Graphene quantum dots/NiTi-LDH as a highly efficient day-night air purification photocatalyst

J. Fragoso,[1] M. Cruz-Yusta,[1] F. Martín,[2] A. Pastor,[1] I. Pavlovic,[1] L. Sánchez [1]

1.- Departamento de Química Inorgánica e Ingeniería Química - IUNAN, Universidad de Córdoba, Córdoba, Spain. (luis-sanchez@uco.es)

2.- Departamento de Ingeniería Química, Universidad de Málaga, Málaga, Spain

UNIVERSIDAD DE CÓRDOBA

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Photocatalytic processes have been deeply studied as adequate environmental remediation tools for the removal of NOx gases (NOx = NO + NO_2 ; **DeNOx** action), causing serious environmental problems and could have negative effects on human health [1]. The typical curve of NOx emission variation in populated cities [2] (Figure 1) shows that NOx concentration levels increase after sunset, a night period in which photocatalysis cannot be developed. Therefore, it is very interesting to study new systems that allow the DeNOx process to be maintained once the solar irradiation is finished. In this work, we have successfully implemented the preparation of graphene quantum dots/layered double hydroxides (GQDs/LDH) as a new and efficient DeNOx photocatalyst. We have prepared $Ni_3Ti\text{-}CO_3$ LDHs nanosheets by the Aqueous Miscible Organic Solvent Treatment (AMOST) [3]. The treated LDH was subsequently mixed with blue luminescent graphene quantum dots to form a 0D/2D composite, Figure 2. We found that GQDs/Ni_3Ti composites show strong persistent DeNOx action even when light irradiation is turned off.

