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Supplementary Information

Precise Growth of Polymer Brushes on Silica-Based Nanocomposites via Visible-Light-Regulated Controlled Radical Polymerization

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Experiment Section

Materials

Tris(2,2′-bipyridyl)dichlororuthenium(II) hexahydrate ($Ru(bpy)_3Cl_2$, 99.95%), tetraethyl orthosilicate (TEOS, 98%), 3-(mercaptopropyl)trimethoxysilane (MPTMS, 95%), ammonium hydroxide solution (28.0~30.0 wt% NH_3 basis), chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, ACS reagent), trisodium citrate dihydrate ($Na_3Cit \cdot 2H_2O$, ≥99%), citric acid monohydrate ($H_3Cit \cdot H_2O$, ≥99%), polyvinylpyrrolidone (PVP, M_w = 10000 g/mol), sodium borohydride ($NaBH_4$, ≥99%), *L*-ascorbic acid (≥99%), iron(III) chloride hexahydrate ($FeCl_3 \bullet 6H_2O$, 95%), 1-octadecene (90%), oleic acid (90%), [3-(2-aminoethylamino)propyl]trimethoxysilane (APMS, 97%), polyoxyethylene (5) nonylphenylether (Igepal CO-520), tris(2-carboxyethyl)phosphine (TCEP, ≥98%) and *S*-dodecyl-*S′*-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate (DDMAT, 98%) were purchased from Sigma-Aldrich and used as received unless otherwise stated. All liquid monomers including *N,N*-dimethylacrylamide (DMA, 99%), ethylene glycol dimethacrylate (EGDMA, 98%) and poly(ethylene glycol) methyl ether methacrylate (PEGMA, M_n = 300 g/mol) were purchased from Sigma-Aldrich and purified by percolating over an inhibitor-removal column. *N*-isopropylacrylamide (NIPAM, 97%) was recrystallized twice from toluene/hexane (7:3, v/v). Hydroxyethyl pyridyldisulfide (HEPS) was synthesized following the previously reported method.[1,2]

Synthesis of 2-(Pyridine-2-yldisulfanyl)ethyl 2-(((dodecylthio)carbonthioyl)thio) propanoate (PDP)

DDMAT (3.65 g, 10 mmol), DCC (2.06 g, 10 mmol), DMAP (0.24 g, 2 mmol) and anhydrous dichloromethane (40 mL) were introduced into a 100 mL single-necked round bottom flask. The flask was immersed in an ice bath and HEPS (2.04 g, 11 mmol) in dry dichloromethane (10 mL) was added dropwise. Upon completion of the addition, the reaction mixture was kept in the ice-water bath for 1 h and then at room temperature for 24 h. The precipitated 1,3-dicyclohexylurea (DCU) was filtered off and the solvent was evaporated. The crude product was purified by column chromatography using ethyl acetate: hexane (3:7, v/v). The PDP chain transfer agent (CTA) was obtained as a yellowish oil (yield ~68%). ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 8.48 (1H, aromatic proton *ortho*-N), 7.74 (1H, aromatic proton *para*-N), 7.68 (1H, aromatic proton *meta*-N), 7.12 (1H, aromatic proton *ortho*-disulfide linkage), 4.34 (2H, $-C(=O)OCH_2-$), 3.27 (2H, $-SC(=S)SCH_2-$), 3.04 (2H, $-SSCH_2-$), 1.62-1.75 (6H, $-C(CH_3)_2$), 1.17-1.42 (18H, $-(CH_2)_9CH_3$), 0.87 (3H, $-CH_3$).

Synthesis of SiO_2@PDMA Nanoparticles

Typically, TEOS (9.0 mL) was added dropwise to a mixture of ethanol (150 mL), deionized water (15 mL) and ammonium hydroxide solution (3.0 mL, 28~30 wt% NH_3 basis). The mixture was stirred vigorously at room temperature for 12 h. Afterward, MPTMS (2.0 mL, 10.8 mmol) was slowly dosed to the reaction suspension and the reaction was allowed to proceed for another 12 h. Finally, the raw product was purified by five cycles of centrifugation/redispersion/washing in excessive ethanol and deionized water. The SiO_2-MPTMS nanoparticles (NPs) were collected by centrifugation and stored in argon-purged ethanol.

About 200 mg of SiO_2-MPTMS NPs were dispersed in DMF (20 mL) by ultrasonication for 30 min. PDP (213.4 mg, 0.4 mmol) was slowly added to the reaction mixture under argon atmosphere. After being stirred vigorously overnight, the SiO_2-PDP NPs were obtained. Afterward, the SiO_2-PDP NPs were purified by extraction with ethanol and dichloromethane five times to remove any leftover reagents. The SiO_2-PDP NPs were collected by centrifugation and stored in argon-purged acetonitrile. About 20 mg of SiO_2-PDP NPs were treated with ethanol containing TCEP (2.0 mg/mL) and incubated at room temperature for 24 h. The residual NPs were purified by extraction with ethanol and dichloromethane five times. The mass difference of the NPs before and after incubation was measured to determine the amount of PDP on the SiO_2-PDP NPs (4.4×10^{-5} mol PDP per 1.0 mg of SiO_2-PDP NPs).

