**Electronic Supplementary Information** 

### Evaluating the Mechanism of Nucleation and Growth of Silver Nanoparticles in Polymer Membrane under Continuous Precursor Supply: Tuning of Multiple to Single Nucleation Pathway

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S1. Experimental Small Angle X-ray Scattering (SAXS) profiles of pristine Nafion-117 membrane in Na+ form



**Figure S1.** Radial averaged SAXS profile of Nafion-117 membrane in Na<sup>+</sup> counter-ionic form and corresponding fit.

#### Fitting of experimental SAXS profile of a pristine membrane:

SAXS profile of pristine Nafion-117 membrane is very well known in literature<sup>1</sup>. Taking guidance from literature, the radial averaged SAXS profile of Nafion-117 membrane has been divided into two regimes for fitting, the membrane matrix (mem) regime at low q value (< 1 nm-1) and the water cluster (WC) regime at high q value ( $> 1 \text{ nm}^{-1}$ ). For fitting, the total scattering intensity I(q) was represented as

$$I(q) = C_{mem} I_{mem}(q) + C_{WC} I_{WC}(q)$$
<sup>(1)</sup>

Where  $C_{mem}$  and  $C_{WC}$  are scale factors and the subscripts mem and WC represent membrane matrix and water clusters respectively. Taking guidance from literature, polydispersed spherical particle model (equation 2) has been adopted to fit the SAXS data for the membrane matrix. In order to fit the low q regime of the SAXS profile, mass fractal structure factor (S(q,R)) has been considered<sup>2</sup>.

$$I_{mem}(q) = \int_{0}^{\infty} P(q, R) R^{6} D(R) S(qR) dR$$
(2)

Where, P(q,R) is the form factor and for a spherical object of radius R it is given as

$$P(q,R) = 9 \frac{(\sin (qR) - qR\cos (qR))^2}{(qR)^6}$$
(3)

D(R) represents the size distribution of the spherical object and is represented as

$$\boldsymbol{D}(\boldsymbol{R}) = \frac{1}{\sqrt{2\pi\sigma^2 R^2}} \exp\left[-\frac{\left[\ln(\boldsymbol{R}/\boldsymbol{R}_0)^2\right]}{2\sigma^2}\right]$$
(4)

Where  $R_0$  represents the median radius and  $\sigma$  represents the variance of the distribution being obtained by fitting the SAXS profiles.

Taking guidance from literature, polydisperse spherical particle model has been adopted to analyze the SAXS data for the water clusters. The term  $(I_{WC}(q))$  in equation 1 under local monodisperse approximation is expressed as:

$$I_{WC}(q) = \int_{0}^{\infty} P_{WC}(q, R) R^{6} D_{WC}(R) S_{WC}(q, R) dR$$
(5)

where,  $P_{WC}(q,R)$  denotes the spherical form factor for water clusters and  $D_{WC}(R)$  denotes the size distribution of water clusters.  $S_{WC}(q,R)$  denotes the structure factor due to the inter water cluster interaction which is responsible for the appearance of the peak at higher scattering vector (~1.7

nm<sup>-1</sup>). A hard sphere type interaction potential between the water clusters has been considered<sup>3</sup>. Fitting of the SAXS data has been carried out using SASfit software<sup>4</sup>. The fitting parameters are given in Table S1.

Table	<b>S1.</b> 5	SASfit	fitting	parameters	for the	analysis	of radial	averaged	SAXS	profiles	of pristine
Nafior	n-117	' memb	orane in	Na <sup>+</sup> counte	erionic	form.					

	Membrane	matrix	Water clusters		
	Size distribution	Structure	Size distribution	Structure factor	
	(Spherical form	Factor	(Spherical form	(Hard sphere)	
Parameter	factor)	(Mass fractal)	factor)		
N (particle number	2.6 x 10 <sup>-4</sup>		9.8 x 10 <sup>-3</sup>	_	
density, arb. unit)					
σ (polydispersity	0.26		0.18		
index)					
μ (median radius,	1.87		1.63	_	
nm)					
r <sub>0</sub> (characteristic		8.0			
dimension of					
individual clusters)					
xi (size of fractal		13.6			
aggregate)					
D (fractal	_	~3		—	
dimension)					

fp (volume fraction)	 	 0.58

# S2. Probing the kinetics of growth of nanoparticles using Small Angle X-ray Scattering (SAXS):

The evolution of growth of silver nanoparticles in the membrane was monitored using time resolved small angle X-ray scattering (SAXS) study. For this purpose, a series of membranes were prepared at the three different temperatures for various experimental times without adding the radioisotope in the precursor solution. The membrane samples containing silver nanoparticles were subjected to SAXS experiments using a laboratory based SAXS instrument with Cu K<sub>a</sub> as probing radiation. Radial averaged scattering intensity (I(q)) was obtained for wave vector transfer (q) ranging from ~0.1 to 1 nm<sup>-1</sup> (q =  $4\pi \sin(\theta)/\lambda$ , where,  $\lambda$  is the wavelength and  $2\theta$  is the scattering angle) and fitted using appropriate mathematical model. The raw radial averaged scattering profiles consist of scattering intensity I(q) was approximated as cumulative contribution of two scattering processes

$$I(q) = C_{mem}I_{mem}(q) + C_{NP}I_{NP}(q)$$
(6)

