Supporting Information

Rapid and Energy-Efficient Synthesis of Graphene-CuCo Hybrid and its High Performance toward Hydrogen Generation from Ammonia Borane

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Chemicals: Graphite flake (C, Alfa Aesar, -325 mesh, 99.8%), ammonia borane (NH_3BH_3, Aldrich, 90%), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, Beijing Chemicals Works, >99%), copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$, Beijing Chemicals Works, >99%), potassium hexachloroplatinate (K_2PtCl_6, Sinopharm Chemical Reagent Co., Ltd, 40-40.3%), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, Beijing Chemicals Works, >98%), sodium borohydride ($NaBH_4$, Sinopharm Chemical Reagent Co., Ltd, 96%), polyvinylpyrrolidone K30 (PVP, $(C_6H_9NO)_n$, Mw: av. 58000, Beijing Chemicals Works). sulfuric acid (H_2SO_4, Beijing Chemical Works, 98%), hydrochloric acid (HCl, Beijing Chemical Works, 36%~37%), potassium peroxodisulfate ($K_2S_2O_8$, Beijing Chemical Works, ≥99%), phosphorus pentoxide (P_2O_5, Beijing Chemical Works, ≥99.99%), potassium permanganate ($KMnO_4$, Sinopharm Chemical Reagent Co., Ltd, ≥99%), hydrogenperoxide (H_2O_2, Beijing Chemical Works, 30%).

Physical Characterization: Transmission electron microscope (Tecnai F20, Philips) and energy-dispersive X-ray spectroscopy (EDS) were applied for the detailed microstructure and composition information. The TEM and EDS samples were prepared by depositing one or two droplets of the NPs suspended in aqueous solution onto the amorphous carbon coated stainless steel grids (containing elements of Fe and

Cr), which were then dried in argon atmosphere. The usage of the stainless steel grids is to avoid the contamination of Cu element in Cu grids.

X-ray photoelectron spectroscopy (XPS) spectra were acquired with an ESCALABMk II (Vacuum Generators) spectrometer using unmonochromatized Al Ka X-rays (240 W).

Atomic force microscopy (AFM) measurements were applied on Bruker MultiMode scanning probe microscope with a Nanoscope IIIA controller in ScanAsyst in Air.

Raman spectra were collected with a Renishaw 1000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter at ambient conditions.

UV-Vis absorption spectra were recorded on an Agilent Cary 50 spectrophotometer in the wavelength range of 200–700 nm.

Powder X-ray diffraction (XRD) patterns were performed on a Rigaku RINT-2000 X-ray diffractometer with Cu Kα.

Synthesis of graphene oxide (GO): Graphene oxide was prepared according to a modified Hummer's method.[S1, S2] Briefly, graphite powder (3 g, 325 mesh) was put into an 80 °C solution of concentrated H_2SO_4 (12 mL), $K_2S_2O_8$ (2.5 g), and P_2O_5 (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 distilled water. Then, the mixture was filtered and washed with distilled water using a 0.2 micron Nylon Millipore filter to remove the residual acid. Next, the pretreated graphite powder was put into cold (0 °C) concentrated H_2SO_4 (120 mL) in a 250 mL round-bottom flask equipped with a magnetic stir bar. 15 g $KMnO_4$ 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 distilled water was added and the suspension was stirred for another 2 h. Subsequently, additional 0.7 L of distilled water was added. Shortly after that, 20 mL of 30% H_2O_2 was added to the mixture to destroy the excess of permanganate. The suspension was then repeatedly centrifuged and washed

firstly with 5% HCl solution and then with water. Exfoliation of graphite oxide to GO was achieved by ultrasonication of the dispersion for 30 min.

Synthesis of graphene-CuCo hybrid: 8.1 mg of $CuCl_2$ and 1.3 mg of $CoCl_2$ were dissolved along with GO solution (300 mg, containing 9‰ GO) and PVP (2 mg) in 10 mL distilled water followed by ultrasonication for 5 min to get the uniform mixture. And then 90 mg of NH_3BH_3 was added while magnetic stirring to reduce metal salts and GO to generate graphene-CuCo hybrid at room temperature. The synthesis progress was traced by UV-Vis spectroscopy. The as-prepared sample was used for TEM, EDS, XPS, AFM, Raman and XRD analyses.

For comparison, the reduction process of GO with/without the presence of the monometallic precursor of Cu or Co salt was also be monitored using UV-Vis spectroscopy.
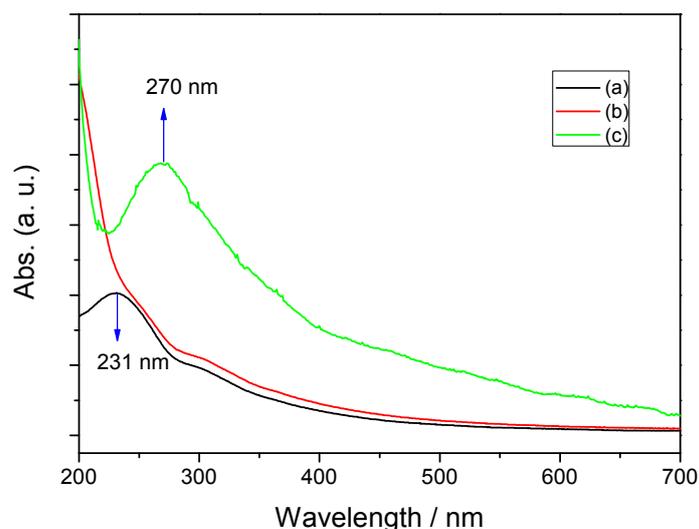

Figure S1. UV-Vis spectra of (a) GO aqueous solution and the monitoring for the synthesis process of graphene-CuCo hybrid at reaction times of (b) 0 min, (c) 1.5 min.

