



Short communication

CuAg nanoparticles immobilized on biomass carbon nanospheres for high-efficiency hydrogen production from formaldehyde

Tao Feng¹, Xu-Feng Meng¹, Shu-Tao Gao*, Cheng Feng, Ning-Zhao Shang, Chun Wang*

College of Science, Hebei Agricultural University, Baoding 071001, China

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ABSTRACT

A low-cost and high-efficient catalyst (denoted as CuAg/BC) was fabricated by immobilizing Cu-Ag bimetal on green and renewable biomass carbon nanospheres derived from sucrose for the first time. The prepared CuAg/BC catalyst exhibited high catalytic activity and stability toward the dehydrogenation of formaldehyde at 30 °C. The rate of H₂ generation can reach 306.7 mL min⁻¹ g_{catalyst}⁻¹, which is among the highest values reported so far. The superior catalytic performance is derived from that the synergistic effect between Cu and Ag nanoparticles, and the relatively small size of CuAg nanoparticles greatly increased the utilization efficiency of the metals.

1. Introduction

Limited fossil resources and growing energy demand have led to a more urgent search for highly efficient, green and sustainable alternative energy sources. Hydrogen is regarded as an extremely promising energy sources for the future because of its non-pollution, full recycle and high energy capacity. However, the conventional means of hydrogen production has some short-comings and can not meet the demands of practical application. Thus, much emphasis has been placed on exploring low-cost, high-efficient and sustainable hydrogen generation technology. As a result, hydrogen generation from hydrogen storage materials, such as borohydride [1], ammonia borane (AB) [2], hydrazine [3], formic acid (FA) [4] and formaldehyde [5] has been widely developed. Notably, formaldehyde is considered as one of the most promising hydrogen storage materials as hydrogen generation from formaldehyde provides a green and renewable route to not only producing hydrogen but also destructing pollutant formaldehyde, in which both formaldehyde and water act as the hydrogen donors: one hydrogen atom comes from formaldehyde and another from water ($\text{HCHO} + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{H}_2$) [6–8].

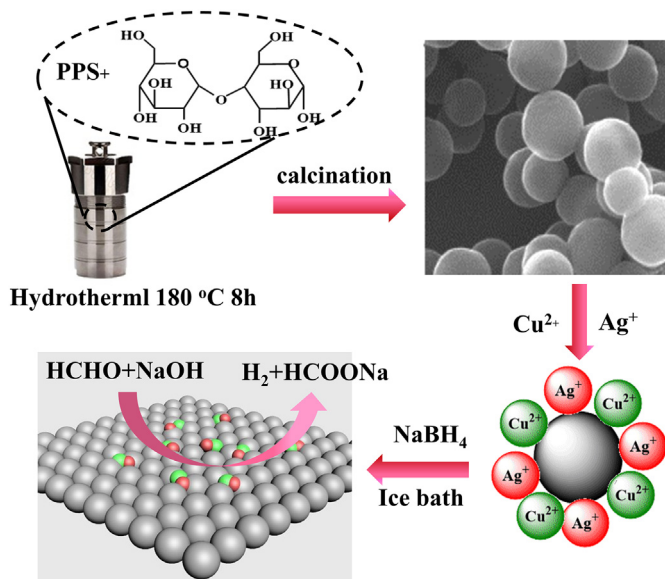
Additionally, this dehydrogenation reaction usually required catalysts and basic media to achieve high dehydrogenation efficiency. Thus, a series of heterogeneous catalysts were recently developed for the hydrogen generation from alkaline formaldehyde solution, such as Pd [9–11], Au [12], Pt [13] and Ag [5,6] and Cu [14]. However, the high cost and low efficiency of the catalytic system have greatly restricted its practical application. To date, various strategies have been proposed to develop low-cost and highly efficient catalysts. One solution is

