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

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Experimental Section

Synthesis of NiFe$_2$O$_4$

To an aqueous solution (24 mL) containing NiCl$_2$.6H$_2$O (2.0 mmol, 0.46 g) and Fe(NO$_3$)$_3$.9H$_2$O (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 °C 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 °C for 10 h.

Synthesis of CoFe$_2$O$_4$

CoCl$_2$. 6H$_2$O (238 mg) and Fe(NO$_3$)$_3$. 9H$_2$O (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 °C 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 °C for overnight.

Synthesis of CuFe$_2$O$_4$ and MgFe$_2$O$_4$

The MFe$_2$O$_4$ (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$_3$.6H$_2$O (5mmol) and MgSO$_4$.7H$_2$O (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 °C for 12 h, then cooled to roomtemperature. The puce products were centrifuged and washed several times with ethanol, finally dried at 60 °C 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)$_3$Cl$_2$ or Na$_2$S$_2$O$_8$ or light.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (gL$^{-1}$)</th>
<th>Na$_2$S$_2$O$_8$ (mM)</th>
<th>[Ru(bpy)$_3$]Cl$_2$ (mM)</th>
<th>light</th>
<th>O$_2$ (μmol)</th>
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<td>yes</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>5</td>
<td>1</td>
<td>no</td>
<td>0</td>
</tr>
</tbody>
</table>

Conditions: LED lamp (λ $\geq$ 420 nm), catalyst is CoFe$_2$O$_4$, 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$_2$O$_4$. C and Cu signal originates from the sample holder and CuFe$_2$O$_4$.

**Figure S2.** EDS of NiFe$_2$O$_4$. C and Cu signal originates from the sample holder.
Figure S3. EDS of MgFe$_2$O$_4$. C and Cu signal originates from the sample holder.

Figure S4. EDS of CoFe$_2$O$_4$. C and Cu signal originates from the sample holder.
Figure S5. Tafel plot of catalyst NiFe$_2$O$_4$.

Figure S6. Tafel plot of catalyst CoFe$_2$O$_4$. 
Figure S7. XRD of fresh CoFe$_2$O$_4$ and recovered CoFe$_2$O$_4$ for the photocatalytic water oxidation.

Comment: Although intensity of fresh CoFe$_2$O$_4$ and recovered CoFe$_2$O$_4$ has changed, no impurity peak was observed.

Figure S8. XRD of fresh NiFe$_2$O$_4$ and recovered NiFe$_2$O$_4$ for the chemical water oxidation.
Comment: Intensity of fresh CoFe$_2$O$_4$ and recovered CoFe$_2$O$_4$ has no changed, no impurity peak was observed.