Detection of the short-lived cation radical intermediate in the electrochemical oxidation of *N*,*N* -dimethylaniline (DMA) by scanning electrochemical microscopy (SECM)

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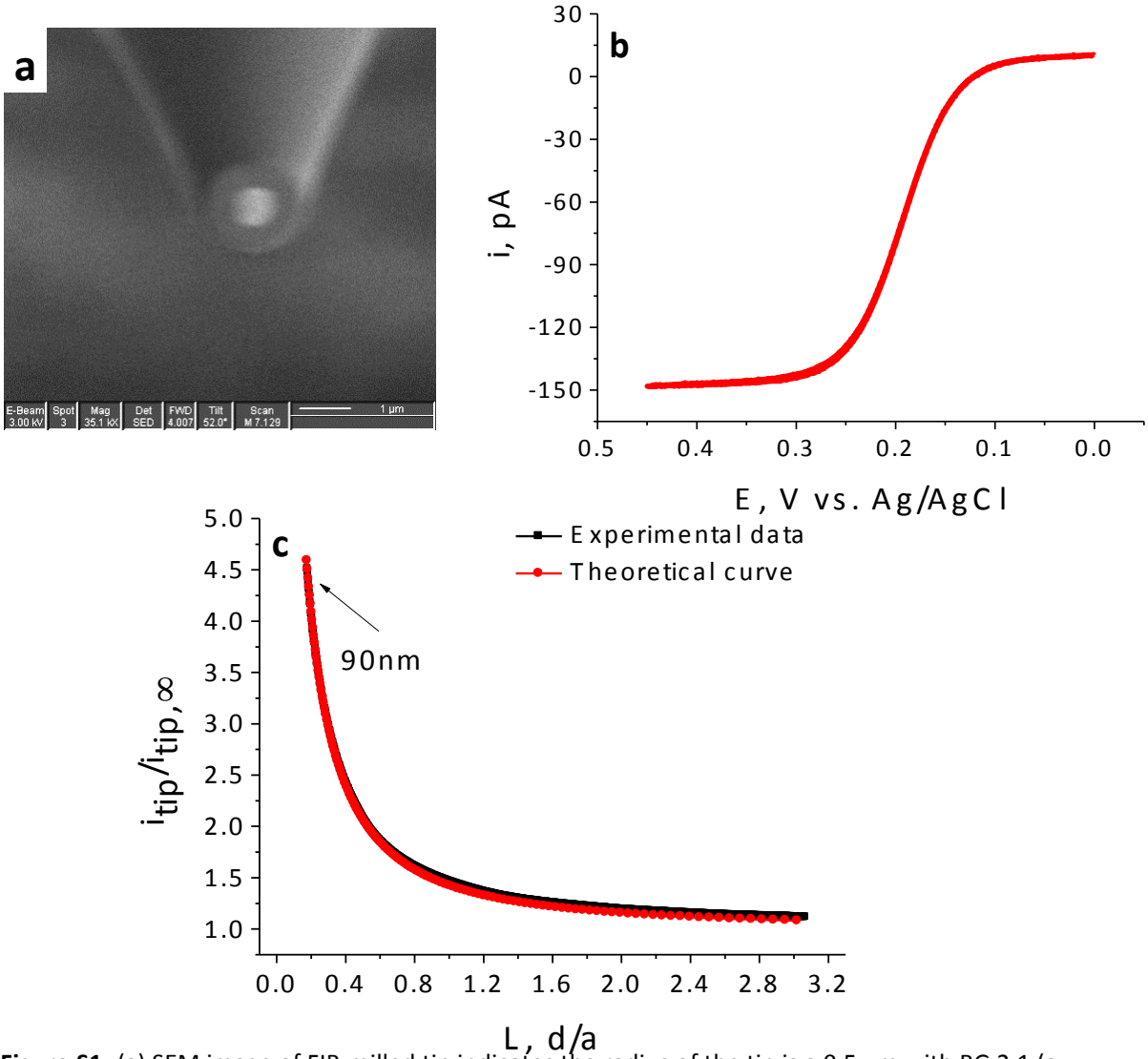

Figure S1. (a) SEM image of FIB-milled tip indicates the radius of the tip is a 0.5 um with RG 2.1 (a, scale bar is 1 µm); (b) the corresponding CV in 1 mM FcMeOH solution containing 0.1 M KNO_3; the radius of the sub-micron electrode is 0.49 µm based on steady-state current; and (c) an SECM approach curve to a 2mM Pt substrate (E=0 V vs. Ag/AgCl in 1M KCl) obtained using 1 mM FcMeOH in 0.1 M KNO_3 with the 0.49 µm radius Pt tip held at 0.45 V vs. Ag/AgCl. Probe scan rate was 60 nm/s. The red line represents a theoretical approach curve to a conductive substrate based on COMSOL fitting with RG = 2.1. The smallest gap obtained between the tip and substrate without contact was 90 nm.

