Probing the Effect of Metal to Ligand Charge Transfer on the Oxygen Evolution Reaction in Au Incorporated $Co(OH)_2$ Thin Film Electrocatalysts

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Supporting Information

Sample preparation and electrochemical experiments:

Three solutions were prepared in three separate 25 ml volumetric flasks. 10 mM $Co(NO_3)_2$ was prepared from $Co(NO_3)_2.6H_2O$. 0.0726g of the salt was taken in a 25 ml volumetric flask and dissolved in water. In another 25 ml volumetric flask 0.0726g of $Co(NO_3)_2.6H_2O$ and 0.0139g of $KAuBr_4.H_2O$ were taken and dissolved in water to prepare a Au incorporated $Co(NO_3)_2$ solution where the concentration of Au was 10% of Co concentration. 1mM Au solution was prepared from dissolving 0.0139g of $KAuBr_4.H_2O$ in a third 25 ml volumetric flask. $Co(OH)_2$, $Co(OH)_2$-Au were electrodeposited on three types of substrates according to the following table:

Table S1: Sample preparation

Sample	Substrate	Deposition time	Experiment name
$Co(OH)_2$, $Co(OH)_2$-Au	Glassy carbon stick electrode	60s	All electrochemical experiments
	Pt coated Silicon wafer	60s	XPS, TEM
	Pt coated Silicon wafer	300s	SEM, EDX, XRD
	Pt coated Si_3N_4 windows	60s	NEXAFS

Au film was deposited on glassy carbon stick electrode and Pt coated Silicon wafer only, to perform cyclic voltammetry and XPS (Figure 1 and 4).

The Si wafer and the Si_3N_4 windows were first coated with a 2nm Ti adhesive layer followed by a 10nm Pt layer by electron beam to increase their conductivity. The films were electrodeposited from the prepared solutions using a potentiostat in a typical three electrode system where a Ag/AgCl electrode was used as the reference electrode and Pt wire was used as counter. Applied voltage for the electrodeposition was -1.05V vs Ag/AgCl. After deposition the films were subjected to OER at 0.75V vs Ag/AgCl for 4 hrs in 0.1M NaOH solution. Au films were not subjected to the 4 hr OER. Cyclic voltammograms (CV) for $Co(OH)_2$, $Co(OH)_2$-Au and Au films were recorded between a range of 0.9 – 1.66 V (vs RHE) at a sweep rate of 20 mVs^{-1} in 0.1 M NaOH to measure their electrochemical performance. To measure electrochemical surface area (ECSA) CV was performed on $Co(OH)_2$ and $Co(OH)_2$-Au films at various scan rates in the double layer charging region of both films.

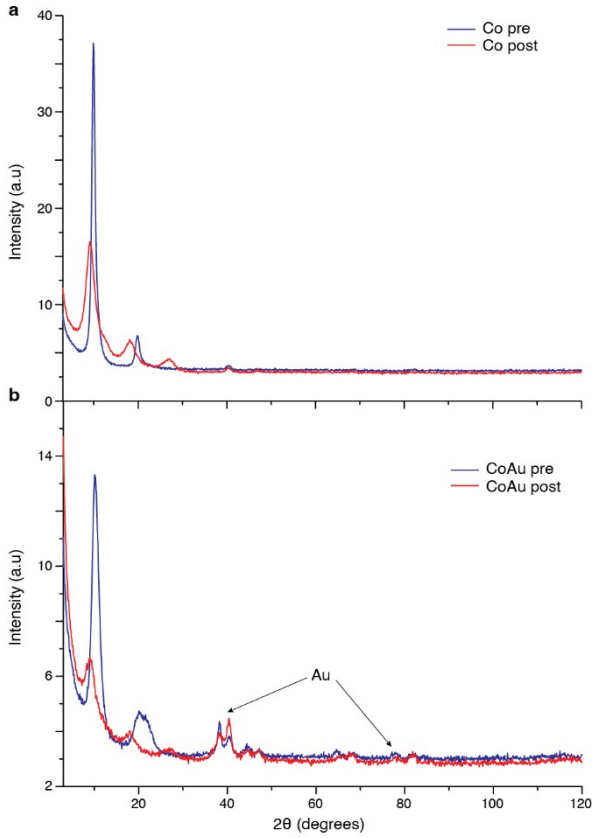

Figure S1: XRD images of (a) $Co(OH)_2$ and (b) $Co(OH)_2$-Au films before and after the OER show presence of crystalline Au *hkl*-111 and *hkl*-311 planes at 2θ of 38° and 77°.[1]

