Electronic Supplementary Information

Solvent Diffusion in Polymer-Embedded Hollow Nanoparticles Studied by *In-situ* Small Angle X-ray Scattering

*Zhi Hong Chen, Sun Hye Hwang, Xiang-bing Zeng, Jongmin Roh, Jyongsik Jang, and Goran Ungar**

Contents

S1. Data analysis procedure

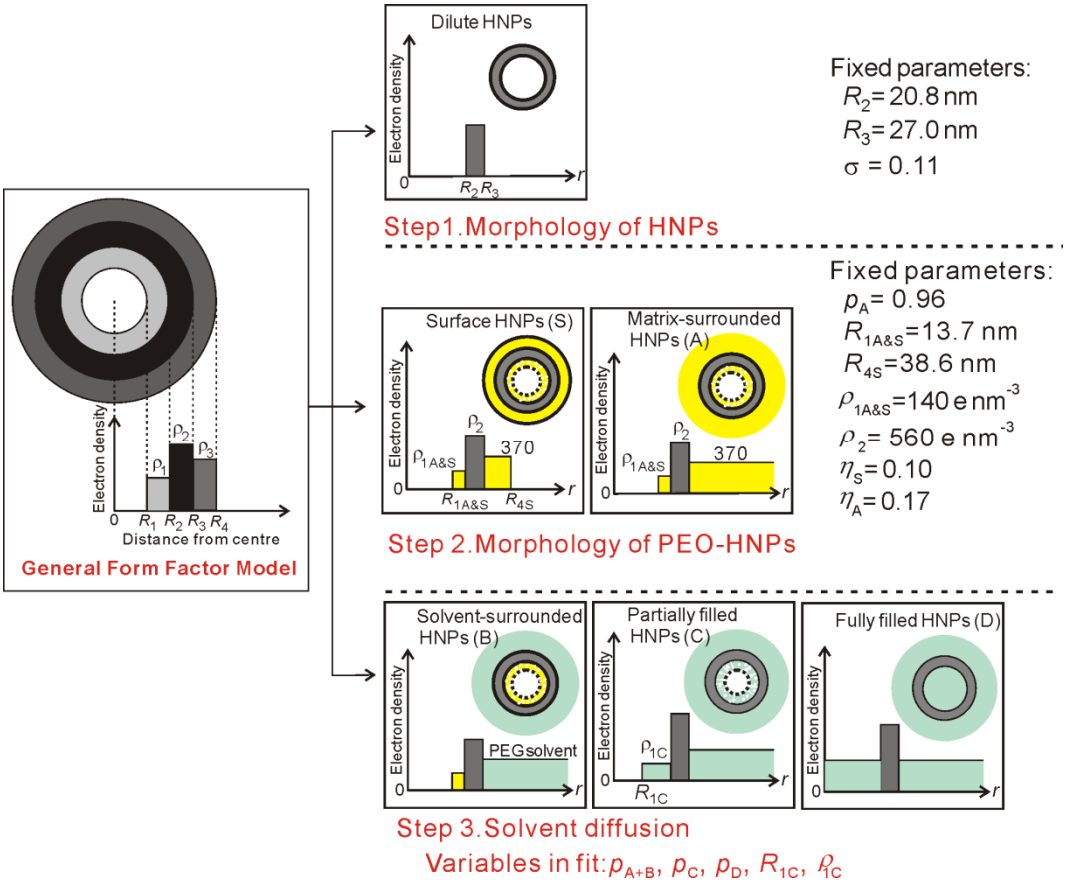

Fig. S1 Schematic illustration of the triple-shell hollow particle model (left), and of the three steps in the SAXS data analysis (right). The parameters obtained at each step are listed on the right and were fixed in the next fitting step.

Table S1. Breakdown of the SAXS analysis process

Analysis steps	Particles Involved	Form factor model	Structure factor	Fittting parameters
1. Morphology of HNPs	HNPs only	Hollow single-shell sphere	PY (3D)	R_2, R_3, σ, η_0
2. Morphology of PEO-embedded HNPs	Surface HNPs (S)	Hollow triple-shell sphere	PY (2D)	$p_A, R_{1A\&S,}, R_{4S}, \rho_{1A\&S}, \rho_2, \eta_A, \eta_S$
	Matrix-surrounded HNPs (A)	Hollow double-shell sphere	PY (3D)	
3.Solvent diffusion	Solvent-surrounded HNPs (B)	Hollow double-shell sphere	PY (3D)	$p_{A+B}, p_C, p_D, R_{1C}, \rho_{1C}$
	Partially filled HNPs (C)	Hollow double-shell sphere	PY (3D)	
	Fully filled HNPs (D)	Hollow single-shell sphere	PY (3D)	

S2. Fitting results on morphology of as-prepared and PEO-embedded HNPs

Table S2. HNP dimensions obtained by fitting SAXS curve for dilute suspension in water

Outer radius R_3 (nm)	Inner radius R_2 (nm)	Shell thickness R_3-R_2 (nm)	Stand. dev. of outer diameter (σ)*	Packing density η_0	χ^2
27.0 ± 0.4	20.8 ± 0.4	6.2	(11 ±1)%	0.05±0.02	108.86

* Here the standard deviation of outer diameter refers to polydispersity of outer diameter.

