SUPPORTING INFORMATION

Electrocatalytic Water Oxidation Reaction Promoted by Cobalt-Prussian Blue and its Thermal Decomposition Product Under Mild Conditions

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1. Raman Spectroscopy

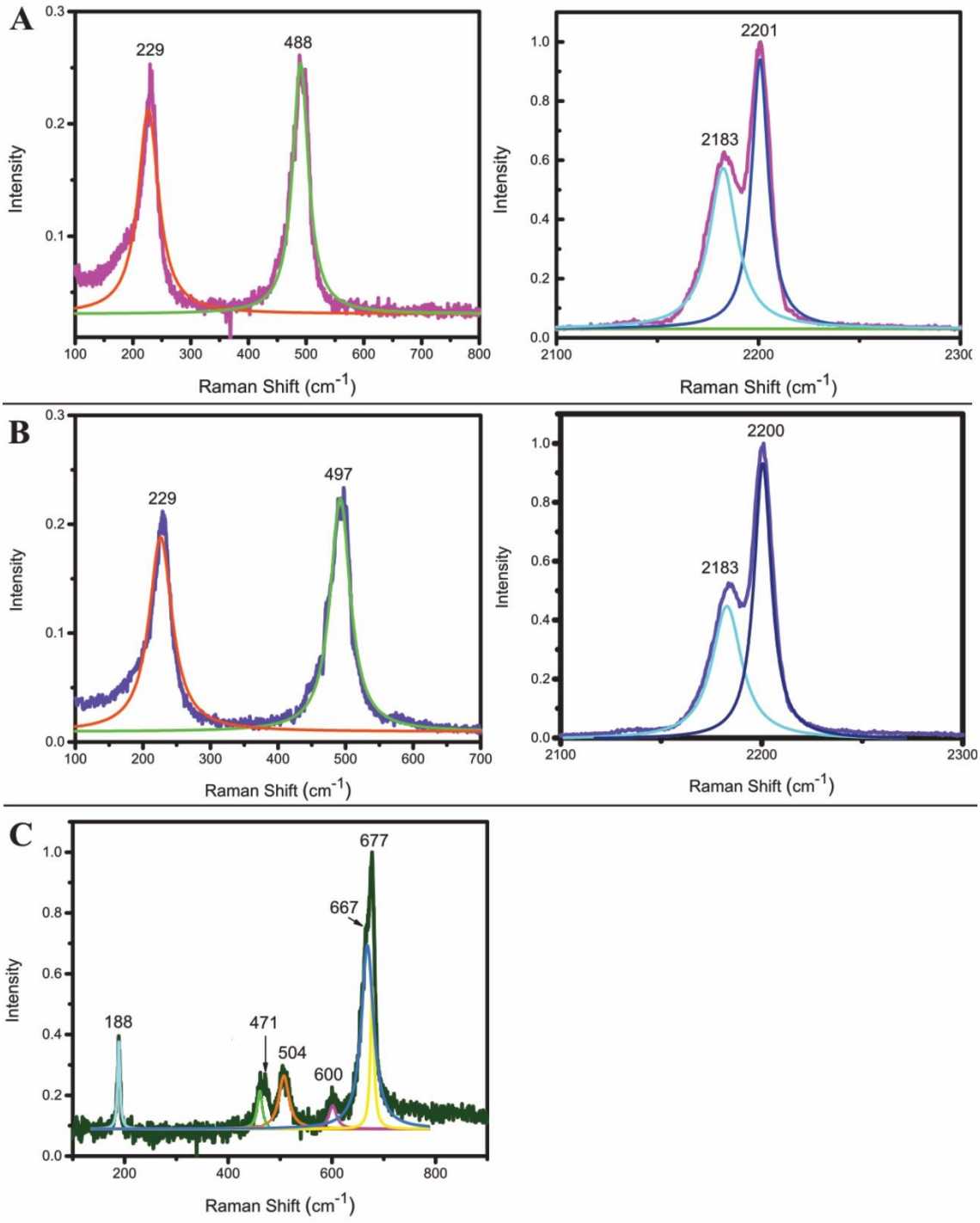

Figure S1. Deconvolution of Raman bands in Lorentz curves for a) Co-Co PBA 60, b) Co-Co PBA 200 and c) Co_3O_4.

Scanning electron microscopy

All catalysts were analyzed by scanning electron microscopy (Figure S2). Co-Co PBA was heated up to 60 °C and showed a smooth surface. After the treatment at 200 °C was observed a slight increase in roughness of the surface of the particle. The thermal treatment up to 400 °C increases the roughness of the particles for the Co_3O_4 oxide.

