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# Bunch-like Copper Oxide Nanowire Array as an Efficient, Durable and Economical Catalyst for Methanolysis of Ammonia Borane

Liang Cui,[a,b] Xueying Cao,[b] Xuping Sun,[c] Wenrong Yang,[b] and Jingquan Liu,*[a,b]

**Abstract:** Dehydrogenation of ammonia borane (AB) offers an effective method for production and storage of hydrogen but suffers from the development of efficient, durable and low-cost dehydrogenation catalysts. In this work, we have successfully prepared a self-supported bunch-like copper oxide nanowire array on copper foam (b-CuO NA/CF) through a facile in-situ wet oxidation and anneal method. This b-CuO NA/CF shows high catalytic activity for AB methanolysis with an initial turnover frequency of 13.3 $mol_{(H2)}$ $mol_{(CuO)}^{-1}$ $min^{-1}$ and an activation energy of 34.7 kJ $mol^{-1}$. Moreover, such self-supported bunch-like nanoarray catalyst can be easily separated from fuel solutions with excellent stability and can still maintain its catalytic activity even after long-time uses, providing a direct, efficient, economical and durable catalyst for hydrogen fuel cells.

Increasing fossil fuels consumption and environmental concerns have greatly promoted the establishment of hydrogen energy system.[1,2] Ammonia borane (AB, $NH_3BH_3$) is considered to be a promising material for hydrogen storage and production due to its high theoretical hydrogen capacity (19.6 wt%), low molecular weight (30.7 g $mol^{-1}$), good stability and safe reaction conditions.[3-11] In general, AB hydrolysis and methanolysis are two practical ways of hydrogen generation from AB for hydrogen fuel cell vehicles, and among them the latter is more advantageous than the former despite its lower hydrogen capacity.[12-14] Similar to AB hydrolysis, in the presence of suitable catalyst, AB methanolysis reaction can be briefly expressed as follows:

$$NH_3BH_3 + 4CH_3OH \longrightarrow NH_4B(OCH_3)_4 + 3H_2 \qquad (1)$$

Compared to AB hydrolysis process, the above reaction even can be initiated below 0 °C, thereby satisfying the applications in cold environment.[15] More importantly, there is no $NH_3$ release in AB methanolysis,[16,17] leading to the generation of pure $H_2$. In addition, the by-product of ($NH_4B(OCH_3)_4$) can be easily reconverted into AB by reaction with LiAlH4 and $NH_4Cl$.[18]

It is well known that the catalyst plays a critical role in AB methanolysis in determining the hydrogen generation rate and AB conversion. Up to now, various noble and non-noble based catalysts, such as Ru,[19,20] Rh,[21-23] Pd[12,17,24] Co,[25] Ni,[25,28] and Cu,[13,27,28] have been widely studied for hydrogen generation from AB methanolysis, among which the Cu species have been regarded as the most promising ones due to its low-cost and high catalytic activity. In 2008, Jagirdar and co-workers designed a nanostructured $Cu_2O$, and found that $Cu_2O$ nanoparticles are more active than the Cu and Cu@$Cu_2O$ nanopowders in catalyzing AB methanolysis reaction.[28] Yang and co-workers further prepared diverse mesoporous CuO nanostructures,[13] and Kaya et al. also reported activated carbon supported Cu-$Cu_2O$-CuO nanoparticles for AB methanolysis,[27] showing that CuO is a promising catalyst in AB methanolysis reaction. However, all these Cu-based catalysts including other metal-based catalyst systems have powder-like structures, suffering from easy aggregation, difficult reuse and mass loss in continuous flow systems. Our previous works have proven that self-supported nanostructures could solve the above issues.[29-31] Thus, it is highly desired but still remains a great challenge to develop an economical self-supported nanostructured Cu-based catalyst for efficient and stable AB methanolysis for hydrogen production.