Surface-initiated PET-RAFT polymerization of DMA monomers in acetonitrile from SiO_2-PDP NPs was conducted using a molar feed ratio [DMA]:[PDP] of 2000:1 and predetermined amounts of $Ru(bpy)_3Cl_2$ photocatalyst.[3-5] Briefly, about 50 mg of SiO_2-PDP NPs were dispersed into acetonitrile (24.5 mL) by ultrasonication for 30 min. DMA (0.45 mL, 4.4 mmol) and $Ru(bpy)_3Cl_2$ (164.5 μg, 50 ppm relative to DMA) were then dosed to the reaction flask. The reaction flask was covered with aluminum foil and degassed with argon for 20 min. The reaction mixture was then irradiated under blue LED light (4.8 W, $\lambda_{max} = 465$ nm, 1.0 mW/cm^2) at 25 ºC. Aliquots of the reaction mixture were withdrawn at regular time intervals by argon-purged syringes. The polymer-grafted hybrid NPs were recovered by centrifugation and carefully washed at least five times with THF and ethanol to eliminate any leftover reagents. The resultant NPs were directly analyzed by TEM observation to monitor the PDMA shell thickness. The residual NPs were treated with ethanol containing TCEP (2.0 mg/mL) and incubated at room temperature for 24 h. Polymer samples were collected by vacuum drying and analyzed by ^{1}H NMR and GPC measurements.

Synthesis of the Pt@SiO$_2$@PNIPAM Core-Shell-Shell Nanoparticles

Monodisperse Pt seeds of 5 nm in diameter were prepared as described in literature by Natan et al with slight modification.[6] All glassware used was cleaned prior to experiment with freshly prepared *aqua regia* (HCl:HNO$_3$, 3:1, v/v) and then rinsed thoroughly with ultrapure water. Briefly, 11 mL of aqueous solution of $Na_3Cit{\cdot}2H_2O$ (134.8 mg, 0.458 mmol) and $H_3Cit{\cdot}H_2O$ (6.0 mg, 0.0287 mmol) were dosed to 500 mL of aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (72.0 mg, 0.139 mmol) under reflux condition. Afterward, about 5.5 mL of a freshly prepared ice-cold aqueous solution of $NaBH_4$ (4.4 mg, 0.116 mmol), $Na_3Cit{\cdot}2H_2O$ (67.4 mg, 0.229 mmol) and $H_3Cit{\cdot}H_2O$ (3.0 mg, 0.0143 mmol) was quickly dosed to the boiling reaction mixture under vigorous stirring. The reaction was allowed to proceed under reflux for another 10 min. After being cooled down to ambient temperature, the as-prepared Pt seed solution was stored at 0 ºC.

Pt nanodendrites of 16 nm in diameter were synthesized by reducing $H_2PtCl_6{\cdot}6H_2O$ with *L*-ascorbic acid from an initial volume of Pt seed solution of 8 mL (per 30 mL reaction solution), respectively, with the following steps.[6-8] i) $H_2PtCl_6{\cdot}6H_2O$ (27.97 mg, 0.054 mmol) and $Na_3Cit{\cdot}2H_2O$ (18.38 mg, 0.0625 mmol) were dissolved in the corresponding Pt seed solution under vigorous stirring. The total volume of solution was then topped up to 90 mL with ultrapure water. ii) About 1.5 mL of a freshly prepared aqueous solution of *L*-ascorbic acid (18.75 mg, 0.107 mmol) was dosed into the reaction solution under vigorous stirring. iii) The reaction flask was heated to 100 ºC with a heating rate of 10 ºC/min. Afterward, reflux was conducted for another 1 h. iv) The reaction mixture was then cooled down to ambient temperature and left at room temperature for 24 h under stabilization of PVP (M_w = 10,000 g/mol, 20 mg). Finally, the Pt nanodendrites were collected and redispersed in ultrapure water (20 mL) for future use.

The silica frameworks were deposited on the Pt nanodendrites using a modified Stöber method to form Pt@SiO_2-MPTMS NPs. In a typical procedure, aqueous solution of PVP-stabilized Pt nanodendrites (20 mL) was dispersed into an ethanol and ammonium hydroxide (100 mL: 2.5 mL) mixture by ultrasonication for 30 min. Subsequently, TEOS (0.1 mL) was dropped into the reaction mixture under vigorous stirring for 12 h. Afterward, MPTMS (0.15 mL, 0.72 mmol) was slowly dosed to the reaction suspension and the reaction was allowed to proceed for another 12 h. Then, the mixture was stirred for 24 h at room temperature. Afterward, the purification of Pt@SiO_2-MPTMS core-shell NPs was done by three cycles of centrifugation/redispersion/washing in a 1:1 (v/v) mixture of ethanol and deionized water. The Pt@SiO_2-MPTMS NPs were collected by centrifugation and stored in argon-purged ethanol.

