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## Hexagonal nanoplates of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite acting as efficient photocatalytic and electrocatalytic water oxidation catalyst

Yukun Zhao<sup>a</sup>, Yan Zhang<sup>a</sup>, Yong Ding<sup>a,b</sup>\*and Mindong Chen<sup>b</sup>

A unique hexagonal sheet-shaped NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite with disordered shaped nanoparticles was fabricated for the first time through a simple co-precipitation and hydrothermal method. The NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite was characterized by multiple experiments (TEM, HRTEM, PXRD, EDX, ICP-AES, BET, XPS) to confirm the structure and the component. This structure of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite may strengthen photocatalytic and electrocatalytic performance of water oxidation. Compared with NiO, CoO and Fe<sub>2</sub>O<sub>3</sub>, NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite exhibits lower overpotential and a much smaller Tafel slope of 49 mV dec<sup>-1</sup> in water oxidation. At the same time, the composite possesses beneficial ferromagnetic properties and superior stability so that it was used repeatedly without the loss in activity.

#### Introduction

Artificial photosynthesis that directly converts solar energy into chemical energy is one of the most promising systems for satisfying humans' thirsty of renewable clean energy.<sup>1-4</sup> One convenient way of energy conversion is to split water which can produce hydrogen and oxygen. In the process of water splitting, the oxidation of water to  $O_2 (2H_2O \rightarrow 4H^+ + 4e^- + O_2)$ is a more complicated reaction as four electrons are needed for the formation of an oxygen molecule.<sup>5, 6</sup> Compared to the reduction of water to hydrogen, the water oxidation process usually holds sluggish kinetics and requires large overpotentials.<sup>7</sup> In order to improve the reaction rate and/or lower the overpotentials, tremendous water oxidation catalysts (WOCs) should be exploited.<sup>8-11</sup> Therefore, extensive efforts have so far been devoted to developing efficient WOCs which can convert solar energy into chemical energy.

Since oxido bridged calcium and manganese cubical subcluster was reported as the active site of water oxidation in the photosystem II (PS II)<sup>12, 13</sup>, multifarious homogeneous and heterogeneous catalysts based on precious metals such as Ir and Ru were reported by many groups<sup>14-18</sup>. Although these catalysts behaved vigorous catalytic activity in PS II, their

finite supplies make them not suitable for large-scale application.<sup>19</sup> Especially in recent years, copious amounts of non-noble metal oxides have been reported as efficient WOCs to replace expensive compounds based on iridium and ruthenium. Among which, WOCs containing nickel<sup>10, 20-22</sup> cobalt<sup>23-27</sup> and iron<sup>28-31</sup> attract significant attentions on account of their earth-abundance and robust activity. However, NiO, CoO and Fe<sub>2</sub>O<sub>3</sub> without any further modification exhibit poor water oxidation activity. To improve their catalytic activity and further simplify synthesis of those WOCs, a mixed-metal composite which is composed of nickel, cobalt and iron should be manufactured to reinforce their photocatalytic and electrocatalytic activity.

Herein, we firstly report the synthesis of mixed-metal oxides NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite and the application as a highly active and robust catalyst for visible light-driven water oxidation with  $Ru(bpy)_3^{2+}$  as a photosensitizer and  $S_2O_8^{2-}$  as a sacrificial oxidant, respectively. The NiO/CoO/Fe2O3 composite exhibits a unique hexagonal sheet-shaped morphology with some disordered shaped nanoparticles. The special structure generates surface charge effect which can strengthen the photocatalytic activity through accelerating electron transfer.<sup>15,</sup>  $^{\rm 16,\ 32-34}$  Compared with that of simple oxides NiO, CoO and

Fe<sub>2</sub>O<sub>3</sub>, the photocatalytic activity of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite is the highest. At the same time, NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite shows a strong electrochemical activity with an extraordinary Tafel slope of 49 mV dec<sup>-1</sup> in water oxidation. Additionally, the ferromagnetic properties of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite are so beneficial that the catalyst can be recovered from the reaction solution without any obvious loss. In the future, there will be a widespread prospect in industrial application.

#### **Results and discussion**



<sup>&</sup>lt;sup>a.</sup> Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China.

