

## **Electronic Supplementary Information**

### **A porous ZnGaNO photoanode for efficient water oxidation modified**

#### **by Co-based electrocatalyst**

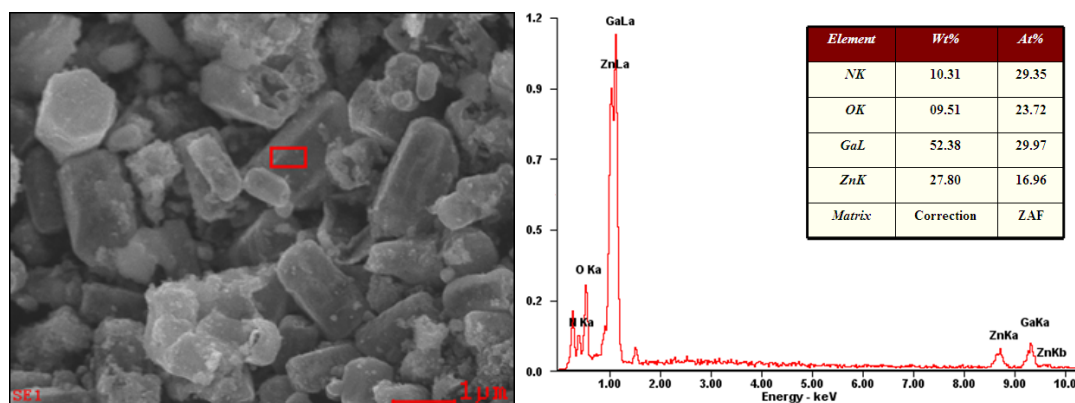
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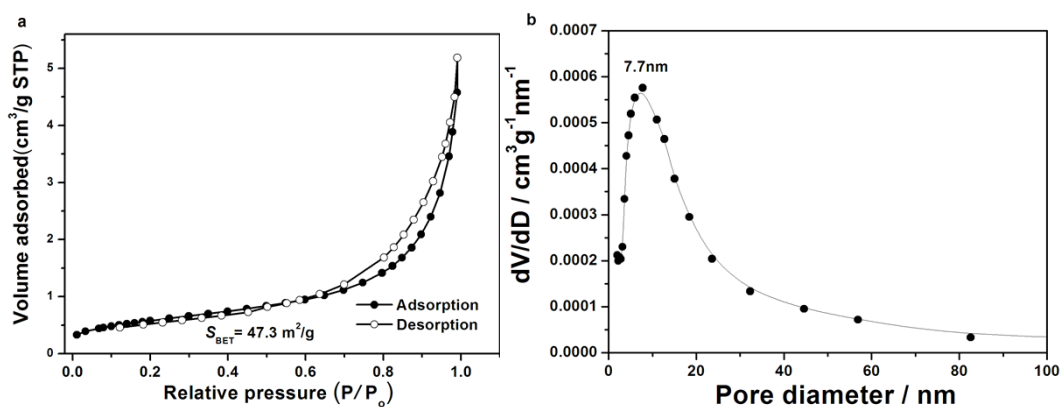
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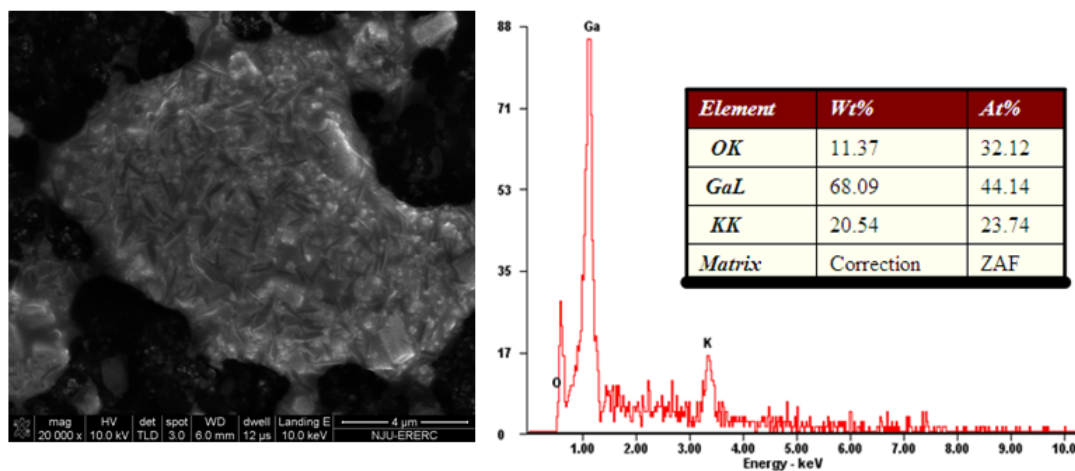
## SI-1 Characterization of porous ZnGaNO microrods



