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SYNTHESIS OF Co BASED LAYERED DOUBLE HYDROXIDES: TOWARD A NOBLE METAL FREE ELECTRO-CATALYSIS AND SENSING

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An electrosynthesis protocol that allows the deposition of thin films of Co/Al and Co/Fe layered double hydroxides (LDHs) on two different supports (Platinum and Grafoil) is hereby described that is more efficient than the one previously proposed by our group. The first material was chosen as a reference for the synthesis, since we had already investigated the electrodeposition mechanism on Pt. Grafoil, instead, was chosen since it can be considered a more versatile substrate to be used in a wide range of applications: it is carbon based, low cost, flexible and environmentally friendly.
The synthetic approach is based on potentiodynamic cathodic reduction of nitrates which is a complex process which leads to a pH increase next to the electrode, necessary for the precipitation of the double hydroxide. [1,2] All the films have been characterized by a lot of analytical techniques including cyclic voltammetry (CV), powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), couple with EDS analysis, Raman and atomic emission spectroscopies. Moreover, LDHs electro-synthesized on Grafoil have also been investigated by X-ray absorption spectroscopy (XAS) to better understand their chemistry and their local metal structure (Fig. 1).
All characterizations confirm the LDH structure of the electro-synthesized materials. In particular, XRD suggests better-formed crystal domains with respect to the previously proposed electrochemical approach, based on a potentiostatic method. [3] Moreover, another remarkable result is related to the morphology of the Co-containing LDHs on Pt, which displayed a tubular nanostructure for Co/Fe-LDs and a cauliflower 3D hierarchical morphology for Co/Al-LDH.
Finally, the modified electrodes were employed both for the sensing and the electro-oxidation of 5-(hydroxymethyl)furfural (HMF), displaying promising performances.
Nowadays, the HMF molecule is considered a fundamental platform chemical, i.e. it is a key precursor for a great number of compounds which find application in the fuel and polymer industry. Among several transforming options of HMF, more and more research focus on the oxidation of HMF to 2,5-furandicarboxylic acid (FDCA) as FDCA may replace terephthalic acid in order to produce environmentally friendly plastic materials, as an alternative to polyethylene terephthalate (PET). Therefore, the detection of this compound, and the investigation of stable catalysts able to selectively oxidize HMF to FDCA and with high yield are nowadays relevant topics and a step forward for a green world and economy.

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All the modified electrodes were tested as sensors for HMF using chronoamperometry at +0.5 V vs SCE, after a preliminary investigation by CV in order to establish the suitable voltage conditions. The sensitivity and the limit of detection values were found to be 0.417 A/(Mcm^2) and 1.69 x 10^{-4} M for the best performing system, respectively.
As to the study of HMF oxidation, an exhaustive electrolysis was carried out, and HPLC, ^{1}H NMR and ESI-MS were utilized to identify and quantitate the reaction products. Two principal products were detected: 5-Hydroxymethyl-2-furancarboxylic acid (HMFCA) and FDCA, but also an unidentified compound was observed. The HMF conversion resulted of 100%.
In conclusion, we propose a robust and highly reproducible electrosynthesis procedure that can be applied to different conductive supports and can be employed in several fields of interest, such as sensing and industrial electrocatalysis.

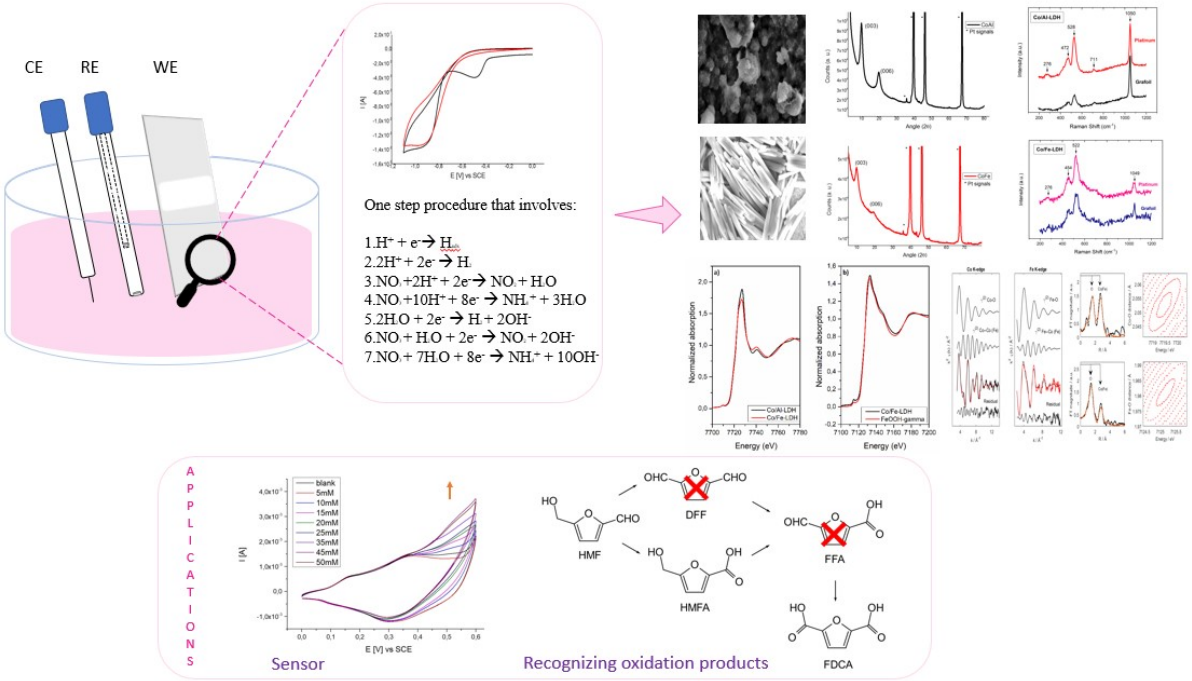

Figure 1. Scheme of the proposed work.

References

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