About 50 mg of Pt@SiO_2-MPTMS core-shell NPs were dispersed in DMF (20 mL) by ultrasonication for 30 min. PDP (53.4 mg, 0.1 mmol) was added to the reaction mixture under argon atmosphere. After being stirred vigorously overnight, the Pt@SiO_2-PDP NPs were obtained. Afterward, the Pt@SiO_2-PDP NPs were purified by extraction with ethanol and dichloromethane five times to remove any leftover reagents. The Pt@SiO_2-PDP NPs were collected by centrifugation and stored in argon-purged acetonitrile. About

10 mg of Pt@SiO_2-PDP NPs were treated with ethanol containing TCEP (2.0 mg/mL) and incubated at room temperature for 24 h. The residual NPs were purified by extraction with ethanol and dichloromethane five times. The mass difference of the NPs before and after incubation was measured to determine the amount of PDP on the Pt@SiO_2-PDP NPs (5.6×10^{-5} mol PDP per 1.0 mg of Pt@SiO_2-PDP NPs).

Surface-initiated PET-RAFT polymerization of NIPAM monomers in acetonitrile from Pt@SiO_2-PDP NPs was conducted using a molar feed ratio [NIPAM]:[PDP] of 2000:1 and predetermined amounts of Ru(bpy)$_3$Cl$_2$ photocatalyst.[4,5] Briefly, about 20 mg of Pt@SiO_2-PDP NPs were dispersed into acetonitrile (10 mL) by ultrasonication for 30 min. NIPAM (0.25 g, 2.32 mmol) and Ru(bpy)$_3$Cl$_2$ (83.8 μg, 50 ppm relative to NIPAM) were then dosed to the reaction flask. The reaction flask was covered with aluminum foil and degassed with argon for 20 min. The reaction mixture was then irradiated under blue LED light (4.8 W, λ_{max} = 465 nm, 1.0 mW/cm^2) at 25 ºC. Aliquots of the reaction mixture were withdrawn at regular time intervals by argon-purged syringes. The polymer-grafted hybrid NPs were recovered by centrifugation and carefully washed at least five times with THF and ethanol to eliminate any leftover reagents. The resultant NPs were directly analyzed by TEM observation to monitor the PNIPAM shell thickness. The residual NPs were treated with ethanol containing TCEP (2.0 mg/mL) and incubated at room temperature for 24 h. Polymer samples were collected by vacuum drying and analyzed by ^{1}H NMR and GPC measurements.

The synthetic method for the creation of vacant space between catalytic nanocore and tunable polymeric shell is based on a compositional difference, by which silica template layer of Pt@SiO_2@PNIPAM core-shell-shell NPs was selectively etched away whereas the PNIPAM shell remains intact. About 5 mg of Pt@SiO_2@PNIPAM NPs were introduced into an etching agent, 5 mL of 12 wt% HF. After 24 h etching reaction at room temperature, the excessive HF and SiF_4 were removed from the raw product by five centrifugation-redispersion runs in ultrapure water and ethanol. Furthermore, the hybrid nanorattles were dialyzed against ultrapure water for two days (MWCO 1,000 g/mol). Finally, the Pt@*h*PNIPAM hybrid nanorattles were centrifuged, redispersed into 20 mL of ultrapure water and stored at ambient temperature for further use.

Synthesis of Fe_3O_4@*a*SiO_2@PPEGMA Hybrid Janus Nanoparticles

Monodisperse oleic acid-capped Fe_3O_4 NPs with a mean diameter of ~12 nm were prepared as described in literature by Part et al.[9] In a typical procedure, 6 mL of aqueous solution of $FeCl_3•6H_2O$ (541 mg, 2 mmol) were dosed to a mixed solution of oleic acid (1.9 mL, 6 mmol), ethanol (8 mL) and hexane (14 mL) under vigorous stirring for 30 min. Afterward, NaOH (160 mg, 4 mmol) was added to the above solution and the reaction was allowed to proceed at 70 ºC for 4 h. After being cooled down to ambient temperature, the organic phase was collected and purified by repeated washing with deionized water. Most of solvents were removed under reduced pressure. The highly viscous iron/oleate complex precursor was redispersed in a mixed solution of oleic acid (0.32 mL, 1 mmol) and 1-octadecene (12.5 mL, 40 mmol), sonicated for 30 min and degassed by bubbling nitrogen for 30 min. The reaction then was allowed to proceed at 320 ºC for 30 min under steady and continuous nitrogen flow. After being cooled down to room temperature, the crude product was purified by repeated precipitation from hexane into excessive ethanol. The oleic acid-stabilized Fe_3O_4 NPs were centrifuged and stored in cyclohexane before use.

The heteroepitaxial deposition of silica frameworks on the Fe_3O_4 NPs were conducted using a reverse microemulsion method.[10-12] Typically, the as-prepared Fe_3O_4 NPs in cyclohexane (10 mL, 2.5 mg/mL) was dispersed in a mixed solution containing Igepal CO-520 (10.0 g), cyclohexane (240 mL) and ammonium hydroxide solution (4.0 mL, 28~30 wt% NH_3 basis) under ultrasonication treatment. Afterward, TEOS (0.2 mL) and APMS (0.2 mL) was dropwise dosed to the reaction suspension in 30 min. The rest of TEOS (0.2 mL × 3) and MPTMS (0.6 mL × 1) was dosed to the reaction mixture at a time interval of 12 h. Finally, the raw product was collected with a magnet, and purified by three cycles of centrifugation/redispersion/washing in excessive ethanol. The Fe_3O_4@*a*SiO_2-MPTMS NPs were collected by centrifugation and stored in argon-purged ethanol.

