

# Supporting information

## Toward the Continuous Production of Multigram Quantities of Highly Uniform Supported Metallic Nanoparticles and Their Application for Synthesis of Superior Intermetallic Pt-Alloy ORR Electrocatalysts

*Luka Pavko<sup>a,b,‡</sup>, Matija Gatalo<sup>a,c,‡,\*</sup>, Gregor Križan<sup>d</sup>, Janez Križan<sup>d</sup>, Konrad Ehelebe<sup>e,f</sup>, Francisco Ruiz-Zepeda<sup>a</sup>, Martin Šala<sup>g</sup>, Goran Dražič<sup>a</sup>, Moritz Geuß<sup>e,f</sup>, Pascal Kaiser<sup>e,f</sup>, Marjan Bele<sup>a</sup>, Mitja Kostelec<sup>a,b</sup>, Tina Đukić<sup>a,b</sup>, Nigel Van de Velde<sup>a</sup>, Ivan Jerman<sup>a</sup>, Serhiy Cherevko<sup>e</sup>, Nejc Hodnik<sup>a</sup>, Boštjan Genorio<sup>b</sup>, Miran Gaberšček<sup>a,\*</sup>*

<sup>a</sup> Department of Materials Chemistry, National Institute of Chemistry, Hajdrihova 19, 1001 Ljubljana, Slovenia

<sup>b</sup> Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1001 Ljubljana, Slovenia

<sup>c</sup> ReCatalyst d.o.o., Hajdrihova 19, 1001 Ljubljana, Slovenia

<sup>d</sup> Ami d.o.o., Trstenjakova 5, 2250 Ptuj, Slovenia

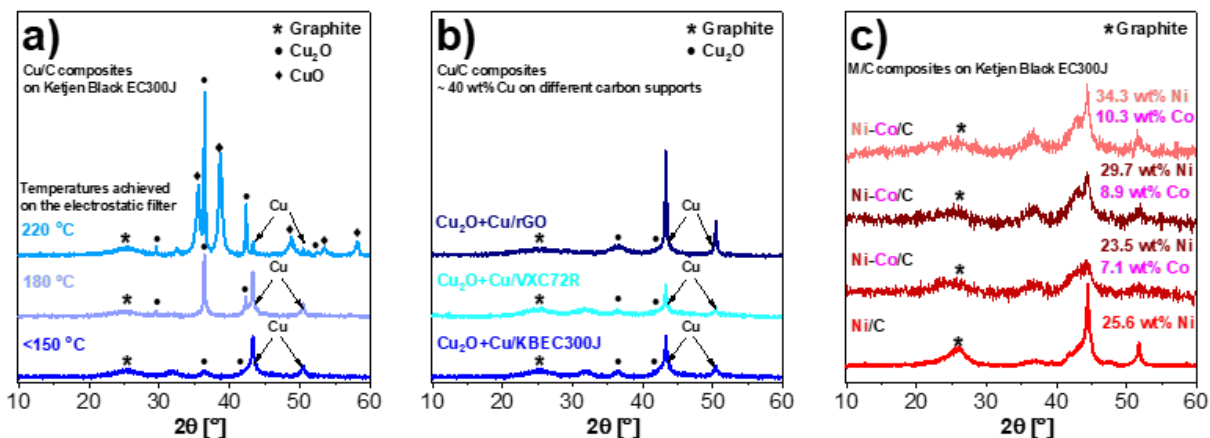
<sup>e</sup> Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (IEK-11), Forschungszentrum Jülich GmbH, Egerlandstr.3, 91058 Erlangen, Germany

<sup>f</sup> Department of Chemical and Biological Engineering, Friedrich-Alexander University Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

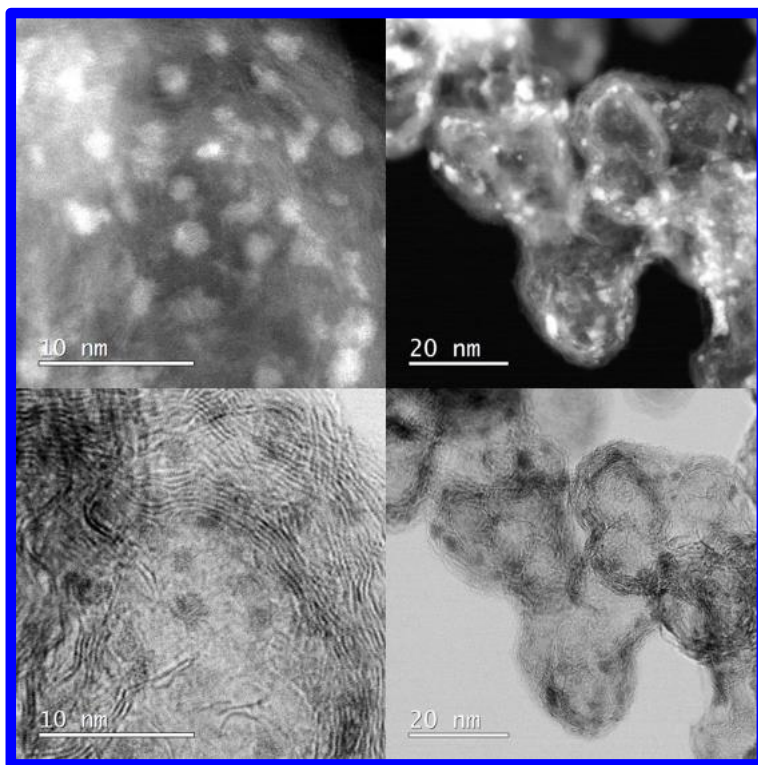
<sup>g</sup> Department of Analytical Chemistry, National Institute of Chemistry, Hajdrihova 19, 1001 Ljubljana, Slovenia

