

# Effects of Electrochemical Tailoring of Monolayers on a Catalytic Redox Entity: An ON–OFF Phenomenon Regulated by the Surrounding Medium

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## ABSTRACT:

Here we report an ON–OFF effect on electrocatalytic amplification when the molecules are connected to each other on an electrode surface. When the molecular connection is achieved, the redox potential of the catalytic redox entity is significantly upshifted with concurrent experience of a more electron-withdrawing atmosphere, and the electron transfer to and from the catalytic center is accelerated, rendering the molecules with strong electroreducing character; however, the overall outcome is dictated by the surface charge. Outer sphere redox probes and X-ray photoelectron spectroscopy evidently revealed that a positive surface charge is preserved in acidic and neutral media after molecular connection which is in parallel with the corresponding electrocatalytic amplifications toward oxygen reduction reaction (ORR), suggesting the electrocatalysis after molecular connection is extremely pH dependent. Surface charge present after molecular connection is significantly neutralized by the abundant hydroxyl groups in alkaline media, making the central metal ion's atmosphere less electron deficient and downshifting its redox potential (compared to the case in acidic and neutral media), thereby reducing the disparity in electroactivity before and after molecular connection. This study underlines that after molecular connection surface charge is the key as it can turn on and turn off the redox entity responsible for electrochemical amplifications. The solvent dependence and redox potential upshift outlined here for monolayer electrodes are nullified during bulk polymerization, indicating the circumstances leading to molecular connection are different from bulk polymerization. Since the surface charge can be modulated by connecting the molecules and tuning the surrounding media, the proposed strategy brings forward a way to tune the interfacial activity and is expected to have implications in electrocatalysis, selective sensing, ion screening, and so on.