Where  $C_{mem}$  and  $C_{NP}$  are scale factors and the subscripts *mem* and *NP* represent polymer membrane and nanoparticles respectively. The scattering contributions due to the water clusters (at q > 1.1 nm<sup>-1</sup>) was intentionally avoided during the analysis of nanoparticles embedded membrane samples to keep the number of fitting parameters minimum. Polydispersed spherical particle model (equation 2) was adopted to fit the SAXS data for both the membrane matrix and silver nanoparticles. For fitting of silver nanoparticles scattering contribution, consideration of the structure factor in equation 2 was not necessary.

For the membrane samples where reactions were carried out for higher reaction time (eg. at 60°C, 80 min-600 min), the scattering data could not be fitted with only two set of variables (size, polydispersity index and number density index) as given in equation 6. This is due to the formation of nanoparticles with two different size ranges; smaller and larger. In such cases, the total scattering intensity was approximated by equation 7.

$$I(q) = C_{mem} I_{mem}(q) + C_{NP_{S}} I_{NP_{S}}(q) + C_{NP_{L}} I_{NP_{L}}(q)$$
(7)

Here, the subscript NP<sub>s</sub> and NP<sub>L</sub> correspond to smaller and larger nanoparticles, respectively.

It is to be noted that, the fitting parameters due to the membrane component has been negligibly varied during the analysis of silver nanoparticles embedded membranes.

S3. Experimental Small Angle X-ray Scattering (SAXS) profiles along with the Model fit.













**Figure S2.** Radial averaged SAXS profiles and corresponding fits at various times during contact of Nafion-117 membrane with silver citrate solution at 60°C (i-x), 80°C (xi-xvii), 92°C in presence of multiple nucleations (xviii-xxiii) and at 92°C in presence of single nucleation (xxiv-xxix)

#### S4. Calculation of number of silver nanoparticles in the membrane:

The number of silver nanoparticles in the membrane at a given reaction time has been obtained from the results of combined radiotracer and SAXS study. Radiotracer study (Section 2.3) gives the number of moles of  $Ag^0$  in the membrane in form of AgNPs, at a given time period.

In case of monomodal size distribution, the number of silver nanoparticles  $(N_{AgNPs})$  has been obtained from the equation

$$N_{AgNPs} = \frac{(n_{Ag^0} \times 3V_m)}{4\pi r^3} \tag{8}$$

Where  $n_{Ag^0}$  represents the number of moles of Ag<sup>0</sup> atoms in the strip,  $V_m$  represents the molar volume of silver (10.28 cm<sup>3</sup>/mol); r represents the median radius of the nanoparticles.

In case of bimodal size distribution, the mutual ratio of smaller to larger nanoparticles was obtained by taking the ratio of number density index as obtained from SAXS analysis (Section S2, S3). The absolute number of smaller and larger nanoparticles was thus obtained using the knowledge of total mass of nanoparticles as obtained from the radiotracer study and the diameter of smaller and larger particles as obtained from SAXS analysis.

### **S5.** Reproducibility of the monomer concentration.

**Table S2.** Concentration of monomer at the three temperatures at different stages of nanoparticle

 synthesis

Temperature	Time	Monomer concentration (mol L <sup>-1</sup> )		
(°C)	(min)	Experiment 1	Experiment 2	
60	30	1.82 x 10 <sup>-9</sup>	2.32 x 10 <sup>-9</sup>	
80	5	1.69 x 10 <sup>-9</sup>	1.91 x 10 <sup>-9</sup>	
80	10	1.87 x 10 <sup>-9</sup>	1.86 x 10 <sup>-9</sup>	
92	2	2.91 x 10 <sup>-9</sup>	2.91 x 10 <sup>-9</sup>	

S6 Representative TEM images of the membranes consisting of silver nanoparticles





**Figure S3.** TEM images showing the spatial distribution of silver nanoparticles across the thickness of Nafion-117 membrane equilibrated with silver citrate solution at 60°C for 40 minutes (a,b) and 600 minutes (c,d). The corresponding size distribution histograms at 40 min (e) and 600 min (f) are also given.

# S7. Variation in size and number of silver nanoparticles formed in Nafion-117 membrane at 80°C and 92°C.

Figure S4 shows the time resolved variation in size and number of nanoparticles in the Nafion-117 membrane during their synthesis as obtained from combined SAXS and radiotracer studies.



**Figure S4.** Time resolved variation in size and number at 80°C (a,b) and at 92°C(c,d) of nanoparticles in Nafion-117 membrane. Solid lines are eye guides only.

#### **S8.** Size distribution of nanoparticles



**Figure S5.** Size distribution profile of AgNPs hosted in Nafion-117 membrane during synthesis by citrate route with condition of multiple nucleation (a) and single nucleation (b).