<sup>‡</sup> these authors contributed equally to this work

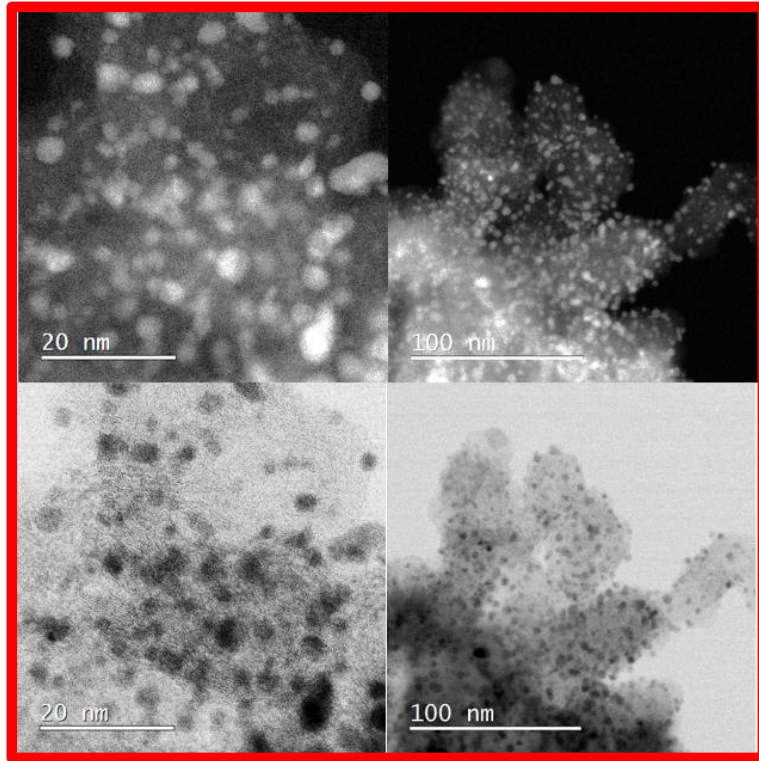
\* to whom correspondence should be addressed: [matija.gatalo@ki.si](mailto:matija.gatalo@ki.si), [miran.gaberscek@ki.si](mailto:miran.gaberscek@ki.si)



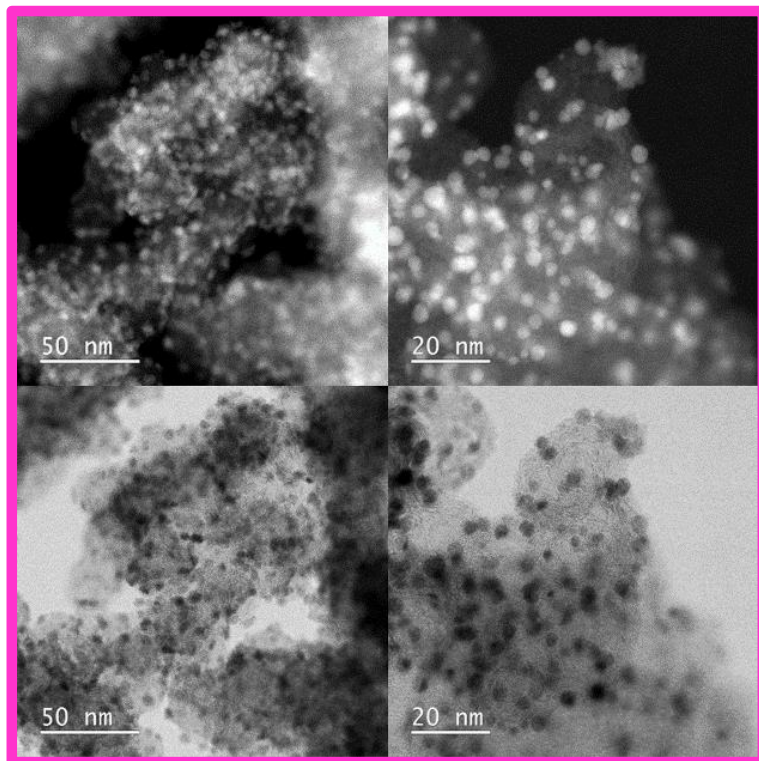
**Figure S1.** (a) XRD spectra comparison of Cu/C composites obtained at various temperatures at the electrostatic filter of the pulse combustion reactor. (b) XRD spectra comparison of Cu/C composites on various carbon-based supports prepared *via* the pulse combustion method. (c) XRD spectra comparison of Ni-Co composites (mix of two metals) with various metal loadings over carbon prepared *via* the pulse combustion method.<sup>1</sup>



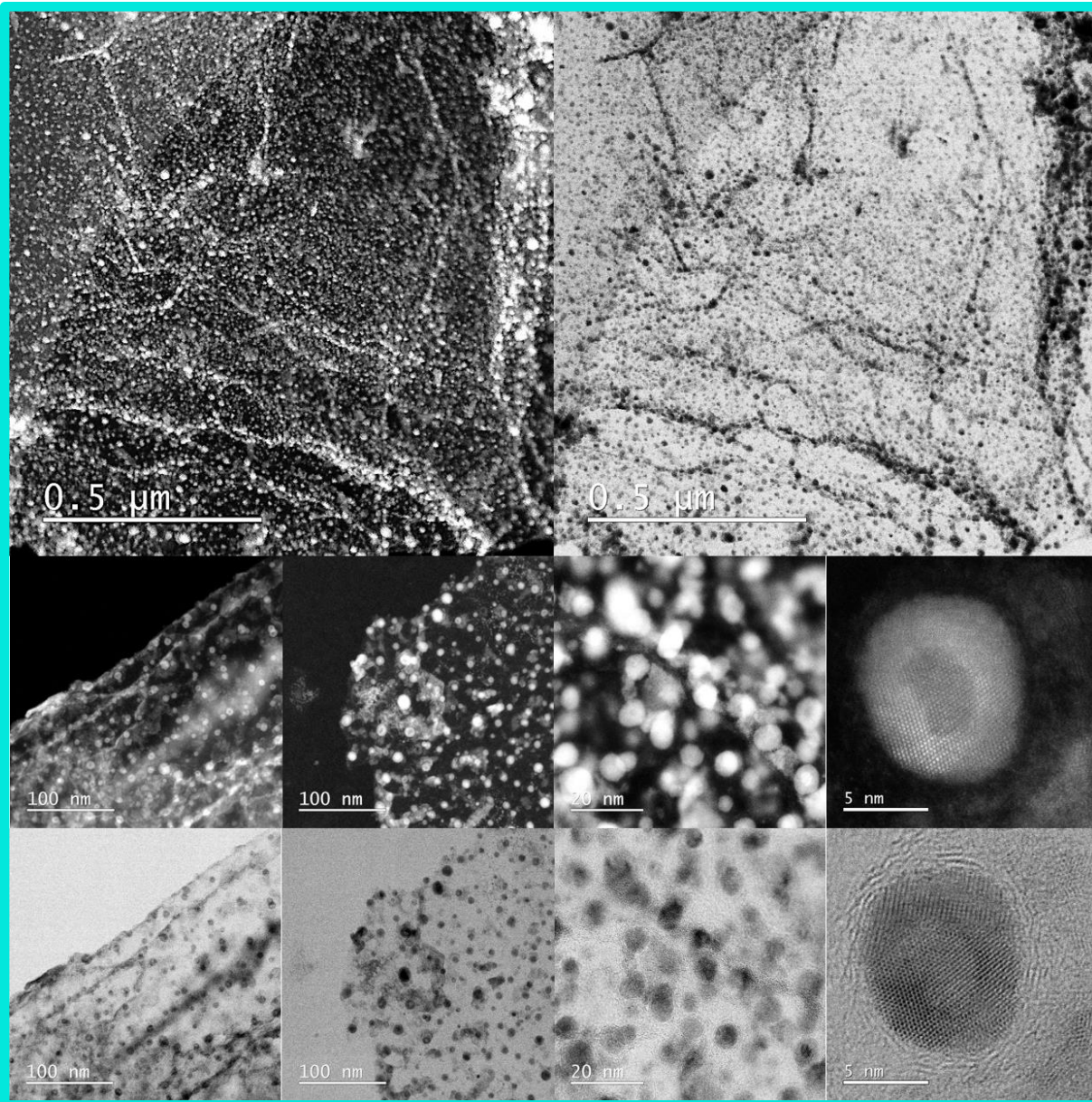
**Figure S2.** ADF and BF STEM images of Cu+Cu<sub>2</sub>O/C (C = Ketjen Black EC300J) composite prepared *via* the pulse combustion method.<sup>1</sup>



