Electronic Supplementary Information

Experimental Section

Materials: $CoSO_4 \cdot 7H_2O$ and urea were purchased from Aladdin Ltd. (Shanghai, China). Hydrochloric acid (HCl), sodium hydroxide (NaOH), and ammonium persulfate (APS) were purchased from Tianjin Fuchen Chemical Reagent Factory. *CF was purchased from* Ailantian Advanced Technology Materials Co. Ltd (Dalian, China). The water used throughout all experiments was purified through a Millipore system. All chemicals were used as received without further purification.

Preparation of $Cu(OH)_2$ NA/CF: $Cu(OH)_2$ NA/CF was made according to our previous report.[1] In brief, copper foam was washed with diluted HCl and water several times to remove the surface impurities. Then a piece of CF was rapidly immersed into a 30 mL mixed solution (4 mmol APS and 80 mmol NaOH) at room temperature for 30 minutes. The resulting $Cu(OH)_2$ NA/CF was dried at 60 °C for 12 h in vacuum oven for use.

Preparation of CuO/Co_3O_4 core-shell NA/CF: In a typical procedure, 0.79 g $CoSO_4 \cdot 7H_2O$ and 0.785 g of urea were dissolved in 37 mL of distilled water and stirred to form a clear pink solution. This solution was transferred to a 50 ml Teflon-lined stainless steel autoclave, followed by inserting of a piece of $Cu(OH)_2$ NA/CF. The autoclave was sealed and maintained at 85 °C for 2 h. The substrates were then taken out from the solution, rinsed with distilled water, and dried at 60 °C for 12 h in vacuum oven. Finally, the resulting $Cu(OH)_2/CoCO_3(OH)_2 \cdot nH_2O$ core-shell NA/CF were annealed at 300 °C in air for 2 h for CuO/Co_3O_4 NA/CF. The actual loading of the CuO/Co_3O_4 core-shell NA on CF is measured by inductively coupled plasma mass spectrometry (ICP-MS) (the loading per unit area is 0.9 mg/cm^{-2}), and we can maintain the ratio of CuO : Co_3O_4 for different loadings by controling the area of the catalyst.

Hydrogen generation measurement: All hydrolysis experiments were performed in a 25 mL two-necked round-bottom flask with 2 mL aqueous solution at ambient

pressure. The solution temperature was controlled by using a constant temperature water bath device. The volume of displaced water was determined using an electronic balance connected to a computer and the weight data were automatically recorded by a data acquisition software (Fig. S1).

Characterizations: Powder X-ray diffraction (XRD) data were collected on a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). Scanning electron microscopy (SEM) measurements were carried out on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. X-ray photoelectron spectroscopy (XPS) data were collected on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed on ThermoScientific iCA.

