

Supporting Information

Quasi-in situ single-grain photoelectron microspectroscopy of Co/PPy nanocomposites under Oxygen Reduction Reaction

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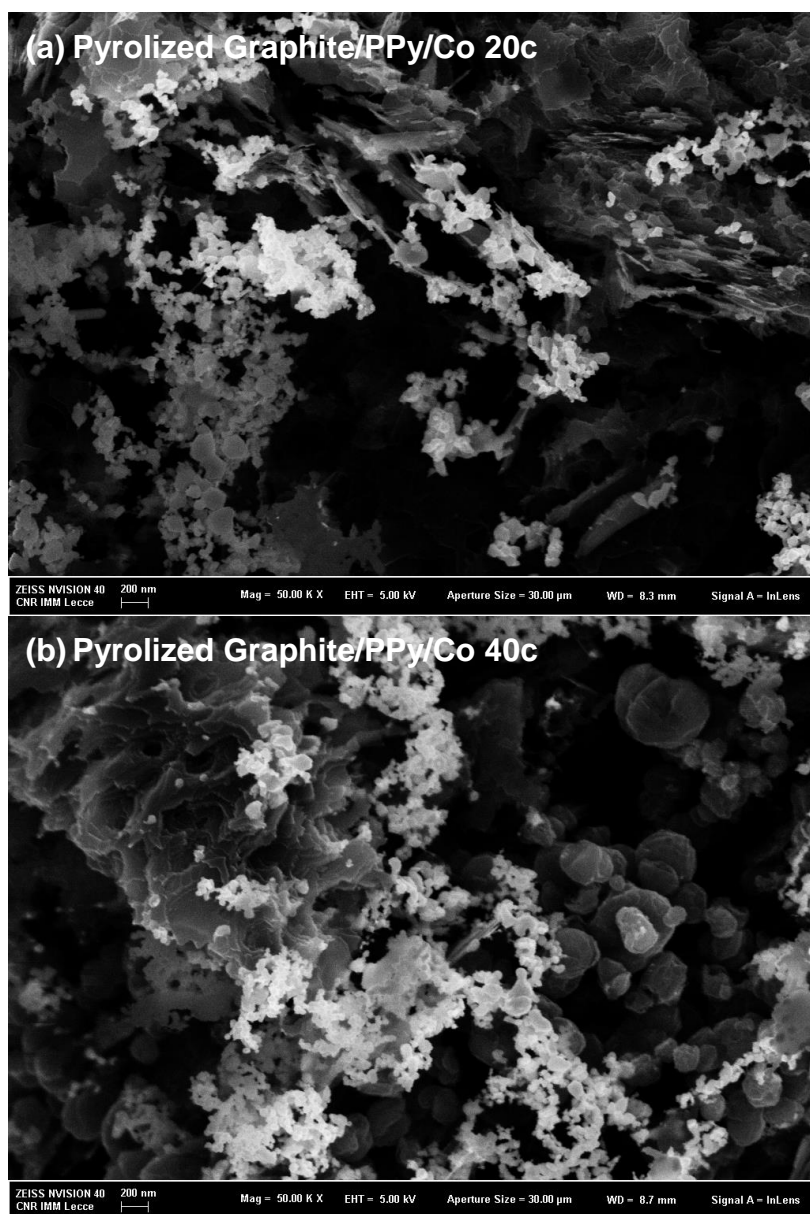


Figure S1. FE-SEM micrographs of pyrolyzed Co/PPy electrocatalyst on graphite electrode after (a) 20 and (b) 40 electrodeposition cycles.

