

Supporting Information

Multifunctional Au-Co@CN Nanocatalyst for Highly Efficient Hydrolysis of Ammonia Borane

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Chemicals:

Ammonia-borane (AB, NH_3BH_3 , Aldrich, 90 %), cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 99.0\%$), chloroauric acid (HAuCl_4 , Aldrich, 48~50 % Au basis), nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Shanghai Hengxin Chemical Reagent Co., Ltd., $\geq 98.0\%$), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 99.0\%$), cyanamide (Aldrich, 50 wt.% in H_2O , contains 0.1 % formic acid as stabilizer), Ludox HS40 solution (Alfa Aesar, Silicon(IV) oxide, 40 % in H_2O , colloidal dispersion), hydrofluoric acid (HF, Sinopharm Chemical Reagent Co., Ltd., $\geq 40.0\%$), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 99.7\%$) were used as received.

Methods:

Synthesis of g- C_3N_4 : 5 g of cyanamide was dissolved in 7.5 g of Ludox HS40 solution (dispersion of 12-nm SiO_2 particles with 40 wt% in water) and heated at 65 °C overnight to remove water. The as-formed white powder was heated at a temperature of 550 °C for 4 h (ramp: 2 °C min^{-1}) under the protection of N_2 . The resulting brown-yellow powder was grinded and treated with a 4 M HF acid for 24 h to remove the silica template. The powders were then filtered and washed twice with distilled water and once with ethanol. Finally the powders were dried at 60 °C overnight.

Synthesis of Au-Co@CN (30 wt.%): 7.1 mg of mesoporous carbon nitride was dispersed into 4.5 mL of water via sonication and vigorous stir. 11 mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added into the dispersion and stirred about 40 h. Then 47 μL of 41.2 mM HAuCl_4 was dropped into this suspension and 0.5 mL freshly prepared NH_3BH_3 aqueous solution (containing 45 mg of AB) was added while stirring at room temperature. The catalyst was thus reduced in situ and used for following catalytic reaction

without separation. After reaction, the catalyst was separated by an external magnet and dried at 60 °C overnight. The as-prepared sample was used for PXRD, BET, TEM and Hysteresis loop measurements.

Samples with different weight percentage of metal loading are prepared by changing the amount of metal solution with other conditions fixed.

Synthesis of Au-Ni@CN (30 wt.%) and Au-Fe@CN (30 wt.%): 7.1 mg of mesoporous carbon nitride was dispersed into 4.5 mL of water via sonication and vigorous stir. 11 mg of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or 12 mg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added into the dispersion and stirred about 40 h. Then 47 μL of 41.2 mM HAuCl_4 was dropped into this suspension and 0.5 mL freshly prepared NH_3BH_3 aqueous solution (containing 45 mg of AB) was added while stirring at room temperature. The catalyst was separated by an external magnet and dried at 60 °C overnight.

Synthesis of Au-Co NPs: 11 mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 4.5 mL water. Then 47 μL of 41.2 mM HAuCl_4 was dropped into this suspension and 0.5 mL freshly prepared NH_3BH_3 aqueous solution (containing 45 mg of AB) was added while stirring at room temperature. The catalyst was separated by an external magnet and dried at 60 °C overnight.

Synthesis of Au@CN (30 wt.%): 7.1 mg of mesoporous carbon nitride was dispersed into 4.5 mL of water via sonication and vigorous stir. 47 μL of 41.2 mM HAuCl_4 was dropped into this suspension and 0.5 mL freshly prepared NH_3BH_3 aqueous solution (containing 45 mg of AB) was added while stirring at room temperature. The catalyst was dried at 60 °C overnight.

Synthesis of Co@CN (30 wt.%): 7.1 mg of mesoporous carbon nitride was dispersed into 4.5 mL of water via sonication and vigorous stir. 11 mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added into the dispersion and stirred about 40 h. Then 0.5 mL freshly prepared NH_3BH_3 aqueous solution (containing 45 mg of AB) was added while stirring at room temperature. The catalyst was separated by an external magnet and dried at 60 °C overnight.

Catalytic Activity Characterization:

0.5 mL freshly prepared NH_3BH_3 aqueous solution (containing 45 mg of AB) was added into the suspension consisting of g- C_3N_4 , CoCl_2 and HAuCl_4 (see the Synthesis of Au-Co@CN) while stirring at room temperature under ambient atmosphere. At the same time, the as-formed H_2 was monitored by a gas burette system. For photocatalytic reactions, the reactor containing the same reactand solution was irradiated under a 150 W Xe lamp with a water filter. The wavelength of the incident light was controlled by using a cut-off filter. The temperature of the reaction solution was maintained at 298 ± 5 K by a water bath during the reaction.

