SUPPORTING INFORMATION

Stabilization of Electrogenerated Copper Species on Electrodes Modified with Quantum Dots

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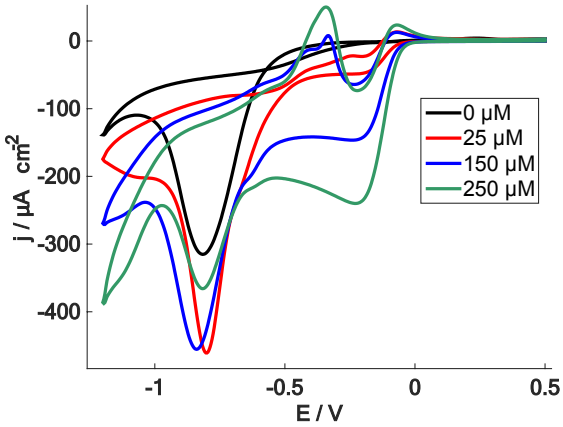

Figure S1. Cyclic voltammograms at 50 mV/s of solutions containing 0, 25, 150 or 250 µM of Cu(II) in 1 M NH_3 at bare electrodes.

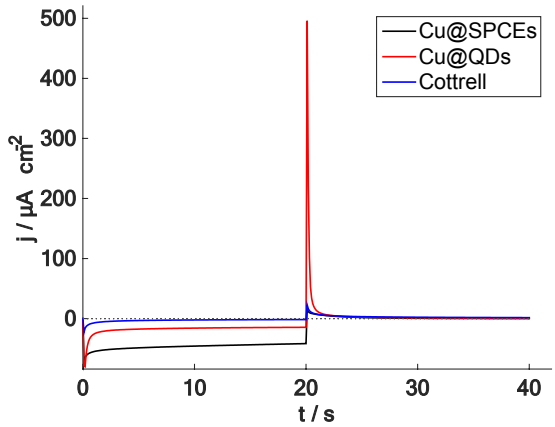

Figure S2. Chronoamperometric responses obtained for a solution of 25 µM Cu(II) in 1 M NH3 after applying -0.3 V and +0.05 V for 20 s at bare SPCEs (black line), QDs-modified SPCEs (red line) and expected response for a diffusion-controlled process following the Cottrell equation (blue line). The cathodic current obtained at bare SPCEs is significantly higher than at QDs-modified electrodes or for a diffusion-controlled process due to the influence of the coupled chemical reaction regenerating the initial species. Both responses were higher than the expected Cottrell response. The subsequent anodic current obtained at QDs-modified electrodes was significantly higher as more Cu(I) was available for the oxidation due to the stabilization by QDs. The anodic response at bare SPCEs was slightly lower than the Cottrell response, as a small amount of Cu(I) is available due to the previous oxidation with O_2. The Cottrell equation is as follows:

$$j = n\,F\,D^{1/2}\,C\,\pi^{-1/2}\,t^{-1/2},$$

where j is the current density, n is the number of electrons exchanged, D is the diffusion coefficient of the electroactive species, C is the initial concentration of the electroactive species and t is the time of experiment.

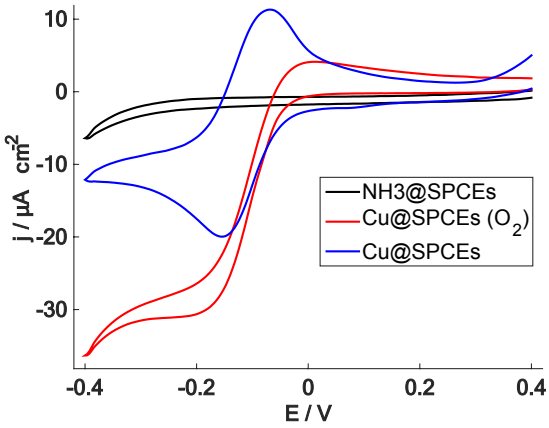

Figure S3. Cyclic voltammograms at 50 mV/s from +0.4 to -0.4 V obtained for a 25 µM Cu(II) solution in presence of O_2 (red line) and absence of O_2 (blue line) and voltammogram for the blank solution in absence of O_2 (black line).