<sup>&</sup>lt;sup>b.</sup> Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), School of Environmental Sciences and Engineering, Nanjing University of Information Science and Technology

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 Scheme 1. Catalytic cycle of visible light-driven water oxidation with Na2S2O8 and How

 Ru(bpy)<sub>3</sub><sup>2+</sup> using NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite as catalyst.

The photocatalytic activity of the mixed-metal oxides was performed under visible light-driven water oxidation with Ru(bpy)<sub>3</sub>Cl<sub>2</sub> as a photosensitizer and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as two-electron oxidant, respectively. The overall catalytic cycle of the visible light-driven water oxidation is depicted in Scheme 1. At first, two equiv. of photosensitizers, 2  $Ru(bpy)_{3}^{2+}$ , which response to the visible light, absorb two photons and form  $2 \operatorname{Ru}^{*}(bpy)_{3}^{2+}$  ( where the \* denotes the excited states). The excited states of photosensitizers can be oxidized by the oxidant of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, forming  $Ru(bpy)_{3}^{3+}$ ,  $SO_{4}^{2-}$  and  $SO_{4}^{--}$ . The produced  $SO_{4}^{--}$  which is known to be a very strong oxidant  $[E_0(SO_4^{-}/SO_4^{2-}) = 2.6 V]^{35}$ can oxidize  $Ru(bpy)_3^{2+}$  to generate two equiv. of  $Ru(bpy)_3^{3+}$ . Eventually,  $Ru(bpy)_3^{3+}$  can oxidize water to evolve  $O_2$  in the presence of the WOCs. The  $Ru(bpy)_3^{3+}$  cannot steadily exist so it will rapidly and irreversibly decompose to inactive products in the absence of catalysts(Fig. 1). The competitive degradation of  $Ru(bpy)_3^{2+}$  appears to be dominant especially at the absence of catalyst where the bimolecular scavenging of the reactive  $Ru(bpy)_{3}^{3+}$  state is slowed down.<sup>36</sup> After the



Fig. 1 UV-Vis absorption of a freshly prepared reaction solution before irradiation (black trace), after irradiation without catalyst (red trace) and after irradiation with catalyst (blue trace).

irradiation without catalyst of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite, the degradation of photosensitizer reaches to about 30%. However, the photosensitizer only has less than 10% degradation in the presence of catalyst, indicating the catalyst (NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite) can stabilize the photosensitizer to make it recycle efficiently (Scheme 1).

The mixed-metal oxides composite (NiO/CoO/Fe<sub>2</sub>O<sub>3</sub>) was synthesized for the first time according to a simple coprecipitation and hydrothermal method (Scheme 2). Fig. 2 elucidates the transmission electron microscope (TEM) image of the sample, from which unique hexagonal sheet-shaped morphology with some disordered shaped nanoparticles can be observed. Moreover, the sizes of hexagonal nanoplates are approximately 100-200 nm, on which surface there are many nanoparticles about 10-30 nm. The different sizes and morphologies nanoparticles represent different metal oxides. The metal oxides adhere to each other and generate surface charge effect which makes great contributions to electron transfer.<sup>32, 37</sup> Fig. 3(a) manifests a high-resolution TEM (HRTEM) image of a piece of a cracked NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> nanoplate, which further reveals the lattice planes with fringe spacing of 0.21, 0.28 and 0.30 nm corresponding to the (200) plane of NiO, the (100) plane of CoO and the (220) plane of  $Fe_2O_3$ , respectively.



Fig. 2 Transmission electron microscope (TEM) image of NiO/CoO/Fe $_2O_3$  composite.



Fig. 3 High resolution TEM images of NiO/CoO/Fe $_2O_3$  composite

The more distinct fringe spacing of NiO lattice plane and  $Fe_2O_3$  lattice plane can be observed in Fig. 3(b) and Fig. 3(d). Although the fringe spacing of CoO lattice plane is some vague, the fringe spacing can be still obtained from the HRTEM image (Fig. 3c). The vague fringe spacing of CoO (100) plane may be assigned to the altitude of TEM detection probe.

The catalyst was characterized by the powder X-ray diffraction (PXRD) measurement as shown in Fig. 4. The dominated peaks of the catalyst are in accordance with the characteristic patterns of NiO, CoO and Fe<sub>2</sub>O<sub>3</sub>. The (200) plane of NiO, the (100) plane of CoO and the (220) plane of Fe<sub>2</sub>O<sub>3</sub> can agree well with the planes of HRTEM observed. Fig. S1 (ESI<sup>+</sup>) demonstrates the energy dispersive X-Ray (EDX) spectrum which indicates the catalyst is composed of the elements Ni, Co, Fe and O. Element mapping characterizations



Fig. 4 Powder XRD pattern of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite.

