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Ni<sub>0.25</sub>Co<sub>0.75</sub>O nanowire array supported on Cu@CuO foam, an inexpensive and durable catalyst for hydrogen generation from ammonia borane

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Abstract: The development of highly active and stable catalysts is desirable for hydrogen generation from ammonia borane (AB). In this study,  $Ni_{0.25}Co_{0.75}O$  nanowire array supported on Cu@CuO foam ( $Ni_{0.25}Co_{0.75}O/Cu@CuO$ ) has been successfully fabricated. The  $Ni_{0.25}Co_{0.75}O/Cu@CuO$  catalyst exhibited high performance towards AB hydrolysis with a high hydrogen generation rate (HGR) of 4.348  $L_{hydrogen}$  min<sup>-1</sup> g<sub>cat</sub>.<sup>-1</sup>. More importantly, the activity of  $Ni_{0.25}Co_{0.75}O/Cu@CuO$  has only decreased slightly after twelve cycles. This work provides a simple method to fabricate an inexpensive film catalyst with high activity and good stability for ammonia borane hydrolysis.

Keywords: Heterogeneous catalysis; Nanowire array; Hydroren generation; Ammonia borane hydrolysis.

### 1. Introduction

Hydrogen energy is one of the most promising substitutes for the transitional fossil fuels due to its high energy density, zero carbon expissions and reproducibility [1-3]. However, the efficient storage and transportation of hydroge i in a safe way is yet a challenge, which are urgent to be solved before practical application. In recent years, hydrolytic dehydrogenation of ammonia borane (NH<sub>3</sub>BH<sub>3</sub>, AB) has attracted considerable research interests since it can produce hydrogen in a simple, safe and effective vav [4-5]. According to the following equation (1), three equivalents of hydrogen can be liberated from one mole of AB. However, this reaction can not occur spontaneously because of the sluggish reaction dynamics [6]. Therefore, it is significant to develop a robust catalyst for hydrogen production from AB hydrolysis.

$$NH_3BH_3 + 2H_2O \rightarrow NH_4BO_2 + 3H_2 \tag{1}$$

In the past few years, a great deal of effort has been made to design robust and inexpensive catalysts, such as non-noble metal catalysts [7] and non-noble metal oxide composites [8-9]. For example, Yang *et al.* [10] have prepared Cu<sub>0.4</sub>Co<sub>0.6</sub>/ BN nanofibers (BNNFs) by an impregnation

reduction method, which exhibited a high hydrogen evolution rate (HGR) of  $3.387 L_{hydrogen} min^{-1} g_{cat.}^{-1}$  towards AB hydrolysis. Figen and co-authors [11] have fabricated Co<sub>3</sub>O<sub>4</sub>/ nanofibrous-1 (Nfs-1) composite with a high HGR of 2.540  $L_{hydrogen} min^{-1} g_{cat.}^{-1}$  towards AB hydrolysis. Although some progresses have been achieved on enhancing catalytic performance towards AB hydrolysis, those catalysts are still facing with some problems, which will worsen their performance in activity and stability. For instance, most of those catalysts are in the form of powder, which is likely to aggregate during hydrolysis [12-14]. In addition, the recovery of powder catalyst from the reaction system is tedious and costly. In contrast, nanocatalyst in the form of film is demonstrated to have good stability and be easy separation from the reaction system [2 15 16].

Herein, we successfully fabricated Ni<sub>x</sub>Co<sub>1-x</sub>O/Cu@CuO vatalysts via a simple hydrothermal process in conjunction with a calcination **•** reat nent. The obtained catalyst of Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO exhibited a high catalytic r er formance with a HGR of 4.348 L<sub>hvdrogen</sub> min<sup>-1</sup> g<sub>cat.</sub><sup>-1</sup> towards AB hydrolysis. More importantly, the Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO catalyst possessed good reusability and stability. The catalytic activity of Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO only slightly decreased after twelve catalytic cycles and its roughology and crystal structure remained unchanged after reaction. Considering its low cost, high activity and good stability, the obtained Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO can be a robust and durable catalyst for hydrogen production from AB hydrolysis.