adulterating less expensive metals such as Ag, Fe, Cu, Co and Ni with noble metals such as Au, Pd and Pt to form alloy or bimetallic catalysts. Owing to the bimetallic synergistic effect, the catalytic activity is greatly enhanced. For example, Li et al. successfully fabricated CoCu alloy nanoparticles (NPs) encapsulated in the pores of MIL-101 and employed in hydrolysis of AB. The CoCu alloy's catalytic activity was superior to corresponding monometal [15]. AgPd NPs was immobilized onto the UIO-66-NH₂ to catalyze the dehydrogenation of AB [2]. AgPd NPs was anchored on Vulcan XC-72 carbon and which was employed as efficient catalyst for hydrogen generation from FA [16]. The results revealed that AgPd based catalytic systems showed a high catalytic activity due to the formation of AgPd alloy nano-facets. Qin and coworkers designed PdNi@Pd/GNs-CB catalyst, which can catalyze the dehydrogenation of formic acid more effectively at room temperature than Pd or Ni alone. Furthermore the Ni-doping changed the electronic state of Pd, and endowed the catalyst with a strong capability of anti-poisoning to CO [17]. Mori et al. revealed that CuPd alloy owns a significantly higher catalytic activity as well as a better tolerance toward CO poisoning compared with monometallic Pd counterparts in the reaction of FA dehydrogenation [18]. The above results demonstrated that bimetallic NPs present improved physical and chemical properties compared with their monometallic NPs, and the doping of second metal can tailor the electronic and geometric structures of NPs, leading to an enhanced catalytic activity and selectivity [19,20].

It should be noted that although bimetallic NPs possess higher catalytic activity than corresponding monometal, supporting materials are usually needed to maintain their improved catalytic activity and life span as the use of supports can restrain the aggregation and achieve the

* Corresponding authors.

E-mail addresses: gaoshutao@hebau.edu.cn (S.-T. Gao), wangchun@hebau.edu.cn (C. Wang).¹ These authors contributed equally to this work.



Scheme 1. Schematic illustration of the preparation process of the CuAg/BC.

homogeneous dispersity of metal nanoparticles [21]. Many supports have been used to anchor metal particle, such as metal oxides [6,9], polymers [22], carbonaceous materials [23,24], metal-organic frameworks [2,4,25] and so on. Among them, carbonaceous materials are commonly used catalyst support material because of its large surface area, good stability, high electrical conductivity, and rich pore structure. Recently, a novel carbonaceous material, biomass carbon nanosphere (BC) has attracted considerable attention [26]. As a green and renewable material, BC has been applied to many catalytic systems, such as dehydrogenation [27], oxidation and reduction reaction [28] [29].

In this work, BC was fabricated by hydrothermal carbonization of sucrose in the presence of kayexalate. Then the bimetal CuAg nanoparticles were immobilized on BC (denoted as CuAg/BC) (Scheme 1), and which was used as a catalyst for the dehydrogenation of formaldehyde for the first time. The as-synthesized CuAg/BC exhibited high catalytic activity for the dehydrogenation reaction under mild conditions.

2. Experimental

The relevant reagents and instruments are given in the Electronic Supporting information.

2.1. Synthesis of biomass carbon nanospheres

BC was synthesized according to the reported procedure [26]. In a typical synthesis, 8 g sucrose and 40 mg sodium polystyrene sulfonate were added into 50 mL of deionized H₂O. Then the mixture was transferred into 100-mL Teflon-lined steel autoclave and sealed. The autoclave was heated to 180 °C for 8 h in an oven. After cooled down naturally, the dark-brown material was washed three times with water and ethanol-water (1,1) solution then dried under 80 °C in an oven. The obtained material was calcined at 800 °C for 1 h under a N₂ atmosphere to obtain BC.

2.2. Synthesis of CuAg/BC via coreduction

For preparation of Cu₂Ag₈/BC, 50 mg BC, 7.62 mL AgNO₃ (1 mg mL⁻¹, 0.045 mmol) and 2.1 mL Cu(NO₃)₂ (1 mg mL⁻¹, 0.011 mmol) were mixed in a round flask and stirred for 12 h at room temperature. The resulting mixture was reduced by NaBH₄ solution

(1 mL, 0.5 mol L⁻¹) at 0 °C for 1 h with vigorous stirring. After centrifugation and washing with deionized water, the obtained Cu₂Ag₈/BC (the molar ratio of Cu and Ag was 2:8) was dried at 80 °C overnight in a vacuum. The Cu₁₀/BC, Cu₁Ag₉/BC, Cu₄Ag₆/BC, Ag₁₀/BC were prepared by the above procedure except that the molar ratios of Cu and Ag were 10:0, 1:9, 4:6, 0:10, respectively. The Pd/BC was prepared by the above procedure except that 50 mg BC was dispersed in the solution of H₂PdCl₄ (13 mL, 1 mg mL⁻¹) solution.

