Low-cost printable metal oxides for electrocatalysis

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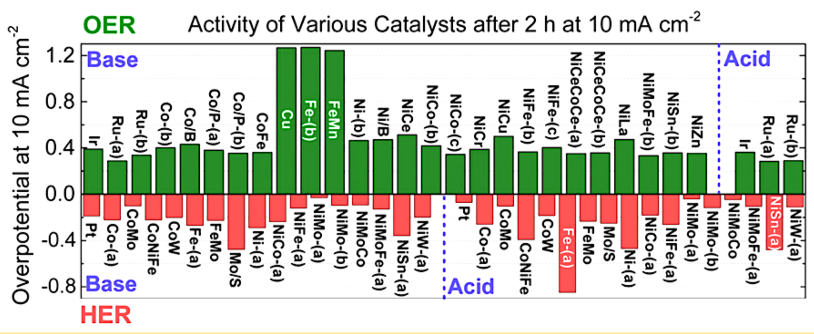
Introduction State-of-the-art

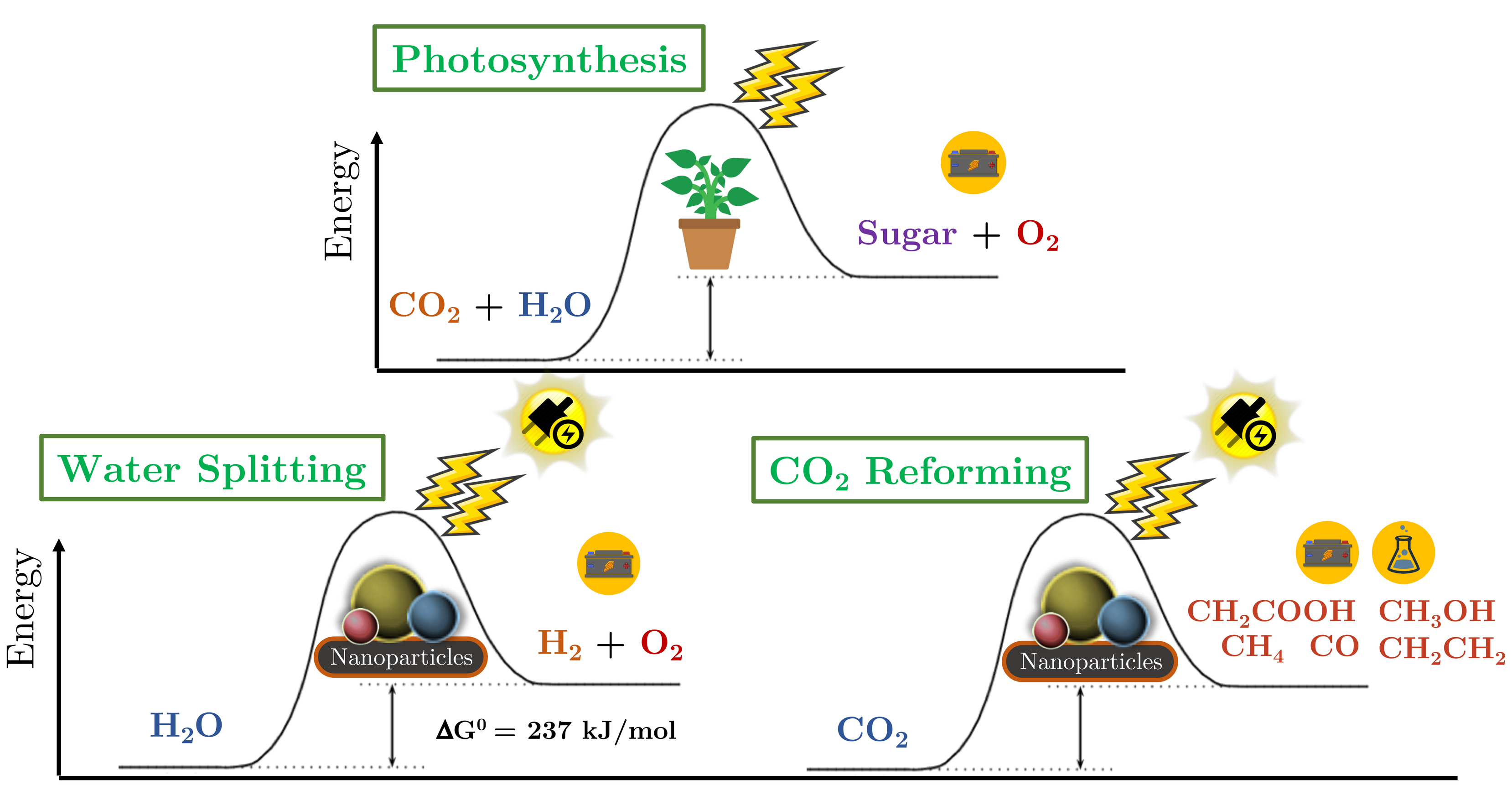
Solution-processed metal oxide semiconductors are believed to play a key role in the research of new materials for low-cost fabrication of future large-area of flexible devices for catalysis, energy generation, electronics, photonics and sensing [1].