Characterization:

The **Nitrogen sorption** experiments were performed with a Quadrasorb at 77 K, and data analysis was performed with Quantachrome software. Samples were degassed at 150 °C for 20 h before measurements. The **PXRD** measurements were performed on a Rigaku D/Max 2550 X-ray diffractometer operating at the Cu K α 1 radiation. The **TEM** measurements were performed on a JEOL JEM-2100 operated at 100 kV. The **FTIR** spectra were recorded using a Bruker IFS 66v/S FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The hysteresis loop The **photoluminescent emission** spectra were recorded on a QM-4-CW (Photo technology international, Int. USA/CAN). The **UV-vis** spectrophotometer (UV-3600) was employed to obtain the diffuse reflectance spectra of the samples. The Hysteresis loop was recorded using a physical property measurement system (PPMS-9T(EC-II)) at 300K.

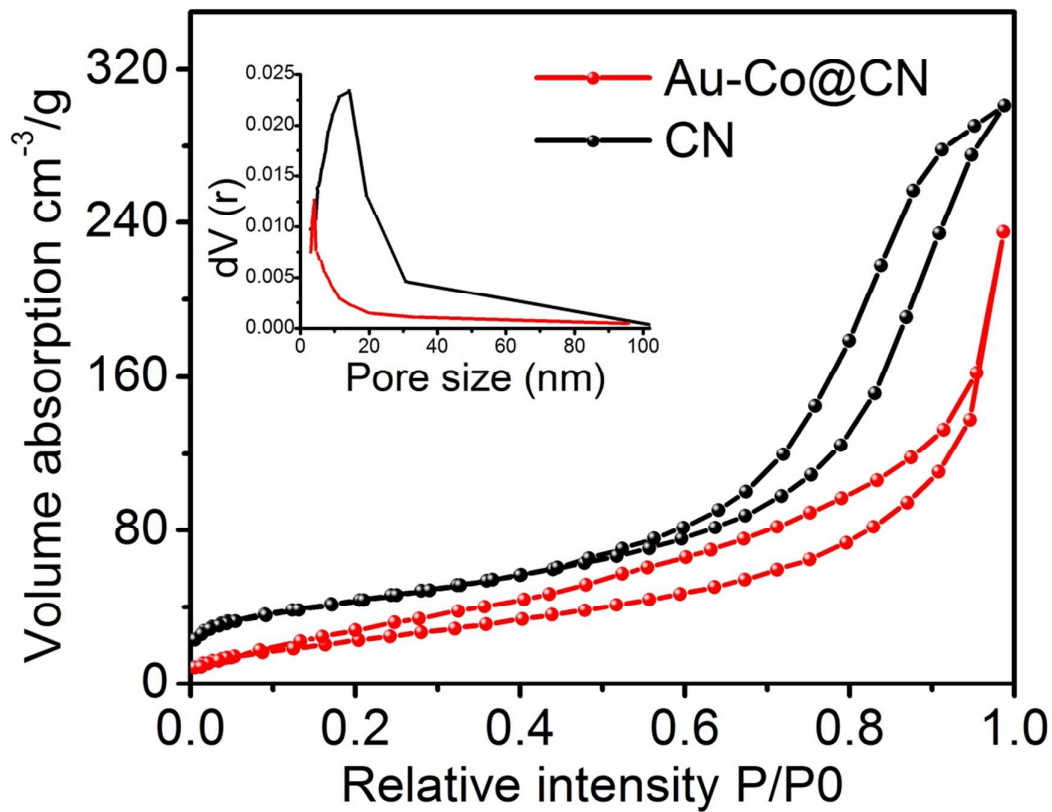


Figure S1. Nitrogen sorption results of bare CN and 30 wt.% Au-Co@CN catalyst. Inset: pore-size distributions. The surface area of bare mesoporous carbon nitride (CN) was 160 m²/g and the pore size distribution was centered at 14 nm. The surface area of Au-Co@CN was 93 m²/g and the pore size is much smaller (mean size: 4 nm). All these results suggest that the metallic Au and Co were successfully deposited in the pore of carbon nitride support.