About 50 mg of Fe_3O_4@*a*SiO_2-MPTMS Janus NPs was dispersed in DMF (20 mL) by ultrasonication for 30 min. PDP (53.4 mg, 0.1 mmol) was added to the reaction mixture under argon atmosphere. After being stirred vigorously overnight, the Pt@SiO_2-PDP NPs were obtained. Afterward, the Fe_3O_4@*a*SiO_2-PDP NPs were purified by extraction with ethanol and dichloromethane five times to remove any leftover reagents. The Fe_3O_4@*a*SiO_2-PDP NPs were collected by centrifugation and stored in argon-purged acetonitrile. About 10 mg of Fe_3O_4@*a*SiO_2-PDP NPs were treated with ethanol containing TCEP (2.0 mg/mL) and incubated at room temperature for 24 h. The residual NPs were purified by extraction with ethanol and dichloromethane five times. The mass difference of the NPs before and after incubation was measured to determine the amount of PDP on the Fe_3O_4@*a*SiO_2-PDP NPs (6.2×10^{-5} mol PDP per 1.0 mg of Fe_3O_4@*a*SiO_2-PDP NPs).

Surface-initiated PET-RAFT polymerization of PEGMA monomers in acetonitrile from Fe_3O_4@*a*SiO_2-PDP NPs was conducted using a molar feed ratio [PEGMA]:[PDP] of 2000:1 and predetermined amounts of Ru(bpy)$_3$Cl$_2$ photocatalyst.[4,5] Briefly, about 20 mg of Fe_3O_4@*a*SiO_2-PDP NPs were dispersed into acetonitrile (9.3 mL) by ultrasonication for 30 min. PEGMA (0.69 mL, 2.48 mmol), EGDMA (70.5 μL, 0.37 mmol) and Ru(bpy)$_3$Cl$_2$ (92.8 μg, 50 ppm relative to PEGMA) were then dosed to the reaction flask. The reaction flask was covered with aluminum foil and degassed with argon for 20 min. The reaction mixture was then irradiated under blue LED light (4.8 W, λ_{max} = 465 nm, 1.0 mW/cm^2) at 25 ºC. Aliquots of the reaction mixture were withdrawn at regular time intervals by argon-purged syringes. The polymer-grafted hybrid NPs were recovered by centrifugation and carefully washed at least five times with THF and ethanol to eliminate any leftover reagents. The resultant NPs were directly analyzed by TEM observation to monitor the PPEGMA shell thickness.

The synthetic method for the creation of vacant space between catalytic nanocore and tunable polymeric shell is based on a compositional difference, by which silica template layer of Fe_3O_4@*a*SiO_2@PPEGMA hybrid NPs was selectively etched away whereas the

PPEGMA shell remains intact. About 5 mg of Fe_3O_4@*a*SiO_2@PPEGMA NPs were introduced into an etching agent, 5 mL of 10 wt% NaOH. After 24 h etching reaction at room temperature, the excessive NaOH and Na_2SiO_3 were removed from the raw product by five centrifugation-redispersion runs in ultrapure water and ethanol. Furthermore, the as-prepared NPs were dialyzed against ultrapure water for two days (MWCO 1,000 g/mol). Finally, the Fe_3O_4@*h*PPEGMA NPs were centrifuged, redispersed into 20 mL of ultrapure water and stored at ambient temperature for further use.

Instrumentation

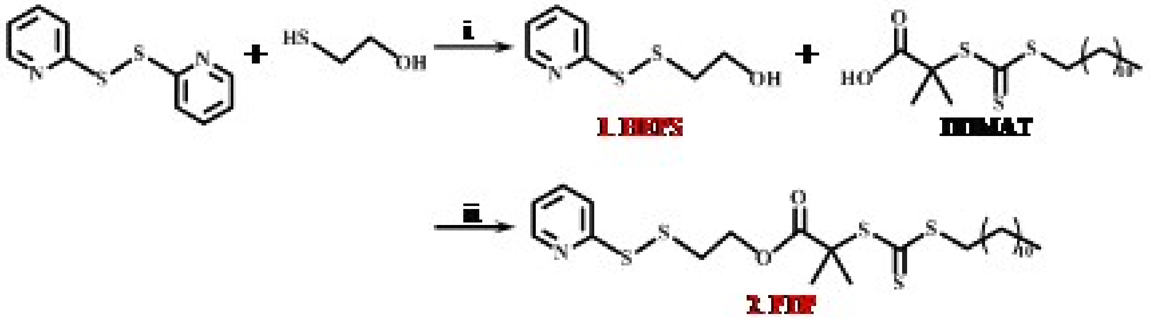
Nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC) were used to characterize the molecular weights and chemical structures of the detached polymers. ^1H NMR spectroscopy were recorded on a Bruker ARX operating at 400 MHz for ^1H using deuterated chloroform ($CDCl_3$), deuterated water (D_2O) and deuterated dimethyl sulfoxide (DMSO-d_6) as the solvents and an internal reference with chemical shifts (δ) reported in ppm. GPC profiles were conducted on a Waters GPC system equipped with an isocratic pump model 1515, a differential refractometer model 2414, a dual-wavelength UV detector model 2487 and Styragel columns. The number-average molecular weight ($M_{n,GPC}$) and polydispersity index ($Đ = M_{w,GPC}/M_{n,GPC}$) were measured with narrow molecular weight distribution poly(ethylene oxide) (PEO) as the standards and THF as the eluent at a flow rate of 1.0 mL/min.

