Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

New insights into water oxidation reactions from photocatalysis, electrocatalysis to chemical catalysis: An example of iron-based oxides doped with foreign elements

Jingwei Huang[a†], Xiaoqiang Du[a†], YingYing Feng[a], Yukun Zhao[a] and Yong Ding[*ab]

[a] State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

[b] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000,China

Experimental Section

Synthesis of $NiFe_2O_4$[1]

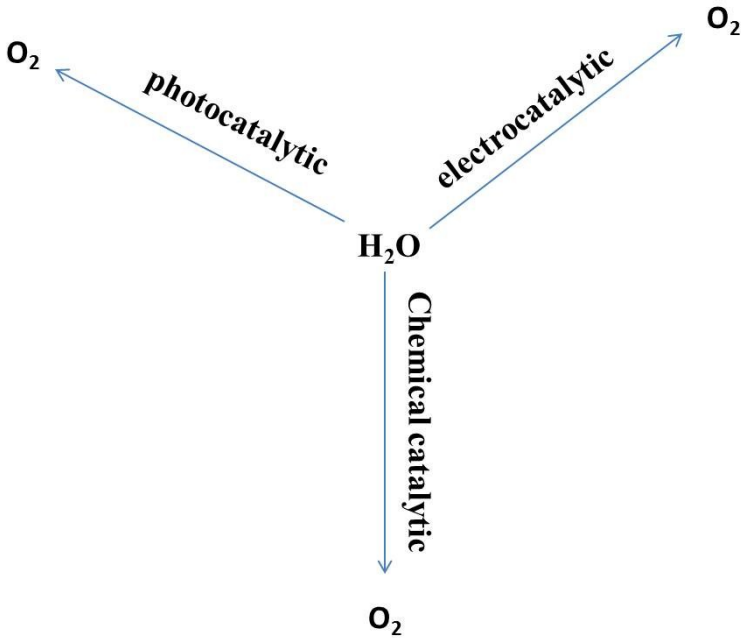
To an aqueous solution (24 mL) containing $NiCl_2.6H_2O$ (2.0 mmol, 0.46 g) and $Fe(NO_3)_3.9H_2O$ (4.0 mmol, 1.62 g) was added KOH solution (2.0 M, 24 mL) with magnetic stirring in room temperature (RT). The mixture was then transferred into a Teflon-lined stainless-steel autoclave of 150 mL capacity. The sealed tank was heated to and maintained at 160 ºC for 10 h in an oven and cooled to RT. The resulting brown precipitates were collected by filtration and washed with water and ethanol for more than 3 times, and finally dried in an oven at 60 ºC for 10 h.

Synthesis of $CoFe_2O_4$[2]

$CoCl_2.6H_2O$ (238 mg) and $Fe(NO_3)_3.9H_2O$ (808 mg) were dissolved separately in 15 mL of water. These two solutions were mixed together; 10 mL of 2 M KOH solution was added to the solution and stirred for 10 minutes at room temperature which was then transferred into a 50 mL autoclave and heated at 160 ºC for 6 hours. The autoclave was cooled down to room temperature. The solid material was centrifuged out and washed several times with water and ethanol, dried at 50 ºC for overnight.

Synthesis of $CuFe_2O_4$ and $MgFe_2O_4$[3]

The MFe_2O_4 (M=Mg,Cu) microspheres were synthesized by coprecipitation of M^{2+} and iron chloride (M^{2+}/Fe^{3+} = 0.5) in ethylene glycol. For example, $FeCl_3 \cdot 6H_2O$ (5mmol) and $MgSO_4 \cdot 7H_2O$ (2.5mmol) was dissolved in ethylene glycol (40ml), then 3.6 g NaAc and 1.0 g polyethylene glycol were added into the above solution. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave with 50ml capacity. The autoclave was heated 200 ºC for 12 h, then cooled to roomtemperature. The puce products were centrifuged and washed several times with ethanol, finally dried at 60 ºC for 6 h before characterization.



Scheme S1. Three driving forces commonly used in evaluating water-oxidation activities of homogeneous and heterogeneous WOCs.

Table S1. Water Oxidation Catalyzed without catalyst or $Ru(bpy)_3Cl_2$ or $Na_2S_2O_8$ or light.