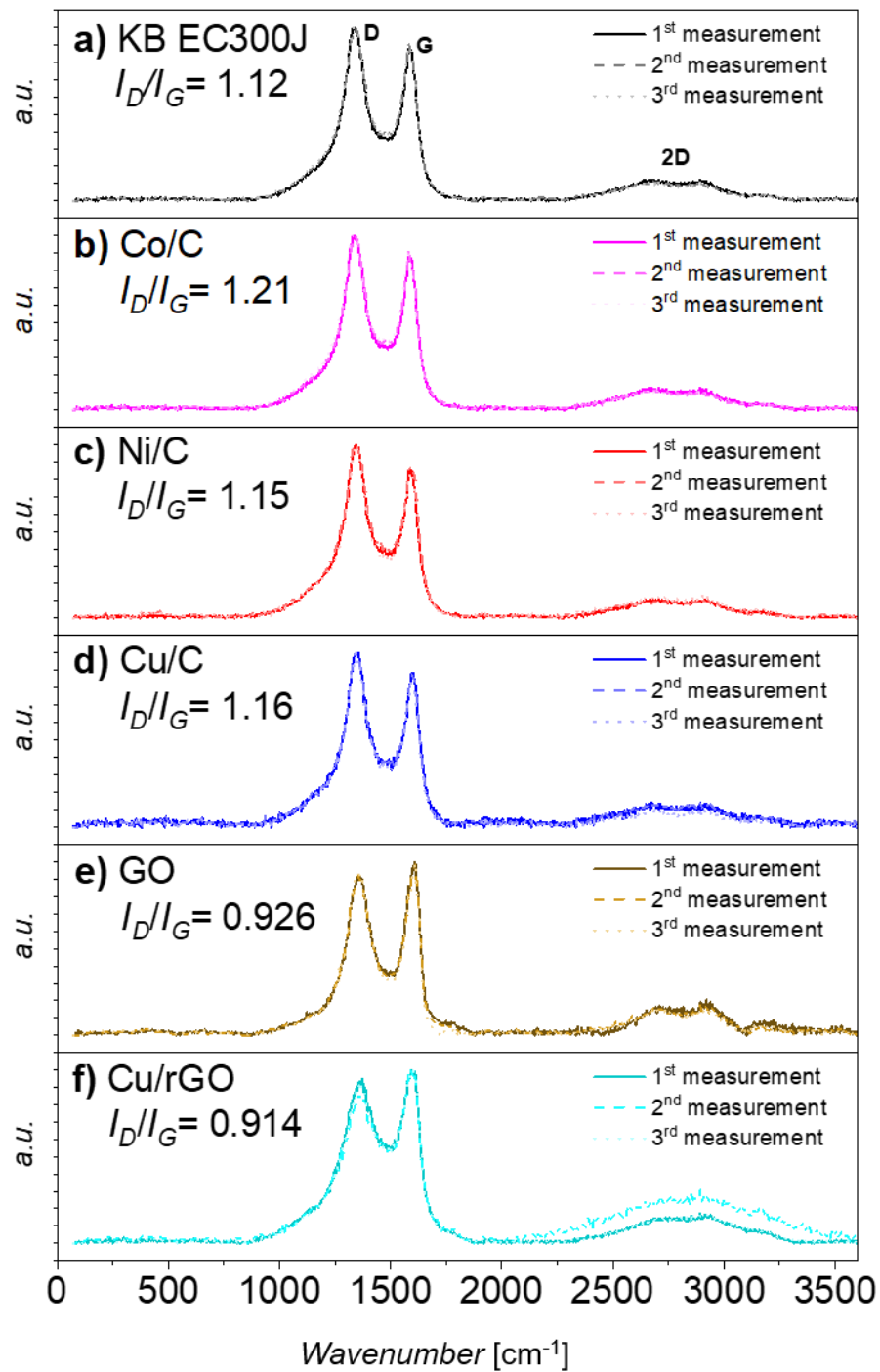
**Figure S3.** ADF and BF STEM images of Ni+NiO/C (C = Ketjen Black EC300J) composite prepared via the pulse combustion method.<sup>1</sup>



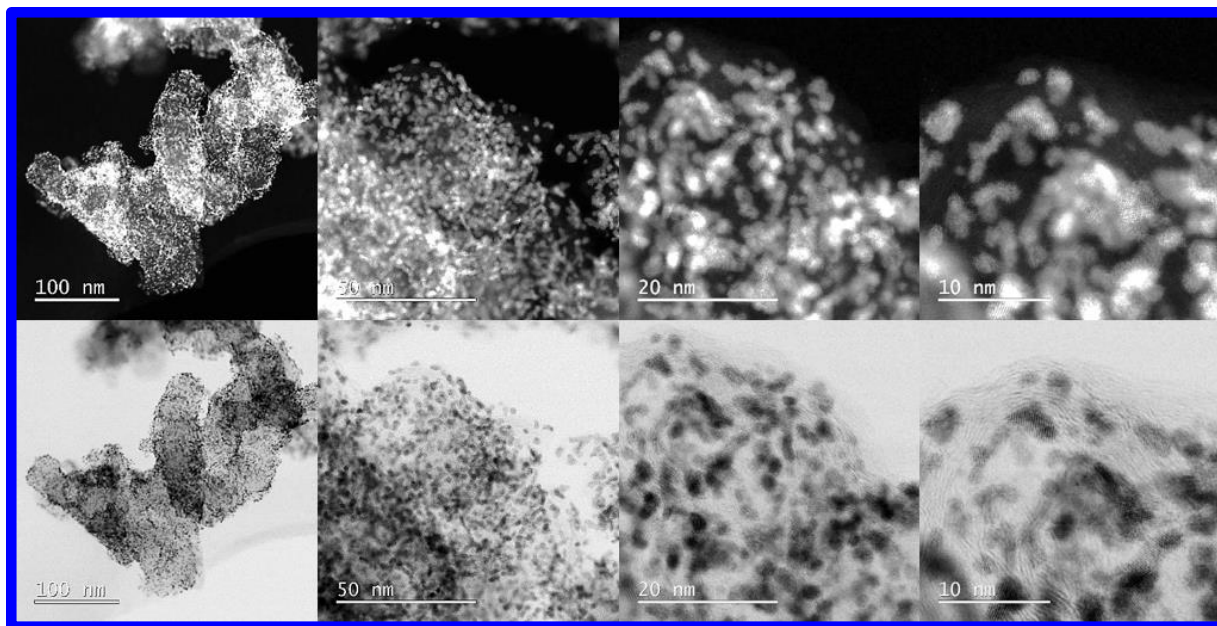
**Figure S4.** ADF and BF STEM images of Co+CoO/C (C = Ketjen Black EC300J) composite prepared via the pulse combustion method.<sup>1</sup>