Surface chemistry of the NPs was analyzed by X-ray photoelectron spectroscopy (XPS) on a Kratos AXIS Ultra DLD spectrometer sourcing with a monochromatized Al Kα X-ray source (1468.71 eV photons). The dynamic laser scattering (DLS) were performed on a Brookhaven 90 plus laser light scattering spectrometer at the scattering angle θ = 90°. The hydrodynamic diameter (D_h) was obtained by averaging the values from five measurements. The morphology of the NPs was observed by transmission electron microscopy (TEM, JEOL-2100, JEOL Ltd., Japan). The thermal stability of the NPs was investigated by thermogravimetric analysis (TGA). The samples were heated from 30 ºC to around 700 ºC with a heating rate of 10 ºC/min under a dry nitrogen atmosphere in a thermal analyzer (TGS-II, PerkinElmer).

The amount of PDP and PDMA grafted onto the surface of the silica NPs was calculated based on the mass differences from the reductive scission of disulfide linkages of the corresponding NPs. The grafting density (*GD*) was estimated according to the following equation:

$$GD(\frac{chain}{nm^2}) = \frac{W_l \times N_a}{M \times m \times S}$$

where W_l is the weight loss, N_a is Avogadro constant, M is the molecular weight, m is the molar mass and S is the specific surface area of the respective components in the silica NPs.



Scheme S1. Synthesis of PDP chain transfer agent. Reagents and conditions: (i) glacial acetic acid, methanol, RT, 3 h; (ii) DCC, DMAP, anhydrous dichloromethane, RT, 24 h.

Table S1. Results on Surface-Initiated PET-RAFT Polymerization of *N,N*-dimethylacrylamide (DMA) on Silica Nanoparticles

Entry	time (h)	W_1 (%)	α^b (%)	$M_{n,NMR}{}^b$ (kg/mol)	$M_{n,GPC}{}^c$ (kg/mol)	$Đ^c$	Shell Thickness (nm)	Grafting Density (chains/nm^2)
1	0	1.8	-	-	-	-	0	1.34
2	0.5	15.2	7.3	14.9	17.9	1.14	6.1±0.8	0.36
3	1.5	32.3	21.5	43.0	48.7	1.11	15.8±1.7	0.33
4	2.5	40.9	33.6	67.1	75.4	1.09	25.6±2.5	0.31
5	4	48.1	47.2	93.9	106.1	1.07	39.8±3.3	0.30

[a] Polymerizations were performed in acetonitrile under blue LED light irradiation (4.8 W, λ_{max} = 465 nm, 1.0 mW/cm^2) with prior deoxygenation at 25 ºC ($[M]_0/[CTA] = 2000:1$).

[b] The molecular weight was calculated using the following equation: $M_{n,NMR} = [M]_0/[CTA] \times MW^M \times \alpha + MW^{CTA}$, where $[M]_0$, [CTA], MW^M, α and MW^{CTA} correspond to initial monomer concentration, initial CTA concentration, molar mass of monomer, monomer conversion derived from ^{1}H NMR spectroscopy, and molar mass of CTA.

[c] Derived from GPC profiles (calibration with PEO molecular weight standards), polydispersity index ($Đ$) = $M_{w,GPC}/M_{n,GPC}$.

