

Supporting Information

Solvent-free Porous Liquid Comprising Hollow Nanorods - Polymer Surfactant Conjugates

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Table of Contents:

- 1. Experimental**
- 2. Supporting Figures**
- 3. Supporting Tables**
- 4. Calculations for Volume fraction of silica and voids for SiNRs**
- 5. References**

1. Experimental

(i) FT-IR spectroscopy:

To study the functional group attachment, IR spectroscopy was employed. FT-IR spectra were obtained on a PerkinElmer Spectrum One FT-IR spectrophotometer as KBr diluted disks. In a typical experiment, a pinch of topic compound (say, SiNRs), was grinded thoroughly with KBr. The samples were pelletized with a hydraulic pressure unit. Prior to analysis, background correction was carried out with air. The range of analysis was fixed to 4500 to 500 cm^{-1} .

(ii) Differential scanning calorimetry (DSC):

DSC was performed using a TA DSC Q20 model in a hermetic pan/lid sample holder. The samples were subjected to three cycles within the range of - 80 to + 80 $^{\circ}\text{C}$. About 1 to 2 mg of the sample was taken in hermetic pan, well-sealed and scanned at 10 $^{\circ}\text{C min}^{-1}$ under N_2 atmosphere. The instrument was calibrated with indium standards prior to measurements.

(iii) Rheology:

To understand the flow behaviour of porous liquid based on hollow silica nanorods (PS-OS@SiNR) of aspect ratio 8 and 11, oscillatory rheological experiments (amplitude sweep and frequency sweep) were performed on MCR302 (Anton Paar) machine. Prior to the experiments the samples (PS-OS@SiNR sample with aspect ratios 8 and 11) were vacuum dried and sealed. First, strain/amplitude sweep experiment were performed to determine the linear region (the amplitude for the linear region was found to be $\sim 0.1\%$). The frequency sweep experiments were carried out at three different temperatures viz. 15 $^{\circ}\text{C}$, 20 $^{\circ}\text{C}$ and 25 $^{\circ}\text{C}$ in the frequency range from 0.1 to 100 radian s^{-1} at 0.1% amplitude using 8 mm parallel plate geometry.

(iv) Thermo gravimetric analysis (TGA):

TGA was carried out on a PerkinElmer Pyris Diamond TG/DTA analysis system under a stream of nitrogen gas from 25 to 600 °C at a heating rate of 10 °C min⁻¹. Before analysis, the sample was thoroughly dried under vacuum and kept in a vacuum desiccator. Roughly 2 mg of the sample was used for the analysis.

2. Supporting Figures:

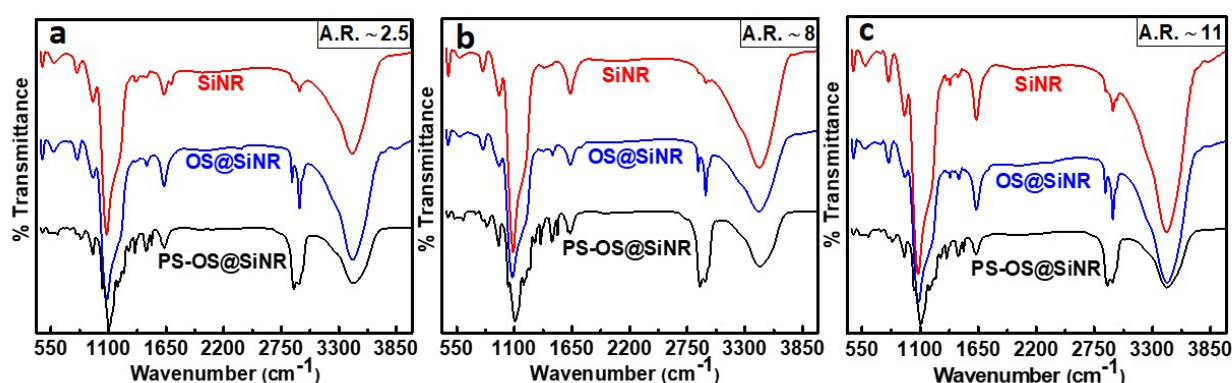


Figure S1: FT-IR spectra of SiNR, OS@SiNR and PS-OS@SiNR. Of aspect ratio (a) 2.5, (b) 8, (c) 11.4. The peak at ~1625cm⁻¹ corresponds to the bending vibration of H₂O molecules which appeared in almost all stages of the sample. There is a broad peak around 3445 cm⁻¹ attributed to the surface bound OH groups and the physisorbed water molecules.^{1, 2}