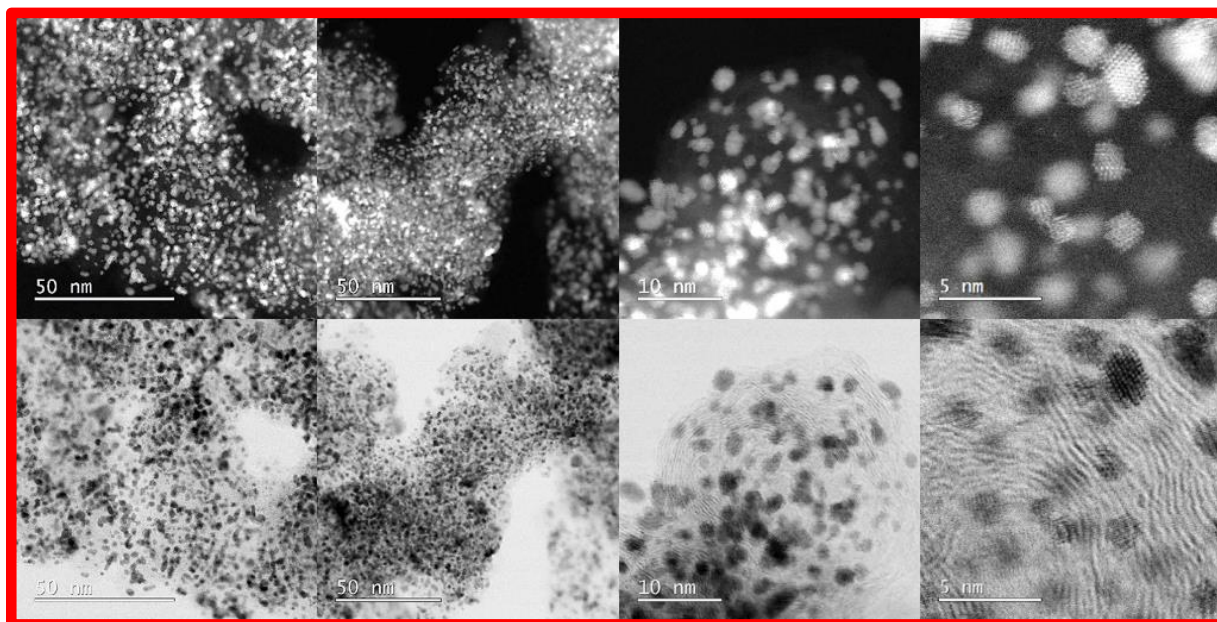
**Figure S5.** ADF and BF STEM images of Cu+Cu<sub>2</sub>O/rGO composite prepared *via* the pulse combustion method.<sup>1</sup>



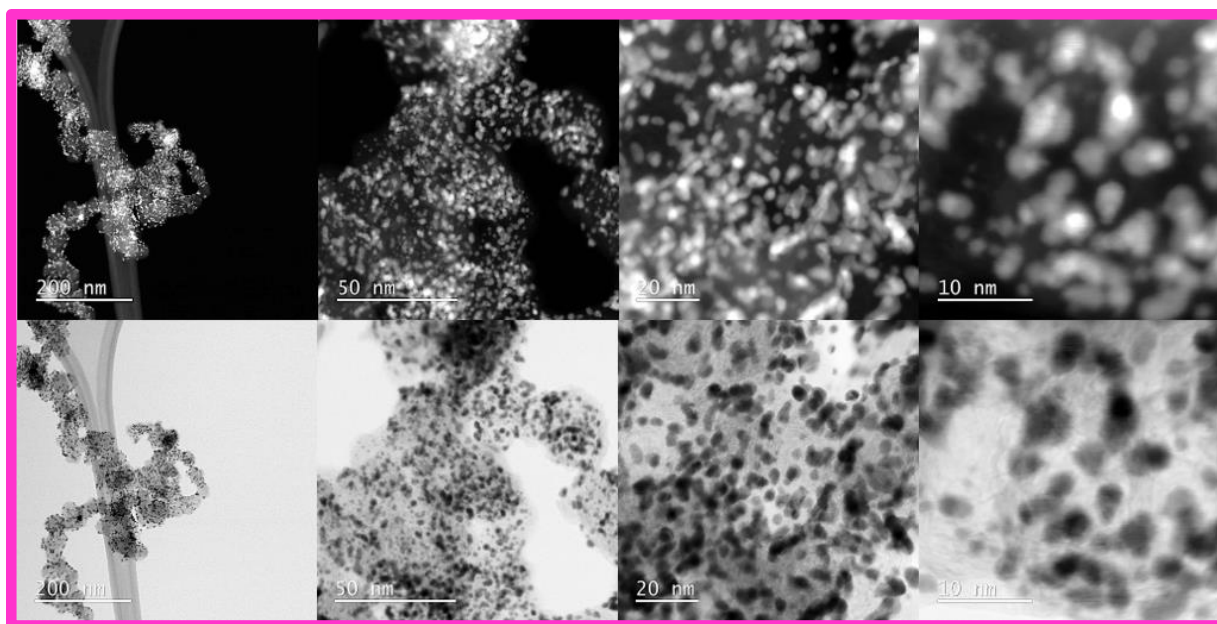
**Figure S6.** (a-f) Comparison of Raman spectra of starting carbon-based supports (Ketjen Black EC300J and GO) and corresponding M/C (M = Co, Ni and Cu) & M/rGO composites prepared *via* the pulse combustion method at 3 different locations for reproducibility.



