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Short Communication

Capping-agent-free Synthesis of Catkin-like CoB Microstrucutres Composed of Untrathin Nanosheets and Their Catalytic Performance in the Hydrolysis of Sodium Borohydride

J.J. Yan[1], J.Y. Liao[2], H. Li[2,], K.J. Feng[2], H. Wang[1], R.F. Wang[1,*], S.X. Li[1], S. Ji[3]*

[1] College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China
[2]Department of Chemical Engineering, Huizhou University, Huizhou, 516007, China
[3]College of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen 518060, China
[*]E-mail: lihao180@126.com, wrf38745779@126.com

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In this work, catkin-like CoB microstructures composed of ultrathin nanosheets were prepared via a ball-milling-assisted liquid–liquid interfacial reaction. In the synthetic process, no capping agents, such as surfactants, complexing agents or polymer stabilizers, were used. The specific surface area of the as-prepared catkin-like CoB sample was very large (224.7 m^2 g^{-1}), which enabled it to be a promising catalyst in many heterogeneous catalytic reactions. When the catkin-like CoB acted as a catalyst for the hydrolysis of sodium borohydride, the hydrogen generation rate could reach ca. 3.12 L min^{-1} g^{-1}, which was higher than the as-prepared CoB nanoparticles with an average size of 20 nm and many CoB catalysts reported in literature. In addition, our CoB catalyst could retain 88% of its origin activity after 7 cycles, exhibiting high durability and good reusability. The high catalytic activity, low-cost, together with its good durability and reusability, make the catkin-like CoB catalyst suitable for sodium borohydride hydrolysis for hydrogen generation in the practical applications.

Keywords: Cobalt boron alloy; Interfacial reaction; nanocatalysis; Hydrogen production.

1. INTRODUCTION

Over the past decade, nanostructured CoB alloys have drawn wide attention on account of their potential applications in different areas, including powder metallurgy, ferrofluids, anode material for secondary alkaline batteries, and heterogeneous catalysis [1, 2, 3]. Recently, fabrication of nanostructured CoB alloys with specific morphology and controlled architecture has become a research hotspot considering the fact that the physicochemical properties of nanomaterials are closely related to their morphology. During the past several years, plenteous differently-shaped CoB nanostructures have been successfully prepared, such as CoB nanospindles [4], CoB nanorods [5], CoB nanospheres [6], CoB hollow spheres [7], CoB nanoworm [1], CoB flowers [8]. In those cases, a large amount of capping agents, such as surfactants, complexing agents or polymer stabilizers, are used in the synthesis, which play a key role in determining the sizes and shapes of the obtained CoB products. The usage of capping agents will remarkably increase the cost of synthetic process. Furthermore, the existence of organic molecules on the surface of the nanomaterials may have detrimental effect on their properties, which may result in difficulty for their potential applications. For example, in heterogeneous catalysis, these capping agents will tightly bind to the surface and make the active sites of the nanocatalysts occupied [9]. On the other aspect, the removal of these capping agents from the surface of nanostructures is both costly and complex. Considering all these factors, fabrication of nanostructured CoB alloys without any capping agents is much more attractive. However, despite the significant progress made on the shape-controlled synthesis of CoB nanomaterials, synthesis of CoB nanoalloys with specific morphology independent of any capping agent is still a challenge.

In our recent work, amorphous NiCo nanoflowers consisting of nanosheets were synthesized via a liquid-liquid interfacial reaction [10]. In this work, the method is modified and applied to prepare catkin-like CoB microstructures composed of ultrathin nanosheets, in which no capping agent is used. As far as we know, fabrication of CoB microstructures via a ball-milling-assisted liquid-liquid interfacial reaction has not been reported previously. Interestingly, the specific surface area of the as-prepared CoB catalyst can reach 224.7 m^2 g^{-1}, which is much larger than those of CoB nanostructures reported in literature. Besides, the catkin-like CoB sample exhibits high catalytic performance in the hydrolysis of $NaBH_4$ for hydrogen generation, which may find practical applications in the hydrogen-oxygen fuel cell systems.

