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Strategic synthesis of graphene supported trimetallic Ag-based core–shell nanoparticles toward hydrolytic dehydrogenation of amine boranes

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ABSTRACT

We reported the synthesis and characterization of two trimetallic (Ag@CoFe, and Ag@NiFe) core–shell nanoparticles (NPs), and their catalytic activity toward hydrolytic dehydrogenation of ammonia borane (AB) and methylamine borane (MeAB). The as-synthesized trimetallic core–shell NPs were obtained via a facile one-step *in situ* procedure using methylamine borane as a reducing agent and graphene as the support under ambient condition. The as-synthesized NPs are well dispersed on graphene, and exhibit higher catalytic activity than the catalysts with other conventional supports, such as the SiO₂, carbon black, and γ -Al₂O₃. Additionally, compared with NaBH₄ and AB, the as-synthesized Ag@CoFe/graphene NPs reduced by MeAB exhibit the highest catalytic activity, with the turnover frequency (TOF) value of 82.9 (mol H₂ min⁻¹ (mol Ag)⁻¹), and the activation energy (E_a) value of 32.79 kJ/mol. Furthermore, the as-prepared NPs exert good durable and magnetically recyclability for the hydrolytic dehydrogenation of AB and MeAB. Moreover, this simple strategic synthesis method can be easily extended to the facile preparation of other graphene supported multi-metal core–shell NPs.

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1. Introduction

Metallic composite nanoparticles (NPs) with core–shell architectures have received considerable attention due to their unique optical [1], electronic [2], magnetic [3], and catalytic properties [4]. The core–shell NPs are very often found to exhibit higher catalytic activity than the alloy and monometallic counterparts, which may be caused by the interplay

of electronic and lattice effects of the neighboring metals [5]. However, until now, reports have mainly focused on the bimetallic systems, while trimetallic core–shell NPs are only developed recently [6].

Graphene is a novel nanomaterial with a single sheet of carbon atoms packed in a sp² lattices. It holds many advantages such as high specific surface area [7], thermal and chemical stability [8], outstanding charge carrier mobility [9], and superior electrical conductivity [10], etc., which could be

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an ideal substrate for growing and loading metal NPs. Recently, many examples of using graphene as support for metal NPs, and then harvesting their catalytic performance have been reported [11]. However, the direct one-step *in situ* growth and anchoring trimetallic core–shell NPs on graphene have been rarely reported. Thus, developing a mild and rapid strategy for facile synthesis of graphene supported trimetallic core–shell NPs with high catalytic activity, and comparing with other conventional supports are of great interests.

Safe storage and effective release of hydrogen under ambient condition are still the most critical issues in hydrogen-based energy [12]. Recently, boron-nitrogen containing compounds have attracted much attention due to their high gravimetric hydrogen densities and favorable kinetics of hydrogen release [13]. Ammonia borane ($\text{NH}_3\text{-BH}_3$, AB), the parent amine borane, with 19.6 wt% hydrogen content, high stability, and environmental benignity, is corresponding an attractive candidate for chemical hydride systems [14]. The hydrogen release from AB could be achieved by catalytic dehydrogenation in non-aqueous solvent [15], thermal decomposition [16], and hydrolysis [17]. With appropriate catalysts, 1 mol AB could release 3 mol H_2 by hydrolysis under ambient condition, which appears to be the most convenient one for the portable hydrogen storage application [18]. A number of transition metals and their alloys have been tested as catalysts for the hydrolysis of AB, and most of them were reduced by NaBH_4 , AB, or a mixture of NaBH_4/AB . However, as a derivative of AB, methylamine borane ($\text{CH}_3\text{NH}_2\text{-BH}_3$, MeAB) has not been widely used as the reducing agent in the synthesis of NPs. As the classical Lewis acid-base adducts, amine-boranes offer much better control in reducing rate and selective reduction of metal ions over the traditional reducing agents like borohydrides. The reducing strength decreases when increasing the alkyl substitution on nitrogen: $\text{H}_3\text{N-BH}_3 > \text{MeNH}_2\text{-BH}_3 > \text{Me}_2\text{NH-BH}_3 > \text{Me}_3\text{N-BH}_3$ [19]. Moreover, MeAB has the high gravimetric hydrogen content (11.1 wt%) [20], its catalytic dehydrogenation in non-aqueous solvent [21], and thermal decomposition [22] has been studied. However, to the best of our knowledge, the hydrolysis of MeAB, which could also release 3 mol H_2 per mol MeAB under ambient condition according to Eq. (1) has been rarely reported. Therefore, exploring new strategies to develop efficient, economical and stable catalysts toward catalytic hydrolytic dehydrogenation from amine–borane systems under moderate conditions is crucial for their practical applications.



