

## Supporting Information

### **Nafion Particles Doped with Methyl Viologen: Electrochemistry**

Haiying Yang <sup>a,b</sup>, Xiuting Li <sup>b</sup>, Christopher Batchelor-McAuley <sup>b</sup>,

Stanislav V. Sokolov <sup>b</sup> and Richard G. Compton <sup>b\*</sup>

<sup>a</sup>Department of Chemistry, Yuncheng University, Yuncheng, 044000, P. R. China

<sup>b</sup>Department of Chemistry, Physical & Theoretical Chemistry Laboratory, Oxford  
University, Oxford, OX1 3QZ, United Kingdom

#### **Corresponding Author**

\*Correspondence to: [Richard.compton@chem.ox.ac.uk](mailto:Richard.compton@chem.ox.ac.uk)

Telephone number: +44(0) 1865 275957

## **Table of contents:**

Section 1: Estimation of the concentration of MV-Nafion particle suspension.

Section 2: Estimation of the amount of  $MV^{2+}$  doped into a single MV-Nafion particle.

Section 3: Dependence of the first reductive current of  $MV^{2+}$  to  $MV^{+}$  on the volume of MV-Nafion particles in dropcast experiments.

Section 4: Overlay of CVs of MV-Nafion particles dropcast on a GC electrode at varying scan rate and the dependence of the first reductive peak current on the square root of scan rate.

Section 5: Estimation of the diffusion coefficient of  $MV^{2+}$  in the Nafion particles.

Section 6: Histogram showing the reduction charges and the number of  $MV^{2+}$  incorporated in signal MV-Nafion particles at -0.8 V vs. SCE.

## Section 1:

### Estimation of the concentration of MV-Nafion particle suspension.

The concentration of the MV-Nafion particles used in the dropcast experiments is  $3.1 \times 10^{-11}$  mol/L, and in nano-impact experiment is  $3.1 \times 10^{-12}$  mol/L. Calculation is given below:

Mass of a single Nafion particle was estimated based on the size of the particle ( $r = 0.43 \pm 0.26 \mu\text{m}$ ) obtained from the SEM analysis and the assumption of a spherical shape and the density of Nafion ( $\rho_{Nafion} = 1.858 \text{ g cm}^{-3}$ )<sup>1</sup>:

$$m_{NP} = \frac{\rho_{Nafion} 4\pi r^3}{3}$$

Thus, the mass of one single particle is estimated to be  $6.4 \times 10^{-13}$  g.

The concentration of the particles  $C$  was calculated according to the following expression:

$$C = \frac{\rho V_{Nafion\ sol} wt\%}{m_{NP} N_A V_{suspension}}$$

where  $\rho$ ,  $V_{Nafion\ sol}$  and  $wt\%$  are the density ( $0.921 \text{ g cm}^{-3}$ ), volume ( $50 \mu\text{L}$ ) and Nafion weight fraction (12.5%) of Nafion solution used for synthesis;  $m_{NP}$  is the mass of one single particle ( $6.4 \times 10^{-13} \text{ g}$ );  $N_A$  is the Avogadro constant ( $6.02 \times 10^{23} \text{ mol}^{-1}$ ) and  $V_{suspension}$  is the volume of the particle suspension ( $0.5 \text{ mL}$ ). Therefore, the concentration of the particles  $C$  is  $3.1 \times 10^{-11}$  mol/L. The suspension was directly used in the dropcast experiments and diluted ten times in the nano-impact experiment ( $3.1 \times 10^{-12}$  mol/L).

