# **Supporting Information**

# Electrochemical oxidation of resorcinol: mechanistic insights from experimental and computational studies

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#### **S1** Electrode characterization

The glassy carbon macro-electrode and the carbon fiber micro-electrode were characterized by the standard redox probe, hexacyanoferrate(II)/hexacyanoferrate(III). The voltammetric peak currents of 1.0 mM hexacyanoferrate(II) ( $[Fe(CN)_6]^{4-}$ ) in the presence of 0.10 M KCl at a glassy carbon electrode showed a linear response with square root of scan rates in accordance with the diffusion-controlled limit. The diffusion coefficient of hexacyanoferrate(II) was determined according to eqn. S1 to be 7.2x x10<sup>-10</sup> m<sup>2</sup> s<sup>-1</sup>, close to the values reported in literature ( $\sim$ 7x10<sup>-10</sup> m<sup>2</sup> s<sup>-1</sup>).<sup>1-2</sup> At a carbon micro-electrode, a steady-state response was observed, giving the diffusion coefficient of hexacyanoferrate(II) of 7.2x x10<sup>-10</sup> (eqn. S2).

For a macrodisc electrode,

$$I_p = 0.446nFAc^* \sqrt{\frac{F\nu nD}{RT}}$$
(S1),

where  $I_p$  is the peak current, n is the number of electrons transfer, F is the Faraday's constant (96,485 C mol<sup>-1</sup>). A is the electrode surface area.  $c^*$  is the bulk concentration of  $[Fe(CN)_6]^{4-}$ .  $\nu$  is the voltage scan rate. D is the diffusion coefficient. R is the molar gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>). T is the absolute temperature.

For a microdisc electrode,

$$I_{ss} = 4nFc^*Dr \tag{S2}$$

where  $I_{ss}$  is the steady-state current. r is the radius of the microdisc electrode.  $n, F, c^*$  and D have the same meaning as the above.



**Figure S1:** Cyclic voltammograms of 1.0 mM hexacyanoferrate(II) ( $[Fe(CN)_6]^{4-}$ ) in the presence of 0.10 M KCl at **a**) a glassy carbon electrode (3.0 mm diameter) at varied scan rates. The inlay shows a plot of the anodic peak currents ( $I_p$ ) against square root of scan rates; and **b**) a carbon microelectrode (7.0 µm diameter) at the scan rate of 10 mV s<sup>-1</sup>.

#### S2 Successive voltammetric scans

Successive voltammetric scans of resorcinol oxidation were performed using the same microelectrode without electrode polishing between scans. The diffusion layers were refreshed by solution stirring before each scan. An anodic peak of resorcinol oxidation was observed in the first scan as usual. However, no oxidation peak was observed in the following scans. After careful polishing, the electrode regained its electroactivity (Figure S2), and thus evidenced the formation of inert film on the electrode surface upon the oxidation of resorcinol.



**Figure S2:** Cyclic voltammograms of 1.0 mM resorcinol at a carbon microelectrode at the scan rate of 10 mV s<sup>-1</sup> with and without electrode polishing between scans.

## S3 Shift of solvent breakdown potential

We found that solvent breakdown shifted to higher overpotentials in the presence of resorcinol (Figure S3).



Figure S3: Cyclic voltammograms of 1.0 mM resorcinol at a carbon macroelectrode at the scan rate of 100 mV s<sup>-1</sup>

#### S4 Calibration curve of resorcinol: cyclic voltammetry measurements

The solutions of varied resorcinol concentrations were subjected to cyclic voltammetry at a microelectrode in the absence of supporting electrolytes. The cyclic voltammograms are demonstrated in Figures S4. The inlay in Figure S4 showed the calibration plot of the peak currents  $(I_p)$  against resorcinol concentrations, with the sensitivity of  $177 \pm 7$  nA M<sup>-1</sup> and the limit of detection  $(3s_B/m)$  of 9.6  $\mu$ M.



**Figure S4:** Cyclic voltammograms of varied concentrations of resorcinol in deionized water at a carbon microelectrode (7  $\mu$ m diameter) at the scan rate of 10 mV s<sup>-1</sup> at 298 K. The inlay shows the calibration plot of the peak currents against resorcinol concentrations.

### References

 Von Stackelberg, M.; Pilgram, M.; Toome, W., Determination of Diffusion Coefficients of Several Ions in Aqueous Solution in the Presence of Foreign Electrolytes. I. *Z. Elektrochem* 1953, 57, 342.

2. Konopka, S.; McDuffie, B., Diffusion coefficients of ferri-and ferrocyanide ions in aqueous media, using twin-electrode thin-layer electrochemistry. *Analytical Chemistry* **1970**, *42* (14), 1741-1746.