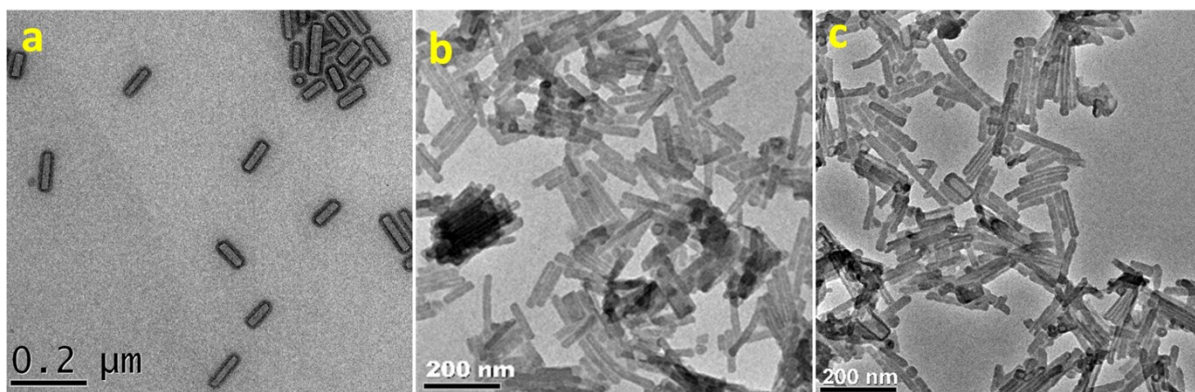


Figure S2: Transmission electron microscopic images of OS@SiNR of aspect ratio (a) 2.5, (b) 8 and (c) 11 showing the retention of rod like shape having hollow core even after modification with organosilane (OS).

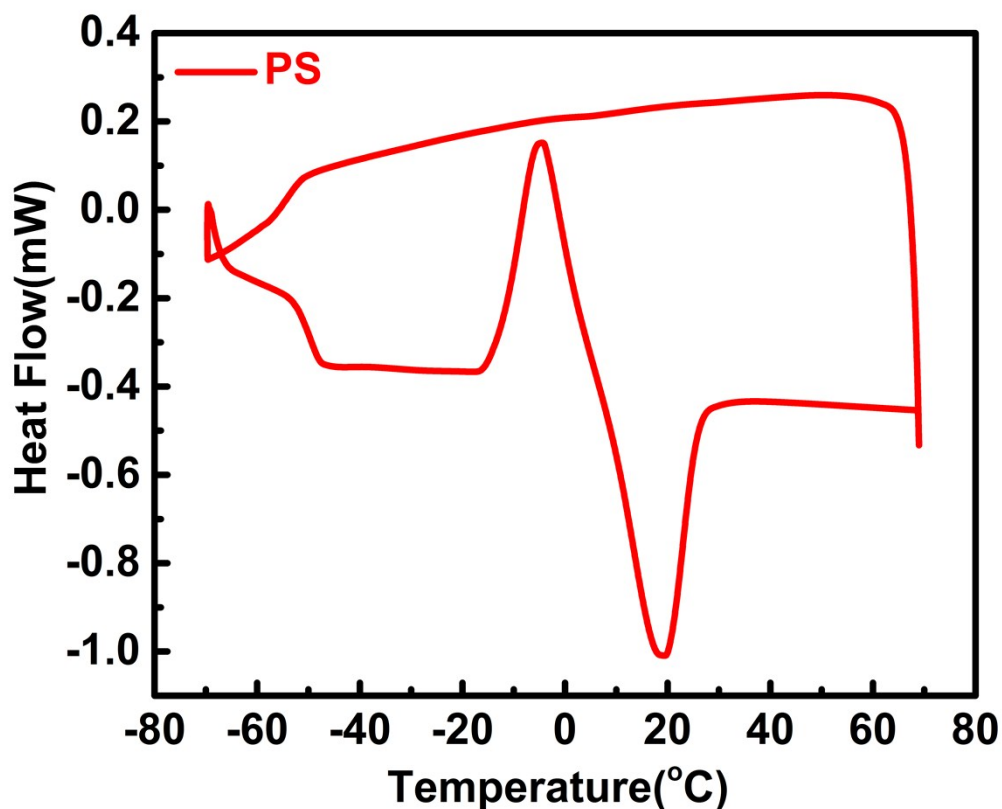


Figure S3: DSC profile of polymer surfactant (PS) showing the endothermic melting transition temperature (T_m) and exothermic crystallization transition temperature at ~ 20 °C and ~ -5 °C respectively.