The prepared GO in aqueous solution demonstrates a characteristic absorption peak at 231 nm (Figure S1a).[14] when GO is dispersed in PVP aqueous solution with certain amount of $CuCl_2$ and $CoCl_2$, the characteristic peak of GO can not be observed any more, which is mainly resulted from the strong absorption of PVP and metal salts in

the spectral region of less than 237 nm (Figure S1b). After NH_3BH_3 is added into the above mixture of GO and metal salts in PVP solution for only 1.5 min, an obvious peak at 270 nm is observed which agrees well with that of graphene in aqueous solution,[14] indicating the complete reduction of GO to graphene within the short period (1.5 min).
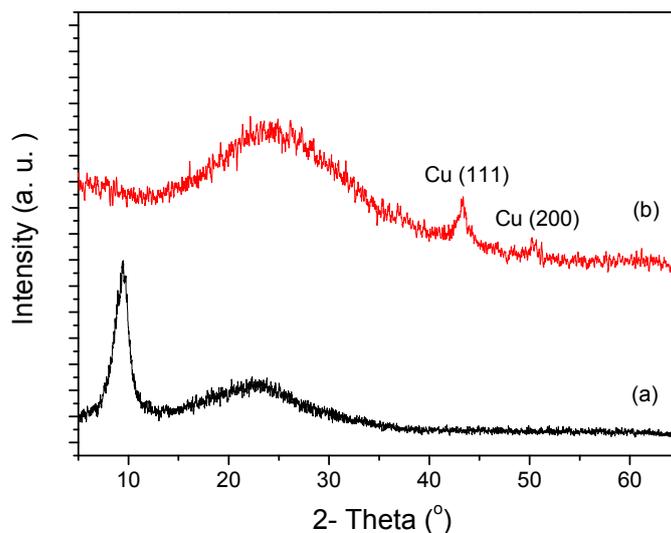

Figure S2. XRD patterns for (a) GO and (b) graphene-CuCo.

The XRD pattern of the prepared GO (Figure S2a) shows a major peak at 9.5° corresponding to an interlayer spacing of 9.30 Å, which indicates a larger interlayer spacing than that of graphite (3.36 Å, (002) graphite peak)[S3] due to the oxygen functional groups of GO as well as water molecules held in the interlayer galleries of hydrophilic GO.[S4] In the XRD pattern of the as-prepared graphene-CuCo (Figure S2b), the diffraction peaks attributed to Cu (JCPDS: 04-0836) are observed. However, no diffraction peak of Co exists. This may be due to the amorphous phase of Co. Besides the diffraction of Cu, another peak is observed at about 24.1°, giving an interlayer spacing of approximately 3.69 Å. This value is closer to the (002) graphite peak of 3.36 Å, and is much smaller than the 9.3 Å for GO. This means that GO is successfully reduced to graphene,[S3] which agrees well with the UV-Vis results.
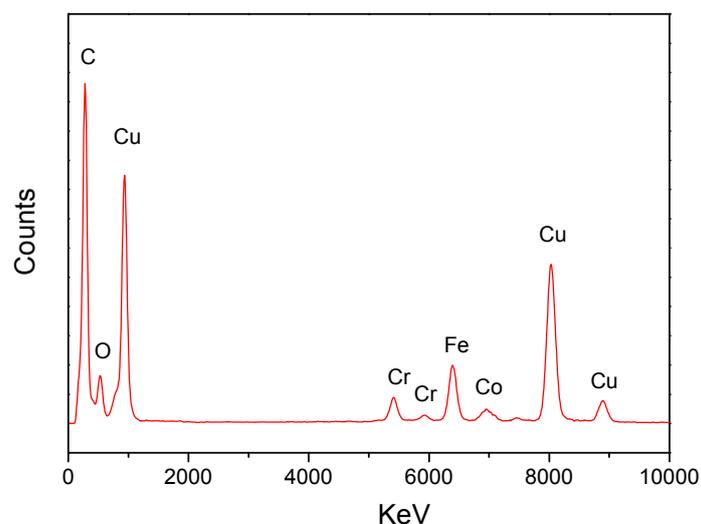
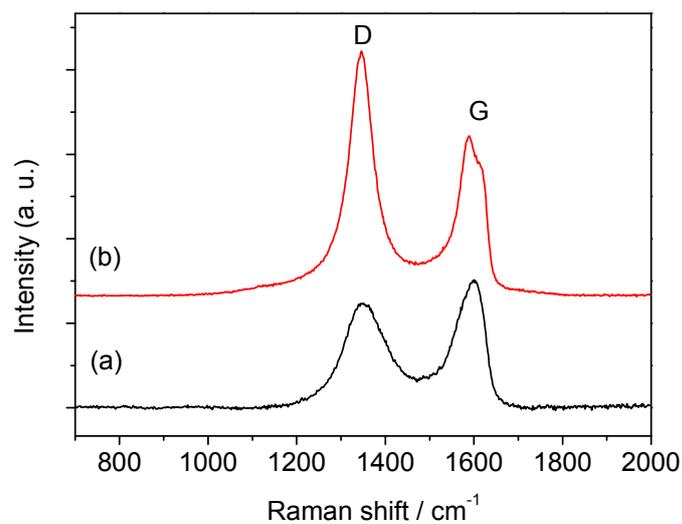**Figure S3.** EDS spectrum of the graphene-CuCo sample.