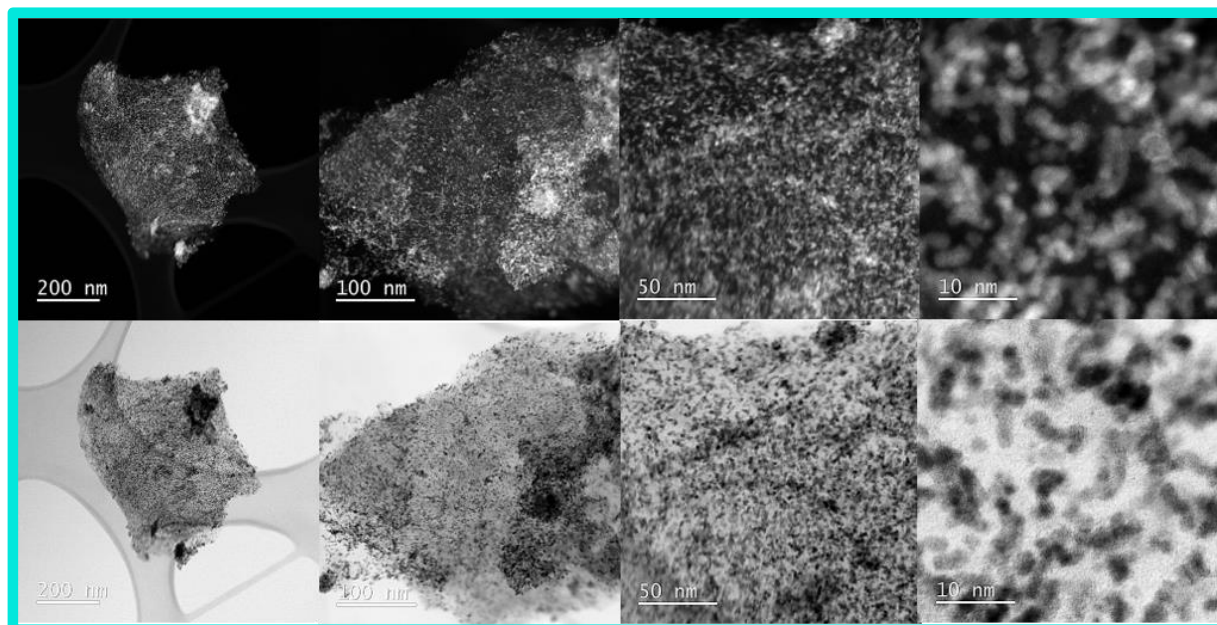
**Figure S7.** ADF and BF STEM images of PtCu+CuO/C (C = Ketjen Black EC300J) after Pt NP deposition step *via* GD method.<sup>1</sup>



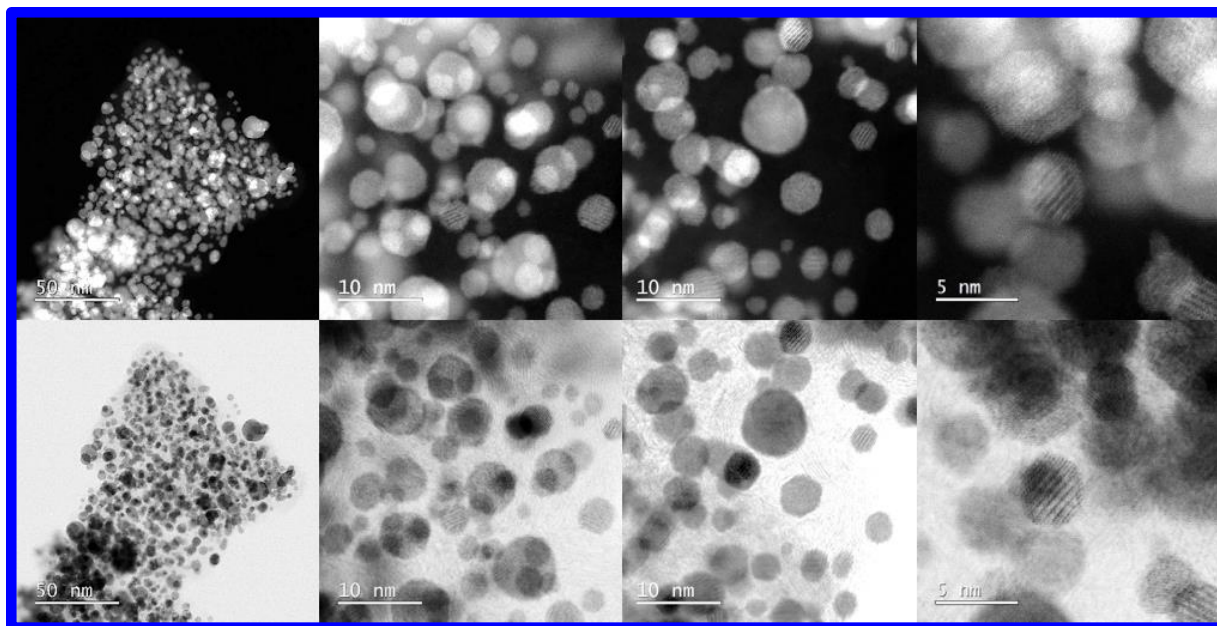
**Figure S8.** ADF and BF STEM images of Pt+Ni/C (C = Ketjen Black EC300J) after Pt NP deposition step *via* GD method.<sup>1</sup>



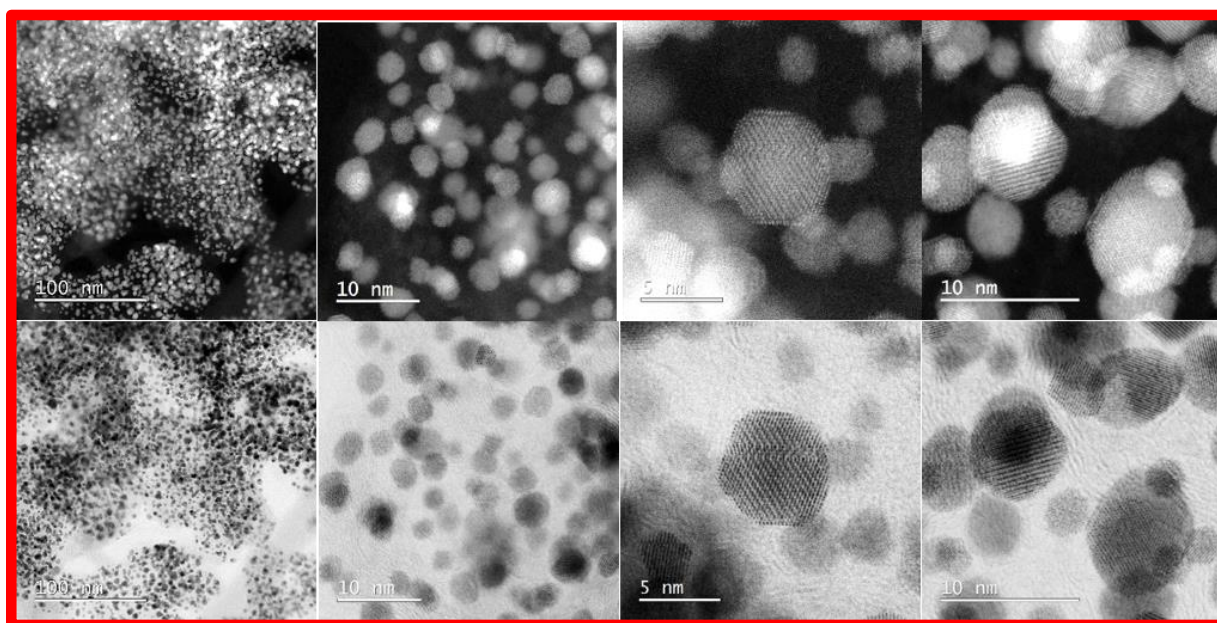
**Figure S9.** ADF and BF STEM images of Pt+Co/C (C = Ketjen Black EC300J) after Pt NP deposition step *via* GD method.<sup>1</sup>



