High-current water electrolysis performance of metal phosphides grafted on porous 3D N-doped graphene prepared without using phosphine

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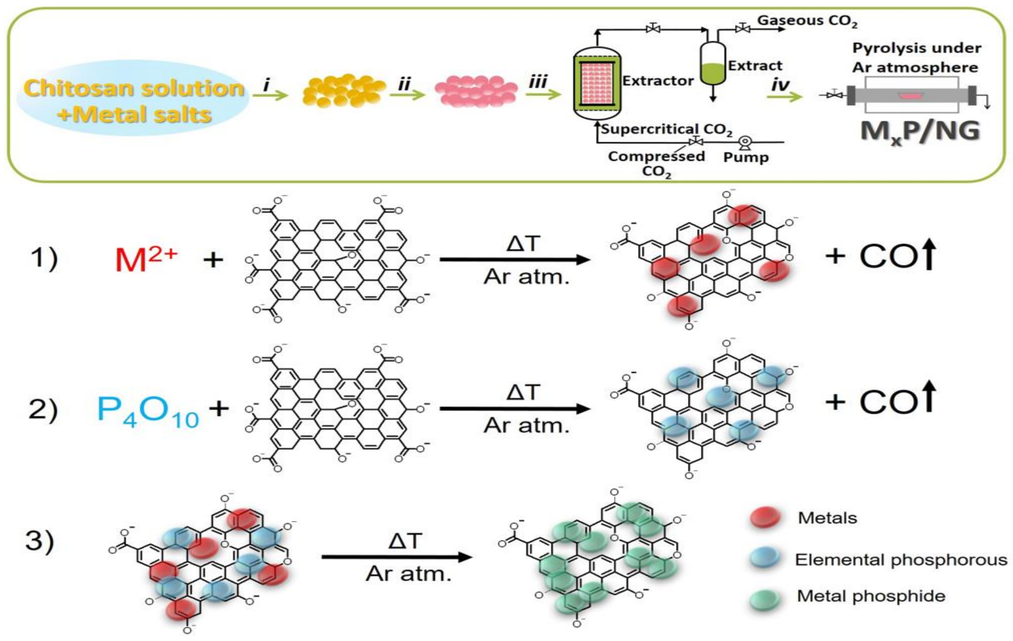
Abstraction

Development of efficient and stable electrodes is of considerable importance for producing green hydrogen from renewable electricity. Here a novel method for the preparation of Ni_2P, Fe_2P and FeP supported on N-doped graphene is reported. The procedure uses metal salts, phosphorous oxide and chitosan as precursors of metal phosphide and N-doped graphene, avoiding the use of undesirable and hazardous precursors, such as PH_3 or NaH_2PO_2. Moreover, NiP/NG and FeP/NG electrodes have demonstrated to be more efficient and stable than the benchmark catalysts Pt/C and RuO_2, water electrolysis was carried out using NiP/NG // FeP/NG at a current density (400 mA/cm^2) near industrial requirements.

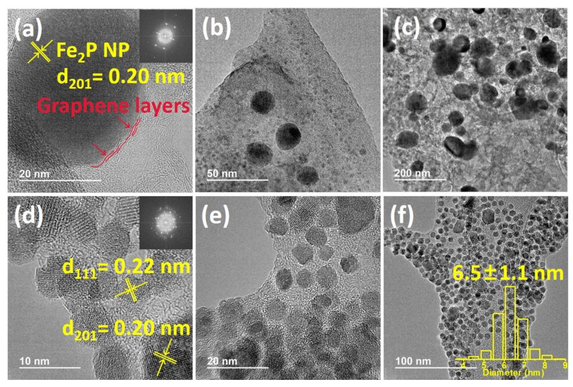
Introduction

The water electrolysis using green electricity from renewable sources, appears as a viable approach for large scale production of high purity H_2. Transition metal phosphides have attracted growing interest as catalyst for water splitting due to their low overpotential, optimum catalytic activity and chemical stability. However, metal phosphides have been typically prepared by phosphidation of metal oxide using extremely **poisonous, hazardous and explosive phosphine.** To facilitate the process, pyrolysis of NaH_2PO_2, plasma treatment, or electrodeposition of precursors have been also reported for metal phosphide preparation. However, some of these alternative methods require high vacuum and expensive equipment, present low purity, forming metal phosphates/phosphides mixtures. Therefore, a green, safe and high phosphorus atom utilization phosphating method needs to be developed urgently.