2.3. Synthesis of Cu₂Ag₈/BC via step-by-step reaction

For the preparation of Cu₂Ag₈/BC via step-by-step reaction (denoted as Cu₂Ag₈-SBS/BC), 50 mg BC and 2.1 mL Cu(NO₃)₂ (1 mg mL⁻¹, 0.011 mmol) were mixed in a round flask and stirred for 12 h at room temperature. The resulting mixture was reduced by NaBH₄ solution (1 mL, 0.5 mol L⁻¹) at 0 °C for 1 h with vigorous stirring. Then 7.62 mL AgNO₃ (1 mg mL⁻¹, 0.045 mmol) was added into the above suspension solution and stirred for 12 h at room temperature. The resulting mixture was reduced by NaBH₄ solution (1 mL, 0.5 mol L⁻¹) at 0 °C for 1 h with vigorous stirring. After centrifugation and washing with deionized water, the obtained Cu₂Ag₈-SBS/BC was dried at 80 °C overnight in a vacuum.

2.4. Catalytic hydrogen production

In a typical catalytic measurement, 7.5 mg catalyst was added into 50 mL mixture solution of NaOH (1 mol L⁻¹) and HCHO (0.4 mol L⁻¹) in a 600-mL sealed flask. The sealed flask was placed in a water bath at a preset temperature (15–30 °C) with stirring vigorously, meanwhile the hydrogen generation reaction started. The amount of hydrogen produced was measured by gas chromatograph equipped with TCD. The evolved gas was extracted 30 uL with syringe every five minutes and which immediately injected into the gas chromatograph for analysis (Fig. S11). The composition of gas was measured by gas chromatograph equipped with TCD and FID.

3. Results and discussion

3.1. Characterization of catalyst

The morphology of the Cu₂Ag₈/BC composite was characterized by transmission electron microscopy (TEM). It can be seen that the Cu-Ag nanoparticles are well dispersed on spheric BC with an average particle size of about 2–8 nm (Fig. 1a). The high resolution TEM image (Fig. 1b) showed that the lattice spacing is 0.22–0.23 nm, which is between the (111) lattice spacing of face-centered cubic (fcc) Cu (0.208 nm) and fcc Ag (0.24 nm), suggesting the formation of a Cu-Ag alloy structure. The crystal structures of the as-prepared BC, Cu₁₀/BC, Cu₂Ag₈/BC and Ag₁₀/BC were investigated by powder X-ray diffraction (PXRD). As illustrated in Fig. 2, all of the samples exhibit a weak and broad peak at 23.74°, which can be assigned to the (002) planes of graphitic carbon [30]. The Ag₁₀/BC gave four distinctive diffraction peaks located at 38.58°, 44.78°, 65.2°, 78.04°, which corresponded to (111), (200), (220) and (311) planes of metallic silver (PDF#04-0783), respectively. The Cu₁₀/BC showed three peaks at 43.66°, 50.54°, 70.38° corresponded to (111), (200), (220) planes of metallic Cu (PDF#04-0836), respectively. The Cu₂Ag₈/BC displayed four diffraction peaks at 38.62°, 44.68°, 65.1°, 78.38°, all of which slightly shifted, compared with that of Ag₁₀/BC, demonstrating that the Cu-Ag alloy structure has formed. The peaks of Cu (200) and (220) disappeared possibly because of the low metal loading and well dispersed of Cu nanoparticles.

X-ray photoelectron spectroscopy (XPS) spectrum (Fig. S1) was used to reveal the valence state of Cu, Ag and C in the catalyst. As shown in the Fig. S1b, the peaks located around 932.82 and 952.72 eV are assigned to Cu⁰ 2p_{2/3} and Cu⁰ 2p_{1/2}, respectively. Also, there are the satellite shakeup feature characteristics of Cu²⁺ species and two peaks

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