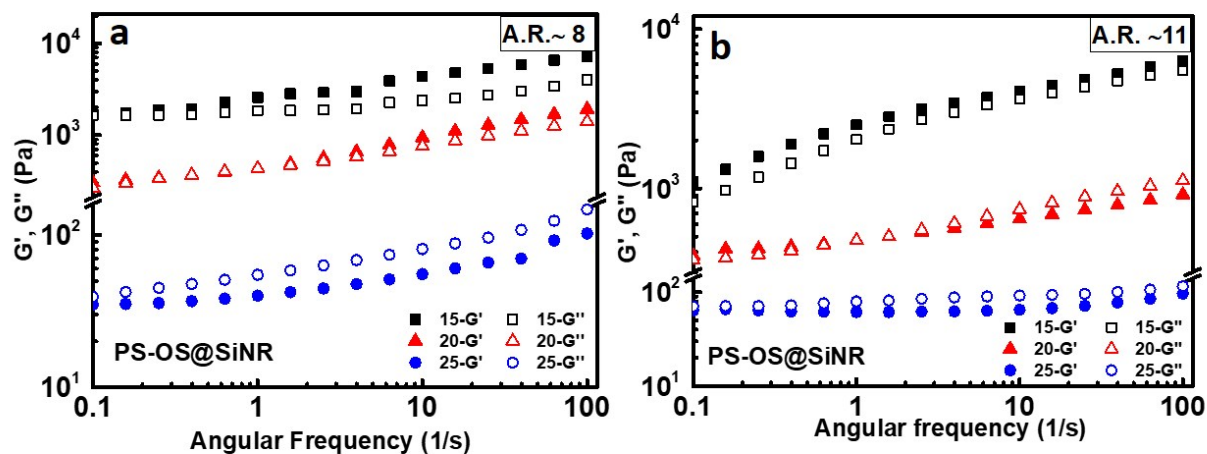


Figure S4: Frequency sweep rheology showing G' (storage modulus) and G'' (loss modulus) at different temperatures for PS-OS@SiNRs with aspect ratio (a) 8 and (b) 11.

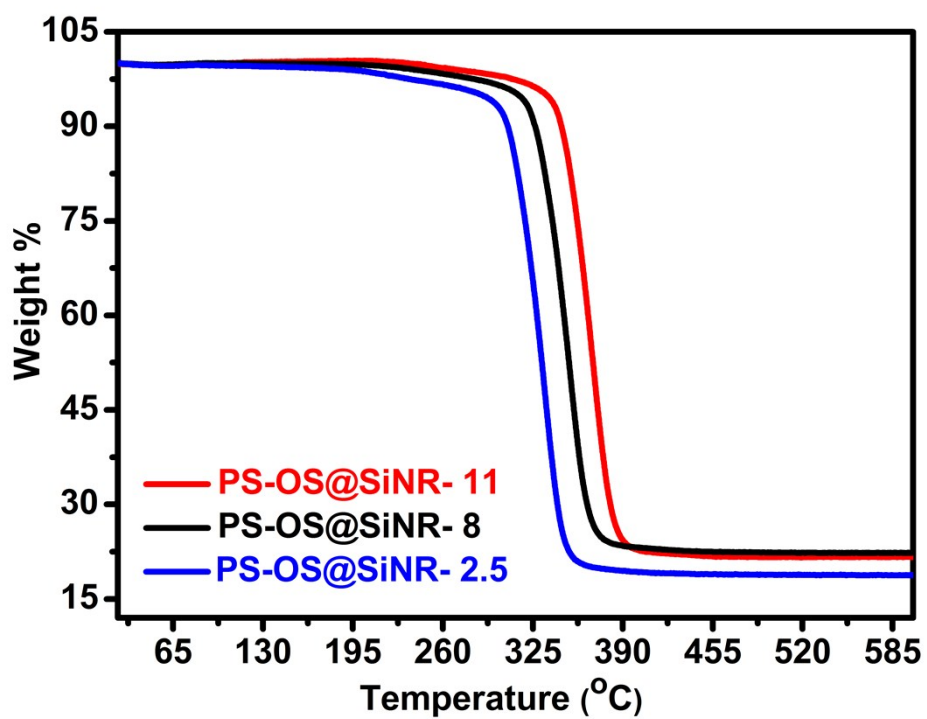


Figure S5: Thermo gravimetric analysis of PS-OS@SiNR of aspect ratio 11(*red curve*) 8(*black curve*), 2.5(*blue curve*),