## Section 2:

### Estimation of the amount of MV<sup>2+</sup> doped into a single MV-Nafion particle.

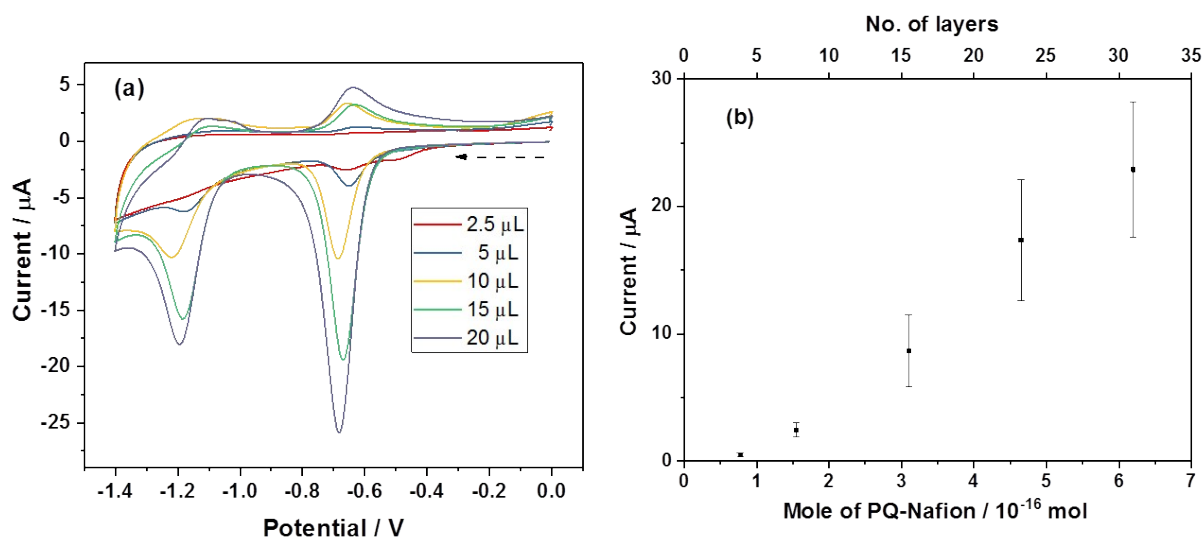
The maximum uptake of MV<sup>2+</sup> onto Nafion can be estimated via measurement of the absorption maximum of MV<sup>2+</sup> in solution at 257 nm using UV-Vis spectroscopy before and after absorption into the Nafion particles. The absorbance loss relates to the amount of MV<sup>2+</sup> incorporated in the MV-Nafion particles. Using the Beer-Lambert law the MV<sup>2+</sup>: Nafion ratio can be calculated to be  $(3.2 \pm 0.4) \times 10^{18}$  MV ions per gram Nafion using the following expression,

$$N_A \times \left( \frac{A_{before} - A_{after}}{\epsilon l} \right) \times \frac{V}{m_{Nafion}} \quad (1)$$

where  $\epsilon$  is the molar extinction coefficient of MV<sup>2+</sup> with a value of  $2.07 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ,<sup>2, 3</sup>  $l$  is the optical path of 1 cm,  $A_{before}$  and  $A_{ater}$  are the absorbance of MV<sup>2+</sup> solution before and after the absorption.  $V$  is the volume of the MV<sup>2+</sup> in solution.<sup>4</sup> The mass of one single particle is  $6.4 \times 10^{-13}$  g (see Section 1). Thus, the maximum number of MV<sup>2+</sup> molecules doped into a single Nafion particle is  $2.0 \pm 0.2 \times 10^6$ .

### Section 3:

**Dependence of the first reductive current of  $MV^{2+}$  to  $MV^{+}$  on the volume of MV-Nafion particles in dropcast experiments.**



**Figure S1.** (a) Cyclic voltammograms of MV-Nafion particles ensembles on GCE with various dropping amount (from inner to outside: 2.5, 5, 10, 15 and 20  $\mu L$ ) in 10 mM PBS (pH 7.4) with 0.1 M KCl at the scan rate of 0.1  $V s^{-1}$ . (b) Dependence of the first voltammetric reduction peak current on the amount and number of layers of MV-Nafion. The error bar was obtained from three repeats. The amount of MV-Nafion particles ranges from  $0.77 \times 10^{-16}$  mol to  $6.2 \times 10^{-16}$  mol equivalent to the number of particles from  $4.6 \times 10^7$  to  $3.7 \times 10^8$ .

In order to estimate the content of MV-Nafion coated on the electrode surface, the volume of material dropcast on the electrode was converted into the moles and an average number of monolayers. A GC macroelectrode dropcast with varying amount of MV-Nafion particles range of  $0.77 \times 10^{-16}$  mol to  $6.2 \times 10^{-16}$  mol (2.5  $\mu L$  to 20  $\mu L$ ) was investigated (Figure S1). The magnitude of the MV-Nafion particle voltammetric response is found to scale with the

number of moles of MV<sup>2+</sup> coated. The first reduction peak current represents the reduction of MV<sup>2+</sup>, and this peak is used to quantify the charge transferred to the MV-Nafion particle. A linear relationship between the current and the mole is obtained.