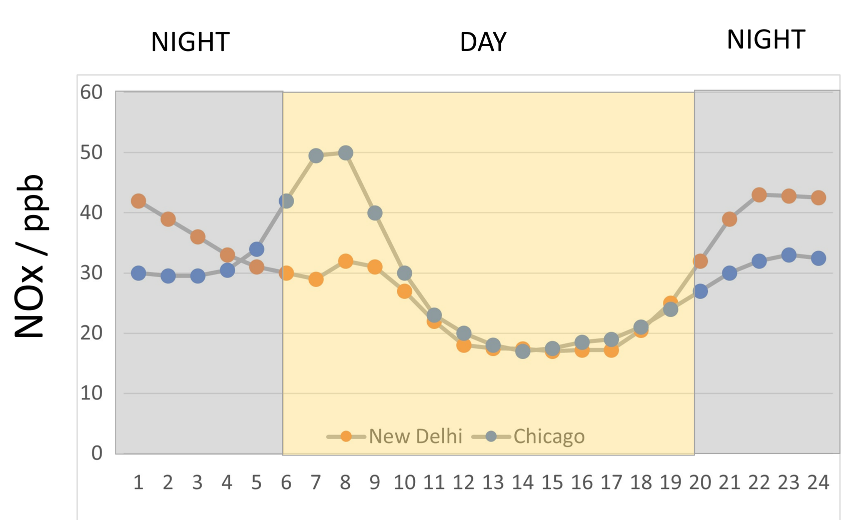


Figure 1: Profiles of daily NOx concentrations at urban centres

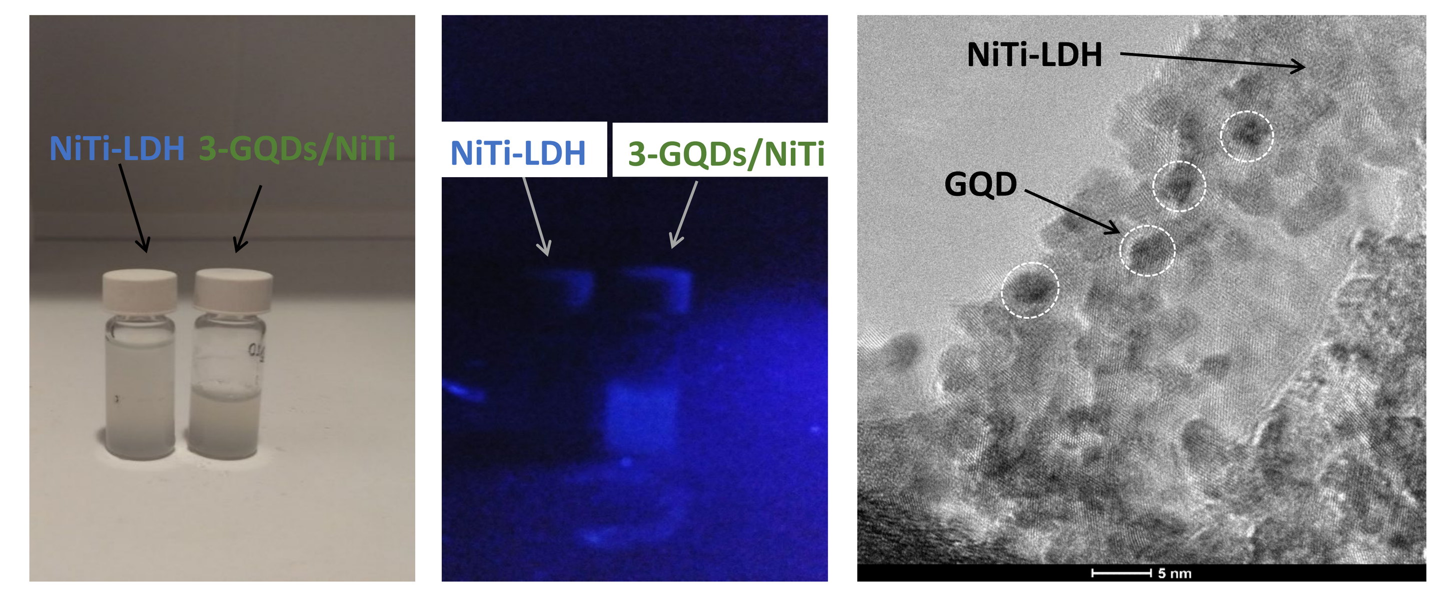


Figure 2: NiTi-LDH and GQDS/NiTi dispersions in light (left) and dark (centre) conditions. HRTEM image (right) for 3-GQD/NiTi sample.

