Electronic Supplementary Information (ESI)

for

Tuning the Growth, Crosslinking, and Gating Effect of Disulfide-Containing PGMAs on the Surfaces of Mesoporous Silica Nanoparticles for Redox/pH Dual-Controlled Cargo Release

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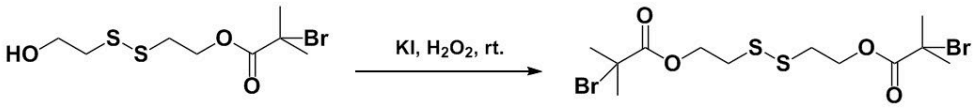
Preparation of 2-2((2-Hydroxyethyl)disulfanyl)ethyl 2-bromo-2-methylpropanoate (HO-SS-Br)

2-Hydroxyethyl disulfide (5 mL, 41.8 mmol) and triethylamine (6 mL, 43.2 mmol) were dissolved in anhydrous THF (350 mL), cooled to 0 °C on an ice-water bath. 2-Bromoisobutyryl bromide (3 mL, 24.3 mmol) was dissolved in THF (20 mL), then added dropwise to the above system. The reaction was kept at 0 °C for 2 h, and then raised to and kept at room temperature for 12 h. Triethylamine hydrogenbromide salt were removed by vacuum filtration. THF was evaporated and crude product was washed with 1 M $NaHCO_3$ (3 × 50 mL) and deionized water (3 × 50 mL). The product was extracted with chloroform and dried by $MgSO_4$. After filtration, solvent was evaporated under vacuum to get 2-2((2-Hydroxyethyl)disulfanyl)ethyl 2-bromo-2-methylpropanoate (HO-SS-Br). Yield: 79.04 % (5.82 g).

KI, H_2O_2 (30 %)-Assisted Disulfide Bond Exchange

HO-SS-Br (200 μL, 0.99 mmol) was dissolved in ethanol (1 mL), then added dropwise to distilled water (5 mL) for dispersion under magnetic stirring. The reaction was carried out in the presence of KI (4.0 mg) and H_2O_2 (20 μl, 30 %) at room temperature (HO-SS-Br : KI: H_2O_2 = 41 : 1 : 16.3). After stirring the reaction mixture for 12 h, the product was extracted with dichloromethane, washed with deionized water (3 × 5 mL), and dried over $MgSO_4$. After filtration, the solvent was evaporated under vacuum to give the final product. Yield: 15.97 % (0.0712 g).



Scheme S1. Reaction of HO-SS-Br and KI, H_2O_2 (30 %) in water for disulfide exchange.