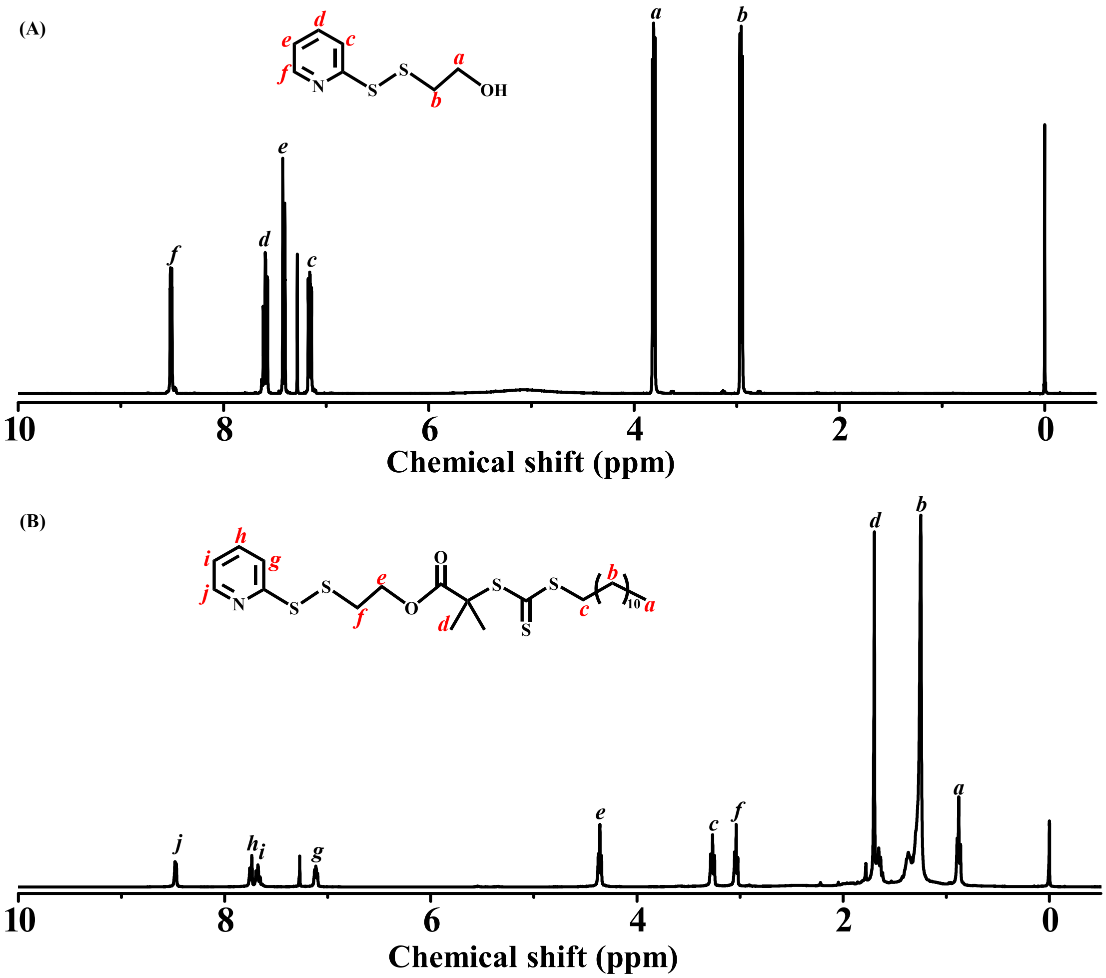


Figure S1. ^{1}H NMR spectra of (A) HEPS and (B) PDP in $CDCl_3$.

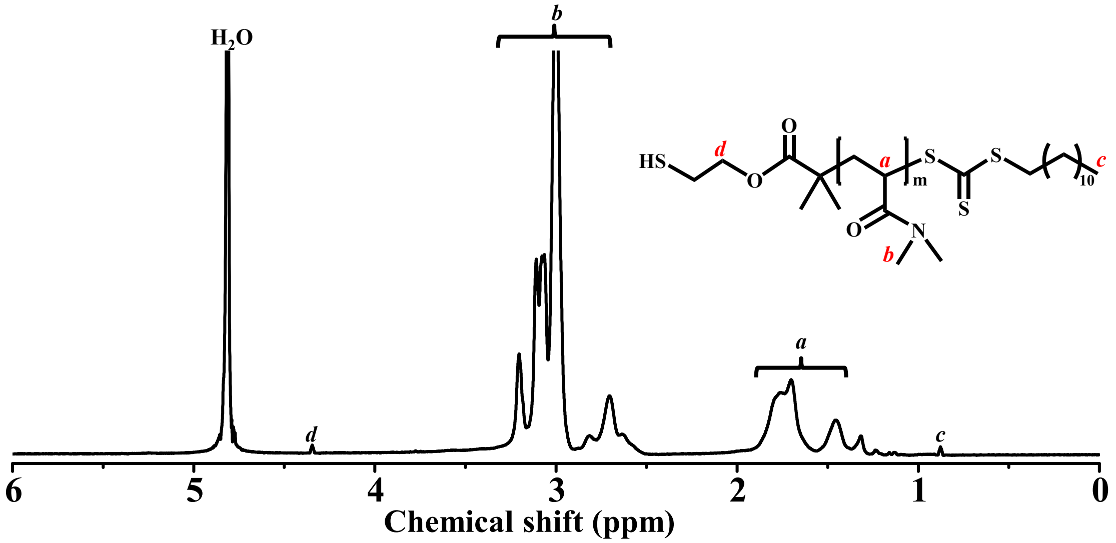


Figure S2. ^{1}H NMR spectrum of PDMA-PDP in D_2O (detached from SiO_2@PDMA-2 nanoparticles with exposure time of 1.5 h).