Pyrolyzed Graphite/PPy/Co 60c

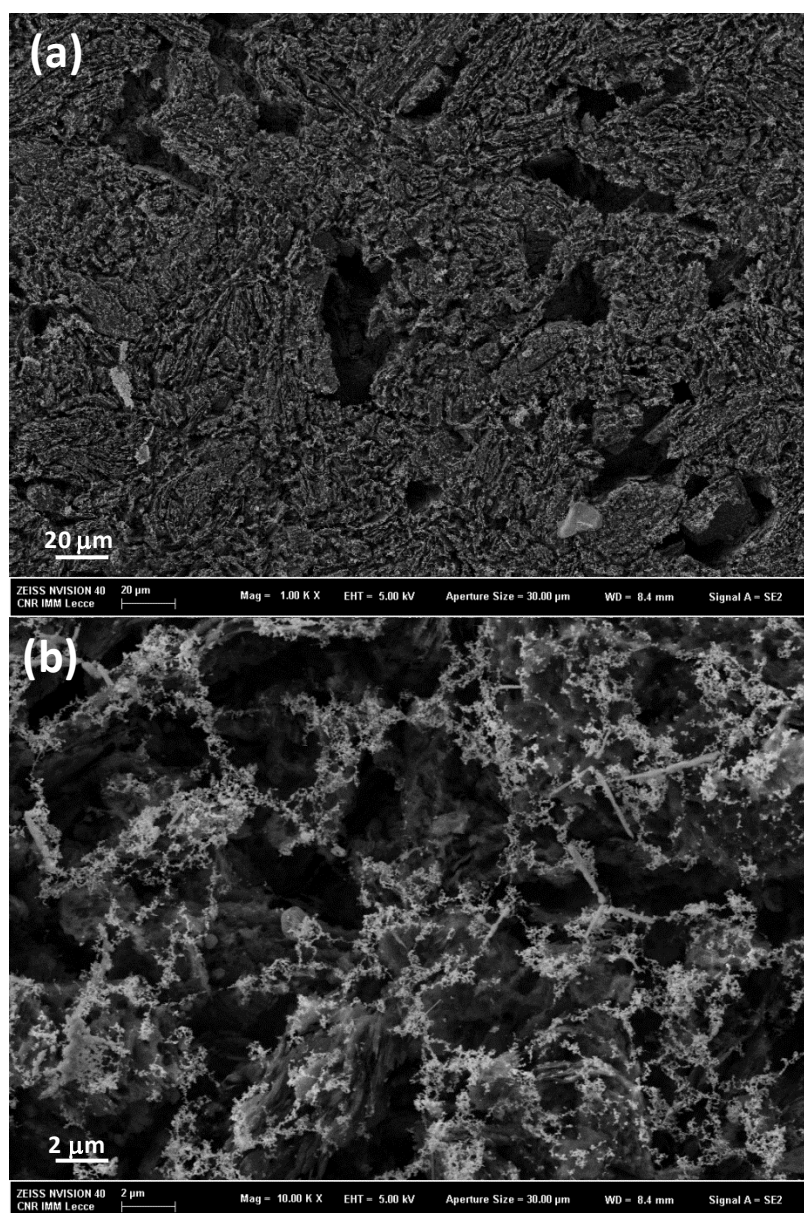


Figure S2. FE-SEM micrographs of pyrolyzed Co/PPy electrocatalyst on graphite electrode after 60 electrodeposition cycles at (a) low magnification and (b) high magnification.