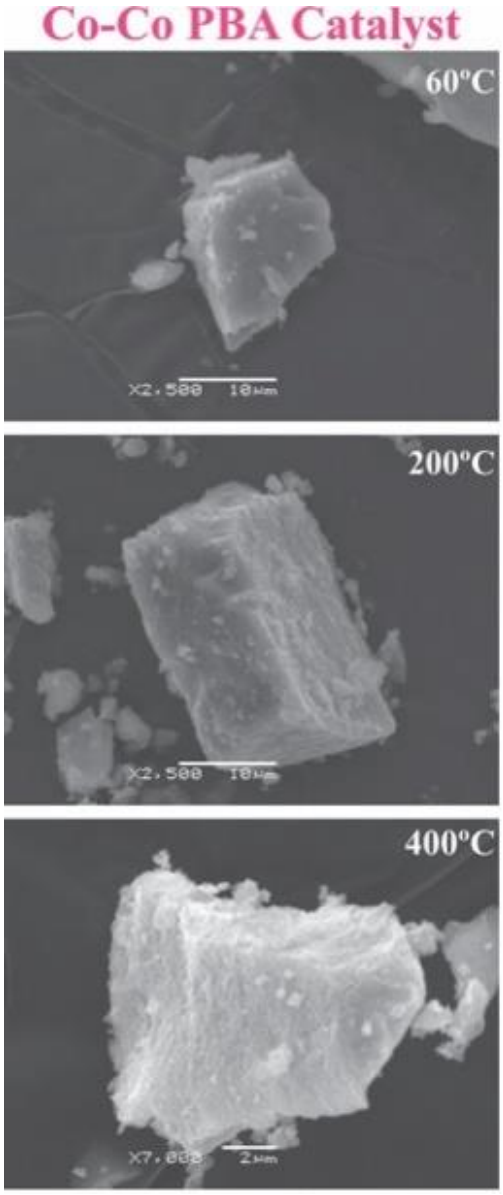

Figure S2. Scanning electron microscopy for each material for cobalt Prussian blue-based materials subjected to heat treatment at (top to botton) 60 °C, 200 °C and 400 °C.

Table S1. Electrochemical parameters and stability data for Co-Co PBA 60, Co-Co PBA 200 and Co_3O_4 films.

	Co-Co PBA		
Thermal treatment	**60 °C**	**200°C**	**400 °C**
	Co-Co PBA 60	**Co-Co PBA 200**	**Co_3O_4**
Onset Potential[a] (RHE)	1.74	1.69	1.81
η@1 mA cm^{-2}	561	480	599
η@5 mA cm^{-2}	910	656	758
η@10 mA cm^{-2}	1141	910	931
Tafel Slope (mV dec^{-1})	155	223	138
Stability[b] (i/ i_0),	1.0	0.98	0.51

[a]onset potential for faradaic process; [b] $i_0 = 20\ min, i = 120\ min$

Table S2. Comparison of the CO_3O_4 catalysts for OER and electrochemical parameters.

Catalysts	**Method preparation**	**Electrolyte**	**η@10 mA cm^{-2}**	**Tafel Slope (mV dec^{-1})**	**REF.**
Co_3O_4	**Co-PBA Thermal Decomposition**	**0.1 M KPi**	**931**	**138**	**This work**
Co_3O_4 UNA	Electrodeposition	1.0 M KPi	207	60	[1]
		0.1 M KOH	148	48	
Co_3O_4	Microwave heating	1 M KOH	298	105	[2]
Co3O4 nanocrystal	Hydrothermal	0.1 M KPi	511	104	[3]
Co_3O_4	Thermal decomposition from $Co(NO_3)_2$ $6H_2O$	1 M NaOH	433	96.7	[4]

*UNA - ultrathin nanosheet arrays

Impedance Spectroscopy

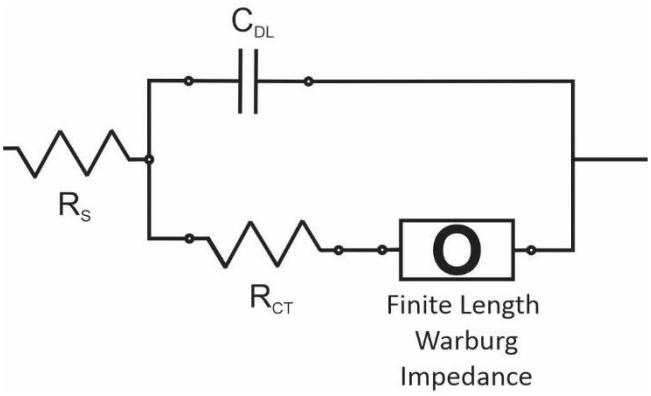

Figure S3. Representation of the modified Randles equivalent circuit used for all catalysts.

