Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Single Entity Electrocatalysis: Oxygen Reduction Mediated via Methyl Viologen Doped Nafion Nanoparticles

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Section 1 Supplementary Experimental Data

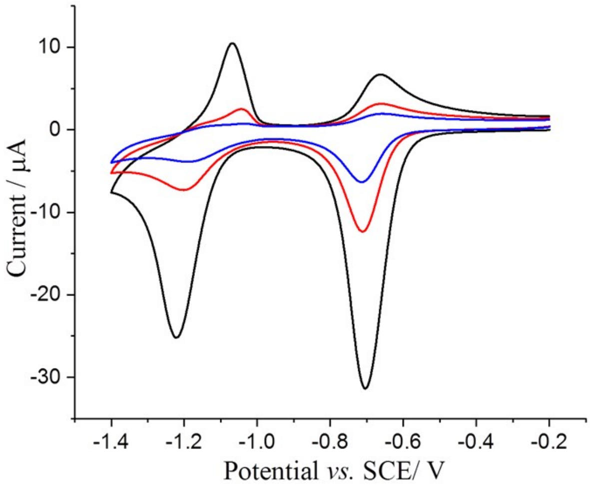

Figure S1. Cyclic voltammograms of a glassy carbon macroelectrode modified with MV-Nafion particles in deaerated PBS buffer (pH = 7.4) at scan rate of 100 mV s^{-1} (black: first scan; red: second scan; blue: third scan).

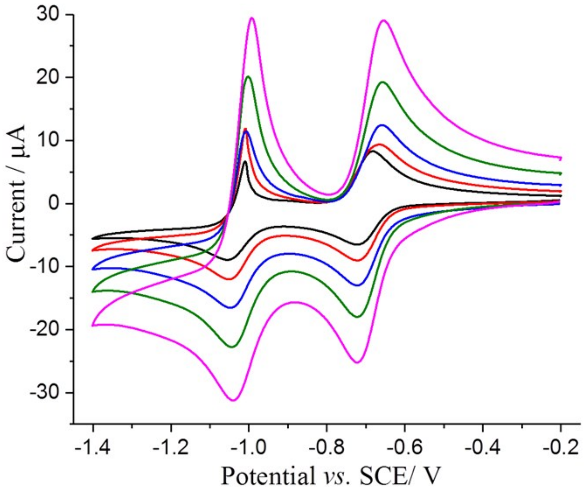

Figure S2. Cyclic voltammograms of a bare glassy carbon macroelectrode in deaerated PBS buffer (pH = 7.4) containing 1 mM $MVCl_2$ record as a function of scan rate (25 mV s^{-1}, black line; 50 mV s^{-1}, red line; 100 mV s^{-1}, blue line; 200 mV s^{-1}, green line; 400 mV s^{-1}, magenta line)

