

## Optimized Immobilization of ZnO:Co Electrocatalysts Realizes 5% Efficiency in Photo-assisted Splitting of Water

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### Supporting Information

#### Used reagents and solvents

Reagent/Solvent	Supplier	Purity
Acetate	Alfa Aesar	p. a.
Sodium perchlorate	Alfa Aesar	p. a.
di-2-pyridylketon	Sigma-Aldrich	p. a.
Ethanol	Sigma-Aldrich	ACS reagent, 99.5%
Acetone	Sigma-Aldrich	ACS reagent, 99.5%
Acetonitrile anhydrous	Sigma-Aldrich	99.8%
Iodine	Sigma-Aldrich	99.99% trace metals basis

**Table T1:** Used reagents and solvents

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### **Synthesis of $[\text{Co}_{4-x}\text{Zn}_x(\text{dpd})_4(\text{OAc})_3(\text{H}_2\text{O})]\text{ClO}_4$**

In a 100 ml Schlenck flask 1.245 g (5 mmol) of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and 1.097 g  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (5 mmol) were dissolved in 50 ml water and stirred under nitrogen atmosphere at 50 °C. After dissolution of the acetates, a solution of 0.911 g (5mmol) di-2-pyridylketone in 10 ml acetonitrile was added dropwise over 15 min. The reaction mixture was cooled to room temperature and a solution of 1.40 g (10mmol)  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  in 1 ml  $\text{H}_2\text{O}$  was added. The crystalline products (1.238 g) were collected after two days from the remaining supernatant by filtration and dried on air.

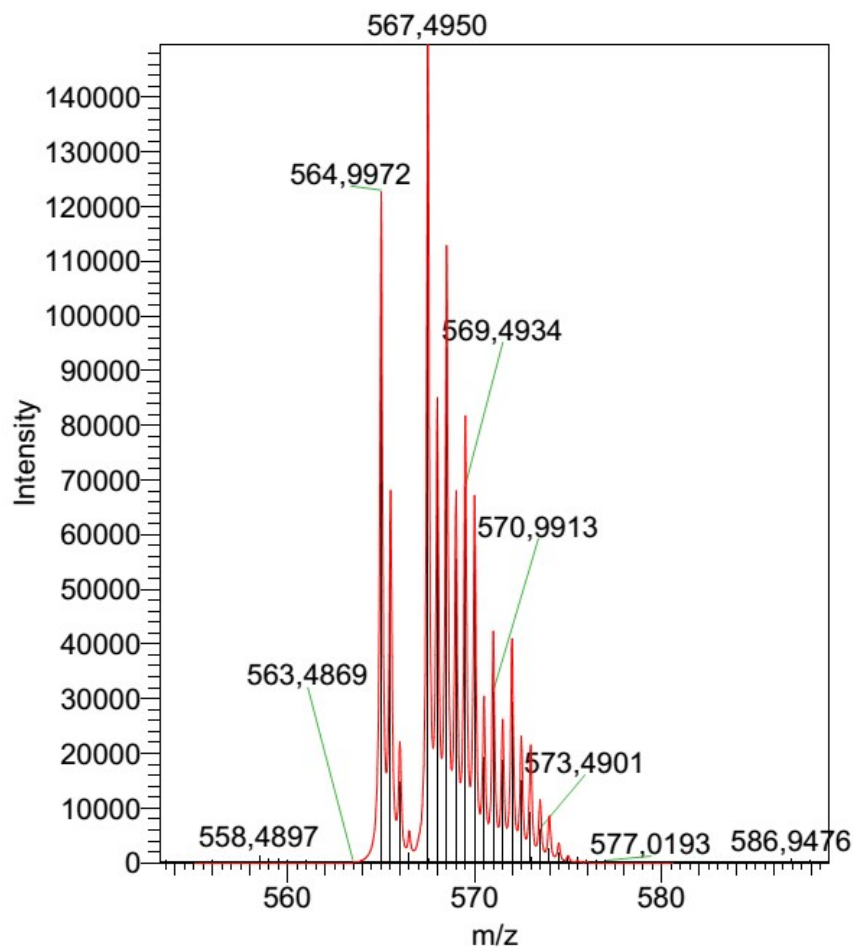
ESI-MS:  $m/z = 564.4950$   $[\text{C}_{46}\text{H}_{38}\text{N}_8\text{O}_{12}\text{Co}_2\text{Zn}_2]^{2+}$

CHN (obs/calc): C (40.1/44.5); H (3,8/3.6); N (7,7/8.3) )  $\text{C}_{50}\text{H}_{50.6}\text{N}_8\text{O}_{20.8}\text{ClCo}_{4-x}\text{Zn}_x$  (x=1-3)

### **Solvolytic preparation of nanoparticles**

200 mg of the precursor mixture and 20 mg of Trioctylphosphine oxide (TOPO) were dissolved in 4ml of Benzylamine and stirred at room temperature until dissolution. The reaction mixture was brought into a 180°C Oil bath and heated for 10 minutes. The tube was removed from the oil bath and cooled to room temperature. Green ZnO:Co Particles were separated from the supernatant by subsequent washing and centrifugation steps with isopropanol, water and acetonitrile.

Yield: 17.9 mg



**Figure S1:** Main Signals in HR-ESI MS of formiate buffered  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  Solutions of the tetrakis-di-2-pyridylmethandiolate precursors.

