

## Supplementary data

### Facile in situ synthesis of copper nanoparticles supported on reduced graphene oxide for hydrolytic dehydrogenation of ammonia borane

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#### Experimental details

##### Chemicals

Ammonia borane (NH<sub>3</sub>BH<sub>3</sub>, AB, Aldrich, 90%), Copper(II) sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O, Sinopharm Chemical Reagent Co., Ltd., ≥99%), potassium permanganate (KMnO<sub>4</sub>, Sinopharm Chemical Reagent Co., Ltd., ≥99%), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, Sinopharm Chemical Reagent Co., Ltd., ≥30%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, Sinopharm Chemical Reagent Co., Ltd., 95~98%), hydrochloric acid (HCl, Beijing Chemical Works, 36%~37%), potassium peroxodisulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Beijing Chemical Works, ≥99%), phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>, Beijing Chemical Works, ≥99.99%), activated charcoal (Aladin Industrial Co.), graphite powder (Sinopharm Chemical Reagent Co., Ltd., ≥99.85%) and nylon filter membranes (Aldrich, pore size 0.2 μm). All chemicals were used as obtained. We use ordinary distilled water as the reaction solvent.

### **Graphite Oxide (GO) preparation.**

GO was made by a modified Hummers method [S1,S2]. Briefly, graphite powder (3 g, 325 mesh) was put into an 80 °C solution of concentrated H<sub>2</sub>SO<sub>4</sub> (12 mL), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2.5 g), and P<sub>2</sub>O<sub>5</sub> (2.5 g). After keeping at 80 °C for 4.5 h using a hotplate, the mixture was cooled to room temperature and diluted with 0.5 L of de-ionized water and left overnight. Then, the mixture was filtered and washed with de-ionized water using a 0.2 micron Nylon Millipore filter to remove the residual acid. The product was dried under ambient condition overnight. Next, the pretreated graphite powder was put into cold (0 °C) concentrated H<sub>2</sub>SO<sub>4</sub> (120 mL) in a 250-mL round-bottom flask equipped with a magnetic stir bar. 15 g KMnO<sub>4</sub> was added gradually under stirring while the temperature of the mixture was kept below 20 °C. The solution was then stirred at 35 °C for 2 h. Afterwards, 250 mL of de-ionized water was added and the suspension was stirred for another 2 h. Subsequently, additional 0.7 L of de-ionized water was added. Shortly after that, 20 mL of 30% H<sub>2</sub>O<sub>2</sub> was added to the mixture to destroy the excess of permanganate. The suspension was then repeatedly centrifuged and washed first with 5% HCl solution and then with water. Exfoliation of graphite oxide to GO was achieved by ultrasonication of the dispersion for 30 min.

### **In situ synthesis of RGO supported Cu NPs and their catalytic activities toward the hydrolysis of AB.**

8 mL aqueous solution containing CuSO<sub>4</sub> (25.22mg) and GO solution (1.77g, containing 0.68% GO) was kept in a 25ml two-necked round-bottom flask. One neck was connected to a gas burette, and the other was connected to a pressure-equalization funnel to introduce 2 mL of aqueous solution containing AB (34.3 mg). The reactions were started when the aqueous AB solution was added to the mixture solution of precursors and GO with vigorous stirring. The evolution of gas was monitored using the gas burette. The reactions were carried out at room temperature under ambient atmosphere.

For comparison, support-free Cu NPs, GO and RGO (GO reduced by NaBH<sub>4</sub>) toward the hydrolysis of AB were used the similar method. And RGO and Cu NPs are together employed in the hydrolysis of AB by using the similar method.

### **Different supported materials**

Sets of experiments with different supported materials (such as activated charcoal, graphite powder) were performed at room temperature. All the experiments were performed in the same way as described in the section above.

