

Supporting information

pH-modulated double LCST behaviors with diverse aggregation processes of random-copolymer grafted silica nanoparticles in aqueous solution

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The detailed formulations in the ATRP reaction are presented in Table S1.

Table S1. Feed Compositions of ATRP reaction

Feed Composition	SiO ₂ -g-P(NIPAM-co-DMAEMA) Sample Code				
	SiO ₂ -N50D50	SiO ₂ -N83D17	SiO ₂ -N33D67	SiO ₂ -N67D33	SiO ₂ -D100
SiO ₂ -Br (mg)	300	300	300	300	300
CuCl (mg)	25	25	25	25	—
bpy (mg)	42.7	42.7	42.7	42.7	—
MeOH/H ₂ O (1:1) (mL)	4	4	4	4	—
CuBr (mg)	—	—	—	—	36
PMDETA (μL)	—	—	—	—	52
Anisole (mL)	—	—	—	—	4
NIPAM (g)	0.312	0.531	0.192	0.384	—
DMAEMA (mL)	0.464	0.155	0.572	0.286	0.928

Table S2. The atomic content analysis of XPS

Samples	Atomic content (%)				
	Br	Si	C	N	O
SiO ₂ -Br	0.52	24.54	25.39	3.01	46.53
SiO ₂ -N50D50	0	1.43	73.30	7.75	17.53
(theoretical value)	(0)	(0)	(73.68)	(10.53)	(15.79)
SiO ₂ -N83D17	0	0.79	71.95	8.24	19.02
(theoretical value)	(0)	(0)	(74.51)	(11.76)	(13.73)
SiO ₂ -D100	0	3.26	66.86	8.01	21.86
(theoretical value)	(0)	(0)	(72.73)	(9.09)	(18.18)

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The XPS data can also be used to roughly confirm the composition of grafted polymer layers. The elemental content analysis is shown in Table S2. As for SiO₂-Br, a high atomic content of O was observed due to the APTES and hydroxyl group on the silica surface. The mole ratio of C and N was 25.39:3.01 $\approx$ 8:1, which was approximately consistent with the theoretical value of 7:1. Furthermore, the content of Br was much less than that of N, indicating the quenching and decreasing of initiator in the post-processing. For PNIPAM and PDMAEMA grafted silica nanoparticles, the Si contents dramatically decreased, indicating the covering of the silica cores by a polymer layer. The experimental contents of different atoms in synthesized samples were similar to those theoretical ones, which suggested that the ratios of two grafted monomers were consistent with the corresponding feeding ones.

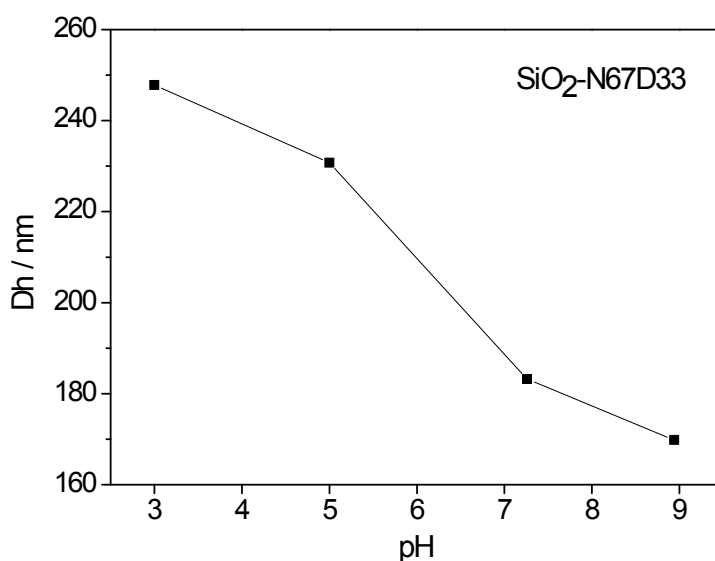


Fig. S1. pH-dependent hydrodynamic diameters of SiO₂-N67D33 at 25 °C.

Table S3. LCSTs of SiO₂-g-P(NIPAM-co-DMAEMA) from DLS results

	LCSTs/ °C				
	Acidic	Neutral		Basic	
	PNIPAM/PDMAEMA	PNIPAM	PDMAEMA	PNIPAM	PDMAEMA
SiO ₂ -N50D50	65 $\pm$ 1	42 $\pm$ 2	52 $\pm$ 1	38 $\pm$ 1	59 $\pm$ 1
SiO ₂ -N83D17	64 $\pm$ 1	42 $\pm$ 2	56 $\pm$ 2	38 $\pm$ 1	57 $\pm$ 1