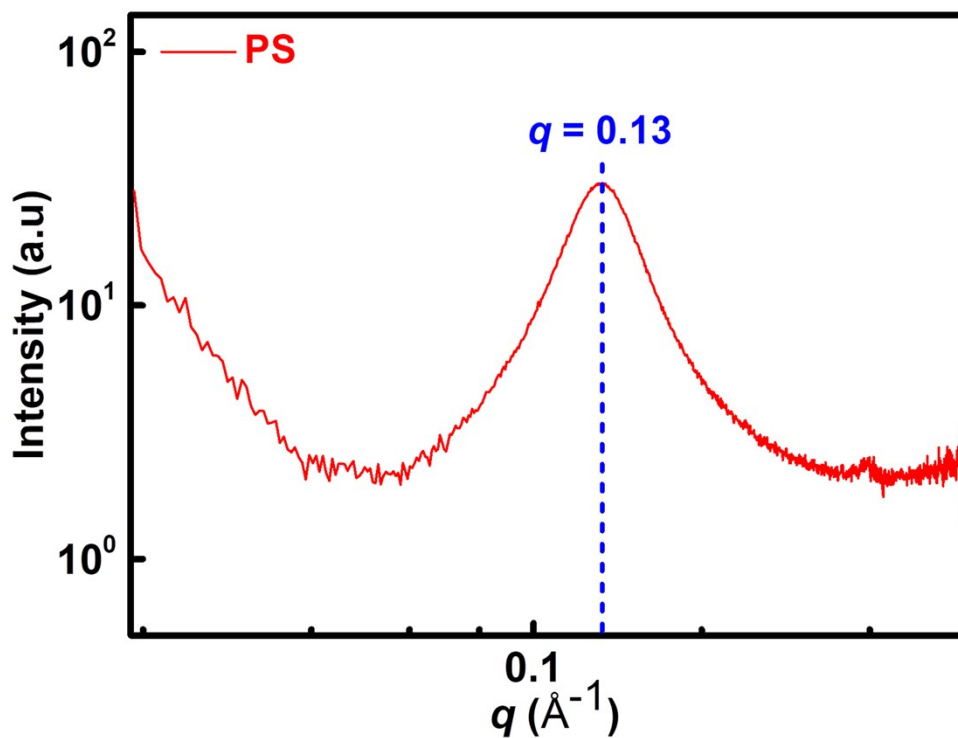


Figure S6: SAXS spectra of neat PS at 25 °C showing a sharp bragg peak at 0.13 \AA^{-1} suggesting a d-spacing of 4.8 nm corresponding to the correlations between polymer surfactant chains. A small peak at $q \sim 0.39 \text{ \AA}^{-1}$ is also seen suggesting a third order bragg peak for a lamellar structure. Interestingly, the second-order bragg peak was absent which can be attributed to the similarity in the thicknesses of lamellar domains in the polymer surfactant. Similar behaviour has also been observed in the literature based on the microphase separated block copolymers, having volume fractions of 0.5 for both the domains.

