Supplementary Information

Au@*m*SiO_2 nanocomposites with large pores for protein transport

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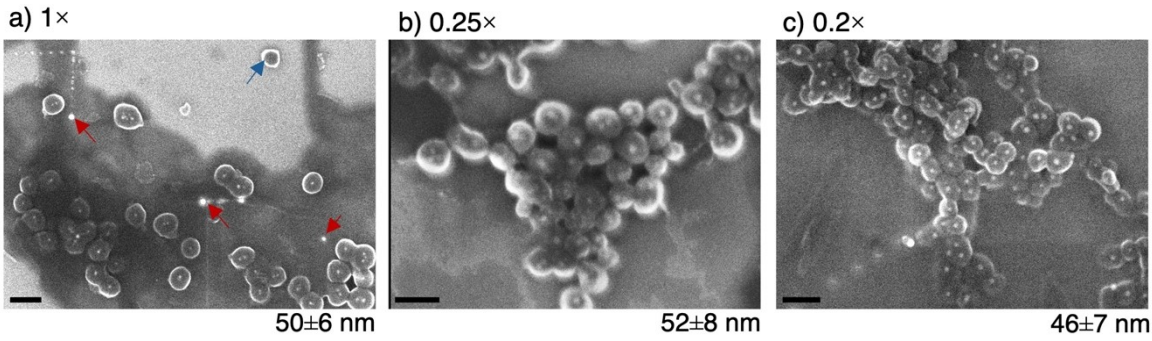

Figure S1. SEM micrographs of Au@mSiO$_2$ seeds synthesized with a) 1x, b) 0.25x, and c) 0.2x TEOS. Red arrows indicate AuNPs that are not coated with a silica shell, while blue arrows point MSN that lack a gold core. Scale bar = 50 nm.

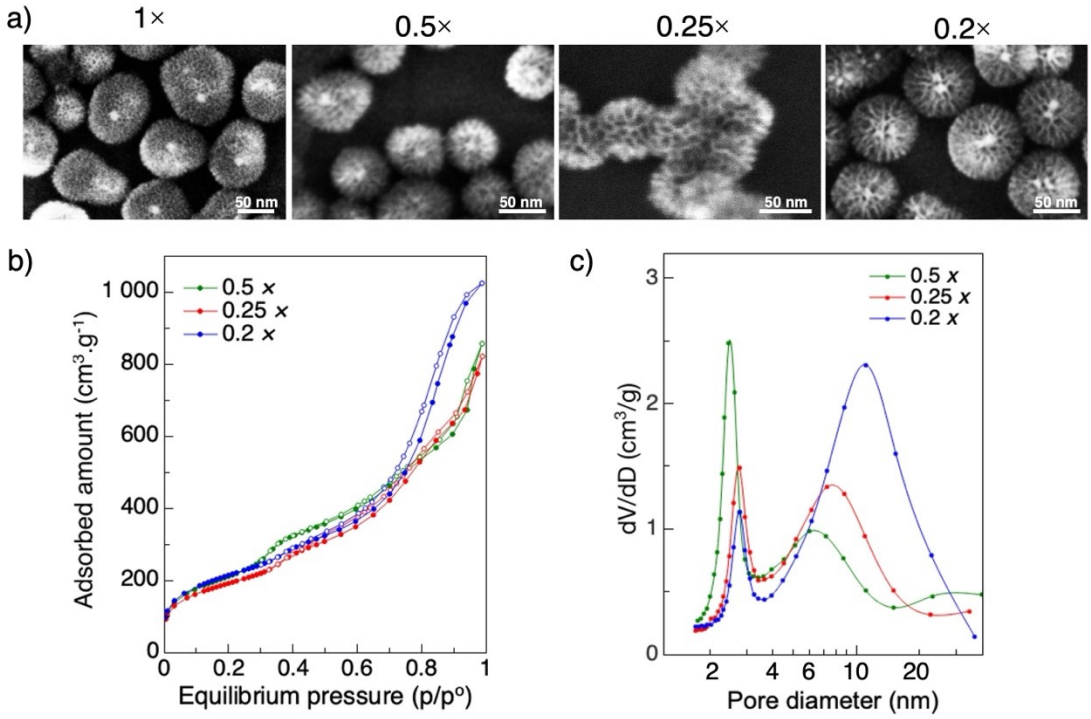

Figure S2. Structural and textural characterization of *lp-Au@m-SiO$_2$* NPs synthesized via biphasic stratification (Method A) using varying concentrations of TEOS during seed formation. (a) SEM images of nanoparticles prepared with 1×, 0.5×, 0.25×, and 0.2× TEOS. (b) N_2 adsorption–desorption isotherms for samples synthesized with 0.5× (green), 0.25× (red), and 0.2× (blue) TEOS. (c) BJH pore size distribution curves of the same samples.

