

## Electrochemical performances of nickel nitride / buckypaper hybrid materials

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The production of hydrogen using clean processes is one of the main challenge of the next decade. Water electrolysis is a promising method to produce green hydrogen. However, platinum-based materials are the state of the art electrocatalyst for the hydrogen evolution reaction (HER). Among the platinum free materials suitable for such application, transition metal nitrides are efficient and cost effective materials for hydrogen production. Buckypapers (BPs) are thin self-supported sheets of interlaced carbon nanotubes (CNTs) that show interesting high flexibility and chemical stability in electrolytes. The objective of the present work is to determine electrochemical performances of nickel nitride ( $\text{Ni}_x\text{N}$ ) thin films deposited on buckypaper substrate. To the best of our knowledge, such hybrid carbon-nitride has never been reported before. In this work, a special attention is devoted to evidence the beneficial combination and synergistic effects between the rough BP and the nickel nitride thin films for their efficiency in HER, including grown phase nature and microstructure.

BPs with a thickness of approx. 80  $\mu\text{m}$  have been prepared by the widely known dispersion-filtration method after dispersing CNTs by sonication in water with the help of an anionic surfactant (sodium dodecyl sulfate). In a second step, the outcome BP disks of 40 mm diameter have been coated by nickel nitride thin films using a reactive magnetron sputtering process. By varying the deposition duration, the thickness of the nickel nitride layer was fixed to 150, 200 and 300 nm.  $\text{Ni}_x\text{N}$  thin films have been also deposited on flat substrates (silicon wafer and polished nickel foil). The films deposited on these various substrates have been characterized by scanning electron microscopy, X-ray diffraction (XRD) and Raman spectroscopy. Thin foil lamella prepared by focused ion beam have been characterized by transmission electron microscopy and electron energy loss spectroscopy.

Our results show that the stoichiometry of the nitride films strongly depends on the nitrogen flow rate introduced into the sputtering chamber. At low nitrogen flow rate, pure  $\text{Ni}_3\text{N}$  films have been evidenced by XRD and Raman, while  $\text{Ni}_2\text{N}$  films have been formed at high nitrogen flow rate. Whatever the nature of the substrate (BP, Si or Ni) the sputtered films exhibit a columnar microstructure. Amazingly, using flat substrates, the columns clearly grow along the direction perpendicular to the surface. Due to the BP roughness, the growth of nickel nitride on BP shows an inclination which leads to a less dense and porous microstructures. Contrary to the commonly used liquid phase approach used to prepare the electrocatalysts of poorly controlled morphology and composition, such  $\text{Ni}_x\text{N}$  / BP hybrid materials of

well controlled microstructure, poorly reported in the field, are highly desired for electrochemical reactions.