

Supporting Information

“Nanoarchitectonics of Metal Organic Frameworks and PEDOT layer-by-layer electrodes for boosting Oxygen Reduction Reaction”

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Table S1. Comparison of recently reported ZIF-8 mass deposited onto gold substrates obtained by QCM (using the same deposition conditions).

Anchoring strategy	Mass deposited from a 1xZIF-8 film (time elapsed)	Reference
Amino-terminated self-assembled monolayer	8.5 $\mu\text{g}/\text{cm}^2$ (40 min)	[1]
Amino-terminated conducting polymer	9.8 $\mu\text{g}/\text{cm}^2$ (40 min)	[2]
Sulfonate-bearing polymer brushes	97.35 $\mu\text{g}/\text{cm}^2$ (1100 min) 18.6 $\mu\text{g}/\text{cm}^2$ (40 min)	[3]
Sulfonate-terminated self-assembled monolayer	31.5 $\mu\text{g}/\text{cm}^2$ (240 min) 11.5 $\mu\text{g}/\text{cm}^2$ (40 min)	[1]
PEDOT:PSS-terminated LbL film	86 $\mu\text{g}/\text{cm}^2$ (50 min)	Present work

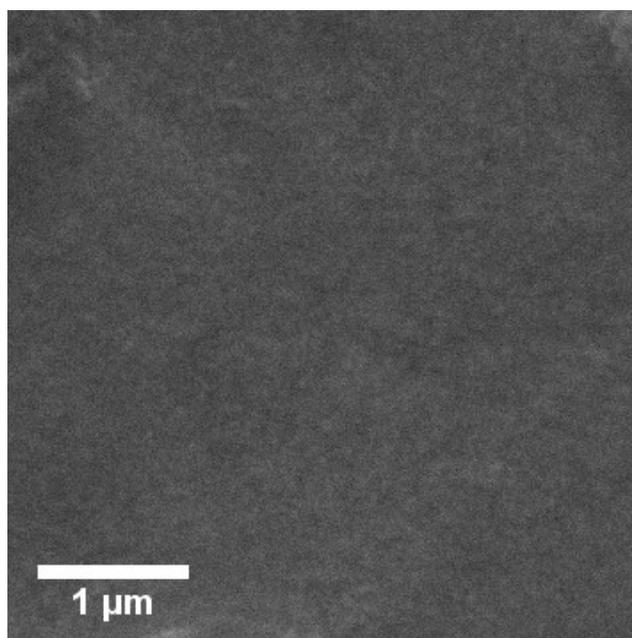


Figure S1. SEM image of the surface of a (PEI/PEDOT)₄-modified electrode.

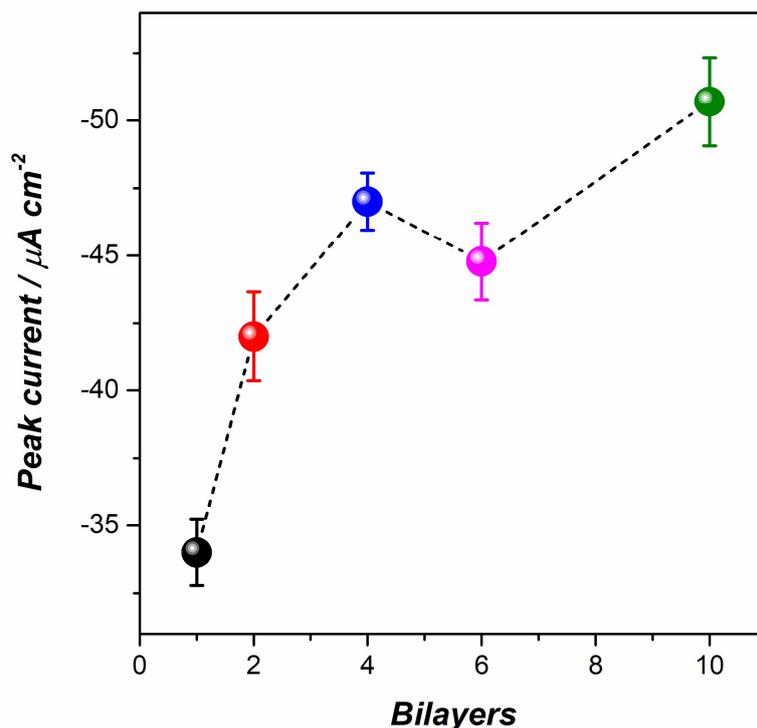


Figure S2. Change in ORR peak current with the number of bilayers ($n=3$).