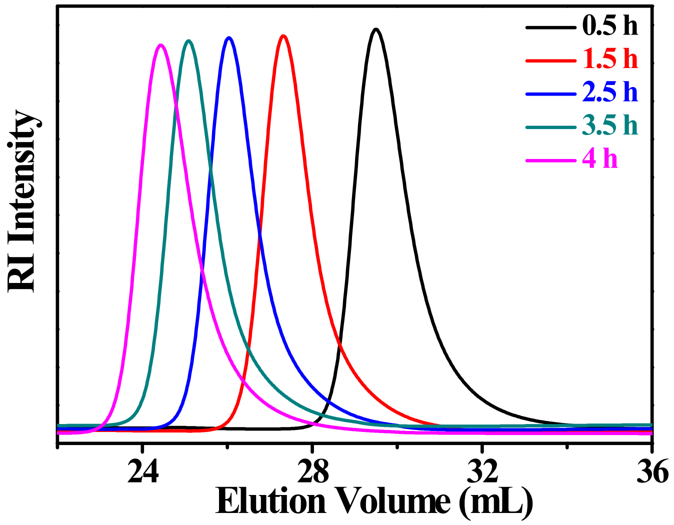


Figure S3. GPC profiles of cleaved PDMA polymers from SiO_2@PDMA core-shell nanoparticles at predetermined time intervals of surface-initiated PET-RAFT polymerization.

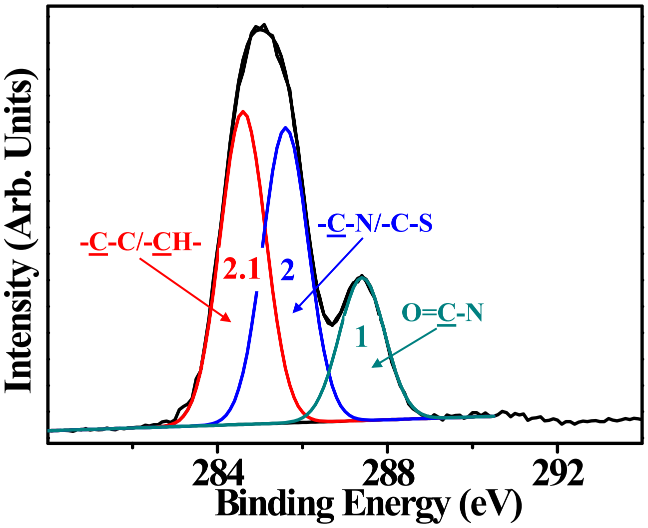


Figure S4. XPS C 1s core-level spectrum of SiO_2@PDMA-2 nanoparticles.

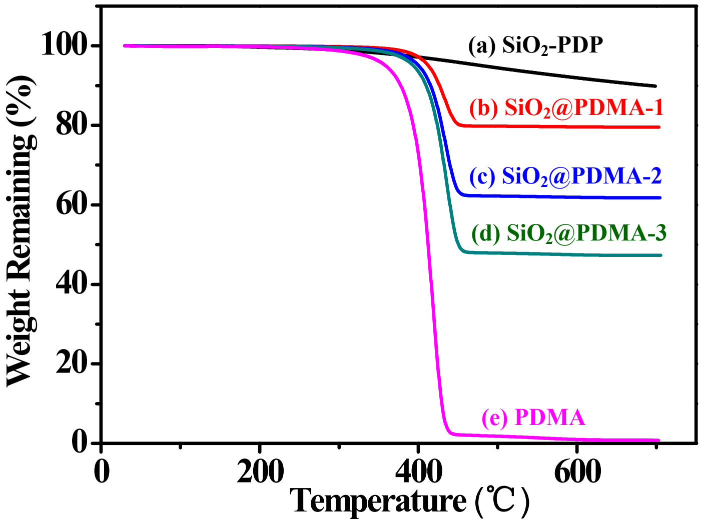


Figure S5. TGA curves of (a) SiO_2-PDP, (b) SiO_2@PDMA-1, (c) SiO_2@PDMA-2, (d) SiO_2@PDMA-3 nanoparticles and (e) PDMA polymer.

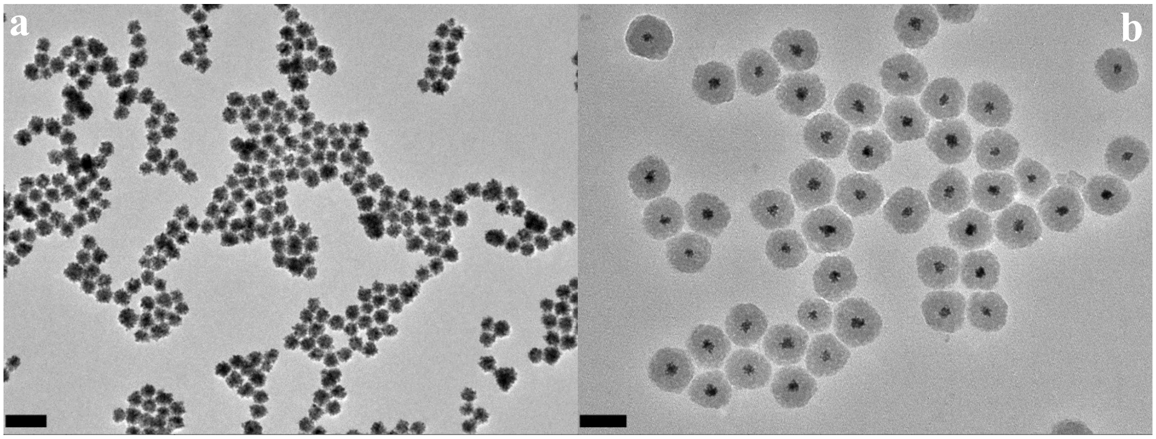


Figure S6. TEM images of (a) Pt and (b) Pt@SiO$_2$-PDP nanoparticles. All scale bars are 50 nm.