### **Catalytic hydrolysis of AB**

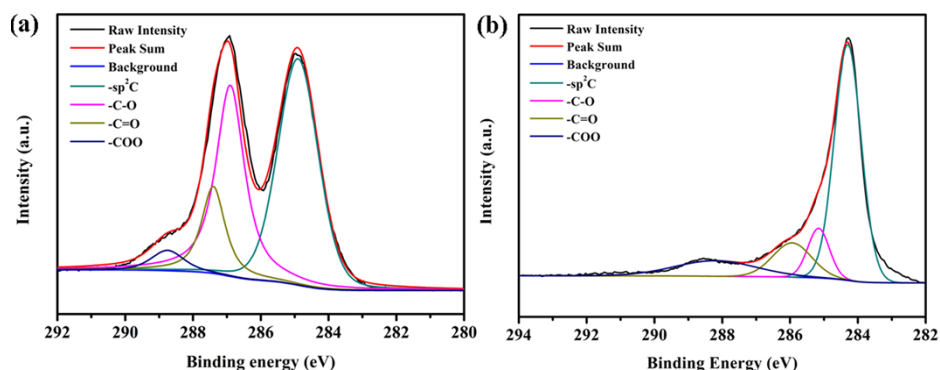
Sets of experiments with different concentration of Cu (0.04, 0.06, 0.08, and 0.1 mmol) were performed at room temperature (25°C) while the AB concentration was kept the same (1 mmol) to determine the rate law of the catalytic hydrolysis of AB. Temperature was varied at 25°C, 30°C, 35°C and 40°C while the ratio of the concentration of Cu (0.1 mmol) and AB (1 mmol) was kept constant of 0.1 to obtain the activation energy ( $E_a$ ).

### **Recyclability test for the hydrolysis of AB**

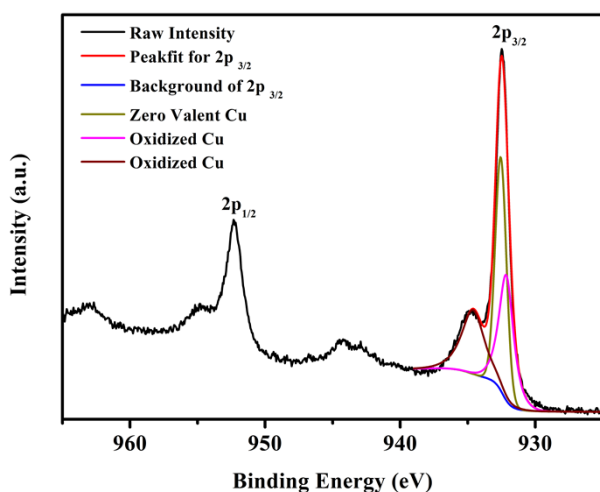
2mL of solution containing  $\text{NH}_3\text{BH}_3$  (34.3 mg, 1 mmol) was added to 8 mL Copper sulfate solution and GO solution, the evolution of gas was monitored as described above. After the hydrogen generation reaction was completed, new aqueous AB (34.3 mg, 1 mmol) was added into the reaction flask. The evolution of gas was monitored using the gas burette. Such cycle tests of the catalyst for the hydrolysis of AB were carried out four times in air.

### **Catalyst characterization**

Powder X-ray diffraction (XRD) studies were performed on a Rigaku RINT-22005 X-ray diffractometer with a  $\text{Cu}_{K\alpha}$  source (40 kV, 20 mA). The morphologies and sizes of the samples were observed by using a transmission electron microscope (TEM, JEM-2010). The TEM samples were prepared by depositing one or two droplets of the nanoparticle suspensions on to the amorphous carbon coated copper grids. FTIR spectra were collected at room temperature by using a Thermo Nicolet 870 instrument using KBr discs in the 500-4000  $\text{cm}^{-1}$  region. Raman spectrometer were carried out using a confocal Raman microscope (LabRAM HR). X-ray photoelectron spectroscopy (XPS) measurement was performed with a Thermo ESCALAB 250XI multifunctional imaging electron spectrometer. The ICP analyses of the reaction mixtures after centrifugal separation of the catalysts were performed by a 725-ES Inductively Coupled Plasma (ICP) spectrophotometer (Varian Corp.).