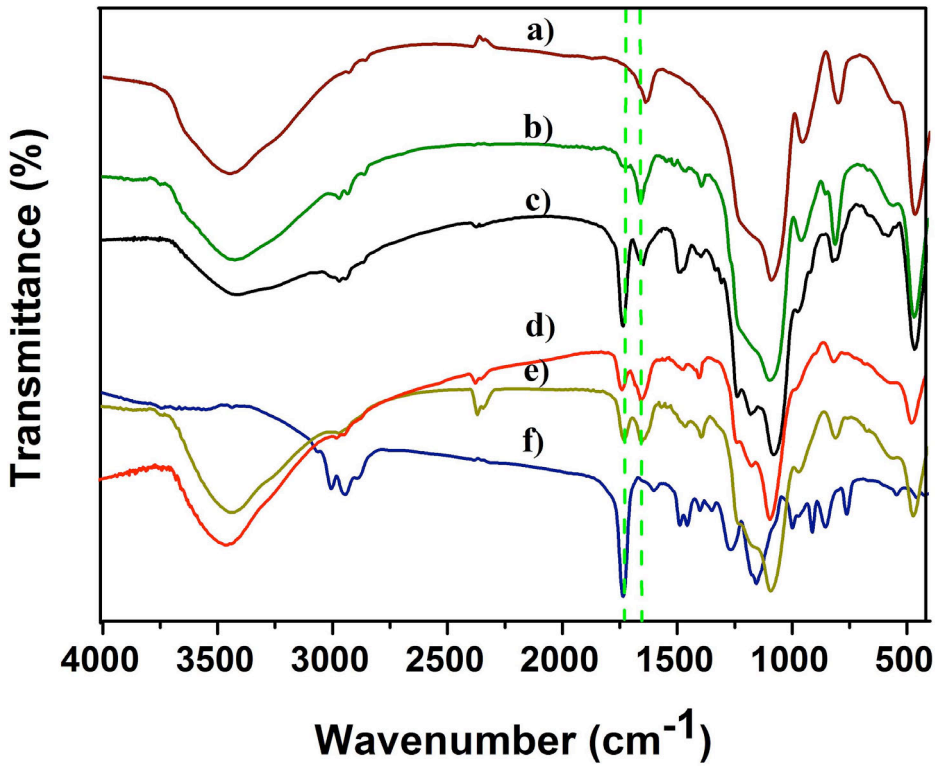


Fig. S1. FT-IR spectra of (a) MSN-OH, (b) MSN-Br, (c) MSN-PGMA, (d) Rh6G@MSN-PSSGMA-1, (e) Rh6G@MSN-PSSGMA-2, and (f) PGMA.

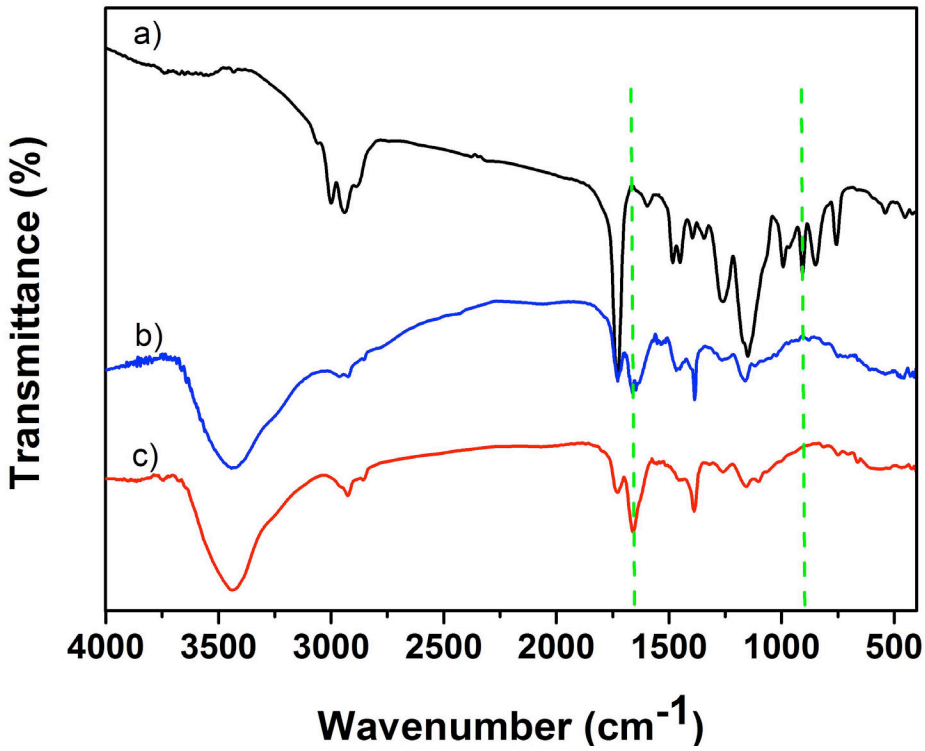


Fig. S2. FT-IR spectra of (a) PGMA, (b) PSGMA, and (c) PSSGMA.

