Synergizing Hole Accumulation and Transfer on Composite Ni/CoO_x for Photoelectrochemical Water Oxidation

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Materials and Methods

A nanostructured hematite was used as a model support for catalyst deposition. Firstly, the β-FeOOH nanorods were synthesized by a hydrothermal deposition onto the F-doped SnO_2 glass (FTO, TEC 15A 3.0 mm, XOP Física glass company) in a solution containing 0.15 M $FeCl_3 \cdot 6H_2O$ (Sigma-Aldrich) and 1.0 M $NaNO_3$ (Sigma-Aldrich) at 95 °C for 1.5 hours. Then this hematite substrate has been annealed in air at 600 °C for 2 hours. Transient electro-reduction of Ni ($NiCl_2.6H_2O$, General-reagent) and Co ions ($CoCl_2.6H_2O$, General-reagent) in the electrolyte (pH=4) containing 0.1 M metal ions at -1.1 V versus Ag/AgCl with a charge density of 0.20 mC cm^{-2} for H2T-NiO_x and H2T-CoO_x, respectively. For the synthesis of H2T-$NiCoO_x$, Ni and Co with a charge density of 0.20 mC cm^{-2} was successively deposited. Several parallel samples were prepared and tested to confirm the repeatability.

TiO_x was prepared on hematite using an atomic layer deposition system at 120°C (PICSUN R-200). Tetrakis(dimethylamido)-titanium(IV) (99.999%, Sigma-Aldrich, kept at 85°C) and H_2O were used as Ti and O sources, respectively. Ti precursor was kept in the chamber for 1.6 seconds under 150 sccm N_2 flow, followed by a 6-second N_2 purge. H_2O was kept for 0.1 seconds under 200 sccm N_2 flow, followed by a 6-second N_2 purge. TiO_x deposition has been calculated to be 0.50 Å per cycle.

A field emission scanning electron microscope (SEM Zeiss Supra 50 VP) was applied to characterize the surface morphology and surface texture. Compositional maps were acquired with the energy-dispersive X-ray spectroscopy (EDX).

The related electrochemical measurements were implemented by using an SP-300 Potentiostat, Bio-logic. All measurements were carried out in a 1.0 M NaOH alkaline electrolyte in a custom-designed Cappuccino Teflon cell with a quartz window.

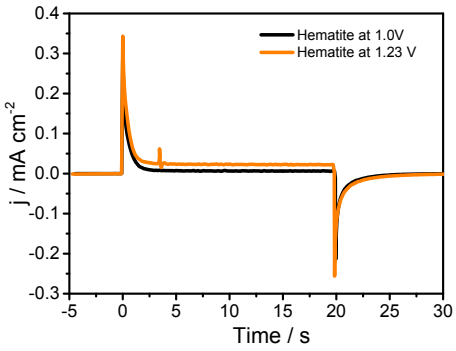

Figure S1. Transient photocurrent response of hematite under chopped light.