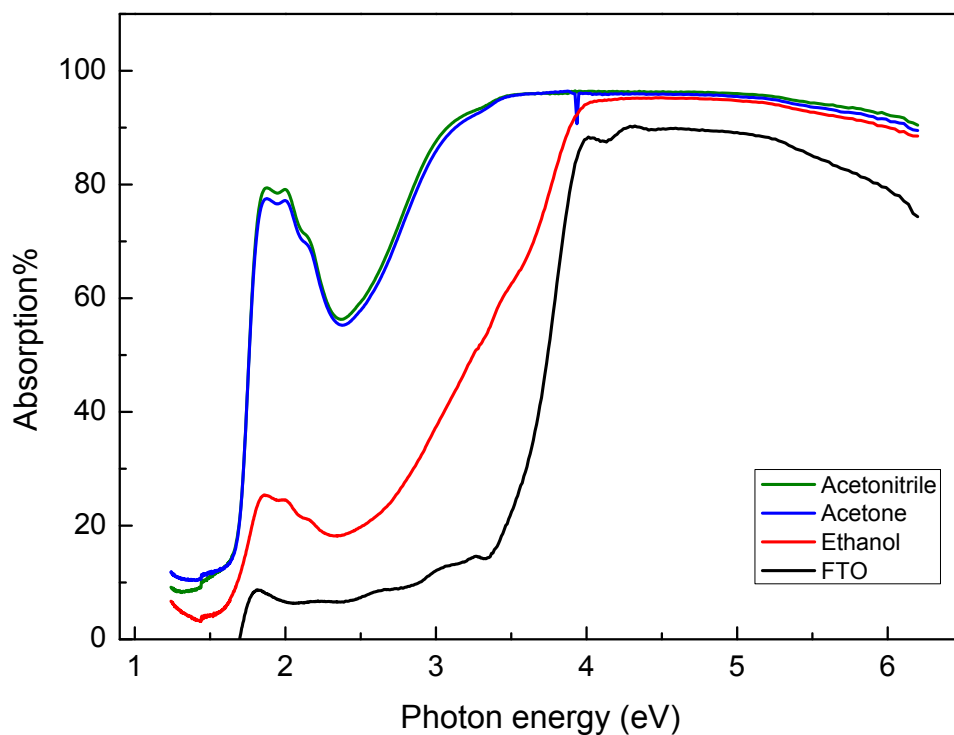
The red line represents a lorentzian fit of simulated spectra  $m/z= 567.4950$   $[\text{C}_{46}\text{H}_{38}\text{N}_8\text{O}_{12}\text{Co}_4]^{2+}$  ( $[\text{Co}_4(\text{dpdH})_4(\text{O}_2\text{CH})_2]^{2+}$  19.7%)  $[\text{C}_{46}\text{H}_{38}\text{N}_8\text{O}_{12}\text{Co}_3\text{Zn}]^{2+}$  ( $[\text{Co}_3\text{Zn}(\text{dpdH})_4(\text{O}_2\text{CH})_2]^{2+}$  52.8%)  $[\text{C}_{46}\text{H}_{38}\text{N}_8\text{O}_{12}\text{Co}_2\text{Zn}_2]^{2+}$  ( $[\text{Co}_2\text{Zn}_2(\text{dpdH})_4(\text{O}_2\text{CH})_2]^{2+}$  26.4%)  $[\text{C}_{46}\text{H}_{38}\text{N}_8\text{O}_{12}\text{CoZn}_3]^{2+}$  ( $[\text{CoZn}_3(\text{dpdH})_4(\text{O}_2\text{CH})_2]^{2+}$  1.1%)

Solvent	Chemical formula	Density	Dielectric constant	Viscosity	Dipole moment
Ethanol	$\text{CH}_3\text{-CH}_2\text{-OH}$	0.789 g/ml	24.55	1.2 cP	1.7
Acetone	$\text{CH}_3\text{-C(=O)-CH}_3$	0.786 g/ml	21	0.32cP	2.7
Acetonitrile	$\text{CH}_3\text{-C}\equiv\text{N}$	0.786 g/ml	37.5	0.37cP	3.44
Toluene	$\text{C}_6\text{H}_5\text{-CH}_3$	0.867 g/ml	2.38	0.59cP	0.36