Herein, we report an *in situ* co-reduction method for preparing graphene supported Ag@CoFe and Ag@NiFe NPs using methylamine borane (MeAB) as the reductant under ambient

condition. Their catalytic activity toward the hydrolytic dehydrogenation of AB and MeAB under ambient condition was also studied.

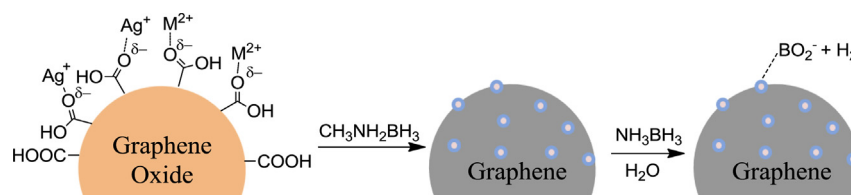
2. Experimental

2.1. Materials

Ammonia borane ($\text{NH}_3\text{-BH}_3$, AB, Aldrich, 90%), sodium borohydride (NaBH_4 , Sinopharm Chemical Reagent Co., Ltd., $\geq 96\%$), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 99\%$), nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 99\%$), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 99\%$), silver nitrate (AgNO_3 , AR), Ketjen black EC-300J (Triquo Chemical Co., Ltd.), neutral silica power (SiO_2 , Branch of Qingdao Haiyang Chemical Co., Ltd.), Aluminum oxide neutral ($\gamma\text{-Al}_2\text{O}_3$, Sinopharm Chemical Reagent Co., Ltd., FCP), methylamine hydrochloride ($\text{CH}_3\text{NH}_2 \cdot \text{HCl}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 96\%$), potassium permanganate (KMnO_4 , Shanghai Chem Co., Ltd., $\geq 99.5\%$), hydrogen peroxide (H_2O_2 , Sinopharm Chemical Reagent Co., Ltd., $\geq 30\%$), sodium nitrate (NaNO_3 , Sinopharm Chemical Reagent Co., Ltd., $\geq 99\%$), sulfuric acid (H_2SO_4 , Sinopharm Chemical Reagent Co., Ltd., 95–98%), tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 99\%$), dimethyl ether anhydrous ($\text{C}_4\text{H}_{10}\text{O}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 99.7\%$), graphite power (Sinopharm Chemical Reagent Co., Ltd., $\geq 99.85\%$). Graphene oxide (GO) and methylamine borane (MeAB) were synthesized by the methods reported in the literature [23–25]. All the chemicals were used as obtained. We use ordinary distilled water as the reaction solvent.

2.2. *In situ* synthesis of Ag@CoFe/graphene, and Ag@NiFe/graphene catalysts

In a typical experiment, 10 mg GO were kept in a 25 mL two-necked round-bottom flask, 1.8 mL cobalt chloride (or nickel chloride) and 0.2 mL ferrous chloride solution (0.0225 mol/L) and 0.1 mL silver nitrate solution (0.05 mol/L) were added into the round-bottom flask. One neck was connected to a gas burette, and the other was connected to a pressure-equalization which used to introduce MeAB. 2.0 mL of aqueous solution containing 90.0 mg MeAB (2 mmol) was kept in the pressure-equalization. The reactions were started when the MeAB solution was added to the flask with vigorously stirring, the evolution of the gas was monitored by the gas



Scheme 1 – Schematic illustration (The orange hemisphere denotes GO; the gray hemisphere represents graphene.). (For interpretation of the references to color in this legend, the reader is referred to the web version of this article.)

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