Discovery of a coherent exchange of multiple electrons within the Au-deposited, self-assembled bio-derived hybrid quasi-2D nano-layers

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We report on the first direct voltammetric observation of a spectacular switch from the easily recognizable single electron exchange pattern, to the multi-electron (up to 10 electrons and more per single elementary act) mechanism, detected through the unprecedented, essentially two-state and fully substituted transformation of the normally-shaped cyclic voltammetry (CV) signal to the "atypical", extremely sharply-peaked CV response, Figure 1, (a). This interplay has been observed for the Au-deposited L-cys self-assembled monolayer films (SAMs) nearly saturated by SAM-coordinated, fully redox-active Cu^{2+} ions, capable of acting either as individual redox-probes (as depicted before) [1] or, as multi-electron-carrier, collectively redox-active quasi-1D clusters, $[(\text{L-cys}–CO_2^-)_2Cu^{2+}]_n$ (where: n = 2, 4, ...10 ...), presumably ordered together through the spin-implicated Boson condensation [2,3] (this work). Careful cross-analysis, based on the combination of complementary rate theories, was applied to explain additional experimental details including effects of temperature and scan-rate variations, by considering direct dynamic control and nonergodic/nonlinear motifs for electronic transport, attributable to the glass-forming (protein-like) interfacial environments [1]. These 2D assemblies displaying unique voltammetric features potentially could be of considerable interest as a novel type of memory storage devices [3].

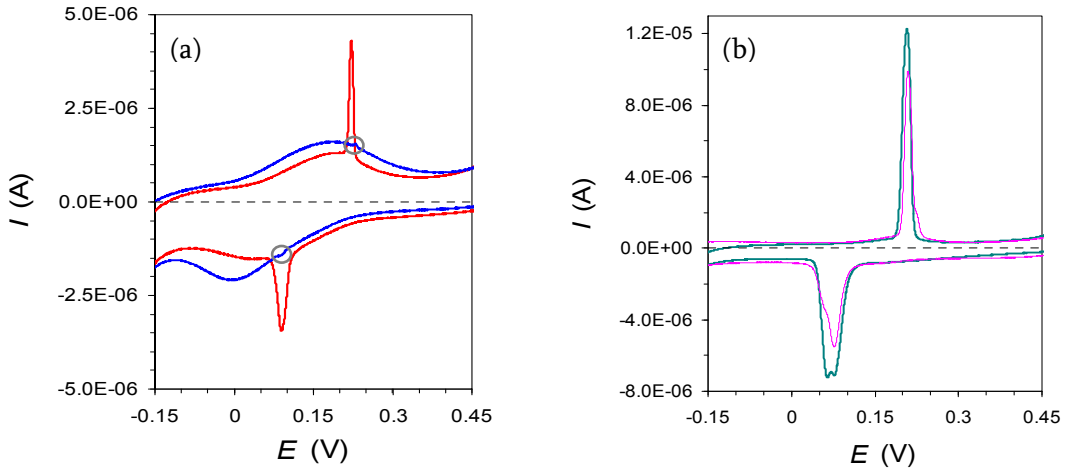

Figure 1. CV curves illustrating single to multiple electron transfer mechanistic changeover within the hybrid Au/L-Cys/Cu^{2+} 2D SAMs at high Cu^{2+} ion concentrations in the film (scan rate 0.1 V s^{-1}; see text below).

Figure 1, (a) demonstrates broad peaks (depicted in blue), attributable to the single electron exchange pattern, after the special treatment, additionally gave birth to new peaks, initially showing up as very small humps (embryos) indicated by small gray circles. Figure 1, (b) depicts CVs of the same system with fully developed sharp peaks (green), and the same peaks taken after a durable multiple potential cycling over the broadly variable scan rates (pink), showing minor degradation.

References

[1] D. E. Khoshtariya *et al.*, J. Phys. D, Appl. Phys. **48** (2015) 255402; [2] J. P. Eisenstein, Ann. Rev. Cond. Matt. Phys., **5** (2014) 159–181; [3] F. Hellman *et al.*, Rev. Mod. Phys. **89** (2017) 025006.