**Figure S10.** ADF and BF STEM images of PtCu+CuO/rGO after Pt NP deposition step *via* GD method.<sup>1</sup>

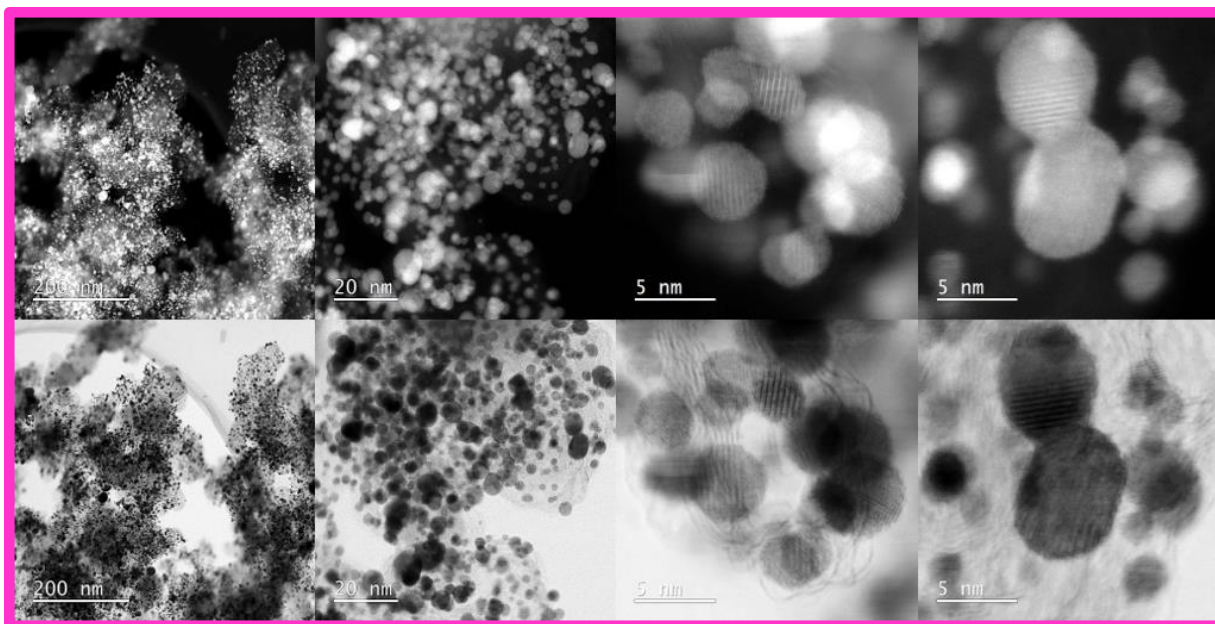


**Figure S11.** ADF and BF STEM imaging of d-int-Pt-Cu/C electrocatalyst.

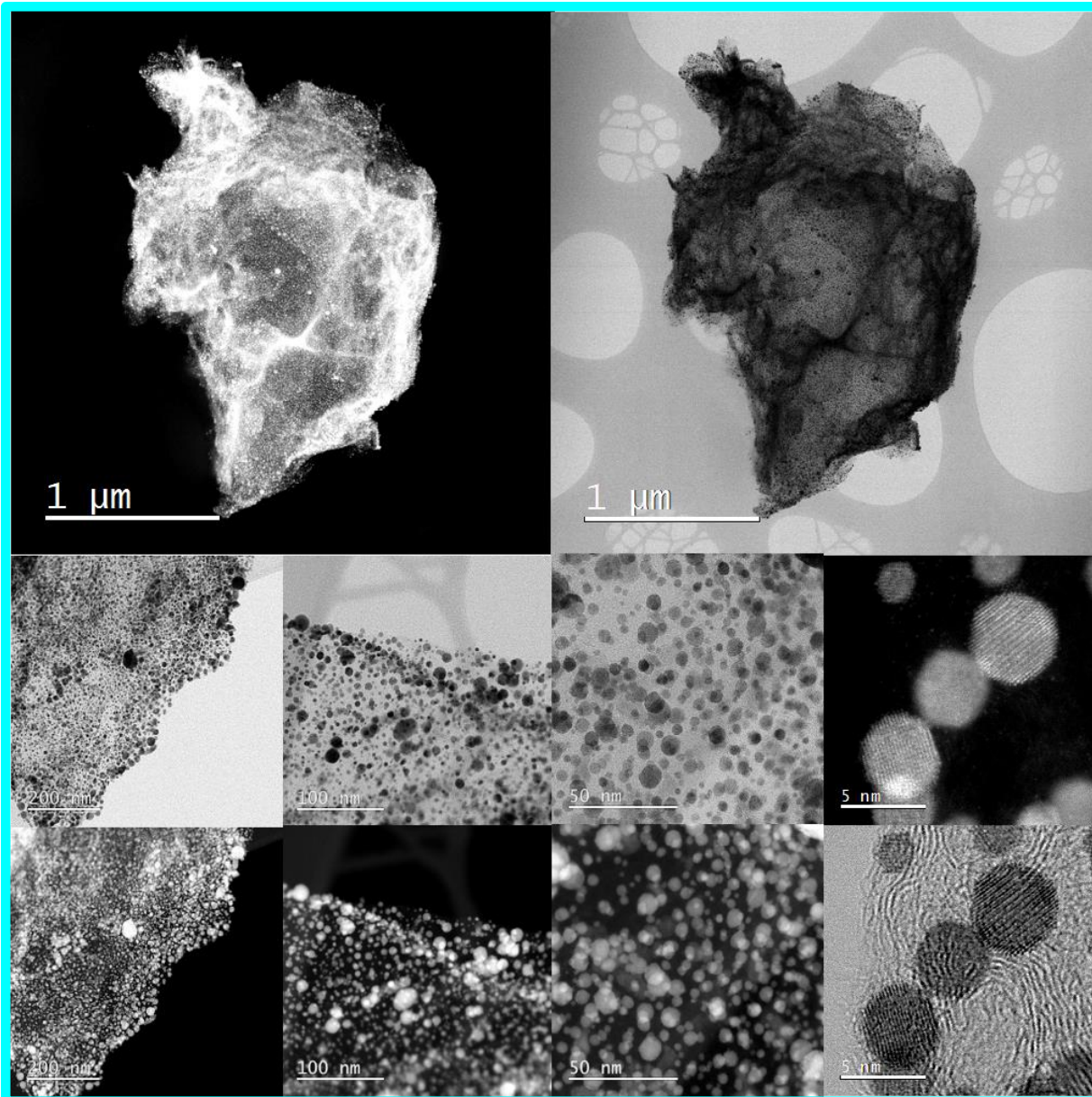


**Figure S12.** ADF and BF STEM imaging of d-int-Pt-Ni/C electrocatalyst.

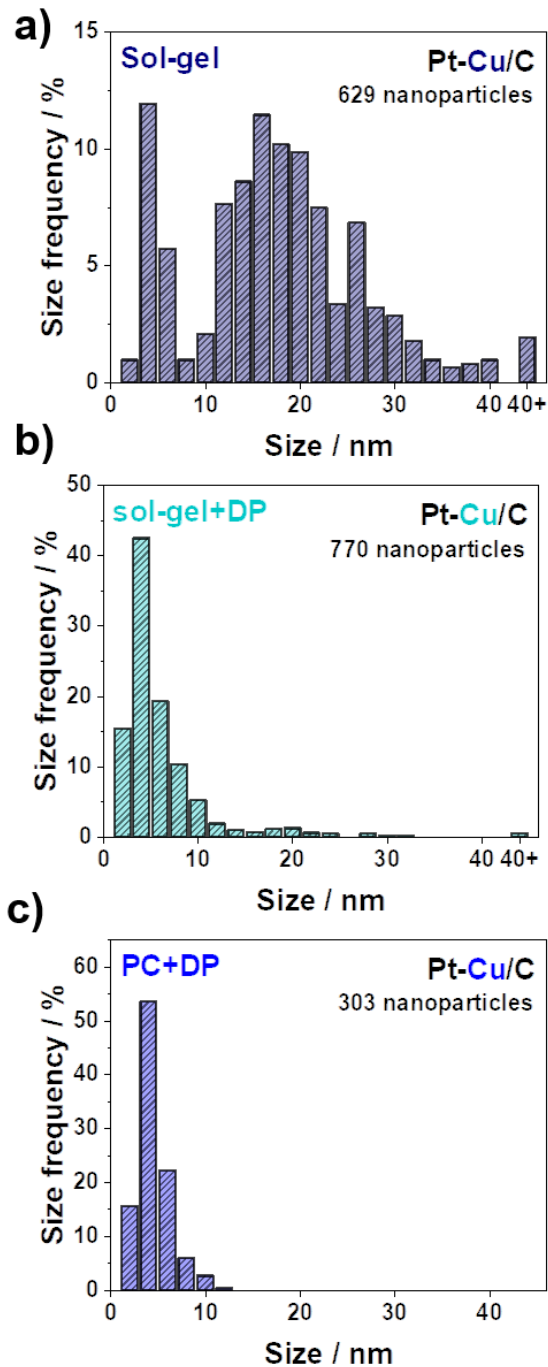


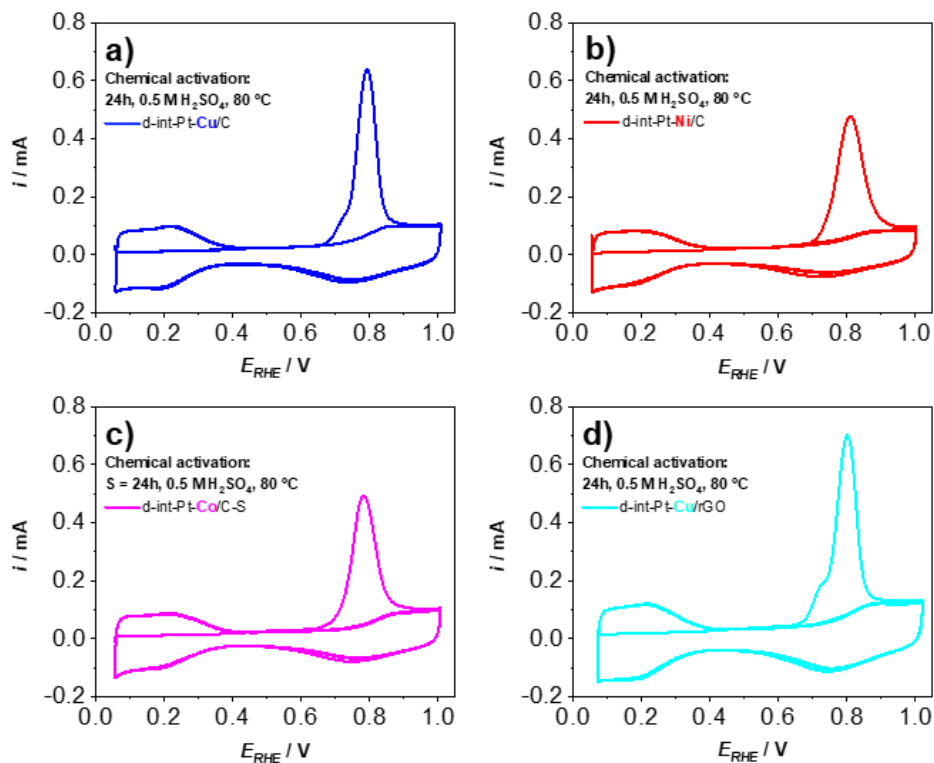


**Figure S13.** ADF and BF STEM imaging of d-int-Pt-Co/C electrocatalyst.

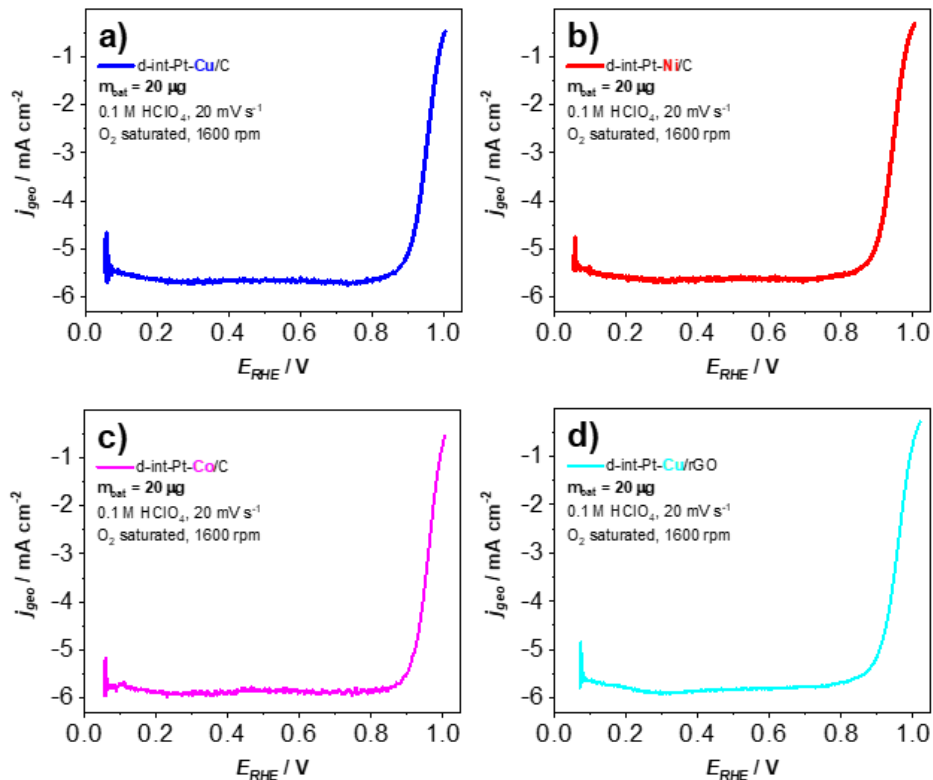


**Figure S14.** ADF and BF STEM imaging of d-Pt-Cu/C-rGO electrocatalyst.

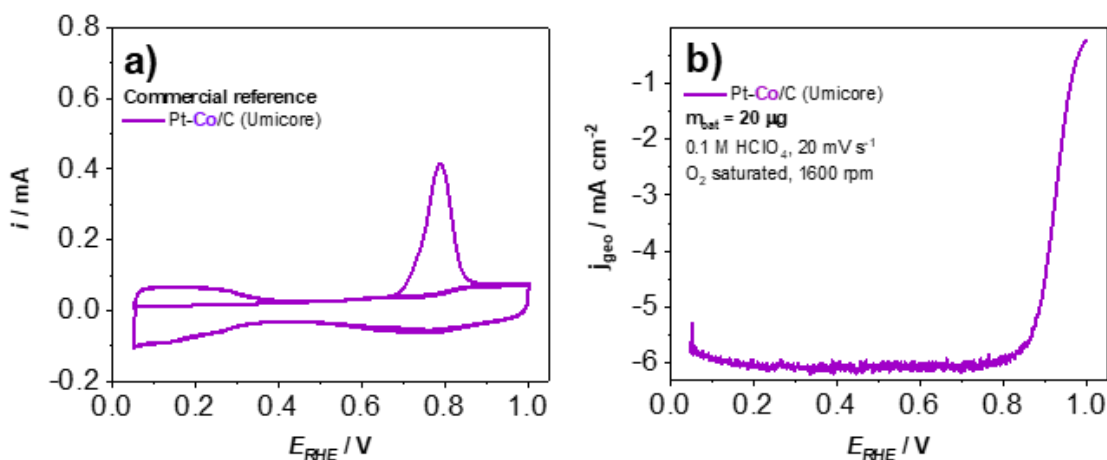




**Figure S16.** CO-electrooxidation CVs (0.05-1.0  $V_{RHE}$ , 20  $mV s^{-1}$ , no rotation, 0.1 M  $HClO_4$ , Ar saturated after  $CO_g$  adsorption) of (a) d-Pt-Cu/C-S, (b) d-Pt-Ni/C-S, (c) d-Pt-Co/C-S and (d) d-Pt-Cu/rGO-S electrocatalysts.



**Figure S17.** ORR polarization curves (0.05-1.0  $V_{RHE}$ , 20  $mV s^{-1}$ , 1600 rpm, iR and background corrected, 0.1 M  $HClO_4$ ,  $O_2$  saturated) of (a) d-Pt-Cu/C-S, (b) d-Pt-Ni/C-S, (c) d-Pt-Co/C-S and (d) d-Pt-Cu/rGO-S electrocatalysts.



