Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

Cube-Like CuCoO Nanostructures on Reduced Graphene Oxide for H_2 Generation from Ammonia Borane

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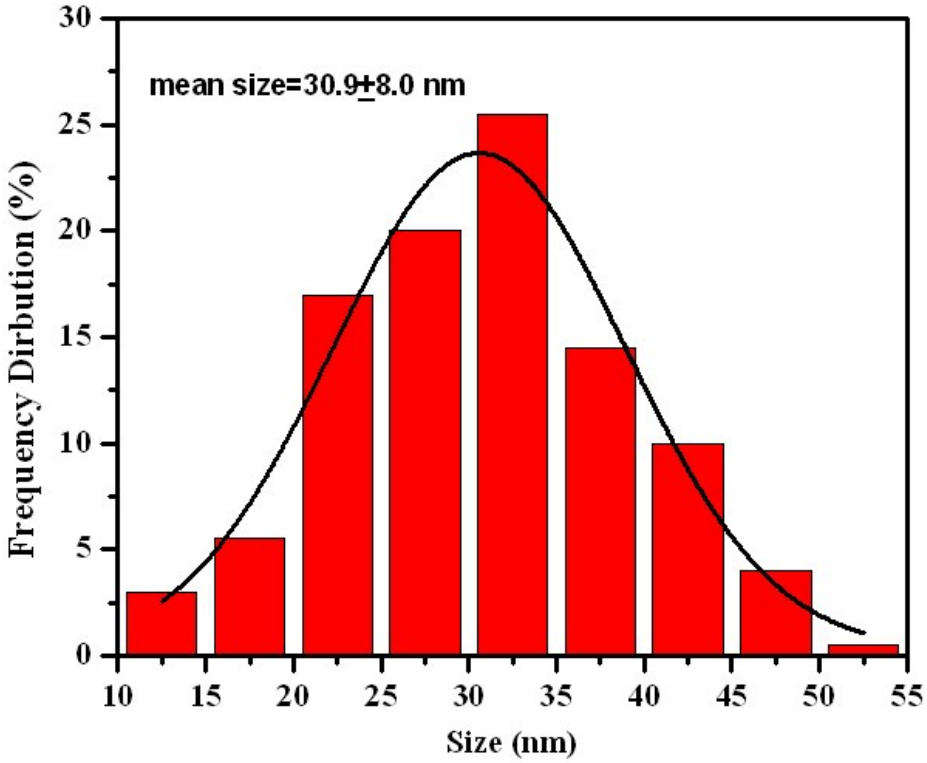

Figure S1: The particle size distribution of $Cu_{0.5}Co_{0.5}O$-rGO with an average size of 30.9 nm.

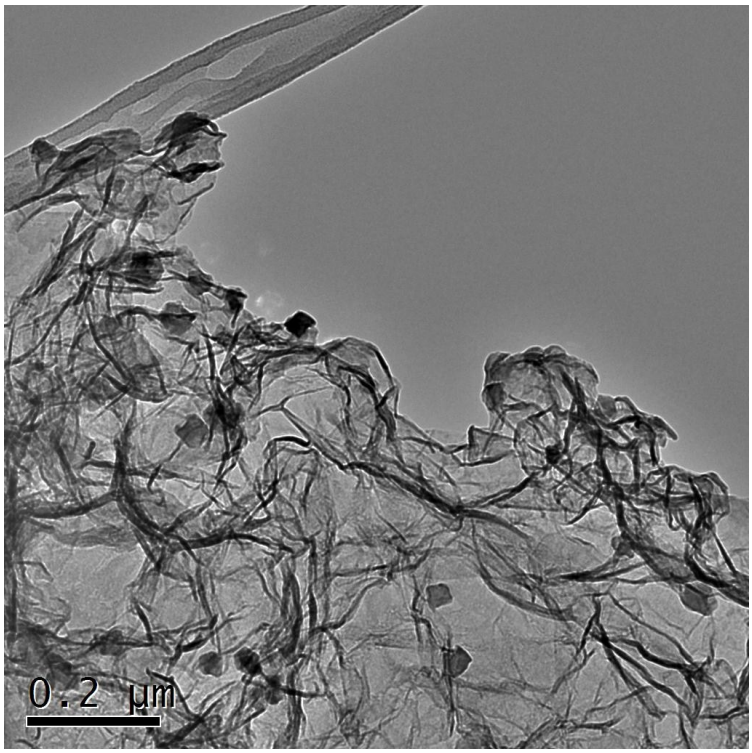

Figure S2: TEM image of the $Cu_{0.5}Co_{0.5}O$-rGO sample.