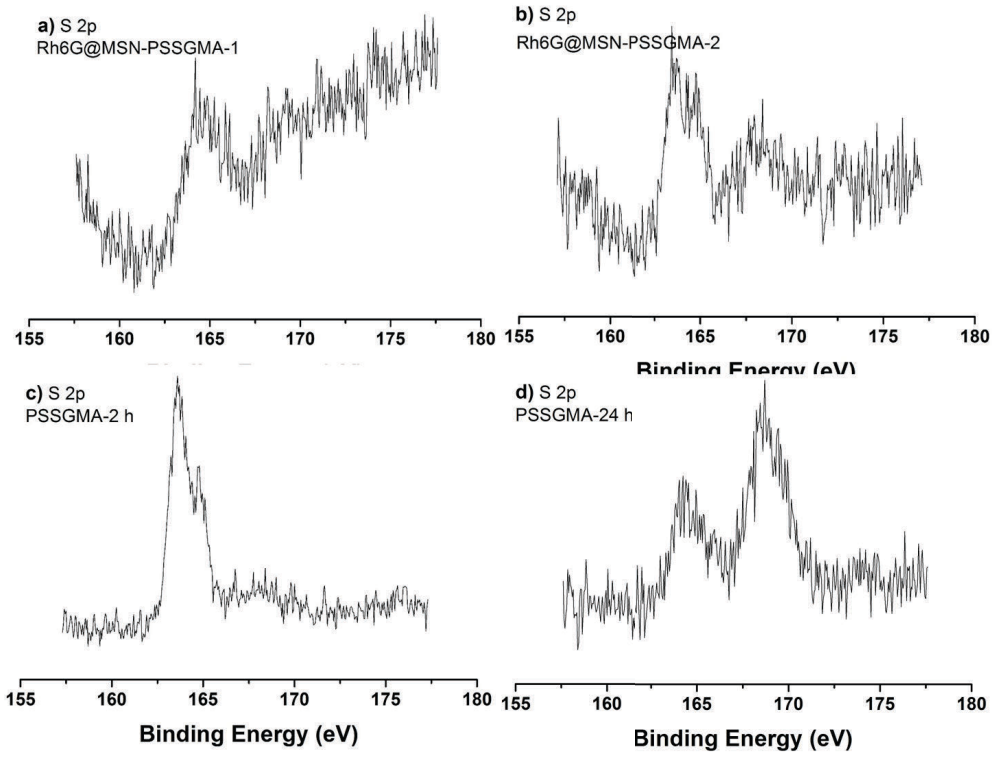


Fig. S3. XPS S 2p Core-level Spectra of (a) Rh6G@MSN-PSSGMA-1, (b) Rh6G@MSN-PSSGMA-2, (c) KI, H_2O_2 2 h catalyzed PSSGMA, and (d) KI, H_2O_2 24 h catalyzed PSSGMA.

Table S1. Elemental Analysis of MSN-OH Based Materials

Name	C	H	N	S
MSN-OH	4.67	2.07	0.47	0
MSN-Br	10.62	2.60	0.65	0
MSN-PGMA	17.54	3.71	1.12	0
MSN-PSSGMA-1	17.63	4.21	3.90	0.82

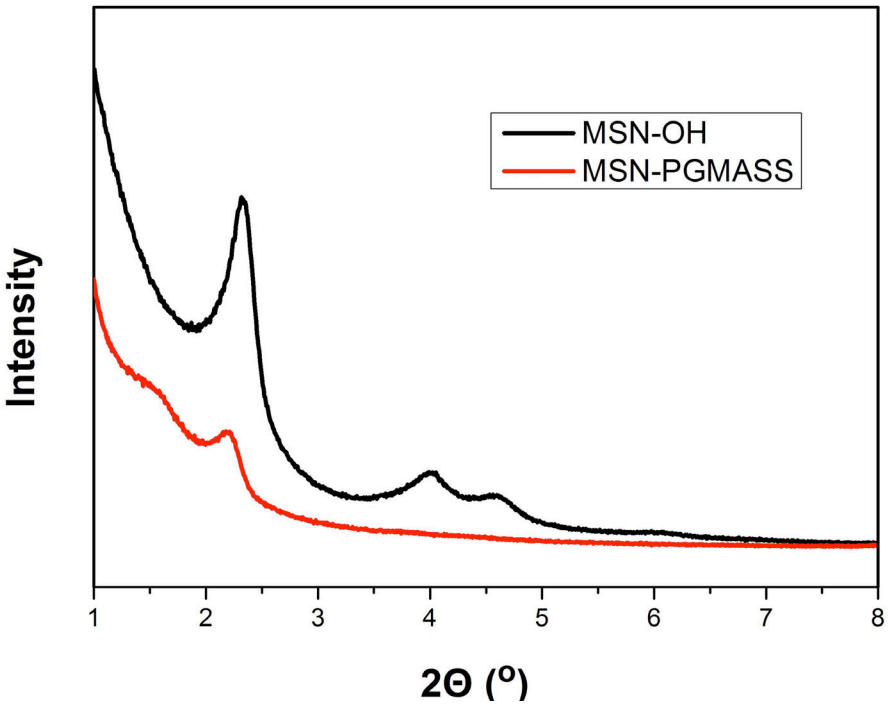


Fig. S4. Small-angle powder XRD of MSN-OH and MSN-PGMA.