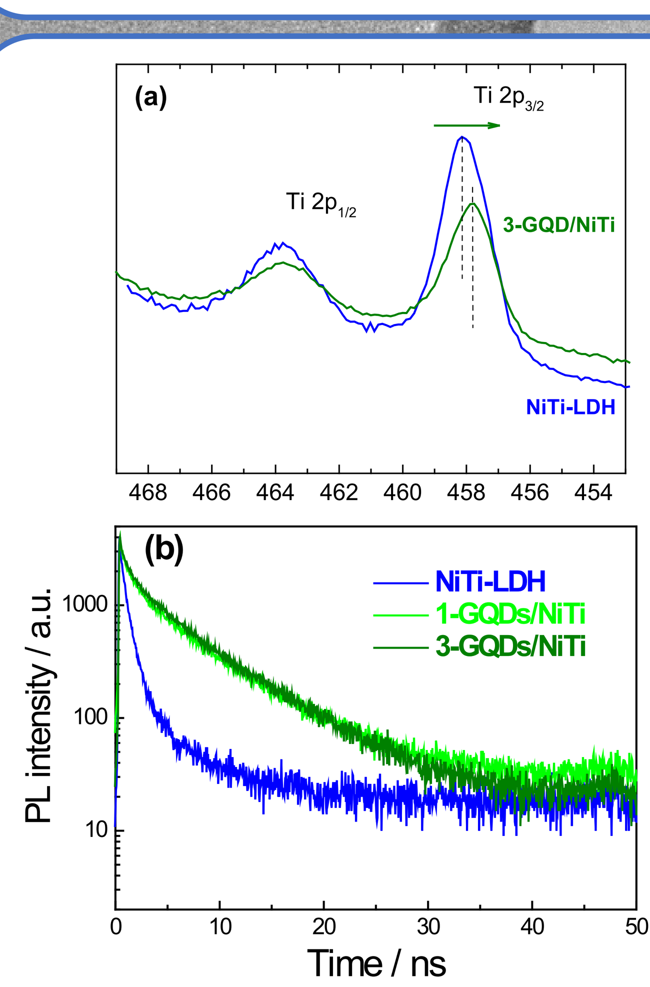
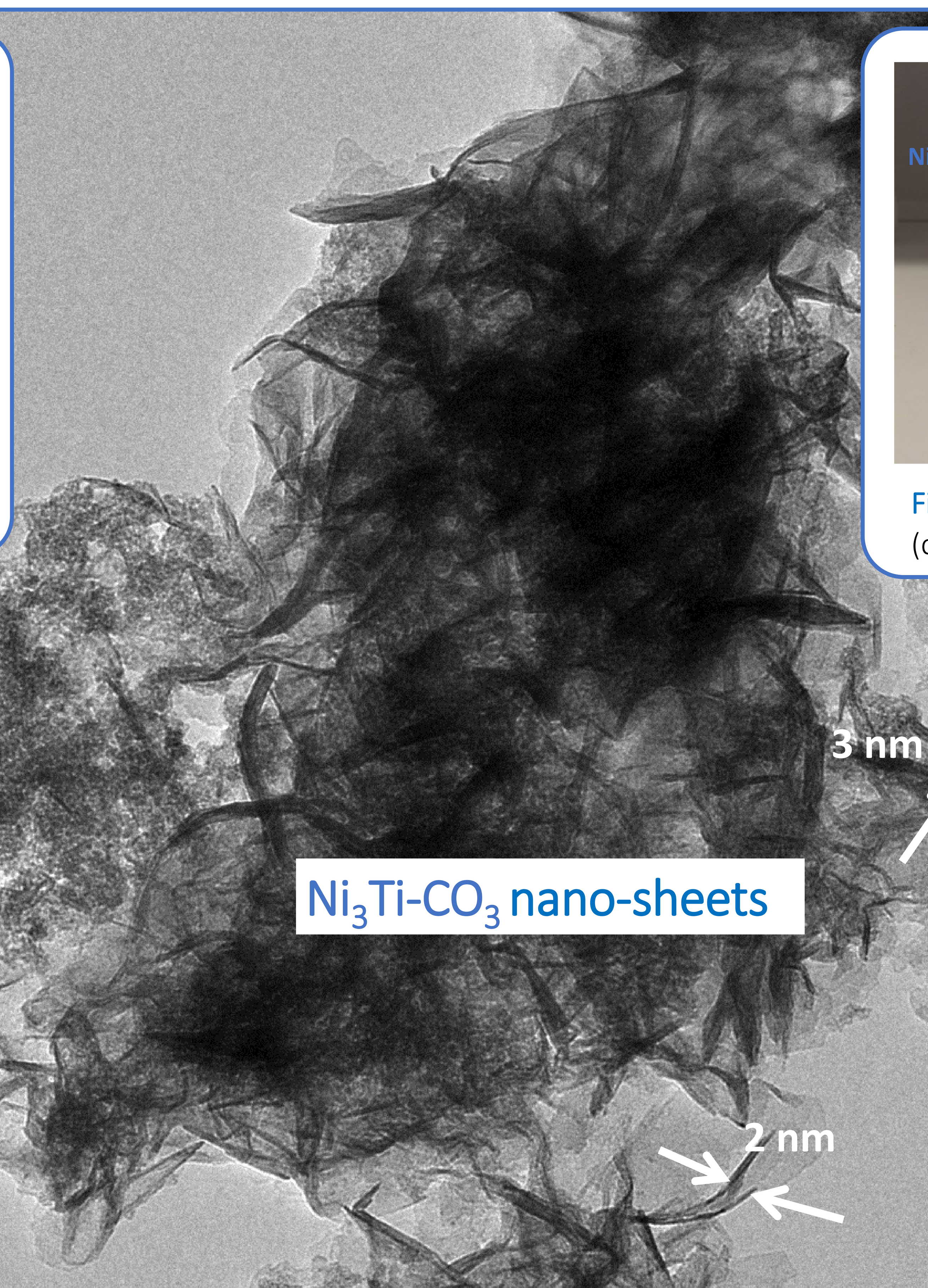