#### 2. Experimental

#### 2.1 Synthesis of catalysts

All reagents used were of analytic grade and received from suppliers without further purification.  $Ni_xCo_{1-x}O/Cu@CuO$  was synthesized via a simple hydrothermal process in conjunction with a calcination treatment. Exemplified by the  $Ni_{0.25}Co_{0.75}O/Cu@CuO$ , the detailed synthesized process is depicted as follow: 1 mmol of  $NiCl_2 \cdot 6H_2O$  and 3 mmol of  $CoCl_2 \cdot 6H_2O$  were dissolved in 80 mL

of deionized water with stirring. Then, 10 mmol of hexamethylenetetramine (HMT) was added into the above solution. After stirring for 10 min, the mixture was transferred into a 100 mL Teflon-lined autoclave in which a copper foam (KunShan Lvchuang Electronic Technology Co. Ltd., Suzhou, China) of  $5 \times 12$  cm was placed in advance and heated at 423 K for 5 h. After the reaction was finished, the product was rinsed and dried at oven. Finally, the obtained precursor was calcined at temperatures in the range of 473-673 K for 3 h in air. The yield of catalyst is measured to be about 30%.

#### 2.2 Characterization of catalysts

The crystal structures of the samples were recorded by Riga xu Ultima IV X-ray powder Diffractometer (XRD) with a Cu K<sub> $\alpha$ </sub> radiation ( $\lambda = 1.5406 \mathring{A}$ , 40 Å, 40 mA). The morphologies of the samples were observed by a Hitachi SU8010 can ing electron microscope (SEM). The elements and oxidation states of the samples were ar a'yzed using a Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer (XPS). The BFT specific surface area of the catalysts were measured using a Micromeritics ASAP 2010 system.

#### **2.3 Catalytic experiments**

Unless specified, hydrolytic deh, drogenation of AB was performed at 298 K maintained by a thermostat. Typically, a piece of callyst foam  $(3 \times 2.5 \text{ cm})$  was added into a glass vessel containing 10 mL of deionized wath. Subsequently, 10 mL of mixed solution containing 3.0 mmol (0.0926 g) of AB and 20 mmol  $(0.8^{\circ} \text{ g})$  of NaOH was quickly added into the vessel. The volume of the produced gas was recorded by measuring the displacement of water in the gas burette. The reusability and stability tests were performed as following procedure. After the completion of AB hydrolysis in the previous cycle, the catalyst was isolated and washed, then dried in a vacuum oven at 343 K for 6 h. Then, the recovered catalyst was mixed with a pristine solution containing 3.0 mmol of AB and 0.8 g of NaOH in the way described above, and a new catalytic cycle of AB hydrolysis reaction started.

#### 3. Results and discussion

XRD analysis was carried out to record the crystal structure of the obtained  $Ni_{0.25}Co_{0.75}O/Cu@CuO$ . As shown in Figure 1, three notable peaks (marked as A) at around  $2\theta =$ 43.3°, 50.4°, and 74.1° were observed, which corresponded to the (111), (200), and (220) crystal planes of Cu (JCPDS 03-1005), respectively. It is worth noting that other three peaks (marked as B) appeared at around 35.6°, 38.7°, and 48.6° were observed. These peaks can be indexed to the (002) and (111) crystal planes of CuO (JCPDS 02-1040), which is a result of partial oxidation of Cu foam during the calcination process. Four diffraction peaks (marked as C) were observed at about 36.5°,  $42.4^\circ$ ,  $61.3^\circ$ , and  $73.3^\circ$ , which can be assigned to the (111), (200), (220), and (311) crystal faces of CoO-NiO, respectively. These results suggest the successful fal rica ion of Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO catalyst. In order to gain a deeper understanding of the form at process of Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO catalyst, we conducted XRD analysis on the precurs: r of Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO. Notably, the quality of the XRD pattern of Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@Cat precursor is low, due to the low intensity of diffraction peaks. Therefore, XRD analysis v as performed on powder instead of foam. As shown in Figure S1 in Supporting Information, the precursor is composed of  $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$ (JCPDS 48-0083) and Ni<sub>2</sub>(CO<sub>3</sub>) (OH) (CPDS 35-0501). According to the literature reported by Baek [17], HMT can decompose in. Nh<sub>3</sub> and HCHO during the hydrothermal reaction. Then, NH<sub>3</sub> dissolved in water and generated  $NH_4^+$  and  $OH^-$ . HCHO will react with  $O_2$  which can further convert to  $CO_3^{2^-}$ . The form ed  $OH^-$  and  $CO_3^{2^-}$  can further combine with  $Co^{2^+}$  and  $Ni^{2^+}$  cations to precursors of  $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$ form the and  $Ni_2(CO_3)$  $(OH)_2$ The  $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$  and  $Ni_2(CO_3)$  (OH)<sub>2</sub> supported on Cu foam will finally decompose into the Ni<sub>x</sub>Co<sub>1-x</sub>O and gases of CO<sub>2</sub> and H<sub>2</sub>O during the calcination process, where Cu foam was partially oxidized to CuO. Hence, the synthesis process of Ni<sub>x</sub>Co<sub>1-x</sub>O/Cu@CuO can be deduced as following equations.

