

## Cu Nanoparticles by Laser Ablation in Liquid for green hydrogen production

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Hydrogen (HER) and Oxygen (OER) evolution reactions play a fundamental role in the field of green sustainability. In fact, they are key reactions for water electrolysis designed as the most prominent source for green hydrogen production. The high-performance materials for these reactions are platinum (HER), iridium and ruthenium oxide (OER). Their rarity and preciousness make them expensive, thus, earth abundant and non-pollutant materials should be employed as electrocatalyst. To this aim, transition metals, both in the metallic and oxide phases, represent a good alternative as catalyst. Pulsed Laser Ablation in Liquid (PLAL) is a high yield and low-cost process suitable for the synthesis of Nanoparticles (NPs), without producing waste materials. In this work, copper (Cu) NPs are synthesized by laser ablation of a metallic Cu target using a Nd:YAG ns-pulsed laser ( $\lambda = 1064$  nm, 12ns, 5W, 10Hz) in different solvents (methanol, ethanol, acetone and water). Characterizations have been performed by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM) and Energy Dispersive X-Ray (STEM-EDX), X-Ray Diffraction (XRD), Raman Spectroscopy and X-Ray Photoelectron Spectroscopy (XPS). Cu NPs produced in methanol, ethanol and acetone show a metallic nature surrounded by carbon. Monte Carlo algorithm based on Mie theory was developed to extract size distribution from UV-Vis-NIR absorbance measurements. Instead, Cu NPs produced in water resulted in two different oxide phases depending on the laser fluence. Electrodes for OER and HER have been realized by drop casting 100 $\mu$ l of the respective colloidal Cu NPs suspensions on 1cm<sup>2</sup> of nickel foam (NF) with an estimated catalyst loading of some  $\mu$ g/cm<sup>2</sup>. A three-electrode setup has been used with platinum wire as the cathode and a saturated calomel electrode (SCE) as the reference electrode in 1M KOH electrolyte. The HER and OER activities were investigated using Linear Sweep Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS). The catalytic activity of the NPs is relevant already at 10mA/cm<sup>2</sup> and the improvement with respect to the bare substrate become more evident at higher current densities. The performance in terms of overpotential ( $\eta$ ) at the standard current density of 10mA/cm<sup>2</sup> reaches the value of  $\eta=0.2$ V in HER and  $\eta=0.3$ V in OER. The ultra-low amount of the catalyst material makes these electrodes competitive in terms of mass activity (more than 10A/mg at 10mA/cm<sup>2</sup>) compared to the state of the art. This work was funded by European Union (Next Generation EU), through the MUR-PNRR project SAMOTHRACE (Grant No.ECS0000022).