**Figure S18.** CO-electrooxidation CV (0.05-1.0  $V_{RHE}$ , 20  $mV s^{-1}$ , no rotation, 0.1 M  $HClO_4$ , Ar saturated after  $CO_g$  adsorption) and ORR polarization curve (0.05-1.0  $V_{RHE}$ , 20  $mV s^{-1}$ , 1600 rpm, iR and background corrected, 0.1 M  $HClO_4$ ,  $O_2$  saturated) of Pt-Co/C electrocatalyst from Umicore (Elyst Pt30 0690) with 27 wt% Pt and approximately 3 wt% Co.

## REFERENCES

- (1) Gatalo, M.; Bele, M.; Ruiz-Zepeda, F.; Šest, E.; Šala, M.; Kamšek, A. R.; Maselj, N.; Galun, T.; Jovanovič, P.; Hodnik, N.; Gaberšček, M. A Double-Passivation Water-Based Galvanic Displacement Method for Reproducible Gram-Scale Production of High-Performance Platinum-Alloy Electrocatalysts. *Angew. Chemie* **2019**, *131* (38), 13400–13404. <https://doi.org/10.1002/ange.201903568>.
- (2) Zhang, J.; Sasaki, K.; Sutter, E.; Adžić, R. R. Stabilization of Platinum Oxygen-Reduction Electrocatalysts Using Gold Clusters. *Science* **2007**, *315* (5809), 220–222.
