

Supporting Information

Investigating interactions between cationic particle and polyelectrolyte brushes with the Total Internal Reflection Microscopy (TIRM)

Xiaoling Wei, Xiangjun Gong*, and To Ngai*

Departments of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong

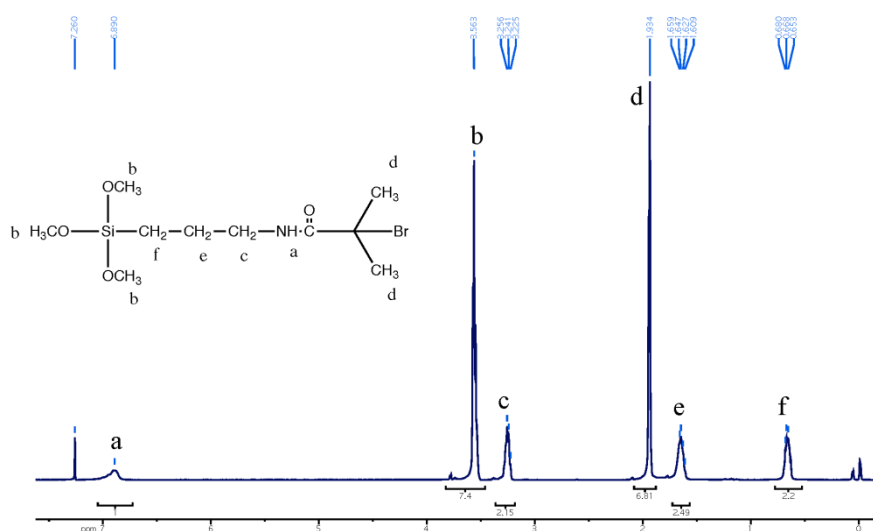


Fig. S1. ¹H NMR spectrum of the synthesized reactive initiator, 2-bromo-2-methyl-N-(3-(trimethoxysily)propyl)pro-panamide (BMTPP).

Synthesis of silica nanoparticles: Silica nanoparticles were synthesized by sol-gel polymerization of tetraethyl orthosilicate (TEOS). To a round flask were added ethanol (99 %, 112 mL), ammonium solution (25 %, 6 mL) and deionized water (7

mL) under stirring. After that, TEOS (8 mL) in ethanol (99 %, 75 mL) were added dropwise under room temperature. After 24 h reaction time, the sample was collected after centrifugation in ethanol and D. I. water respectively for three times. Then the sample was freeze dried. The sample was redispersed in D. I. water and characterized by Scanning Electron Microscopy (SEM) and Dynamic Light Scattering (DLS).

ATRP initiator deposition: Ammonium solution (25 %, 1.5 g) in ethanol (99 %, 10 mL) were added dropwise to the mixture of the above synthesized silica particle (0.25 g) and ethanol (99 %, 5 g) in a round flask under 40 °C. Then the ATRP initiator BMTTP (0.2 g) in ethanol (99 %, 2.5 mL) was added to the above mixture. The reaction was conducted for 24 h under continuous stirring. After centrifugation in ethanol and D. I. water at 5000 rpm for 3 times, the final product Silica-Br was obtained after drying.

ATRP synthesis of PDMAEMA brushes on silica nanoparticles: 0.15 g Silica-Br, PMEDTA (432 µL, 0.22 mmol), DMF (10 mL), CuBr (63.2 mg, 0.44 mmol) were added to a flask and degassed. Then DMAEMA (7.36 mL, 44.0 mmol) was added in and the reaction was started after three freeze-thaw cycles. The reaction was conducted at 60 °C, quenched by liquid nitrogen and exposed to air. The final product Silica-PDMAEMA was collected by centrifugation at 7000 rpm for 3 times in D. I. water, 2 times in EDTA sodium salt and 3 times in ethanol. The final product was dried before further use.

