# AMO-NiTi layered double hydroxide nanosheets for photocatalytic removal of NOx pollutant

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## INTRODUCTION

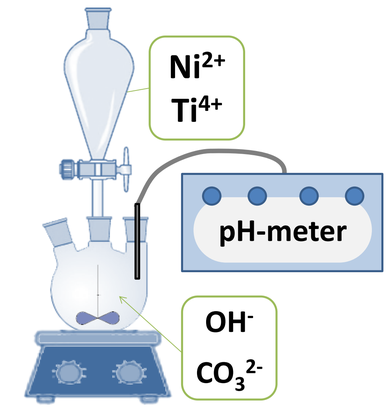
Nowadays, it is greatly concerning the harmful effects provoked over the environment and citizens by the urban pollution of NOx (NO + $NO_2$) gases [1].

With the aim to remediate this problem, photocatalytic Layered Double Hydroxides (LDH) have been applied recently to remove these pollutants (De-NOx action) directly from the air [2]. LDHs have a type-brucite structure consisting of sheets of metal hydroxications, while the interlaminar space contains certain inorganic or organic anions. To avoid the characteristic stacking of LDH, O'Hare et al. have devised a treatment (AMOST, Aqueous Miscible Organic Solvent Treatment) consisting of replacing the interlaminar water molecules of the LDH structure with molecules of an organic solvent. After drying, LDHs with a large specific surface can be obtained, since the LDH structure is partially exfoliated, grouping itself into nanosheets [3].

In this work, $Ni^{2+}Ti^{+4}$-LDH with the interlayer anion carbonate have been synthesized by the co-precipitation method (NiTi-LDH). In addition to this preparation procedure, the AMOST treatment was applied to the samples in order to increase the surface area and particle dispersion (NiTi-AM samples). Moreover, two Ni/Ti ratios were prepared to examine the influence of the metal ratio on the De-NOx performance.

## SYNTHESIS

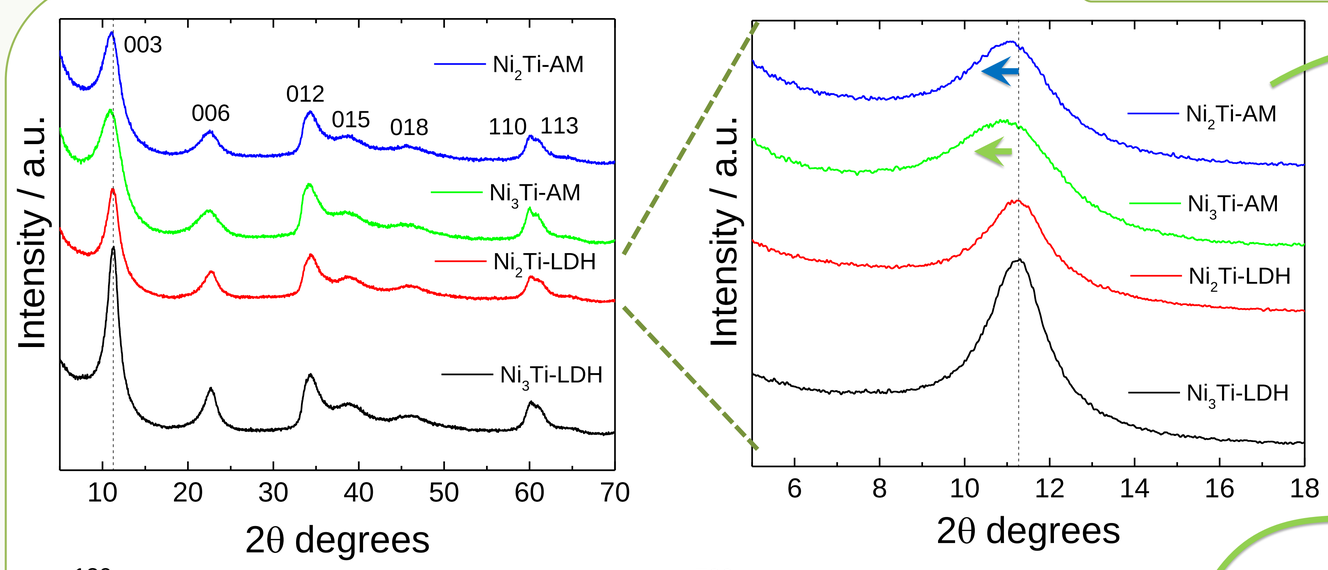
**Metal ratio:**
- $Ni^{2+}$:$Ti^{4+}$ = 3:1 → ***$Ni_3Ti$***
- $Ni^{2+}$:$Ti^{4+}$ = 2:1 → ***$Ni_2Ti$***