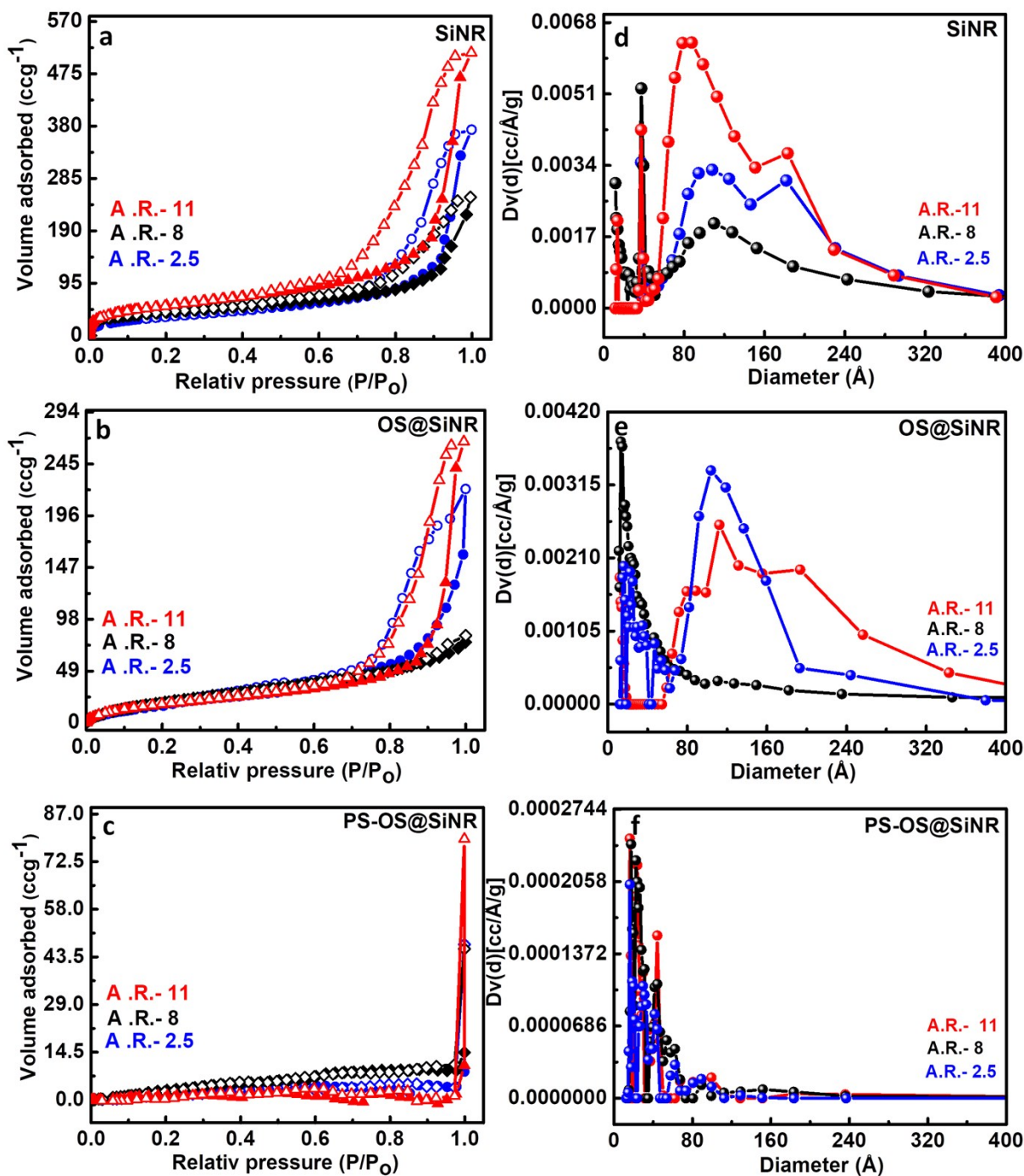


Figure S7: N₂ adsorption isotherms for (a) SiNR, (b) OS@SiNR, (c) PS-OS@SiNR and their respective pore size distributions from (d) to (f), respectively, for rods with aspect ratios 2.5, 8, and 11. Pore size distributions were calculated from N₂ adsorption isotherms with the help of BJH method. It was important to note that the BET surface area calculation for PS-OS@SiNR composite samples were done by considering only the silica content in each sample (~ 20 wt%).