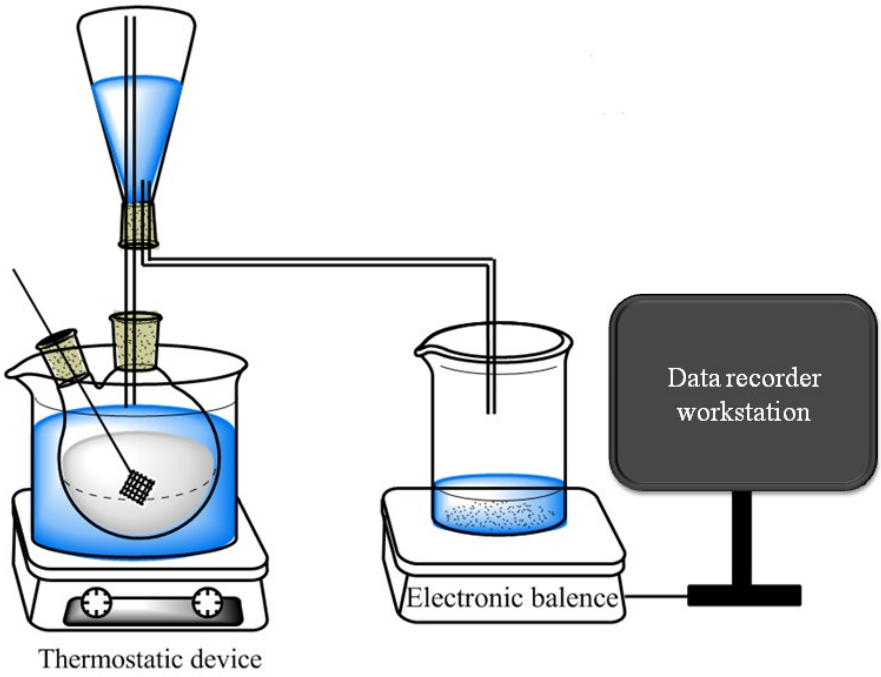

Fig. S1. Schematic diagram of HGR measurement system.

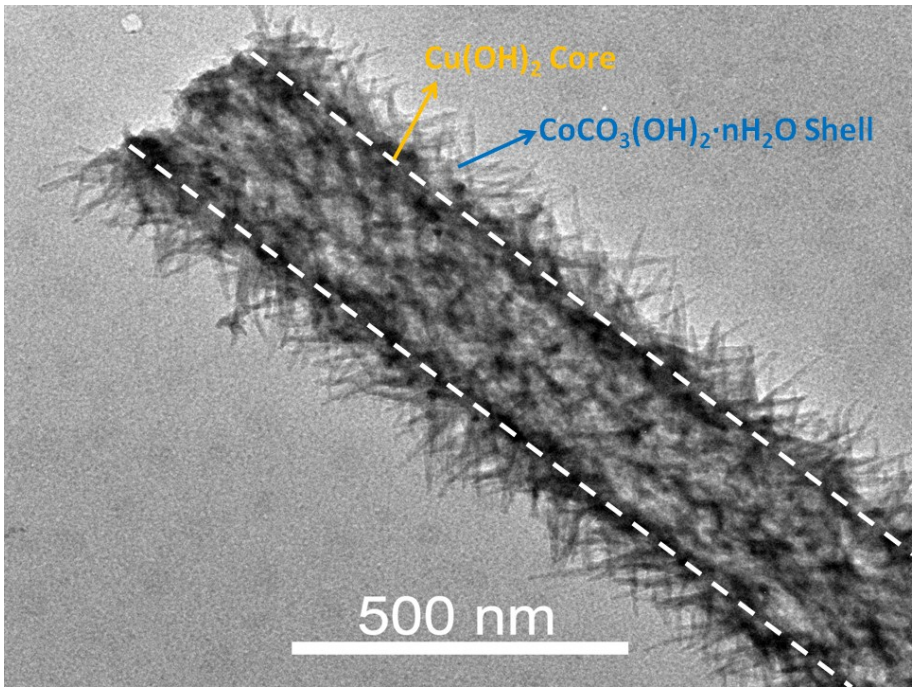

Fig. S2. TEM image for $Cu(OH)_2/CoCO_3(OH)_2 \cdot nH_2O$ core-shell NA/CF.

