Electronic Supplementary Information

A porous ZnGaNO photoanode for efficient water oxidation modified by Co-based electrocatalyst

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SI-1 Characterization of porous ZnGaNO microrods

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

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

Figure S3 SEM observation for sample obtained by heating the KGaO$_2$ coated ZnO
microrods at 780 °C for 1h in flowing NH₃. EDS analysis confirmed that the needle-shaped particles shown in SEM image are the KGaO₂.

**Figure S4** SEM observation for sample obtained by heating the KGaO₂ coated ZnO microrods at 780 °C for 1h in flowing NH₃ 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 KGaO₂.

**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 CoGa$_2$O$_4$

The NaGaO$_2$ solid powders, as a raw material, were first prepared by heating stoichiometric mixture of Na$_2$CO$_3$ and Ga$_2$O$_3$ at 850 °C for 12h. The preparation procedure of CoGa$_2$O$_4$ was as follows: in a typical procedure, 10mL of NaGaO$_2$ colloidal suspension (0.2 molL$^{-1}$) was added into 20mL of CoCl$_2$ (0.05 molL$^{-1}$) aqueous solution and stirred for 3h at room temperature to form the CoGa$_2$O$_4$, then the sedimentation was separated by centrifugation and dried at 60 °C for 2h.
Figure S8 XRD pattern for the CoGa$_2$O$_4$. Two broadening peaks can be observed in the XRD pattern, indicating that the as-prepared CoGa$_2$O$_4$ has the low crystallinity.

Figure S9 TEM image for the as-prepared CoGa$_2$O$_4$. The TEM image shows that the as-prepared CoGa$_2$O$_4$ presents a porous structure.
Figure S10 XPS spectra for the as-prepared CoGa$_2$O$_4$. a) Ga2p. b) Co2p. c) O1s. The composition of as-prepared CoGa$_2$O$_4$ is confirmed by XPS to be Co:Ga:O=1:2:4.

Figure S11 High-resolution TEM image for the CoGa$_2$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)$_2$+CoOOH or Co$_3$O$_4$.

Figure S13 The photocurrent for the ZnGaNO microrod photoanode with dense Co(OH)$_2$+CoOOH electrocatalytic layer.