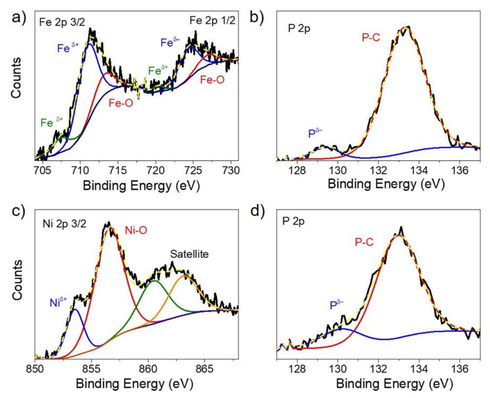
Synthesis



Characterization

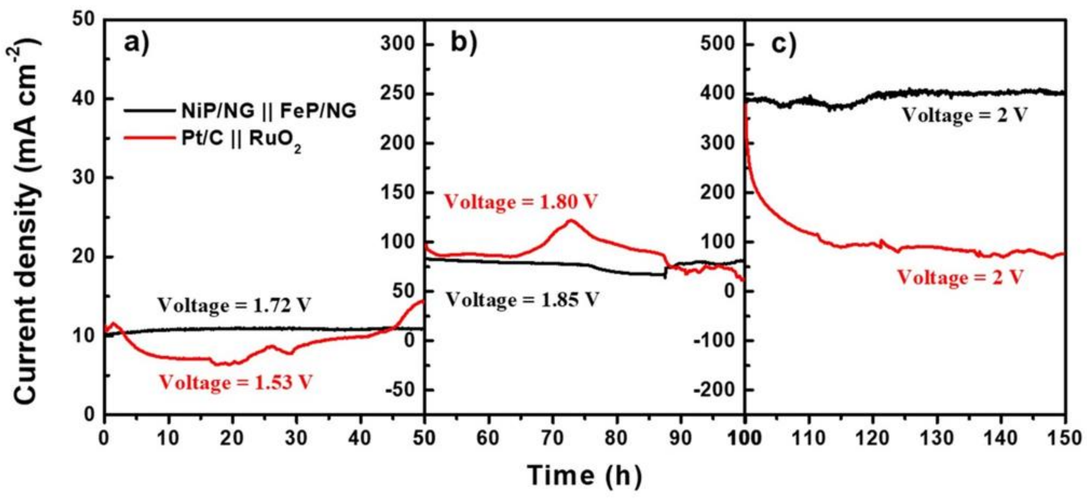


i. TEM shows that metal phosphide nanoparticles have been homogenerously dispersed on the graphene surface.



ii. XPS shows the formation of metal phoshide and the strong interation between MP and N,P-codoped graphene.

Application



Water electrolysis using NiP/NG-FeP/NG and the benchmark catalysts Pt/C-RuO_2 have been tested at different potential. NiP/NG-FeP/NG has outperformed the benchmark catalysts at high current density, 400 mA/cm^2, for 50 h.

Conclusion

i. A green and sustainable procedure for the preparation of metal phosphides that avoids the use or generation of extremely hazardous PH_3, was developed.
ii. It enhances the interaction between the electrically conductive graphene and the metal phosphide resulting in improved HER and OER electrodes.
iii. These metal phosphides on graphene outperform the performance of benchmark electrodes made of Pt or Ru for high current densities required in commercial water electrolysis.

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