Co-precipitation + Stirring in water → ***NiTi-LDH***

Co-precipitation + Stirring in organic solvent → ***NiTi-AM***

## RESULTS





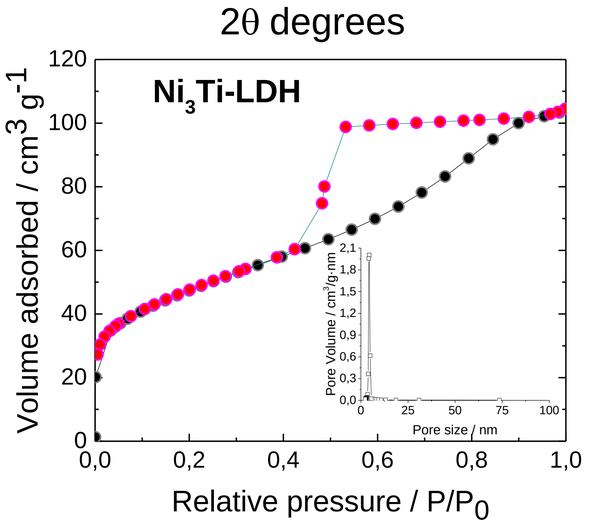


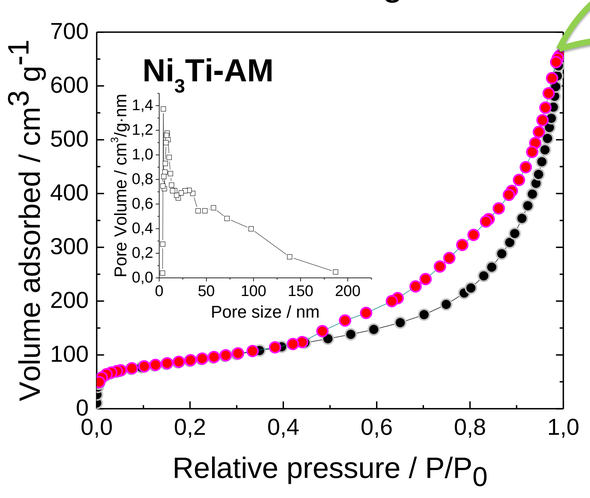
### X-ray diffraction

- Pure LDH phases.
- Decreased crystallinity of NiTi-AM samples compared to NiTi-LDH, is indicative of less stacking of the LDH sheets.
- Interlayer distance of NiTi-LDH $d_{003}$ = 7.8 Å ($CO_3^{2-}$ anion).
- NiTi-AM samples showed an increase in basal spacing with respect to NiTi-LDH, that been possibly caused by the incorporation of ethanol molecules into the interlayer space.

### Nitrogen adsorption isotherms

- Isotherm type shift: from type II (NiTi-LDH) to type IV (NiTi-AM).
- The water molecules adsorbed on the LDH are replaced by ethanol molecules. The evaporation of these leads to the collapse of the stacked structure, obtaining meso- and macroporous compounds which are quite exfoliated with high specific surfaces.

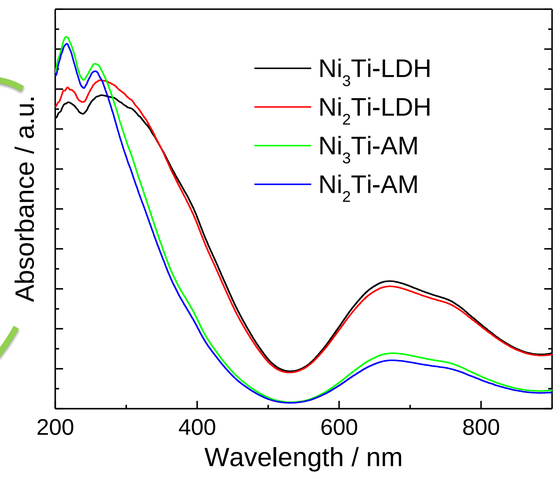



| Sample | $S_{BET}$ / $m^2g^{-1}$ | Band Gap / eV |
|---|---|---|
| $Ni_3Ti$-LDH | 166 | 2.54 |
| $Ni_2Ti$-LDH | 254 | 2.56 |
| $Ni_3Ti$-AM | 314 | 2.91 |
| $Ni_2Ti$-AM | 311 | 2.94 |

