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Graphene supported Ru@Co core-shell nanoparticles as efficient catalysts for hydrogen generation from hydrolysis of ammonia borane and methylamine borane

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#### Abstract

Well-dispersed graphene supported Ru@Co core-shell nanoparticles were synthesized by one-step *in situ* co-reduction of aqueous solution of ruthenium(III) chloride hydrate, cobalt(II) chloride hexahydrate and Graphite Oxide (GO) with ammonia borane under ambient condition. The as-synthesized nanoparticles exert excellent catalytic activities, with the turnover frequency (TOF) value of 344 mol H<sub>2</sub> min<sup>-1</sup> (mol Ru)<sup>-1</sup> for catalytic hydrolysis of ammonia borane, which is the second highest value ever reported. The as-synthesized catalysts exert superior catalytic activities than the monometallic (Ru/graphene), alloy (RuCo/graphene), and graphene-free Ru@Co counterparts towards the hydrolytic dehydrogenation of AB. Moreover, the catalytic hydrolysis of MeAB at room temperature was also studied. These Ru@Co NPs are a promising catalyst for amine-borane hydrolysis and for developing a highly efficient hydrogen storage system for fuel cell applications.

Keywords: core-shell, ruthenium, cobalt, graphene, hydrogen storage

#### 1. Introduction

Safe and efficient storage of hydrogen is essential for the development of a hydrogen-based energy infrastructure [1]. Recently, numerous hydrogen storage approaches are currently under investigation, including metal hydrides [2], sorbent materials [3], and chemical hydride systems [4]. Among the chemical hydrides, ammonia borane (NH<sub>3</sub>-BH<sub>3</sub>, AB) has recently received a great interest because of its 19.6 wt% hydrogen content, highly stability, and environmentally benign [5]. Hydrolytic dehydrogenation of AB is considered to be the most convenient approach for portable hydrogen storage application [6]. However, the methyl-substituted AB, methylamine borane (CH<sub>3</sub>NH<sub>2</sub>-BH<sub>3</sub>, MeAB) with the 11.1 wt% hydrogen content, has not been widely studied [7]. Furthermore, to the best of our knowledge, the hydrolysis of MeAB, which could also release 3 mol H<sub>2</sub> per mol MeAB at room temperature has been rarely reported. Therefore, searching for suitable catalysts that meet efficient, economical, and stable requirements toward hydrogen generation from the amine-borane systems under moderate conditions, is crucial for their practical applications.

On the other hand, bimetallic transition metal core-shell nanoparticles (NPs) have attracted considerable interest owing to their unique optical properties [8], electronic properties [9], and exciting potential for application in biological [10], chemical sensing [11], optoelectronics [12], magnetics [13], and catalysis [14]. Such materials

are often found to possess enhanced catalytic properties in contrast to the monometallic counterparts and alloys, due to the interplay of electronic and lattice effects of the neighboring metals [15]. Ru nanoparticles, including monometallic Ru-based NPs [16] and bimetallic RuCo [17], RuNi [18], and Ni@Ru [19] NPs, have showed extremely high activities for catalytic dehydrogenation of AB. Recently, the synthesis of Ru@Ni core-shell NPs has been reported by a spray-pyrolysis method [20], however, as far as we know, there are no reports about synthesis and characterization of Ru@Co core-shell NPs. Therefore, developing a facile one-step route to construct the Ru-based core-shell NPs with high catalytic activities are highly desirable.

Herein, we first report the *in situ* synthesis of magnetically recyclable graphene supported Ru@Co core-shell NPs using AB as reductant in a one-step co-reduction route at room temperature under ambient atmosphere. Graphene was chosen as a support because it has been reported to be a suitable substrate to grow active materials and maintain the stability of the metal NPs during the catalytic process [21], due to its outstanding charge carrier mobility [22], thermal and chemical stability [23], and high specific surface area [24], *etc.*. The as-synthesized catalysts exert superior catalytic activities than the monometallic (Ru/graphene), alloy (RuCo/graphene), and graphene-free Ru@Co counterparts towards the hydrolytic dehydrogenation of AB. Moreover, the catalytic hydrolysis of MeAB at room temperature was also studied.

#### 2. Experimental

The detail experimental process could be found in the supporting information.