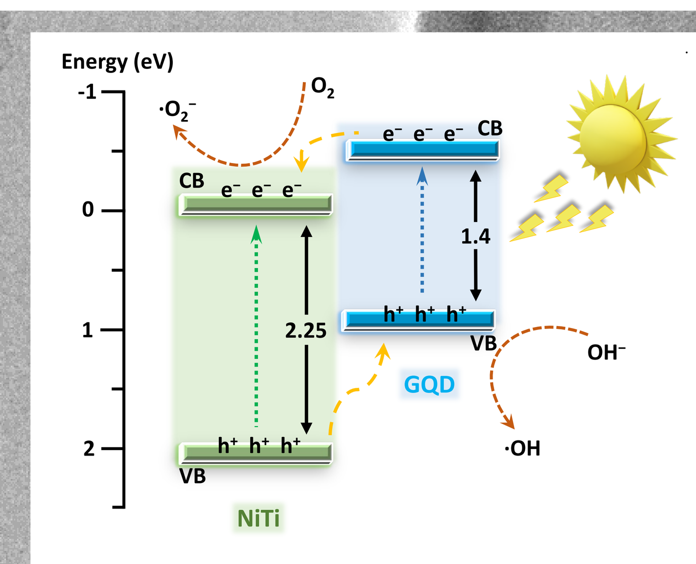


