Supporting Information

Ultrathin CoO_x Modified Hematite with Low Onset Potential for Solar Water Oxidation

Chun Du,^a Jun Wang,^a Xiao Liu, ^b Jie Yang, ^a Kun Cao, ^b Yanwei Wen,^a Rong Chen ^{b,c}*and Bin Shan ^{a,d}*

^{a.}State Key Laboratory of Materials Processing and Die & Mould Technology, School of

Materials Science and Engineering, Huazhong University of Science and Technology,

Wuhan 430074, Hubei, People's Republic of China.

^{b.}State Key Laboratory of Digital Manufacturing Equipment and Technology, School of

Mechanical Science and Engineering, Huazhong University of Science and Technology,

Wuhan 430074, Hubei, People's Republic of China.

^{c.}School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, Hubei, People's Republic of China.

^{d.}Department of Materials Science and Engineering, The University of Texas at Dallas, Richardson, Texas 75080, USA



Fig. S1. Top-view (a) and side-view (b) SEM images of bare hematite nanostructured film. The scale bar is 500 nm.



Fig. S2. (a) High-resolution TEM image of hematite with ALD CoO_x modification layer. (b) TEM image of single hematite nano-structure unit.



Fig. S3. First-order derivative of the photocurrent density as a function of voltage was calculated. The onset potential is defined as the voltage at which $dJ/dV \ge 0.2$ mA cm⁻ $^{2}V^{-1}$. The onset potential was read as 0.85 V_{RHE} and 0.60 V_{RHE} for Fe₂O₃ and Fe₂O₃/CoO_x, respectively.



Fig. S4. Steady-state *J*-V curves for hematite photanode with 10 cycles and 250 cycles of ALD CoO_x overlayer. Solid and dashed curves represent the response collected in light and dark condition respectively. Both light curves express improvement in turn on potential compared to bare hematite film.



Fig. S5. Polarization *J*-V curve for CoO_x coated hematite photoanode with growth temperature at 250 °C. Water oxidation turn on potential is around 0.7 V_{RHE}.



Fig. S6. XPS characterizations of O 1s on CoO_x coated hematite sample. Green curve is the raw data and grey lines are fitted results.



Fig. S7. Polarization *J*-V curves of bare Fe_2O_3 (a) and Fe_2O_3/CoO_x (b) tested in 1 M KOH, under chopped AM 1.5 illumination. Positive and negative spikes show up when light was switched on and off.



Fig. S8. *J*-V curves with opposite scan directions on (a) bare (left) and (b) CoO_x coated hematite (right) photoanode. Positive scan means the applied potential start from low value, while the negative scan starts from high potential value.



Fig. S9. (a) Dark *J*-V curves on hematite with 0 , 25 and 250 cycles of ALD CoOx overlayer. Hematite with 250 cycles of ALD CoOx with the highest OER activity exhibits the earliest Von potential. (b) Representative Nyquist plot data for various hematite photoanodes collected in dark condition.



Fig. S10. CV scans on CoO_x coated hematite photoanode. CV scan was done for 10 times with a scan rate of 10 mV/s. Negligible oxidation or reduction features are exhibited in the CV results.



Fig. S11. *J*-V curves for CoO_x coated hematite photoanode with post annealing in air at 300 °C. Compared to as-prepared CoO_x/Fe_2O_3 photoanode, turn on potential shifts positively to 0.9 V_{RHE} after thermal treatment.