Highly efficient activity for photocatalytic water splitting to produce hydrogen under visible light irradiation over Pd/g-C_3N_4 catalyst modified by trace Ag

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Abstract: PdAg bimetallic nanoparticles (NPs) are important in catalytic process. Here, we used Ag nanoparticles as seeds which induced the reduction of Pd precursor to produce Pd, and named as Pd@Ag. Then, the photocatalytic activity of the Pd@Ag loaded on g-C_3N_4 was assessed by water splitting reaction under visible-light irradiation. The results indicated that Pd@Ag/g-C_3N_4 showed higher activity than Pd/g-C_3N_4. Calculating from the amount of Pd, the TOFs of Pd@Ag and Pd were 126.7 and 13.4 h^{-1}, respectively. This work is a useful method to enhance the catalytic performance of noble metals.

Keywords: Photocatalysis, Water splitting, Pd@Ag/g-C_3N_4.

1. Introduction

The production of hydrogen through photocatalytic water splitting has become a promising approach to remedy the current environmental and energy crisis. Graphitic carbon nitride (g-C_3N_4) has received tremendous attention due to its unique property and photocatalytic application under visible light [1]. To enhance the visible light photocatalytic performance of g-C_3N_4, some strategies have been employed including doping with noble metal Pt, Pd, Au, etc [2]. Furtherly, bimetallic particles such as PdAu, PdAg, PtAu, PtAg were supported on g-C_3N_4 to improve the catalytic activities [3]. Here, we synthesized palladium nanoparticles modified by trace Ag, and investigated its photocatalytic performance for water splitting under visible light.

2. Experimental

Pd nanoparticles was synthesized using the polyol reduction method [4]. In principle, poly (vinylpyrrolidone) (PVP, MW=58000, 50 mg) was dissolved in ethylene glycol (15 mL) in a flask with magnetic stirring and the temperature was brought to 150 °C in an oil bath (methyl silicone oil). $NaPdCl_4$ dissolved in the ethylene glycol (5 mL) were injected into the flask and reaction at this temperature for 30 minutes. Then, the mixture was rapidly cooled by quenching in an ice-water bath. The resulting Pd particles were washed by acetone and collected by centrifugation. Pd particles modified with Ag noted as Pd@Ag were synthesized sequential reduction. Ag nanoparticles were obtained using the above method, which were dispersed into the flask with ethylene glycol and PVP, the other steps were as the same as Pd nanoparticles. As prepared Pd or Pd@Ag particles were loaded on the g-C_3N_4 to obtain the Pd/g-C_3N_4 and Pd@Ag/g-C_3N_4 catalysts, respectively [4]. The amount of noble metal was 5 mg and g-C_3N_4 was 200 mg. The photocatalytic hydrogen evolution reaction was carried out in a top-irradiation type vessel linked to a glass closed gas system under visible-light ($\lambda \geq 420$ nm) irradiation [5].

3. Results and discussion

TEM images (Fig.1) revealed that Pd NPs and Pd@Ag NPs were highly dispersed on the surface of g-C_3N_4 with average size about 4-5 nm. EDS mapping of Pd@Ag indicated that both Pd and Ag were observed clearly.

The photocatalytic water splitting of H_2 evolution was used as the model reaction to determine the catalytic performance of Pd@Ag NPs, and the corresponding results are compared in Fig. 2. It can be found that the amount of H_2 improved markedly with the noble metal Ag or Pd loaded on the g-C_3N_4. The enhancement could be due to the Schottky barrier formation [2]. Furtherly, the activity was strengthened as Pd NPs modified by trace Ag. The turnover frequencies (TOFs) of Pd and Pd@Ag were calculated, i.e., 13.3 and 126.7 h^{-1}, respectively. It suggests that the role of Ag was important, Pd@Ag had about 10 fold TOFs value than that of Pd. The Mott-Schottky results indicated that the level of lowest unoccupied molecular orbital (LUMO) of Pd@Ag/g-C_3N_4 was - 0.56 V, which is higher than that of Pd/g-C_3N_4 (- 0.70 V).