Figure 3: (a) XPS Ti 2p and (b) Time evolution of the PL signals for NiTi-LDH and GQDs/NiTi samples.



0D/2D Heterojunction



Persistent DeNOx action in the dark

Photocatalytic NO removal

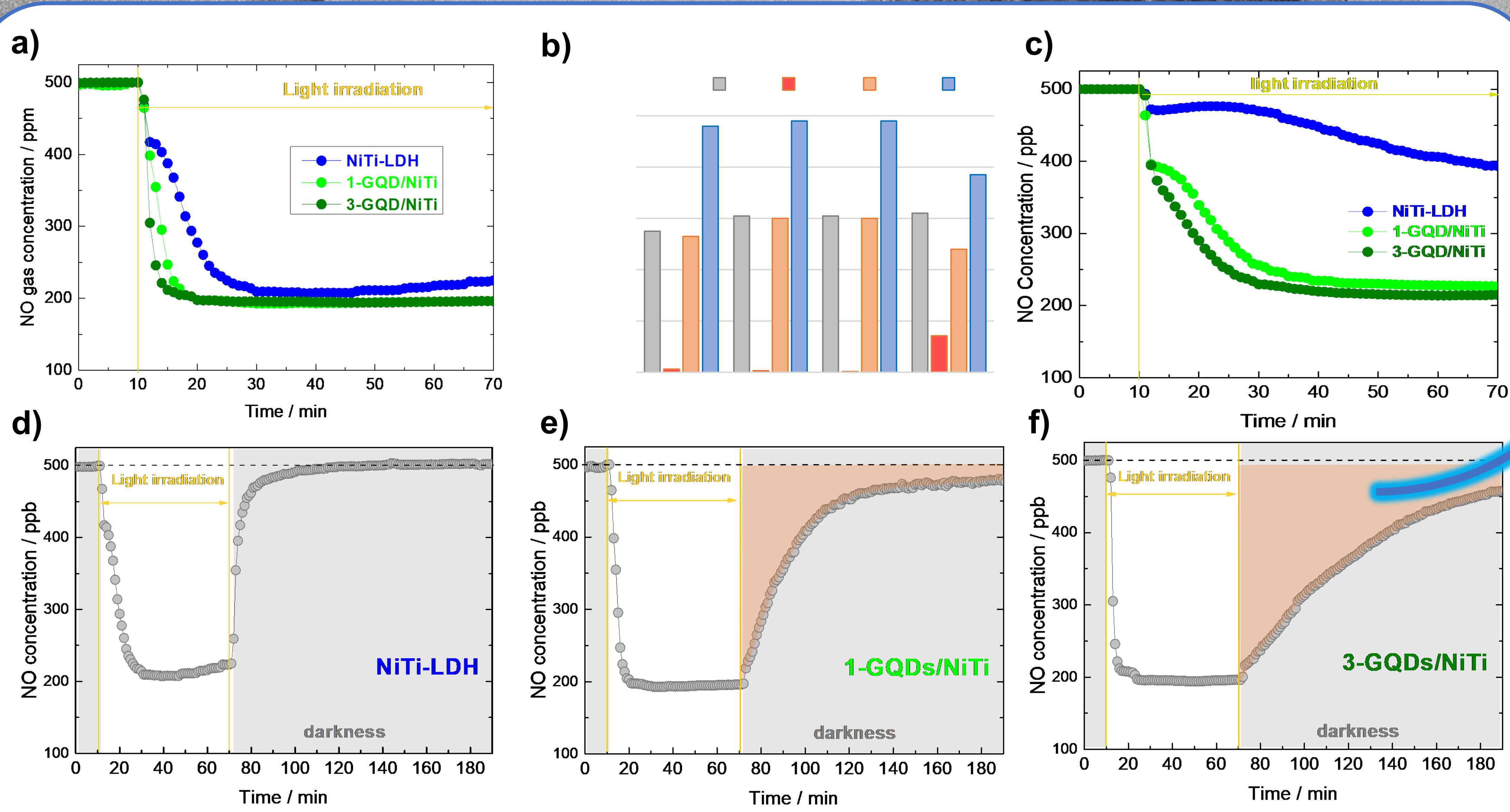


Figure 4: (a) Gas concentration evolution during the photodegradation of NO under (a) UV-Vis or (c) visible light irradiation on NiTi-LDH and GQDs/NiTi samples. (b) NO conversion, NO_2 emitted, NOx conversion and selectivity values (%). (e - f) Gas concentration evolution during the catalytic reaction of NO in light/dark periods on NiTi-LDH and GQDs/NiTi samples.