- (3) Zhang, J.; Vukmirović, M. B.; Xu, Y.; Mavrikakis, M.; Adžić, R. R. Controlling the Catalytic Activity of Platinum-Monolayer Electrocatalysts for Oxygen Reduction with Different Substrates. *Angew. Chemie* **2005**, *117* (14), 2170–2173. <https://doi.org/10.1002/ange.200462335>.
- (4) Gong, K.; Su, D.; Adžić, R. R. Platinum-Monolayer Shell on AuNi<sub>0.5</sub>Fe Nanoparticle Core Electrocatalyst with High Activity and Stability for the Oxygen Reduction Reaction. *J. Am. Chem. Soc.* **2010**, *132* (41), 14364–14366. <https://doi.org/10.1021/ja1063873>.
- (5) Sasaki, K.; Naohara, H.; Choi, Y.; Cai, Y.; Chen, W.-F.; Liu, P.; Adžić, R. R. Highly Stable Pt Monolayer on PdAu Nanoparticle Electrocatalysts for the Oxygen Reduction Reaction. *Nat. Commun.* **2012**, *3*, 1115. <https://doi.org/10.1038/ncomms2124>.
- (6) Gatalo, M.; Hodnik, N.; Gaberšček, M.; Bele, M. Method for Preparation of a Supported Noble Metal-Metal Alloy Composite, and the Obtained Supported Noble Metal-Metal Alloy Composite. PCT/EP2020/057334, 2020.