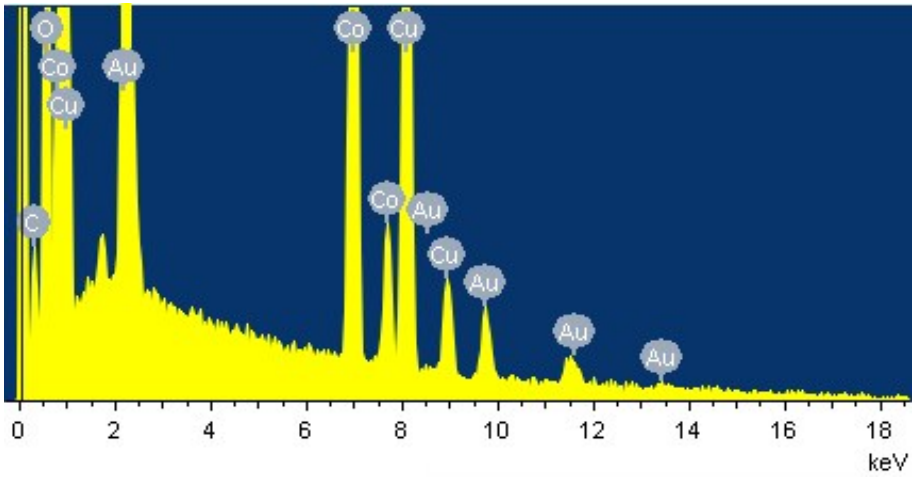

Fig. S3. EDX spectrum for CuO/Co_3O_4 core-shell NA/CF.

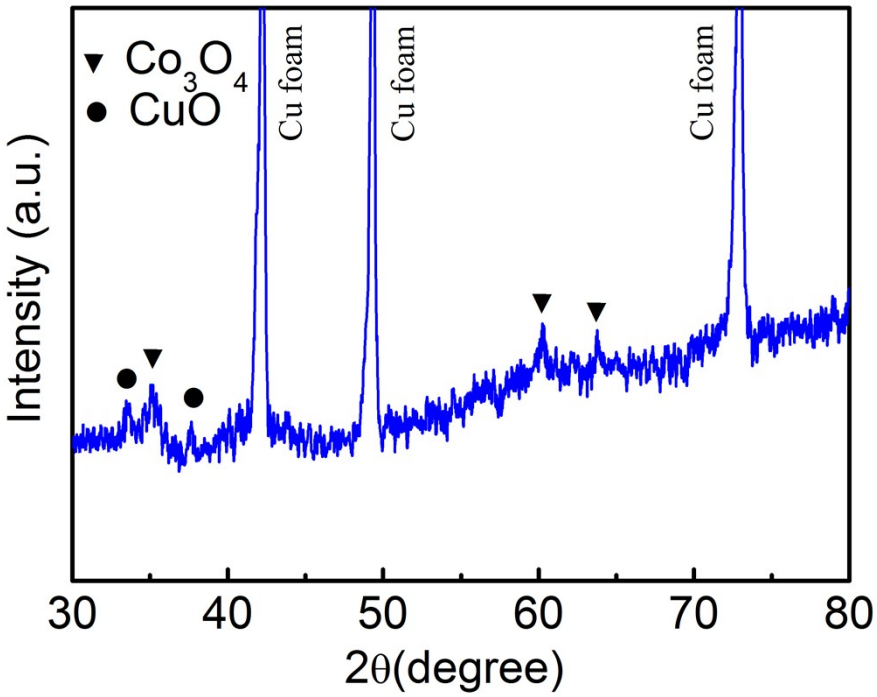

Fig. S4. XRD pattern for CuO/Co_3O_4 core-shell NA/CF.