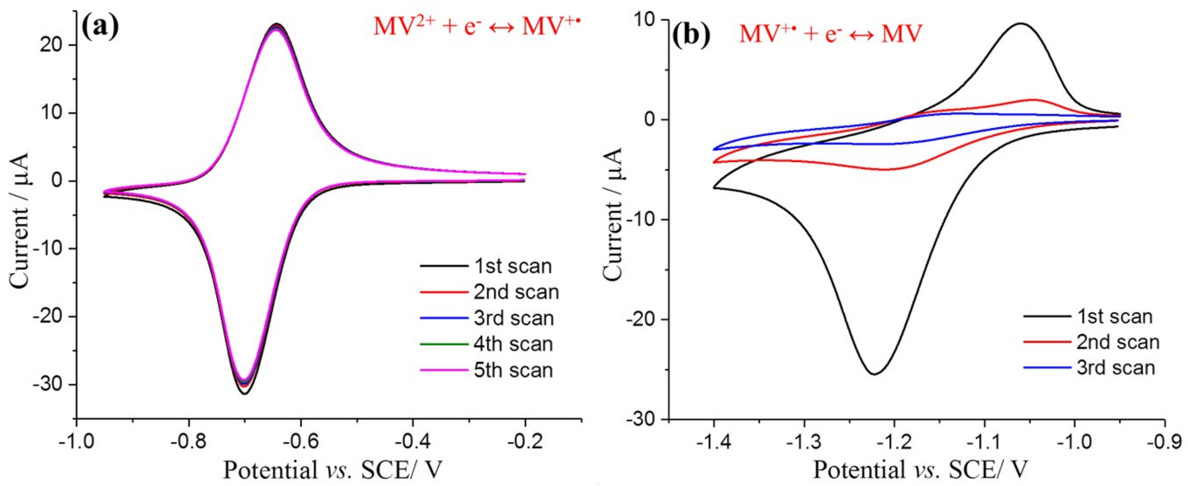

Figure S3. Cyclic voltammograms of a glassy carbon macroelectrode modified with MV-Nafion particles in deaerated PBS buffer (pH = 7.4) at scan rate of 100 mV s^{-1}. (a) recorded from -0.2 to -0.95 V and reversed back to -0.2 V (a) recorded from -0.95 to -1.4 V and back to -0.95 V

It is evident that, as shown in Figure S3(a), the charge of reduction and oxidation peaks for the $MV^{2+}/MV^{+\bullet}$ couple doped in Nafion particles is conserved and the reaction is reversible, suggesting that both cationic forms of MV are retained and stable in the Nafion particles. In contrast (Figure S3b), the reduction peak is much larger than the oxidation peak for the $MV^{2+}/MV^{+\bullet}$ couple, and the charge decays progressively with number of scans, suggesting that the neutrally charged MV is rapidly lost from the particles. This was further confirmed by the ‘stop’ voltammetric experiment as followed. Note that ‘stop at -0.2 V for 10s’ means holding the potential at -0.2 V for 10 seconds during cyclic voltammetry measurements.