**Figure S1** EDS analysis for the porous ZnGaNO microrods prepared by heating the  $\text{KGaO}_2$  coated ZnO microrods at 780 °C for 5h in flowing  $\text{NH}_3$ . EDS analysis indicated that the composition of the final product is  $\text{Zn}_{0.17}\text{Ga}_{0.3}\text{N}_{0.3}\text{O}_{0.24}$ .

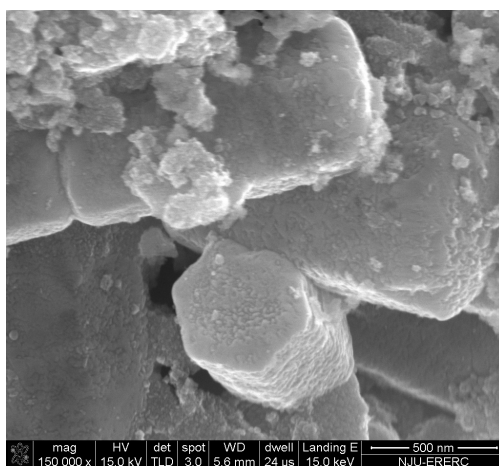


**Figure S2** BET analysis for the porous ZnGaNO microrods. a) Nitrogen adsorption-desorption isotherms. b) Pore-size distribution.