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3$$
(2)

$$\mathrm{NH}_3 + \mathrm{H}_2\mathrm{O} \to \mathrm{NH}_4^+ + \mathrm{OH}^- \tag{3}$$

$$2\text{HCHO} + \text{O}_2 \rightarrow 2\text{HCOOH} \tag{4}$$

$$2\text{HCOOH} + \text{O}_2 \rightarrow 2\text{H}_2\text{CO}_3 \rightarrow 4\text{H}^+ + 2\text{CO}_3^{2-}$$
(5)

$$2Ni^{2+} + 2OH^{-} + CO_{3}^{2-} \rightarrow Ni_{2}(CO_{3})(OH)_{2}$$
(6)

$$\text{Co}^{2+} + \text{OH}^{-} + 0.5\text{CO}_3^{2-} + 0.11\text{H}_2\text{O} \rightarrow \text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$$
 (7)

 $xNi_2(CO_3)(OH)_2 + 2 - 2xCo(CO_3)_{0.5}(OH) \cdot 0.11H_2O \rightarrow 2Ni_xCo_{1-x}O + CO_2 + 1.22 - 0.22xH_2O$  (8)

Figures 2a-2c displays the SEM images of Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO. It is clearly to observe that well-defined nanowires in the form of array are obtained, which are perpendicular to the Cu@CuO foam. The average diameter of nanowires is about 40 nm seen from the magnified images in Figure 2b and 2c. The two-dimensional elemental mapping alorlysis was further performed on Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO. The uniform distribution of Co, Ni and Cu as well as O elements on Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO (Figure 2d) reveals that the ortained catalyst is a nanocomposite. The SEM images of the precursor of Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO are shown in Figure S2. It is clearly to observe that the surface of precursor is rough and numerous nanoparticles with mean sizes of 40 nm were observed. Obviously, the morphology of precursor has changed from nanoparticles to nanowire array after calcination treatment at C3 K.

The surface electronic structure and chemical compositions of the obtained catalyst were analyzed by XPS. In high-resolution XPS spectrum of Ni2p (Figure S3a), six peaks are observed. The peaks located at 880.1 and 861.3 eV are the satellite peaks of Ni2p. The peaks at about 874.5 and 856.5 eV are indexed to Ni<sup>3+</sup> and the peaks at about 872.9 and 855.0 eV are assigned to Ni<sup>2+</sup>, respectively [18]. These results are in line with the XPS data of NiO [18]. In Co2p spectrum (Figure S3b), two peaks at 795.5 and 780.3 eV are observed [19]. The spin-orbit splitting is measured to be 15.2 eV, suggesting that Co element in our catalyst is in the form of CoO [19]. In the Cu2p spectrum (Figure S3c), the peaks at 952.9 and 932.9 eV can be assigned to Cu [20], and the peaks appeared at 954.9 and 935.0 eV are indexed to Cu<sup>2+</sup> [21], arising from the oxidation of Cu during calcination. This result demonstrates that Cu and CuO coexisted in our sample.