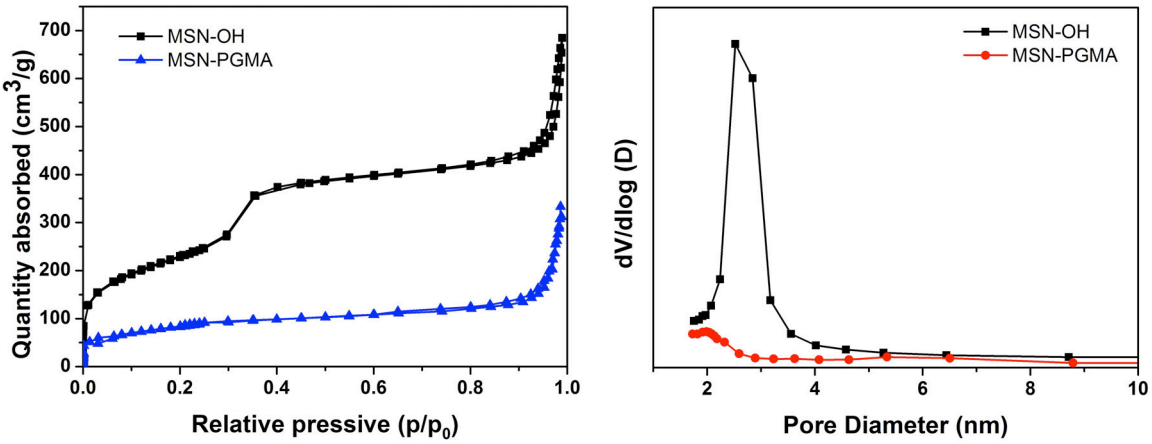


Fig. S5. BET N_2 sorption-desorption isotherms and BJH pore size distribution of MSN-OH and MSN-PGMA.

Table S2. Surface Areas and Pore Volumes of MSN-OH and MSN-PGMA Calculated From BET

Name	BET surface area $m^2 g^{-1}$	Pore volume /$cm^3 g^{-1}$
MSN-OH	829.32	0.97
MSN-PGMA	302.63	0.45

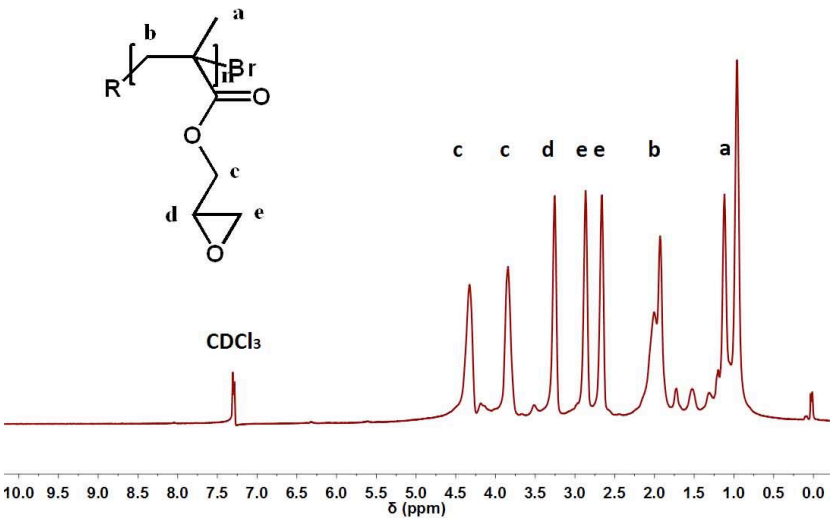


Fig. S6. Typical ^{1}H NMR spectrum of PGMA (in $CDCl_3$).

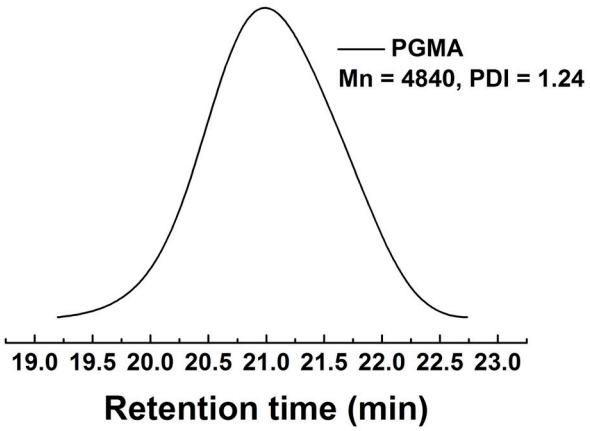


Fig. S7. GPC trace of PGMA.