Entry	Catalyst (gL^{-1})	$Na_2S_2O_8$ (mM)	$[Ru(bpy)_3]Cl_2$ (mM)	light	O_2 (μmol)
1	0	5	1	yes	0.5
2	0.5	0	1	yes	0
3	0.5	5	0	yes	0
4	0.5	5	1	no	0

Conditions: LED lamp ($\lambda \geq 420$ nm), catalyst is $CoFe_2O_4$, 80 mM sodium borate buffer (initial pH 8.5), and total reaction volume is 15 mL and overall volume is ~28 mL, vigorous agitation using a magnetic stirrer.

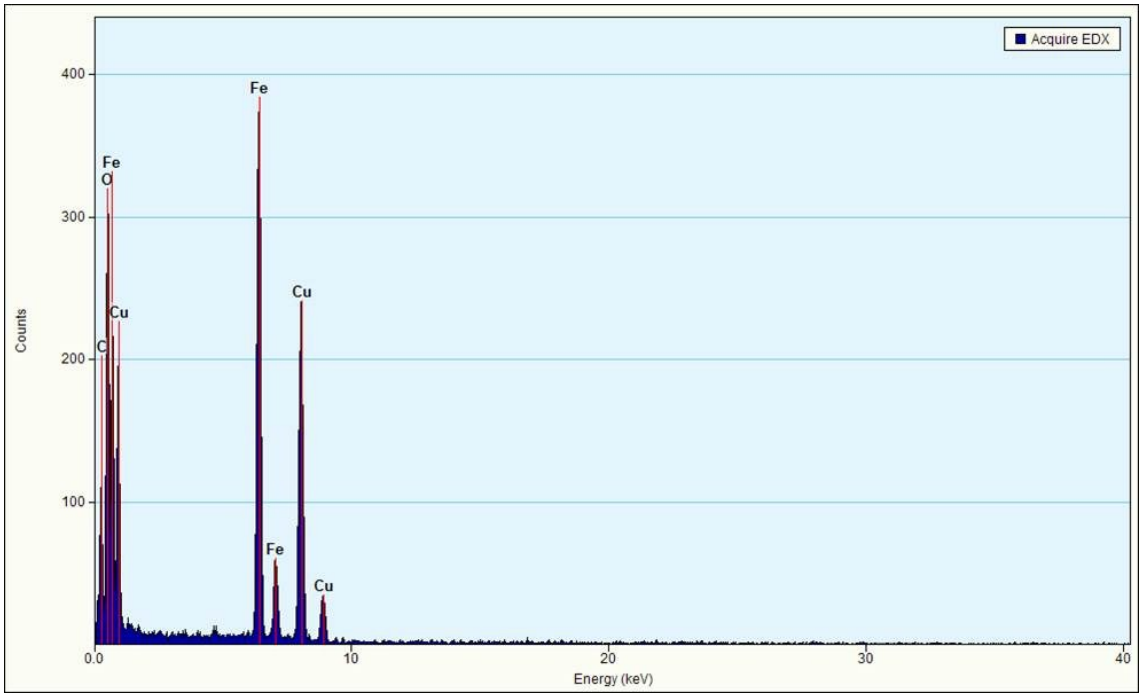


Figure S1. EDS of $CuFe_2O_4$. C and Cu signal originates from the sample holder and $CuFe_2O_4$.