In this work, for the first time, a bunch-like CuO nanowire array on copper foam (b-CuO NA/CF) is developed via a facile and economical method and it behaves as an efficient catalyst for methanolytic dehydrogenation of AB. b-CuO NA/CF exhibits high catalytic activity for AB methanolysis with an initial turnover frequency (TOF) of 13.3 $mol_{(H2)}$ $mol_{(CuO)}^{-1}$ $min^{-1}$ and an activation energy of 34.7 kJ $mol^{-1}$. Moreover, this self-supported bunch-like nanoarray catalyst can be easily separated from fuel solutions with excellent stability and can still maintain its catalytic activity even after long-time uses.

b-CuO NA/CF was derived through a simple thermal treatment of its $Cu(OH)_2$ NA/CF precursor which was prepared via a facile in situ wet-oxidation treatment of copper foam (CF) at room temperature (Figure 1a).[32] The reddish brown copper foam was converted to light blue after oxidation and further transformed into black after thermal annealing at 300°C, indicating the formation of new phase and phase transformation, respectively (Figure S1, ESI). Figure S2 depicts XRD patterns of bare CF, $Cu(OH)_2$ NA/CF and b-CuO NA/CF. The $Cu(OH)_2$ product shows diffraction peaks indexed to the orthorhombic phase of $Cu(OH)_2$ (JCPDF 35-0505), demonstrating the successful formation of $Cu(OH)_2$. Following the thermal treatment, only peaks for CuO (JCPDF 48-0937) are observed except for those of bare CF (JCPDF 04-0836), clearly indicating the complete conversion of $Cu(OH)_2$ into CuO. Scanning electron microscopy (SEM) image for bare CF (Figure 1b) shows that CF has a 3D cross-linked grid structure and clean surface, which was fully covered with crossed $Cu(OH)_2$ nanowires after the wet-oxidation process (Figure 1c). Following thermal treatment, $Cu(OH)_2$ will be decomposed into CuO with connected tops, forming a bunch-like

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CuO nanowire array (Figure 1d). The energy-dispersive X-ray (EDX) spectrum and corresponding element mapping images of b-CuO NA/CF reveal it has a Cu:O atomic ratio of 1:1 with a uniformly distributed elements (Figure 1e). Figure 1f presents the transmission electron microscopy (TEM) image of $Cu(OH)_2$ nanowire, giving a diameter of approximately 130 nm with a smooth surface. TEM image of CuO nanowire shows a rough surface with a decreased diameter of about 100 nm (Figure 1g). The selected area electron diffraction (SAED) image of CuO nanowire reveals an almost single-crystal-like diffraction pattern. All these observations confirm the successful fabrication of integrated bunch-like CuO nanowire array on copper foam.

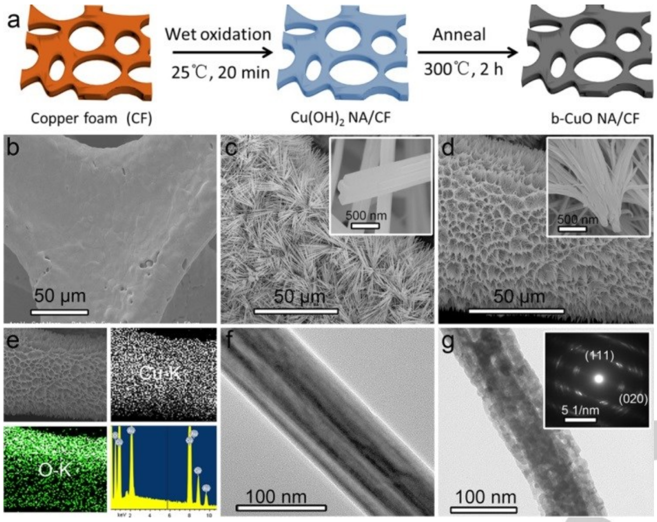

**Figure 1.** (a)Illustration for the stepwise preparation of b-CuO NA/CF. (b-d) SEM images of bare CF, $Cu(OH)_2$ NA/CF and b-CuO NA/CF (e) EDX elemental mapping of b-CuO NA/CF and its corresponding SEM image. (f) TEM image of single $Cu(OH)_2$ nanowire and (g) TEM images of single CuO nanowire and its corresponding SAED pattern.