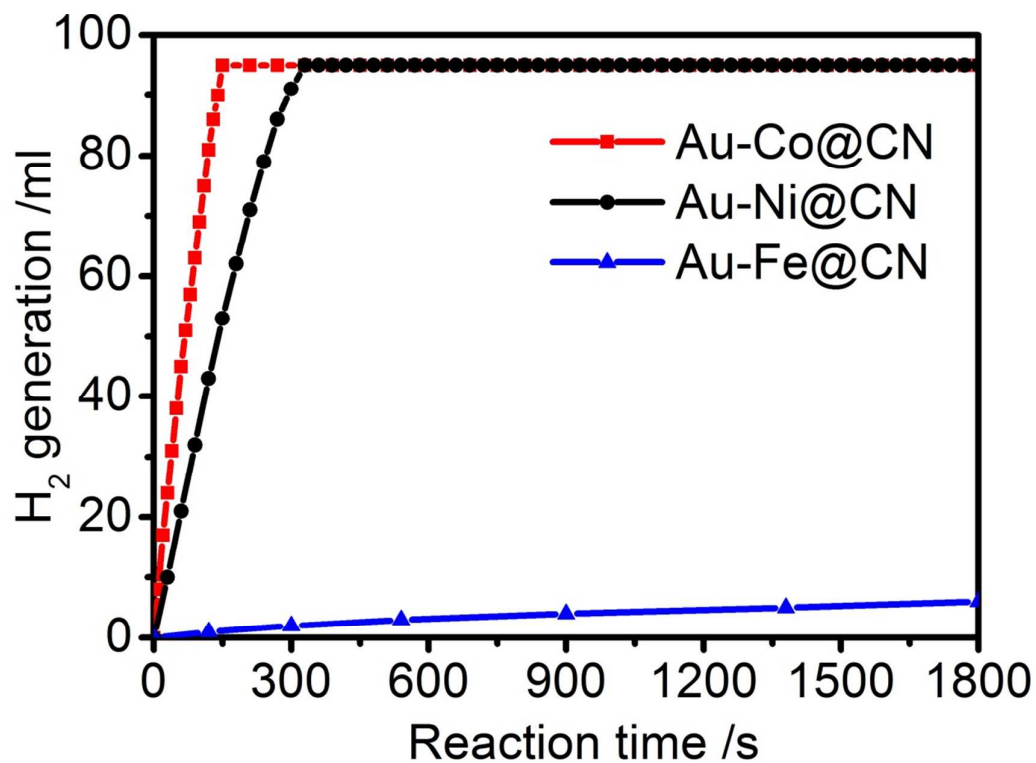


Figure S2 Hydrolysis of aqueous AB solution catalyzed by Au-Co@CN, Au-Ni@CN and Au-Fe@CN with photo-irradiation. Au-Co@CN show the best catalytic activity while the H₂ generation rate of Au-Ni@CN was about a half slower than that of Au-Co@CN. Au-Fe@CN displayed almost no activity in this reaction. Typical conditions: 0.26 M aqueous AB solution (5 mL), Catalyst/AB: 0.02 molar ratio, ambient atmosphere, 298 K.