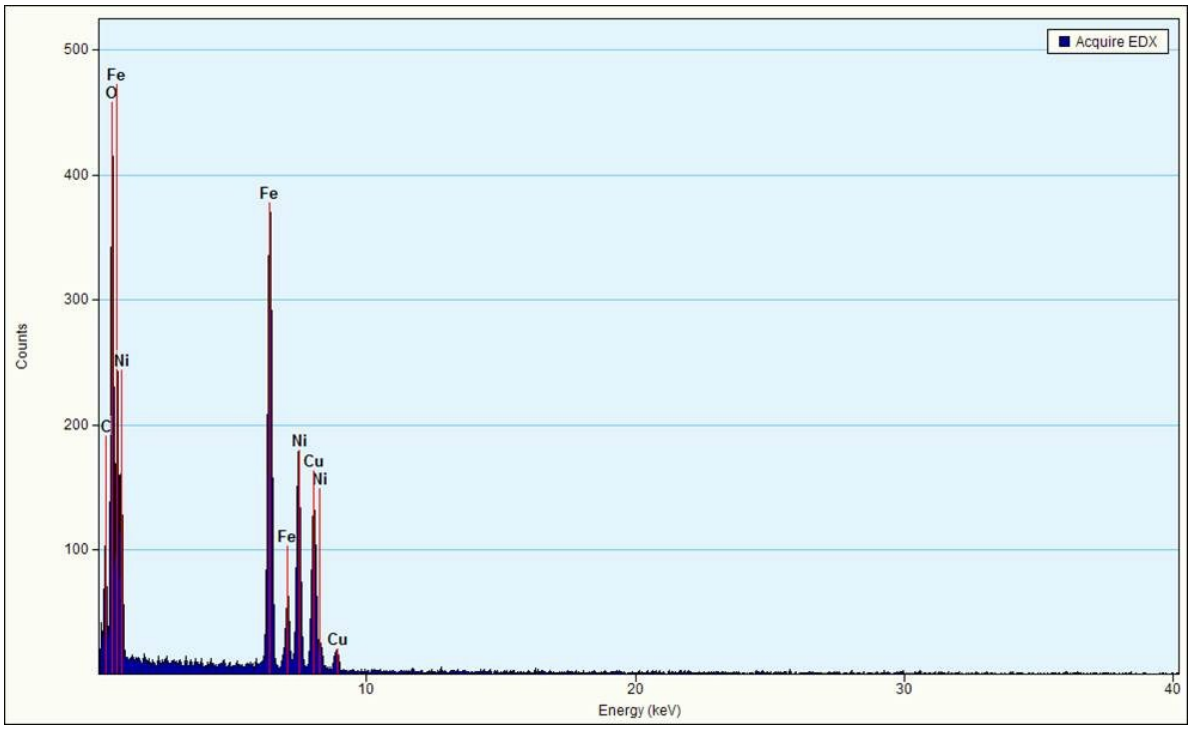


Figure S2. EDS of $NiFe_2O_4$. C and Cu signal originates from the sample holder.

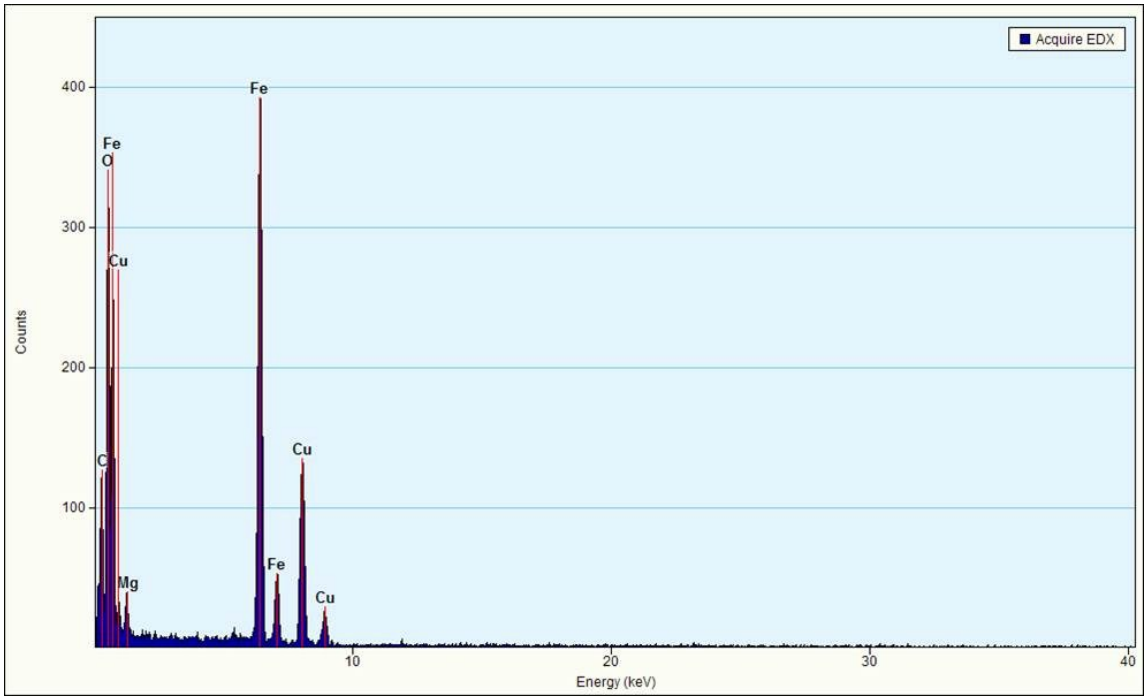


Figure S3. EDS of $MgFe_2O_4$. C and Cu signal originates from the sample holder.