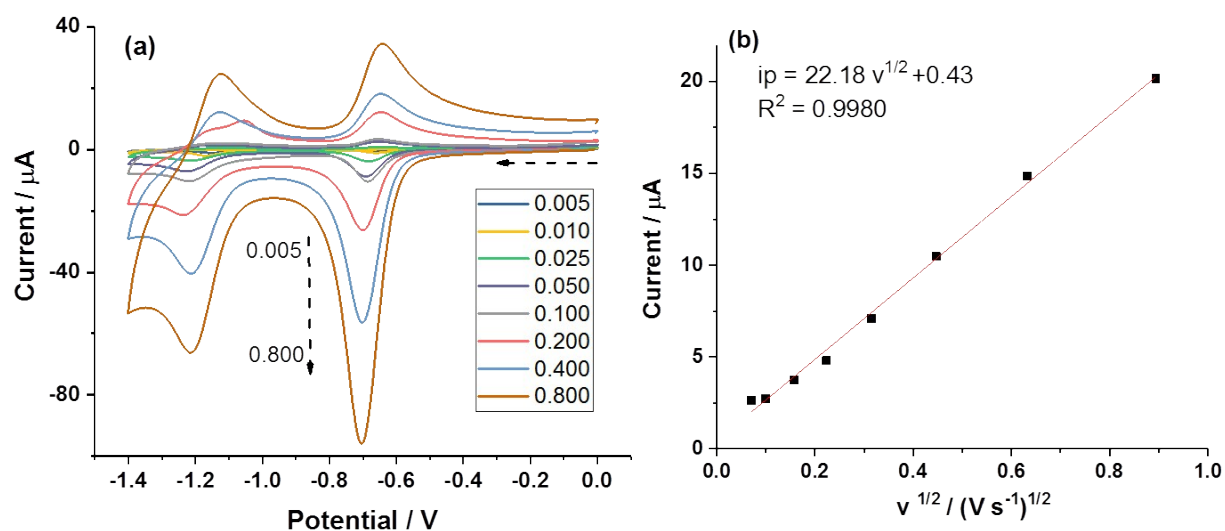
The thickness of the MV-Nafion particles coated on the electrode surface was estimated by converting the mass of dropcast material into the average number of monolayers. Assuming the MV-Nafion particles is quasi-spherical, and the number of layers ( $N_l$ ) of particles is calculated based on the following Equation (1):

$$N_l = \frac{cV}{\frac{A}{\pi r^2} \times \rho \times \frac{4}{3}\pi r^3} = \frac{3cV}{4A\rho r} \quad (1)$$

where  $c$  is the concentration of MV-Nafion particles,  $V$  is the dropcast volume,  $\rho$  represents the Nafion density in water (1.858 g m<sup>-3</sup>),<sup>1</sup>  $A$  is the geometric surface area of the electrode, and  $r$  is the radius of the particles from SEM analysis.  $6.2 \times 10^{-16}$  mole MV-Nafion particles casted on a GC electrode corresponding to 30 layers of particles gives the highest oxidation current. It becomes difficult to observe the MV<sup>2+</sup> reduction at less than 3 layers, which is likely due to the less content of electroactive molecules in the particles. The linear increase of current with the amount of dropcast materials seen in Figure S1 (b) probably reflects an increase in the number of particles directly in electrical contact with the electrodes. Note that it is likely that the particles form aggregation on the surface (see also below).

#### Section 4:

**Overlay of CVs of MV-Nafion particles dropcast on a GC electrode at varying scan rate and the dependence of the first reductive peak current on the square root of scan rate.**



**Figure S2.** (a) The overlaid voltammograms of a  $1.8 \times 10^8$  MV-Nafion particles dropcast on a GC electrode ( $d = 3$  mm) in 10 mM PBS with 0.1 M KCl at varying scan rates of 0.005, 0.010, 0.025, 0.050, 0.100, 0.200, 0.400 and 0.800  $\text{V s}^{-1}$ . (b) The first reductive current versus square root of scan rates at the range of 0.005 to 0.800  $\text{V s}^{-1}$ .