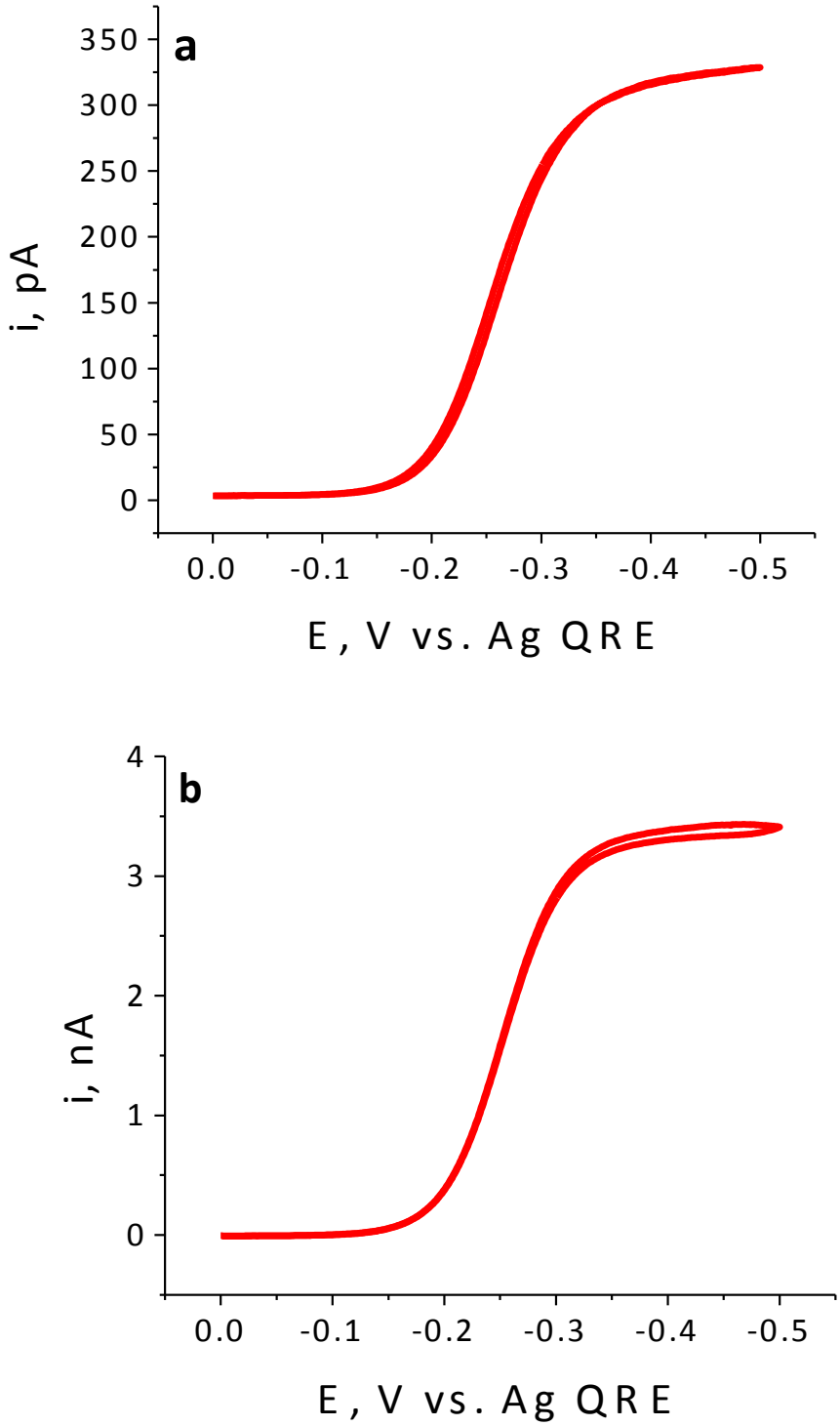

Figure S2. Cyclic voltammogram of 1 mM EVD in MeCN with 0.1 M $TBAPF_6$ as supporting electrolyte. (a) at the tip, Pt disk UME (a = 0.5 µm); (b) at the substrate, Pt disk UME (a = 5 µm).

