Rare earth element modified nickel phosphide nanoparticles as electro- and photocatalysts for hydrogen generation reactions

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Introduction

With the rising global energy demand and urgent environmental issues, sustainable and renewable energy sources are essential to replace fossil fuels. Hydrogen fuel stands out due to its eco-friendliness and high energy output through combustion.[1] Hydrogen production via hydrogen evolution reaction (HER) can be achieved through electrocatalysis or photocatalysis. Platinum group metals (PGMs) are highly effective HER electrocatalysts, but their scarcity and high cost limit their practicality.[2] Recently, transition metal phosphides (TMPs) -such as nickel phosphide - have emerged as promising catalyst candidates due to their excellent stability under various conditions and ability to perform reversible association or dissociation of H to H_2.[3]

This work investigates the use of lanthanide ion-modified nickel phosphide (NiP) nanoparticles as highly efficient catalysts for hydrogen generation reactions: both electrochemical and photochemical HER. This class of materials displayed tunable electronic properties for optimized catalytic activities.

Materials and Methods

Pristine and various lanthanide-modified nickel phosphide nanoparticles (denoted as Ln-Ni_2P) were synthesized through a facile wet-chemistry method using a high-precision heating mantle and inert atmosphere. The resulting nanoparticles were characterized by PXRD, XPS, UPS and TEM. Particles were dropcasted onto carbon paper for alkaline electrochemical HER tests. Dye-sensitized photochemical HER was carried out using eosin Y dye and triethanolamine as sacrificial agent.

Results and Discussion

Electrochemical activities of the nanoparticles were evaluated using linear sweep voltammetry (LSVs) and results are shown on Figure 1. While all of them showed activity towards HER, incorporation of lanthanides did not improve catalytic activities. All catalysts showed relatively higher Tafel slopes, suggesting that the rate-determining step is associated with the Volmer step of HER, which involves the adsorption of hydrogen onto the catalyst surface.

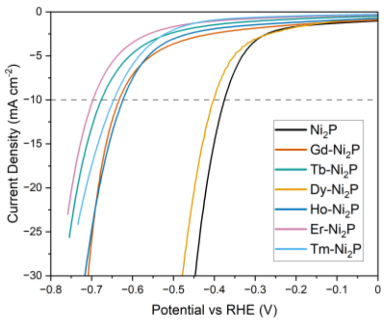

Figure 1. LSV of pristine and lanthanide modified NiPs in alkaline HER.

Ultraviolet photoelectron spectroscopy (UPS) was used to establish the metallic properties of all materials. The lack of band gap in these catalysts means they cannot be utilized in conventional colloidal semiconductor systems. However, their ability to act as cathodes in hydrogen reduction allows them to be used in efficient dye-sensitized photochemical HER in the presence of a sacrificial agent. Here, the only requirement of the catalyst is the ability carry out HER. This mechanism is illustrated on Figure 2b and involves 4 key steps: 1) excitation of electron from HOMO to LUMO of dye, 2) electron transfer, 3) production of H_2 and 4) electron transfer from sacrificial agent to dye. An interesting reverse-Vulcanic relationship was observed in the lanthanide series

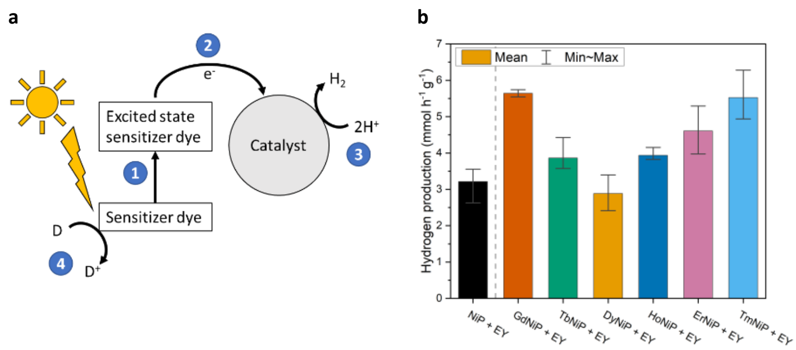

Figure 2. a) . Proposed mechanism scheme of dye-sensitized photochemical HER. b) Photocatalytic activity of pristine and Ln-Ni_2P.

Significance

Despite their misleading name, rare-earth elements are quite abundant. Replacing the currently used platinum group metals - that are expensive and are at risk of depletion - in hydrogen generation reactions would be an important step towards more efficient production of clean hydrogen energy at an industrial level. It is demonstrated the incorporation of small amounts of rare-earth elements into transition metal phosphides can alter catalytic permormances.

References

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