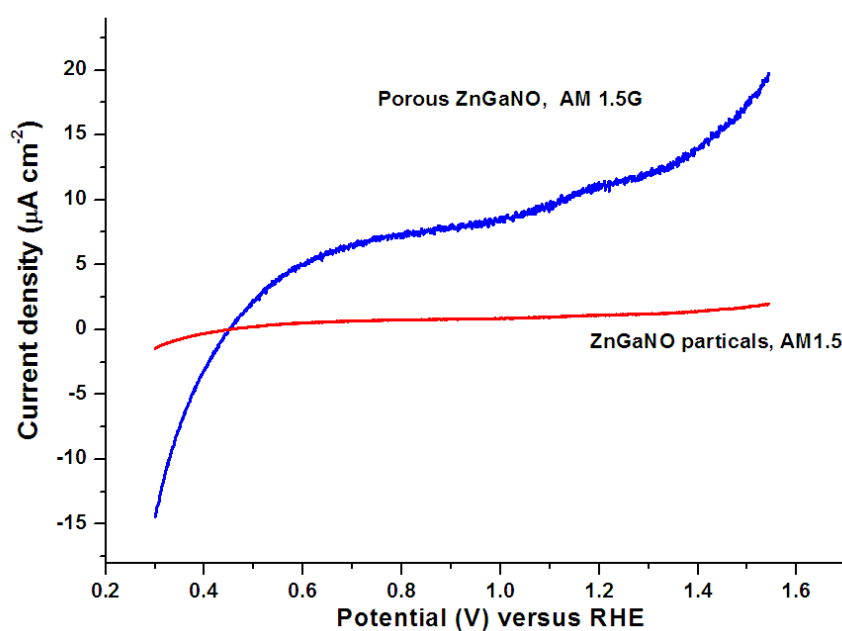


**Figure S3** SEM observation for sample obtained by heating the  $\text{KGaO}_2$  coated ZnO

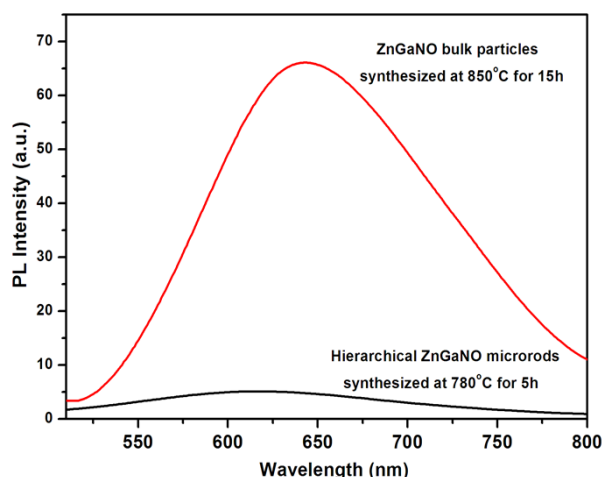
microrods at 780 °C for 1h in flowing  $\text{NH}_3$ . EDS analysis confirmed that the needle-shaped particles shown in SEM image are the  $\text{KGaO}_2$ .



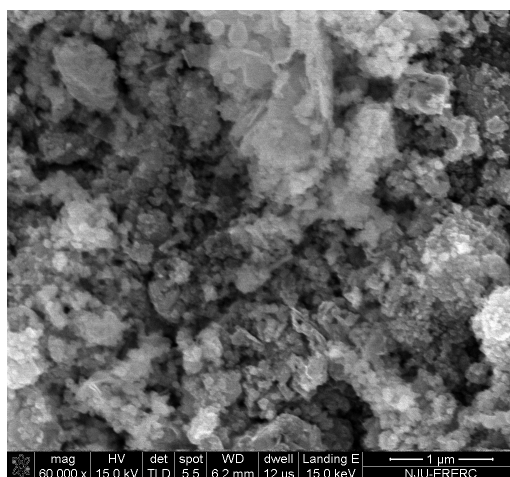
**Figure S4** SEM observation for sample obtained by heating the  $\text{KGaO}_2$  coated ZnO microrods at 780 °C for 1h in flowing  $\text{NH}_3$  after washing by water. The SEM image shows an intermediate process for formation of ZnGaNO. After washing by water, the needle-shaped particles disappeared, further confirming that the needle-shaped particles shown in Figure S3 are water-soluble  $\text{KGaO}_2$ .



**Figure S5** Photocurrent for ZnGaNO particles and porous ZnGaNO photoanodes



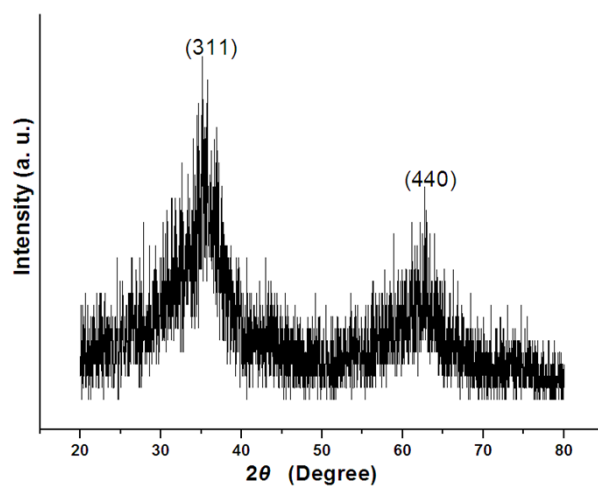
**Figure S6** Room temperature PL spectra of ZnGaNO bulk particles and hierarchical ZnGaNO microrods with a fluorescent light excitation of 410 nm and filter wavelength of 420 nm.