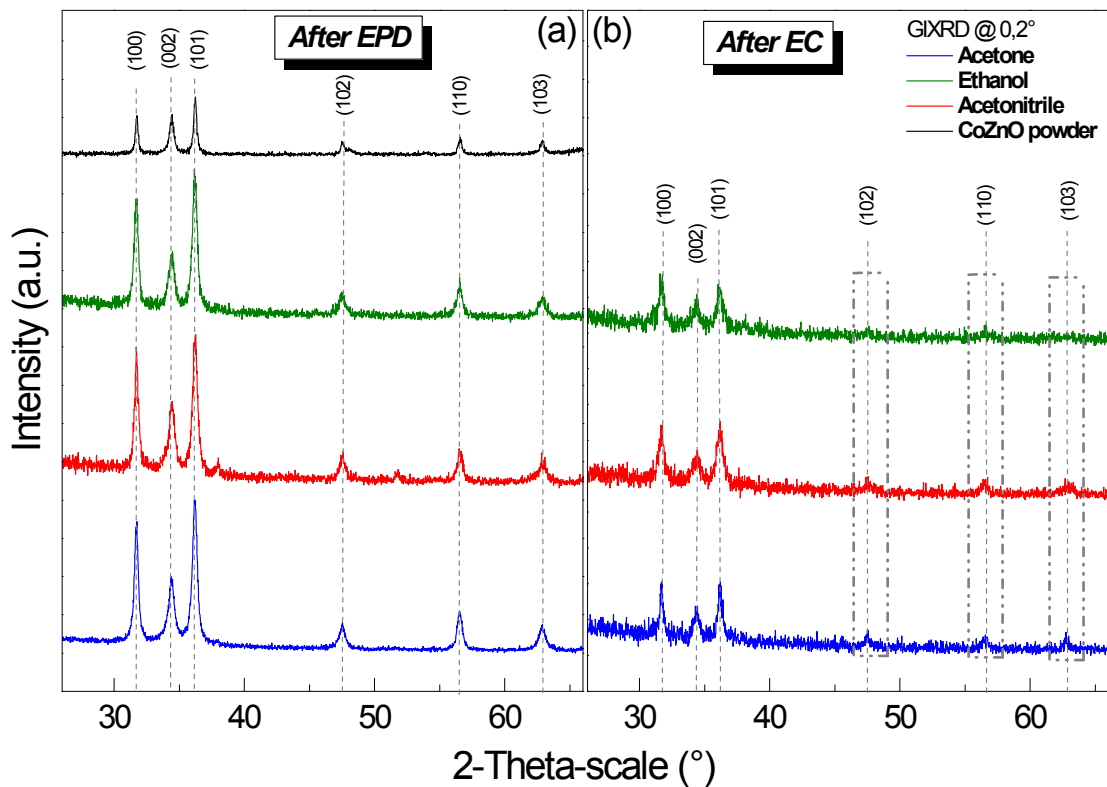
**Table T2:** Physical parameters of the used organic solutions.

	ZnO:Co in Ethanol	ZnO:Co in Acetone	ZnO:Co in Acetonitrile
<b><math>\mu</math> (<math>cm^2V^{-1}S^{-1}</math>) <math>\times 10^{-8}</math></b>			
4 min EPD	1.46	18.3	25.5
7 min EPD	1.46	16.7	23
10 min EPD	1.17	16.1	22.5
<b><math>\zeta</math> potential (mv)</b>			
4 min EPD	12.1	47.9	42.7
7 min EPD	12.1	43.7	38.4
10 min EPD	9.7	42.2	37.1
<b>Deposited Mass (mg)</b>			
4 min EPD	0.04	0.5	0.7
7 min EPD	0.07	0.8	1.1
10 min EPD	0.08	1.1	1.5
<b>Thickness (nm)</b>			
4 min EPD	49	654.58	1102.74
7 min EPD	125.29	1496.94	2318.36
10 min EPD	165.34	2330.87	3585.11

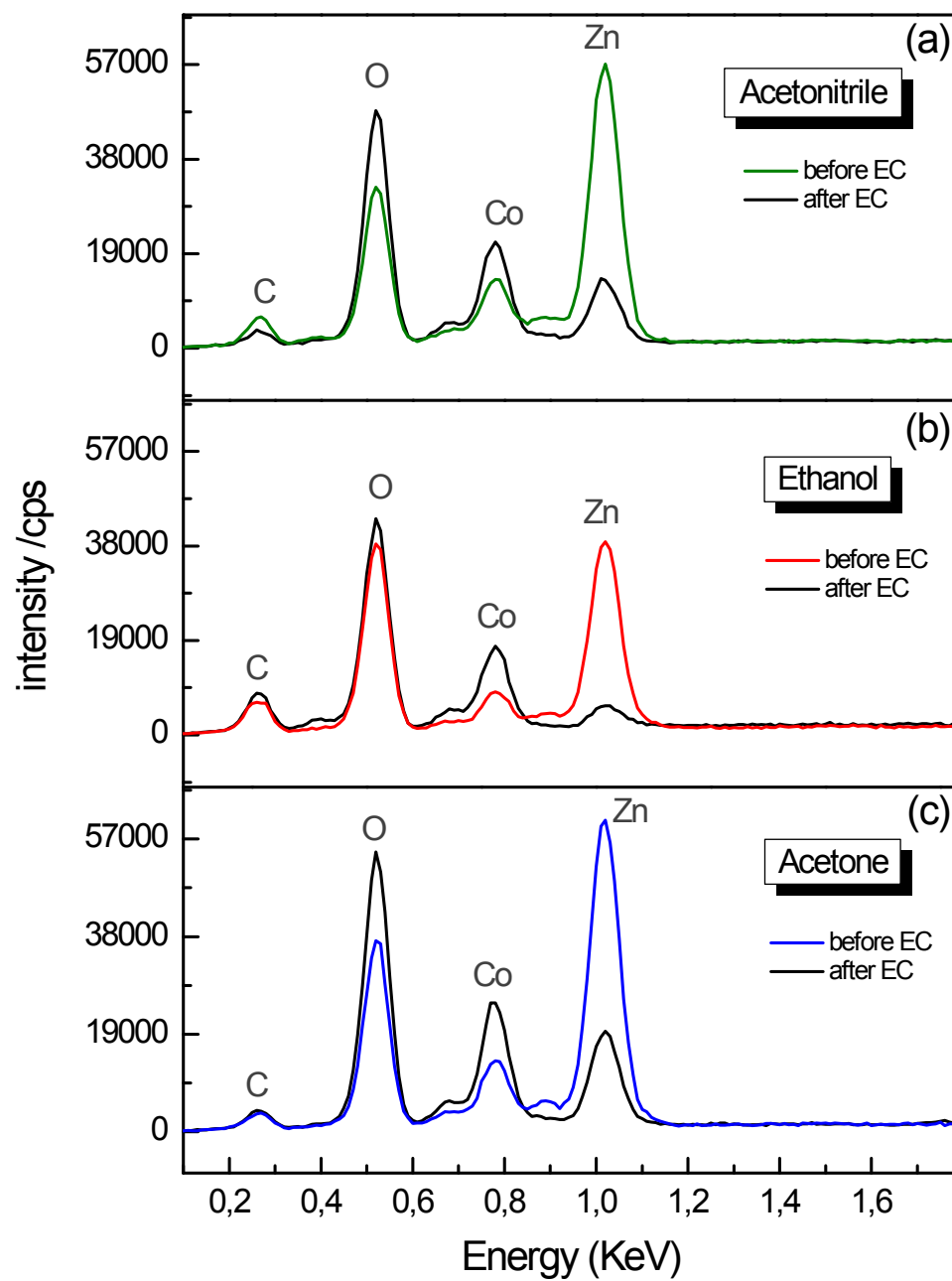
**Table T3: Electrophoretic deposition data**