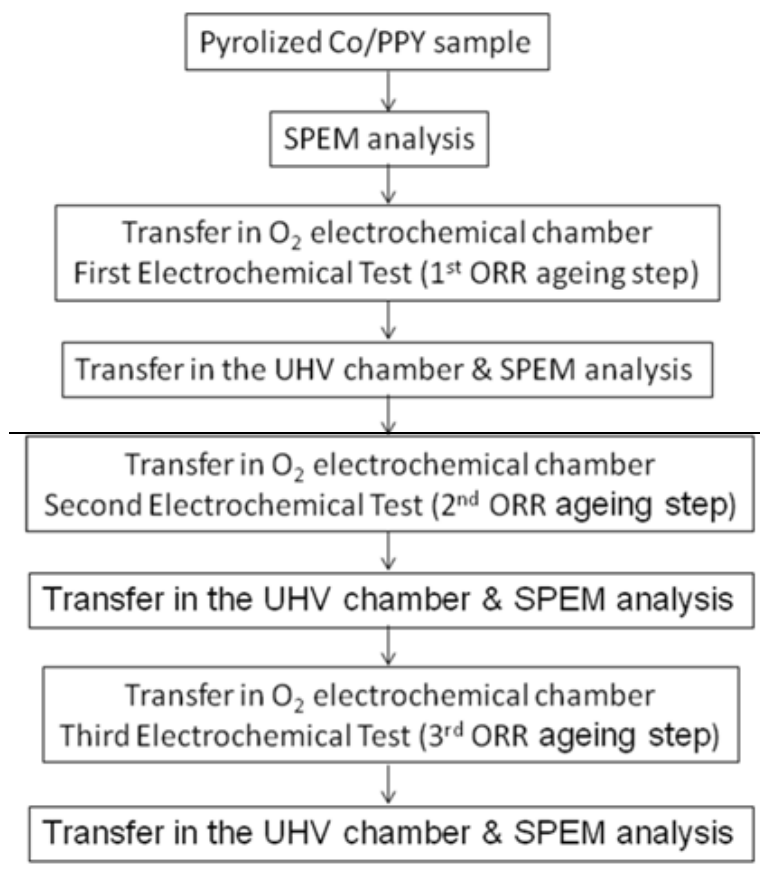


Figure S3. Steps of the procedure adopted for electrochemical quasi-in situ SPEM measurements.

Table S1. Oxygen reduction electrocatalytic parameters extracted from cyclic voltammograms recorded in O₂-saturated 0.5 M H₂SO₄ aqueous solution at scan rate 5 mV s⁻¹ (*i*_{peak}= peak current density; *E*_{onset}= onset potential; *E*_{1/2}= half-wave potential) for pyrolyzed Co/PPy samples electrosynthesized at different pulse cycles.

Co/PPy electrodeposition cycles	<i>E</i> _{onset} , V	<i>E</i> _{1/2} , V	<i>i</i> _{peak} , mA cm ⁻²
2	0.12	0.0148	2.89
20	0.071	0.0510	0.68
40	0.075	0.0355	0.66
60	0.083	0.0530	3.33

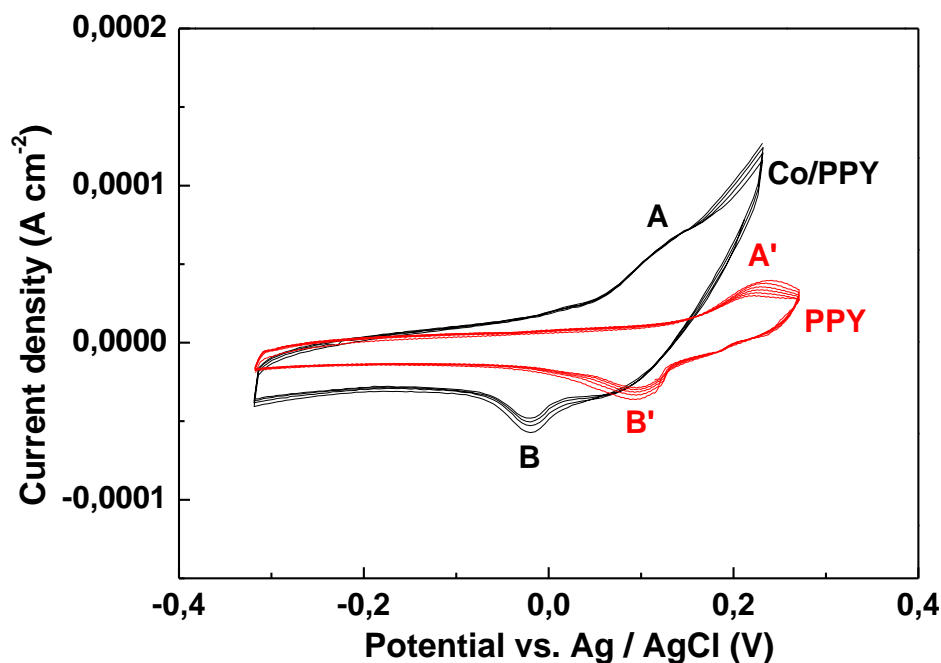


Figure S4 - Quasi-steady state cyclic voltammograms recorded in 0.5 M H₂SO₄ aqueous solution at scan rate 5 mV s⁻¹ under Ar atmosphere of pyrolyzed Co/PPy (60 electrodeposition cycles) and pyrolyzed PPy electrode.

In Figure S4 we report the cyclic voltammetries of a pyrolyzed PPy sample in the presence and in the absence of cobalt. From the comparison it appears that the redox behavior of pyrolyzed PPy is very similar to that of pyrolyzed Co/PPy. The peaks A (0.121 V) and B (-0.025 V) of the Co/PPy curve are shifted by about 100 mV with respect to the peaks A' (0.23 V) and B' (0.1 V) in the Co-free PPy sample (the potential values of the latter peak are very close to those reported for the 10th cycle of Figure 5a in Ref. S1 for unpyrolyzed Co/PPy, prepared in similar conditions similar to those employed in this work). By considering the literature reports of redox activity of PPy in sulphuric acid (expected to be great in non pyrolyzed sample)^{S2, S3} and the observed cathodic shift in the doping/undoping waves of PPy after the electrochemical incorporation of cobalt^{S4}, we conclude that these peaks cannot be straightforwardly attributed to the Co(III)/Co(II) couple (as suggested in Ref. 1), but a deeper analysis also accounting for the presence of PPy should be carried out.