Figure S4. Raman spectra of (a) GO and (b) graphene-CuCo.

It can be seen from Figure S4 that graphene-CuCo and GO exhibit two peaks centered at 1347 and 1600 cm^{-1}, corresponding to the D and G bands of carbon products, respectively.[2c] The D peak indicates the disorder band created by the attachment of hydroxyl and epoxide groups on the carbon basal plane or edge, while the G peak is related to the graphitic C(sp^2)-C(sp^2) bond stretching vibrations.[2c, S5] Obviously, the D/G intensity ratio for graphene-CuCo is higher than that of the as-made GO, which is due

to the increase in the number of smaller graphene domains after reduction of GO.[S5, S6]
Therefore, the Raman results confirm the reduction of GO during the preparation of
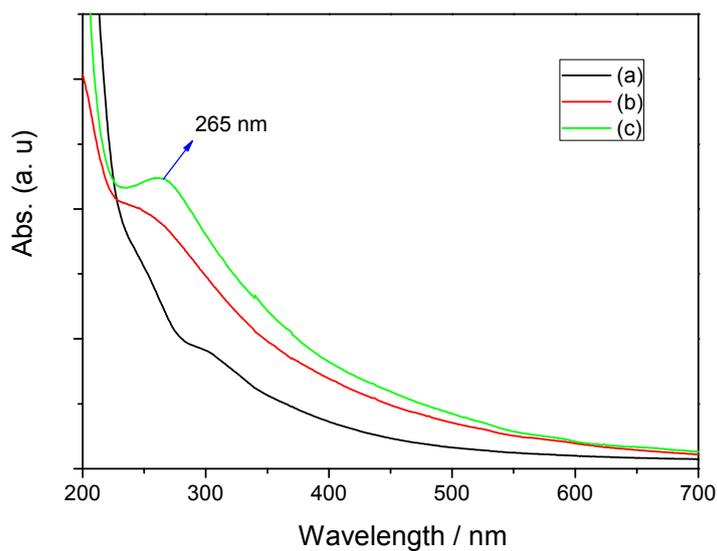the graphene-CuCo.

Figure S5. UV-Vis spectra of the monitoring for the process of reduction of GO with the presence
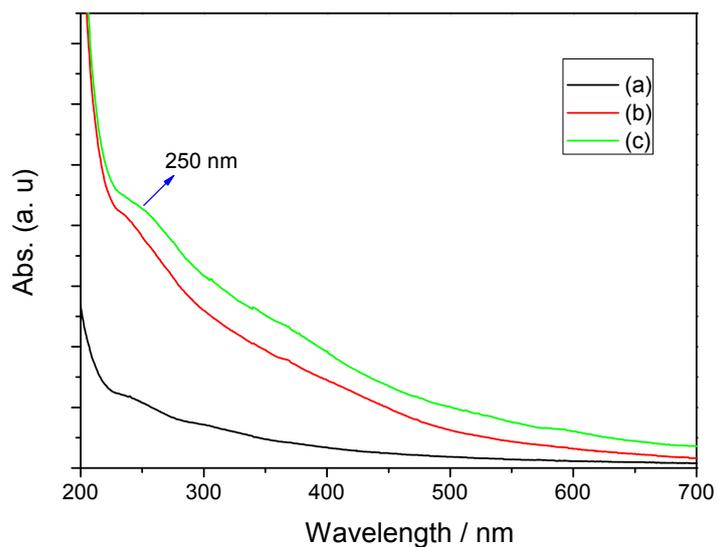of Cu salt at reaction times of (a) 0 min, (b) 60 min, and (c) 130 min.

Figure S6. UV-Vis spectra of the monitoring for the process of reduction of GO with the presence
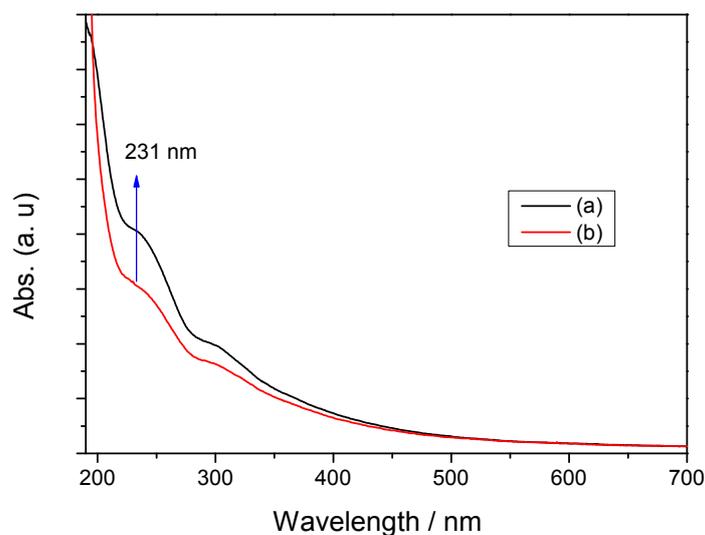of Co salt at reaction times of (a) 0 min, (b) 130 min, and (c) 200 min.