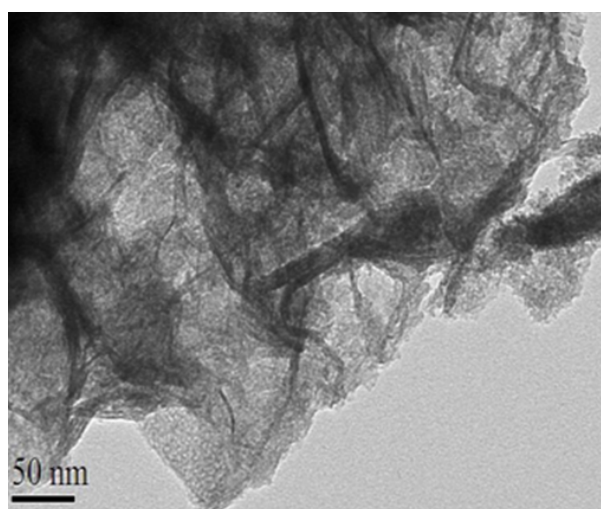
**Figure S7** SEM image for the porous ZnGaNO microrods after mechanically milling. It can be seen that the porous structure of ZnGaNO microrods was destroyed into a dispersed nanocrystals.

## SI-2 Synthesis and characterization of $\text{CoGa}_2\text{O}_4$

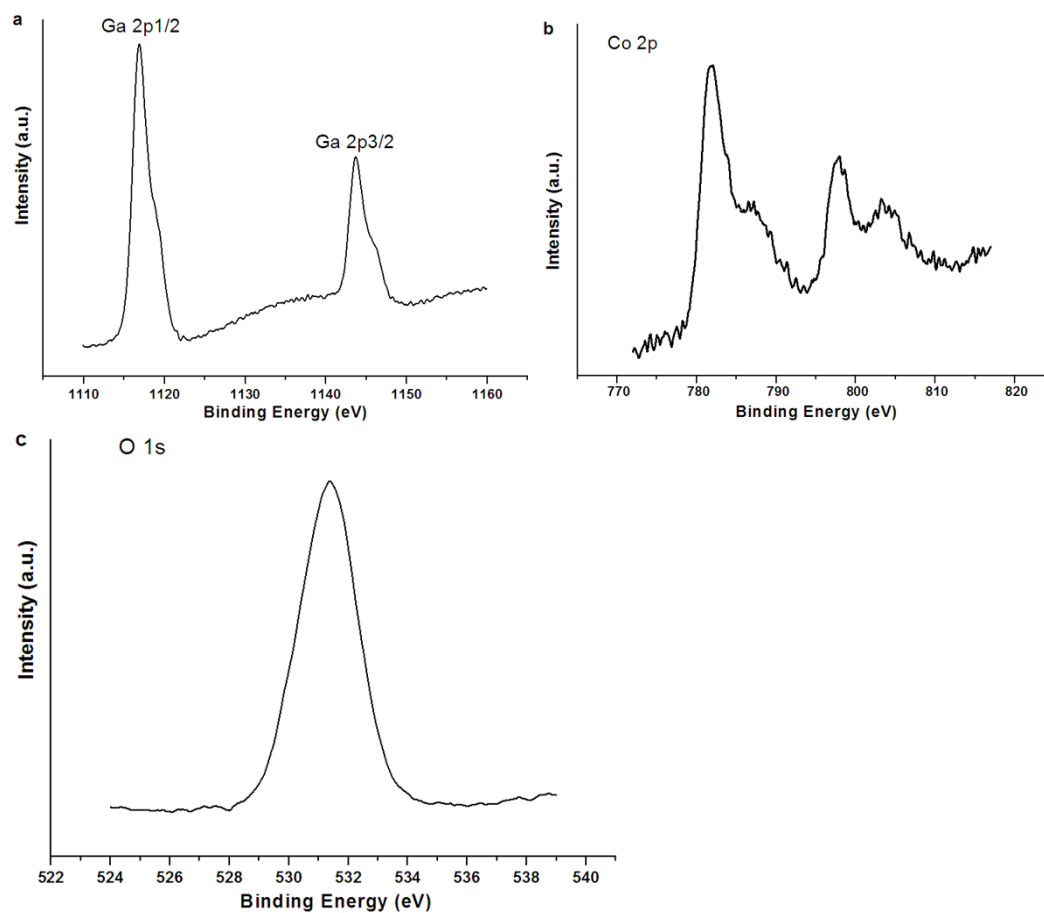
The  $\text{NaGaO}_2$  solid powders, as a raw material, were first prepared by heating stoichiometric mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{Ga}_2\text{O}_3$  at 850 °C for 12h. The preparation procedure of  $\text{CoGa}_2\text{O}_4$  was as follows: in a typical procedure, 10mL of  $\text{NaGaO}_2$  colloidal suspension ( $0.2 \text{ molL}^{-1}$ ) was added into 20mL of  $\text{CoCl}_2$  ( $0.05 \text{ molL}^{-1}$ ) aqueous solution and stirred for 3h at room temperature to form the  $\text{CoGa}_2\text{O}_4$ , then the sedimentation was separated by centrifugation and dried at 60 °C for 2h.