**Figure S2:** Calculated absorption for the FTO support (black) and acetonitrile-, acetone- and ethanol-prepared FTO/ZnO:Co samples shown as green, blue and red curves, respectively.



**Figure S3:** GIXRD diagram of ZnO:Co prepared in Ethanol (red line), Acetone (blue line) and Acetonitrile (green line) (a) after electrophoretic deposition (b) after electrochemical measurements.



**Figure S4.** EDX spectra of ZnO:Co deposited on FTO in acetonitrile (a), ethanol (b) and acetone (c) before and after electrochemistry measurements.

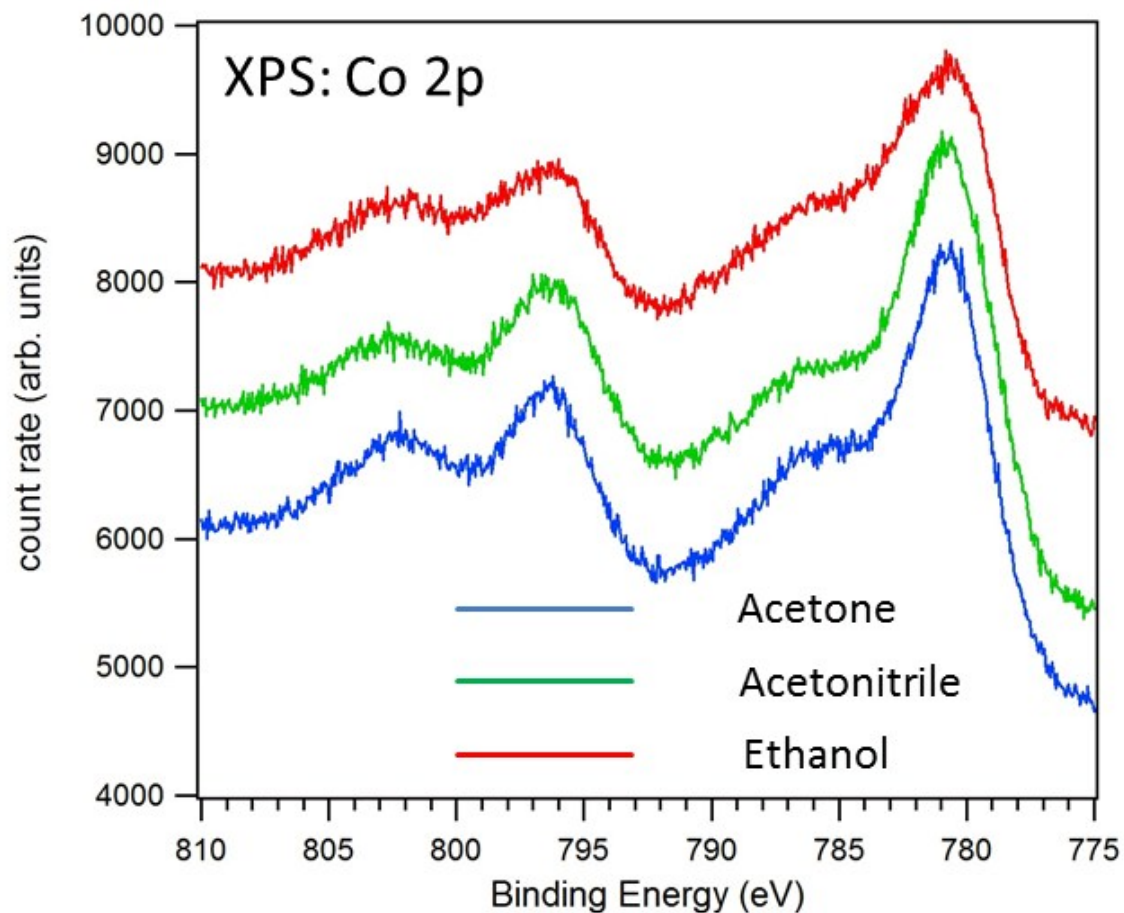
<b>solvent</b>	<b>EDX: Co:O:Zn - before EC</b>	<b>EDX: Co:Zn:O - after EC</b>
acetonitrile	C K 3.81+/-0.10 O K 19.13+/-0.20 K K 2.31+/-0.15 Co L 21.07+/-0.44 Zn L 53.68+/-0.38	C K 1.22+/-0.04 O K 26.34+/-0.24 K K 2.29+/-0.11 Co L 37.27+/-0.50 Zn L 13.86+/-0.25
acetone	C K 2.12+/-0.05 O K 20.91+/-0.19 K K 3.70+/-0.17 Co L 20.60+/-0.41 Zn L 52.67+/-0.36	C K 2.08+/-0.07 O K 28.64+/-0.22 K K 1.53+/-0.17 Ca K 1.05+/-0.09 Co L 43.69+/-0.52 Zn L 22.68+/-0.32
ethanol	C K 5.86+/-0.17 O K 28.71+/-0.32 Co L 17.24+/-0.50 Zn L 45.77+/-0.40 Sn L 2.41+/-0.54	C K 2.14+/-0.06 O K 24.15+/-0.26 K K 2.84+/-0.21 Co L 29.43+/-0.43 Zn L 3.88+/-0.10 Sn L 37.56+/-0.43