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ARTICLE

Catalysts	Apparent TOF <sup>b</sup> (μmol s <sup>-1</sup> m <sup>-2</sup> )	$O_2$ yield (%) <sup>c</sup>	Ref.
NiO/CoO/Fe <sub>2</sub> O <sub>3</sub>	0.20	64	This work
NiO	0.06	25	This work
CoO	-	45	This work
Fe <sub>2</sub> O <sub>3</sub>	0.19	34	This work
NiO+CoO+Fe <sub>2</sub> O <sub>3</sub>	-	47	This work
γ-Fe <sub>2</sub> O <sub>3</sub> @NiO	0.19	52	38
γ-Fe₂O₃@NiO	0.29	34	38

<sup>a</sup> Conditions: LED lamp (≥420 nm), 15.8 mW; 1.0 mM Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, 5.0 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 0.33 g L<sup>-1</sup> NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite, 80 mM sodium borate buffer (initial pH 8.5); total reaction volume 15 mL and head space volume 13.5 mL; vigorous agitation using a magnetic stirrer. <sup>b</sup> Turnover frequency normalized by a catalyst surface area for O<sub>2</sub> evolution. <sup>c</sup> Yield is defined as twice the number of moles of O<sub>2</sub> per mole of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.



Fig. 5 Time courses of O<sub>2</sub> evolution under photoirradiation (LED lamp,  $\lambda \ge 420$  nm, 15.8 W) of a borate buffer solution (pH 8.5, 15.0 mL) containing Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (5.0 mM), Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (1.0 mM).

(Fig. S2, ESI<sup>+</sup>) were carried out to further investigate the main constituent of the samples. The data of EDX spectrum manifests that the ratio of these atoms (Ni: Co: Fe) is approximately 1.1: 0.9: 1. The radio of these atoms is also authenticated through X-ray photoelectron spectra (XPS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses. These results match well with the atomic percentages of Ni, Co and Fe in the composite. The Brunauer-Emmett-Teller (BET) surface area determined by N<sub>2</sub> absorption measurements at 77 K is 76 m<sup>2</sup> g<sup>-1</sup> for NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite.

The photocatalytic water oxidation activity of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite was investigated in the borate buffer solution (initial pH 8.5) with Ru(bpy)<sub>3</sub>Cl<sub>2</sub> as photosensitizer and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as sacrificial electron acceptor. The time courses of evolved O<sub>2</sub> with different catalysts are shown in Fig. 5. Table 1 tabulates that the apparent turnover frequency (TOF) and O<sub>2</sub> yield were obtained for all of the metal oxides studied. Compared with NiO (26%), Fe<sub>2</sub>O<sub>3</sub> (35%) and

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Fig. 6 Time courses of O<sub>2</sub> evolution under photoirradiation (LED lamp,  $\lambda \ge 420$  nm, 15.8W) of a borate buffer solution (pH 8.5, 15.0 mL) containing Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (5.0 mM), Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (1.0 mM) and NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite (0.33 g L<sup>-1</sup>) at room temperature in five repetitive experiments.

CoO (45%), oxygen yield of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite can reach to 64% and it has a considerable apparent TOF (0.20  $\mu$ mol s<sup>-1</sup> m<sup>-2</sup>). However, the physical mixture of NiO, CoO and Fe<sub>2</sub>O<sub>3</sub> exhibits lower oxygen yield (47%) than the composite, which may be attributed to the surface charge effect of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite.<sup>38</sup> The high catalytic activity of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite was maintained perfectly even after the fifth run (Fig. 6). As illustrated in Fig. S3 (ESI+), the catalyst demonstrated extremely strong ferromagnetic properties, which can explain the same high catalytic activity in repetitive experiments. Isotope-labelling water oxidation experiments using <sup>18</sup>O enriched water instead of H<sub>2</sub><sup>16</sup>O were carried out with NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite to confirm that the water is the source of the evolved oxygen. The ratio of  ${}^{16}O{}^{16}O$  :  $^{16}\text{O}^{18}\text{O}$  :  $^{18}\text{O}^{18}\text{O}$  is determined to be 83 : 16: 1, which is in great agreement with the simulated ratio of 81 : 18 : 1 for oxygen coming exclusively from water (Fig. S4, ESI<sup>+</sup>). The above data clearly reveal that the evolved O<sub>2</sub> originates exclusively from the water. Thus, NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite is a robust and efficient water oxidation catalyst and can be recycled many times