Possible explanations of the observed electrochemical stability of pyrolyzed Co/PPy in argon atmosphere can be found in the presence of multiplicity of chemical and morphological states of Co/PPy forming as a result of pyrolysis. As a consequence, the Co₃O₄ and CoO grains do not exhibit a perfect crystallographic structure, but rather they consist in aggregates of varied and complex chemical nature (such as Co(II,III) containing O-Co, N-Co and N-C moieties^{S5}, fragments of the original Co/PPy and graphitized PPy), where Co(III) can be kinetically and/or mechanically protected by electrochemical reduction in argon atmosphere. The presence of insoluble Co-N moieties after pyrolysis in the inner part of Co oxide grains cannot be excluded by XPS spectra (Figure 5), nevertheless a clear identification is not possible due to the high overlap of the Co-N and Co-O spectral components. The formation of a graphitic protective layer during pyrolysis of the polymeric film covering the Co grain is also a possible explanation^{S6, S7} similarly to the case of pyrolyzed cobalt macrocycles, where the presence of a graphitic envelope and its action against dissolution of catalytic particles in acidic media have been demonstrated^{S8-S9}. Of course, experimental verifications of these hypothesis need a detailed separate study, beyond the scope of this paper.

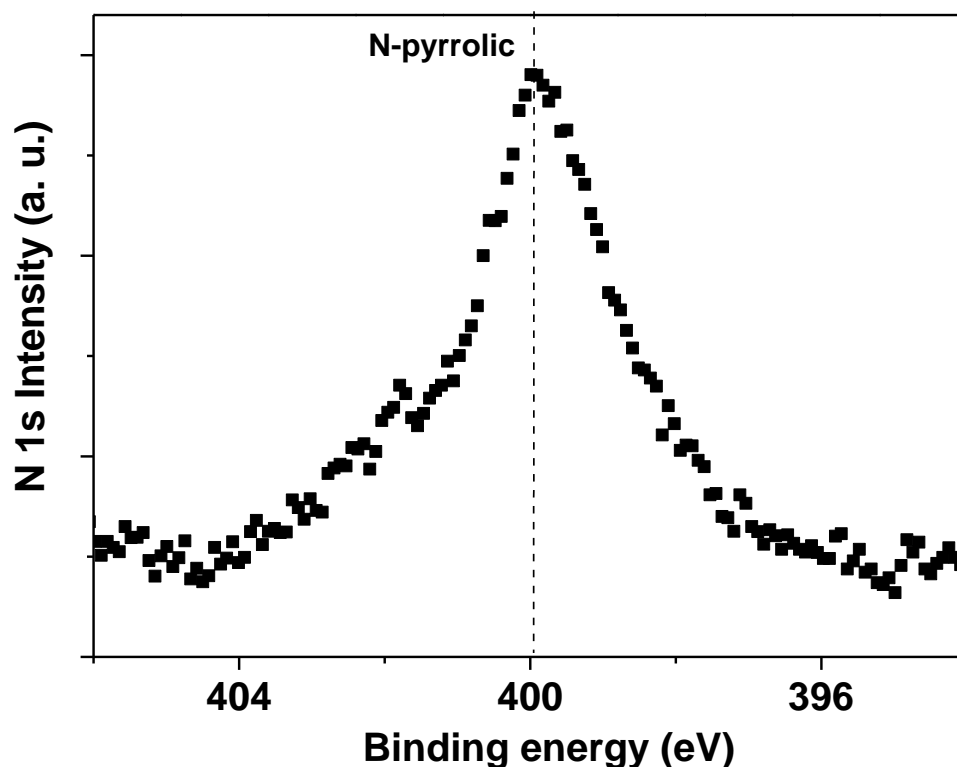


Figure S5 – Micro-XPS N 1s spectrum measured at the surface of an unpyrolyzed Co/PPy (60 electrodeposition cycles) sample.

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