**Table T4:** EDX-quantitative elemental analysis of ZnO:Co films deposited on FTO supports. Data are given before and after electrochemical (EC) operation.

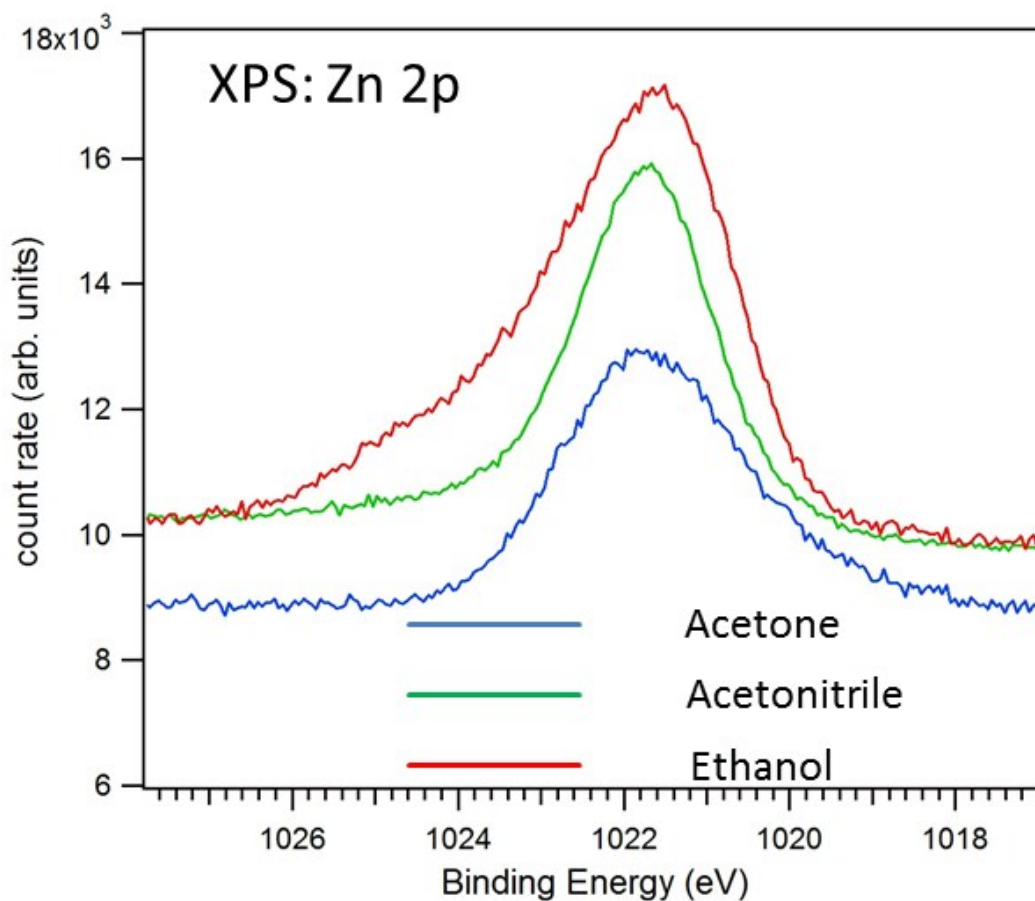
<b>Solvent</b>	<b>EDX: Co:O:Zn – before EC</b>	<b>EDX: Co:Zn:O – after EC</b>
acetonitrile	1 : 1 : 2.5	1 : 0.7 : 0.4
acetone	1 : 1 : 2.5	1 : 0.7 : 0.5
ethanol	1 : 1.6 : 2.6	1 : 0.8 : 0.1(3)