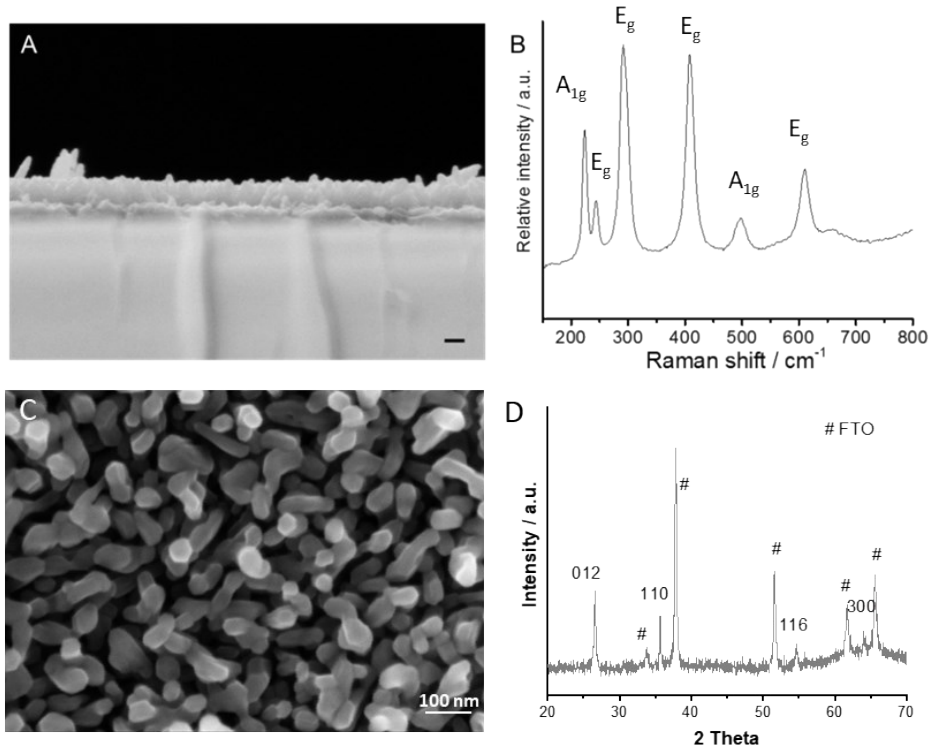

Figure S2. A, C) TEM image of cross-section and surface morphology of H2T (scale bar 100 nm), B) Raman and D) XRD of H2T.

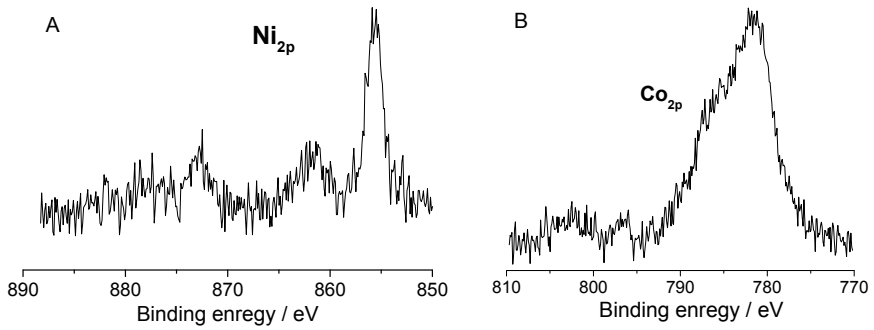

Figure S3. X-Ray Photoelectron Spectroscopy (XPS) plots after background subtraction show the formation of A) NiO_x and B) CoO_x in air.

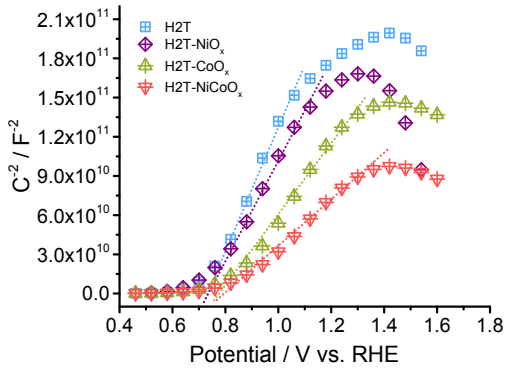

Figure S4. Mott–Schottky plots of H2T, H2T-NiO_x, H2T-CoO_x and H2T-Ni/CoO_x collected at 1 kHz in the dark. The slope of the Mott–Schottky plots,[1] slope=$\frac{2}{D_N e\varepsilon\varepsilon_0}$, are used to evaluate the donor density D_N, meaning lower slope, higher donor density.

1. F. Fabregat-Santiago, G. Garcia-Belmonte, J. Bisquert, P. Bogdanoff and A. Zaban, *J. Electrochem. Soc.*, 2003, **150**, E293-E298.