We studied the catalytic activity of bare copper foam, $Cu(OH)_2$ NA/CF and b-CuO NA/CF for hydrogen generation via AB methanolysis. It is very interesting to have found that vigorous bubbles occur for $Cu(OH)_2$ NA/CF and b-CuO NA/CF in AB methanol solution (Figure S3a). Besides, bare CF shows almost no activity towards AB methanolysis. Thus, the copper oxides ($Cu^{1+}$ or $Cu^{2+}$) are the active species for AB methanolysis.[25] A water displacement equipment was designed to measure the insight activities of bare copper foam, $Cu(OH)_2$ NA/CF and b-CuO NA/CF in the catalytic methanolysis of AB. As shown in Fig. S3b, b-CuO NA/CF exhibits the best catalytic activity (45% conversion in 5 min) which slows down continuously with the decreasing AB concentration as the reaction proceeds. Interestingly, the catalytic activity for $Cu(OH)_2$ NA/CF decreased more rapidly than that of b-CuO NA/CF, which can be due to the collapsed $Cu(OH)_2$ nanowires after the methanolysis process (Figure S4a and b). In sharp contrast, b-CuO NA/CF can maintain its nanoarray structure during the catalytic process (Figure S4c and d), leading to the higher catalytic activity and stability.

To obtain more insight into the active sites, we explore the different valence states of Cu and O elements in b-CuO NA/CF before and after methanolysis process using X-ray photoelectron spectroscopy (XPS). Particularly, the sample after catalyzing the methanolysis reaction was kept in $N_2$ atmosphere before characterization. Figure 4a shows the Cu LMM region for b-CuO NA/CF, the strong feature at 917.7 eV indicates the existence of $Cu^{2+}$, while two peaks at 916.8 and 918.6 eV appeared after methanolysis which can be assigned to $Cu^{1+}$ and $Cu^0$, respectively.[33] Figure 4b shows the Cu 2p peaks at 934.0 (2p3/2) and 953.8 eV (2p1/2) with strong statellite peaks, indicating the existence of CuO.[34,35] However, both the two peaks are negatively shifted after the catalyzing process to 932.2 and 952.1 eV, respectively, and the statellite peaks have also disappeared, confirming the reduction of $Cu^{2+}$ to $Cu^{1+}$ and $Cu^0$ by AB in the methanolysis reaction.[10] Figure 4c illustrates the O 1s spectra before and after the AB methanolysis process, showing the existence of $Cu^{1+}$-O and $Cu^{2+}$-O, proving the reduction mechanism in catalyzing AB methanolysis.[36] Thus, $Cu^{1+}$ and $Cu^0$ are the real active sites for AB methanolysis in our case and a plausible mechanism is provided to illustrate the $H_2$ generation process. As shown in Figure 4d, the b-CuO NA/CF having $Cu^{2+}$ on its surface can interact strongly with AB forming the activated complex which was further dissociated to generate hydrogen when being attacked of $CH_3OH$ molecule to form Cu-H bond. According to this mechanism, $Cu^{2+}$ is firstly reduced to $Cu^{1+}$ and $Cu^0$ among which the latter is then oxidized to $Cu^{1+}$ during the dehydrogenation process for repeated catalysis.[13,28,37]

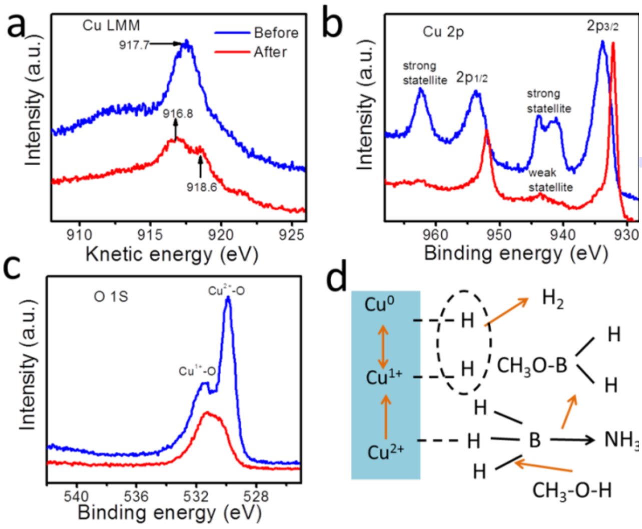

**Figure 2.** (a-c) Cu LMM, Cu 2p and O 1s XPS spectra of b-CuO NA/CF before (blue) and after (red) catalyzing AB methanolysis reaction; (d) The proposed mechanism of b-CuO NA/CF in catalyzing the methanolysis of AB for hydrogen generation.