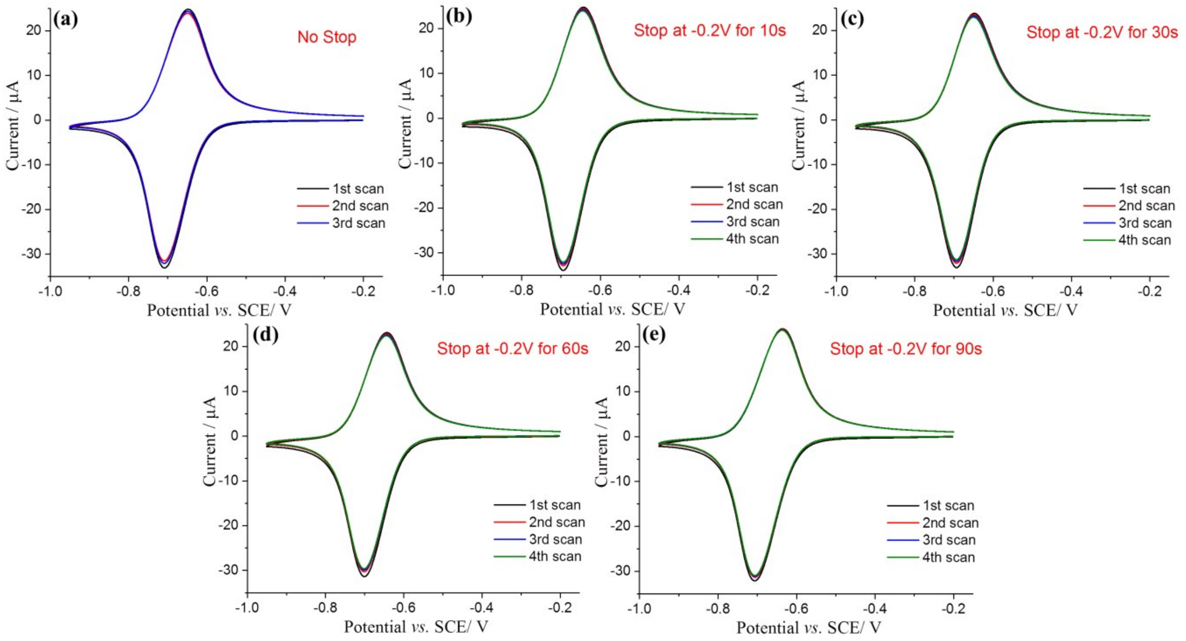

Figure S4. Cyclic voltammograms of a glassy carbon macroelectrode modified with MV-Nafion particles in deaerated PBS buffer (pH = 7.4) at scan rate of 100 mV s^{-1}. The potential was held at -0.2 V for various time then recorded from -0.2 to -0.95 V and back to -0.2 V. (a) 0 s, (b) 10 s, (c) 30 s, (d) 60 s, (e) 90 s.

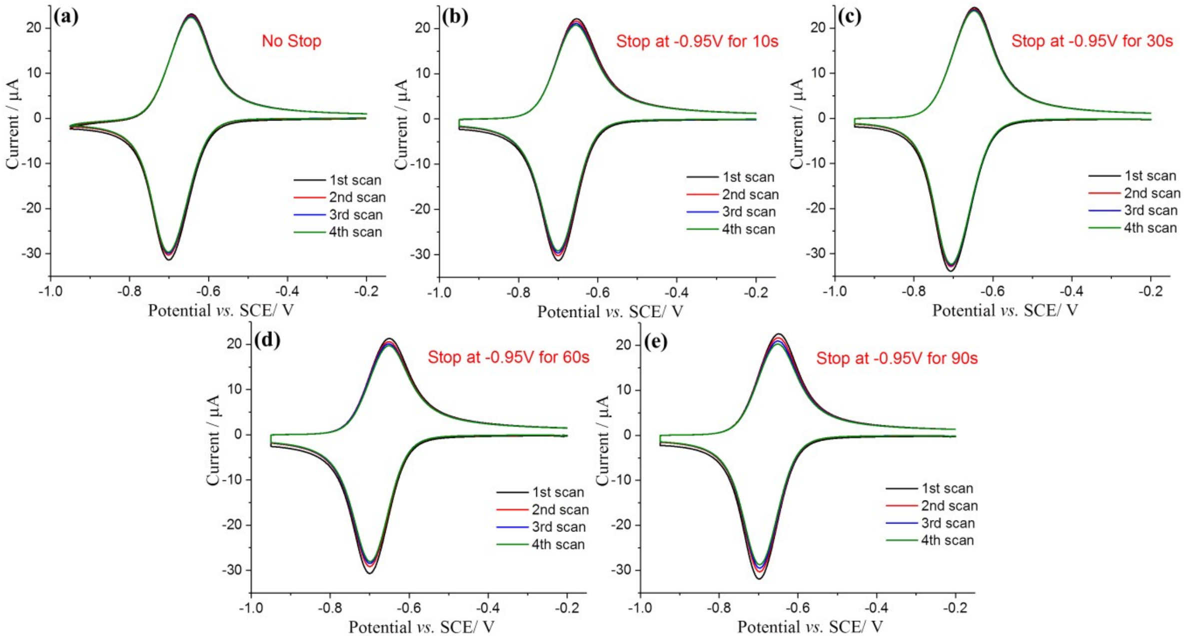

Figure S5. Cyclic voltammograms of a glassy carbon macroelectrode modified with MV-Nafion particles in deaerated PBS buffer (pH = 7.4) at scan rate of 100 mV s^{-1}. The CVs were recorded from -0.2 to -0.95 V and held at -0.95 V for various time then reversed back to -0.2 V. (a) 0 s, (b) 10 s, (c) 30 s, (d) 60 s, (e) 90 s.