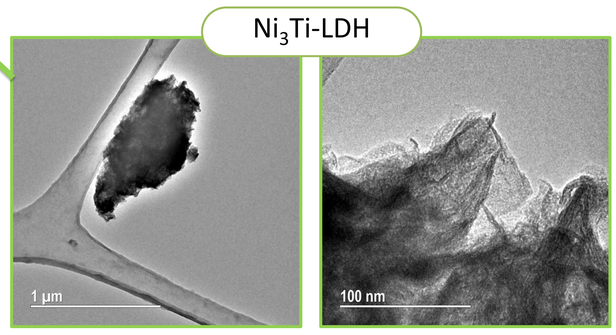
### UV-Vis

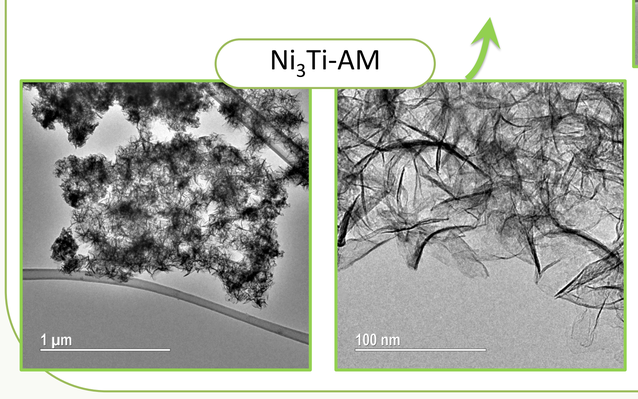
- 200-400 nm → ligand-to-metal charge for $Ti^{4+}$ in octahedral environment; 600-800 nm → $Ni^{2+}$ located in the layers
- NiTi-AM had a greater band-gap value




### TEM

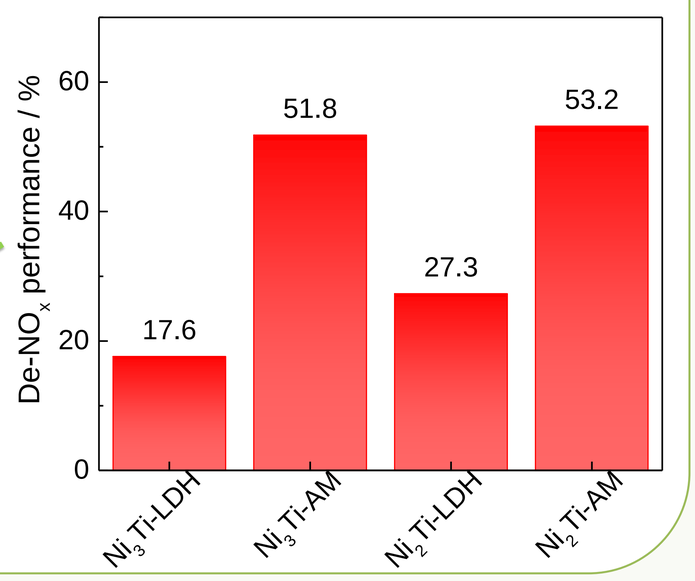
- Intense sheets aggregation for NiTi-LDH (stacking on the *ab* side).
- NiTi-AM exhibited greater exfoliation and flower-like morphology.




### De-NOx photocatalytic tests

- NiTi-AM performance was superior to NiTi-LDH → the high surface area of NiTi-AM samples allows the reactant molecules of NOx gases to find a greater number of active sites in the NiTi-LDH photocatalyst, facilitating the photocatalytic process.
- In spite of the increased amount of Ti in LDH, the $Ni_2Ti$ performance was similar to than $Ni_3Ti$.




## CONCLUSIONS

The AMOST treatment for Ni- and Ti-based LDHs allows obtaining pure LDH samples with high specific surface area values. This treatment is easy to apply and does not affect the hexagonal structure of LDH. For ever both The De-NOx activity corresponding to the NiTi-AM samples was around 50%.

## REFERENCES

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[3] Q. Wang, D. O'Hare, *Chem. Commun*. 49 (2013) 6301–6303.

## ACKNOWLEDGMENTS

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