Synthesis of Ni_5P_4 as cocatalyst for promoting photocatalytic H_2 production

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Abstract: The Ni_5P_4 nanoparticle was prepared through an annealing method using an inorganic phosphorus source, which is used as suitable cocatalysts in photocatalytic hydrogen generation. The results demonstrated that Ni_5P_4 can be utilized as electron cocatalysts to markly boost the visiable-light H_2 generation over g-C_3N_4 semiconductor. Thus, Ni_5P_4 was shown to be efficient cocatalysts that can replace noble metals as low-cost photocatalytic H_2 production. Significantly, no catalyst degradation is seen in the recycle application.

Keywords: Ni_5P_4, g-C_3N_4, hydrogen generation.

1. Introduction

Photocatalytic water splitting into hydrogen has received significant attention as a renewable and environmentally friendly method to solve energy crisis. Metal-free g-C_3N_4, an n-type semiconductor with appropriate bandgap and conduction band, is widely used as a photocatalyst to produce H_2 by splitting water[1]. However, the fast recombination rate of photoinduced electron–hole pairs still leads to inefficient photocatalytic performance[2]. It is generally believed that loading of a cocatalyst on an active substrate is essential for the realization of efficient photocatalytic hydrogen production[3]. Transition metal phosphide offers exciting opportunities to promote charge separation of g-C_3N_4 due to the low-cost and easy to obtain[4].

2. Experimental

First, the Ni–P precursor was synthesized as follow. 0.5 g $NiCl_2$ $6H_2O$, 2.44 g NaH_2PO_2 H_2O, and 0.29 g NaAc were dissolved in deionized water to obtain a clear solution; then, KOH (2 M) was added to adjust the pH value to 8 with stirring. The solution was kept at 363 K for 1 h, then separated and washed with ammonia solution (25–28 wt%), deionized water, and ethanol to obtain the resultant black sample. The as-prepared Ni-P mixed with red phosphorus and the mixture was treated by a thermal treatment at 773 k for 1 h for the phase transformation to obtain Ni_5P_4 nanoparticles. A given amount of g-C_3N_4 and Ni_5P_4 was dissolved into DMF and kept under ultrasound for 1 h and stirred for another 12 h. The resultant solution was separated by centrifugation, washed with water and ethanol once, and then dried at 303 K for 6 h. The final hybrid was signed as Ni_5P_4/g-C_3N_4.

3. Results and discussion

The crystal structure of the as-prepared Ni_5P_4 and Ni_5P_4/g-C_3N_4 indicates the successful formation of the Ni_5P_4 phase and the Ni_5P_4/g-C_3N_4 hybrid. The unchanged peaks belonging to g-C_3N_4 and Ni_5P_4 in hybrid catalyst confirm that the structure of g-C_3N_4 and Ni_5P_4 remains the same after hybridization.

The elemental mapping of Ni_5P_4/g-C_3N_4 further demonstrates that Ni_5P_4 particles were deposited on the surface of g-C_3N_4. Ni_5P_4 particles in Ni_5P_4/g-C_3N_4 exhibit an irregular structure and an average particle size of 150–250 nm.

Ni_5P_4/g-C_3N_4 (5 wt% Ni_5P_4) show comparable photocatalytic activity for H_2 generation to that for Pt/g-C_3N_4 (5 wt% Pt), which is approximately 39 times the amount obtained on pure g-C_3N_4 under visible light irradiation (> 420 nm). Ni_5P_4/g-C_3N_4 shows negligible degradation after the circulation of the H_2 production reaction under prolonged irradiation for 9 h, suggesting that Ni_5P_4/g-C_3N_4 acts as a stable photocatalyst.

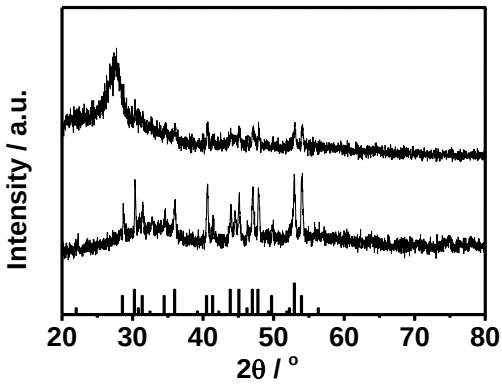

Figure 1. XRD patterns of the as-prepared Ni_5P_4 and Ni_5P_4/g-C_3N_4 (5 wt% Ni_5P_4).

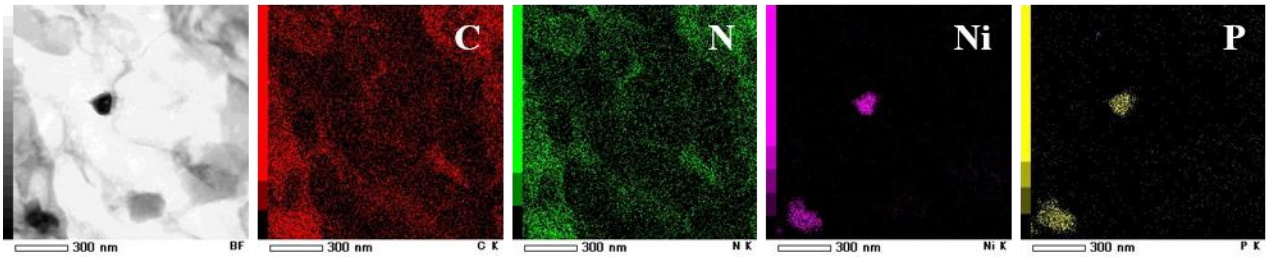

Figure 2. EDX mapping images for Ni_5P_4/g-C_3N_4.

Table 1. Photocatalytic H_2 generation rates for g-C_3N_4, Ni_5P_4/g-C_3N_4, and Pt/g-C_3N_4.

Catalyst	Catalyst / mg	MeOH / mL	Water / mL	H_2 / μmol·g^{-1}·h^{-1}
g-C_3N_4	2	1	4	4.4
Ni_5P_4/g-C_3N_4 (5wt%)	2	1	4	171.8
Pt/g-C_3N_4 (5wt%)	2	1	4	175.5

4. Conclusions

In conclusion, Ni_5P_4 was prepared through an annealing method. After hybridization with g-C_3N_4, Ni_5P_4 exhibits good photocatalytic H_2 generation activity and stability. This combination of superior efficiency and stability among earth abundant elements makes Ni_5P_4 a promising candidate for the future development of renewable H_2 via photocatalytic water splitting.

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