We present the recent progress in solution-processed NiO_x thin films as a development of novel nanomaterials for electrocatalysis. Also, in this work we report our methodology to build ultrathin film layers based on sol-gel synthesis coupled by spin-coating [2] and adopted with a mild annealing process on a hot-plate. NiO_x thin films are in-situ synthesized after deposition during a bake in a single step. The resulting film looks homogeneous without cracks nor pinholes. Our study demonstrated that NiO_x films exhibit significantly enhanced electrocatalytic properties in comparison with bibliography results (as shown on the chart) [3]. The most encouraging results were for NiO_x films baked at low temperatures (below 150 ºC) showing the best results regarding overpotential (η) for OER reaction.

We believe that our advances in solution-processed NiO_x thin films baked at mild temperatures, may form the basis of a new platform for the fabrication flexible devices with potential applications in light-driven water splitting and solar fuel cells.

Artificial Photosynthesis

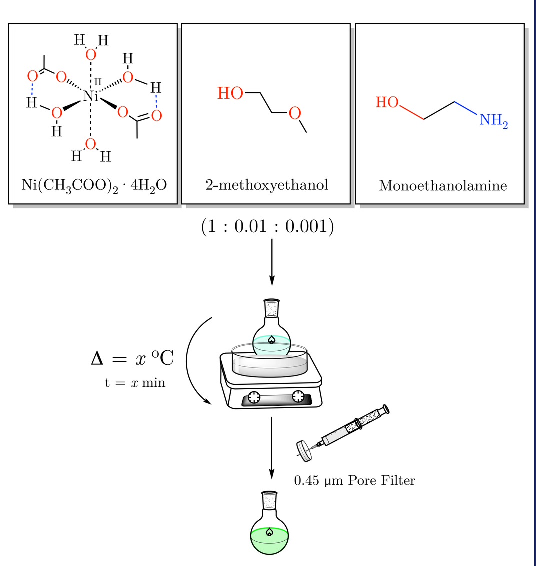


Method Sol-gel synthesis - bottom-up approach

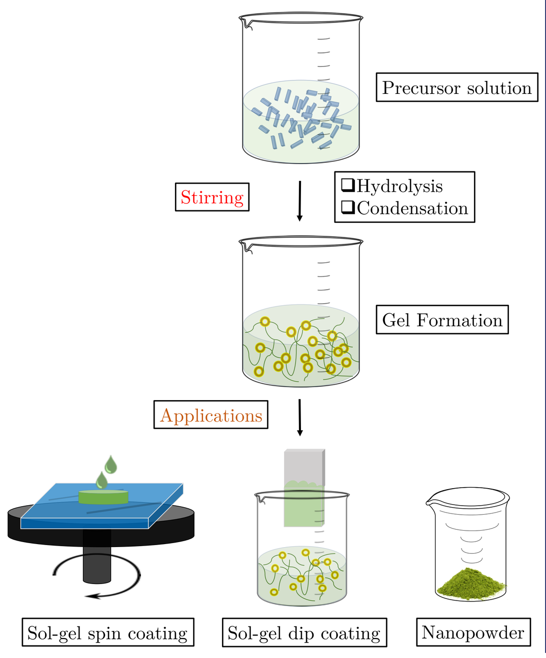
A sterically stabilizing surfactant (**stabilizer**) is often used in sol-gel synthesis of nanocrystalline oxide particles. Its use is compulsory to avoid *gelification.*

- Surfactants must permit the reaction products to diffuse through its adsorbed layer.
- Surfactants should not be incorporated into the structure of the growing particles.