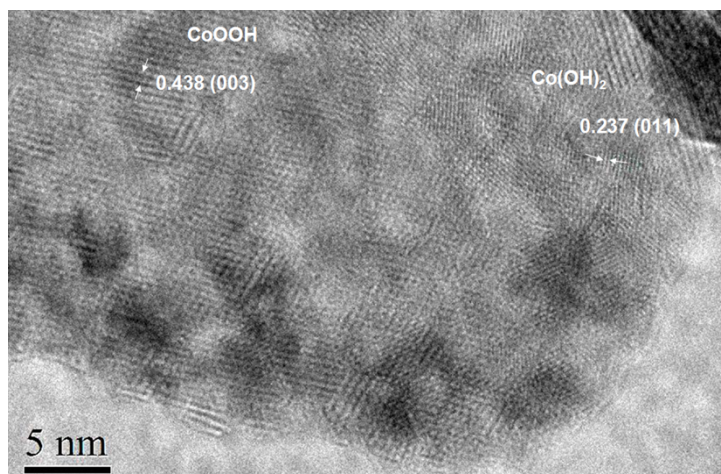
**Figure S8** XRD pattern for the  $\text{CoGa}_2\text{O}_4$ . Two broadening peaks can be observed in the XRD pattern, indicating that the as-prepared  $\text{CoGa}_2\text{O}_4$  has the low crystallinity.