### **S9.** Optical quality of nanoparticles

**Figure S6.** Time resolved evolution of UV-visible absorption spectra of AgNPs in Nafion-117 membrane during synthesis at 92°C, under the condition of multiple nucleation (a) and single nucleation condition (b).

#### Calculation of integrated absorption cross section

Table S3. Parameters of the AgNPs quantitatively calculated by SAXS and radiotracer techniques

	Diameter		Absorbance at	Absorption cross	Integrated absorption
	of AgNPs	No. of	peak max	section at peak max	cross section (315-
Route of	(SAXS	particles in	(λ=400 nm)	(λ=413 nm), for a	800 nm) for a single
synthesis	data)	the strip	of the strip	single AgNP	AgNP
	d (nm)	N <sub>AgNPs</sub>	$A_{\lambda-max}$	C <sub>abs-max</sub> (nm <sup>2</sup> ) <sup>†</sup>	$\int C_{abs} \Delta \lambda$ ( nm <sup>3</sup> )
Multiple nucleation	21.93	1.63 x 10 <sup>13</sup>	1.92	1.08 x 10 <sup>5</sup>	9.91 x 10 <sup>7</sup>
Single nucleation	20.94	1.77 x 10 <sup>9</sup>	1.91	9.92 x 10 <sup>8</sup>	1.16 x 10 <sup>11</sup>

<sup>+</sup>The values of  $C_{abs}$  have been calculated using the formula  $C_{abs} = (2303 \times A \times V_{strip})/(N_{AgNPs} \times L)$ ; where A denotes the absorbance,  $V_{strip}$  denotes the volume of the strip,  $N_{AgNPs}$  denotes the number of nanoparticles in the strip, and L denotes the optical path length (thickness of the strip)<sup>5</sup>.

#### S10. Theoretical description of Classical Nucleation Theory

The thermodynamics of nucleation is described by the popular "classical nucleation theory", which states that the nucleation involves a free energy barrier, originating from the balance between the surface and volume energy term as shown in equation 9. Considering a first order rate equation for nucleation, the nucleation rate constant can be given by simple Arrhenius equation (equation 10)

$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_V$$

$$k = A \exp\left(\frac{-\Delta G_{crit}}{k_B T}\right)$$
(10)

Where; r and  $\gamma$  are the radius and surface energy of a nucleus respectively,  $\Delta G_v$  is the change in Gibbs free energy per unit volume of the solid phase (the nucleus), k is the rate constant; A is the pre-exponential factor,  $\Delta G_{crit}$  is the critical free energy of activation for nucleation;  $k_B$  is Boltzmann constant and T is temperature. The critical free energy of activation ( $\Delta G_{crit}$ ) and the critical radius above which the nuclei are thermodynamically stable ( $r_{crit}$ ) are given by equation 11 and 12.

$$\Delta G_{crit} = \frac{16\pi\gamma^3 v_m^2}{3R^2 T^2 N_A^2 (\ln S)^2}$$
(11)

$$r_{crit} = \frac{2\gamma v_m}{RN_A T(\ln S)}$$
(12)

Where,  $v_m$  is the molar volume of the monomer species and S is the supersaturation, mathematically defined as the ratio of the monomer concentration [C] at a given time to the equilibrium monomer concentration [C<sub>s</sub>] and R is gas constant. For a system, the  $\Delta G_V$  has a strong dependence on supersaturation (S) which depends on temperature. On the other hand surface energy ( $\gamma$ ) will also change with temperature. Therefore,  $\Delta G_{crit}$  and  $r_{crit}$  will modify with temperature. In the present synthesis, within the temperature range under study (60 to 92 °C), both the  $C_s$  and  $C_{max}$  have been seen to be nearly constant. In this situation, therefore, it is reasonable to approximate that the  $\Delta G_V$  and the surface energy will be independent of temperature within this temperature range in the present study. This allowed us to assume the validity of Arrhenius type equation (equation 10) and subsequent measurement of  $\Delta G_{crit}$  under the present range of temperature.

## S11. Determination of rate constant for the decay of monomer concentration during nucleation:

The rate constant for the decay of monomer concentration during the formation of nuclei have been calculated assuming it to be a first order reaction. Following the first order rate kinetics, natural logarithm of concentration of monomer was plotted against time at three different temperatures. A representative plot is shown in figure S7 at 60<sup>o</sup>C. The parameters obtained from the fitting are given in Table S4.



**Figure S7.** Plot of natural logarithm of monomer concentration with time during nucleation ( $T=60^{\circ}C$ ). The slope is related to the rate of nucleation.

**Table S4.** Fitting parameters and rate constants of monomer consumption at the three different

 temperatures under the present investigation.

Temperature	C1	<b>T</b>	1 ( 1)
(°C)	Slope	Intercept	K (S <sup>-1</sup> )
( 0)			
60	$-0.011 \pm 0.003$	$-19.77 \pm 0.08$	0.01
80	$-0.040 \pm 0.022$	$-19.49 \pm 0.31$	0.04
92	$-0.121 \pm 0.07$	$-19.49 \pm 0.25$	0.12

#### References

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