Figure S7. UV-Vis spectra of the monitoring for the process of reduction of GO without any metal salt at reaction times of (a) 0 min, (b) 300 min.

Synthesis of CuCo NPs: 8.1 mg of $CuCl_2$ and 1.3 mg of $CoCl_2$ were dissolved along with PVP (2 mg) in 10 mL distilled water followed by ultrasonication for 5 min to get the uniform mixture. And then 90 mg of NH_3BH_3 was added while magnetic stirring to reduce metal salts to generate CuCo NPs at room temperature. The as-prepared sample was used for TEM and XRD analyses.
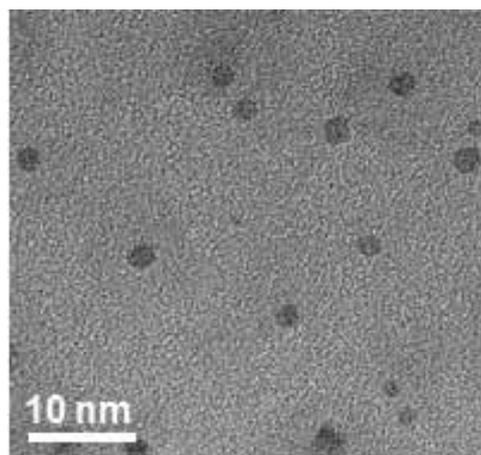

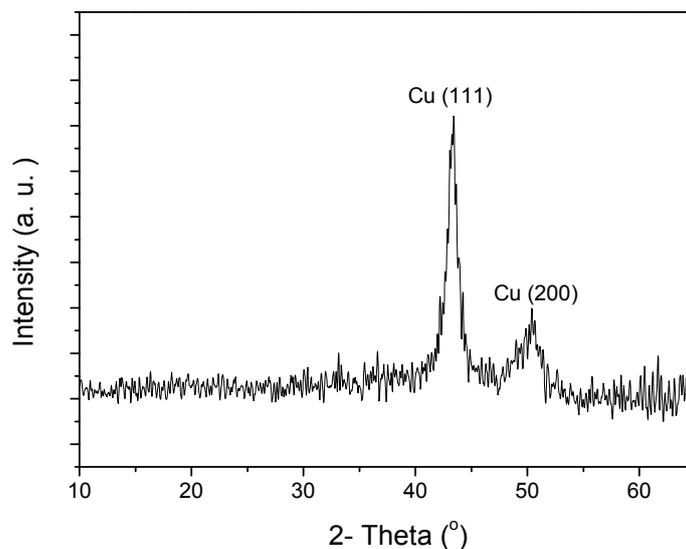**Figure S8.** TEM image of CuCo NPs.

Figure S9. XRD pattern of CuCo NPs.

Synthesis of Cu NPs: 8.1 mg of $CuCl_2$ was dissolved along with PVP (2 mg) in 10 mL distilled water followed by ultrasonication for 5 min to get the uniform mixture. And then 90 mg of NH_3BH_3 was added while magnetic stirring to reduce metal salt to generate Cu NPs at room temperature. The as-prepared sample was used for TEM and XRD analyses.