Counter electrode test

In order to discard any effect caused by the nature of the Pt counter electrode employed in the electrochemical measurements on the ORR performance, comparative experiments employing both Pt and graphite electrodes were performed. Identical working electrodes modified by a $(\text{PEI/PEDOT})_4$ construction were tested in 5 mM HEPES 0.1M KCl. For these experiments, the electrochemical cell was thoroughly cleaned. Then, one $(\text{PEI/PEDOT})_4$ -modified electrode was measured by CV using a graphite bar counter electrode. Afterwards, a ZIF coating layer was deposited as using the same electrochemical cell, as described in the experimental section, and new CV measurements were performed for the $(\text{PEI/PEDOT})_4$ -1xZIF8 construction using the graphite counter electrode. Then, the electrochemical was disassembled and cleaned and a new configuration with the Pt counter electrode was assembled. In this configuration, a new $(\text{PEI/PEDOT})_4$ -modified working electrode was evaluated by CV before and after the MOF deposition. Voltammetric results corresponding to these measurements are presented in **Figure S2**. From the analysis of this figure, it can be concluded that no effects can be attributed to the use of a Pt counter electrode, as it could happen if a small amount of Pt was deposited on the working electrode. These results reinforce the idea that the increment in the ORR after MOF

deposition can be exclusively attributed to the preconcentration effect caused by this component.

On the other hand, the effect of the Pt deposition on the conducting polymer layer was recently reported to cause a shift in the ORR onset potential as it is expected from its proved electrocatalytic activity.⁴ In the case of the MOF layer, the ORR enhancement takes place without change in the onset potential as the effect of this electrochemically inactive component is augmenting the O₂ availability in the electrode surface.

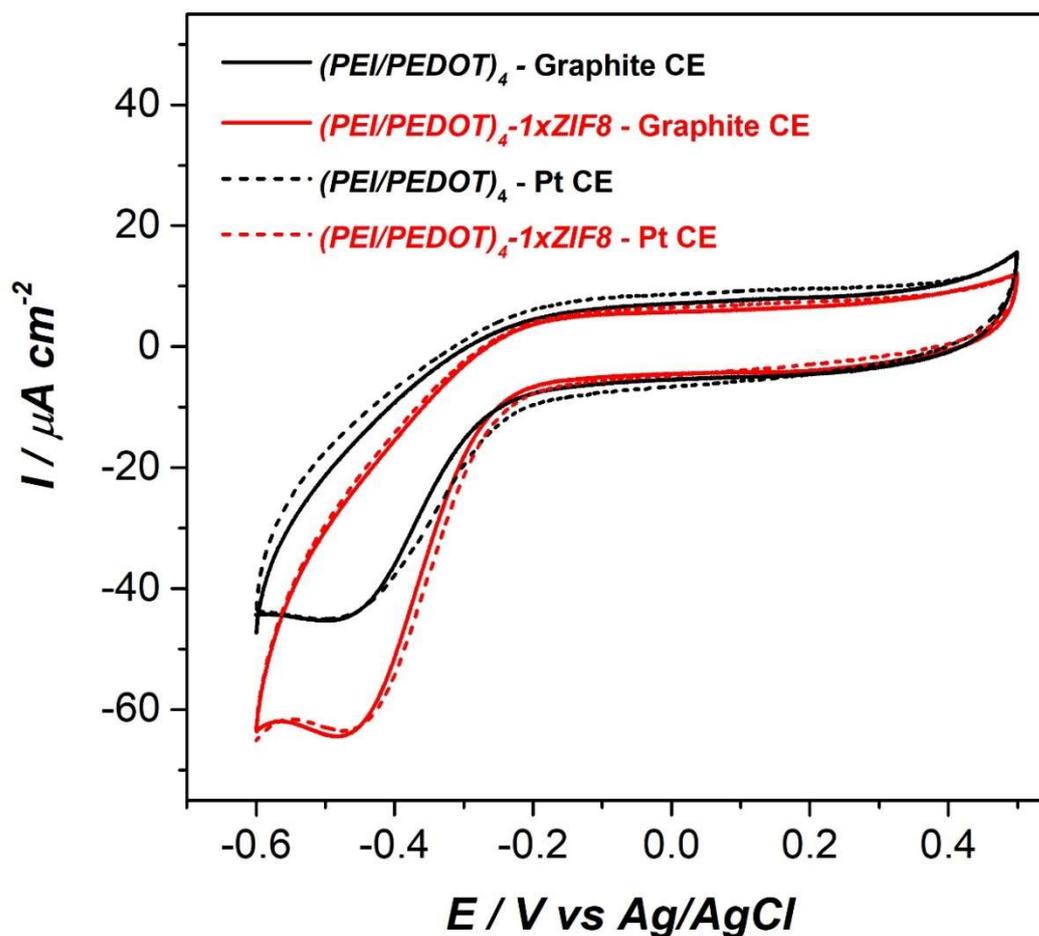


Figure S3. CV curves for the ORR of a 4 bilayers-modified Au electrode before and after the deposition of a 1xZIF-8 layer employing a graphite rod or a Pt wire as counter electrode. The measurements were performed in air-saturated 5 mM HEPES 0.1M KCl solution; $\nu = 10 \text{ mV s}^{-1}$.

References

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