The temperatures of calcination on catalysts have been demonstrated to have significant impacts on their structural and catalytic properties [22]. Therefore, we have fabricated a series of Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO catalysts calcined at different temperatures ranging from 473 K to 673 K. The SEM images of those catalysts are shown in Figure S4. It is worth noting that the morphologies of Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO catalysts calcined at 473 and 523 K are in the form of nanoparticles instead of nanowires. However, the morphologies of Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO catalysts have been converted to the form of nanowire array as the calcined temperatures increased to 573, 623 and 673 K. Generally, the precursor of transition metal oxide can convert to their corresponding transition metal oxide without morphology deformation by controlling thermal decomposition process in a delicate way [23]. Interestingly, morphology of our sample has changed distinctly from nanoparticles array to nanowires array when our precure or was calcined at temperature above 573 K. This may because the precursors of  $Co(CO_3)_{0.5}(Jr.) \cdot 0.11H_2O$  and  $Ni_2(CO_3)(OH)_2$  can quickly release CO<sub>2</sub> and H<sub>2</sub>O when the calcination temperature is elevated to 573 K, accompanied by lattice contraction of the precursor, which finally cauled a change in morphology. A similar finding that  $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$  nanobelts w is inverted to necklace-like 1D  $Co_3O_4$  nanochains after a calcination treatment was also reported in literature [23]. The catalytic performances of those obtained Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO cotalysts calcined at different temperatures towards AB hydrolysis are shown in Figure 3a It is c ear that all samples are active towards AB hydrolysis. When the Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO ca<sup>1</sup>c<sup>2</sup> ned at 473 K act as a catalyst, the catalytic activity is sluggish with an initial HGR of 0.128 L<sub>hvdrogen</sub> min<sup>-1</sup> g<sub>cat.</sub><sup>-1</sup>. As the calcined temperatures increased to 523, 573 and 623 K, the initial HGR is improved to 0.786, 2.153 and 4.348 L<sub>hydrogen</sub> min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, respectively. However, the initial HGR decreased as the temperature further increased to 673 K. On the other hand, the composition of the catalysts is also found to has an important effect on their catalytic performances [24]. Therefore, we have synthesized a series of Ni<sub>x</sub>Co<sub>1-x</sub>O/Cu@CuO catalysts with different Ni/Co ratios and the morphologies of those obtained catalysts are shown in Figure S5. As shown, the morphologies of CoO/Cu@CuO and NiO/Cu@CuO are nanosheet array. The mean

thickness of those nanosheets on CoO/Cu@CuO and NiO/Cu@CuO is about 30 nm. The morphologies of Ni<sub>0.5</sub>Co<sub>0.5</sub>O/Cu@CuO and Ni<sub>0.75</sub>Co<sub>0.25</sub>O/Cu@CuO are similar to that of Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO though the molar ratio of Ni/Co has changed. These results suggest that the compositions of catalysts show significant effects on their morphologies. In addition, the composition of the Ni<sub>x</sub>Co<sub>1-x</sub>O/Cu@CuO may also affect their crystal structure according to the vegard's law [25]. In order to know more detailed information about the crystal structure of those catalysts with different molar ratio of Ni/Co, we performed XRD analysis on Ni<sub>x</sub>Co<sub>1-x</sub>O/Cu@CuO and the results are shown in Figure S6. As shown, no obvious hange has been observed in the XRD patterns of Ni<sub>0.5</sub>Co<sub>0.5</sub>O/Cu@CuO and Ni<sub>0.75</sub>Co<sub>0.25</sub>O/Cu@CuO compared with that of  $Ni_{0.25}Co_{0.75}O/Cu@CuO$ . These may because the Ni and Co have a similar atomic radius. When the Ni replaced Co in NiO-CoO, the interplanar distance of Ni D-CoO did not change obviously. The catalytic activities of Ni<sub>x</sub>Co<sub>1-x</sub>O/Cu@CuO catalyst, t/wards AB hydrolysis were tested and shown in Figure 3b. Obviously, the catalytic activities of CoO/Cu@CuO and NiO/Cu@CuO are poor with an initial hydrogen evolution rate of 1.878 and 1.993  $L_{hydrogen}$  min<sup>-1</sup>  $g_{cat}$ <sup>-1</sup>, respectively. However, the hydrogen evolution rate has been nureased when NiO was combined with CoO to form Ni<sub>x</sub>Co<sub>1-x</sub>O/Cu@CuO. Among all the samples, the Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO possessed the highest HGR, which reached to 4.348  $L_{hy, ogen}$  min<sup>-1</sup>  $g_{cat.}^{-1}$ . In the field of heterogenous catalysis, the BET surface areas of catalysts n ay have significant effect on their activity [26]. In order to know more information about their B'T surface areas, N2 adsorption-desorption isotherm analysis was performed on Ni<sub>x</sub>Co<sub>1-x</sub>O/Cu@CuO and the results are shown in Table S1. Obviously, the catalytic activity of Ni<sub>x</sub>Co<sub>1-x</sub>O/Cu@CuO catalysts did not increase as the increase of their BET surface areas. According to the literatures [26], the morphologies of catalysts also have remarkable influence on their catalytic activity. As shown in Figure 3b, nanowire array Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO, Ni<sub>0.5</sub>Co<sub>0.5</sub>O/Cu@CuO and Ni<sub>0.75</sub>Co<sub>0.25</sub>O/Cu@CuO have exhibited higher activity than nanosheet array CoO/Cu@CuO and NiO/Cu@CuO. In recent year, many researchers [4, 27] have demonstrated that catalysts with nanowires morphology exhibited high activity toward AB