2. EXPERIMENTAL SECTION

2.1. Synthesis

All chemical reagents were of analytic grade and ultrapure water was used in the experiments. In a typical synthesis, 150 mg $CoCl_2 \cdot 6H_2O$ and 3 mL $CHCl_3$ were mixed into a ball-milling vessel, with which 20 balls with a diameter of 5 mm are filled. After that, 3 mL $NaBH_4$ solution (0.84 mol L^{-1}) was slowly added into the above mixture. Then, the ball grinder was operated at a rotation rate of 750 rpm for 2 h. The resultant black precipitate was washed with ethanol and deionized water. Finally, the obtained precipitate was dried in a vacuum oven at 60 ^oC for 8 h. For reference, CoB nanoparticles were also prepared. Typically, 150 mg $CoCl_2 \cdot 6H_2O$ and 3 ml ultrapure water were placed into a reaction, and then 3 mL 0.84 mol L^{-1} $NaBH_4$ solution were slowly added into the above solution. The mixed solution was sealed for 6 h at room temperature.

2.2 Characterization

The morphology of the samples were studied by a Carl Zeiss Ultra Plus field emission scanning electron microscope (SEM) and a Joel JEM-2010 transmission electron microscope (TEM). The specific surface area was measured on a Quantachrome Autosorb-1 volumertic analyzer, using nitrogen adsorption and the Brunauer-Emmett-Teller method, and the pore size distribution was calculated from the isotherms using the BJH (Barett-Joyner- Halenda) procedure. X-ray diffraction (XRD) patterns of the CoB samples were recorded on a Shimadzu XD-3A diffractometer with Cu Kα radiation (λ = 1.5406Å). The molar ratios of Co to B in CoB samples were determined by a Varian 720 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES).

2.3 Hydrogen generation testing

Catalytic reaction was carried out at 30 ^{o}C in a three-necked glass container connected with a water-filled gas burette to measure the volume of H_2 produced from the hydrolysis of $NaBH_4$. In a typical process, 3.6 mmol $NaBH_4$ and 2.5 mmol NaOH were mixed into a three-necked glass container containing 10 ml ultrapure water, followed by the addition of 10 mg CoB catalyst under mechanical stirring. For the durability and reusability testing, the used CoB catalyst was separated from the reaction solution by a magnet, and then washed and dried. Another run of catalytic activity testing was carried out by using the recovered CoB as a catalyst. Similar process was repeated 7 times.

3. RESULTS AND DISCUSSION

The morphology of the as-synthesized CoB sample was investigated by SEM and TEM, and the results are displayed in Fig.1. As shown in Fig.1a, numerous irregularly-shaped aggregations with a typical size of 1-2 μm are obtained.

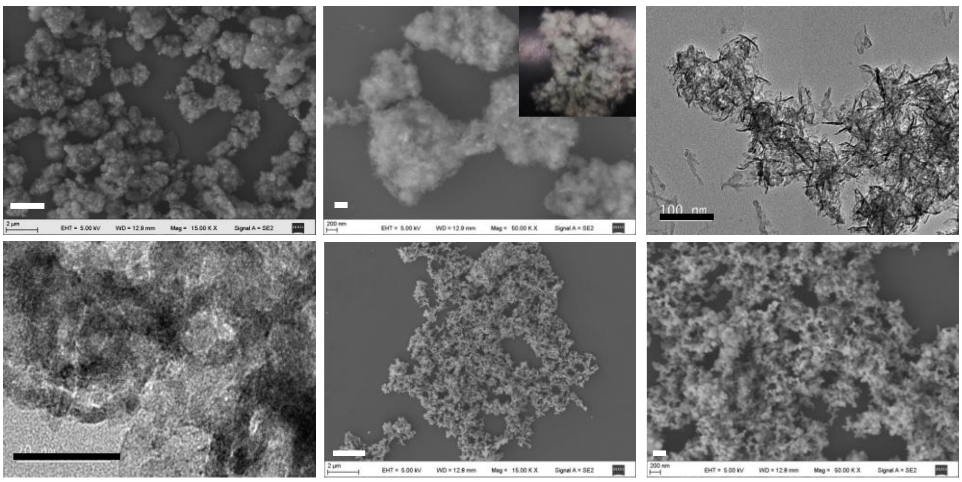

Figure 1. SEM (a, b), TEM (c), HRTEM (d) images of the as-prepared catkin-like CoB microstructures and SEM images (e, f) images of the CoB nanoparticles. Inset in Fig.1b is the photograph of catkin.

