Supporting Information

Investigating the behavior of various cocatalysts on $LaTaON_2$ photoanode for visible light water splitting

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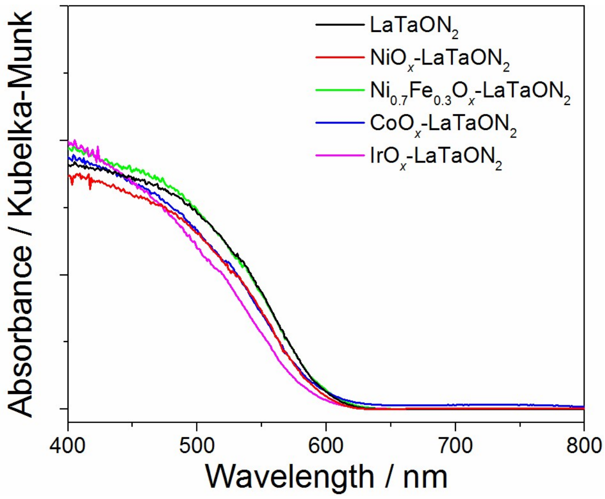

Fig. S1 Kubelka–Munk absorbance for $LaTaON_2$, NiO_x–$LaTaON_2$, $Ni_{0.7}Fe_{0.3}O_x$–$LaTaON_2$, and CoO_x–$LaTaON_2$ as well as post–loaded IrO_x–$LaTaON_2$.

In comparison with the bare $LaTaON_2$, only slight changes occur in the absorbance at 405 nm (light source for PEC measurement) for the cocatalysts loaded $LaTaON_2$. This is understandable if considering quite low nominal loading amount (2 wt%) of these cocatalysts. In addition, the absorption edge is also slightly blue shifted after loading cocatalysts, which could be due to the shading effect of cocatalysts.

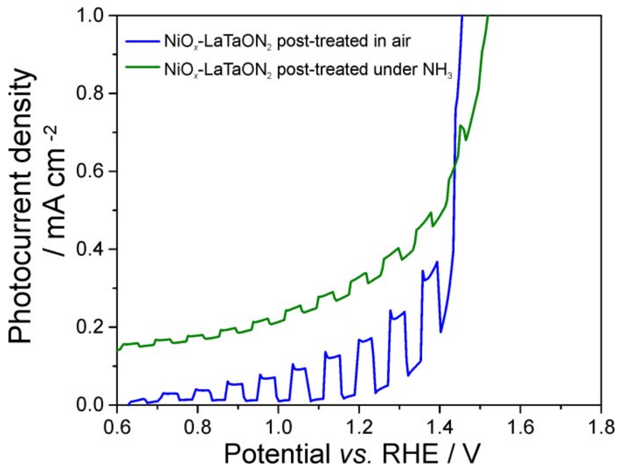

Fig. S2 Potentiodynamic measurements in 0.5 M NaOH (pH=13.0) for NiO_x–$LaTaON_2$ after treatment in air and under NH_3.

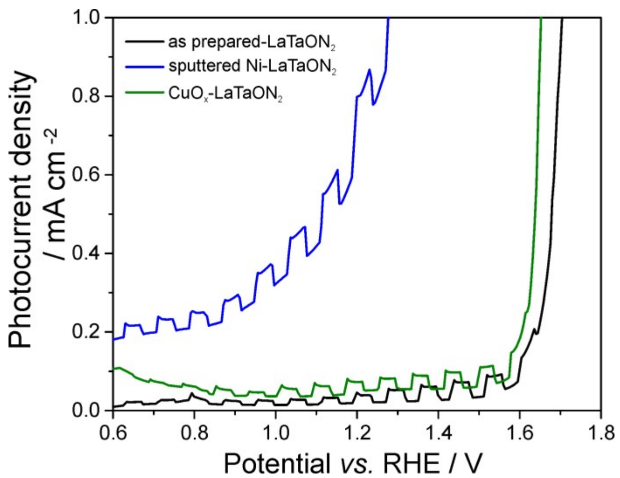

Fig. S3 Potentiodynamic measurements in 0.5 M NaOH (pH=13.0) for sputtered Ni–$LaTaON_2$ and CuO_x–$LaTaON_2$ in comparison to as prepared–$LaTaON_2$.