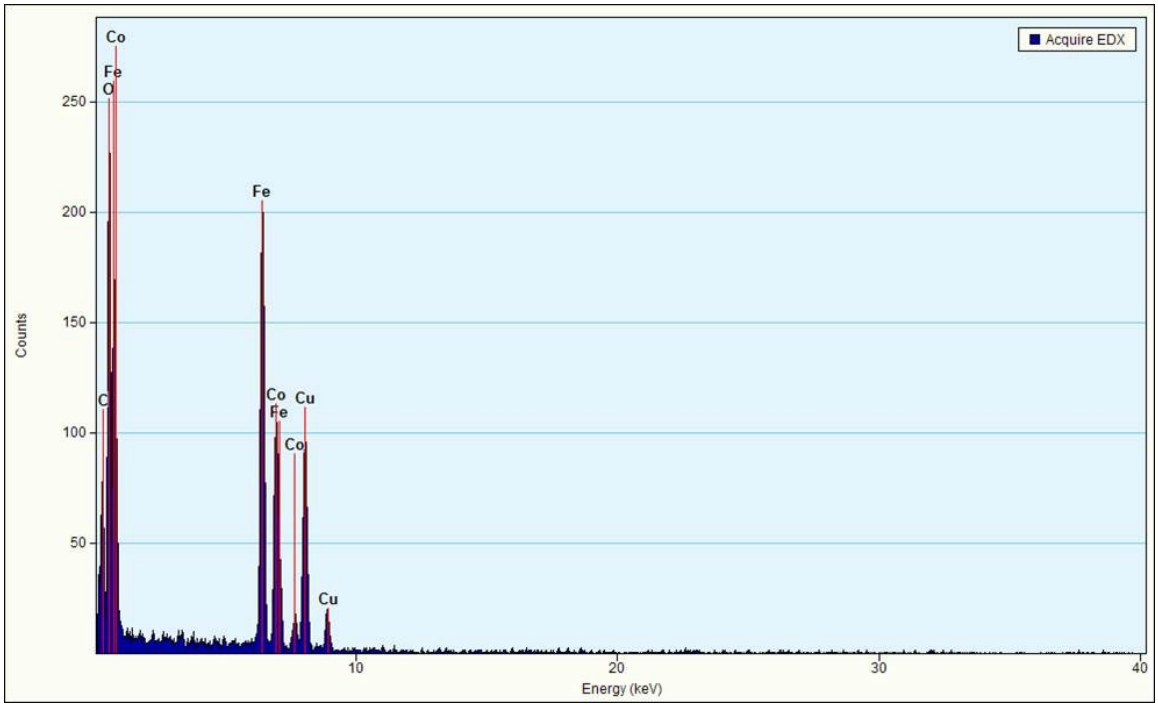


Figure S4. EDS of $CoFe_2O_4$. C and Cu signal originates from the sample holder.