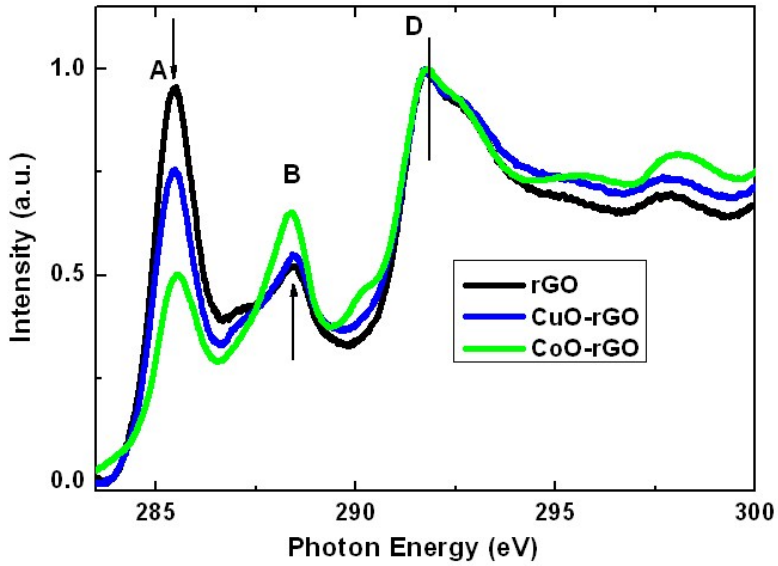

Figure S3: XAS spectra of rGO, CuO-rGO and CoO-rGO samples at C *K*-edge.

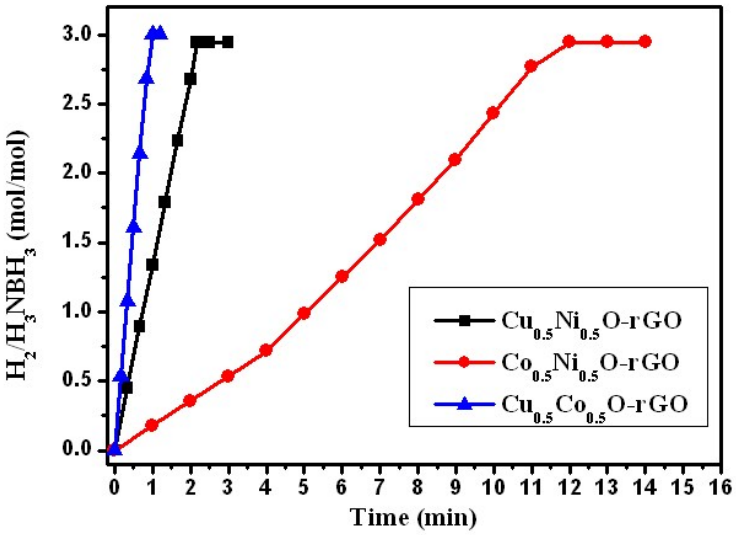

Figure S4: Hydrogen evolution curves of the hydrolysis of AB aqueous solution catalyzed by $Cu_{0.5}Co_{0.5}O$-rGO, $Cu_{0.5}Ni_{0.5}O$-rGO and $Co_{0.5}$ $Ni_{0.5}O$-rGO samples.