Synthesis of Co NPs: Typically, 1.3 mg of $CoCl_2$ was dissolved along with PVP (2 mg) in 10 mL distilled water followed by ultrasonication for 5 min to get the uniform mixture. And then 90 mg of NH_3BH_3 was added while magnetic stirring to reduce metal salt to generate Co NPs at room temperature. The as-prepared sample was used for TEM and XRD analyses. Moreover, the prepared sample (ca. 30 mg) was heat treated at 873 K for 3 h in Ar atmosphere, and then the obtained sample was used for XRD analysis.
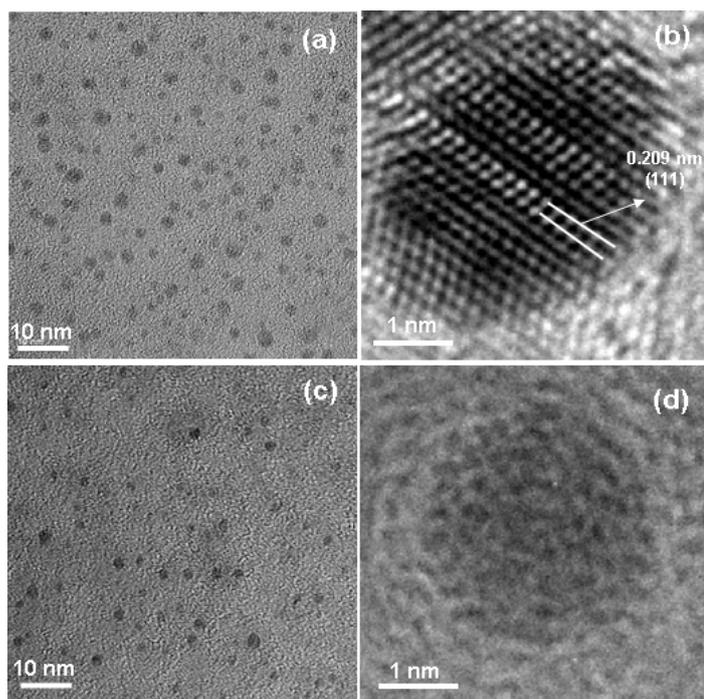
Figure S10. TEM images of (a) low magnification of Cu, (b) high resolution of Cu, (c) low magnification of Co, and (d) high resolution of Co.
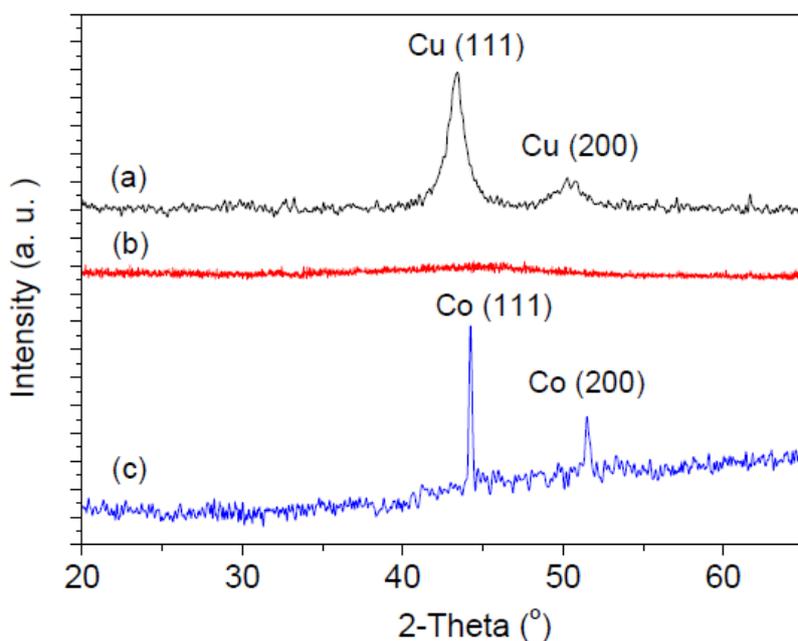

Figure S11. XRD patterns of (a) Cu and (b) Co NPs prepared at room temperature, and (c) Co NPs after heat treatment at 873K for 3 h in Ar atmosphere.

From Figure S11, it can be seen that, after heat treatment, the Co sample is crystallized in cubic Co^0 (JCPDS: 15-0806), indicating that the amorphous sample (Figure S11 b) is in the state of metallic Co^0.

Synthesis of graphene-Pt hybrid: 7.1 mg of K_2PtCl_6 was dissolved along with GO

solution (147 mg, containing 9‰ GO) and PVP (2 mg) in 10 mL distilled water followed by ultrasonication for 5 min to get the uniform mixture. And then 45 mg of NH_3BH_3 was added while magnetic stirring to reduce metal salt and GO to generate graphene-Pt hybrid at room temperature. The synthesis progress is traced by UV-Vis spectroscopy. The as-prepared sample was used for XRD analysis.
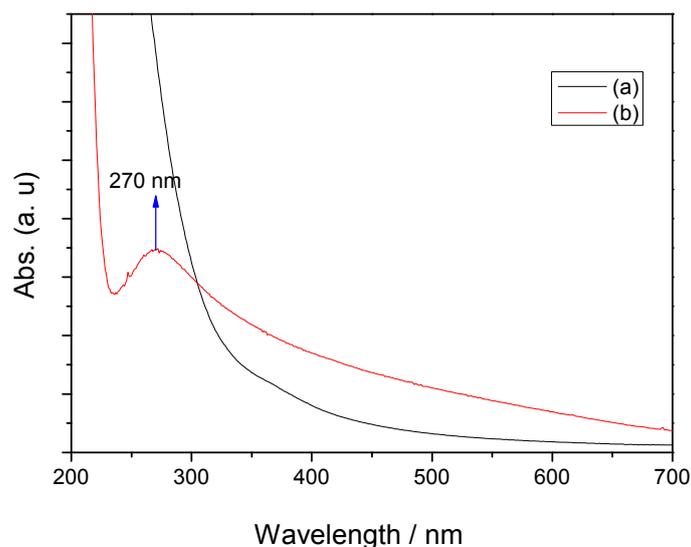
Figure S12. UV-Vis spectra of the monitoring for the synthesis process of graphene-Pt at reaction times of (a) 0 min, (b) 1 min.
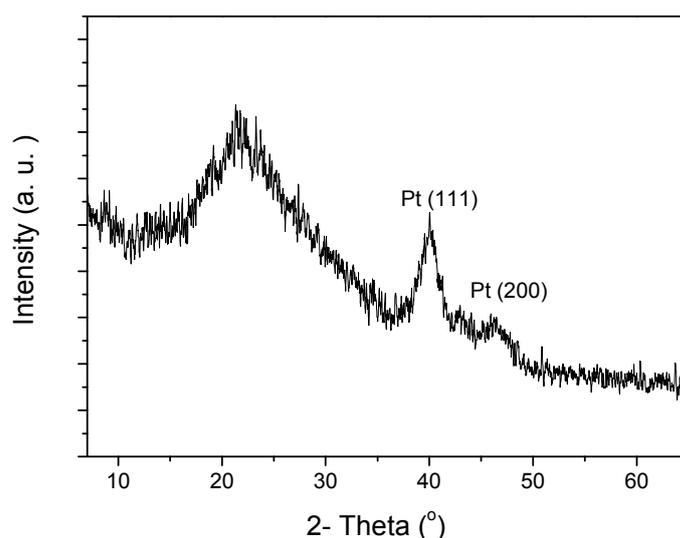
Figure S13. XRD pattern of graphene-Pt hybrid.