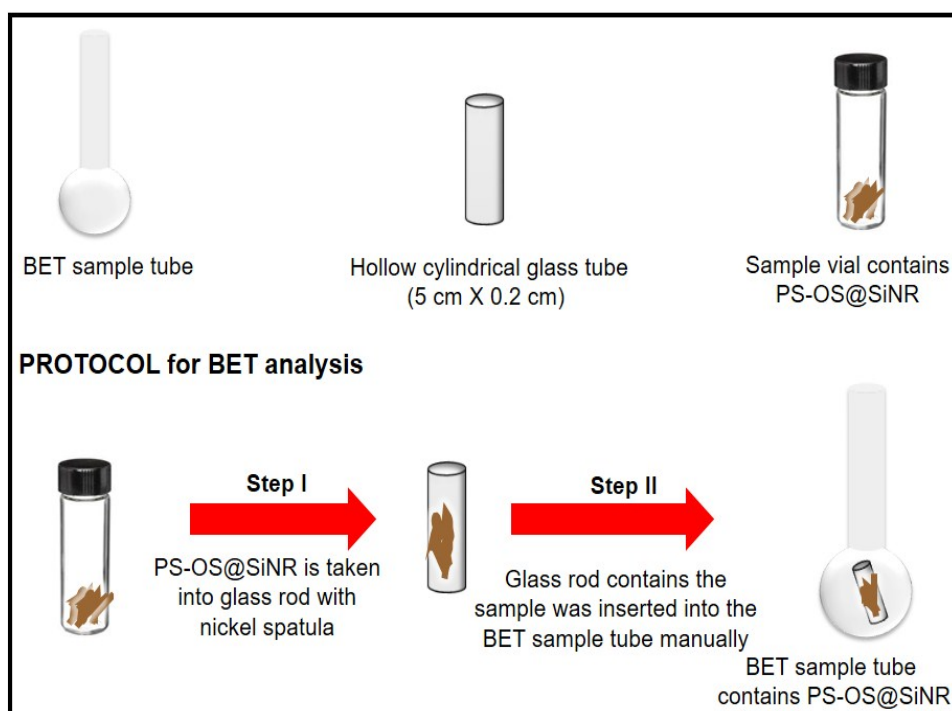


Figure S8: Schematic shows the standard protocol used for BET analysis of PS-OS@SiNR.

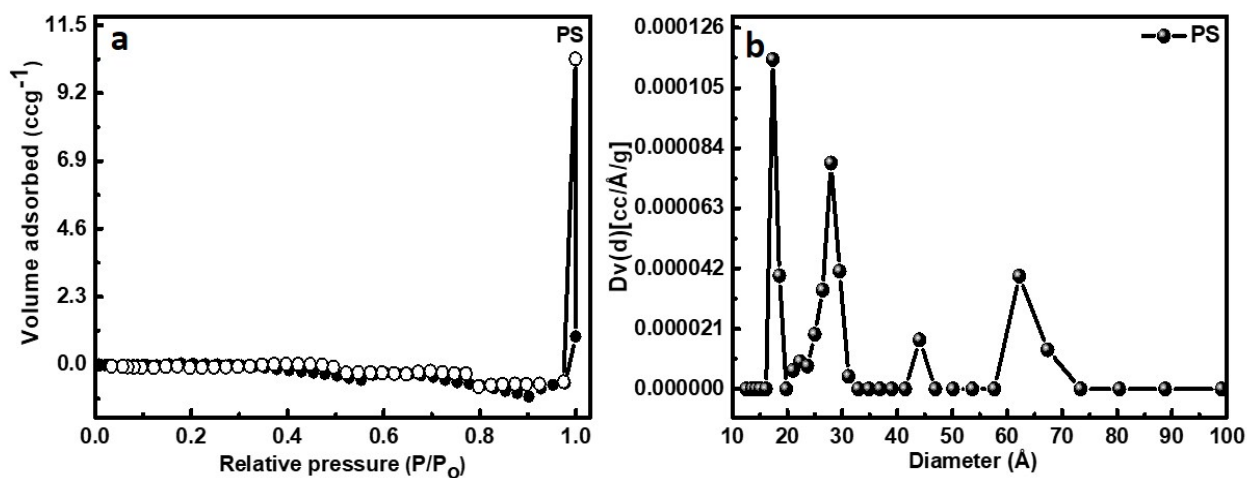


Figure S9: (a) N_2 adsorption isotherm of polymer surfactant (PS). (b) Pore size distribution as calculated using BJH method.