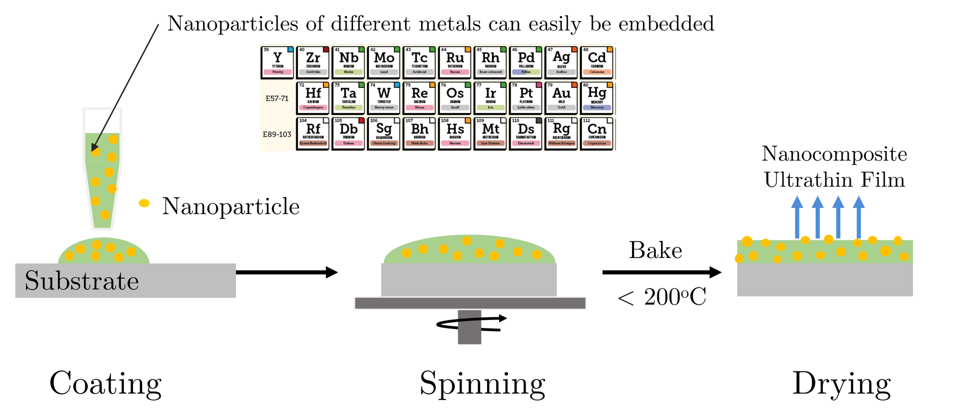
Experimental flowchart



Sol-gel allows higher purity and homogeneity and also lower processing temperatures. This method presents important advantages in the preparation of nanostructured materials. Primarily, the aim of using sol-gel processing usually rely on the **control of the surface and interface** of materials during the earliest stages of production.



Sol-gel processing is a **bottom-up** approach towards high performance nanomaterials, and, thus, it allows the possibility of controlling unique physical properties and generate in second phases homogeneous structures at nanoscale.

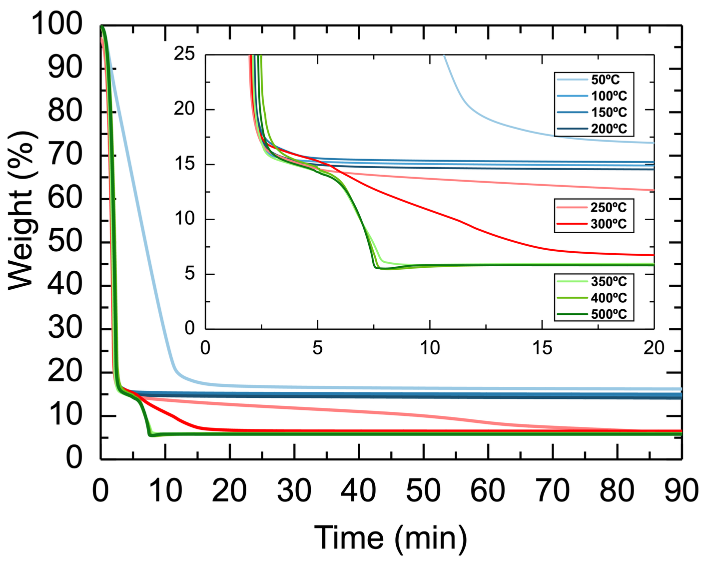


Results Characterization (TGA, HR-TEM, EDX and XPS) and electrochemical performance

Precursor solution

The **weight loss** of the wet NiO_x solution occur in three stages where the following reaction takes place:

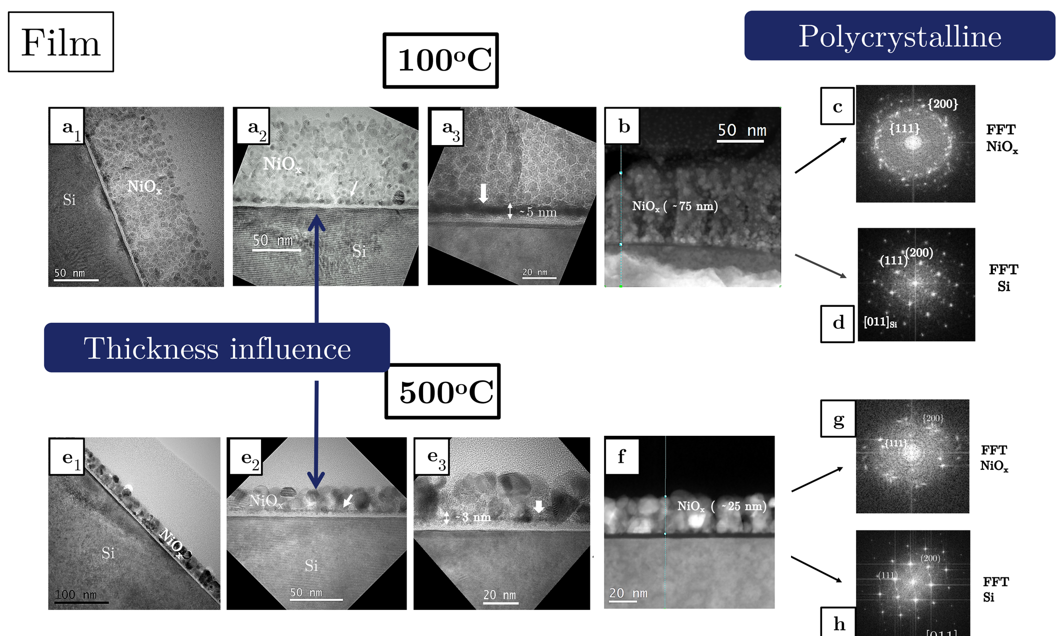
$$Ni(ac)_2 + H_2O \rightarrow NiO + 3H_2O + 4CO_2$$