From Figure S12, it can be seen that before adding NH_3BH_3, the characteristic peak

of GO can not be observed, resulting from the strong absorption of PVP and Pt salt in the spectral region of less than 250 nm (Figure S12a). After addition of NH_3BH_3 for only 1 min, an obvious peak attributed to graphene is observed at 270 nm[14] which agrees well with its XRD result (Figure S13, where an diffraction peak at about 23° can be observed), indicating the reduction of GO to graphene within the short period (1 min). Besides the diffraction peak of graphene, the XRD pattern also shows the formation of metallic Pt (JCPDS: 04-0802). As a result, graphene-Pt hybrid has been synthesized in 1 min.

Synthesis of graphene-Ni hybrid: 7.0 mg of $NiCl_2$ was dissolved along with GO solution (290 mg, containing 9‰ GO) and PVP (2 mg) in 10 mL distilled water followed by ultrasonication for 5 min to get the uniform mixture, and then 45 mg of NH_3BH_3 and 2.5 mg $NaBH_4$ were added while magnetic stirring to reduce metal salt and GO to generate graphene-Ni hybrid at room temperature. The synthesis progress was traced by UV-Vis spectroscopy. The as-prepared sample was used for XRD analysis.

From Figure S14, it can be seen that after addition of NH_3BH_3 for only 1.5 min, an obvious peak attributed to graphene is observed at 270 nm[14] which also agrees well with its XRD result (Figure S15), indicating the reduction of GO to graphene within the short period. The XRD pattern of the as-prepared sample also shows a broad halo diffraction peak at about 44°, which could be assigned to (111) of cubic Ni (JCPDS: 65-0380). Therefore, graphene-Ni hybrid has been successfully prepared within 1 min.
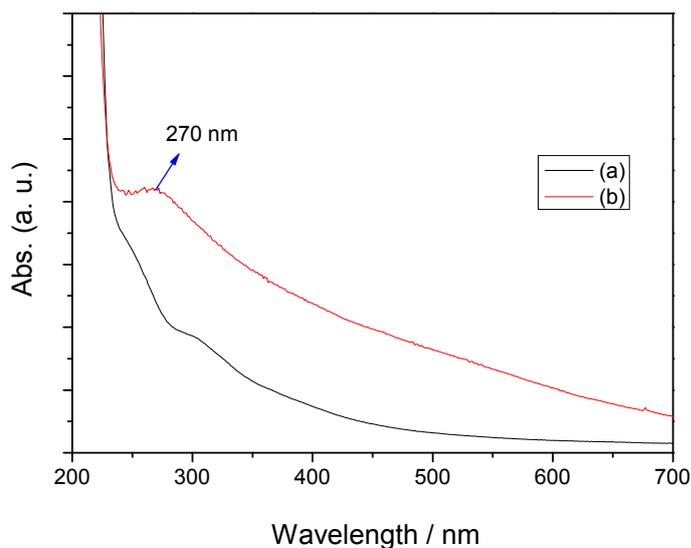
Figure S14. UV-Vis spectra of the monitoring for the synthesis process of graphene-Ni at reaction times of (a) 0 min, (b) 1.5 min.
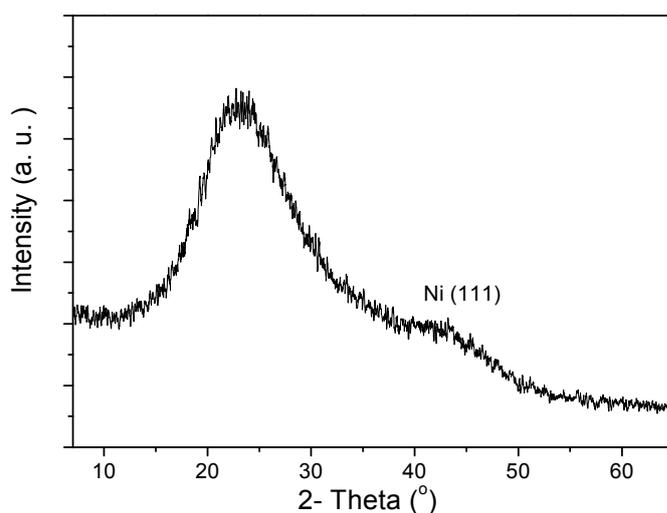

Figure S15. XRD pattern of graphene-Ni hybrid.