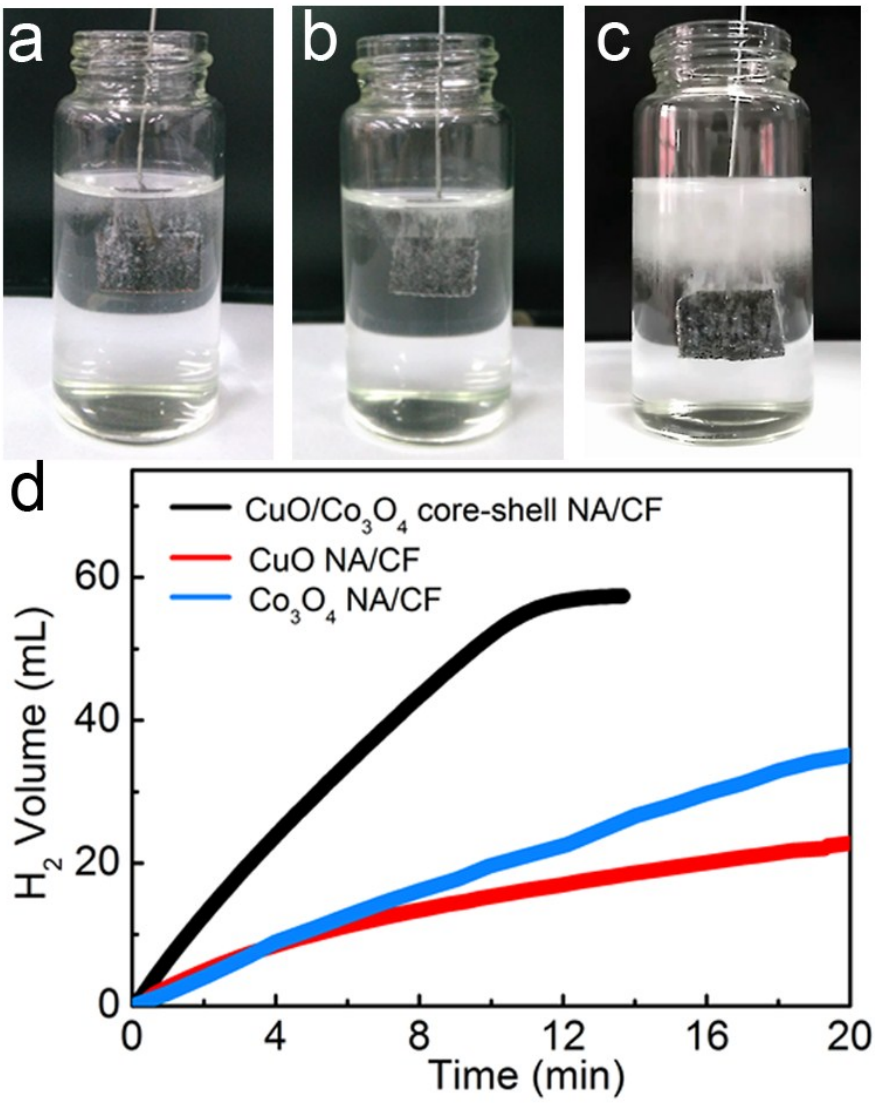

Fig. S5. Optical photograph of $NaBH_4$ hydrolysis reaction catalyzed by (a) CuO NA/CF, (b) Co_3O_4 NA/CF ,and (c) CuO/Co_3O_4 core-shell NA/CF using 1 wt.% NaOH and 1 wt.% $NaBH_4$ solution at 298 K and the corresponding plots of the volume of hydrogen vs time (d).