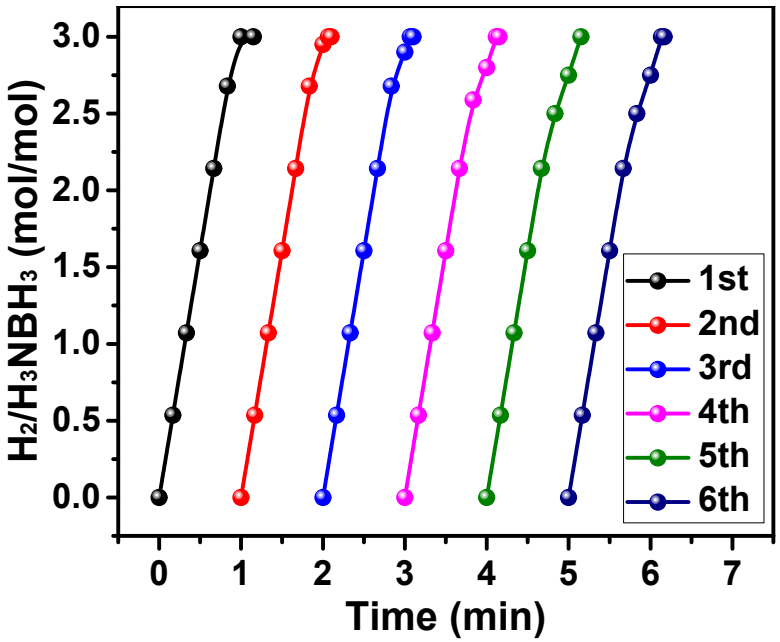

Figure S5: Stability test of $Cu_{0.5}Co_{0.5}O$-rGO in 6 runs for the hydrolysis of AB. The TOF value decreases from 81.7 to 72.1 (the 6th cycle, 88.3% left).

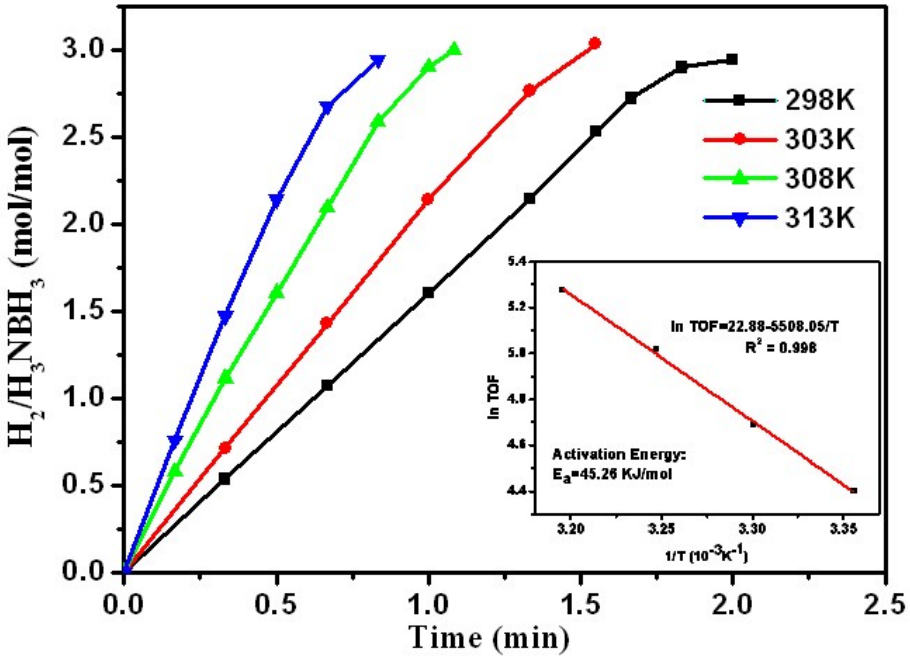

Figure S6: Hydrogen-generating rate as a function of temperature in the hydrolysis of AB catalyzed by $Cu_{0.5}Co_{0.5}O$-rGO. Since at a high temperature the reaction will be finished very quickly, we have used less $Cu_{0.5}Co_{0.5}O$-rGO (2.6 mg) in this reaction. Inset: Arrhenius plot of ln(TOF) versus $1/T$. The activation energy is 45.26 kJ/mol.