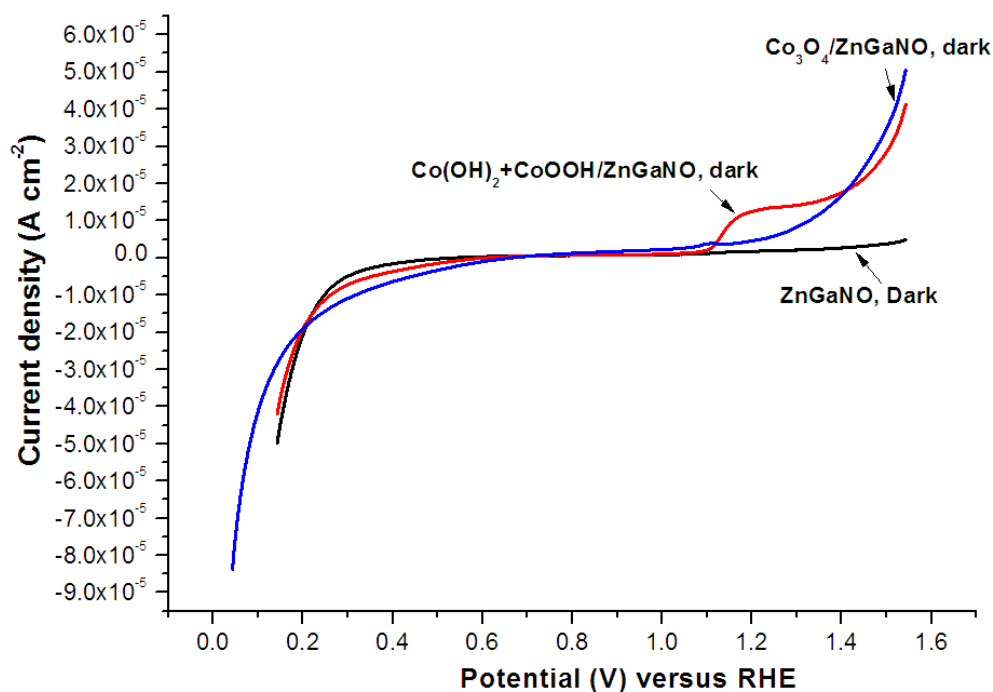
**Figure S9** TEM image for the as-prepared  $\text{CoGa}_2\text{O}_4$ . The TEM image shows that the as-prepared  $\text{CoGa}_2\text{O}_4$  presents a porous structure.



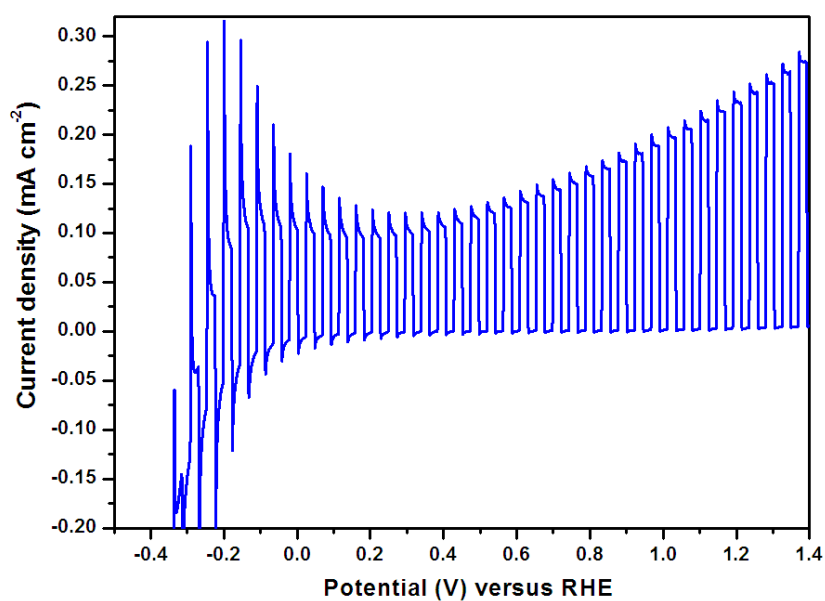
**Figure S10** XPS spectra for the as-prepared  $\text{CoGa}_2\text{O}_4$ . a) Ga2p. b) Co2p. c) O1s. The composition of as-prepared  $\text{CoGa}_2\text{O}_4$  is confirmed by XPS to be Co:Ga:O=1:2:4.



**Figure S11** High-resolution TEM image for the  $\text{CoGa}_2\text{O}_4$  after current-time scan at 1.72 V vs RHE in 1M NaOH electrolyte for 10h



**Figure S12** The dark current for the porous ZnGaNO without or with Co(OH)<sub>2</sub>+CoOOH or Co<sub>3</sub>O<sub>4</sub>.



**Figure S13** The photocurrent for the ZnGaNO microrod photoanode with dense Co(OH)<sub>2</sub>+CoOOH electrocatalytic layer.