#### **3. Results and Discussion**

#### 3.1 Synthesis and characterization

The graphene supported core-shell Ru@Co/graphene NPs were prepared by adding AB into the precursor solution containing RuCl<sub>3</sub>, CoCl<sub>2</sub>, and graphene oxide (GO) at room temperature. The Ru<sup>3+</sup> and Co<sup>2+</sup> were reduced in sequence to produce core-shell structured NPs during the reduction process. Considering the reduction potentials of Ru<sup>3+</sup> and Co<sup>2+</sup> ( $E^0(Ru^{3+}/Ru) = +0.40 \text{ eV } vs$ . SHE;  $E^0(Co^{2+}/Co) = -0.28 \text{ eV } vs$ . SHE), Ru<sup>3+</sup> with higher reduction potential was first reduced by AB, and formed the *in situ* seed to induce the successive growth of the Co as the shell.

The microstructure of Ru@Co/graphene NPs were characterized by transmission electron microscopy (TEM). As shown in Fig. 1a, the NPs were well dispersed on graphene, which help to prevent the agglomeration. In Fig. 1b, there are three kinds of NPs, the big particles are around ~15 nm, some of them are monometallic Co NPs, while the others are bimetallic Ru@Co NPs, with the core-shell structures; the small ones with the particle sizes around ~2 nm are monometallic Ru NPs. The high resolution TEM (HRTEM) image indicates the core-shell NPs are mostly amorphous, and a distinct contrast of core and shell can be observed clearly in Fig. 1c. The dark core is Ru, and the gray shell is Co, indicating that Ru is initially reducing by AB, and subsequently acting as the seed helping for the reducing Co to form the shell. The lattice fringes of the small NPs can be clearly observed, with the lattice separation is 0.234 nm, which is consistent with the (100) plane of Ru (Fig. 1d). Therefore, it can be conclude that the as-synthesized NPs are the composite of the Ru, Co, and Ru@Co

core-shell NPs [25]. This may be caused by the discontinuous growth of Co shell on parts of the Ru seeds. Due to the small amount of Ru, the X-ray diffraction (XRD) pattern (Fig. S1) of the as-synthesized NPs has no obvious diffraction peak, indicating the sample is almost in an amorphous state, which is in good agreement with the TEM results. Furthermore, the most intense peak at around 8.3° corresponds to the GO disappeared, and new broad peak around 23.8° appeared in the as-prepared NPs indicating that the GO is successfully reduced to graphene. In the Raman spectroscopy (Fig. S2), the GO and graphene supported Ru@Co exhibit two peaks centered at 1354 and 1608 cm<sup>-1</sup>, corresponding to the D and G bands of the carbon products, respectively. The intensity ratio of the D to G band  $(I_D/I_G)$  is generally accepted to reflect the degree of graphitization of carbonaceous materials and defect density. After loading of the as-synthesized NPs, the  $I_D/I_G$  of GO is increased from 1.0 to 1.8. The relative changes in the D to G peak intensity ratio confirm the reduction of GO during the *in situ* fabrication. It can be seen clearly from the FTIR spectra (Fig. S3) that the disappearance of C=O peak at 1736 cm<sup>-1</sup>, C-OH peak at 1224 cm<sup>-1</sup> and the C-O peak at 1052 cm<sup>-1</sup> of GO after the formation of the as-synthesized NPs, further indicating the GO was reduced to graphene during the process.

#### 3.2 Catalytic activities for hydrolysis of AB

Without  $Ru^{3+}$ , the Co<sup>2+</sup> cannot be reduced by AB, resulting in no activity toward catalytic hydrolysis of AB as shown in Fig. 2. When Ru NPs were supported on graphene, keeping the molar ratio of Ru/AB as 0.004, AB cannot be catalytic decomposed completely, and only 89% of H<sub>2</sub> is released for about 1 h. Unexpectedly,

when Co was introduced into the NPs to form the core-shell NPs, and still keeping the molar ratio of Ru/AB as 0.004, the decomposed of AB was completed, and the reaction time was decreased. When the Co/Ru molar ratio is 7.5, the release of  $H_2$  can be completed within 2 min, further increased the Co/Ru molar ratio to 10 results in the prolonging of the reaction time, indicating the positive effect of the Ru@Co core-shell nanostructures to the catalytic hydrolysis of AB, and the best Co/Ru molar ratio in the Ru@Co core-shell NPs is 7.5. The activity in terms of turnover frequency (TOF) is 344 (mol H<sub>2</sub> min<sup>-1</sup> (mol Ru)<sup>-1</sup>) for this as-synthesized NPs, moreover, to the best of our knowledge, this is the second highest value ever reported for the catalytic hydrolysis of AB among the Ru-based catalyst, and higher than most of other reported noble metal-based catalysts, if the TOF is normalized in terms of mol noble metal (Table 1). Interestingly, the TOF value of the as-synthesized NPs is much higher than the Ni@Ru core-shell NPs, which have a more reactive Ru as the shell [19]. The results may be attributed to the positive synergistic effect between Ru and Co in the core-shell nanostructure, and more active sites deriving from the higher amorphous Co contents [21].