Fig.1b indicates that these aggregations look somewhat like catkins, which is illustrated in the inset of Fig.1b. TEM image in Fig.1c clearly reveals these catkin-like aggregations are not solid, but composed of plenteous ultrathin nanosheets with a thickness of less than 10 nm. High-magnification TEM image in Fig.1d shows there are no regular crystal fringes in the CoB sample, hinting its amorphous structure. In contrast, the CoB products obtained by a traditional chemical reduction method are spherical nanoparticles with an average size of 20-30 nm (Fig. 1e and 1f).

Fig.2 shows the XRD patterns of the catkin-like CoB microstructures and CoB nanoparticles. Obviously, there is only a broad peak centered at about $2\theta = 45.5^{o}$ in both XRD patterns, which can be indexed to the amorphous state of cobalt boron alloy [1, 4]. Note that no characteristic peaks of metallic Co was observed, demonstrating the obtained sample are CoB rather than Co. The molar ratios of Co to B for both samples determined by ICP-OES are around 1:0.32, implying that the composition of the samples is not affected by the synthetic methods.

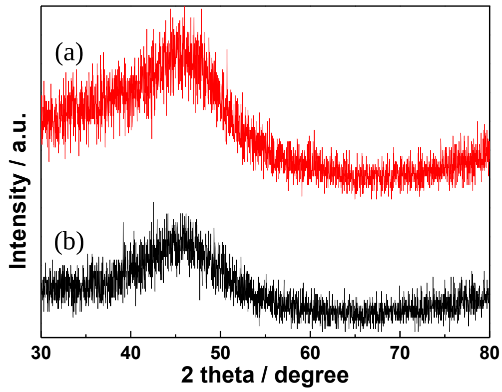

Figure 2. XRD patterns of the catkin-like CoB microstructures (a) and the CoB nanoparticles (b).

Fig.3a displays the adsorption-desorption isotherm of nitrogen and the corresponding pore size distribution curve of the catkin-like CoB microstructures. The adsorption-desorption isotherm of the CoB sample belongs to Type IV in the classification of IUPAC, with an adsorption-desorption hysteresis loop at the high pressure range. This implies that the as-prepared CoB sample possesses mesoporous structures, which was supported by the porous size distribution curve in the inset in Fig.3a. For comparison, the adsorption-desorption isotherm of the CoB nanoparticles belongs to Type II in the classification of IUPAC, indicating that the CoB nanoparticles is non-porous. The BET surface of the CoB nanoparticles calculated from the adsorption-desorption isotherm is 20.9 $m^2\ g^{-1}$, while that of catkin-like CoB microstructures can reach ca. 224.7 $m^2\ g^{-1}$, which is much higher than that of CoB nanostructures recently reported in literature, such as CoB nanoparticles (65 $m^2\ g^{-1}$) [1], CoB nanoworm (163.77 $m^2\ g^{-1}$) [1], CoB hollow spheres (100.7 $m^2\ g^{-1}$) [7], CoB hollow nanospindles (143.09 $m^2\ g^{-1}$) [4]. Such a large BET surface may lead to its high catalytic activity for many heterogeneous catalytic reactions.

In contrast to the traditional electrochemical method for preparing CoB [12], the synthetic process for the catkin-like CoB catalyst presented in this work was very simple, in which no capping agent was used. Furthermore, the specific surface area of our catkin-like CoB catalyst is 224.7 m^2 g^{-1}, which is much higher compared to those of CoB nanostructures prepared by other methods [1, 4, 7]. This large specific surface area will be beneficial to enhance the activity for the hydrogen generation reaction.

