Supporting Information

Double Shelled Polymer Nanocontainers Decorated with Poly(ethylene glycol) Brushes by Combined Distillation Precipitation Polymerization and Thiol-Yne Surface Chemistry

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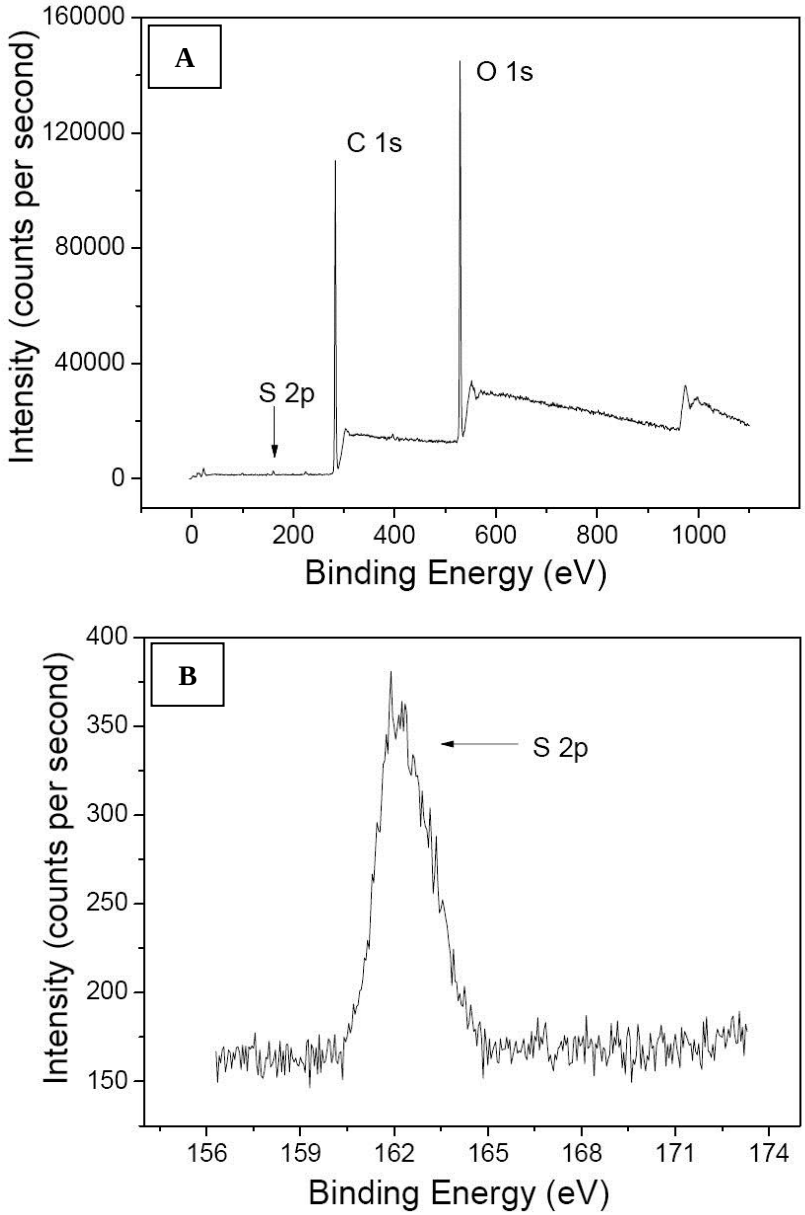

Figure S1 XPS (a) wide-scan and (b) S 2p core-level spectrum of the telechelic PEG-SH chains. The S 2p signal is associated with the functional thiol groups.