**Table T5:** Ratios of cobalt, oxygen and zinc calculated from table T4, above.

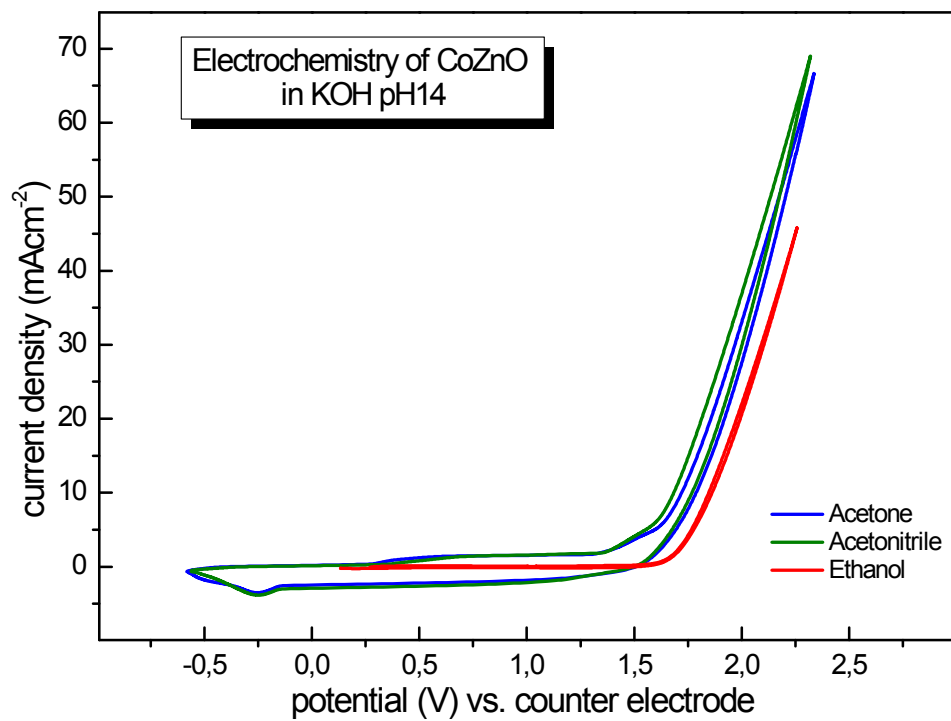




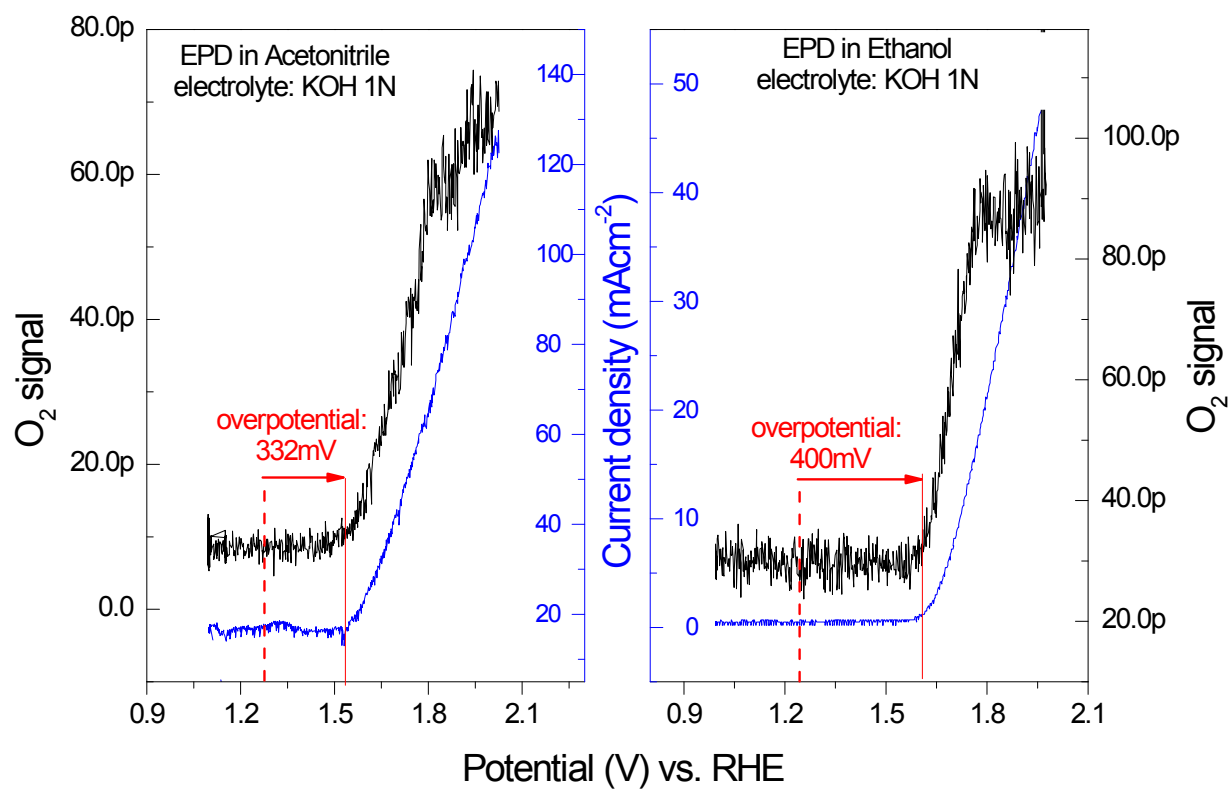
**Figure S5.** XPS analysis of the Co 2p core level for samples deposited from ethanol-, acetone- and acetonitrile-containing suspensions. The samples showed electrostatic charging which was corrected (with an accuracy of about  $\pm 0.5$  eV) by the C 1s line of adventitious carbon. The strong shake-up features of the curves near 785 and 802 eV suggest the presence of Co(II).