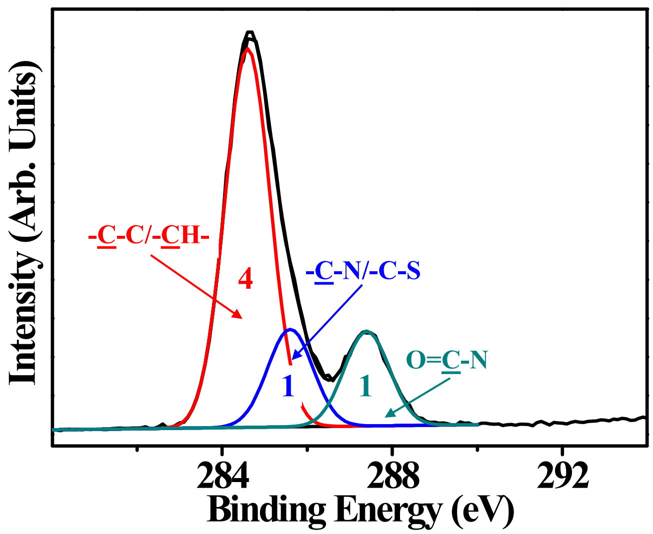


Figure S7. XPS C 1s core-level spectrum of Pt@SiO$_2$@PNIPAM-2 nanoparticles.

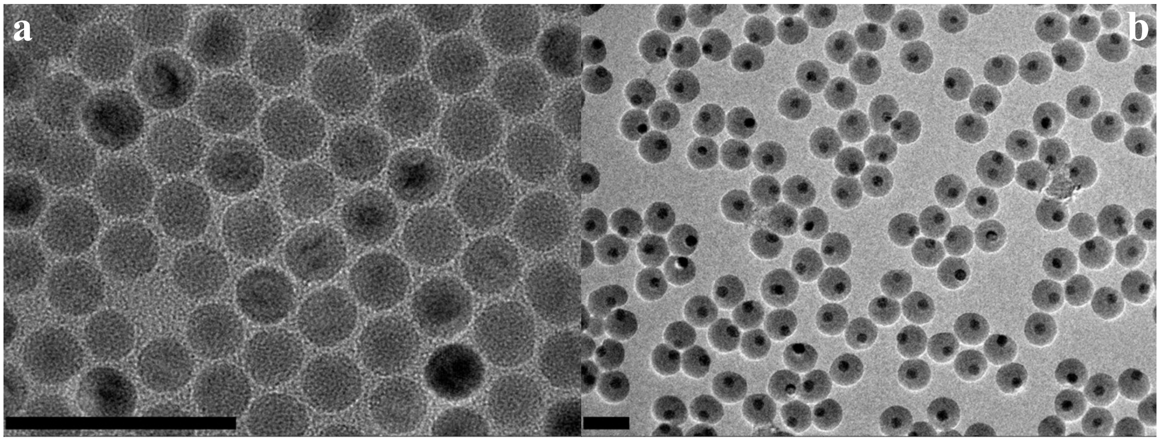


Figure S8. TEM images of (a) Fe_3O_4 and (b) Fe_3O_4@*a*SiO_2-PDP nanoparticles. All scale bars are 50 nm.

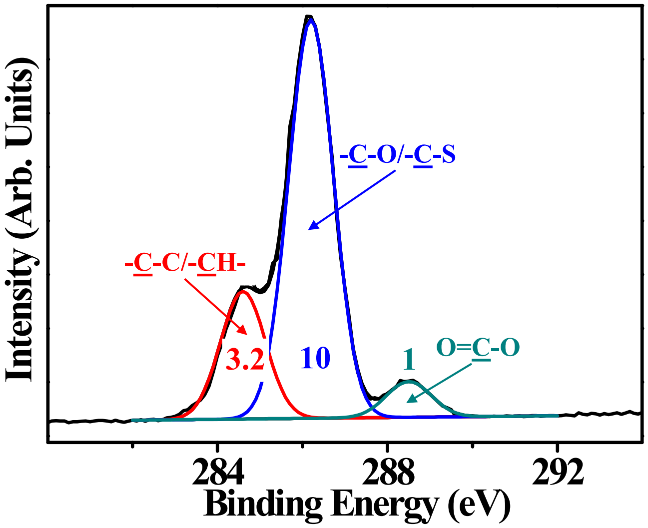


Figure S9. XPS C 1s core-level spectrum of Fe_3O_4@*a*SiO_2@PPEGMA-2 nanoparticles.

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