Stages

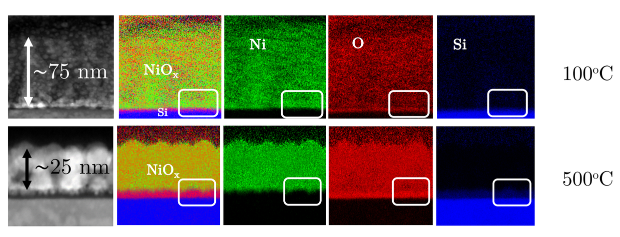
- **50 – 200 ºC** removing solvent and hydration water
- **200 – 300 ºC** reaction occuring *gradually*
- **300 – 500 ºC** reaction occuring *abruptly*

Film



Compositional analysis

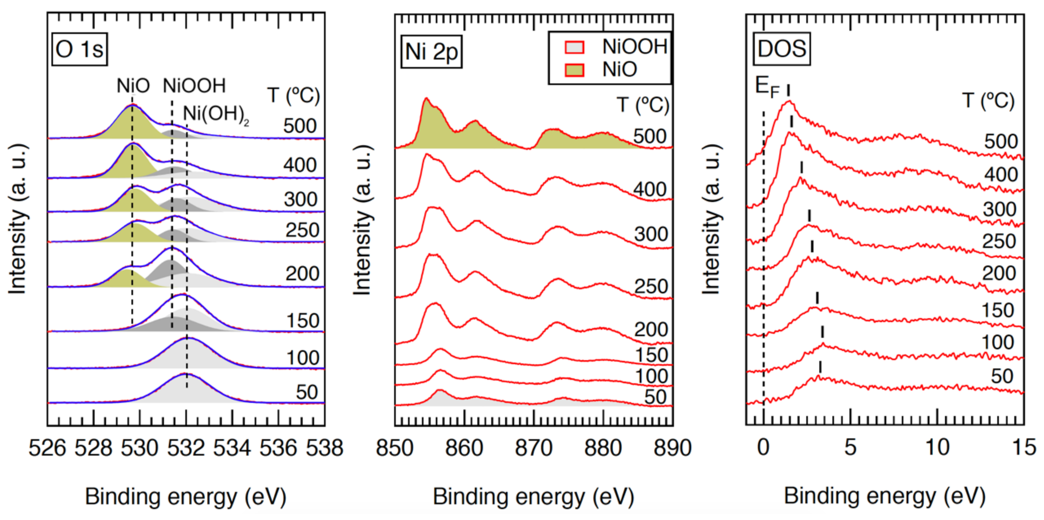
- 100 ºC Oxygen and Nickel widely distributed
- 500 ºC Compressed layer and organic matter loss



Film

The region of 534-532 eV usually illustrates organic adsorbate species [4]:

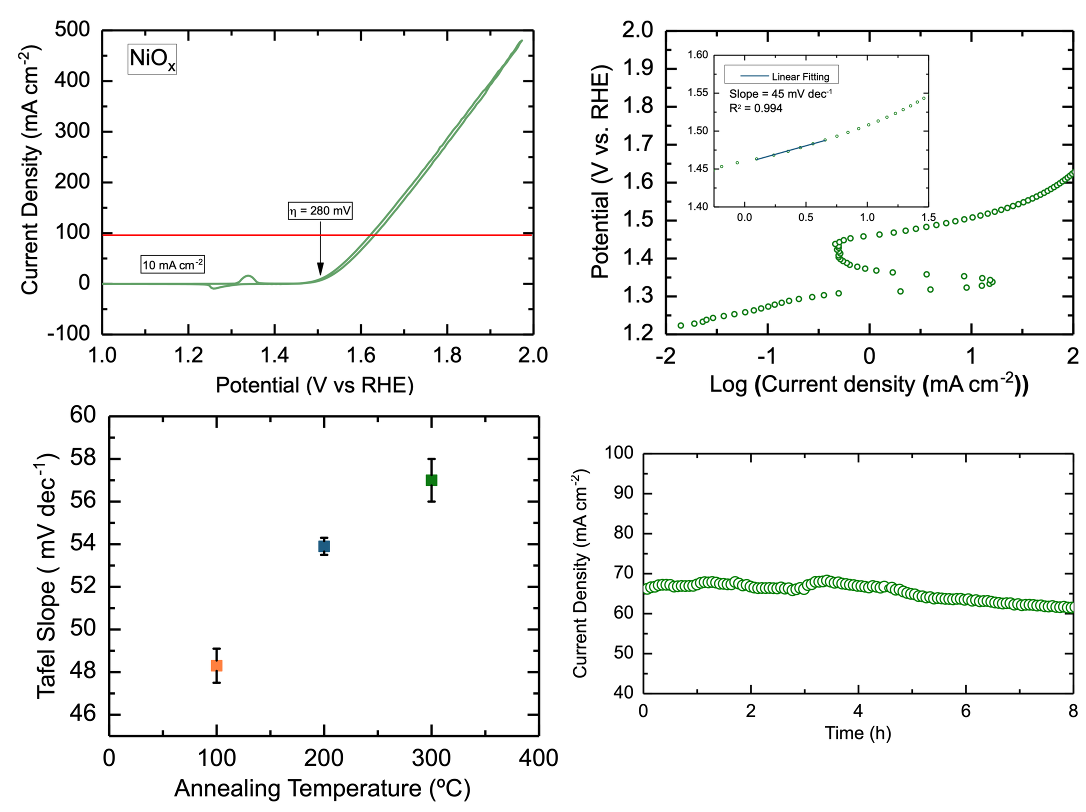
- -COH (532.7 ± 0.2 eV)
- -COO- (532.1 ± 0.3 eV, 533.6 ± 0.1 eV)
- -CO (532.1 ± 0.1 eV)



Organic matter presence
Region from 532 to 534 eV

Being close to E$_F$
Presence of nickel oxide

Film



Suitable conditions

- MEA (stabilizer)
- 2-methoxyethanol
- Concentration 0.45 M
- Spin-rate 1000 rpm
- Anneling
  - 30 min
  - 100 ºC

OER Values

- η = 280 mV
- Tafel Slope = 45 mV dec^{-1}

Conclusions Further work

We report solution-processed NiOx ultra thin films (under 100 nm thickness) prepared by one-step procedure. These layers were prepared at mild temperatures. XPS and TGA show that organic matter still remaining on films after baking. This is also in agreement with HR-TEM images. As a result, the active surface area increases. XRD measured with HR-TEM shows the formation of cubic phase (bunsenite) of NiO nanocrystals.

The electrochemical performance of NiO_x thin films exhibits an outstanding overpotential values comparing with literature [3] for OER electrocatalysts.

Further work will include:

- Test the same material but used as HER electrode.
- Addition of other metals to enhance its light response.
- XPS comparison between NiO_x before and after CVs.
- Other material exploration for sol-gel@spin-coating synthesis.

References Acknowledgements

[1] Trotochaud, L. , Ranney, J. K. , Williams, K. N. , and Boettcher, S. W. Solution-cast metal oxide thin film electrocatalysts for oxygen evolution. *Journal of the American Chemical Society* **2012**, 134, 17253–17261.

[2] Charlesbabu, J. , Gopalakrishnan, K. , Elango, M. , and Vadivelan, K. Preparation and characterization of Cd-doped ZnO thin films by spin coating method. *Inorganic and Nano-Metal Chemistry* **2017**, 47, 1298–1303.

[3] Nadzirah, S. , Foo, K. L. , and Hashim, U. Morphological reaction on the different stabilizers of titanium dioxide nanoparticles. *International Journal of Electrochemical Science* **2015**, 10, 5498–5512.

[4] Payne, B. P. , Biesinger, M. C. , and McIntyre, N. S. The study of polycrystalline nickel metal oxidation by water vapour. *Journal of Electron Spectroscopy and Related Phenomena* **2009**, 175, 55–65.

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