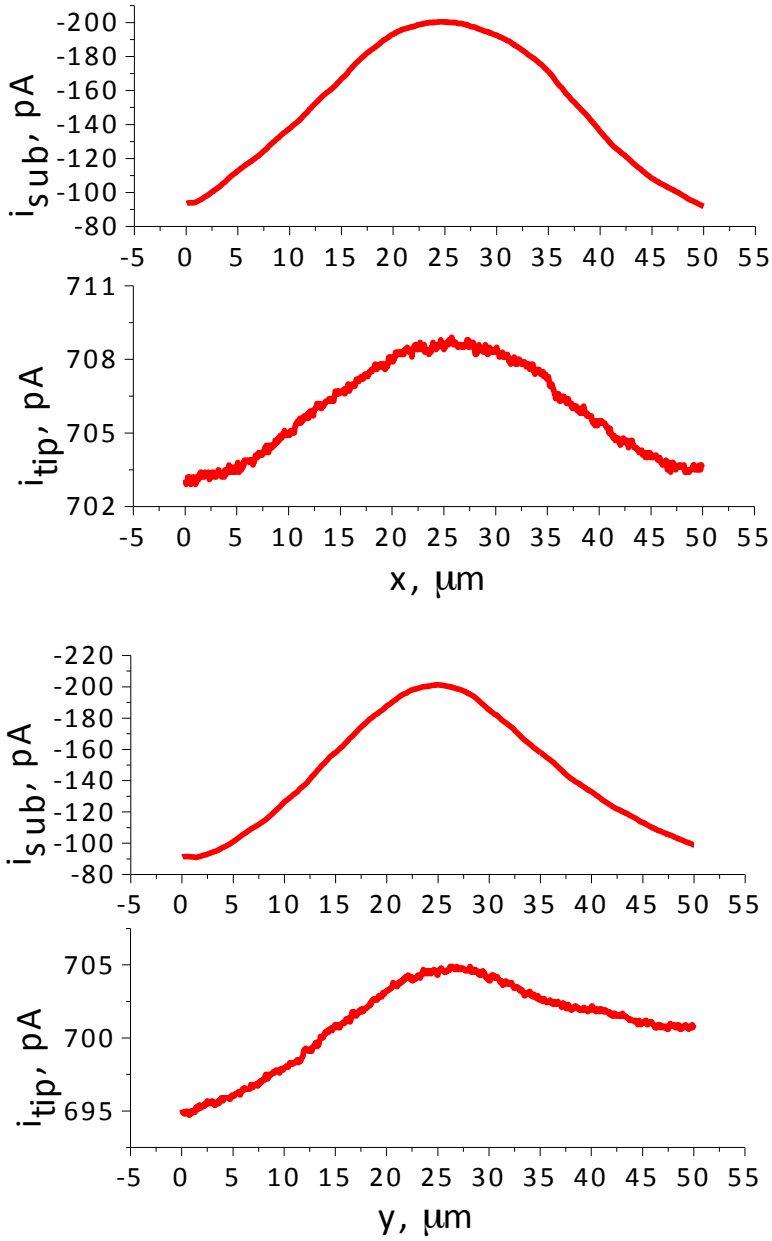

Figure S3. Alignment of tip and substrate by x and y axis line scanning. The tip potential is -0.45V, while the substrate potential is 0V. The scanning rate is 0.05μm/0.016667s, controlled by a piezoelectric motor. These figures indicate that when the tip is scanned over the substrate, significant positive feedback can be observed both tip and substrate electrode.