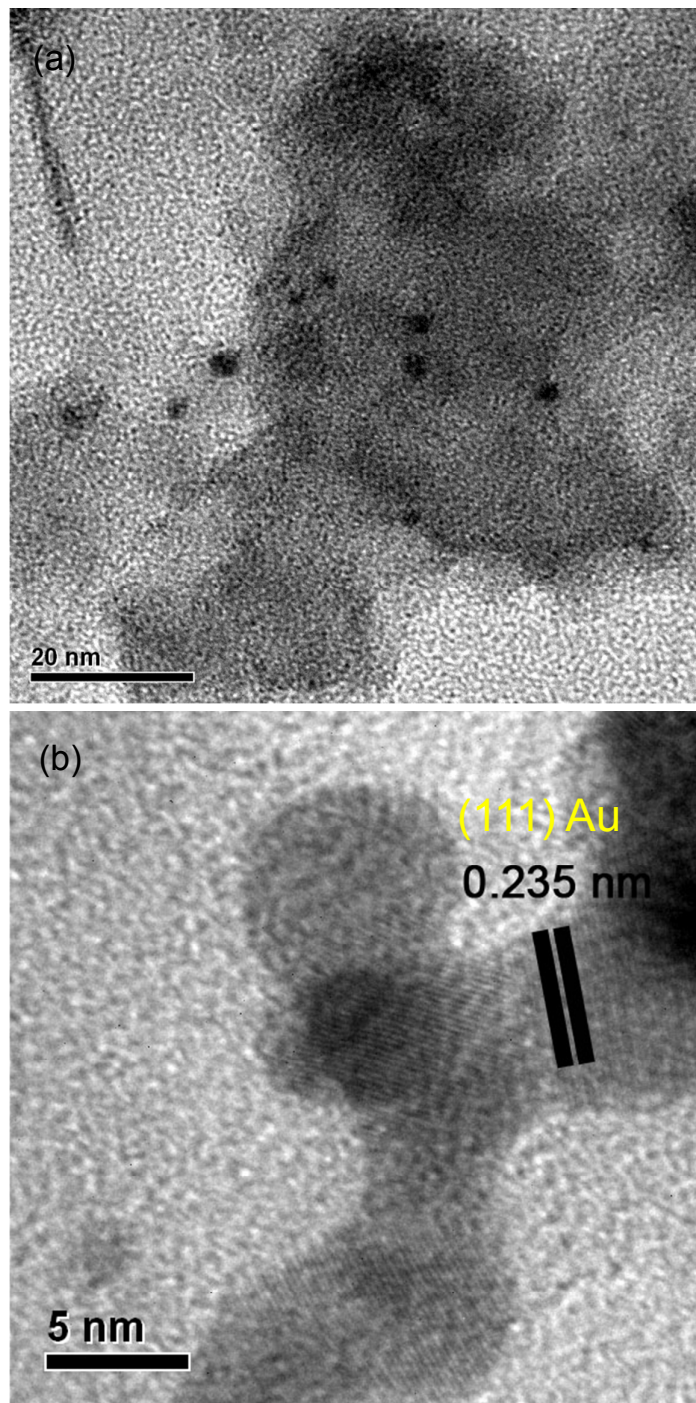


Figure S3 The transmission electron microscopy (TEM) images of Au-Co@CN. The Au NPs on carbon nitride are roughly spherical in shape. The (111) facet of Au nanoparticles was observed and the sizes of the Au nanoparticles were mainly smaller than 10 nm.

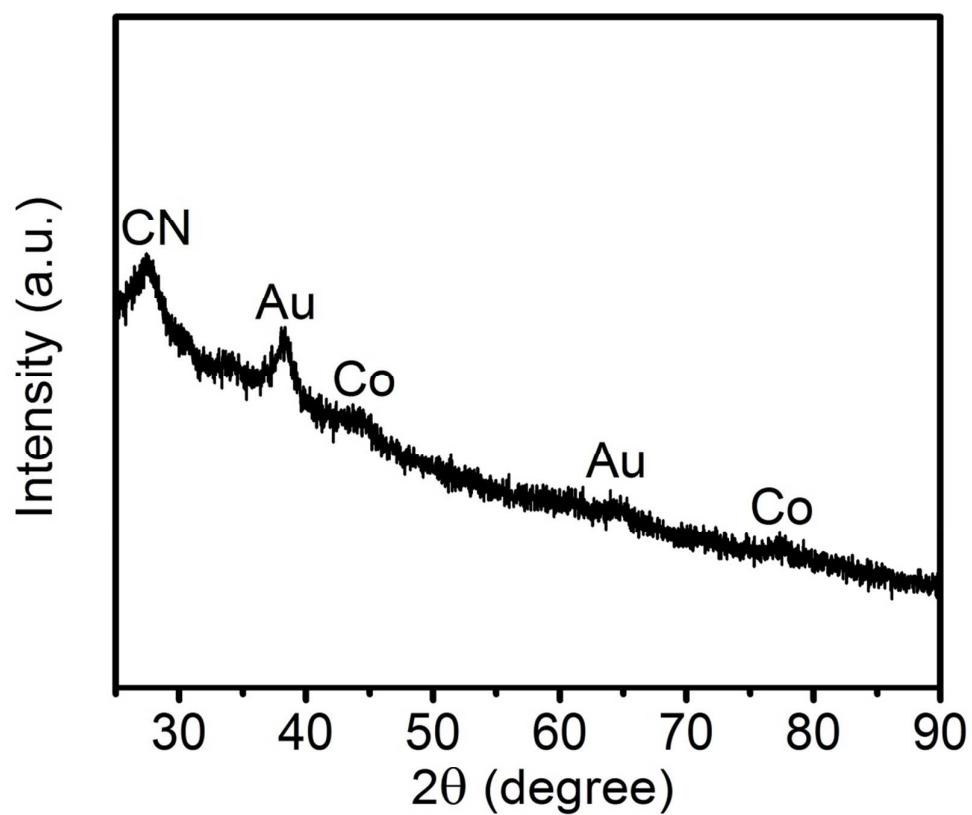


Figure S4 PXRD patterns of Au-Co@CN. The powder X-ray diffraction (PXRD) patterns of Au-Co@CN exhibit peaks of carbon nitride and metallic Au, Co. The intensity of peaks of the Co metals (96 at.% of the metal components) is relatively weak, suggesting that the Co metal nanoparticles are roughly in the amorphous phase.