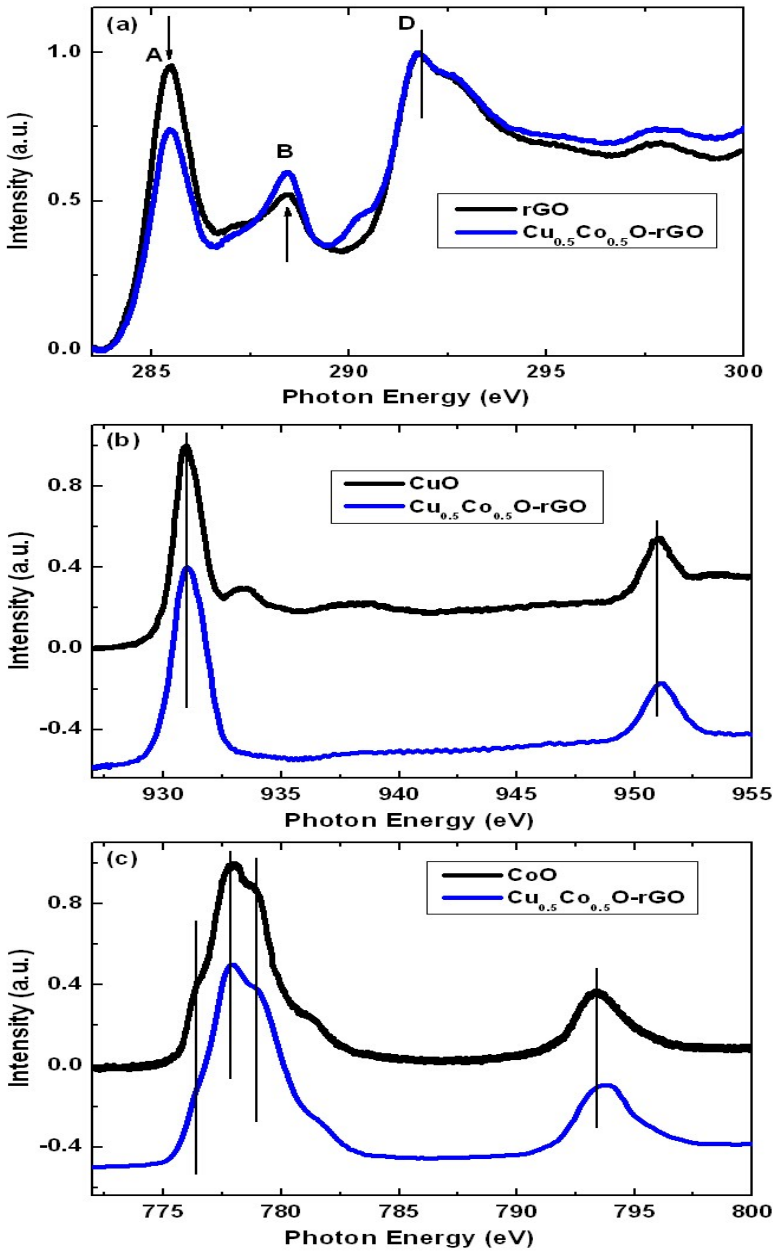

Figure S7: XAS spectra of $Cu_{0.5}Co_{0.5}O$-rGO and the reference samples at C *K*-edge (a); Cu *L*-edge (b); and Co *L*-edge (c).