H_2O_2 as hole scavenger

H_2O_2/O_2 has a relatively negative oxidation potential (0.682 V_{RHE}) and its rate constant is 10 to 100 times higher than that of water.[1] Thus, H_2O_2 is an efficient hole scavenger in electrolyte to suppress surface recombinations. Holes that come to the surface will be immediately captured and participate in the oxidation of H_2O_2. Assuming that all samples have the same bulk recombination, any difference seen in the photocurrent of H_2O_2 oxidation should therefore be due to the recombination at the interfaces between $LaTaON_2$ and the cocatalysts as well as the electrolyte.

As shown in Fig. S3, the photocurrent of NiO_x–$LaTaON_2$ is the highest followed by that of $Ni_{0.7}Fe_{0.3}O_x$–$LaTaON_2$, both higher than that of bare $LaTaON_2$. The improvement in the photocurrent indicates a reduced recombination and good passivation at the interface of $LaTaON_2$ and the cocatalysts, which is consistent with our conclusions.

CoO_x– and IrO_x–loaded $LaTaON_2$ exhibit huge background cathodic and anodic currents, which makes the chopped photocurrent characteristics undetectable. This is probably due to their high catalytic activity for H_2O_2 oxidation and the photocurrent–doubling phenomena, which causes the oxidized form of H_2O_2 to be oxidized again through injection of an electron into the conduction band of the semiconductor. [1–4] The oxidation procedures can be described as follows: $H_2O_2 + h^+ \rightarrow 2H^+ + O_2^-$ and $O_2^- \rightarrow O_2 + e^-$.[4] In comparison to NiO_x– and $Ni_{0.7}Fe_{0.3}O_x$–$LaTaON_2$, CoO_x– and IrO_x–loaded $LaTaON_2$ have higher background currents, which is also consistent with the PEC measurement without H_2O_2, indicating the more dependency of the system's photocurrent on the catalytic effect of CoO_x and IrO_x.

However, the presence of a hole scavenger and cocatalyst still did not significantly enhance the photocurrent up to the mA cm^{-2} range, implying that the PEC performance is not limited by surface or interface recombination, but rather by the recombination or low electronic conductivity in the bulk of $LaTaON_2$.

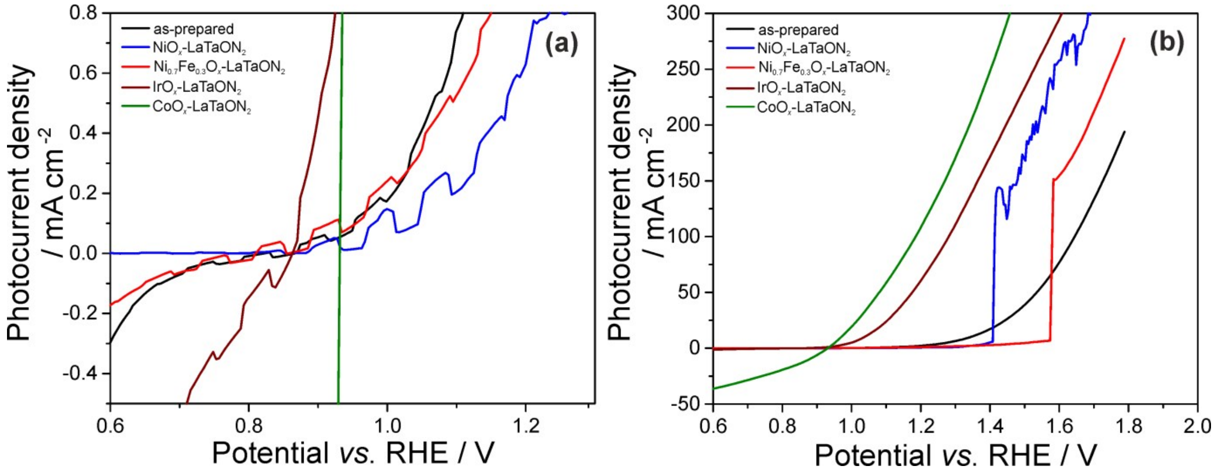

Fig. S4 PEC performance under chopped light in 0.5 M NaOH with the presence of 0.1 M H_2O_2 for pre−loaded NiO_x−$LaTaON_2$, $Ni_{0.7}Fe_{0.3}O_x$−$LaTaON_2$, and CoO_x−$LaTaON_2$ as well as post−loaded IrO_x−$LaTaON_2$. (a). Zoomed−in view of PEC performance. (b). PEC performance between 0.6−1.8 V_{RHE}, calculated based on the illuminated area of 3 mm^2.

References

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