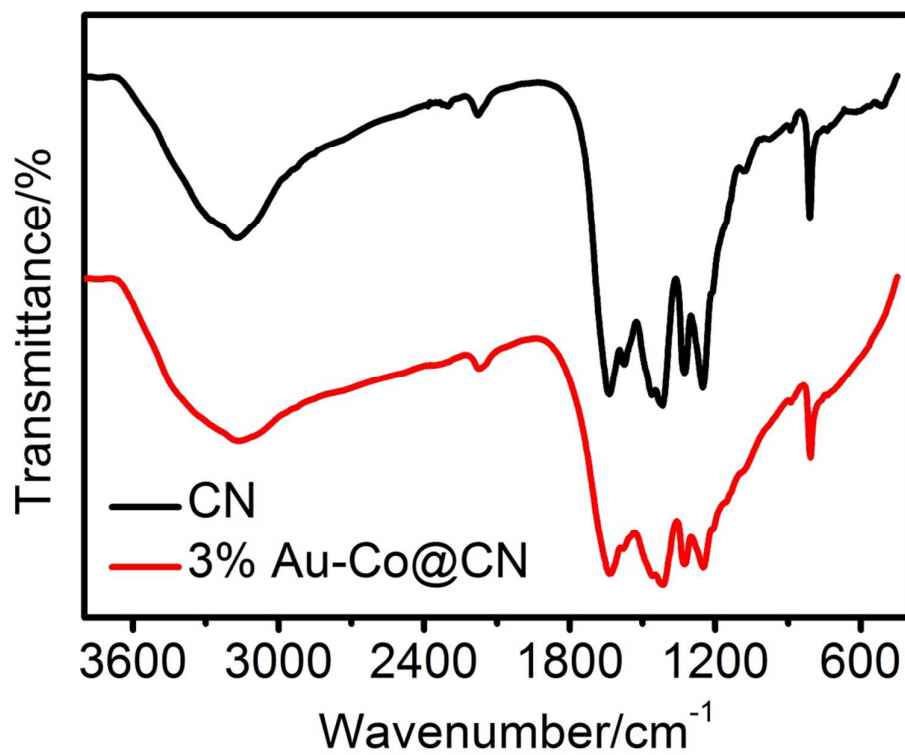


Figure S5 FTIR spectra of Au-Co@CN (3 wt.%) and bare mesoporous carbon nitride (CN). There was no obvious changing in the FTIR spectra of the samples after the metal loaded, showing that the carbon nitride support was chemical stable.

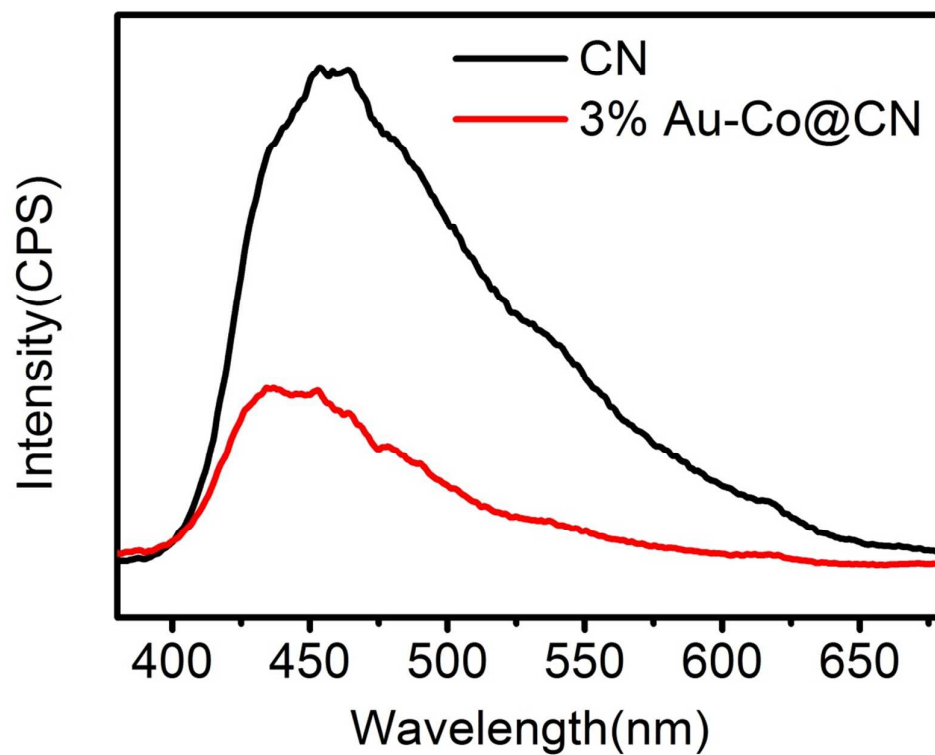


Figure S6 Photoluminescence spectra of Au-Co@CN (3 wt.%) and bare mesoporous carbon nitride (CN). The notable decreased photoluminescence intensity (red line) of carbon nitride after the introduction of Au-Co NPs indicates the electron transfer from carbon nitride to Au-Co NPs.