The catalysis behavior of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite for visible light-driven water oxidation was also scrutinized under electrocatalysis conditions. The cyclic voltammograms (CVs) using a working electrode modified with NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite in a pH 8.5 borate buffer solution are demonstrated as Fig. 7. The anodic currents with NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite started growing at a lower potential (0.70 V) than that of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (1.05 V) and it could reach approximately 120  $\mu$ A at 1.50 V, which is a strong catalytic current. The result reveals that the composite is active for the water oxidation. The onset of the catalytic wave due to water oxidation is observed at ca. 0.70 V, and the redox potential of Ru(bpy)<sub>3</sub><sup>2+/3+</sup> in our system is



Fig. 7 Cyclic voltammograms (CVs) of 80 mM sodium borate buffer solution at pH 8.5 with 1.0 mM Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (red line) and NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite (blue line). The black line displays the CV of 80 mM sodium borate buffer solution (pH 8.5).

Conditions: CV was recorded on a CHI660D electrochemical analyzer with a glassy carbon pasting 0.01 mg catalyst, Ag/AgCl, and Pt wire electrodes as the working, reference, and auxiliary electrode, respectively, at room temperature with a scanning rate of 100 mV s<sup>-1</sup>.



Fig. 8 The powder XRD patterns of NiO/CoO/Fe $_2O_3$  composite before the reaction (black); after the reaction (red).

1.12 V (Fig. S5, ESI<sup>†</sup>). Therefore,  $Ru(bpy)_{3}^{3+}$  is thermodynamically capable of facilitating water oxidation.

In contrast to the homogeneous catalysts, the heterogeneous ones possess an enviable preponderance that they are easy recycling for many times. Due to the strong ferromagnetic properties of the catalyst, the high catalytic activity of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite maintained well even after the fifth run (Fig. 6). Compared to the powder XRD patterns before and after the reaction (Fig. 8), all the peaks of two samples were consistent completely, which indicates that it is a stable catalyst in the process of water oxidation. As depicted in Fig. 9 and Fig. S6 (ESI<sup>†</sup>), the changes of the surface

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Fig. 9 X-ray photoelectron spectra (XPS) of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite before (black) and after (red) the reaction in the energy regions of (a) Ni 2p, (b) Co 2p, (c) Fe 2p and (d) O 1s.

conditions and the valence changes of each component before and after photocatalytic reaction were observed by X-ray photoelectron spectra. The XPS was performed in the Ni 2p, Co2p, Fe 2p, O 1s and survey binding energy regions, which were corrected using the C 1s peak from residual carbon (284.8 eV). Fig. 9(a) displays the XPS spectrum for the Ni  $2p_{3/2}$ and Ni  $2p_{1/2}$  peaks at 854.3 and 872.1 eV with strong satellite peaks before the reaction, at 854.5 and 872.3 eV with strong satellite peaks after the reaction. The binding energies of these peaks indicate that the Ni species in the samples are Ni<sup>2+</sup> by comparison with the Ni 2p peak positions of NiO.<sup>39</sup> The Co  $2p_{3/2}$  and Co  $2p_{1/2}$  peaks were located at 779.3 and 795.1 eV with satellite peaks before the photocatalytic reaction (Fig. 9b), and at 779.6 and 795.6 eV with satellite peaks after the reaction. These satellite peaks are characteristic of Co<sup>2+</sup> species.<sup>40</sup> As illustrated in Fig. 9(c), the XPS spectrum of Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  exhibited characteristic peaks at 709.9 and 723.1 eV for NiO/CoO/Fe2O3 composite before the reaction and that at 710.1 and 723.8 eV after the reaction. These peaks are assigned to Fe<sup>3+</sup> species by comparison with the Fe 2p peaks of Fe<sub>2</sub>O<sub>3</sub>.<sup>41</sup> Fig. 9(d) elucidates the XPS spectrum of O 1s peak for NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite which appeared at 530.0 eV and 530.2 eV before and after the reaction. At the same time, they both have a weak shoulder peak on the main peak, which may be ascribed to the common influence between these three different metal oxides. These data insinuates that the surface conditions of two samples were the same even after the photocatalytic reaction.