Table S3. Experimental Conditions of KI, H_2O_2 (30 %)-Assisted Disulfide Bond Exchange

No.	Water/mL	PSGMA DMF aq/μL	KI/mg	H_2O_2/μL	Appearance
1	5	400	2.0	10	Precipitation
2	5	400	-	10	No change
3	5	400	2.0	-	No change
4	5	PEGMA DMF aq 400 μL	2.0	10	No change

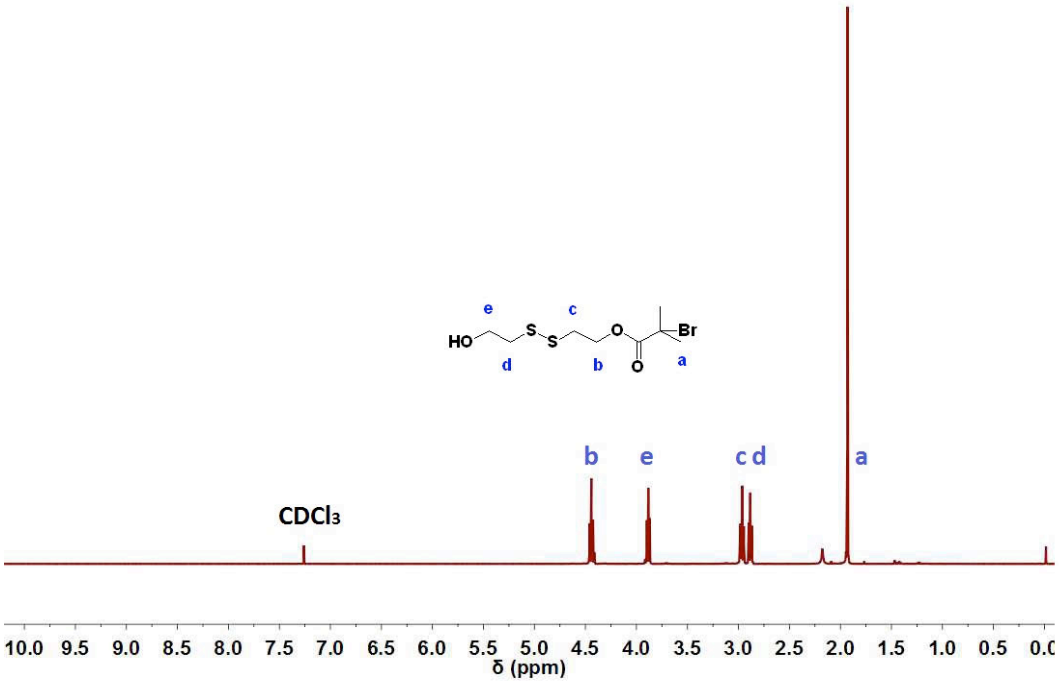


Fig. S8. ^{1}H NMR spectrum of HO-SS-Br.