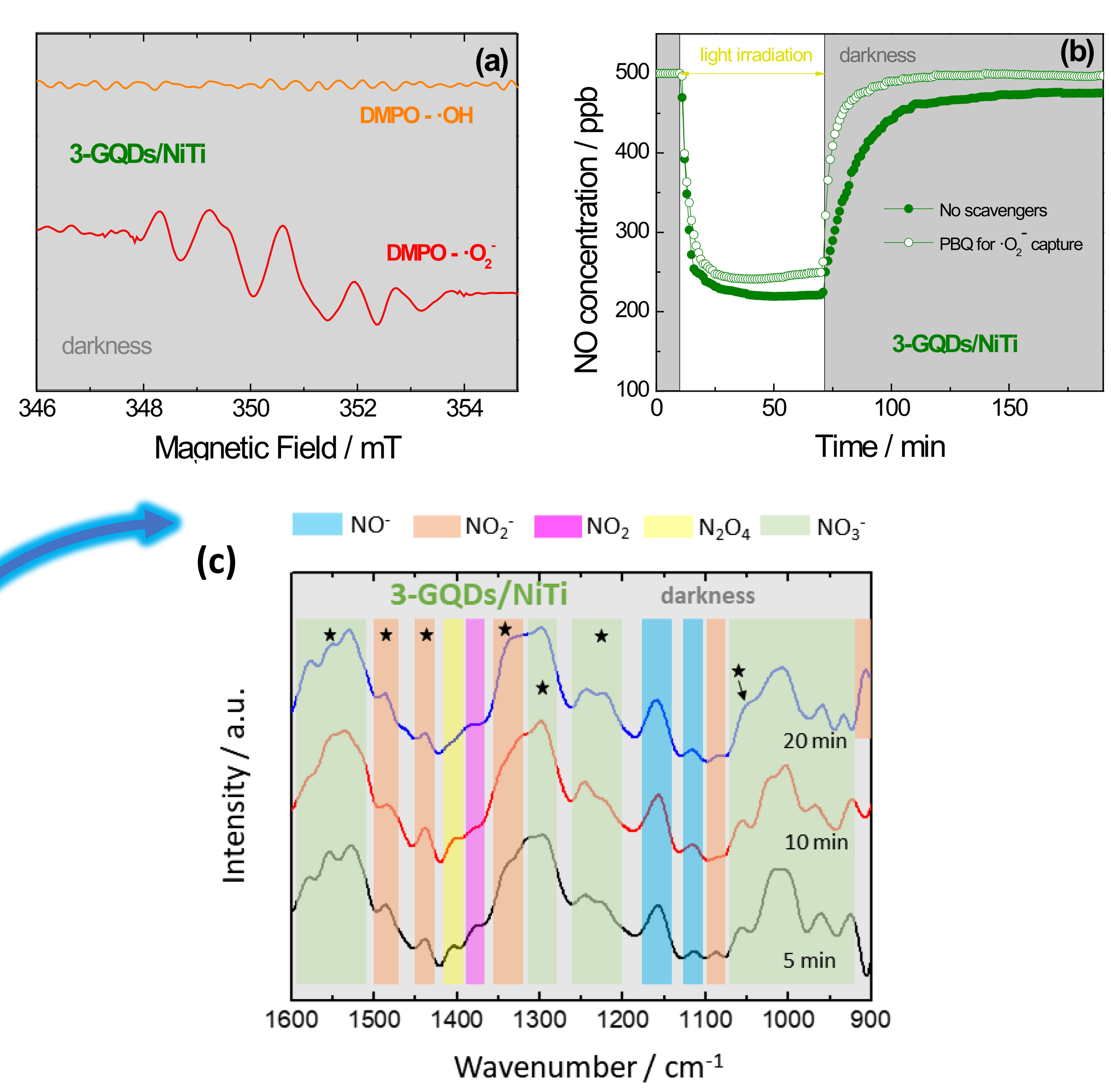


Figure 5: (a) DMPO spin-trapping EPR spectra, (b) active species trapping experiments and (c) in situ DRIFTS spectra for 3-GQD/NiTi sample. (a) and (c) measurements were done in the dark for the pre-illuminated 3-GQDs/NiTi sample.

RESULTS

Preparation of 0D/2D heterostructures between NiTi-LDH and luminescent GQDs (**Figure 2**) brings several advantages to the DeNOx process, as a consequence of lower electron/hole recombination (**Figure 3**). GQDs incorporation led to a better DeNOx response of GQDs/NiTi photocatalysts compared to NiTi-LDH, mainly under visible light. GQDs/NiTi are highly selective towards the NO photo-oxidation process and, therefore, exhibit higher NOx gases abatement values than standard TiO_2 P25 photocatalyst. Once the light is off, a large persistence of the catalytic process is observed for the GQDs/NiTi compounds (**Figure 4**). Simultaneously to the NO → NO_2^- → NO_2 → NO_3^- photo-oxidative process, a part of excited electrons occurring during the light irradiation period are trapped and stored by the GQDs particles. In the dark the stored electrons are released again, favouring the formation of superoxide radicals which maintain the DeNOx process in the dark (**Figure 5**). We can conclude that GQDs/NiTi heterostructure provide a new approach to develop novel persistent photocatalytic systems with the goal of practical day/night photocatalysis applications.

References: [1]: 10.1166/jnn.2015.10871;
[2]: 10.1016/j.atmosenv.2017.12.028;
[3]: 10.1016/j.cej.2021.132361

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