Catalytic Activity Characterization for hydrolysis of NH$_3$BH$_3$: 90 mg of NH$_3$BH$_3$ was kept in a 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 CuCl$_2$, CoCl$_2$ and GO (300 mg, containing 9‰ GO) in PVP (2 mg) aqueous solution (10 mL), where the molar ratio of Cu/Co and (Cu+Co)/NH$_3$BH$_3$ are kept as the constants of 9 and 0.02, respectively. The solution of metal salts, GO and PVP was firstly ultrasonicated for 5 min, and then it was added into the round-bottom flask

containing NH_3BH_3 solid with magnetic stirring. The evolution of gas was monitored using the gas burette. The reactions were carried out at 20 and 65 °C under ambient atmosphere. For comparison, NH_3BH_3 hydrolytic reactions catalyzed by CuCo, Cu, Co, Cu-GO, Co-GO and PVP have also been applied at 20 °C. The hydrolysis of NH_3BH_3 can be briefly expressed as follows:
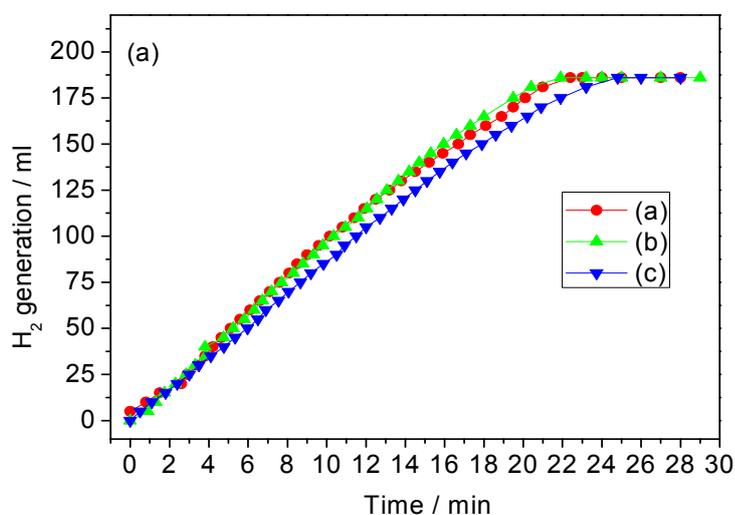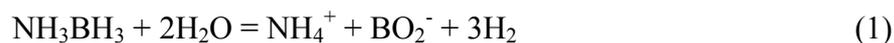
$$NH_3BH_3 + 2H_2O = NH_4^+ + BO_2^- + 3H_2 \tag{1}$$

Figure S16. Hydrogen generation from NH_3BH_3 aqueous solution (0.26 M, 10 mL) catalyzed by graphene-CuCo NPs at the (a) 1st, (b) 2nd and (c) 3rd recycle experiment.

After the hydrogen generation reaction was completed, the as-synthesized graphene-CuCo NPs were kept in their reaction solution in air and another equivalent of NH_3BH_3 (90 mg) was added to the reaction system and the released gas was monitored by the gas burette. Such recycle experiments for the synthesized catalyst were repeated for 3 times at 20 °C. As shown in Figure S16, after 3 times of the recycle test, the activity of the as-prepared graphene-CuCo catalyst has no obvious decrease.
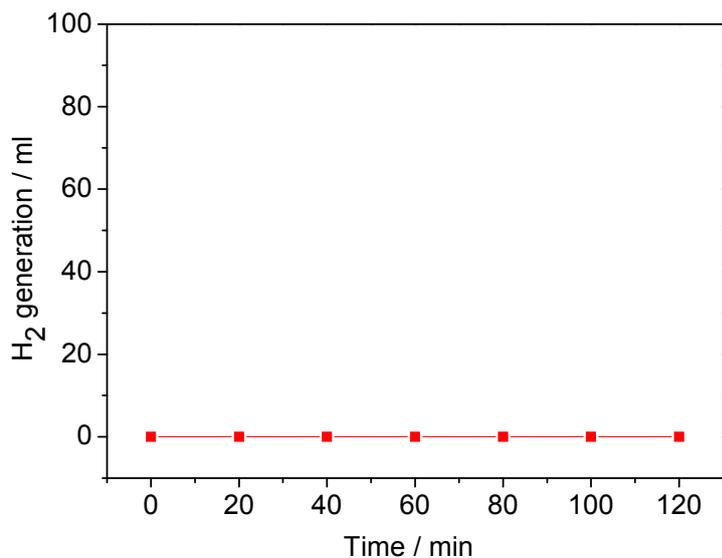
Figure S17. Hydrogen generation from NH_3BH_3 aqueous solution (0.26 M, 10 mL) in the presence of PVP (2 mg).

Table S1. Hydrogen generation from aqueous NH_3BH_3 catalyzed by Cu-, Co- and Pt-based catalysts.