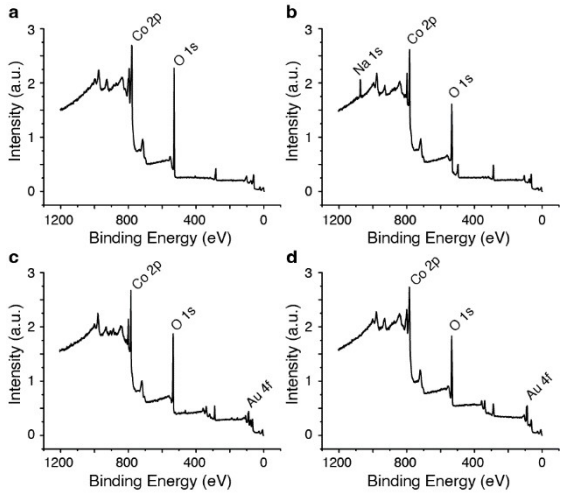

Figure S2: XPS survey scans of (a) $Co(OH)_2$ pre, (b) $Co(OH)_2$ post, (c) $Co(OH)_2$-Au pre and (d) $Co(OH)_2$-Au post OER films show presence of Co 2p, O 1s in all four films, Na 1s in Co post and Au 4f in $Co(OH)_2$-Au films.

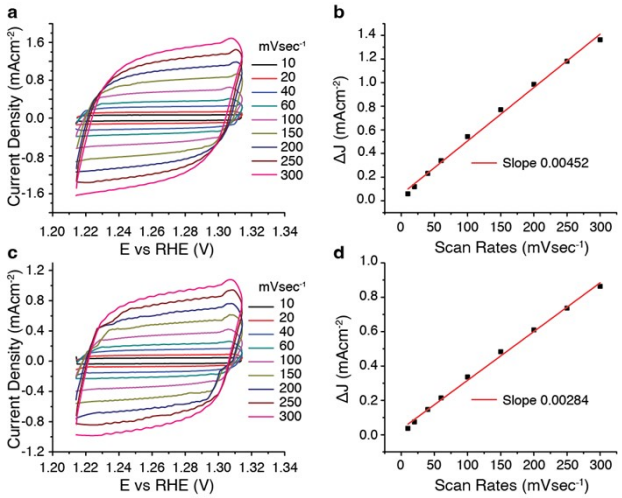

Figure S3. (a) and (c) Cyclic voltammograms recorded for $Co(OH)_2$ and Co(OH) -Au films in 0.1M NaOH at various scan rates in the double layer charging region. (b) and (d) Plots of capacitive current obtained at 1.26 V vs RHE against sweep rate.

The surface area was determined from the slope of the plots in Figure S3 (b) and (d) which is given below in Table S2. The electrochemically active surface area was calculated by assuming that a flat surface has a specific capacitance of 40 μFcm^{-2} for $Co(OH)_2$. [2]

Table S2. Electrochemically active surface area of Co and CoAu thin films.

Sample	Slope	ECSA (cm^2)
$Co(OH)_2$	0.00452	113
$Co(OH)_2$-Au	0.00284	71

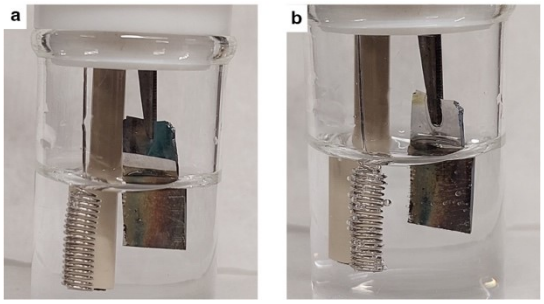

Figure S4: (a) Electrodeposited $Co(OH)_2$-Au film on Si wafer submerged in 0.1M NaOH before applying voltage, (b) Oxygen bubbles accumulating on the $Co(OH)_2$-Au film surface after applying the voltage for OER.

References

1. G. Geng, P. Chen, B. Guan, Y. Liu, C. Yang, N. Wang and M. Liu, *RSC advances*, 2017, **7**, 51838-51846.
2. H. Deng, C. Zhang, Y. Xie, T. Tumlin, L. Giri, S. P. Karna and J. Lin, *Journal of Materials Chemistry A*, 2016, **4**, 6824-6830.