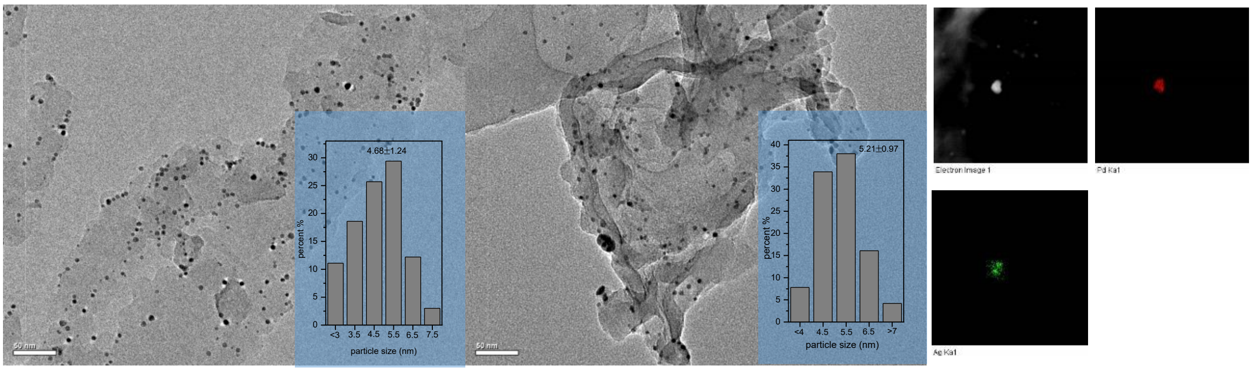

Figure 1. TEM images of (a) Pd/g-C_3N_4, (b) Pd@Ag/g-C_3N_4, and the insets: NPs size histographs, (c) STEM image of Pd@Ag, EDS maps of (d) Pd and (e) Ag

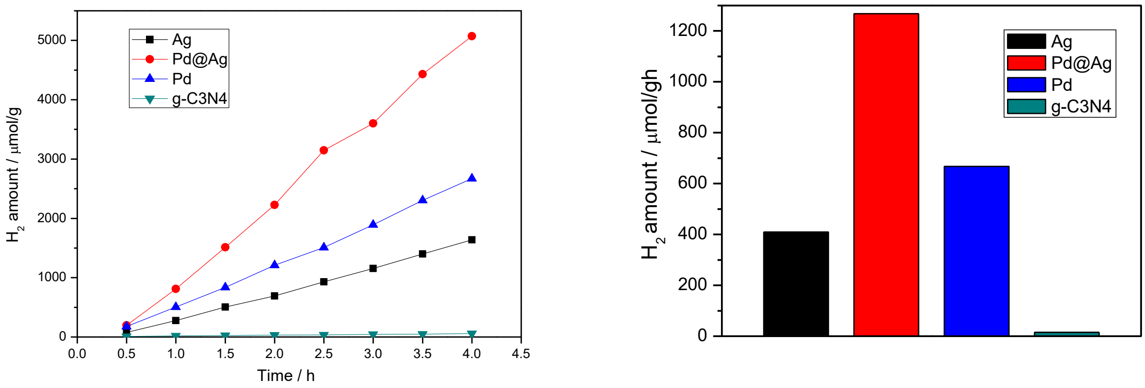

Figure 2. H_2 production of Ag, Pd, Pd@Ag loading on g-C_3N_4.

4. Conclusions

We can synthesized Pd and Pd@Ag NPs using polyol reduction method with average size of 4-5 nm. Pd and Pd@Ag NPs can strengthen the photocatalytic activity of g-C_3N_4 for the water splitting reaction. Additionally, the catalytic performance of Pd NPs was enhanced tremendously by inducing trace Ag NPs. Furthermore, the TOFs of Pd@Ag/g-C_3N_4 was about 10 fold than that of Pd/g-C_3N_4, due to the Mott-Schottky barrier.

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