A kinetic study was performed to gain further insight into the catalytic activity of b-CuO NA/CF for hydrogen generation from AB methanolysis. Figure 3a shows the plots of volume of hydrogen versus time under various CuO/AB molar ratios with a fixed amount of AB (0.6 mmol, 3 mL) at room temperature. It suggests that when the catalyst content increased, the reaction

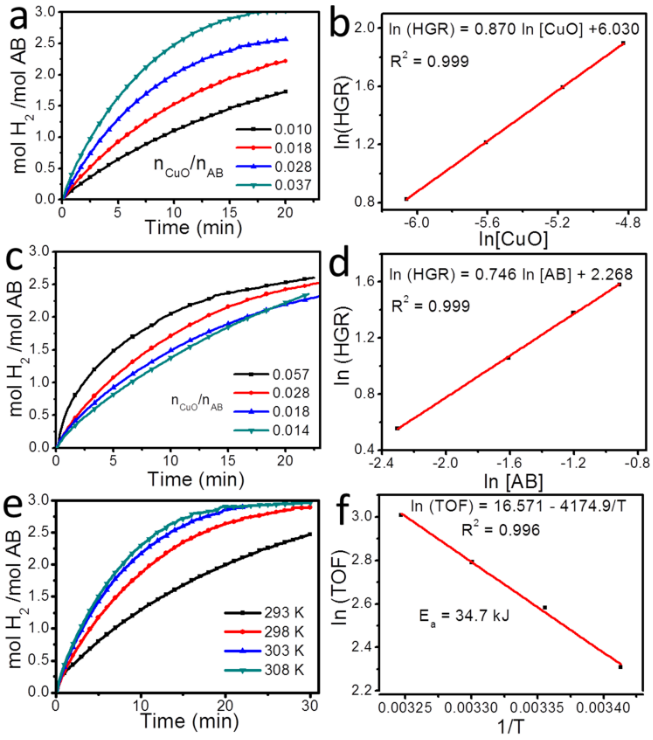

**Figure 3.** (a) Plots of mol $H_2$ evolved per mol of AB versus time for the methanolysis of AB in methanol solution containing fixed amount of of AB (0.6 mmol) in the presence of b-CuO NA/CF with various CuO/AB molar ratios at 298 K and (b) its corresponding logarithmic plot of HGR versus [CuO]; (c) Plots of mol $H_2$ evolved per mol of AB versus time for the methanolysis of AB at fixed CuO amount (0.017 mmol) with different AB concentrations at 298 K and (d) its corresponding logarithmic plots of HGR versus [AB]; (e) Plots of mol $H_2$ evolved per mol of AB versus time for the methanolysis of AB in the presence of b-CuO NA/CF at 298-308 K ([CuO]/[AB] = 0.018) and its corresponding Arrhenius plot. 3 mL fuel solution was applied for each experiment.

time for generating hydrogen (60% conversion) decreased obviously from 20 to 5.3 min. Hydrogen generation rate (mL min$^{-1}$) is calculated from the initial stage of each plot (experimental section for details), and the obtained logarithmic plot shows a slop of 0.87 which is close to 1.0 (Figure 3b). This result indicates that the catalytic methanolysis of AB is first order with respect to the CuO concentration, which is similar to the reports by others. [13,19,27,38,39] The highest initial turnover frequency (TOF) was obtained at CuO/AB molar ratio of 0.01, which is calculated to be 13.3 mol($H_2$) mol (CuO)$^{-1}$ min$^{-1}$. Though this value is not the highest one ever reported for the methanolysis of AB using various catalysts as listed in Table 1, it is still higher than many other relevant catalyst systems, such as PVP-stabilized Ni (12.1 min$^{-1}$), Co-Ni-Bi (10 min$^{-1}$) and nanostructured CuO powder (2.41 min$^{-1}$). Those methanolysis catalysts with higher TOF than that of b-CuO NA/CF are either noble-metal (Rh, Ru and Pd) based systems or powder-like catalysts (Cu-$Cu_2O$-CuO/C and CuNi/graphene) which should be deposited onto substrate in the application of hydrogen fuel cells.

