$Ni_{12}P_5$ Nanoparticles as an Efficient Catalyst for Hydrogen Generation *via* Electrolysis and Photoelectrolysis

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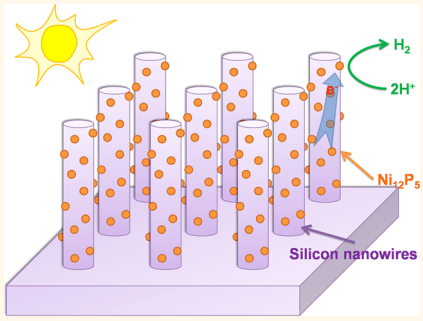
ABSTRACT The exploitation of a low-cost catalyst is desirable for hydrogen generation from electrolysis or photoelectrolysis. In this study we have demonstrated that nickel phosphide ($Ni_{12}P_5$) nanoparticles have efficient and stable catalytic activity for the hydrogen evolution reaction. The catalytic performance of $Ni_{12}P_5$ nanoparticles is favorably comparable to those of recently reported efficient nonprecious catalysts. The optimal overpotential required for 20 mA/cm^2 current density is 143 $\pm$ 3 mV in acidic solution (H_2SO_4, 0.5 M). The catalytic activity of $Ni_{12}P_5$ is likely to be correlated with the charged natures of Ni and P. $Ni_{12}P_5$ nanoparticles were introduced to silicon nanowires, and the power conversion efficiency of the resulting composite is larger than that of silicon nanowires decorated with platinum particles. This result demonstrates the promising application potential of metal phosphide in photoelectrochemical hydrogen generation.



KEYWORDS: hydrogen generation · electrolysis · photoelectrolysis · nickel phosphide · silicon nanowires · electrocatalyst

The increasingly serious energy crisis and environmental issues have stimulated considerable research concerning renewable clean energy.[1,2] Solar-driven water splitting into hydrogen (H_2) is one of the most promising approaches to produce clean energy,[3−5] because it can harvest solar energy and store the energy as clean fuel (H_2), and the storage of energy in H_2 has the largest mass storage density and the longest storage time.[5] Efficient photoelectrochemical hydrogen generation requires the modification of a photocathode with an active catalyst for the hydrogen evolution reaction (HER), because of native slow HER kinetics at semiconductor surfaces. Although platinum and other noble metals have been successfully incorporated into photocathodes for hydrogen generation,[6−9] the widespread practical application of these HER catalysts is limited because of high cost and low abundance. Therefore, the exploitation of efficient photocathodes modified with a low-cost and effective HER catalyst is attracting extensive attention.

Recently reported nonprecious HER catalysts include molybdenum sulfide,[10,11] first-row transition metal dichalcogenides,[12,13] molybdenum carbide,[14,15] tungsten carbide,[16] nickel phosphide (Ni_2P),[17] cobalt phosphide (CoP),[18−20] and so on. The edge sites of molybdenum sulfide are analogous to the active centers of nitrogenase,[10] while some surface cations of the first-row transition metal dichalcogenides resemble the ligand number and symmetry of active centers in hydrogenase ([NiFe]-hydrogenase, [FeFe]-hydrogenase, or [Fe]-hydrogenase).[13] The electronic structures of group VI transition metal carbides are similar to those of Pt-group metals.[21] Metal (Ni or Co) and P in metal phosphide have similar charged natures to those of the hydride acceptor and proton acceptor in [NiFe] hydrogenase and its analogues.[22] These reports suggest that mimicking the coordination structures or electron structures of active sites of high-performance noble metal catalysts or hydrogenases is an efficient approach to the development of new nonprecious HER catalysts.

On the other hand, only limited kinds of nonprecious HER catalysts have been incorporated into photocathodes to promote solar-driven hydrogen generation (*e.g.*,

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