Table S1. Characterization data of *lp-Au@mSiO$_2$* NPs obtained using different biphasic stratification and seeds synthesized with 1*x*, 0.5*x*, 0.2*x*, and 0.25*x* TEOS (Method A). Particle diameters (D_{part}) and nanoparticle percentages were determined from SEM micrographs. Hydrodynamic diameters were measured using DLS. The textural parameters were derived from the N_2-sorption isotherms showed in Figure S2

Sample name	TEOS in seed	Hydrodynamic diameter (nm)	D_{part} (nm)	% NP without Au core	S_{BET} (m^2/g)	Mesopore volume (cm^3/g)	BJH Pore diameters (nm)
M9	1*x*	243	98 ± 12	48	ND	ND	ND
M10	0.5*x*	117	58 ± 7	31	772	1.3	2.7 & 6
M11	0.25*x*	240	60 ± 6	17	695	1.2	3.0 & 7
M5	0.2*x*	130	109 ± 14	3.1	778	1.5	3.0 & 11

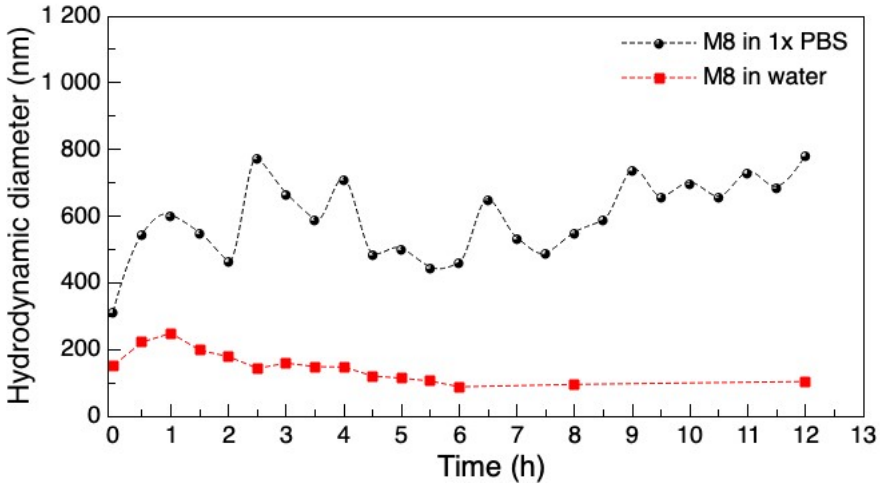

Figure S3. Hydrodynamic diameter as a function of degradation time for sample **M8** suspended at 0.1 mg/mL in (black) PBS 1× and (red) water.

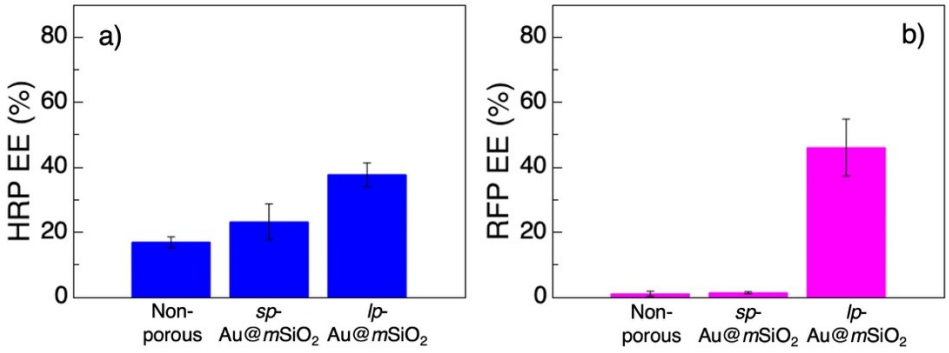

Figure S4. Encapsulation efficiency of Au@*m*SiO₂ NPs. a) HRP encapsulation efficiency (%) on non-porous, *sp*-Au@*m*SiO₂ (3 nm pores), and *lp*-Au@*m*SiO₂ (5–20 nm pores). b) RFP loading, showing minimal adsorption on non-porous and *sp*-Au@*m*SiO₂, but significant encapsulation within *lp*-Au@*m*SiO₂ mesopores. Error bars represent standard deviation (*n*=3). The loading experiment was conducted at 25 °C in 10 mM PB, pH 7 with initial protein concentrations of 100 µg/mL (HRP) and 5 µg/mL (RFP), and NP concentrations of 500 µg/mL (HRP) and 50 µg/mL (RFP).