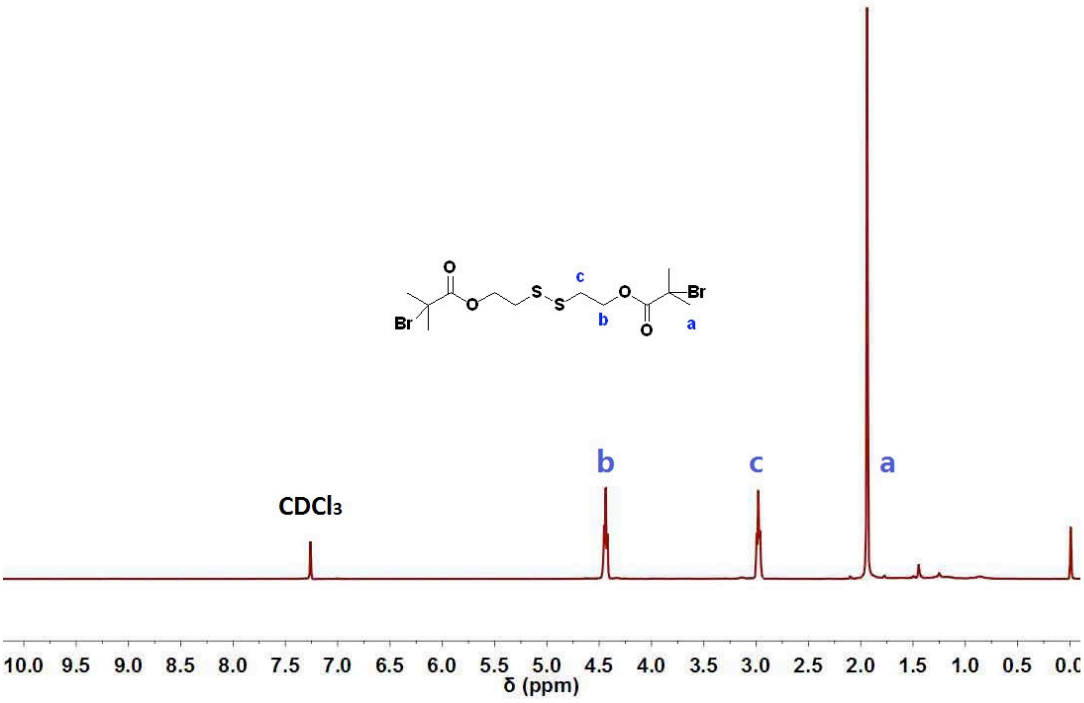


Fig. S9. ^{1}H NMR spectrum of Br-SS-Br.

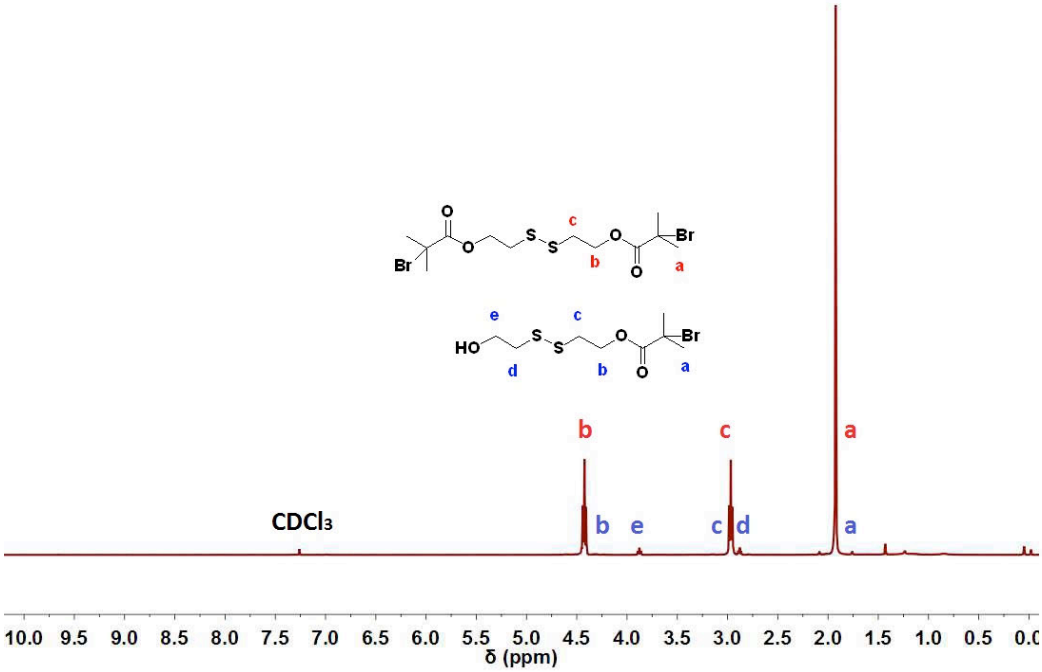


Fig. S10. ^{1}H NMR spectrum of the collected mixture of after 12 hours' disulfide bond exchange reaction.