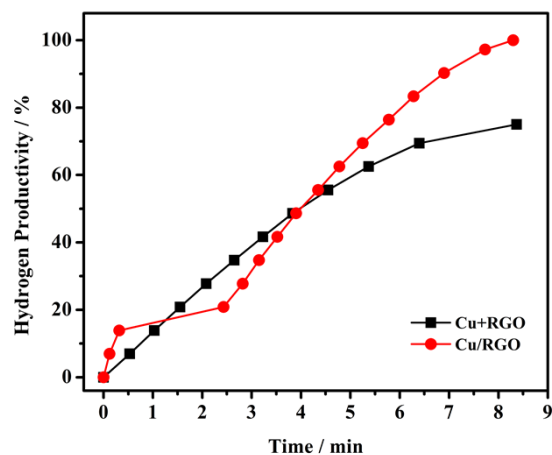
**Fig. S1.** (a) XPS spectra of C 1s of GO and (b) XPS spectra of C 1s of Cu/RGO.



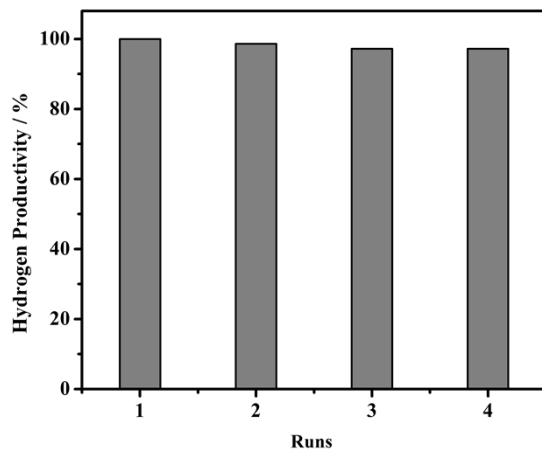
**Fig. S2.** XPS spectra of Cu/RGO showing the Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> at 934.9 and 952.3 eV, respectively, with their shake-up satellite peaks and the peakfit of Cu 2p<sub>3/2</sub> peak.

Cu/RGO was characterized by X-ray photoelectron spectroscopy (XPS). Compared with the peaks of GO (Fig. S1a), the intensities of oxygen containing functional groups (such as -C-O, -C=O, -COO) in Cu/RGO (Fig. S1b) decrease significantly, which reveal the reduction of GO to RGO. The XPS spectrum of Cu/RGO shows two prominent peaks at 934.9 and 952.3 eV which are assigned to Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub>, respectively (Fig. S2). The peakfit of Cu 2p<sub>3/2</sub> core level reveals three peaks, the peak at 932.6 eV is attributed to zero valent Cu, while the other two peaks at 932.1 and 934.6 eV stand for oxidized Cu. The

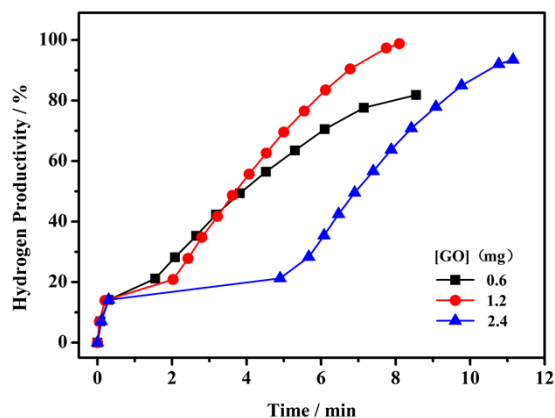
formation of the oxidized Cu most likely occurs during the sample preparation process for XPS measurements [16].



**Fig. S3.** Hydrogen generation from hydrolysis of ammonia borane (0.10M, 10 mL) catalyzed by as-synthesized Cu/RGO and Cu NPs mixed with RGO. (Cu/AB=0.1).