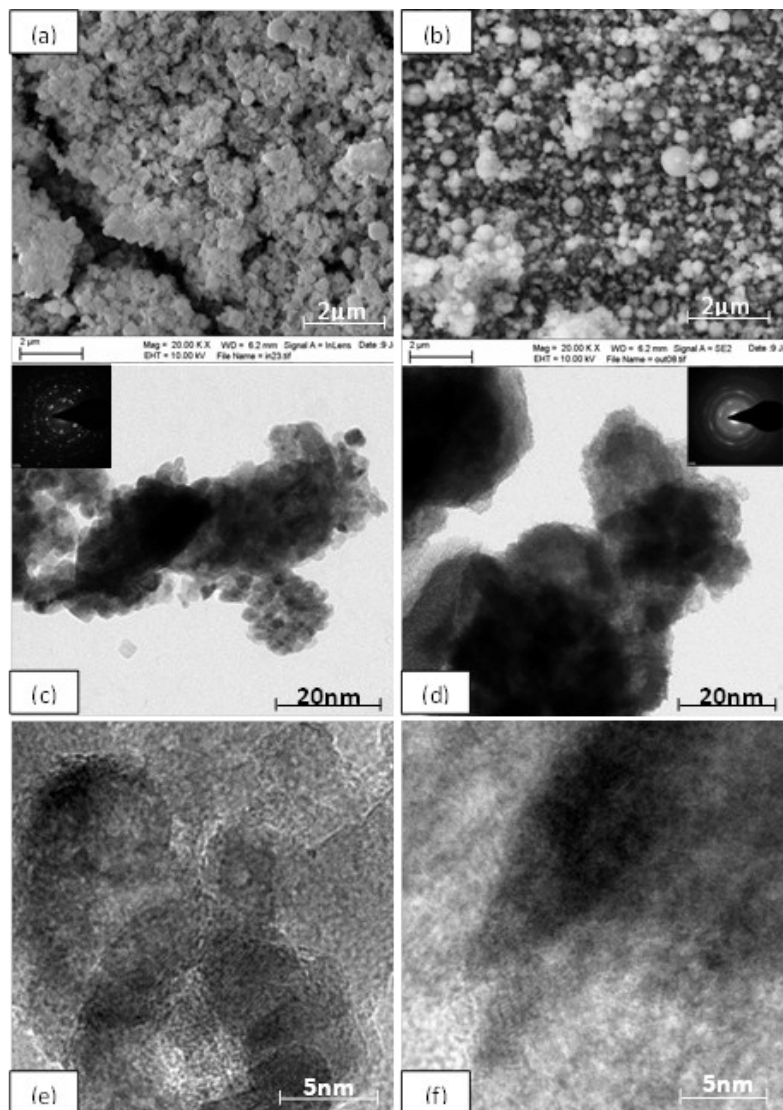
**Figure S6.** XPS analysis of the Zn 2p core level for samples deposited from ethanol-, acetone- and acetonitrile-containing suspensions. Asymmetric features particularly for ethanol- and acetone-prepared samples point to chemical transformations already during electrophoretic deposition. Due to sample charging and remnant inaccuracy of the binding energy after correction, the corresponding line positions cannot be unambiguously attributed to specific chemical states.



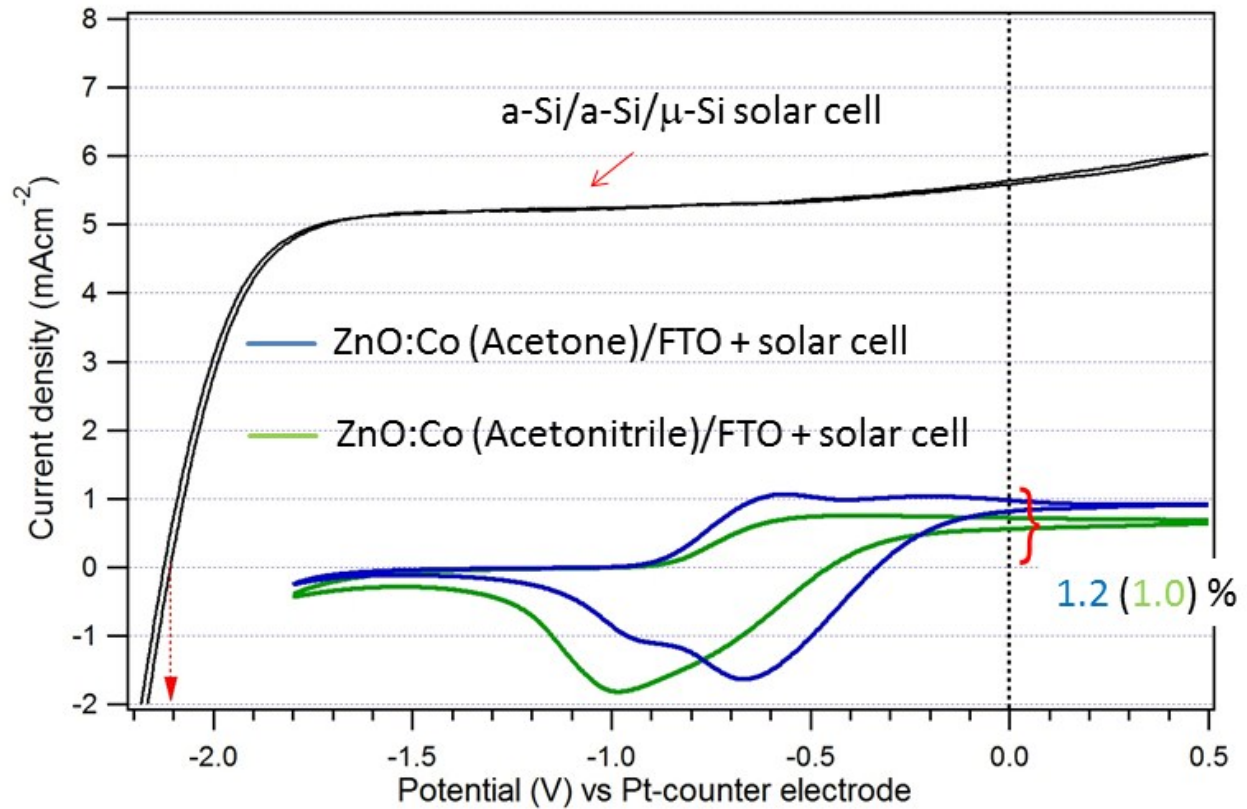
**Figure S7.** Two-electrode current-voltage measurements for ZnO:Co /FTO heterojunctions prepared from ethanol (red), acetone (blue) and acetonitrile (green) containing suspensions (compare Fig. 4 in the main manuscript).