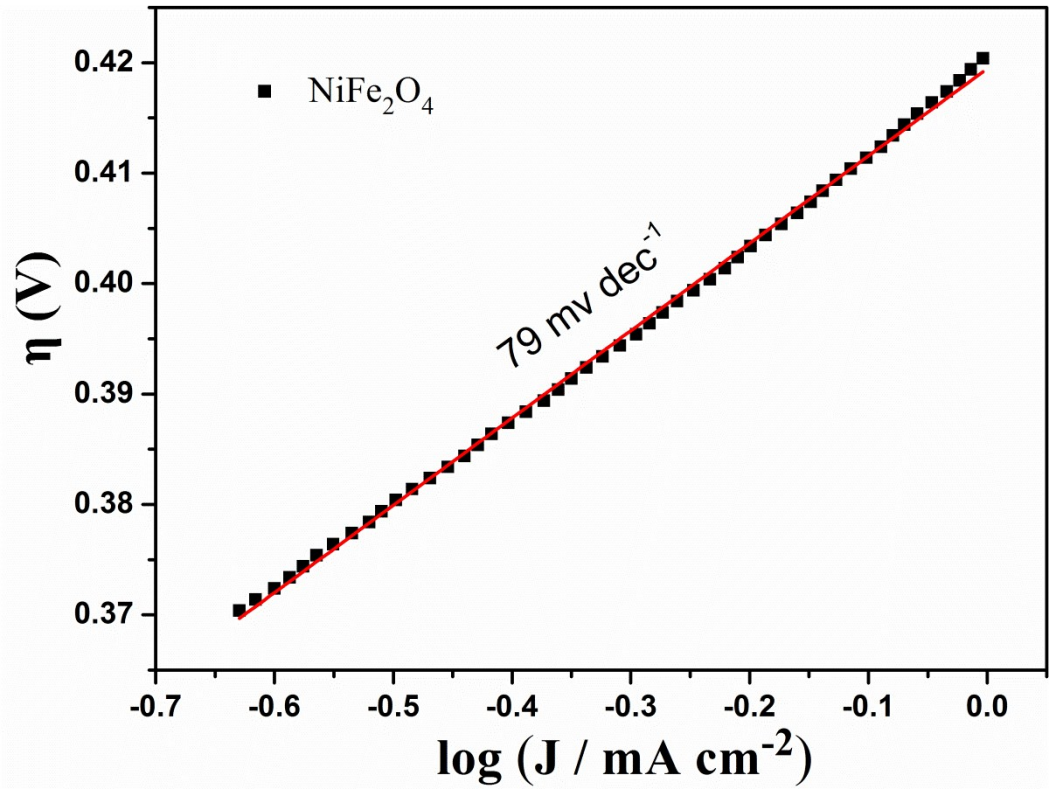


Figure S5. Tafel plot of catalyst $NiFe_2O_4$.

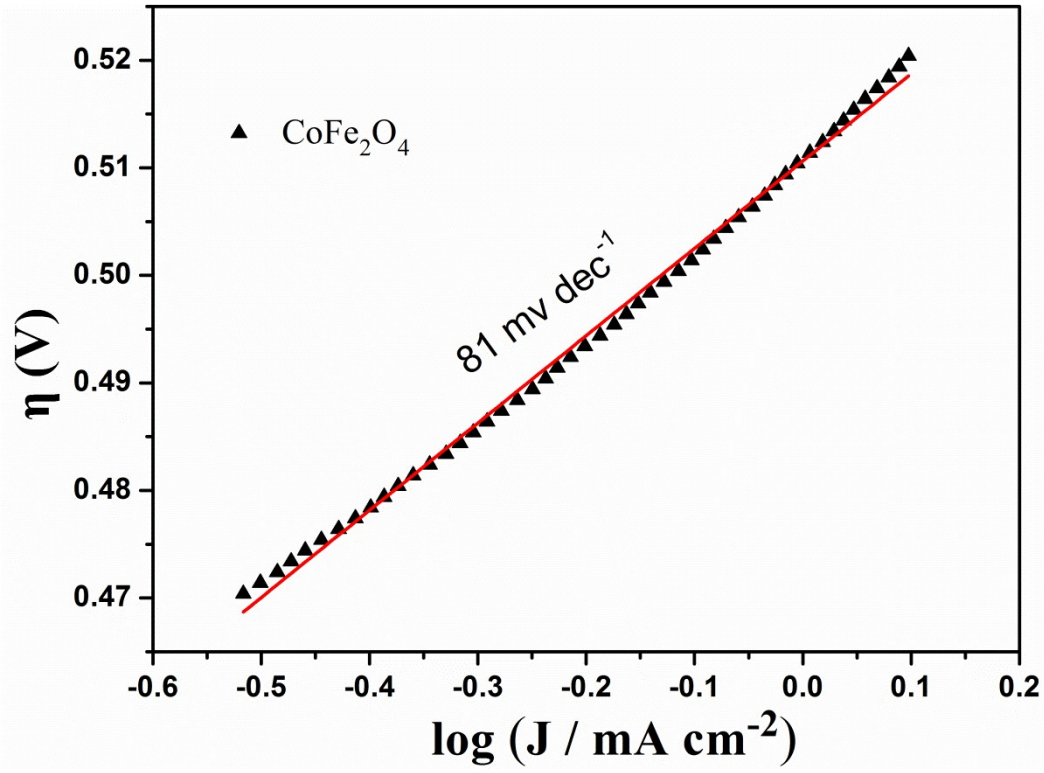


Figure S6. Tafel plot of catalyst $CoFe_2O_4$.