Although the peaks of Ni 2p, Co 2p, Fe 2p and O 1s from the samples before and after the reaction shifted slightly, the identical separation between different peaks in both samples and the consistency of peak shapes obviously verify that there were no changes in the valence state of Ni<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>3+</sup> and O<sup>2-</sup>. The surface conditions of the composite before and after the photocatalytic water oxidation were the same which can also



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ARTICLE

Fig. 10 Linear sweep voltammograms (LSVs) of the catalysts in 1 M potassium hydroxide with a scan rate of 1 mV s $^{-1}$ .

results from the TEM images before and after the reaction (Fig. S7, ESI<sup>+</sup>). Therefore, NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite is a highly stable catalyst in the visible light-driven water oxidation process.

The electrochemical activity of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite and reference samples in the water oxidation was evaluated in 1 M potassium hydroxide solution using a standard threeelectrode system. Catalysts (0.01 mg) were uniformly dropcasted on a glassy carbon electrode. The electrocatalytic activity of water oxidation was investigated by linear sweep voltammograms (LSVs) with a scan rate of 1 mV s<sup>-1</sup>. As shown in Fig. 10, the electrocatalytic water oxidation started at an electrode potential of ~+1.52 V vs RHE for NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite which is the minimum one among the samples measured. At the same overpotential, the highest anodic current density was obtained for NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite in comparison to other samples. To reach a current density of 10 mA cm<sup>-2</sup> (Fig. S9, ESI<sup>+</sup>), the as-prepared NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite requires 0.41 V whereas 0.43 V and 0.45 V are required for NiO and CoO, respectively. Moreover, Fe<sub>2</sub>O<sub>3</sub> requires much more than 0.50 V to reach the same current density. Thus, the good activity of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite obviously outperformed those of the rest materials over the entire potential range (1.5 V to 1.7 V vs RHE) of water oxidation.

The Tafel slopes curves were calculated by plotting overpotential (η) against log(J), which are significant kinetic parameters of water oxidation. Fig. 11 shows that the Tafel slope of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite is 49 mV dec<sup>-1</sup>, which is lower than that of NiO (60 mV dec<sup>-1</sup>) and CoO (66 mV dec<sup>-1</sup>). The Tafel slope of the Fe<sub>2</sub>O<sub>3</sub> sample is 183 mV dec<sup>-1</sup> (Fig. S10, ESI<sup>+</sup>), which is much higher than the value of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite. The excellent Tafel slopes of 49 mV dec<sup>-1</sup> for NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite is comparable to 49 mV dec<sup>-1</sup> for IrO<sub>2</sub> and superior to other mixed metal oxide composites such as CoFeO<sub>n</sub> (89 mV dec<sup>-1</sup>). Co<sub>3</sub>O<sub>4</sub>-carbon (70 mV dec<sup>-1</sup>) and MnCo<sub>2</sub>O<sub>4+δ</sub> (84 mV dec<sup>-1</sup>). <sup>42, 43</sup> The Tafel slopes are frequently influenced by electron and mass transport while they might be used to examine the mechanism of WOCs.<sup>44</sup> Recently, Hu et al.

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reported that the slow electron transport gave larger Tafel slopes for hydrogen evolution.<sup>45</sup> Therefore, the lower Tafel slope of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite probably results from faster electron transportation on the sample nanoplates. The stability of the catalyst was studied at  $\eta$  = 300 mV in 1 M potassium hydroxide solution (Fig. S11, ESI+). The anodic current density sostenuto increased from 0.5 to 0.8 mA cm<sup>-2</sup> in 2 hours. Some speculations were reported previously that the determined step for water oxidation of  $\text{CoO}_x$  was the protoncoupled one-electron oxidation of  $Co^{III}$ -OH to  $Co^{IV}$ -O.<sup>46-51</sup> The increase of current density may be attributed to the accumulation of Co(IV) species or other element high state species to enhance the water oxidation activity.<sup>42</sup> These high state species come from the continuous anodic conditioning. When the species accumulated to some certain level, the anodic current density will remain stationary.

