Magnetic ferrite-based materials for hydrogen generation via water photo-electrolysis

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Significance and Relevance

In the present study, magnetic Cu, Co, Ni, and Zn ferrites were synthesized following a co-precipitation approach carried out at mild conditions (*i.e.*, 90 °C, 2 hours), followed by a thermal treatment (*i.e.*, 700 °C, 5 hours). Subsequently, after performing morphological (SEM), structural (XRD), physicochemical (ICP-OES, FTIR spectroscopy), and magnetic (VSM) characterizations, the most promising materials were tested in the photo-induced hydrogen evolution reaction (*photo*-HER) at neutral pH, showing a significant increase in terms of current density under irradiation, and a consequent increase in H_2 productivity. These results, although preliminary, highlight how these systems can be promising photocatalysts for promoting photo-induced HER processes.

Preferred and 2nd choice for the topic:

- Photocatalysis and photoelectrocatalytic approaches, solar energy utilization.
- H_2 storage and transportation, green H_2 production, hydrogen vectors.

Preferred presentation: Poster

Introduction and Motivations

The consumption of fossil fuels represents the current energetic model for the energy production. However, the growing attention toward the challenges related to the energy green transition and the reduction of CO_2 emissions has made the search for alternative technological solutions for the clean energy production an essential current task. In this context, the exploitation of H_2 (better if obtained through green processes, and from renewable sources) is one of the most promising strategies, given its ability to act as a clean energy carrier.[1] Unfortunately, the possibility of exploiting catalytic routes to produce fuels at large scale is still strongly affected by the selection of the best catalyst (hopefully avoiding the use of platinum group metals).[2] In this regard, magnetic spinel ferrite nanomaterials represent a class of magnetic compounds promising for the energy field, due to their high catalytic activity, presence of active surfaces, selectivity toward the hydrogen evolution reaction (HER), and chemical versatility.[3]

Materials and Methods

Magnetic ferrites were synthesized applying a co-precipitation route,[4] by introducing into an aqueous solution containing the desired metallic cations (*i.e.*, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Fe^{3+}, fixing the M^{2+}:Fe^{3+} molar ratio equal to 1:2) an alkaline 5 M NaOH solution (precipitating agent). The synthesis took place at constant temperature (90 °C), and time (2 hours). Once purified by performing several centrifugations, and washing runs, solid particles were dried, manually ground, and calcined in a muffle oven at 700 °C for 5 hours.[5] The as-prepared samples, fully characterized, were loaded on a ITO support by drop-casting and tested in photo-electrocatalytic (PEC) HER using a three-electrode compact cell, consisting of two compartments (anodic and cathodic) separated by a Nafion membrane and equipped with a quartz window for irradiation of the catalyst. The produced H_2 was analyzed by gas chromatography (GC) equipped with a TCD.

Results and Discussion

In all cases, XRD analyses confirmed the crystal structure of ferrites. Morphological analysis performed by SEM revealed distinct morphologies for the different samples of ferrites (Figure 1). In detail, bare Cu ferrite ($CuFe_2O_4$) showed the presence of rounded particles (40-600 nm) together with larger anisotropic structures (*ca*. 500 nm), attributable to a secondary phase of CuO (corroborated by XRD and FTIR analyses). Bare Co ferrite ($CoFe_2O_4$) showed the presence of micrometric aggregates with rounded edges and the co-presence of considerably small particles (few tens of nm). Both bare Ni ($NiFe_2O_4$) and Zn ($ZnFe_2O_4$) ferrites, instead, showed needle-like structures, with average diameters of *ca*. 450 nm, and *ca*. 100-500 nm, respectively. Magnetic characterization highlighted an overall superparamagnetic behavior for all bare ferrites, with a hint of hysteresis in the case of Co ferrite, and a weak magnetic response in the case of Zn ferrite. Magnetic saturation values follow the order $CoFe_2O_4$ (55.7 emu g^{-1}) > $CuFe_2O_4$ (31.3 emu g^{-1}) > $NiFe_2O_4$ (18.7 emu g^{-1}) > $ZnFe_2O_4$ (6.4 emu g^{-1}).

A comparative study was carried out over different spinel ferrites to thoroughly investigate the effect of M = Cu, Co, Ni, and Zn on water photo-electrolysis at neutral pH. Among all the catalysts tested, Cu and Zn ferrites demonstrated the most impressive performances. Specifically, $CuFe_2O_4$ exhibited the highest Faradaic Efficiency (FE of 87%) over three hours of photo-electrocatalytic testing (with a correspondence hydrogen evolution rate of 75 mmol h^{-1} g^{-1}). This interesting performance can be attributed to the superior photocurrent response of $CuFe_2O_4$ compared to the other ferrite-based materials. Under light irradiation, there was a significant increase in current density (more than 15% compared to the dark) which is crucial for enhancing the overall efficiency of the photo-electrolysis process.

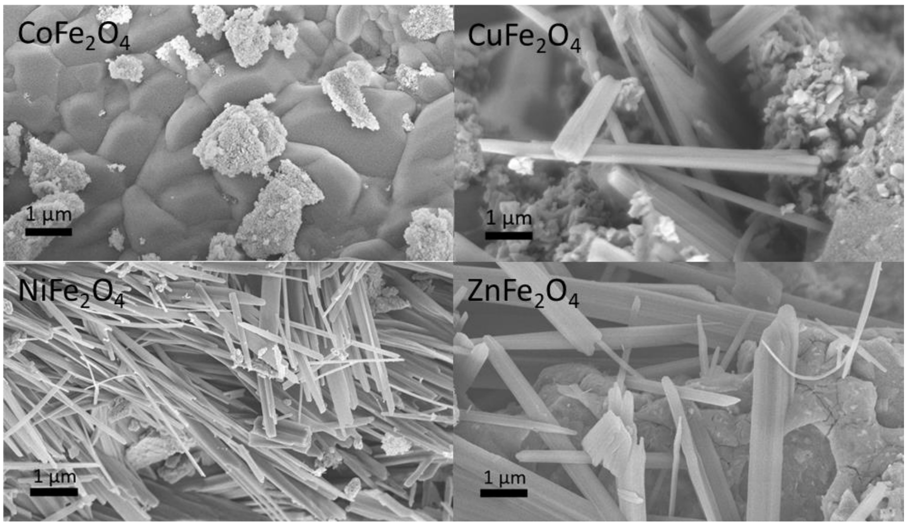

Figure 1 SEM micrographs of magnetic ferrites.

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