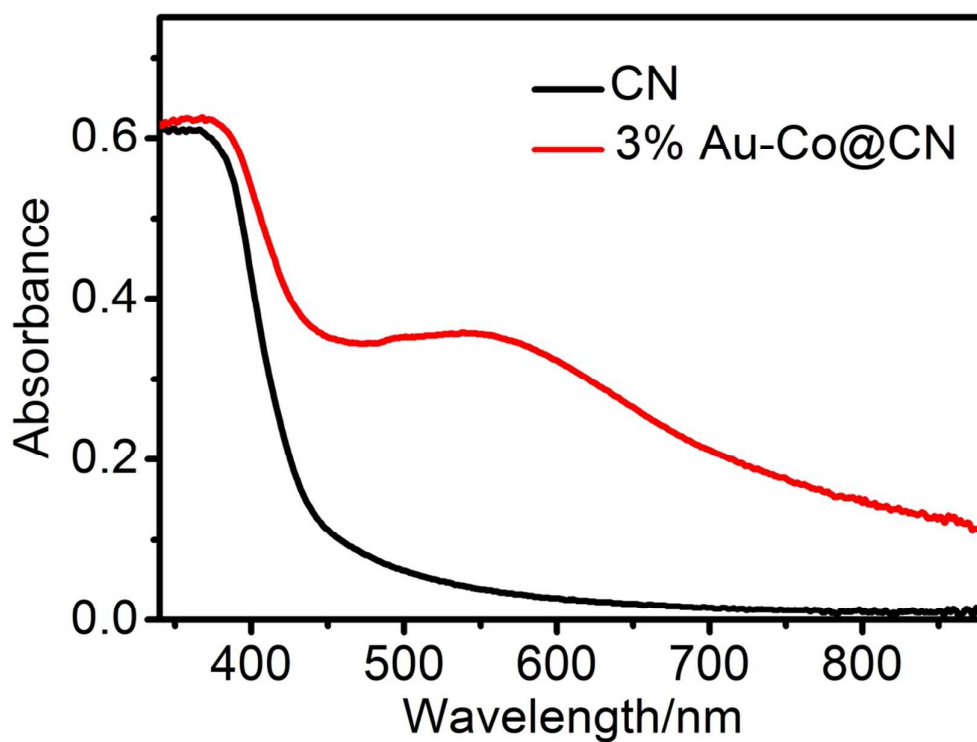
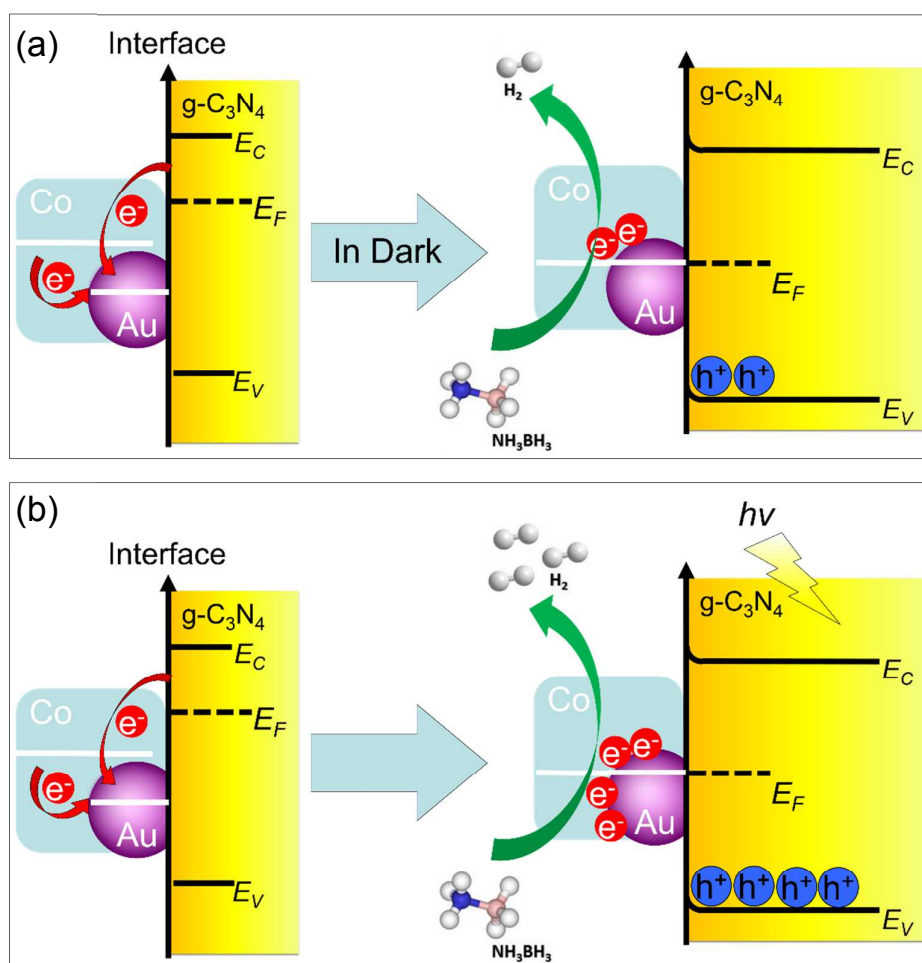


Figure S7 UV-Vis adsorption spectra of Au-Co@CN (3 wt.%) and bare carbon nitride (CN). The notable absorption peak of the Au-Co@CN around 570 nm was attributed to the plasma absorption of Au NPs.



