**ΠΑΝΕΠΙΣΤΗΜΙΟ ΚΡΗΤΗΣ**
**ΤΜΗΜΑ ΕΠΙΣΤΗΜΗΣ ΚΑΙ ΤΕΧΝΟΛΟΓΙΑΣ ΥΛΙΚΩΝ**

**ΠΑΡΟΥΣΙΑΣΗ ΜΕΤΑΠΤΥΧΙΑΚΗΣ ΔΙΠΛΩΜΑΤΙΚΗΣ ΕΡΓΑΣΙΑΣ**

## Τίτλος

# «Ανάπτυξη και Χαρακτηρισμός Σύνθετων Νανοδομών $Ni_2P/CuCo_2S_4$ για Ηλεκτροκαταλυτική Διάσπαση Νερού»

# «Development and Characterization of $Ni_2P/CuCo_2S_4$ Composite Nanostructures for Electrocatalytic Overall Water Splitting»

της **Σοφίας Μπρα,** μεταπτυχιακής φοιτήτριας του
Τμήματος Επιστήμης και Τεχνολογίας Υλικών του Πανεπιστημίου Κρήτης

**Επιβλέπων Καθηγητής: Γεράσιμος Αρματάς**

## Δευτέρα 07/11/2022

## 10:00

Η παρουσίαση θα πραγματοποιηθεί στην **αίθουσα Τηλε-εκπαίδευσης Ε-130, στο κτήριο του Τμήματος Μαθηματικών και Εφαρμοσμένων Μαθηματικών,** του Πανεπιστημίου Κρήτης.

ABSTRACT

The development of highly effective, stable and inexpensive catalysts is an important target in the research of water electrolysis and hydrogen production. A key pursuit of current research efforts is to increase the exposure and accessibility of the catalyst's active sites as well as to improve the kinetics of the reaction. This is achievable by combining suitable chemical components in the same material, which could induce electronic band structure modulation and efficient charge-transfer dynamics, with a properly designed nanostructured morphology, which offers a rich density of active sites and large interfacial

contact area. The purpose of this master's thesis is to fabricate and characterize new nanostructured heterostructures of $Ni_2P$ and $CuCo_2S_4$ composition and to investigate the electrocatalytic activity of these materials towards the electrochemical water splitting and hydrogen evolution reaction (HER). The morphology, composition and crystal structure of the $Ni_2P/CuCo_2S_4$ composite catalysts were characterized by a combination of electron microscopy, EDS microprobe analysis, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction techniques. These results indicated that $Ni_2P/CuCo_2S_4$ heterostructures adopt a cubic thiospinel structure and a hexagonal $Ni_2P$ phase (in 10-15 nm size), while their surface is endowed with various loadings of nickel phosphide, i.e., 15, 20, 30 and 40 wt.%. Experimental optical absorption, valence band XPS and electrochemical spectroscopy studies coupled with theoretical DFT calculations indicated that p-n $Ni_2P/CuCo_2S_4$ junctions provide an increased number of electrochemically active surface sites and an efficient interfacial electronic transport with lower resistance, resulting in a remarkable enhancement in the electrocatalytic $H_2$ evolution performance. The unmodified $CuCo_2S_4$ sample showed moderate to low electrocatalytic behavior for the hydrogen evolution reaction, giving an overpotential of 348 mV at a current density of 10 $mA \cdot cm^{-2}$ in an alkaline electrolyte (1M KOH). We show that $Ni_2P$-modification of the $CuCo_2S_4$ surface markedly increases the electrochemical activity by improving the transport efficiency of electrons at the $Ni_2P/CuCo_2S_4$ interface. Thus, the optimized $Ni_2P/CuCo_2S_4$ catalyst at 30 wt.% $Ni_2P$ content reached the lowest overpotential of 183 mV at 10 $mA \cdot cm^{-2}$ current density under alkaline conditions, which is associated with a 78 $mV \cdot dec^{-1}$ Tafel slope, indicating a Volmer-Heyrovsky type mechanism. Chronoamperometric studies revealed that $Ni_2P/CuCo_2S_4$ is quite stable during the reaction, operating stably for 30 h under a current density of 10 $mV \cdot cm^{-2}$. In addition, the 30% $Ni_2P$-loaded catalyst showed a very good oxygen evolution reaction (OER) activity with an overpotential of 360 mV at 40 $mA \cdot cm^{-2}$ current density in 1 M KOH electrolyte. When 30% $Ni_2P/CuCo_2S_4$ is used as both anode and cathode in a two-electrode electrochemical cell, it requires only a 1.78 V potential for overall water electrolysis under 10 $mA \cdot cm^{-2}$ current density. Overall, these $Ni_2P$-modified $CuCo_2S_4$ catalysts demonstrate great potential for renewable hydrogen production technologies, including water electrolysis.