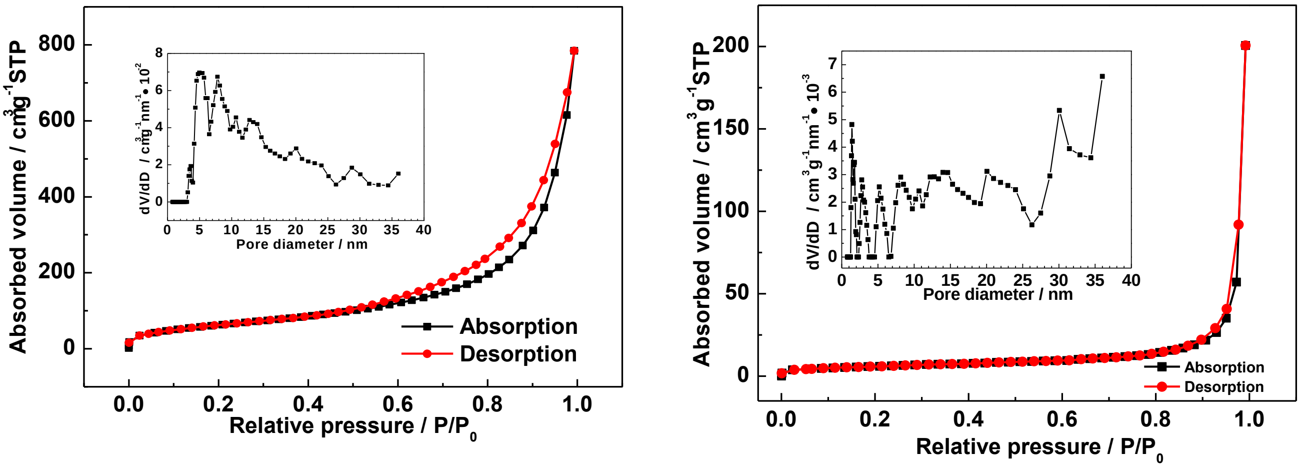

Figure 3. The adsorption-desorption isotherms and porous size distribution curve of the catkin-like CoB microstructures (a) and the CoB nanoparticles (b).

In this study, the hydrolysis of $NaBH_4$ for H_2 generation is applied as a model reaction to test the catalytic activity of the as-synthesized catkin-like CoB microstructures. As shown in Fig. 4, both the catkin-like CoB microstructures and the CoB nanoparticles can effectively catalyzed the hydrolysis of $NaBH_4$ to produce hydrogen. The hydrogen generation rate is 2.24 L min^{-1} g^{-1} for the CoB nanoparticles and 3.12 L min^{-1} g^{-1} for the catkin-like CoB microstructures, respectively. That value for catkin-like CoB catalyst is higher than the hydrogen generation rates reported for many other CoB catalysts, such as CoB catalyst (0.75 L min^{-1} g^{-1}) [11], electroless and electroplanted thin-film CoB/Ni-foam catalysts (1.64 and 0.3 L min^{-1} g^{-1}, respectively) [12], CoB catalyst prepared by a sonochemical approach (ca. 1.8 min^{-1} g^{-1}) [13], CoB nanoparticles (2.4 L min^{-1} g^{-1}) [14], CoB/open-CNTs (3.041 L min^{-1} g^{-1}) [15].

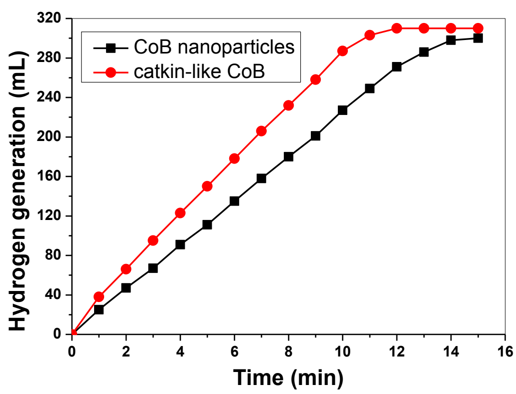

Figure 4. Hydrogen generation at different reaction time.

In addition to the catalytic activity, the durability and the reusability of a heterogeneous catalyst are important concerns in the practical applications. In this study, it was found that the CoB nanoparticles lost ca. 50% activity of its origin activity after 7 catalytic cycles. Interestingly, the as-prepared catkin-like CoB still retained ca. 88% activity of its origin activity after 7 catalytic cycles, demonstrating the good durability and the reusability of our catalyst.

4. CONCLUSION

In summary, catkin-like CoB microstructures composed of ultrathin nanosheets were synthesized via a ball-milling-assisted liquid–liquid interfacial reaction free of any capping agent. The specific surface area of the as-prepared catkin-like CoB sample could reach 224.7 m^2 g^{-1}. When the catkin-like CoB acted as a catalyst in the hydrolysis of sodium borohydride, the hydrogen generation rate could reach ca. 3.12 L min^{-1} g^{-1}, which is higher than the as-prepared CoB nanoparticles and many CoB catalysts reported in literature. In addition, our CoB catalyst could retain 88% of its origin activity after 7 cycles, exhibiting high durability and good reusability. The high catalytic activity, low-cost, together with its good durability and reusability, make the catkin-like CoB catalyst suitable for hydrogen generation from the hydrolysis of sodium borohydride in the practical application. Besides, the catkin-like CoB catalyst can find other applications in the heterogeneous catalysis due to its large BET surface.

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