For comparison, RuCo/graphene and graphene-free Ru@Co NPs are also prepared and their catalytic activities to hydrolysis of AB are studied. As shown in Fig. 3, their catalytic activities are both inferior to that of Ru@Co/graphene NPs, which confirms that the positive synergistic effect of Ru@Co core-shell nanostructure. Furthermore, the catalytic activities of RuCo/graphene NPs are better than that of the Ru@Co NPs, highlighting the cooperative effect between graphene and NPs for AB

dehydrogenation.

#### 3.3 Recycle ability

The recyclability of the catalyst is crucial in the practical application. The recyclability of as-synthesized composite of Ru/graphene and Ru@Co/graphene NPs up to fifth run for hydrolysis of AB and MeAB are shown in Fig. 4 and 5 respectively. The as-prepared catalysts retain 51% of their initial catalytic activities in the hydrolysis of AB in the fifth run. In Fig. 5, with our as-synthesized NPs, MeAB can release 3 equiv. H<sub>2</sub> in less than 4 min at room temperature, with the TOF measured to be 226 (mol  $H_2 \text{ min}^{-1}$  (mol Ru)<sup>-1</sup>), and retain 51% of their initial catalytic activities after fifth run. Furthermore, the *in situ* synthesized NPs are magnetic and thus can be separated from the reaction solution by an external magnet (Fig. 5 inset), which makes the practical recycling application of the NPs more convenient. Additionally, when the recycled cycles increased to ten, there are only 32% and 25% of their initial catalytic activities were left for the catalytic hydrolysis of AB and MeAB, respectively (Fig. S4, S5). Further study about increase the stability and recyclability of the as-synthesized catalysts should be done toward their practical application. Fig. 1d and Fig. 1e show the representative TEM images of the as-synthesized NPs after the fifth run durability test. As clearly seen from the TEM images, there is no noticeable change in the morphology, and no obvious aggregation of the Ru NPs on graphene, but the Ru@Co core-shell NPs are readily agglomerate on graphene after five cycles. Therefore, the observed decrease in the catalytic activity may be attributed to the agglomeration of Ru@Co core-shell NPs, highlighting the positive

effect of Ru@Co core-shell NPs toward to catalytic hydrolysis of AB and MeAB. Further study about synthesis of the pure Ru@Co core-shell NPs is in process in our lab, which are supposed to exert higher catalytic activities for the hydrolytic dehydrogenation of AB and MeAB.

To better understand the hydrolysis of MeAB in the presence of as-synthesized NPs, and confirm the completely decomposed of MeAB after the catalytic reaction, we performed the <sup>11</sup>B NMR studies (Fig. S4). The <sup>11</sup>B peak at -19.8 ppm which assigned to MeAB is disappeared after the catalytic reaction, and a new peak around 11.4 ppm is observed indicating three moles of hydrogen has been generated from the one mole of MeAB *via* the catalytic hydrolysis according to Eq. (1). Furthermore, there is no change in the <sup>11</sup>B NMR of the MeAB after stay 7 days under ambient condition, indicating the catalytic activities of the as-prepared NPs toward catalytic hydrolysis of MeAB at ambient condition.

 $MeNH_2-BH_3+2H_2O \xrightarrow{catalyst} (MeNH_3)BO_2+3H_2 (1)$ 

#### Conclusion

In summary, for the first time, the Ru@Co core-shell NPs were synthesized by a one-step *in situ* method using graphene as the supported material. The as-synthesized NPs exhibit superior catalytic activities than the monometallic Ru and Co, alloy RuCo, and graphene-free Ru@Co counterparts. The turnover frequency (TOF) value of the as-synthesized NPs is 344 mol  $H_2 \text{ min}^{-1}$  (mol Ru)<sup>-1</sup> for catalytic hydrolysis of ammonia borane, which is the second highest value ever reported. In addition, the as-synthesized NPs show good durable stability and magnetically recyclability for the

hydrolytic dehydrogenation of AB and MeAB. Moreover, this simple synthetic method can be extend to other Ru-based bimetallic or trimetallic core-shell systems for more applications.