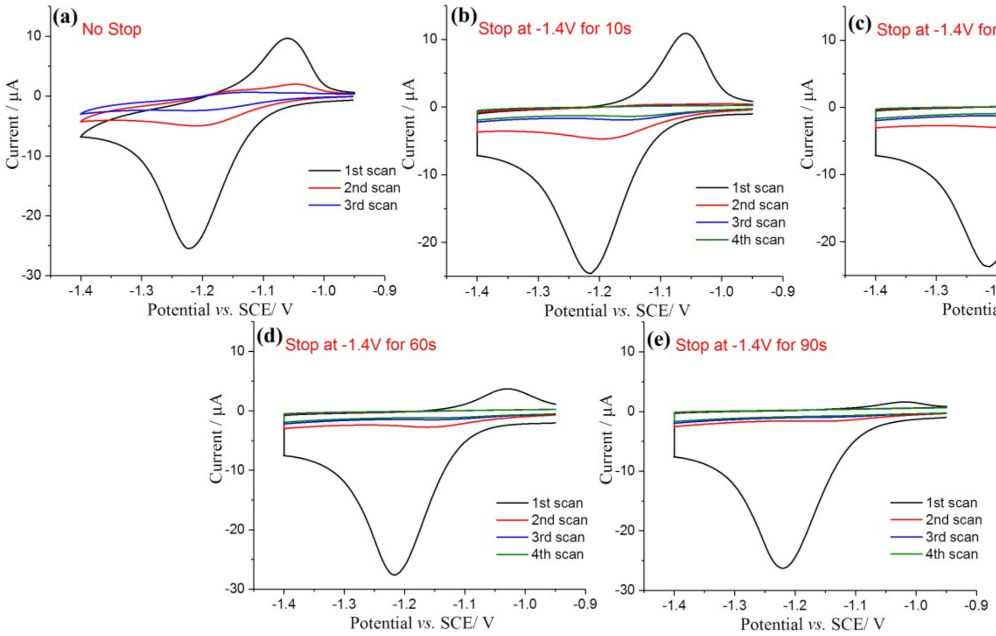

Figure S6. Cyclic voltammograms of a glassy carbon macroelectrode modified with MV-Nafion particles in deaerated PBS buffer (pH = 7.4) at scan rate of 100 mV s^{-1}. The CVs were recorded from -0.95 to -1.4 V and held at -1.4 V for various time then reversed back to -0.95 V. (a) 0 s, (b) 10 s, (c) 30 s, (d) 60 s, (e) 90 s.

As shown in Figure S4-6, both of the reductive and oxidative peaks are identical with number of scans even when the potential was held at -0.2 V or -0.95 V for various times, further confirming that both MV^{2+} and $MV^{+\bullet}$ are very stable in the Nafion particle. As for the neutral form, MV, it is clearly observed that the oxidative (backward) peak markedly decays when increasing the ‘stop’ time at -1.4 V, as neutrally charged MV has more time to diffuse out of the particles. Note that the equilibrium time in the cyclic voltammetry experiments was set as 3 seconds to equilibrate the electrode at the start potential. Therefore, all the MV^{2+} species in the Nafion particles would be reduced into $MV^{+\bullet}$ when the start potential being -0.95 V as shown in Figure S3b and S6.

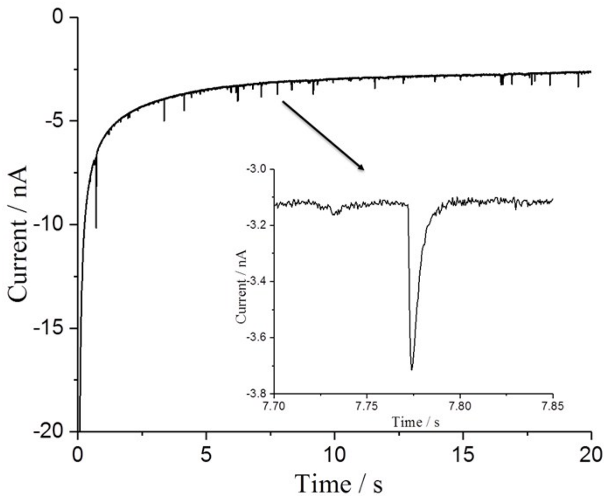

Figure S7. Representative chronoamperometric profiles of nano-impacts at +0.90 V versus SCE in deaerated pH 7.4 PBS buffer containing MV-Nafion particles only.