hydrolysis. Therefore, we believe that the high catalytic activities of  $Ni_{0.25}Co_{0.75}O/Cu@CuO$ ,  $Ni_{0.5}Co_{0.5}O/Cu@CuO$  and  $Ni_{0.75}Co_{0.25}O/Cu@CuO$  are mainly attributed to their nanowire morphology. For comparison, we list the representative catalysts towards AB hydrolysis in Table S2. Obviously, our catalyst of  $Ni_{0.25}Co_{0.75}O/Cu@CuO$  is one of the robust non-noble metal catalysts for hydrolytic dehydrogenation of AB.

The reusability and stability of heterogenous catalyst are crucial in practical application. Therefore, we have repeated the AB hydrolysis reaction catalyzed by Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO for twelve cycles and the result is shown in Figure S7. The HGR 'owards AB hydrolysis remains almost unchanged over the first seven cycles and only slight.v d creased after twelve catalytic cycles, indicating that our catalyst is stable during AB hydrolysis reaction. The good stability of our catalyst is mainly because that the active species of Ni<sub>v</sub>  ${}_{25}$ C  ${}_{0.75}$ O is tightly anchored on Cu@CuO foam, which can avoid the agglomeration of nanor ar icles during the reaction. The morphology of used Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO was characterices' and shown in Figure S8. Clearly, the morphology has maintained the nanowire array. The XRL pattern of used Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO was also recorded. The XRD result suggests that the crystal structure of our Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO remains unchanged after AB hydrolysis.

### Conclusions

In summary, Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO have been successfully fabricated via a simple hydrothermal method followed by a calcination treatment. In the hydrolysis of AB, Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO exhibited a high catalytic activity with a HGR of 4.348  $L_{hydrogen}$  min<sup>-1</sup> g<sub>cat.</sub><sup>-1</sup>, higher than many reported non-noble metal catalysts. The effects of calcination temperatures and compositions of catalysts on their catalytic performances were also demonstrated. The obtained Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO catalyst showed a good stability with only a slight decrease in activity after

twelve catalytic cycles. This study can provide a simple method and some new insights into the design of unexpensive and durable film catalysts towards AB hydrolysis.

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### Figure and Table cartions

Figure 1 XRD pattern of Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO

Figure 2 SEM images (a-c), two-dimensional elemental mapping analysis (d).

Figure 3 Catalytic performance. of  $Ni_{0.25}Co_{0.75}O/Cu@CuO$  calcined at different temperatures ranging from 473 K to 673 K (a) and catalytic performances of  $Ni_xCo_{1-x}O/Cu@CuO$  with different Ni/Co ratios.

## **Credit author statement**

Yufa Feng: Investigation, Writing - original draft.

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#### **Declaration of interests**

In the authors declare that they have no known competing financial interests or personal relationships

that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be

considered as potential competing interests:







Figure 2



Figure 3



## Highlights

- $Ni_{0.25}Co_{0.75}O/Cu@CuO$  was prepared by a simple two-steps process.
- Performance of Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO toward ammonia borane hydrolysis was studied.
- Ni<sub>0.25</sub>Co<sub>0.75</sub>O/Cu@CuO exhibited high activity and good stability.

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