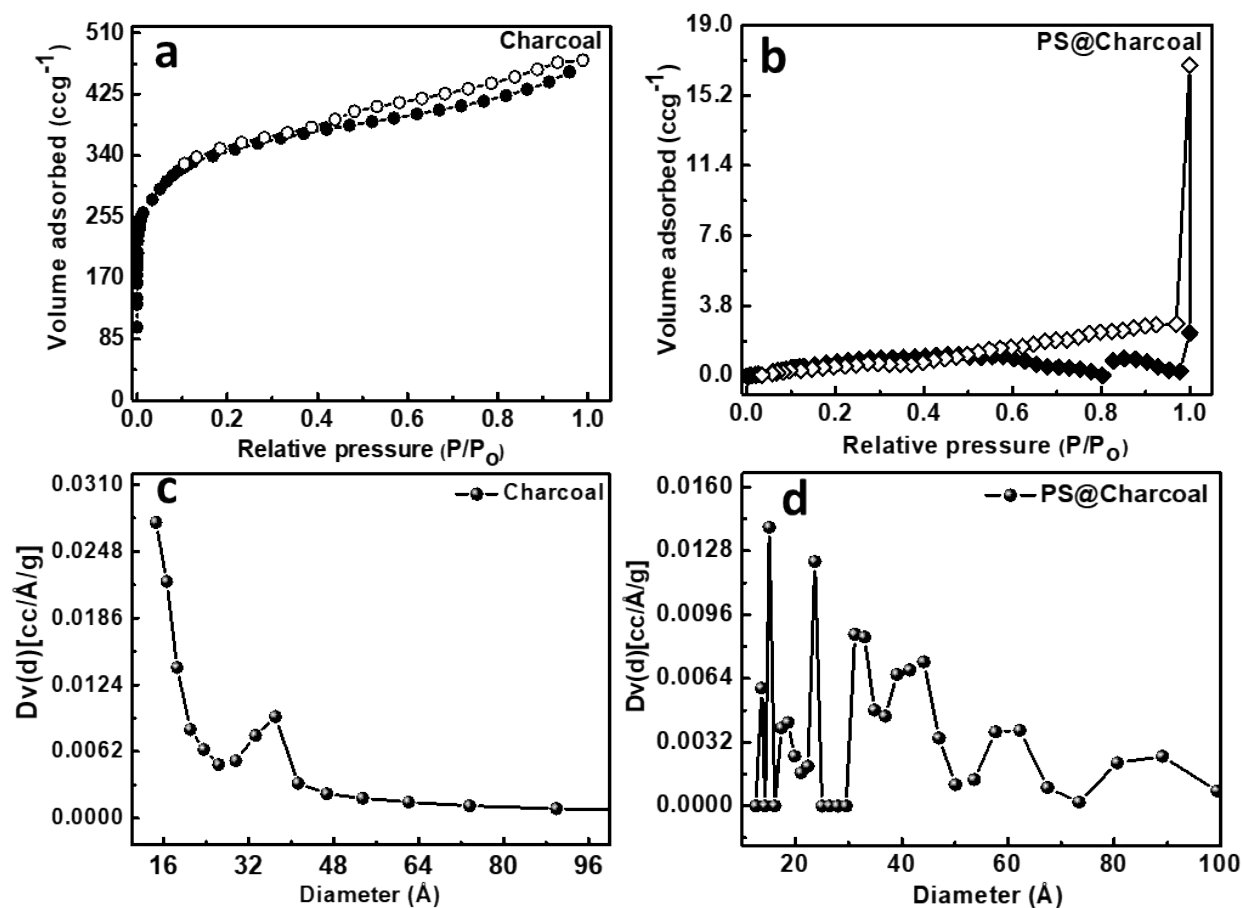


Figure S10: N₂ adsorption isotherm of (a) charcoal and (b) after treating with polymer surfactant (PS@charcoal), (c) Pore size distributions of charcoal and (d) pore size distribution of PS@charcoal. Pore size distribution was calculated from N₂ adsorption isotherm by BJH method.

3. Supporting tables:

Table S1: The tabulated data shows the surface area and average pore diameter, pore volume, and gas uptake of SiNR, OS@SiNR, PS-OS@SiNR of aspect ratio 2.5, 8, 11 and for polymer surfactant (PS), charcoal, PS@Charcoal. Average pore diameter was calculated by BJH method.

Sample Name		BET Surface Area (m ² g ⁻¹)	BJH Pore Size (Å)	Pore volume (ccg ⁻¹)	Gas Uptake (N ₂) (ccg ⁻¹)
SiNR	A.R. 2.5	127	37.1	0.60	373.7
	A.R. 8	143	37.3	0.39	250.9
	A.R. 11	196	88	0.84	513.4
OS@SiNR	A.R. 2.5	81	104	0.38	221.3
	A.R. 8	86	13.2	0.16	82.7
	A.R. 11	70	112	0.44	266.1
PS-OS@SiNR	A.R. 2.5	12.1	16.1	0.017	47.3
	A.R. 8	26.9	17.4	0.088	46.0
	A.R. 11	5.1	16.1	0.155	79.4
PS		0.42	17.3	0.018	10.4
PS@Charcoal		3.89	15.1	0.028	16.8
Charcoal		1046	14.6	0.43	472.5

Table S2: SAXS parameters obtained by fitting the polydisperse core-shell cylinder model for the different aspect ratio rods dispersed in ethanol and as shown in **Figure 2** of the main manuscript.³ Aspect ratios was calculated based on the parameters obtained by fitting has been shown in in the **Table S2**