#### Conclusions

In summary. we synthesized mixed-metal oxides NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite to develop a highly efficient visible light-driven water oxidation catalyst for the first time. The unique hexagonal nanoplate morphology of the catalyst, to which some nanoparticles adhere, produces surface charge effect which mav strengthen photocatalytic and electrocatalytic performance. The mixed-metal oxides composite exhibited lower overpotential and a much smaller Tafel slope than that of CoO, NiO and Fe<sub>2</sub>O<sub>3</sub>. Moreover, this catalyst possesses superior durability and stability in the recycling experiments. The beneficial durability and stability are certified by multiple experiments and are assigned to the beneficial ferromagnetic properties of the catalyst. There will be important applications for developing novel and robust water oxidation catalysts in the future.

#### **Experimental section**

#### Materials

All chemicals used for synthesizing catalysts were obtained from a chemical company and used without further purification. Purified water ( $18.2M\Omega$  cm) for the preparation of solutions was provided by a Milli-Q water purification system (Millipore, Direct-Q 3 UV).

#### Synthesis of NiO<sup>52</sup>

Porous NiO nanostructure powders were obtained by annealing as-prepared Ni(OH)<sub>2</sub> samples at 300  $^{\circ}$ C for 2 h. After calcination, a color change from light green to gray was visualized, confirming the transformation of Ni(OH)<sub>2</sub> into NiO.

#### Synthesis of CoO<sup>53</sup>

72.8 mg Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in 10 mL deionized water, and then 10 mL 0.1M NH<sub>3</sub>·H<sub>2</sub>O was added to the solution slowly. After stirring for about 15 min, the precipitation was washed with deionized water by centrifugation for 5-7 times, then transferred into a 20 mL Teflon-lined autoclave, which was filled with solvents (water/methanol = 1/1, V/V) up to 80% of the total volume. And then these systems were sealed and heated at 250 °C for 24 h.

#### Synthesis of Fe<sub>2</sub>O<sub>3</sub><sup>6</sup>

To an aqueous solution (30 mL) containing  $FeSO_4$  (1.0 M) was added NaOH (6.0 M) drop wisely to pH 11 with magnetic stirring in room temperature. The mixtures were stirred vigorously for 1.5 h with bubbling air. The products were collected by filtration and washed with water several times, dried at 65 °C.

#### Synthesis of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite

NiCl<sub>2</sub>·6H<sub>2</sub>O (2.0 mmol), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.0 mmol) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (2.0 mmol) were dissolved in 24 mL deionized water with strong stirrings. Subsequently, 24 mL KOH solution (2 M) was added to this aqueous solution with magnetic stirring in room temperature. After continuous stirring for 10 min, the mixture was transferred into a Teflon-lined autoclave and maintained at 160 °C overnight. After being cooled to ambient temperature naturally, the brown powders in the autoclaves were collected by centrifugation, washed with deionized water, followed by ethanol (99.7%) three times, and dried at 60 °C for 8 h. The synthesis process for mixed-metal oxides composite is shown in scheme 2.

#### **Catalysts characterization**

Transmission electron microscope (TEM) images were obtained with a TecnaiG<sup>2</sup>F30. Crystalline structures were determined by X-ray diffraction (XRD) using a Rigaku D/MAX 2400 diffractometer (Japan) with Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) operating at 40 kV and 60 mA. X-ray photoelectron spectra (XPS) were measured by ESCALAB250Xi with X-Ray monochromatisation. The binding energy of each element was corrected by the C 1s peak (284.8 eV) from residual carbon. Nitrogen adsorption-desorption at 77 K was performed within

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a relative pressure range from 0.01 to 101.3 kPa. A sample mass of about 200 mg was used for adsorption analysis after pretreatment at 437 K for 30 min under vacuum conditions and kept in a N<sub>2</sub> atmosphere until N<sub>2</sub>-adsorption measurements. Cyclic voltammetry (CV) was recorded on a CHI660D electrochemical analyser with a glassy carbon, Ag/AgCl and Pt wire electrode as the working, reference and auxiliary electrodes, respectively, using sodium borate buffer solutions (pH 8.5, 80 mM) as a supporting electrolyte at room temperature with a scanning rate of 100 mV s<sup>-1</sup>.