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#### **Figure Captions**

Table 1. TOF values for hydrolysis of AB catalyzed by different catalysts.

Fig. 1 (a)-(d) TEM images of the composite of Ru/graphene and Ru@Co/graphene NPs with different magnifications; (e)-(f) TEM images of the as-synthesized NPs after the fifth cycle.

Fig. 2 Time plots of catalytic dehydrogenation of AB over the as-synthesized catalysts at ambient condition. Ru/AB = 0.004 (molar ratio).

Fig. 3 Time plots of catalytic dehydrogenation of AB over RuCo/graphene, composite of Ru/graphene and Ru@Co/graphene, and composite of Ru and Ru@Co catalysts at ambient condition. Ru/AB = 0.004, Co/Ru = 7.5.

Fig. 4 Time plots of catalytic dehydrogenation of AB over the as-synthesized catalysts from 1st to 5th cycle at  $25 \pm 0.2$  °C. Ru/AB = 0.004, Co/Ru = 7.5.

Fig. 5 Time plots of catalytic dehydrogenation of MeAB over the as-synthesized catalysts from 1st to 5th cycle at  $25 \pm 0.2$  °C. Ru/MeAB = 0.004, Co/Ru = 7.5.

Catalyst	$TOF(mol H_2 mol^{-1} M min^{-1})$	Ref.
	M=Pt, Ru, Pd, Au	L
Ru/C	429.5	16(a)
Pd@Co/graphene	408.9	21
Ru@Co/graphene	344	This study
Ru(0)@MWCNT	329	16(b)
Ni <sub>0.33</sub> @Pt <sub>0.67</sub> /C	280.3	26
Pt@MIL-101	258.6	27
Co <sub>0.32</sub> @Pt <sub>0.68</sub> /C	248.5	28
Ni <sub>0.74</sub> Ru <sub>0.26</sub> alloy NPs	194.8	18
PSSA-co-MA stabilized Ru	187.6	29
nanoclusters		
Ni@Ru	114	16(b)
Ru@Al <sub>2</sub> O <sub>3</sub> after acetic acid	83.3	30
treatment		
$Ru@Al_2O_3$	39.6	30
RuCo (1:1)/γ-Al <sub>2</sub> O <sub>3</sub>	32.9	17
PSSA-co-MA stabilized Pd	19.9	29
nanoclusters		
RuCu (1:1)/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	16.4	17

Table 1 TOF values for hydrolysis of AB catalyzed by different catalysts.



Fig. 1 (a)-(d) TEM images of the composite of Ru and Ru@Co/graphene NPs with different magnifications; (e)-(f) TEM images of the as-synthesized NPs after the fifth cycle.



Fig. 2 Time plots of catalytic dehydrogenation of AB over the as-synthesized catalysts at ambient condition. Ru/AB = 0.004 (molar ratio).



Fig. 3 Time plots of catalytic dehydrogenation of AB over RuCo/graphene, composite of Ru/graphene and Ru@Co/graphene, and composite of Ru and Ru@Co catalysts at ambient condition. Ru/AB = 0.004, Co/Ru = 7.5.



Fig. 4 Time plots of catalytic dehydrogenation of AB over the as-synthesized catalysts from 1st to 5th cycle at  $25 \pm 0.2$  °C. Ru/AB = 0.004, Co/Ru = 7.5.



Fig. 5 Time plots of catalytic dehydrogenation of MeAB over the as-synthesized catalysts from 1st to 5th cycle at  $25 \pm 0.2$  °C. Ru/MeAB = 0.004, Co/Ru = 7.5.

#### Graphical abstract

Well dispersed Ru@Co/graphene nanoparticles were synthesized via a one-step *in situ* co-reduction route. The as-synthesized NPs exerted satisfied catalytic activity and recycle stability towards the hydrolysis of ammonia borane and methylamine borane.



Highlights:

First synthesize Ru@Co core-shell NPs supported on graphene The catalysts exhibit excellent catalytic activity toward hydrolysis of AB and MeAB Second highest TOF value for the catalytic hydrolysis of AB

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