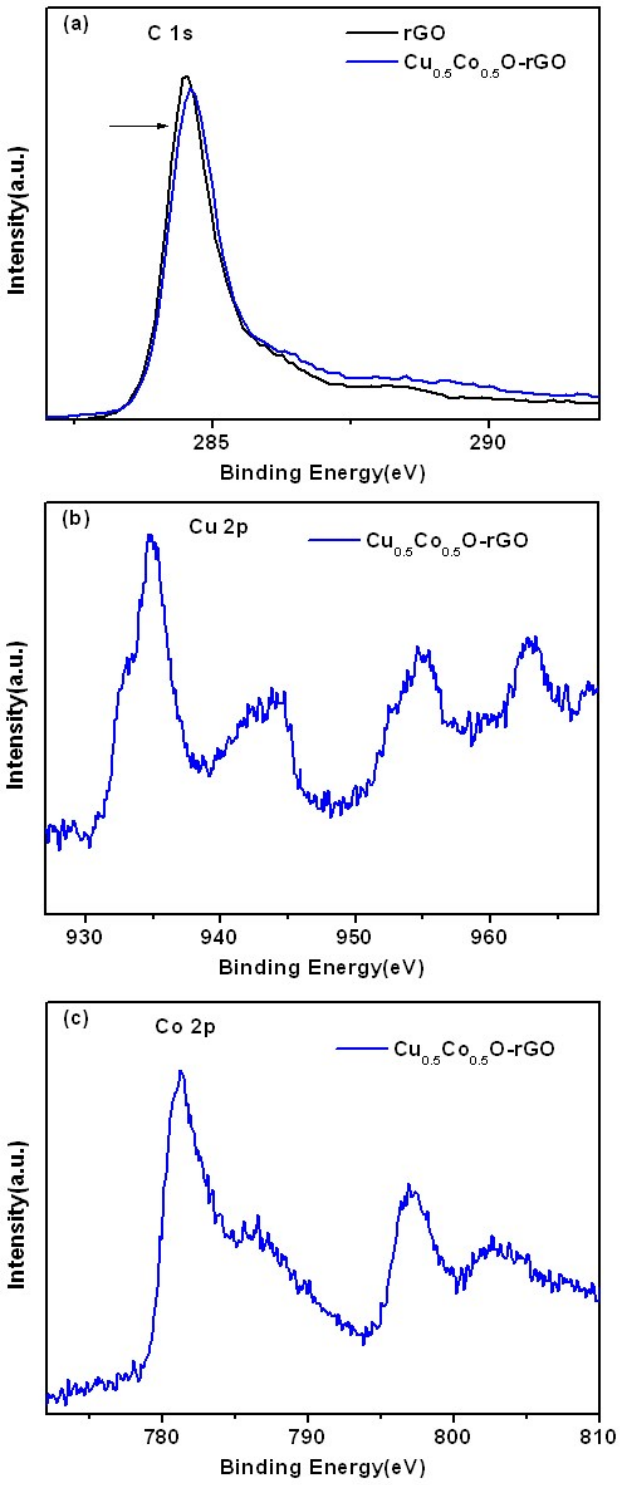

Figure S8: XPS spectra of $Cu_{0.5}Co_{0.5}O$-rGO at C 1s (a), Cu 2p (b) and Co 2p (c) edges, respectively.

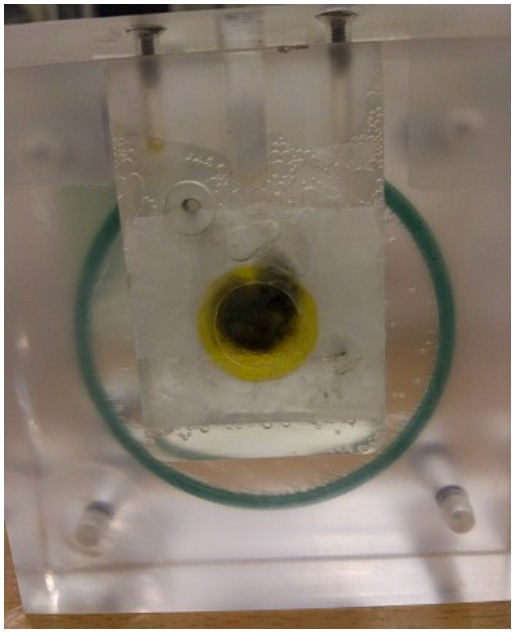

Figure S9: *In-situ* XAS cell with bubbles observed in the hydrolysis process.