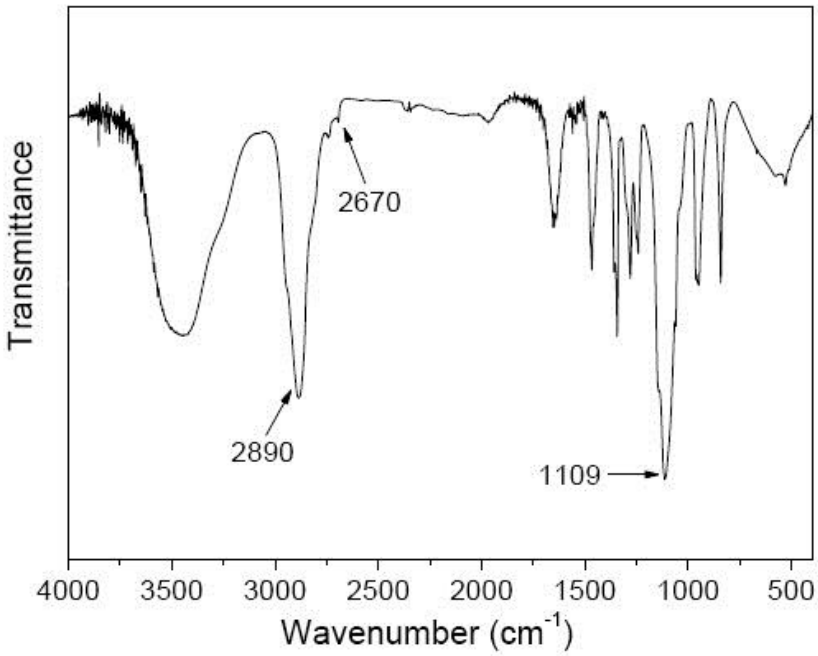

Figure S2 FT-IR spectrum of the thiol-terminated poly(ethylene glycol) (PEG-SH) chains. The characteristic absorption peaks at 1109 cm^{-1}, 2890 cm^{-1} and 2670 $cm^{-1}$are associated with stretching vibrations of the C-O-C, $–CH_2$ and -SH groups, respectively.

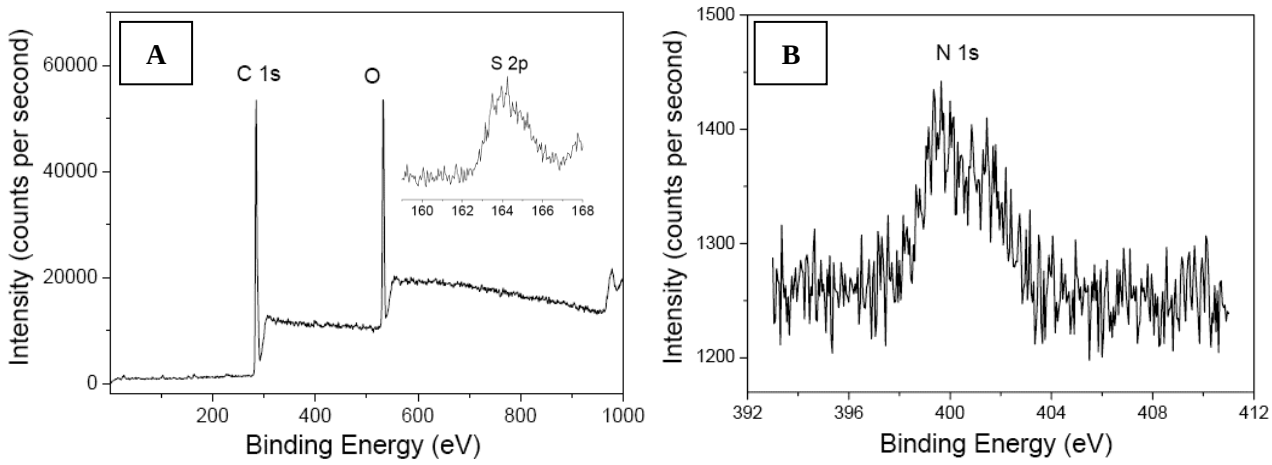

Figure S3 XPS wide-scanned (A) and N 1s core-level spectra (B) of the SiO_2@poly(PMA-*co*-MAA-*co*-EGDMA)-*click*-cysteamine nanospheres.

The photo-initiated thiol-yne coupling reaction was performed in DMF under a 1000 W high-pressure mercury lamp at room temperature for 3 hrs. The propargyl groups on the core-shell nanospheres allow for double hydrothiolation of alkyne groups. After grafting of cysteamine, the core-shell particle surfaces were functionalized with amine groups. Figure S3 shows the XPS wide-scan spectrum of the SiO_2@poly(PMA-*co*-MAA-*co*-EGDMA)-*click*-cysteamine core-shell hybrid nanospheres. The new photoelectron lines at the BE of 164 and 400 eV are associated with the S 2p and N 1s species from the grafted cysteamine, respectively. The surface grafting of cysteamine on the nanocontainers leads to an increase in the C 1s signal intensity and to appearance of the S 2p and N 1s signals. The elemental analysis suggests that the mass content of the sulfur element in the SiO_2@poly(PMA-*co*-MAA-*co*-EGDMA)-*click*-cysteamine nanospheres is about 1.38 wt%. Thus, the grafted cysteamine on particle surfaces is calculated to be 0.43 mmol/g, which means, that the accessible alkyne groups on the SiO_2@poly(PMA-*co*-MAA-*co*-EGDMA) hybrid surface are around 0.215 mmol/g.