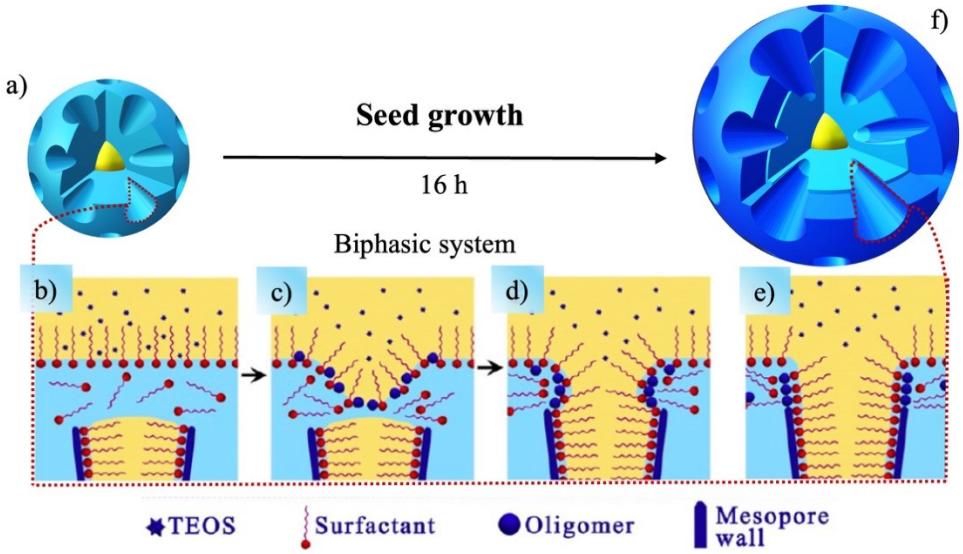

Figure S5. Schematic illustration of the formation mechanism of large-pore Au@*m*SiO₂ particles via a biphasic stratification method. The process begins with Au@*m*SiO₂ seed particles introduced into a biphasic oil–water system (a). Upon addition of TEOS to the oil phase, silica oligomers begin to nucleate and diffuse across the interface (b). Panels (c–e) depict the growth mechanism of a single mesopore channel in the oil-water media. Final structures (f) exhibit large radial mesopores emanating from the gold core. Adapted from [1]

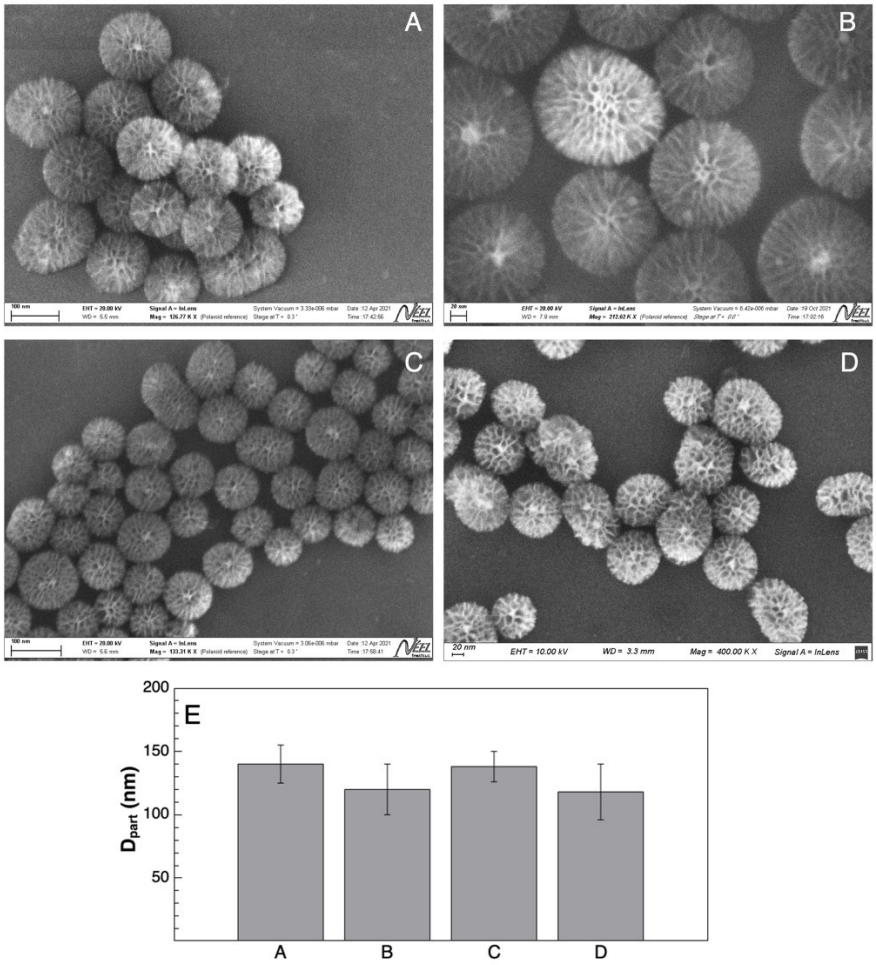

Figure S6. SEM micrographs of large-pore Au@*m*SiO_2 nanoparticles synthesized using biphasic stratification (method D). Panels A–D represent four independent synthesis batches to demonstrate reproducibility in morphology and structure. Panel E shows the average nanoparticle diameters measured from SEM images (n = 50 particles per batch), confirming consistent particle size across batches. Error bars indicate standard deviation.

References

(1) Shen, D.; Yang, J.; Li, X.; Zhou, L.; Zhang, R.; Li, W.; Chen, L.; Wang, R.; Zhang, F.; Zhao, D. Biphase Stratification Approach to Three-Dimensional Dendritic Biodegradable Mesoporous Silica Nanospheres. *Nano Lett* **2014**, *14* (2), 923–932. https://doi.org/10.1021/nl404316v.