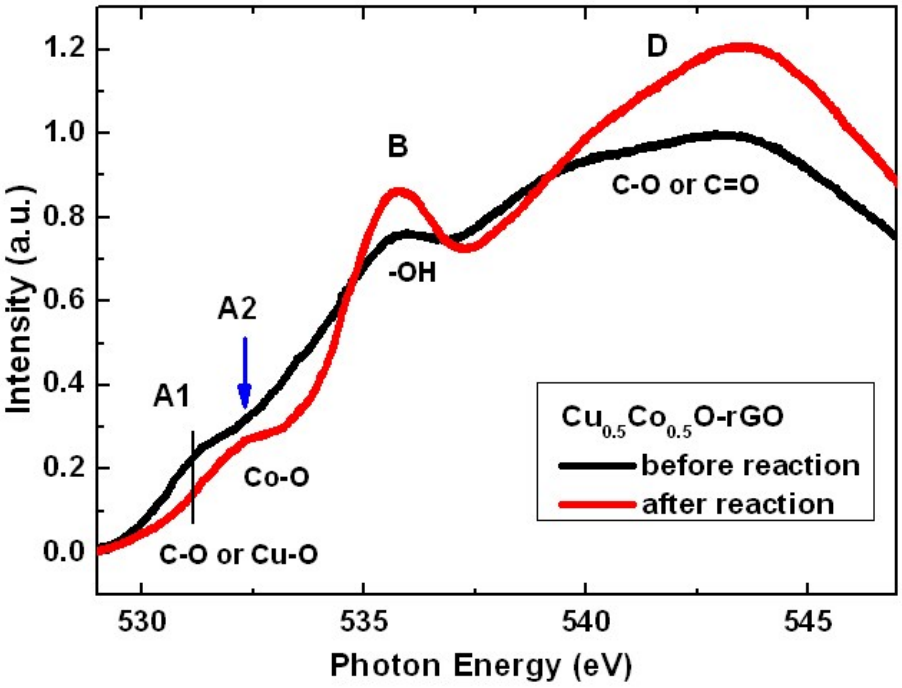

Figure S10: XAS spectra of $Cu_{0.5}Co_{0.5}O$-rGO before and after the reaction at O *K*-edge.

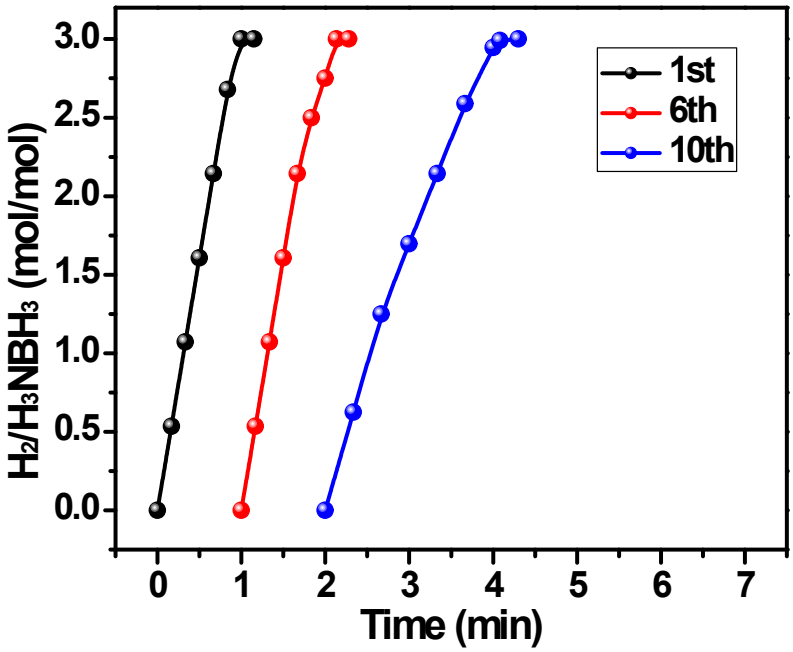

Figure S11: Stability test of $Cu_{0.5}Co_{0.5}O$-rGO after 9 runs. The TOF value slightly decreases from 81.7 to 72.1 in the 6th cycle (88.3% left), while sharply decreases to 43.5 in the 10th cycle (53.2% left).