In another group of tests, CuO amount was fixed at 0.017 mmol but the AB was varied from 0.3-1.2 mmol. The kinetic and corresponding logarithmic plots are given in Figure 3c and d, respectively. It can be seen that the HGR increased with the increased AB concentrations, giving a final AB conversion of approximately 92.1% (Figure 3c). Particularly, the reaction is nearly half-order with respect to the AB concentration (Figure 3d) due to the Cu cations re-reduction during the methanolysis process, which is similar to other Cu-based catalysts. [19,39,40]

The methanolysis activation energy ($E_a$) was evaluated by measuring the hydrogen evolution capability at different temperature. Figure 3e shows the temperature-dependent hydrogen generation of the b-CuO NA/CF catalyst from 293 to 308 K. As observed, HGR increased dramatically at higher temperature, which should be due to the accelerated movement of AB and methanol molecules, leading to increasing number of effective collision that passes the threshold energy barrier.[41] However, the final AB conversion remains almost constant under high temperatures(>298K). From the slop of the straight line in Figure 3f, $E_a$ was calculated to be 34.7 kJ mol$^{-1}$ for AB methanolysis reaction using Arrhenius equation (experimental section for details). This value compares favourably to those of many other Cu-based catalysts, such as Cu-$Cu_2O$-CuO/C (67.9 kJ mol$^{-1}$)[27] and CuO powder (34.2 ± 1.2 kJ mol$^{-1}$)[13] and even lower than those of other noble and non-noble metal catalysts as listed in Table 1. The high catalytic activity of b-CuO NA/CF can be attributed to its nanowire structures, which expose more active sites and facilitate mass transfer during methanolysis process.

**Table 1** Comparison of $E_a$ and TOF for the methanolysis of $NH_3BH_3$ using various catalysts.

| Catalyst | $E_a$ (kJ mol$^{-1}$) | TOF (min$^{-1}$) | T (K) | Ref |
|---|---|---|---|---|
| Rh/$SiO_2$ | 62 | 168 | 298 | [22] |
| Rh/nanoHAP | 56 | 147 | 298 | [23] |
| Ru/MMT | 23.8 | 118.1 | 298 | [19] |
| Ru/graphene | 54.1 | 99.4 | 298 | [20] |
| PVP-stabilized Ru | 58 | 66.9 | 298 | [42] |
| Rh/CC3-R-hetro | NG | 65.5 | 298 | [21] |
| CuPd/C | NG | 53.2 | 298 | [24] |
| CuNi/graphene | 24.4 | 49.1 | 298 | [39] |
| CoPd/C | 25 | 27.7 | 298 | [12] |
| Cu-$Cu_2O$-CuO/C | 67.9 | 24 | 298 | [27] |
| PVP-stabilized Pd | 35 | 22.3 | 298 | [17] |
| b-CuO NA/CF | 34.7 | 13.3 | 298 | This work |
| PVP-stabilized Ni | 63 | 12.1 | 298 | [27] |
| Co-Ni-B | NG | 10 | 293 | [25] |
| Co-$Co_2B$ | NG | 7.5 | 293 | [25] |
| Rh/zeolite | 40 | 6.3 | 298 | [38] |
| Ni-$Ni_3B$ | NG | 5 | 293 | [25] |
| $CoCl_2$ | NG | 3.7 | 298 | [18] |
| $NiCl_2$ | NG | 2.9 | 298 | [18] |
| Nanostructured CuO | 34.2 | 2.41 | 298 | [13] |
| Pd/C | NG | 2.0 | 298 | [18] |
| $PdCl_2$ | NG | 1.6 | 298 | [18] |
| $Cu_2O$ | NG | 0.21 | 298 | [28] |
| Nano Cu@$Cu_2O$ | NG | 0.16 | 298 | [28] |
| Nano Cu | NG | 0.12 | 298 | [28] |