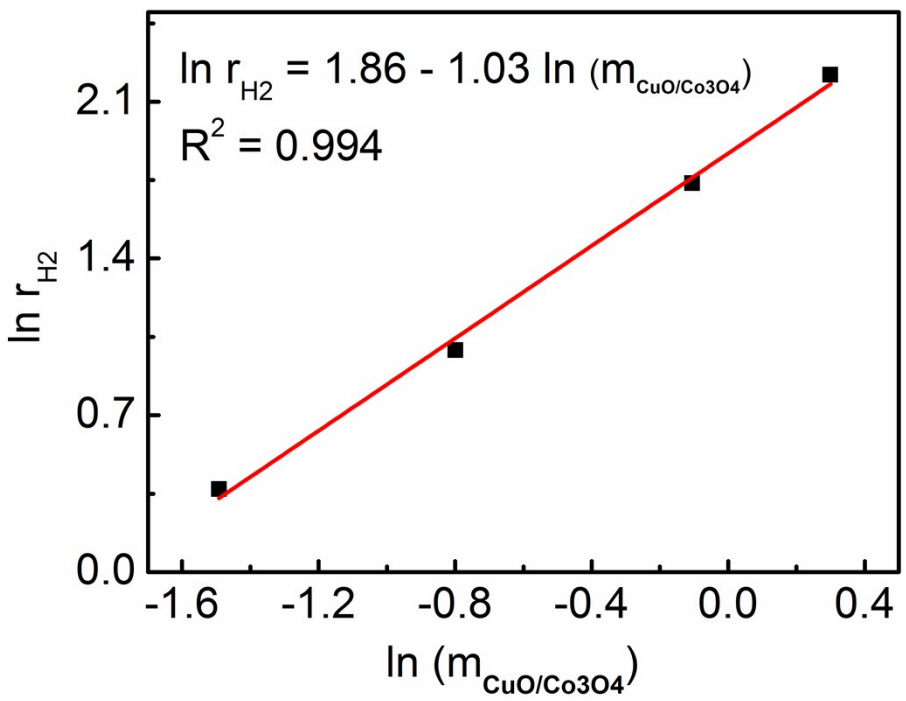

Fig. S6. Plot of the hydrogen generation rate versus the catalyst loading (both in logarithmic scale) for the same reactions.

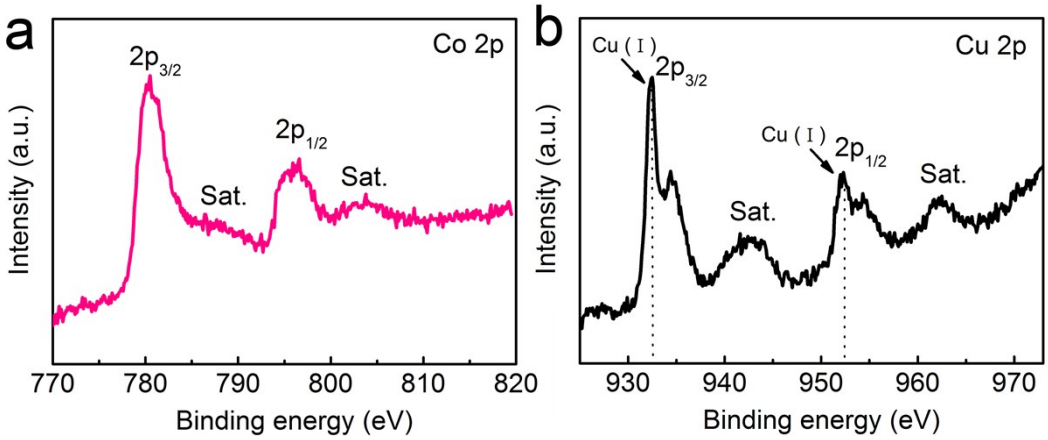

Fig. S7. XPS spectra for CuO/Co_3O_4 core-shell NA/CF after hydrolysis. (a) Cu 2p and (b) Co 2p regions.

Table S1. Comparison of E_a and HGR for the hydrolysis of $NaBH_4$ using Co-based catalysts.

Catalyst	**E_a (KJ/mol)**	**HGR (L/min/g_{cat})**	**Temperature (K)**	**Ref.**
Co-P	60.2	3.30	303	2
CoO nanocrystals	59.7	8.33	303	3
$LiCoO_2$	-	1.54	303	4
Co_3O_4	-	3.90	303	5
$CoCl_2$	52.86	1.16	298	6
Co	-	0.10	293	7
Co-B/CB	57.8	3.90	303	8
Ni-Co-B	62.0	2.68	301	9
Co_2B (Co_3O_4)	77.96	1.80	298	10
$Ru/LiCoO_2$	68.5	0.20	298	11
Co-B	64.87	1.10	293	12
Co/IR-120	54.1	1.24	293	13
CuO/Co_3O_4 core-shell NA/CF	**56.38**	**6.16**	**298**	**This work**

References

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