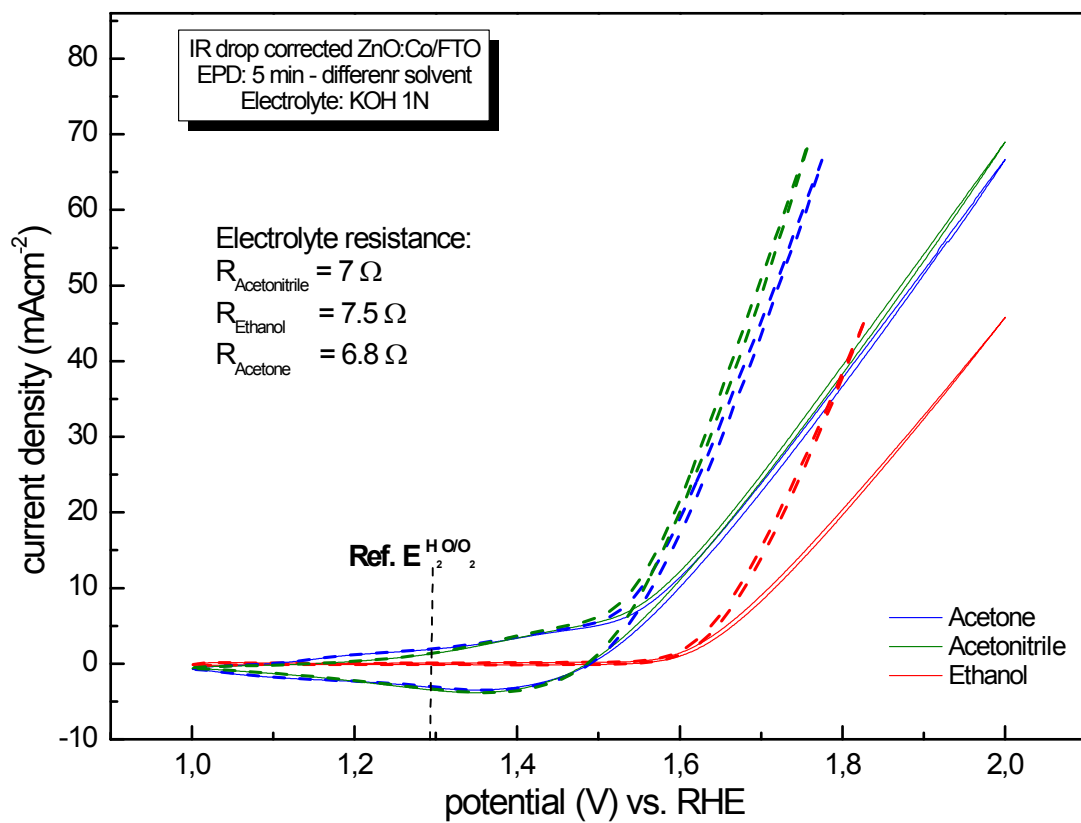
**Figure S8:** Differential electrochemical mass spectroscopy (DEMS) measurements for O<sub>2</sub> evolution on ZnO:Co deposited on FTO, dissolved in acetonitrile (a) and ethanol (b). Electrolyte: KOH 1N.



**Figure S9:** Microscopy characterization of ZnO:Co morphologies after EPD using acetone as electrolyte. (a) and (b) SEM surface view before and after electrochemistry, respectively. (c) and (d) corresponding TEM images of ZnO:Co lamellae before and after electrochemistry, respectively. (e) and (f) Magnified TEM images of ZnO:Co lamellae before and after the electrochemistry, respectively.



**Figure S10:** Photocurrent-voltage behavior of ZnO:Co /FTO samples on top of a triple-junction silicon solar cell. Black curve: with ZnO:Co prepared from acetonitrile solutions. Green curve: with ZnO:Co prepared from acetone solutions. The solar cell characteristic under illumination of 100 mWcm<sup>-2</sup> is shown in red.



**Figure S11:** IR-drop corrected current-voltage curves measured in 1N KOH, pH14 (dashed curves). The solid curves represent the respective measured data.