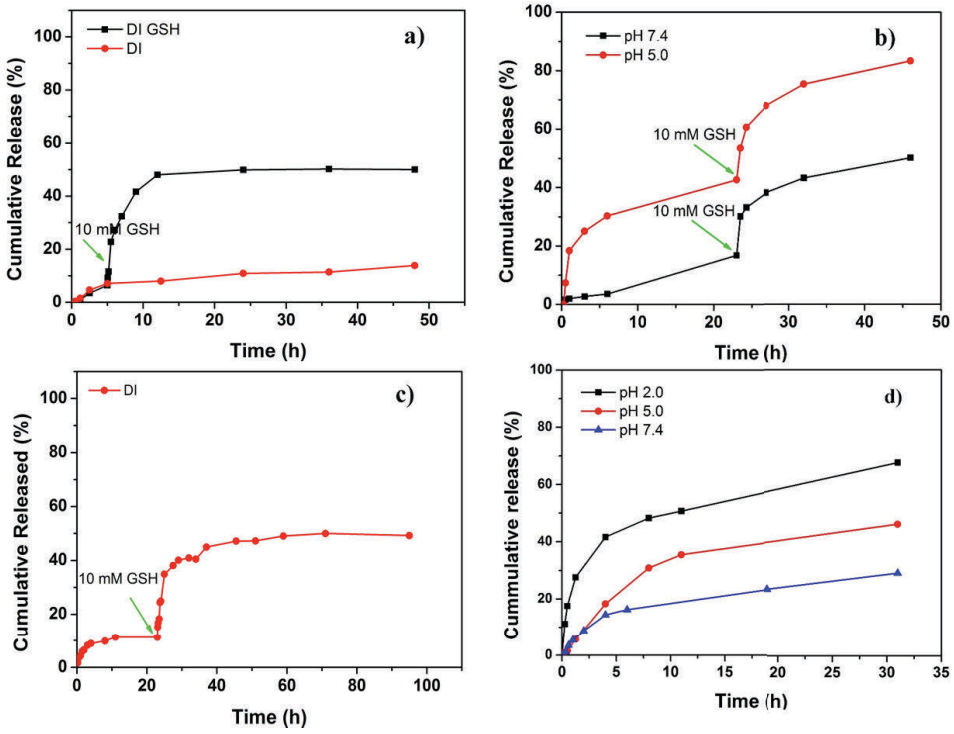


Fig. S11. The release profiles of Rh6G from MSN-PSSGMA (a) Rh6G @MSN-PSSGMA-2 in distilled water, (b) Rh6G@MSN-PSSGMA-1 in different PBS buffers, (c) Rh6G@MSN-PSSGMA-1 in distilled water, (d) Rh6G@MSN-PSSGMA-2 in different PBS buffers.

Table S4. Zeta Potential of MSNs and PSGMA Aggregates

No.	Sample	Average Zeta Potential (mV)
1	MSN-OH	-20.4
2	MSN-PGMA	-9.3
3	MSN-PSGMA	31.6
4	Rh6G@MSN-PSSGMA-1	5.5
5	Rh6G@MSN-PSSGMA-2	12.6
6	Cat. PSGMA-0 h	23.8
7	Cat. PSGMA-2 h	15.4
8	Cat. PSGMA-24 h	13.9

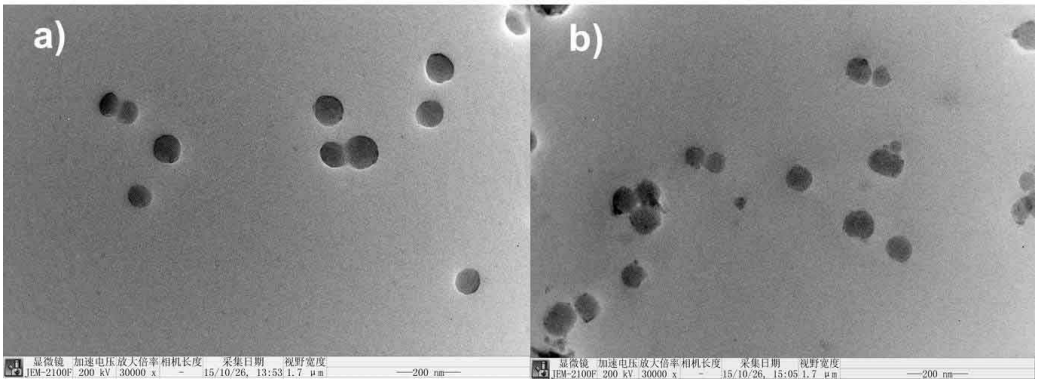


Fig. S12. Wide range TEM images of (a) MSN-OH and (b) MSN-PGMA.