Table S1 Size and size distribution and shell thickness of nanospheres.

Sample[a]	D_n[b] (nm)	D_h[b] (nm)	PDI[b]	CV[c] (%)
SiO_2@poly(PMA-*co*-MAA-*co*-EGDMA) -*click*-cysteamine	272	321	1.20	6

[a]PMA = propargyl methacrylate, [b]D_n is the number-average diameter from FESEM images, D_h is the hydrodynamic diameter in ethanol from dynamic light scattering (DLS)and PDI is the polydispersity index. [c]CV is the coefficient of variation or ratio of the standard deviation to the mean of particle size (CV =δ/D_n).

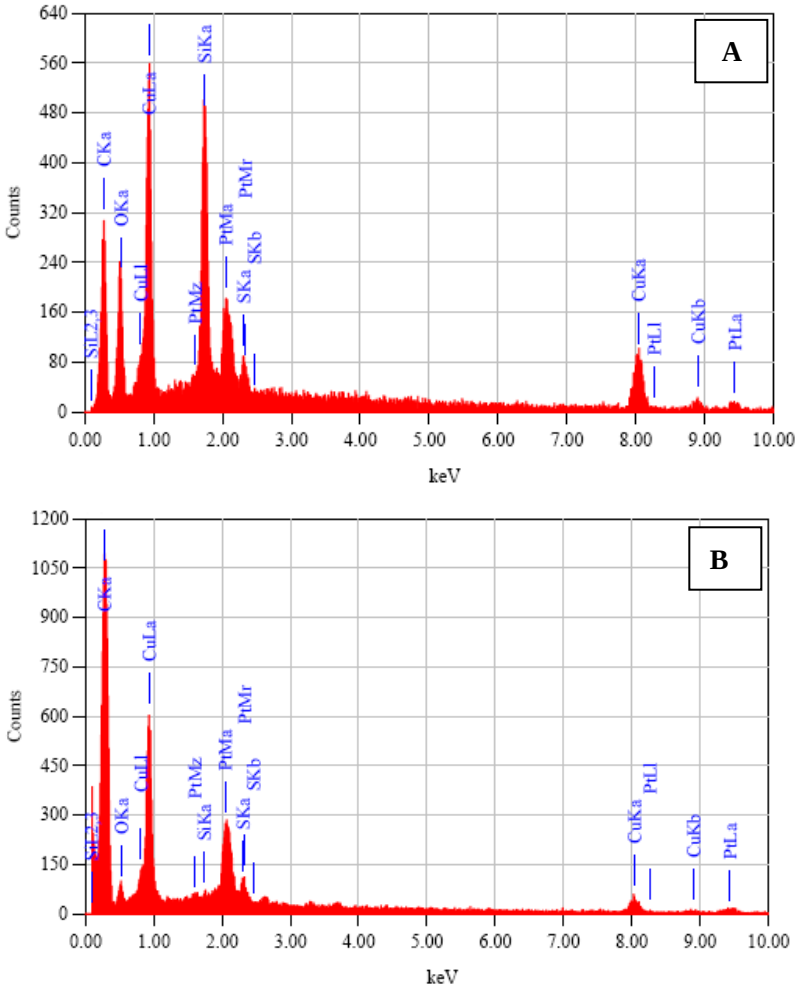

Figure S4 Energy dispersive X-ray **(**EDX) spectra of the (A) SiO_2@poly(PMA-*co*-MAA-*co*-EGDMA)-*click*-PEG hybrid nanospheres and (B) air@poly(PMA-*co*-MAA-*co*-EGDMA)-*click*-PEG hollow nanocontainers.

Table S2 The summary of element contents of nanospheres from EDX measurement.