Parameters/SiNRs	A.R 2.5	A.R. 8	A.R. 11
<i>Shell Radius (Å)</i>	120 (0.18)	85 (0.50)	80 (0.45)
<i>Thickness (Å)</i>	75 (0.20)	95 (0.20)	100 (0.10)
<i>Shell Length (Å)</i>	500 (0.20)	2000 (0.40)	2500(0.20)
<i>SLD core ($\times 10^{-6} \text{Å}^{-2}$)</i>	7.59	16.70	16.70
<i>SLD solvent($\times 10^{-6} \text{Å}^{-2}$)</i>	7.59	7.59	7.59
<i>SLD Shell ($\times 10^{-6} \text{Å}^{-2}$)</i>	16.76	16.76	16.76
<i>Scale</i>	0.00004	0.00070	0.00008
<i>Final A.R.</i>	1.7	6.1	7.5

4. Calculations for Volume fraction of silica and voids for PS-OS@SiNR (Aspect Ratio = 8)

Parameter calculated from TEM images and SAXs results

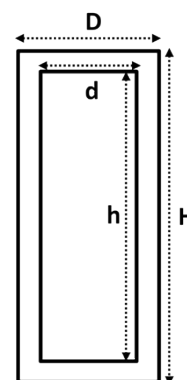
Thickness of silica in silica Nano rods = 6.18nm

$$H = 205.26\text{nm}$$

$$h = 191.29\text{nm}$$

$$R = 11.66\text{nm}$$

$$r = 5.49 \text{ nm}$$



The mass of silica in one nanorod [M] = (V – v) × d

Where **V** = volume occupied by silica by one rod, **v** = volume occupied by void from one rod, **d** = density of silica.

$$\mathbf{M} = \{\pi [R^2H-r^2h]\} \times \mathbf{d}$$

$$\mathbf{M} = \{3.14[[(11.66 \times 10^{-7})^2 \times 205.26 \times 10^{-7}] - [(5.49 \times 10^{-7})^2 \times 191.29 \times 10^{-7}]] \times 2.65\}$$

$$\mathbf{M} = 18.44 \times 10^{-17}\mathbf{g}$$

Volume occupied by one silica nanorod $[V] = \pi R^2 H$

$$V = 3.14 \times (11.66 \times 10^{-7})^2 \times 205.26 \times 10^{-7} \text{ cm}^3$$

$$V = 8.8 \times 10^{-17} \text{ cm}^3$$

Volume occupied by void of one nanorod $[v] = \pi r^2 h$

$$v = 3.14 \times (5.49 \times 10^{-7})^2 \times 191.29 \times 10^{-7}$$

$$v = 1.81 \times 10^{-17} \text{ cm}^3$$

Silica (wt%) : polymer surfactant(wt%) = 20 : 80 (from TGA)

Total number of silica nanorods in 20 wt% of silica = 20g / (18.44 × 10⁻¹⁷g)

Total number of silica nanorods in 20 wt% of silica = 1.085 × 10¹⁷

$$[V]_{\text{Fraction}} = \{[V]_{\text{Si-nanorods}} + ([V]_{\text{void}} \times \text{total number of Si nanorods in 20 wt\% silica})\}$$

Where $[V]_{\text{Fraction}}$ = volume fraction of silica in porous liquid, $[V]_{\text{void}}$ = volume occupied by void

$$[V]_{\text{Fraction}} = \{(20/2.65) + (1.81 \times 10^{-17} \times 1.085 \times 10^{17})\}$$

$$[V]_{\text{Fraction}} = 9.5$$

$$\text{Volume fraction of voids} = \frac{[\text{Volume occupied by void} \times \text{total number of Si nanorods in 20 wt\% silica}]}{\text{Total volume of material}}$$

Total volume of material = Volume of silica + volume of voids + volume of polymer surfactant

$$\text{Volume of silica} = \pi [R^2 H - r^2 h]$$

$$\text{Volume of voids} = \pi r^2 h$$

$$\text{Volume of polymer surfactant} = m/d = 80 \text{ g} / 1.08 \text{ g cm}^{-3}$$

Volume occupied by void × total number of Si nanorods in 20 wt% silica

$$= (1.81 \times 10^{-17}) \times (1.085 \times 10^{17}) = 1.964$$

$$\text{Volume of silica} = \pi R^2 H - \pi r^2 h = (8.8 - 1.81) \times 10^{-17} = 6.99 \times 10^{-17}$$

$$\text{Total volume of material} = 6.99 \times 10^{-17} + 1.81 \times 10^{-17} + 74.1$$

$$\text{Total volume of material} = 74.1$$

$$\text{Volume fraction of voids} = 1.964/74.1$$

$$\% \text{ Volume fraction of voids} = \text{ca. } 3 \%$$

5. References:

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3. A. Guiner, G. Fournet, C. Walker and K. Yudowitch, *Jahn Willey-Champan, New-York*, 1955.