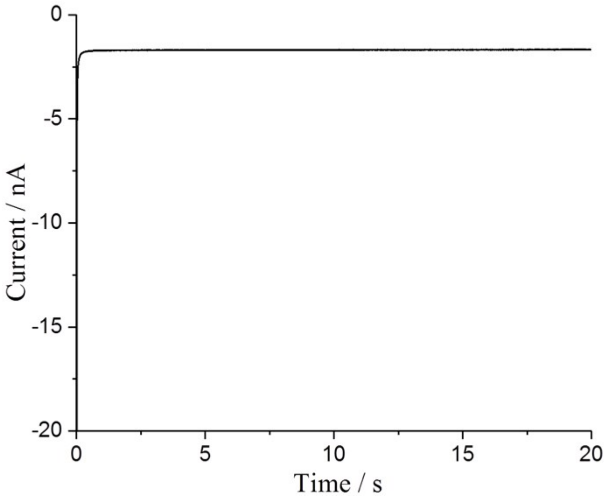

Figure S8. Representative chronoamperometric profiles of nano-impacts at +0.90 V versus SCE in deaerated pH 7.4 PBS buffer without addition of MV-Nafion particles suspensions

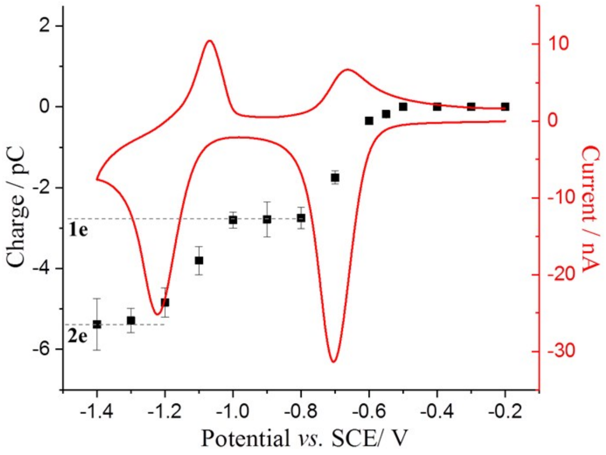

Figure S9. Potential variable study of single MV-Nafion particles in deaerated pH 7.4 PBS. The error bars are derived from SD/(n)$^{1/2}$, where SD is the standard deviation and n is the number of the spikes. Overlayed voltammogram was recorded at a glassy carbon macroelectrode modified with MV-Nafion particles in deaerated PBS buffer (pH = 7.4) at scan rate of 100 mV s^{-1}.

Section 2 Number of Electrons Transferred in the Mediated Oxygen Reduction Reaction

The reversible Randles–Sevcik equation[1] for a n_e-electron transfer reaction is expressed as:

$$I_p = 0.446 n_e F S c^* \sqrt{\frac{n_e F D v}{RT}} \qquad \text{* MERGEFORMAT (S1)}$$

where S is the electrode geometry area, c^* is the bulk concentration of the reactant, D is the diffusion coefficient of the reactant and v is the scan rate. Using the I_p-$v^{1/2}$ relationship measured in the experiment (Figure 3), the effective number of electrons transferred in the mediated oxygen reduction reaction is calculated to be *c.a.* 2.

Section 3 Amounts of Nafion Particles in drop-casting and nano-impact experiments

For single MV-Nafion particle, the average radius is 0.43 ± 0.26 μm (estimated from scanning electron microscopy[2]) and the density of Nafion in water ρ_{Nafion} is 1.858 g cm^{-3}.[3]

Hence the mass for single particles is

$$m_{Nafion} = \frac{4}{3}\pi r^3 \rho_{Nafion} = 6.36 \times 10^{-13}\, g$$

Total mass of Nafion used to synthesize Nafion particles is

$$m_{total} = V\rho_{bluk} \times wt\% = 50\mu L \times 0.921 g/cm^3 \times 12.5\% = 5.76 \times 10^{-3}\, g$$

Where ρ_{bluk} is the density of Nafion perfluorinated resin solution, whose value obtained from the supplier Sigma-Aldrich.