## Section 5:

### Estimation of the diffusion coefficient of MV<sup>2+</sup> in the Nafion particles.

The first reductive peak current is found to vary linearly with the square root of the scan rate ( $I/\mu\text{A} = 22.18 v^{1/2} - 0.43$ ,  $R^2 = 0.998$ ), suggesting that it is a diffusional control process. Then, the diffusion coefficient (D) of MV<sup>2+</sup> incorporated Nafion particles was estimated according to the Randles-Sevcik equation,

$$I = 2.69 \times 10^5 n^{3/2} A D^{1/2} C_{MV} v^{1/2}$$

where  $n$  is the transfer electron of 1, D is the diffusion coefficient,  $C_{MV}$  is MV<sup>2+</sup> incorporated into Nafion particles, A is the electrode area ( $7.07 \times 10^{-6} \text{ m}^2$ ),  $v$  is the scan rate.

For the concentration of MV<sup>2+</sup> incorporated Nafion particles can be estimated by the following equation:

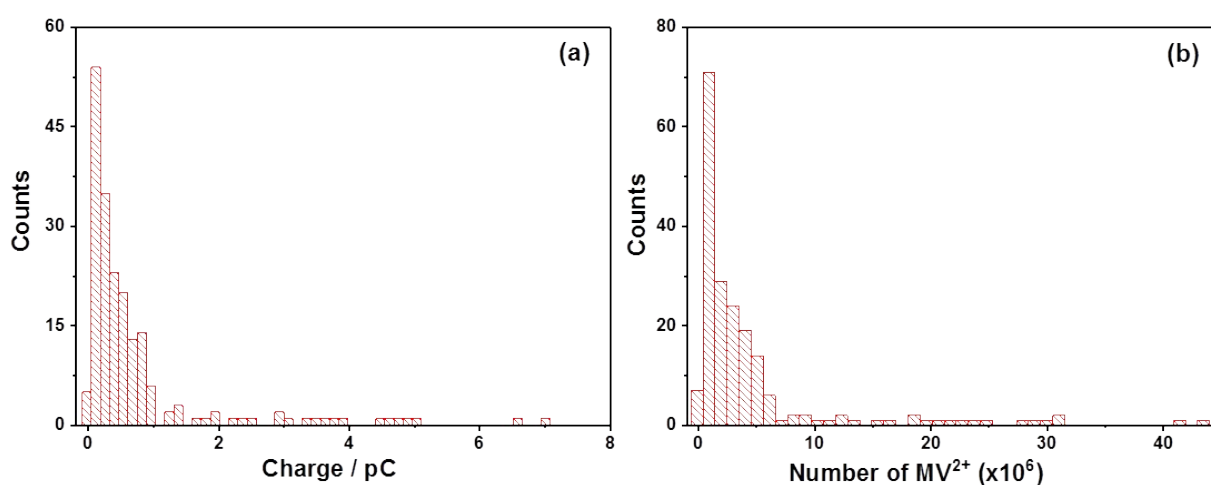
$$C_{MV} = \frac{n_{MV}}{m_{\text{Nafion,tot}} / \rho}$$

$n_{MV}$  is the moles of MV<sup>2+</sup> from UV-Vis results,  $m_{\text{Nafion,tot}}$  is the mass of Nafion in the particles,  $\rho$  is the density of Nafion.<sup>4</sup> So, the diffusion coefficient is estimated to be  $1.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  was obtained. However the above argument is based on semi-infinite, one dimensional diffusion and a fixed geometric area A corresponding to that of the electrode substrate. In reality (see main text) the value of D may likely be lower and the 'true' value of A to increase with coverage as a result of particle aggregation leading to underestimation of D at lower coverage.



## Section 6:

Histogram showing the reduction charges and the number of  $MV^{2+}$  incorporated in signal MV-Nafion nanoparticles.



**Figure S3.** (a) Histogram showing the MV-Nafion particles charges of the 350 spikes reductive from nano-impact experiments at  $-0.8$  V vs. SCE. (b) The histogram of the number of  $MV^{2+}$  incorporated in signal MV-Nafion particles.

## References and Notes

1. T. Takamatsu and A. Eisenberg, *J. Appl. Polym. Sci.*, 1979, **24**, 2221-2235.
2. J. H. Ross and R. I. Krieger, *J. Agric. Food Chem.*, 1980, **28**, 1026-1031.
3. T. Watanabe and K. Honda, *J. Phys. Chem.*, 1982, **86**, 2617-2619.
4. Noting that the absorbance of MV-Nafion particles was not directly used to calculate the amount of  $MV^{2+}$  incorporated in MV-Nafion particles. This is because the absorbance of  $MV^{2+}$  is sensitive to the surrounding environment of the complex cation of Nafion and

shows smaller extinction efficient than that in aqueous soltuion, which will lead to inaccurate estimation.