Sample	Element	KeV	Mass%	At%	Error%
SiO_2@poly(PMA-*co*-MAA-*co*-EGDMA)-*click*-PEG	C	0.277	48.47	60.17	0.41
	O	0.525	31.63	29.47	0.97
	Si	1.739	16.65	8.84	0.44
	S	2.307	3.26	1.51	0.47
air@poly(PMA-*co*-MAA-*co*-EGDMA)-*click*-PEG	C	0.277	72.56	79.70	0.46
	O	0.525	21.75	17.93	2.82
	Si	1.739	0.74	0.35	0.98
	S	2.307	4.92	2.02	0.93

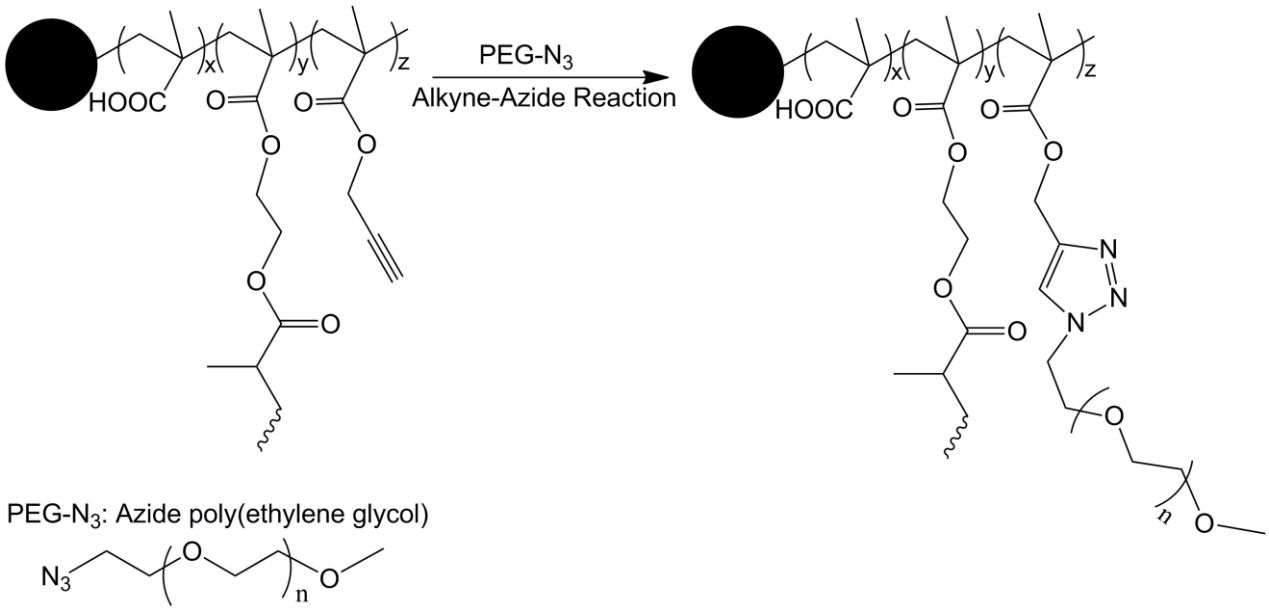

Figure S5 Surface grafting of PEG chains on the core-shell nanospheres via alkyne-azide surface "click" reaction.

Surface grafting of PEG brushes on the SiO_2@poly(PMA-co-MAA-co-EGDMA) core-shell nanospheres via alkyne-azide "click" reaction

Briefly, about 0.15 g of as-synthesized SiO_2@poly(PMA-*co*-MAA-*co*-EGDMA) core-shell nanospheres, 0.40 g of azide-terminated poly(ethyleneglycol) chains (PEG-N_3, M_n = 5,000 g/mol, Sigma-Aldrich), and 14 mg of CuBr powder were introduced into 10 mL of dimethylformamide (DMF) under sonification. After degassing over a period of 30 minutes, pentamethyldiethylenetriamine (PMDETA, 0.018 mL) was added quickly into the flask and the reaction mixture was kept at 60^{o}C for 24 hrs. The as-prepared PEG-grafted core-shell nanospheres by alkyne-azide "click" reaction were collected by centrifugation and then transferred into an EDTA (5 wt%) solution to remove the copper catalyst. Finally the PEG-grafted core-shell nanospheres were dried till a constant weight in a vacuum oven at room temperature, after 5 times of dispersion/centrifugation cleaning cycles. The solvent used for the colloid dispersion is a mixture of water and ethanol. The THF/hexane solvent pair was utilized to clean nanoparticles in the last dispersion/centrifugation cleaning cycle. The grafting density of PEG brushes on the

SiO_2@poly(PMA-*co*-MAA-*co*-EGDMA)-*click*-PEG nanospheres from TGA curves is calculated as 0.72 chains/nm^2.