Table S3. Morphological parameters of matrix-surrounded and surface HNPs in freeze-dried sample*

Parameters	Matrix-surrounded HNPs (A)	Surface HNPs (S)
Fraction of all HNPs (p_A or (1-p_A))	0.96 ± 0.01	0.04 ± 0.01
Particle packing density (η_A or η_S)	0.17 ± 0.05	0.10 ± 0.05
Thickness of outer PEO R_{4S}-R_3 (nm)	NA	11.6 ± 1.0
Thickness of inner PEO (R_2-$R_{1A\&S}$) (nm)	7.1 ± 0.4	
Electron density of inner PEO $\rho_{1A\&S}$ (e nm^{-3})	140 ± 20	
Electron density of HNP shell ρ_2 (e nm^{-3})	560 ± 20	
χ^2	15.82	

* The electron densities of inner PEO layer and HNP shell had been scaled according to the electron density of PEO with a value of 370 e nm^{-3}. The electron density was calculated by $\rho_e = (\frac{\rho_m \cdot V}{M_m} \cdot N_A \cdot N_e)/V$ with ρ_e the electron density, ρ_m the mass density, V the volume of the sample, M_m the molar mass of a molecule, N_A the Avogadro's constant and N_e the number of electrons in a molecule. The mass density of bulk PEO in the calculation was 1.13 g/cm^3.[S1]

S3. Detailed results of fitting SAXS curves recorded during PEG diffusion

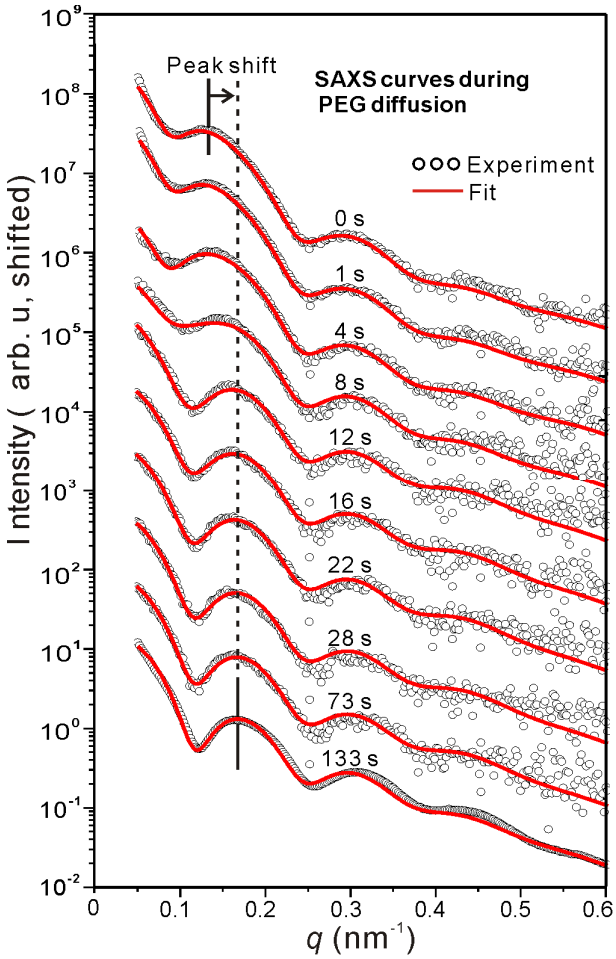

Fig. S2. Experimental (open circles) and fitted (red solid line) SAXS curves for PEG diffusion in PEO-embedded HNPs. For clarity, only a few curves are shown here, and they are vertically shifted. The lateral shift of the main scattering peak during solvent diffusion is shown by vertical reference lines.