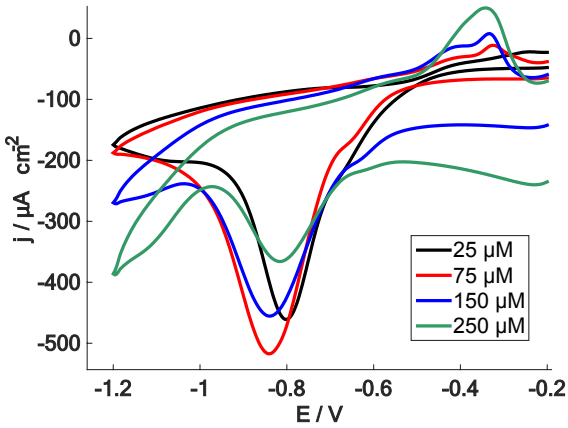

Figure S4. Cyclic voltammograms at 50 mV/s from -0.2 to -1.2 V obtained for solutions of 25, 75, 150 and 250 µM of Cu(II) using bare electrodes.

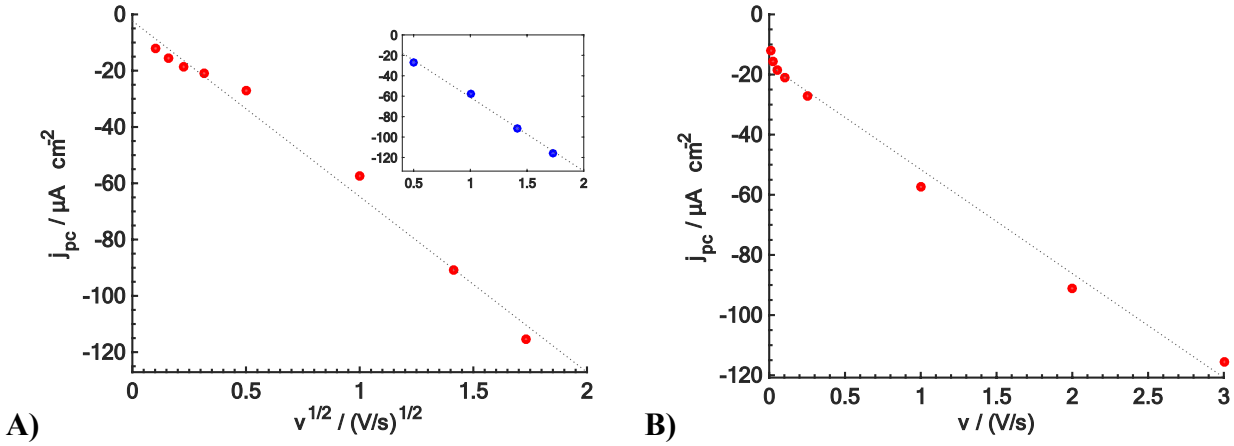

Figure S5. A) Relationship between the cathodic peak current obtained at QDs-modified electrodes and the square root of the scan rate. Inset: same plot for the highest scan rates (0.25-3 V/s) showing their linear relationship. **B)** Relationship between the cathodic peak current obtained at QDs-modified electrodes and the scan rate.

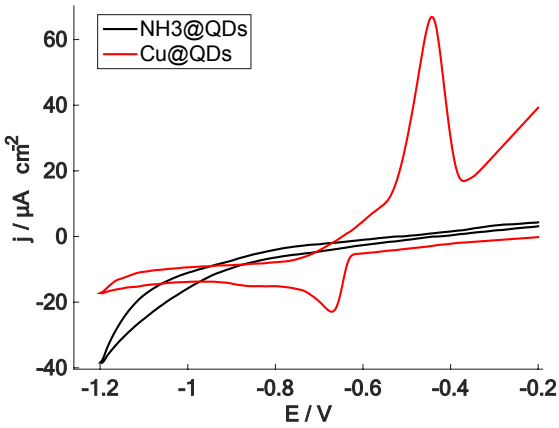

Figure S6. Cyclic voltammograms at 50 mV/s from -0.2 to -1.2 V obtained for a solution of 25 µM of Cu(II) (red line) and blank (black line) at QDs-modified electrodes in absence of oxygen.

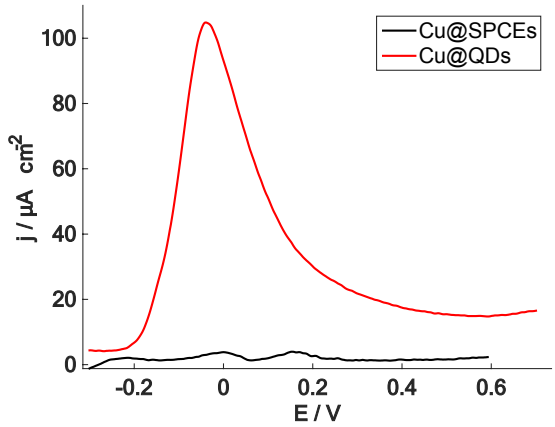

Figure S7. Linear-sweep anodic stripping voltammograms obtained in 0.1 M H_2SO_4 for bare and QDs-modified electrodes after electrodeposition at -1 V for 30 s of a solution of 25 µM of Cu(II) in 1 M NH_3 and washing with ultrapure water.