In flow fuel systems for practical applications, controllability and stability are vital for the dehydrogenation catalyst. Such self-supported b-CuO NA/CF catalyst can offer more advantages than traditional powder catalyst systems in this respect.[29,30,43] As shown in Figure 4a, the methanolysis process can be well controlled by b-CuO NA/CF. When the catalyst, b-CuO NA/CF (ON) was separated from fuel solution, the reaction stopped quickly (OFF); while in the presence of catalyst hydrogen release occurs immediately with almost the same rate, demonstrating good sensitivity and stability of b-CuO NA/CF to AB methanolysis. The recyclability of b-CuO NA/CF catalyst was also examined in the methanolysis of AB (Figure 4b). It can be seen that the HGR (slop of the line) is constant even after seven cycles of repeated uses and the final conversion remains almost the same for each cycle, indicating a stable catalytic activity and good recyclability of b-CuO NA/CF in AB methanolysis. The remarkable durability for b-CuO NA/CF could be attributed to its unique bunch-like nanostructure, which is more stable than separate nanowires and nanopowders.

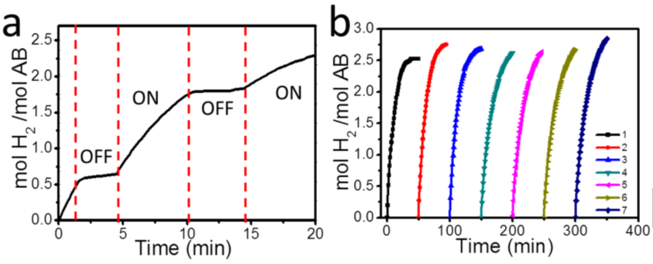

**Figure 4.** (a) Plots of mol $H_2$ evolved per mol of AB versus time for the controllability test of b-CuO NA/CF in AB methanolysis reaction; (b) Plots of mol $H_2$ evolved per mol of AB versus time for b-CuO NA/CF catalyzed methanolysis of AB. (0.6 mmol AB, 0.017 mmol CuO, 3 mL fuel solution was applied for each experiment at 298 K).

In summary, a bunch-like CuO nanowire array on copper foam (b-CuO NA/CF) was developed as an efficient and stable catalyst for AB methanolysis for hydrogen generation via a simple oxidation process. This method is facile, scalable and economical, and the as-prepared b-CuO NA/CF exhibits high catalytic activity for AB methanolysis with an initial turnover frequency (TOF) of 13.3 $mol_{(H2)}$ $mol_{(CuO)}^{-1}$ $min^{-1}$ and an activation energy of 34.7 kJ $mol^{-1}$. Furthermore, b-CuO NA/CF can be easily separated from fuel solutions and has excellent stability due to its unique bunch-like nanowire structure. Moreover, such self-supported bunch-like nanoarray catalyst can be easily separated from fuel solutions with excellent stability and can still maintain its catalytic activity even after long-time uses, providing a direct, efficient, economical and durable catalyst for hydrogen fuel cells.

## Experimental Section

### Materials

Copper foam was purchased from Jiangsu Jiayisheng Foam Metal Co., Ltd. $NH_3BH_3$, $(NH_4)_2S_2O_8$, and NaOH were bought from Aladdin Ltd. (Shanghai, China). Hydrochloric acid (HCl) and methanol were purchased from Tianjin Fuyu Ltd.. All the reagents were used as received. The ultrapure water used throughout all experiments was prepared through a FLOM water purified system.