Scheme S1 Proposed reaction mechanism of hydrolysis of aqueous AB solution over Au-Co@CN in dark (a) and under visible light (b). Considering the reaction mechanism of hydrolysis of AB over metal nanocatalysts has been well elucidated in the literature, we thus discuss more on the electron transfer at the metal-CN interface and thus the Mott-Schottky effect on the final catalytic activity. Generally speaking, electron will flow from CN to metal to balance once the rectified interface formed, resulting in a balanced work function (E_F) at both sides of the metal-CN interface. The electron will also flow from Co to Au due to the variation in the E_F . All these electron flows lead to an enriched electron-intensity at metal-CN interface or Co-Au-CN interface. For dark reaction as depicted in (a), the slightly enriched electron-intensity could obviously elevate the catalytic activity of Au nanoparticles by following the manner of organic ligands or moieties for activating metal active centers in the literature. That's why CN supported nanocatalyst was more active than bare one. For photocatalytic reaction (b), the light irradiation excited more electrons to the interface, resulting in higher enrichment of electron intensity. The obviously promoted hydrogen evolution rate under visible light irradiation rather suggested the direct interaction between the electron intensity and catalytic activity for hydrolysis of AB. It should be noted that the photothermal effect was excluded here because photoirradiation could not obviously elevate the activity of bare Au-Co nanoparticles.

Table S1 TOF values for decomposition of AB catalyzed by various Au and/or Co NPs based catalysts.^a

Catalyst	[AB](M)	T (K)	TOF ^a (metal)	TOF ^b (noble metal)	Note	Reference
Au-Co@CN	0.26	298	2897	71410	Visibile light	This work
Au-Co@CN	0.26	298	1704	42006	dark	This work
Au@Co	0.26	298	960	11838		15
Ru@Co/graphene	0.21	298	2428	20640		16
Pd@Co/graphene	0.19	298	2454	24540		37
Fe _{0.3} Co _{0.7} /rGO	0.16	298	2162	-		20
AuCo@MIL-101	0.2	298	1410	23500		17
Ag@Co/graphene	0.1	298	614	6144		21
RuCo/ γ -Al ₂ O ₃	1.0	338	987	1974		38
Cu-Co	0.05	298	163	-		S1
Cu@FeCo	0.2	298	630	-		S2
Au/Co/Fe	0.17	298	113	1883	Ar atmosphere	S3

^a TOF values were calculated in the format of mol H₂ per mol catalyst (metal) per hour. The amounts of catalyst were calculated on the basis of the total moles of metal components involved.

^b TOF values were calculated in the format of mol H₂ per mol catalyst (noble metal) per hour. The amounts of catalyst were calculated on the basis of the moles of noble metal components involved.