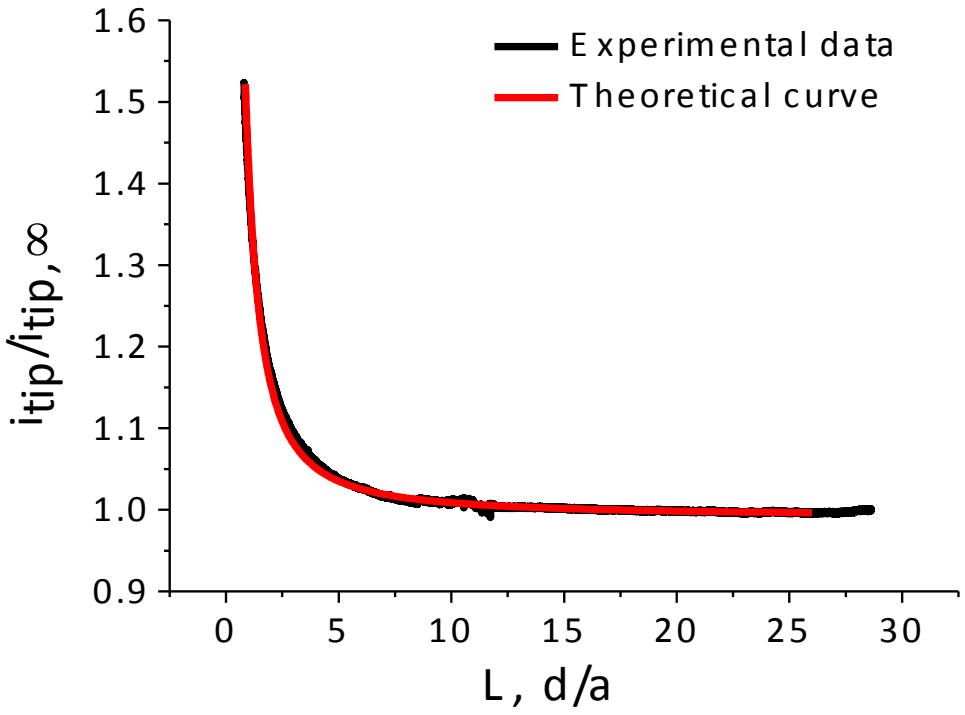

Figure S4. Approach curve of 0.5 µm radius Pt tip with RG = 2 (E = -0.45 V vs. Ag QRE) on 5 µm radius Pt substrate (E=0 V vs. Ag QRE), obtained using 1 mM EVD in MeCN with 0.1 M $TBAPF_6$ as supporting electrolyte. Probe scan rate is 60 nm/s. The red line represents a theoretical approach curve to a conductive substrate from COMSOL simulation results. At the end of the approach curve, the gap between the tip and the substrate is 0.43 µm. The tip was not approached any closer in order to avoid crashing it into the substrate. The SECM stage and cell were put in an argon filled glove bag to avoid the effect of oxygen.