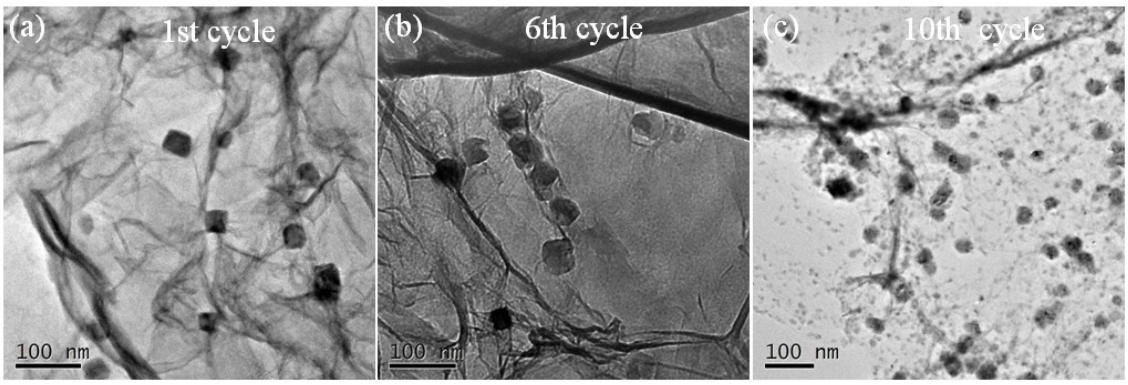

Figure S12: TEM images of the $Cu_{0.5}Co_{0.5}O$-rGO samples in the first cycle (a), the 6^{th} cycle (b), and the 10^{th} cycle (c).

Samples	Cu-loading/wt%	Co-loading/wt%	TOF (H_2) mol/(Cat-M)mol·min
$Cu_{0.9}Co_{0.1}O$-rGO	21.0	1.8	57.8
$Cu_{0.7}Co_{0.3}O$-rGO	16.1	5.7	59.6
$Cu_{0.5}Co_{0.5}O$-rGO	11.7	10.0	81.7
$Cu_{0.3}Co_{0.7}O$-rGO	7.2	10.0	64.4
$Cu_{0.1}Co_{0.9}O$-rGO	2.7	14.3	34.0
CuO-rGO	15.2	-	7.5
CoO-rGO	-	13.2	17.2
rGO	-	-	0

Table S1. Cu and Co contents and the TOF values of various $Cu_xCo_{1-x}O$-rGO samples.

Catalyst	TOF (H_2) mol/(Cat-M)mol·min	Solution	T (°C)	Ref.
$Cu_{0.5}Co_{0.5}O$-rGO cube	81.7	Water	25	This work
$Ni_{0.3}Co_{1.3}P$/GO	109.4	NaOH	25	1
Ni/ZIF-8	85.7	NaOH	25	2
CoP	72.2	NaOH	25	3
$Cu_{0.8}Co_{0.2}O$-GO	70.0	Water	25	4
CuO-NiO	60.0	Water	25	5
$Cu_{0.5}Ni_{0.5}$/CMK-1	54.8	Water	25	6
CuCo/MIL-101-1-U	51.7	Water	25	7
Co NPs (in-situ)	49.8	Water	25	8
Ni NPs@3D-(N)GFs	41.7	Water	25	9
Ni_2P	40.4	Water	25	10
Cu NPs@SCF	40.0	Water	25	11
PEI-GO/Co	39.9	Water	25	12
Ni@MCS-30	30.7	Water	25	13
$Cu_{0.49}Co_{0.51}$/C	28.7	Water	25	14
Ni/CNT	26.2	Water	25	15
Ni NPs/CNT	23.5	Water	25	16
$Cu_{0.1}$@$Co_{0.45}Ni_{0.45}$/graphene	15.46	Water	25	17
Ni NPs/C	8.8	Water	25	18
Pt/C	111.0	Water	25	19
Pt black	14.0	Water	25	19

Table S2. TOF values reported in the literatures. The red color indicates the TOF values obtained in a NaOH solution instead of pure water.

References listed in Table S1:

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Cycles	TOF (H_2) mol/(Cat-M)mol·min	Catalytic Efficiency
1st	81.7	100%
2nd	76.6	93.8%
3rd	76.6	93.8%
4th	73.2	89.6%
5th	72.1	88.3%
6th	72.1	88.3%

Table S3. TOF values and the catalytic efficiencies of $Cu_{0.5}Co_{0.5}O$-rGO in different cycles during the stability test.