The number of Nafion particle synthesized is

$$N = \frac{m_{total}}{m_{Nafion}} = \frac{5.76 \times 10^{-3}\, g}{6.36 \times 10^{-13}\, g} = 9.05 \times 10^9$$

Final Nafion particle suspension volume is 0.5 mL.

Then the concentration of Nafion particle suspension is

$$C = \frac{N}{V} = \frac{9.05 \times 10^9}{0.5\, mL} = 1.81 \times 10^{10}\, particles/mL$$

Hence the number of Nafion particle drop-casted on the GC electrode is

$$N_{GC} = C \cdot V_{GC} = 1.81 \times 10^{10}\, particles/mL \times 10\mu L = 1.81 \times 10^8\, particles$$

For nano-impact experiments, 0.5 mL of stock Nafion particle suspension is diluted to 5 mL suspension. Hence the concentration of Nafion particles for nano-impact experiments can also be determined as

$$C_{Impact} = \frac{1.81 \times 10^{10}\, particles/mL}{N_A} \times \frac{0.5\, mL}{5\, mL} = 3.0 \times 10^{-12}\, mol/L$$

Section 4 Doping Amount of MV^{2+} in individual Nafion Particles (ratio of MV^{2+}:SO_3^-)

For single MV-Nafion particle, the average radius is 0.43 ± 0.26 μm (estimated from scanning electron microscopy[2]) and the density of Nafion in water ρ_{Nafion} is 1.858 g cm^{-3}.[3]

Hence the mass for single particles is

$$m_{Nafion} = \frac{4}{3}\pi r^3 \rho_{Nafion} = 6.36 \times 10^{-13}\, g$$

Equivalent weight (EW) of Nafion is defined as the number of grams of dry Nafion per mole of sulfonic acid groups when the material is in the acid form.[4] Nafion used in this work is 1100 EW.

The amount of SO_3^- can be then determined as

$$n_{SO_3^-} = \frac{6.36 \times 10^{-13}\, g}{1100\, g/\,mol} = 5.78 \times 10^{-16}\, mol$$

The average charge of individual impacts at first plateau, Q, is 2.74 ± 0.26 pC.

Hence the amount of MV^{2+} in single Nafion particle is

$$n_{MV^{2+}} = \frac{Q}{neN_A} = 2.84 \times 10^{-17}\, mol$$

The doping amount of MV^{2+} in individual Nafion Particles (ratio of MV^{2+}:SO^{3-}) is

$$\frac{n_{MV^{2+}}}{n_{SO_3^-}} = \frac{2.84 \times 10^{-17}\, mol}{5.78 \times 10^{-16}\, mol} = \frac{1}{20}$$

Therefore, the doping amount of MV^{2+} in Nafion Particles is 1:20, 1:40, 1:80, 1:160, and 1:320 corresponding to doping level 100%, 50%, 25%, 12.5% and 6.25% in this work, respectively.

Section 5 Supported Spherical Electrode Model vs Isolated Spherical Electrode Model

The spherical electrode located on a flat substrate which partly shields the particle from diffusion is simulated in the cylindrical coordinates as illustrated in Figure S10a, where *r* and *z* are the two dimensions parallel and perpendicular to the supporting electrode surface. For the isolated spherical electrode, only the concentration distribution at the dimension *r* needs to be solved. Comparing the two geometries in Figure S10a, solving a partial differential equation in the isolated sphere model is much easier than the attached sphere model. As the steady-state currents of the two models have analogous expressions when the electrode size is small, we suggest that the overall cyclic voltammetric wave of the shielded sphere model can be approximated by the isolated sphere model for a simple one-electron-transfer reaction. The steady-state expressions of the two models are:[5, 6]

$$I_{\mathrm{attached}} = 4\pi \ln 2 F D r_{\mathrm{el}} c^{*} \qquad \text{\\* MERGEFORMAT (S2)}$$

$$I_{\mathrm{isolated}} = 4\pi F D r_{\mathrm{el}} c^{*} \qquad \text{\\* MERGEFORMAT (S3)}$$

I_{attached} equals I_{isolated} times a coefficient of ln2.