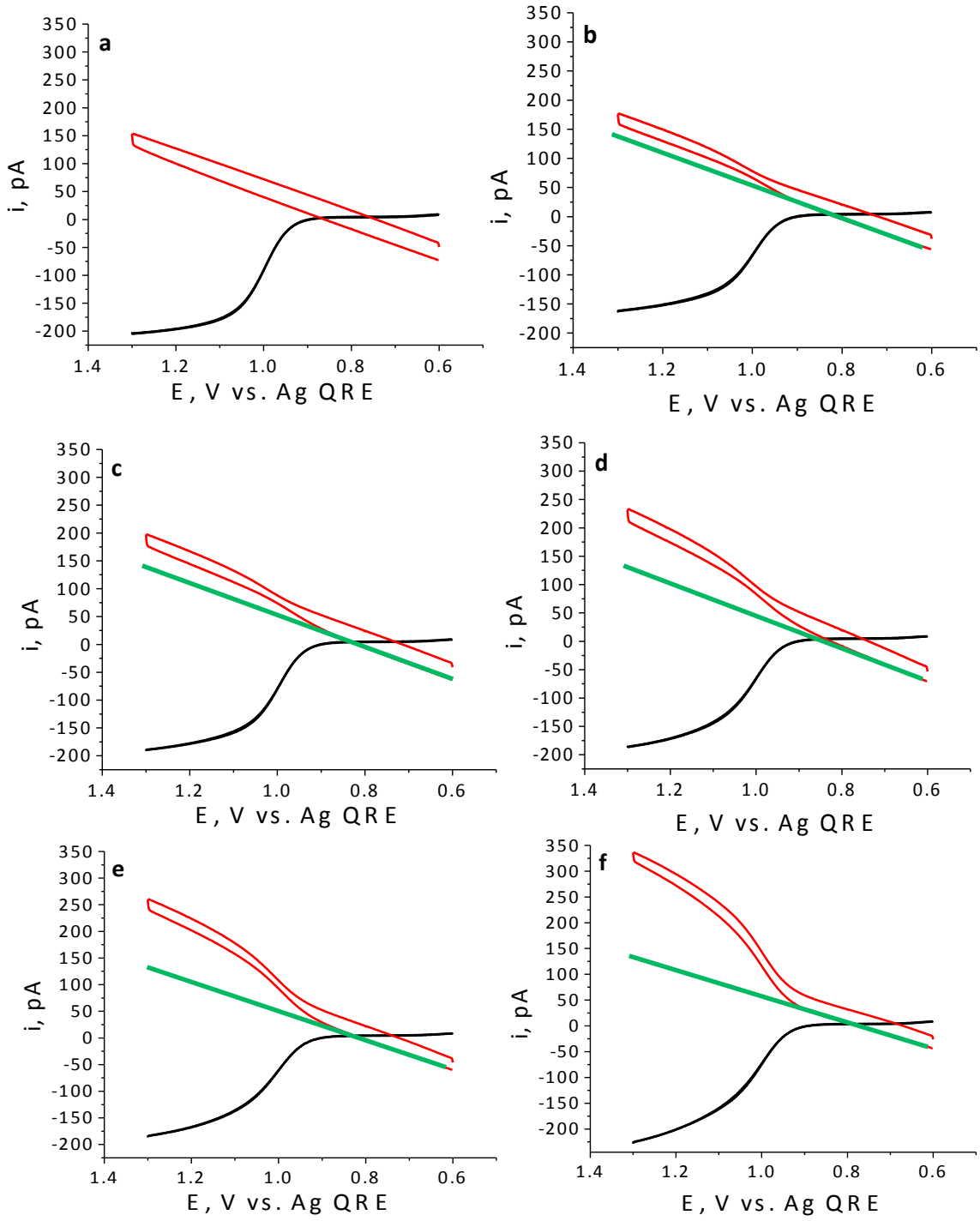

Figure S5. Typical collection curves of 0.4 mM DMA oxidation in acetonitrile solution with 0.1 M $TBAPF_6$ at different *d*: (a) 10 μm, (b) 1.4 μm, (c) 1.1μm, (d) 0.8 μm, (e) 0.5 μm and (f) 0.2 μm. The black and red lines are the tip and substrate currents respectively, while the green line is the baseline of substrate current to calculate the collection current. The tip potential is swept from 0.6 to 1.3 V vs. Ag QRE at a scan rate of 50 mV/s to electro-oxidize DMA, while the substrate potential is held at 0.76 V vs. Ag QRE to collect the $DMA^{\cdot+}$ radical.

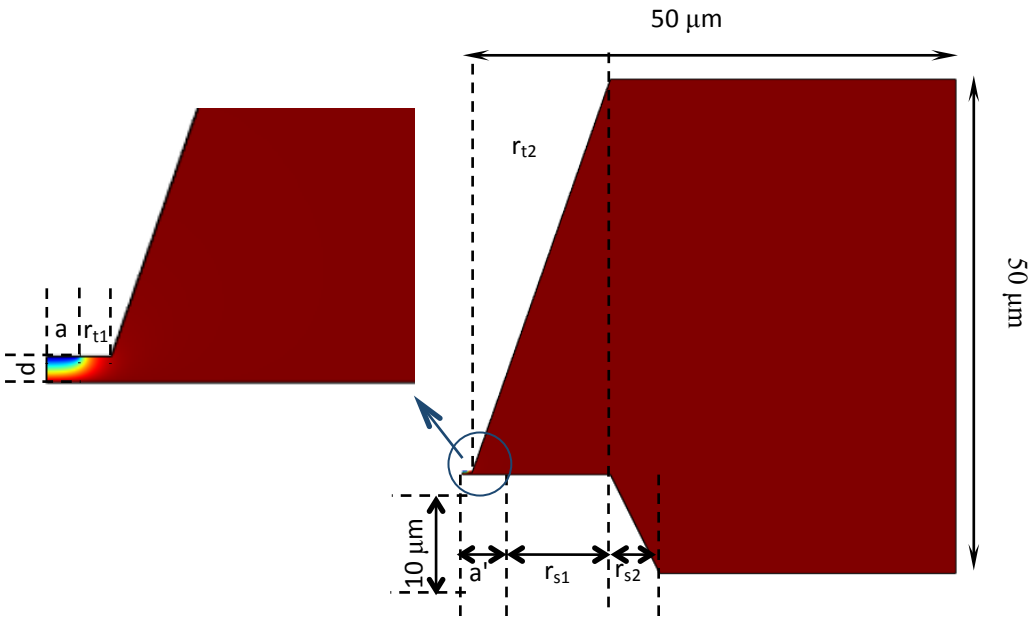

Figure S6. Two-dimensional axial symmetry dimension image with parameters for COMSOL simulation, and its corresponding boundary conditions are shown in the Table 1.