Table S4. Fitting results for the change in the fraction of surface HNPs, matrix- and solvent-surrounded empty HNPs, partially filled HNPs, and fully filled HNPs, and for the change in thickness and electron density of the inner solvent layer in the case of partially filled HNPs

	Surface HNPs (S)	Matrix- & solvent-surrounded empty HNPs (A+B)	Partially Filled HNPs (C)			Filled HNPs (D)	χ^2
Time	Fraction $(1-p_{A+B}-p_C-p_D)$ (±0.01)	Fraction p_{A+B} (±0.04)	Fraction p_C (±0.03)	Thickness of inner solvent layer R_2-R_{1C} (±1.7 nm)	Electron density of inner solvent* ρ_{1C} (±50 e nm^{-3})	Fraction p_D (±0.03)	
0 s	0.04	0.96	0	-	-	0	15.82
1 s	0.04	0.93	0.03	7.4	129	0	15.20
2 s	0.03	0.89	0.08	9.7	99	0	10.13
3 s	0.02	0.82	0.16	10.1	143	0	11.97
4 s	0.02	0.68	0.24	9.1	129	0.06	11.68
5 s	0.01	0.56	0.29	9.9	104	0.14	12.86
6 s	0.01	0.51	0.30	10.4	119	0.18	12.55
7 s	0.01	0.45	0.31	10.3	159	0.23	11.80
8 s	0	0.32	0.31	9.2	114	0.37	15.07
9 s	0	0.24	0.33	9.5	133	0.43	10.13
10 s	0	0.11	0.37	9.2	110	0.52	12.19
11 s	0	0.05	0.36	8.8	118	0.59	10.38
12 s	0	0	0.39	12.6	137	0.61	13.65
13 s	0	0	0.37	13.4	150	0.63	10.76
16 s	0	0	0.36	14.0	164	0.64	10.22
22 s	0	0	0.33	14.7	170	0.67	15.35
28 s	0	0	0.32	14.9	181	0.68	15.58
73 s	0	0	0.31	18.0	190	0.69	14.85
133 s	0	0	0.29	21.1	198	0.71	4.55

*The electron density of inner solvent was obtained by scaling to that of outside pure PEG solvent. The reason why the electron density of the inner solvent layer in the partially filled HNPs did not reach the value of bulk PEG, i.e. 370 e nm^{-3}, is thought to be the presence of air bubbles trapped inside the inner solvent of partially filled HNPs, which gave a lower average electron density.

Table S5. Sensitivity of the fits to deviations of individual parameters for scattering curves recorded during solvent diffusion*

Parameter	Parameter increased/decreased by 30%	χ^2	Deviation of χ^2 from best fit
	Best fit	12.86	----
Fraction of fully filled HNPs (p_D)	Increased	30.79	140%
	Decreased	16.64	30%
Fraction of surface HNPs (1 - p_{A+B} - p_C - p_D)	Increased	14.90	16%
	Decreased	26.94	109%
Fraction of partially filled HNPs (p_C)	Increased	14.90	16%
	Decreased	16.99	32%
Electron density of inner solvent layer (ρ_{1C})	Increased	17.93	39%
	Decreased	16.95	31%
Thickness of inner solvent layer (R_2-R_{1C})	Increased	14.80	15%
	Decreased	18.51	44%

* The effect of the fraction of empty-surrounded HNPs on the fit is not evaluated here since this value is constrained by the total fraction of HNPs measured independently.

S4. Estimation of diffusion coefficient of solvent in HNPs

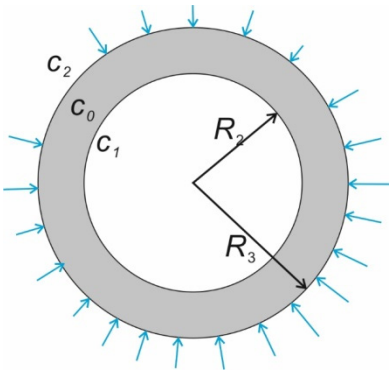

Fig. S3. Illustration of the model for radial diffusion of solvent in a hollow particle. R_2 and R_3 are inner and outer radii of the HNP, c_0, c_1 and c_2 are, respectively, the initial concentrations of solvent in the shell, at the inner surface and at the outer surface. The blue arrows indicate the flow direction of solvent.

Having defined the parameters in Fig. S4, the general expression for radial diffusion of solvent through spherical shell can be given by[S2]

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{\mathrm{r}} \cdot \frac{\partial c}{\partial r}\right) \tag{S1}$$

where c is the concentration of sovlent at radial distance r from the center at time t. The initial and boundary conditions of eqn (S1) are

$$\begin{cases} c = c_0 & (t = 0, R_2 < r < R_3); \\ c = c_1 & (t > 0, r = R_2); \\ c = c_2 & (t > 0, r = R_3). \end{cases} \tag{S2}$$