### Preparation o Preparation of $Cu(OH)_2$ nano array on copper foam ($Cu(OH)_2$ NA/CF)

A piece of Cu foam (2 × 2 $cm^2$) was pretreated with hydrochloric acid and washed with water and ethanol several times to ensure the surface of the copper foam was well cleaned before use. The pretreated copper foam was immersed into a 30 mL aqueous solution containing 4 mmol $(NH_4)S_2O_8$ and 80 mmol NaOH at room temperature for 20 min. After that the sample was taken out and washed with pure water and ethanol several times and then dried in air at room temperature ($Cu(OH)_2$ loading = 0.72 mg $cm^{-2}$).

### Preparation of bunch-like CuO nanoarray on copper foam (b-CuO NA/CF)

b-CuO NA/CF was prepared through a facile and simple thermal annealing treatment of the above $Cu(OH)_2$ NA/CF. Typically, the above obtained $Cu(OH)_2$ NA/CF was put into a porcelain boat in a furnace and heated to 300 °C with a heating rate of 5 °C $min^{-1}$ and held at this temperature for 2 h. CuO loading amount was obtained via inductively coupled plasma mass spectrometry (ICP-MS) analysis, in which CuO was dissolved by acetic acid, .and the result was calculated to be 0.65 mg $cm^{-2}$.

### Characterizations

X-ray diffraction (XRD) data were acquired on a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). SEM measurements were made on a HITCHI S-4800 with scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were taken on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) at 200 kV. X-ray photoelectron spectrometer measurements (XPS) were performed on an ESCALABMK II using Mg as the exciting source, and b-CuO NA/CF sample was kept in $N_2$ atmosphere after methanolysis process before characterization. ICP-MS analysis was performed on Thermo Scientific iCAP6300.

### Hydrogen generation measurement

The volume of hydrogen was measured using water displacement method. Typically, the methanolytic dehydrogenation experiments were performed in a 25 mL two-necked round-bottom flask with one neck connected to a gas burette and the other sealed with a rubber cap. The temperature of the reaction system was kept at the desired value by using a constant temperature bath. b-CuO NA/CF was put into $NH_3BH_3$ methanol solution in the two-necked round-bottom flask and the volume of displaced water was automatically calculated using an electronic balance (SHIMADZU, AUW220D, d = 0.01 mg) connected to a computer (Figure S5). The systematic and personal error can be substantially reduced in such a way. The catalytic activity of b-CuO NA/CF can be expressed with three parameters, hydrogen generation rate (HGR, mL $min^{-1}$), turnover frequency (TOF, mol($H_2$) mol $(CuO)^{-1}$ $min^{-1}$) and activation energy. The corresponding calculating formulas are as follow:

$$HGR = \frac{\mathrm{V}}{\mathrm{t}}$$

$$TOF = \frac{\mathrm{P}}{\mathrm{nRT}} \times HGR$$

$$\ln(TOF) = \ln A - \frac{E_a}{\mathrm{RT}}$$

where $V$ ($m^3$) is the volume hydrogen which can be obtained from the volume of drained water; $t$ (min) is the corresponding time; $P$ ($1.01\times10^5$ Pa) is the standard atmospheric pressure; n is the mole of CuO; $R$ is a constant (8.314 J $K^{-1}$ $mol^{-1}$); $A$ is the pre-experimental factor and $T$ (K) is the absolute temperature.

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**Keywords:** bunch-like nanostructure • CuO nanocatalyst • ammonia borane • methanolysis • hydrogen

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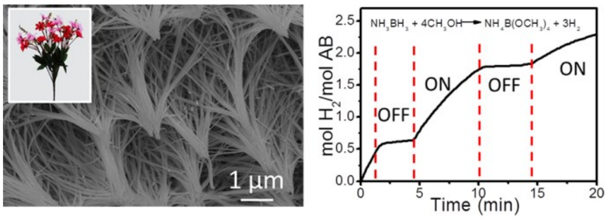
# COMMUNICATION



Bunch-like CuO nanowire array on copper foam (b-CuO NA/CF) is obtained via a facile and economical method and behaves as an efficient and durable catalyst for hydrogen generation from controlled methanolysis of ammonia borane.

*Liang Cui, Xueying Cao, Xuping Sun, Wenrong Yang, and Jingquan Liu **

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