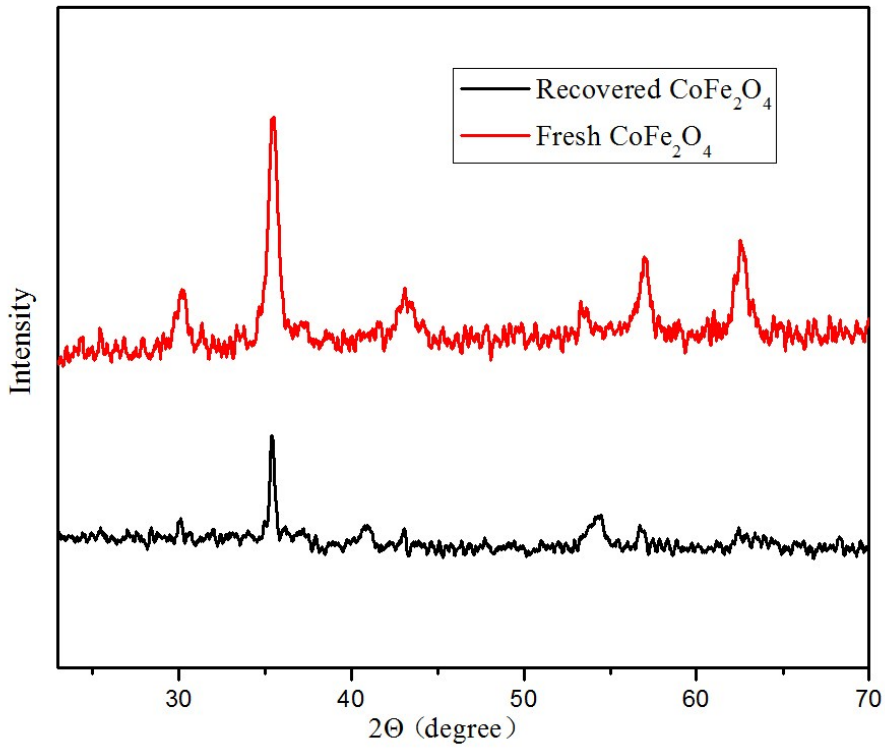


Figure S7. XRD of fresh $CoFe_2O_4$ and recovered $CoFe_2O_4$ for the photocatalytic water oxidation.

Comment: Although intensity of fresh $CoFe_2O_4$ and recovered $CoFe_2O_4$ has changed, no impurity peak was observed.

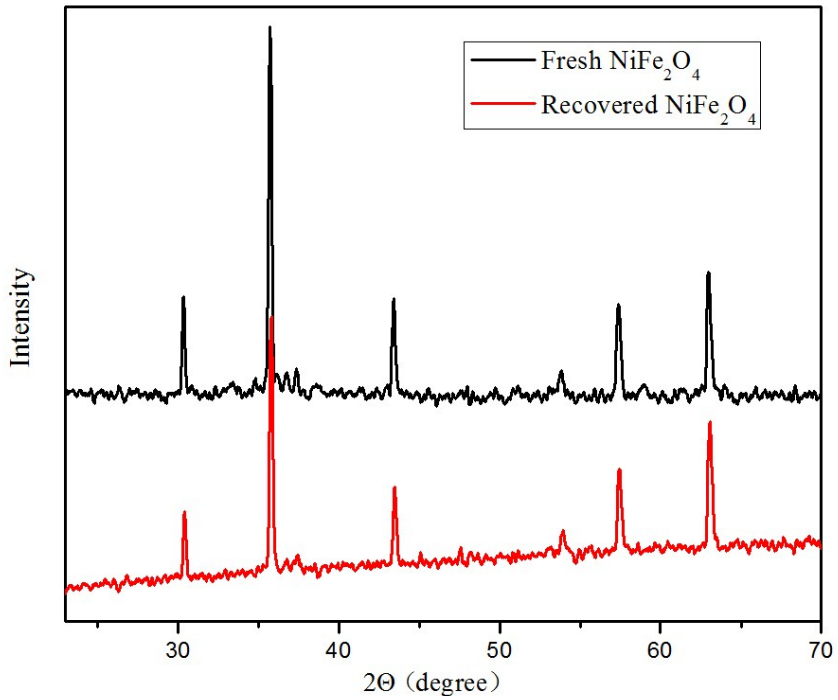


Figure S8. XRD of fresh $NiFe_2O_4$ and recovered $NiFe_2O_4$ for the chemical water oxidation.

Comment: Intensity of fresh $CoFe_2O_4$ and recovered $CoFe_2O_4$ has no changed, no impurity peak was observed.

1. D. Hong, Y. Yamada, T. Nagatomi, Y. Takai and S. Fukuzumi, *J Am Chem Soc*, 2012, **134**, 19572-19575.
2. A. Indra, P. W. Menezes, N. R. Sahraie, A. Bergmann, C. Das, M. Tallarida, D. Schmeißer, P. Strasser and M. Driess, *J Am Chem Soc*, 2014, **136**, 17530-17536.
3. H. Deng, H. Chen and H. Li, *Mater Chem Phys*, 2007, **101**, 509-513.