Catalyst	Cu Content (wt%)	Temp. (°C)	Volume of H_2 (mL)	Mol of Catalyst (mmol)	Time (min)	TOF (mol H_2· mol catalyst^{-1}·min^{-1})	Ref.
Graphene-CuCo	90.70	20	187	0.052	16.3	9.18	This study
Cu (supported on γ-Al$_2$O$_3$)	100	20	220	0.058	590	0.27	11a
CuCl$_2$	100	20	33	0.035	170	0.23	11c
Cu	100	20	23	0.150	100	0.06	11b
Cu$_2$O	88.81	20	65	0.150	100	0.18	11b
Cu2O-Co3O4	16.55	20	1.3 (mmol)	0.066	7.5	2.63	S7
Cu-Co$_3$O$_4$	2.04	20	36	0.053	4	7.06	11d
Graphene-CuCo	90.70	65	189	0.052	3	50.4	This study
RuCu (supported on γ-Al$_2$O$_3$)	38.60	65	175	0.39	14	1.33	11e
RuCo (supported on γ-Al$_2$O$_3$)		65	175	0.4	5	3.64	11e
Co$_{0.32}$@Pt$_{0.68}$(supported on C)		25	100	0.062	6	10.99	S8
Au@Co		20	187	0.052	11	13.64	7f
Pt (supported on γ-Al$_2$O$_3$)		25	237	0.058	0.75	222.8	8
Pt (supported on C)		25	237	0.058	1.5	111.4	8
Pt (supported on SiO$_2$)		25	237	0.058	3	55.7	8

From Figure S1, and S5-7, it can be seen that the *in situ* prepared CuCo, Cu and Co NPs has catalytic activity on the reduction of GO. Moreover, the catalytic activities of

S14

the metal NPs for GO reduction by NH_3BH_3 have a great relationship with their activities for hydrolysis of NH_3BH_3 (Figure 4). The stronger the catalytic activity of metal NPs for hydrolysis of NH_3BH_3, the faster the reduction of GO. Therefore, the rapid self-catalytic synthesis of graphene-CuCo may be easily understood as follows: since the firstly formed Cu NPs by NH_3BH_3 reduction has the weak catalytic activity for NH_3BH_3 hydrolysis (Figure 4 inset b), the B-H$^{\delta-}$ bond in NH_3BH_3 should be slowly weakened or broken on the surface of Cu NPs, and thus a few intermediate species of Cu-H$^{\delta-}$ are generated, which could be then enough to help only the rapid adsorbtion and reduction the Co^{2+} on the surface of Cu NPs, but not the rapid reduction of GO. However, after the generation of surface decorated CuCo NPs, large amount of CuCo-H$^{\delta-}$ intermediate species are quickly built due to the relatively strong catalytic activity for NH_3BH_3 hydrolysis of CuCo NPs (Figure 4 inset a). As results, GO is easily reduced and the final product of graphene-CuCo hybrid is self-catalytically synthesized in a very short time. Consequently, all metallic NPs having catalytic activities for NH_3BH_3 hydrolysis has the potential to enhance the reduction rate of GO by NH_3BH_3.

Catalytic Activity Characterization for electrochemical hydrogen evolution reaction (HER): Cyclic voltammetry (CV) tests were carried out with a Biologic VMP3 station. The reference was Ag/AgCl electrode while Pt/C was used as counter
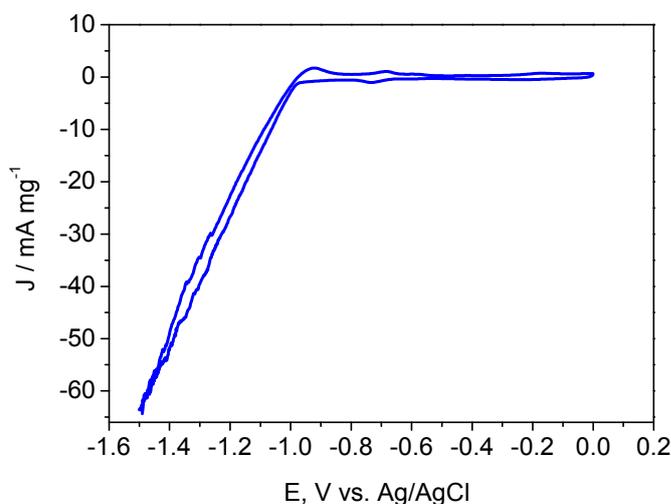

Figure S18. Cyclic voltammograms of Pt/C on glassy carbon electrode.

electrode. Glassy carbon electrodes (0.2 cm^2) used as a working electrode were first polished with 1 μm diamond polishing paste then ultrasonicated in distilled water for 5 min before immobilizing the different materials for hydrogen evolution reactions (HER). Electrode materials (Graphene-CuCo, Cu, Co and Pt/C) containing 5 mg of metals were dissolved in 1 ml ethanol with 1 μl naphthol, and then 10 μl of the above solution was placed on glassy carbon electrode and dried in air. The electrode was then placed in the cell containing 50 mL of 0.5 M KOH solution. CV was carried out at a scan rate of 20 mV/s with a peak window between 0 and -1.5 V versus Ag/AgCl electrode at room temperature.

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