Calibration curve for oxygen evolution determination

All oxygen evolution data were based on GC measurements. The GC was calibrated for oxygen through the dilution of analytical standard of O_2 in the photoelectrochemical cell previously filled with an Argon gas (Ar). The PEC was purged with Ar for at least 30 minutes to completely remove gas impurities. A known volume of O_2 was then added to the system and the resulted mixture was sampled and analysed. At least three injections were made for each data point, and the average values were used to make the calibration curve. Each sample was analyzed a single time, maintaining the same conditions used in the previous calibration.

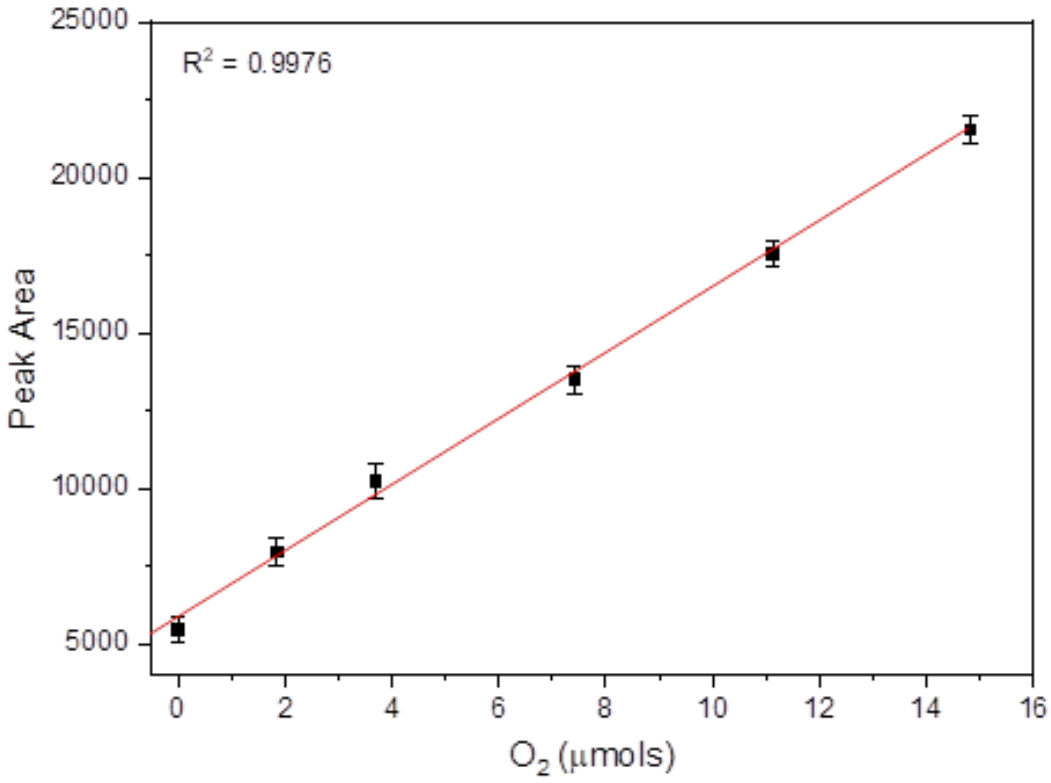

Figure S4. Calibration curve obtained different amounts of added O_2 in the PEC system filled with Argon.

References

[1] Zhang, L., Liu, B., Zhang, N., Ma, M., 2018. Electrosynthesis of Co3O4 and Co(OH)2 ultrathin nanosheet arrays for efficient electrocatalytic water splitting in alkaline and neutral media. Nano Research. doi:10.1007/s12274-017-1634-z

[2] Jadhav, A.R., Puguan, J.M.C., Kim, H., 2017. Microwave-Assisted Synthesis of a Stainless-Steel Mesh-Supported Co3O4 Microrod Array As a Highly Efficient Catalyst for Electrochemical Water Oxidation. ACS Sustainable Chemistry & Engineering.. doi:10.1021/acssuschemeng.7b03027

[3] Wu, J., Xue, Y., Yan, X., Yan, W., Cheng, Q., Xie, Y., 2012. Co3O4 nanocrystals on single-walled carbon nanotubes as a highly efficient oxygen-evolving catalyst. Nano Research. doi:10.1007/s12274-012-0237-y

[4] Jeon, H. S., Jee, M. S., Kim, H., Ahn, S. J., Hwang, Y. J., & Min, B. K. (2015). Simple Chemical Solution Deposition of Co3O4 Thin Film Electrocatalyst for Oxygen Evolution Reaction. ACS Applied Materials & Interfaces, 7(44), 24550–24555. doi:10.1021/acsami.5b06189