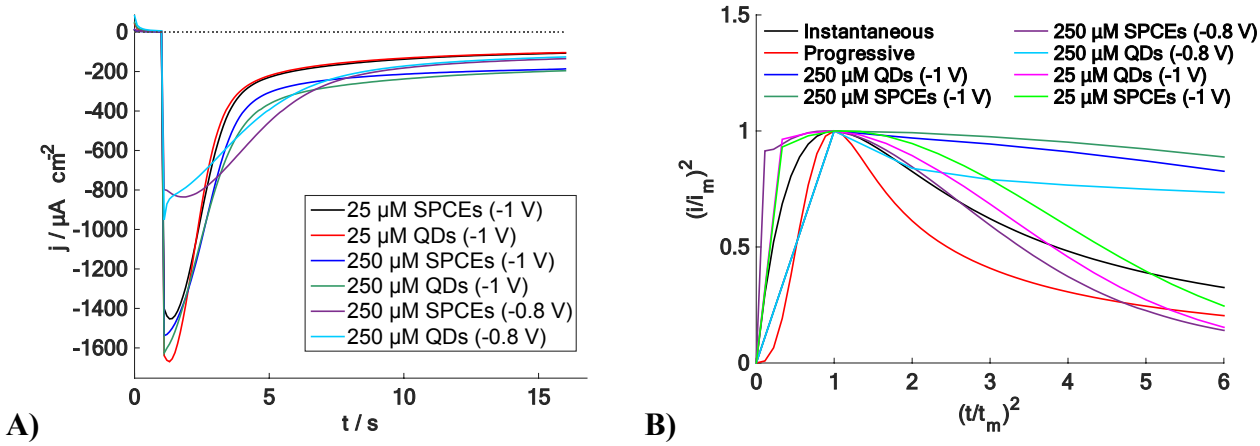

Figure S8. A) Chronoamperometric responses for the electrodeposition of copper in 1 M NH_3 at bare and QDs-modified electrodes under different experimental conditions. **B)** Scharifker-Hills model i-t transients for the electrodeposition of copper at bare and QDs-modified electrodes under different experimental conditions.

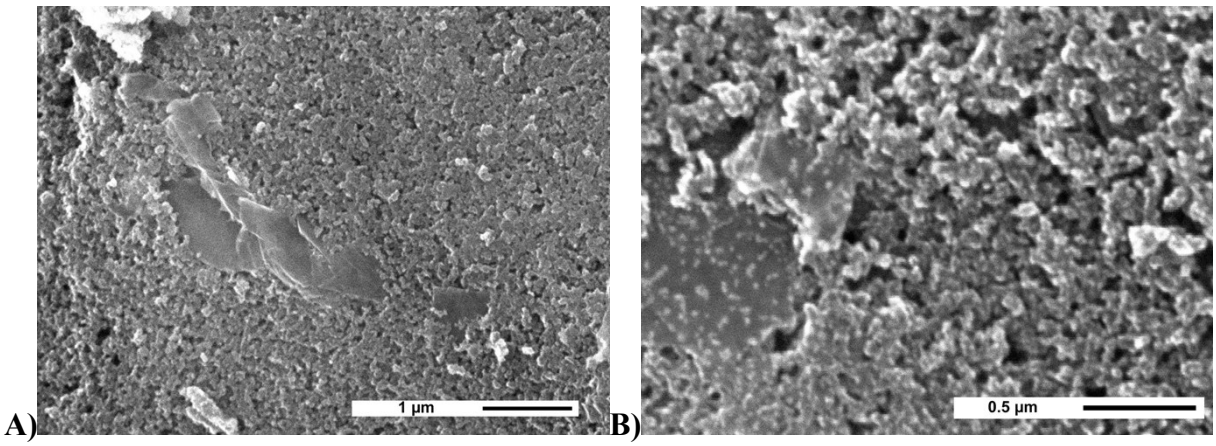

Figure S9. A) SEM micrograph of the electrode surface after electrodeposition of 25 µM of Cu(II) in 1 M NH_3 at -1 V for 30 s at bare electrodes. **B)** SEM micrograph of the electrode surface after electrodeposition of 25 µM of Cu(II) in 1 M NH_3 at -1 V for 30 s at QDs-modified electrodes.