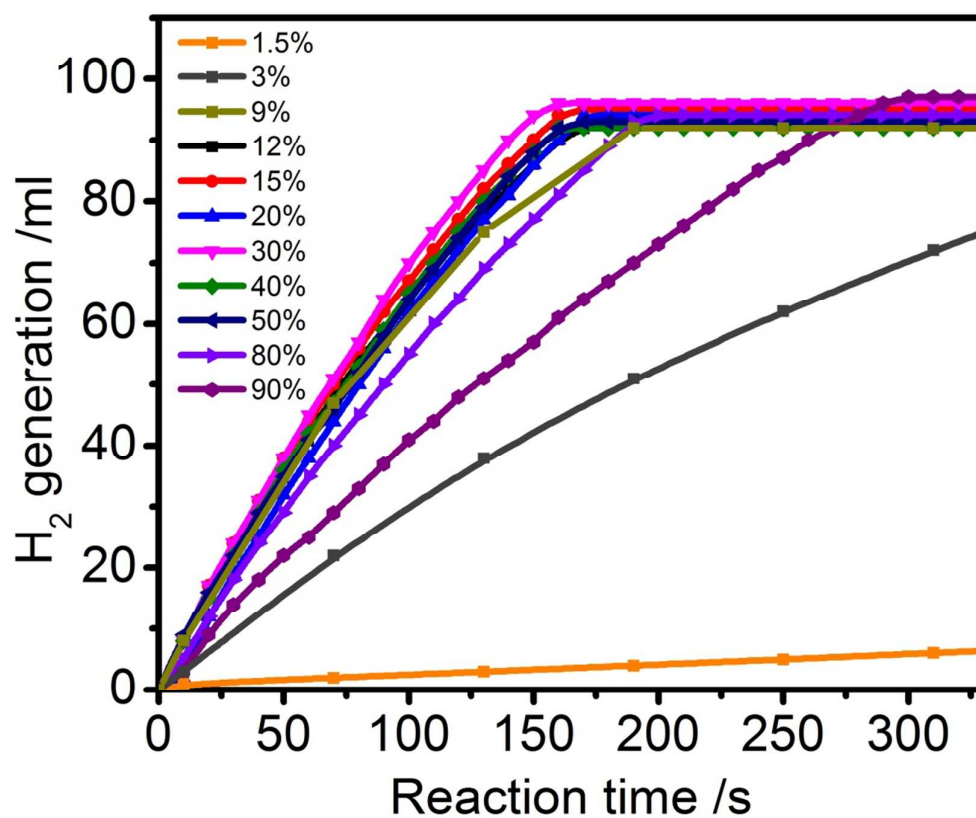


Figure S8 Hydrolysis of aqueous AB solution catalyzed by Au-Co@CN-x% with photo-irradiation. The gas evolution rate generally increases with the increasing of the weight percentage of metal loading till the optimum proportion of 30 wt.%. Typical conditions are described in Figure S1.

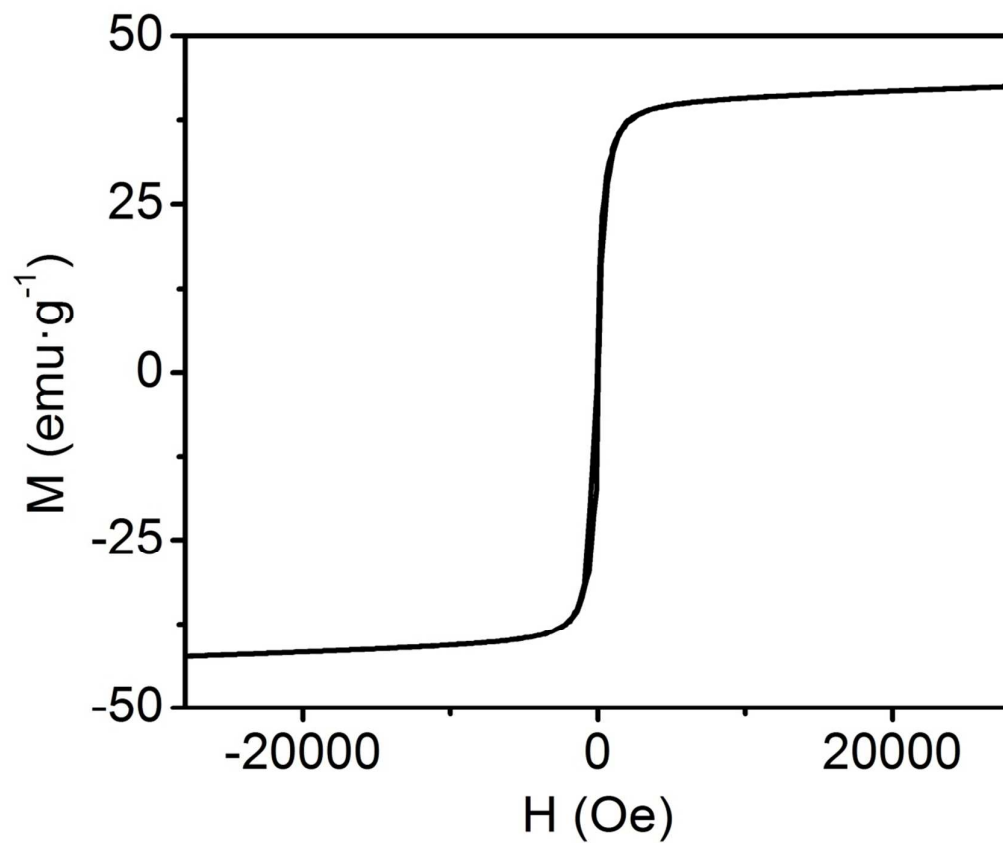


Figure S9 Hysteresis loop of Au-Co@CN (30 wt.%). The Au-Co@CN is superparamagnetic according to its negligible hysteresis loop at 300 K, making it easy for recycling via external magnetic field.

REFERENCES

- S1 Li, C. M.; Zhou, J. Y.; Gao, W.; Zhao, J. W.; Liu, J.; Zhao, Y. F.; Wei, M.; Evans, D. G.; Duan, X. *J. Mater. Chem. A*. **2013**, 1, 5370-5376.
- S2 Qiu, F. Y.; Dai, Y. L.; Li, L.; Xu, C. C.; Huang, Y. N.; Chen, C. C.; Wang, Y. J.; Jiao, L. F.; Yuan, H. T. *Int. J. Hydrogen Energy*. **2014**, 39, 436-441.
- S3 Aranishi, K.; Jiang, H. L.; Akita, T.; Haruta, M.; Xu, Q. *Nano Res.* **2011**, 4, 1233-1241.