

Accepted Manuscript

Title: Transition Metal-doped Nickel Phosphide Nanoparticles as Electro- and Photocatalysts for Hydrogen Generation Reactions

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PII: S0926-3373(18)30946-9
DOI: <https://doi.org/10.1016/j.apcatb.2018.09.103>
Reference: APCATB 17086

To appear in: *Applied Catalysis B: Environmental*

Received date: 4-8-2018
Revised date: 22-9-2018
Accepted date: 30-9-2018

Please cite this article as: Man H-Wing, Tsang C-Shan, Li MM-Jung, Mo J, Huang B, Yoon Suk Lee L, Leung Y-chung, Wong K-Yin, Chi Edman Tsang S, Transition Metal-doped Nickel Phosphide Nanoparticles as Electro- and Photocatalysts for Hydrogen Generation Reactions, *Applied Catalysis B: Environmental* (2018), <https://doi.org/10.1016/j.apcatb.2018.09.103>

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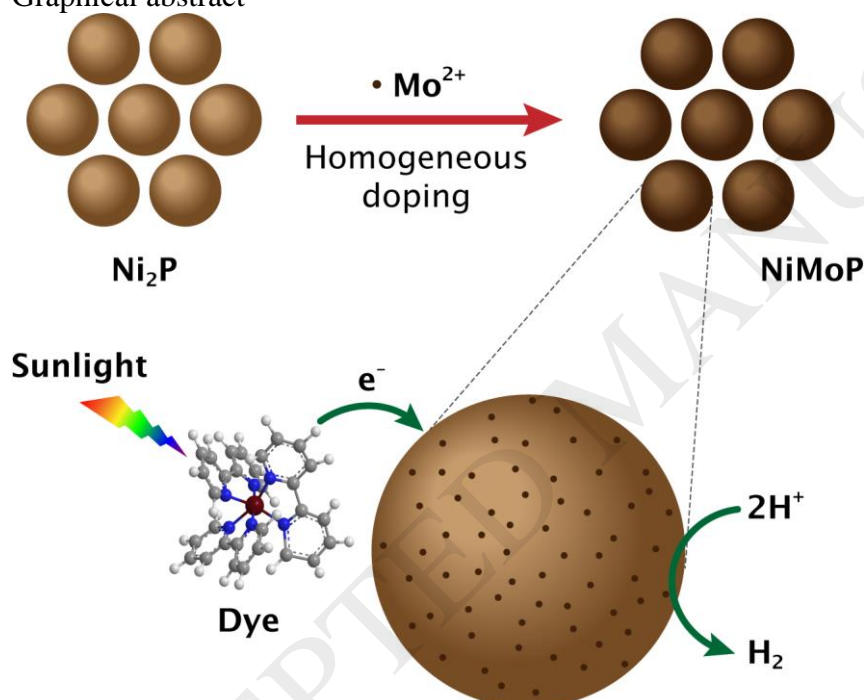
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Graphical abstract



Highlights

- transition metal-doped nickel phosphides prepared by wet-chemical method
- Fe, Co, Ni and Mo atomic substitute Ni in phosphide lattice as a single phase
- electro- and photocatalysts for hydrogen evolution reactions
- tunable activities dependent on electron filling

Abstract

Transition metal-doped nickel phosphide nanoparticles with metallic properties are prepared by a simple and facile wet-chemical method. It is shown for the first time that these transition metals: iron, cobalt, manganese, and molybdenum, can atomically substitute nickel in the parent *hcp* phosphide lattice as a single phase without significant change in its metallic structure and morphology. They are employed as electro- and photocatalysts for hydrogen evolution reaction, which show highly tunable activities dependent on electron filling of their metallic bands and H coverage according to our experimental and theoretical rationalizations.

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