#### Photocatalytic and electrocatalytic water oxidation

Photocatalytic water oxidation was performed as follows: the desired concentration of catalyst (0.33 g L<sup>-1</sup>) was prepared by dissolving the appropriate amount of catalyst in a borate buffer solution (80 mM, pH 8.5) containing Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (1.0 mM) and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (5.0 mM). The above solution was deaerated by purging with Ar gas for 10 min in a flask (28.5 mL) sealed with a rubber plug (the total volume of the reaction solution was 15 mL). The reaction was then started by irradiating the solution with a LED light source<sup>54</sup> (light intensity 15.8 mW, beam diameter 2 cm) through a transmitting glass filter ( $\lambda \ge$ 420 nm) at room temperature. After each sampling time, 100  $\mu L$  of Ar was injected into the flask and then the same volume of gas sample in the headspace of the flask was withdrawn by a SGE gas-tight syringe and analyzed by gas chromatography (GC). The O<sub>2</sub> in the sampled gas was separated by passing through a 2 m × 3 mm packed molecular sieve 5 Å column with an Ar carrier gas and quantified by a Thermal Conductivity Detector (TCD). The total amount of evolved O<sub>2</sub> was calculated based on the concentration of  $O_2$  in the headspace gas. Contamination of the head-space with air was corrected by measuring the  $N_2$  concentration present in the head-space. The solution pH was monitored after the reaction by a METTLER TOLEDO FEP20 pH meter.

Linear scan voltammograms (LSVs) were recorded on a CHI660D electrochemical analyser with a glassy carbon, Ag/AgCl and Pt wire electrode as the working, reference and auxiliary electrodes, respectively. LSVs were conducted in potassium hydroxide solutions (1 M) as a supporting electrolyte at room temperature with a scanning rate of 1 mV s<sup>-1</sup>. The experiments were measured from 0.4 to 0.7 V vs. Ag/AgCl with a glassy carbon pasting 0.01 mg catalyst as a working electrode. Tafel slopes were calculated from the LSVs curves by plotting overpotential  $\eta$  against log (J).

#### Isotope-labelled experiment

The 10.8 atom%  $H_2^{18}O$  of borate buffer solution (pH 8.5, 80 mM) containing NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite (0.33 g L<sup>-1</sup>), Ru(bpy)<sub>3</sub><sup>2+</sup> (1.0 mM) and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (5.0 mM) was deaerated with helium gas before irradiation by LED light ( $\geq$  420 nm) in a quartz flask that was sealed with a rubber plug. After 10 min, 50 µL of gas sample was withdrawn using a gas-tight syringe for gas analysis. An Agilent Series 7890A model chromatograph interfaced with an Agilent Series 5975C model mass spectrometer operating in electron impact ionization mode was used to collect the mass spectrometry data. The MS

detector was tuned for maximum sensitivity (quadruple temperature, 150 °C; ion source temperature, 230 °C). The single ion mode was used to scan for the ions m/z = 28, 32, 34, 36 with a dwell time of 100 ms, resulting in 8.3 cycles per second. Ions in the m/z range 30 to 50 were also scanned in order to observe the abundance change of  $^{16}O^{18}O$  and  $^{18}O^{18}O$ , which evolved from  $H_2^{\ 16}O$  and  $H_2^{\ 18}O$ , respectively. The total flow rate into the spectrometer was limited to 0.6 mL min-1. The GC was equipped with a molecular sieve column (30 m  $\times$  0.32 mm  $\times$  15  $\mu$ m), and the vaporizing chamber temperature and column temperature was set for 100 °C and 35 °C, respectively.

#### Definition of half-wave potential (E<sub>1/2</sub>)

 $E_{1/2} = (Epa + Epc) / 2$ 

Epa : the oxidation potential of  $Ru(bpy)_{3}^{2+/3+}$ Epc : the reduction potential of  $Ru(bpy)_{3}^{2+/3+}$ 

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### **Graphic abstract**

# Hexagonal nanoplates of NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite acting as an efficient photocatalytic and electrocatalytic water oxidation catalyst

Yukun Zhao<sup>a</sup>, Yan Zhang<sup>a</sup>, Yong Ding<sup>a,b</sup>\* and Mindong Chen<sup>b</sup>



The unique hexagonal sheet-shaped NiO/CoO/Fe<sub>2</sub>O<sub>3</sub> composite fabricated through a co-precipitation and hydrothermal method demonstrates robust photocatalytic and electrocatalytic performance of water oxidation.