Figure S10 shows the cyclic voltammogram of a simple one-electron-transfer reaction at spherical electrodes of 1 um. The black solid line is the simulation with the model of a spherical electrode attached on the substrate; while the blue dashed line is from the model of an isolated spherical electrode with a correcting coefficient of ln2. The two voltammetric waves fully overlap with each other in the same simulation conditions and different approaches to calculate the electrode current. For both models, the initial concentration of the reactant is taken as 1 mM; the diffusion coefficient is 10^{-9} m^2 s^{-1}; and the electron transfer rate constant is 1 m s^{-1}. The concentration distribution at the electrode-electrolyte interface can be calculated from solving the diffusion equation. In the simulation of the attached spherical electrode, the current is calculated by:

$$I = 2\pi r_{\mathrm{el}} F D \int_0^{\pi} \left(r_{\mathrm{el}} \sin(\theta) \left. \frac{\partial c}{\partial n} \right|_{r=r_{\mathrm{el}}} \right) \mathrm{d}\theta \qquad \text{\\* MERGEFORMAT (S4)}$$

where θ is the angel of a point at the electrode surface deviating from the z axis. The current expression in the simulation of the isolated spherical electrode with the correcting coefficient ln2 is written as:

$$I = 4\pi {r_{\mathrm{el}}}^{2} FD \frac{\partial c}{\partial n}\bigg|_{r=r_{\mathrm{el}}} \qquad \text{* MERGEFORMAT (S5)}$$

From Figure 10b, it is found that the simulation results based on the two models fully overlap in the case of 1 μm radius spherical electrodes, proving the possibility of replacing the simulation of a one-electron-transfer reaction on a microsize attached spherical electrode by the isolated sphere model. In this work, as the radius of the Nafion sphere is about 0.43 μm and the electrochemical oxygen reduction reaction on Nafion is treated as a simple two-electron-transfer process, it is possible to use the corrected isolated sphere model in the simulation.

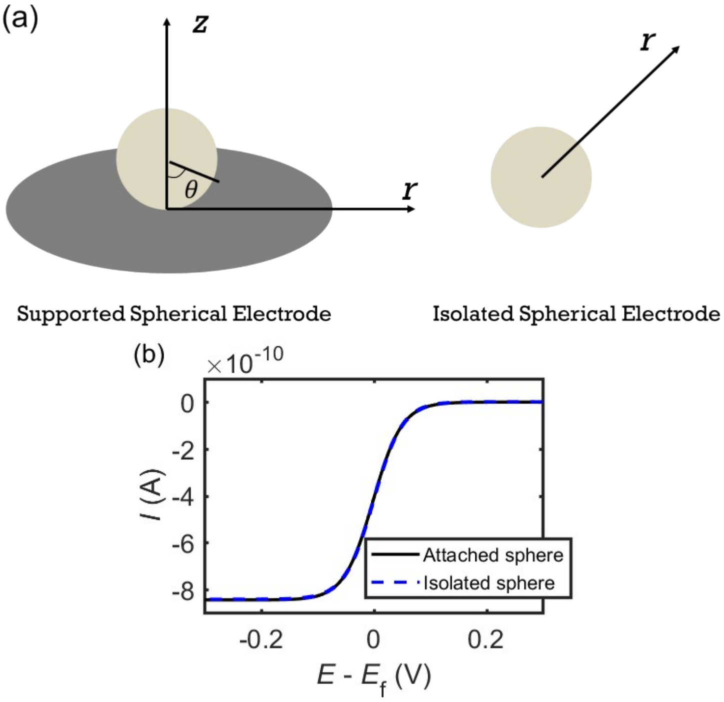

Figure S10. (a) Illustration of the geometries of the two spherical electrodes. (b) Cyclic voltammogram of the one-electron-transfer reaction. Black solid line: a spherical particle supported on a supporting electrode; blue dashed line: an isolated spherical electrode.