The general solution of eqn (S1) has been given in the literature and can be written as[S3]

$$\begin{aligned} c = {} & \frac{c_1 R_2}{r} + \frac{c_2 R_3 - c_1 R_2}{(R_3 - R_2)} \cdot \frac{(r - R_2)}{r} \\ & + \frac{2}{\pi r} \sum_{n=1}^{\infty} \frac{c_2 R_3 cosn\pi - c_1 R_2}{n} sin \frac{n\pi (r - R_2)}{(R_3 - R_2)} \cdot exp\left(-\frac{Dn^2\pi^2 t}{(R_3 - R_2)^2}\right) \\ & - \frac{2c_0}{\pi r} \cdot \sum_{n=1}^{\infty} sin \frac{n\pi (r - R_2)}{(R_3 - R_2)} \cdot \frac{(R_3 cosn\pi - R_2)}{n} \cdot exp(-\frac{Dn^2\pi^2 t}{(R_3 - R_2)^2}) \end{aligned} \tag{S3}$$

The total amount of solvent that had flown through the outer surface of the hollow spherical shell within time *t* can be expressed by

$$M_t = -4\pi D \int_0^t {R_3}^2 \left(\frac{\mathrm{d}c}{\mathrm{d}r}\right)_{r=R_3} \mathrm{d}t \tag{S4}$$

M_t can be further expanded into[S3]

$$\begin{aligned} M_t = {} & 4\pi D(c_1 - c_2) \frac{R_3 R_2}{(R_3 - R_2)} t - \frac{4\pi}{3} {R_3}^2 (R_3 - R_2)(c_2 - c_0) \left[1 - \frac{6}{\pi^2} \cdot \sum_{n=1}^{\infty} \frac{1}{n^2} exp\left(-\frac{Dn^2\pi^2 t}{(R_3 - R_2)^2}\right)\right] \\ & - \frac{2\pi}{3} R_3 R_2 (R_3 - R_2)(c_1 - c_0) \left[1 - \frac{12}{\pi^2} \cdot \sum_{n=1}^{\infty} -\frac{cosn\pi}{n^2} exp\left(-\frac{Dn^2\pi^2 t}{(R_3 - R_2)^2}\right)\right] \end{aligned} \tag{S5}$$

In our case, when only the diffusion of solvent through the HNP shell is considered, *i.e.* c_0=0 and c_1=0. M_t is further reduced to

$$M_t = -4\pi D c_2 \frac{R_3 R_2}{(R_3 - R_2)} t - \frac{4\pi}{3} {R_3}^2 (R_3 - R_2) \cdot c_2 \cdot \left[1 - \frac{6}{\pi^2} \cdot \sum_{n=1}^{\infty} \frac{1}{n^2} exp\left(-\frac{Dn^2\pi^2 t}{(R_3 - R_2)^2}\right)\right] \tag{S6}$$

Within a timescale that equals the half-life of solvent surrounded HNPs, half of the solvent surrounded HNPs changed into partially filled HNPs, meaning the shell of those HNPs was filled by solvent. Hence, the amount of solvent filling the shell of half solvent surrounded HNPs derived from SAXS can be considered to equal to that derived by Fick's law. We have

$$(M_t)_{\text{Fick}'\text{s law}} = (M_t)_{\text{SAXS}} \tag{S7}$$

where

$$(M_t)_{\mathrm{SAXS}} = -\frac{1}{2}\cdot\frac{4\pi(R_3^3 - R_2^3)}{3}\cdot\rho_{\mathrm{solvent}}\cdot x$$

and $c_2 = \rho_{\mathrm{solvent}}\cdot x$ with ρ_{solvent} the density of solvent and x the HNP shell porosity. Therefore, the diffusion coefficient of solvent through the shell of HNPs can be expressed by

$$R_3^3 - R_2^3 = 6D\frac{R_3R_2}{(R_3 - R_2)}t_{½} + 2R_3^2(R_3 - R_2)\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-\frac{Dn^2\pi^2t_{½}}{(R_3 - R_2)})\right] \quad \text{(S8)}$$

From the SAXS results, the diffusion coefficient of PEG in HNP shell is estimated to be ~8×10^{-18} m^2/s.

References

S1 Value of density was taken from safety data sheet of the product on the website of Sigma Aldrich chemical company. Website: http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=CN&language=zh&productNumber=181986&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3Dpolyethylene%2Boxide%26interface%3DAll_ZH%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Dzh%26region%3DCN%26focus%3Dproduct. (Accessed 2017/4/20)

S2 R. M. Barrer, *Phil. Trans. R. Soc. A Math. Phys. Eng. Sci.,* 1944, **35**, 802-811.

S3 J. Crank, *The mathematics of diffusion (2nd Edt),* Clarendon Press, Oxford, **1975**.