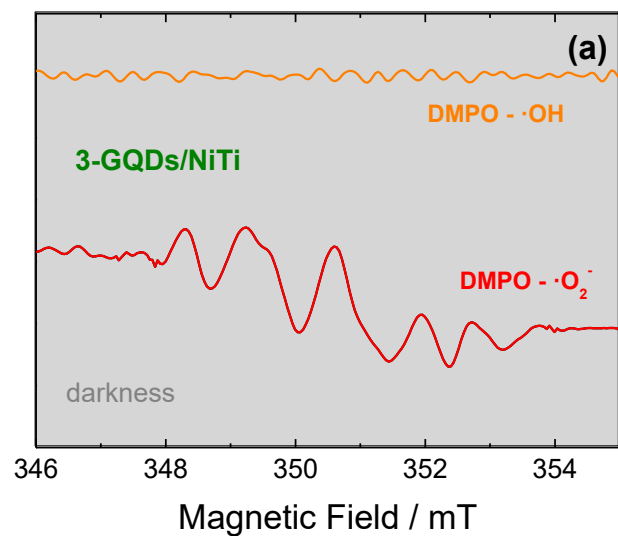


**Figure 3:** (a) XPS Ti 2p and (b) Time decay of the PL signals for NiTi-LDH and GQDs/NiTi samples.





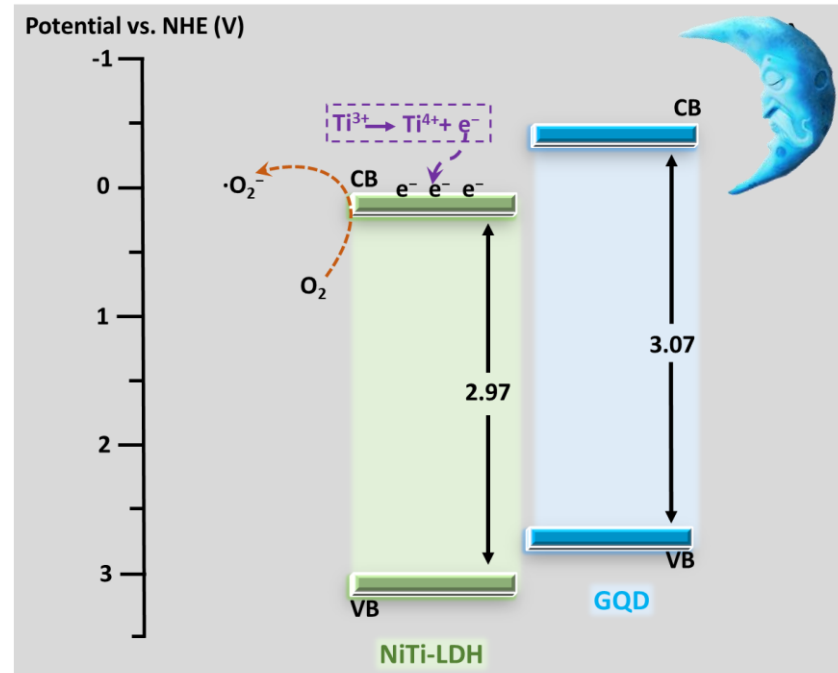
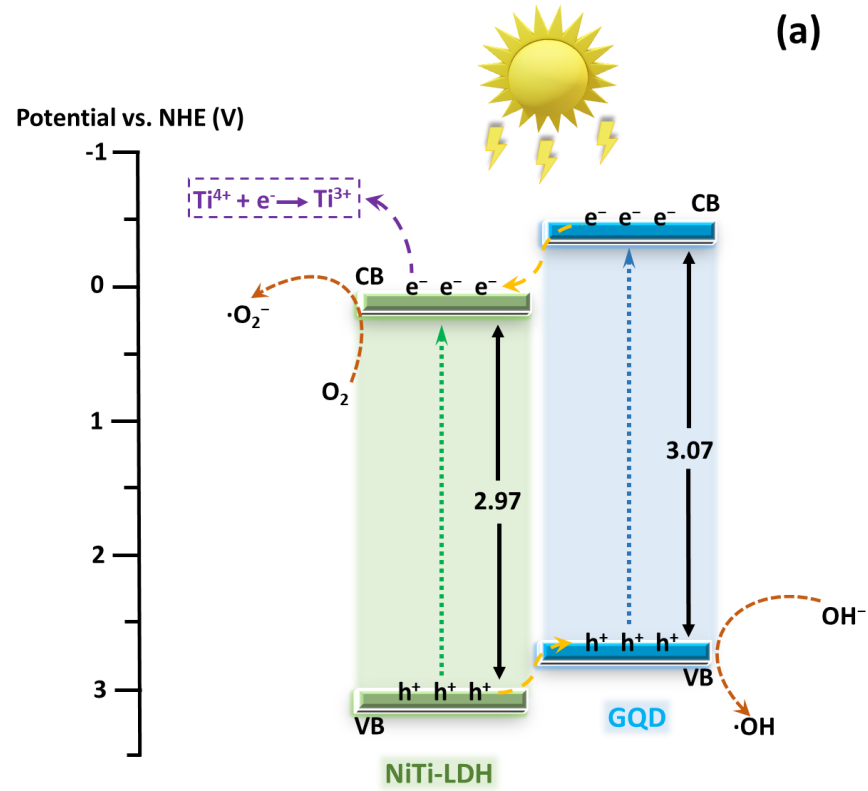
**Figure 4:** (a) Gas concentration evolution during the photodegradation of NO under (a) UV-Vis or (c) visible light irradiation on NiTi-LDH and GQDs/NiTi samples. (b) NO conversion, NO<sub>2</sub> emitted, NO<sub>x</sub> conversion and selectivity values (%). (e - f) Gas concentration evolution during the catalytic reaction of NO in light/dark periods on NiTi-LDH and GQDs/NiTi samples.



**Figure 5:** (a) DMPO spin-trapping EPR spectra, (b) active species trapping experiments and (c) in situ DRIFTS spectra for 3-GQD/NiTi sample. (a) and (c) measurements were done in the dark for the pre-illuminated 3-GQDs/NiTi sample.



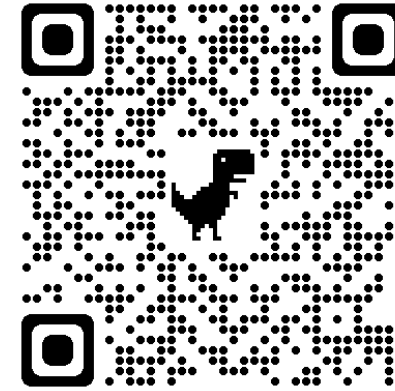
# Photocatalytic and energy storage mechanisms



Thanks for your attention!!



Visit us on: <https://www.2d2denox.org/>



### Acknowledgements.

This work was partly financed by **FEDER 2014-2020** program (Consejería de Economía, Conocimiento, Empresas y Universidad de la Junta de Andalucía) and Agencia Estatal de Investigación (Spain; **PID2020-117516GB-I00**).