Section 6 Simulation and Experiment under Various MV^{2+} doping Levels.

Figure S11 shows the comparison between the simulations including (Figure S11 a and b) and excluding (Figure S11 c and d) the electrochemical oxygen reduction reaction. In the experiments of fully-doped MV^{2+} and half-doped MV^{2+}, the model including the electrochemical oxygen reduction reaction fits the experiment results much better, showing that it is available to distinguish the two competing catalytic reactions, the MV^{+} catalysed ORR and the electrochemical ORR, on a micro-/nano-size electrode.

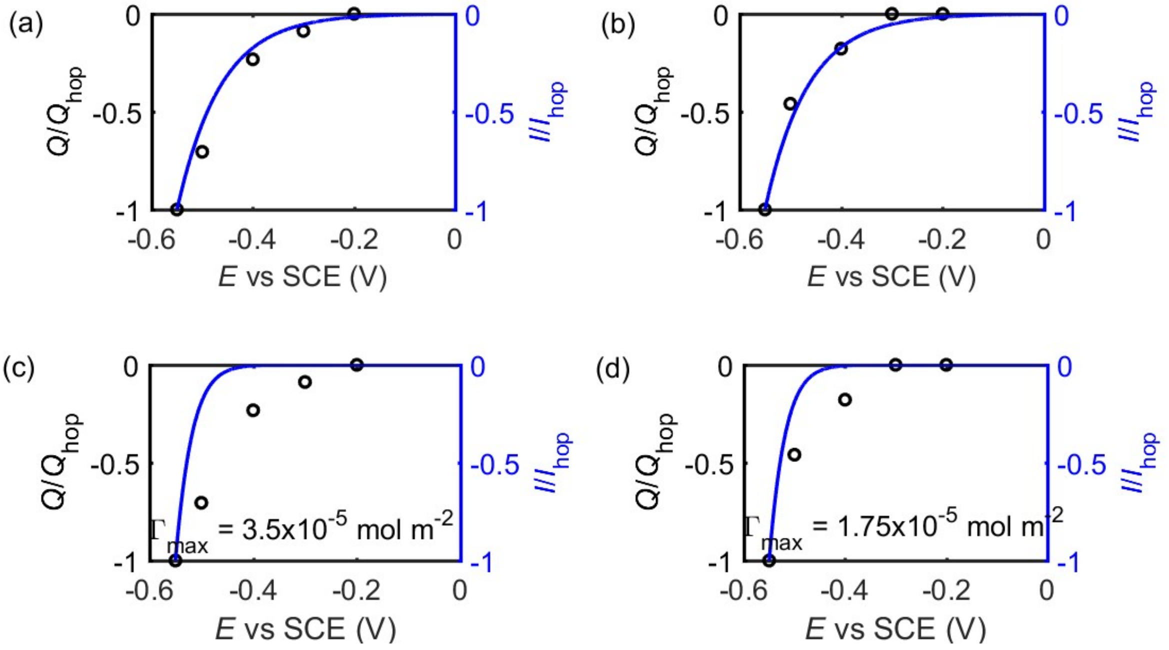

Figure S11. Potential dependence of the nano-impact charge and the simulated current-potential response. (a) fully-doped Nafion particles, where the MV^{2+} doping concentration in Nafion particles is 4.1 mM (the effective surface coverage of MV^{2+} $\Gamma_{max} = 2.6\text{x}10^{-6}$ mol m^{-2}); (b) half-doped Nafion particles, where the MV^{2+} doping concentration in Nafion particles is 2.55 mM (the effective surface coverage of MV^{2+} $\Gamma_{max} = 1.3\text{x}10^{-6}$ mol m^{-2}). (c) and (d) are the simulation excluding the electrochemical oxygen reduction reaction. Other simulation parameters are the same as used in Figure 5. The measurement is implemented in air saturated solution where $c_{O2}^* = 0.26$ mM. $r_{el} = 0.43$ μm.

References

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