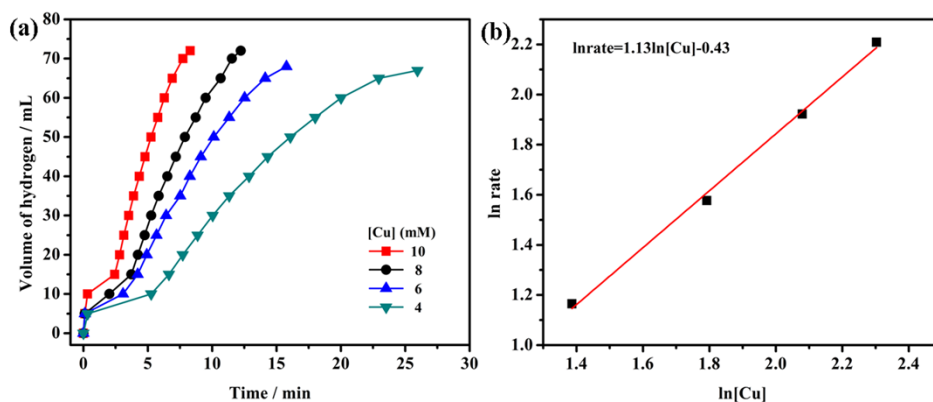


**Fig. S4.** Hydrogen productivity vs. reaction time for hydrogen release from an aqueous AB solution (0.10M, 10 mL) catalyzed by the Cu/RGO nanocatalysts during a four cycle reusability test. (Cu/AB =0.1).

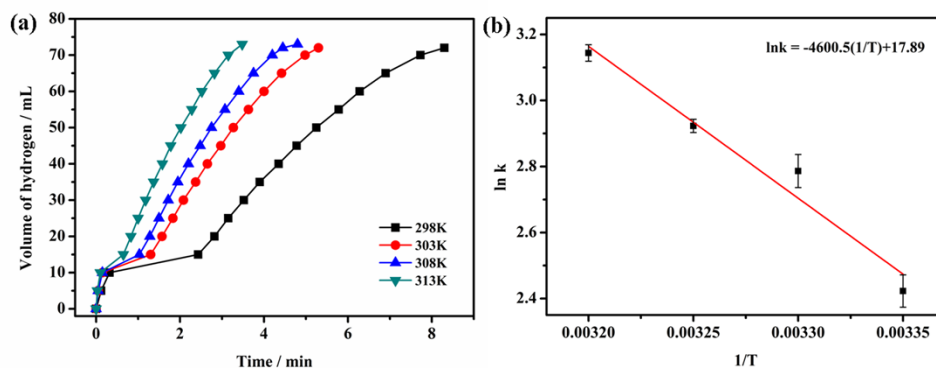


**Fig. S5.** Hydrogen generation from hydrolysis of ammonia borane (0.10M, 10 mL) catalyzed by Cu/RGO with different amount of GO (0.6, 1.2, 2.4 mg), catalyst/AB=0.1.

With increasing GO from 0.6 mg to 1.2 mg, the catalytic performance increases, while GO continues to increase to 2.4 mg, the catalytic performance decreases, indicating the best amount of GO in our system is 1.2 mg (1.77g GO solution, containing 0.68% GO).



**Fig. S6.** Plots of volume of hydrogen generated vs. time. (a) The hydrolysis of AB ammonia borane (0.10M, 10 mL) was catalyzed by the Cu/RGO nanocatalysts at different catalyst concentrations. (b)  $\ln [\text{Cu/RGO}]$  vs.  $\ln$  rate plot.



**Fig. S7.** (a). Plots of volume of hydrogen generated vs. time. for Cu/RGO catalyzed hydrolysis of AB at four different temperatures in the range of 298-313K, Cu/AB = 0.1; (b) Arrhenius plot obtained from the data of Fig. S7a with standard deviation bars.

**Table S1.** TOF values ( $\text{mol H}_2 \text{ mol catalyst}^{-1} \text{ min}^{-1}$ ) of Cu nanocatalysts tested in hydrogen generation from aqueous  $\text{NH}_3\text{BH}_3$  at room temperature.

Catalyst	TOF ( $\text{H}_2 \cdot \text{mol catalyst}^{-1} \cdot \text{min}^{-1}$ )	Ref.
Cu/RGO	3.61	This study
Zeolite-confined Cu	1.25	[16]
p(AMPS)-Cu	0.72	[15]
Cu/ $\gamma$ - $\text{Al}_2\text{O}_3$	0.27	[9]
$\text{CuCl}_2$	0.23	[11]
$\text{Cu}_2\text{O}$ NPs	0.18	[20]
Cu NPs	0.06	[20]

## References

- [S1] W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, 80, 1339-1399.
- [S2] N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva, and A. D. Gorchinskiy, *Chem. Mater.*, 1999, 11, 771-778.