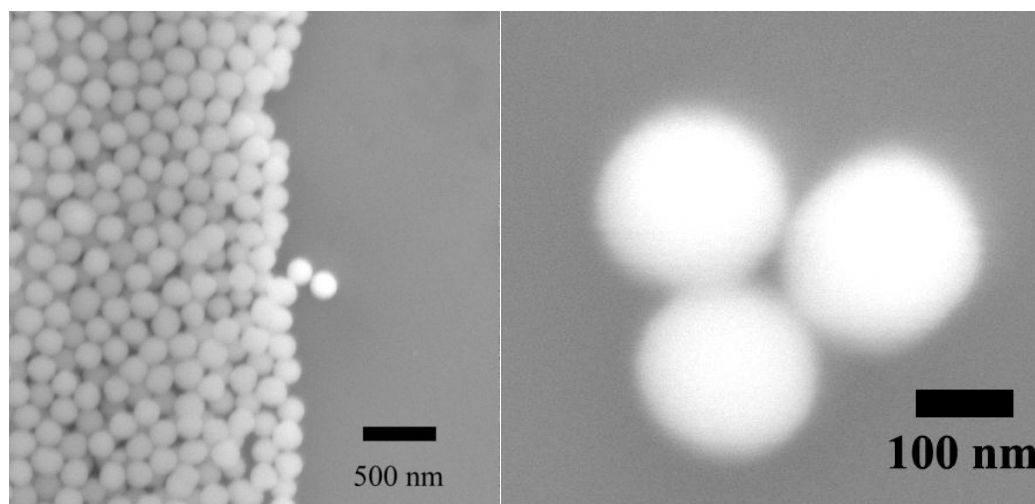


Fig. S 2. SEM images of the synthesized silica nanoparticles

Laser light scattering (LLS). A modified commercial light scattering spectrometer (ALV/DLS/SLS-5022F) equipped with a multi- τ digital time correlator and a cylindrical 22 mW He-Ne laser ($\lambda_0 = 632.8\text{nm}$, Uniphase) was used as light source. In dynamic LLS, the intensity-intensity time correlation function $G^{(2)}(\tau)$ in the self-beating mode was measured in the scattering angle range 20° - 150° . The Laplace inversion of $G^{(2)}(\tau)$ can lead to a line-width distribution $G(\Gamma)$, which can be further converted to a translational diffusive coefficient distribution $G(D)$ by $\Gamma = Dq^2$ or a hydrodynamic radius distribution $f(R_h)$ by use of the Stokes-Einstein equation, $R_h = k_B T / 6\pi\eta D$, where η , k_B , and T are the solvent viscosity, the Boltzmann constant, and the absolute temperature, respectively. The silica nanoparticle sample was dissolved in water at 25°C for at least 24 h and was further filtered through a $0.45\ \mu\text{m}$ Milipore Millex-LCR filter to remove dust for LLS experiments. The details of the LLS theory can be found elsewhere.^{1,2}

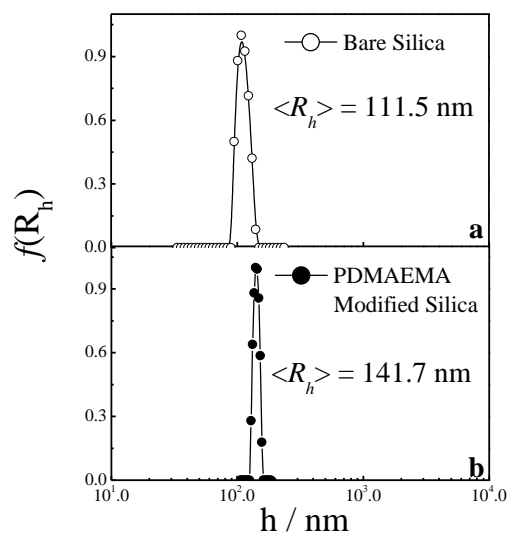


Fig. S3. Hydrodynamic radius distributions ($f(R_h)$) of the a) bare and b) PDMAEMA-modified silica nanoparticle in aqueous solution as measured by dynamic laser light scattering, where the measured angle is 20° . The thickness of the grafted brushes is 30.2 nm.

Table S 1. Zeta potential of the bare silica nanoparticle, initiator modified silica Silica-Br and polymer grafted silica Silica-PDMAEMA in different environments.

Sample	pH	Mobility	Zeta Potential (mV)
Silica	D.I. Water	- 3.52	- 46.81
Silica-Br	D.I. Water	- 2.99	- 38.28
Silica-PDMAEMA	D.I. Water	+ 0.32	+ 4.05
Silica-Br	pH = 3.2	+ 0.47	+ 5.97
Silica-PDMAEMA	pH = 3.2	+ 2.98	+ 38.16

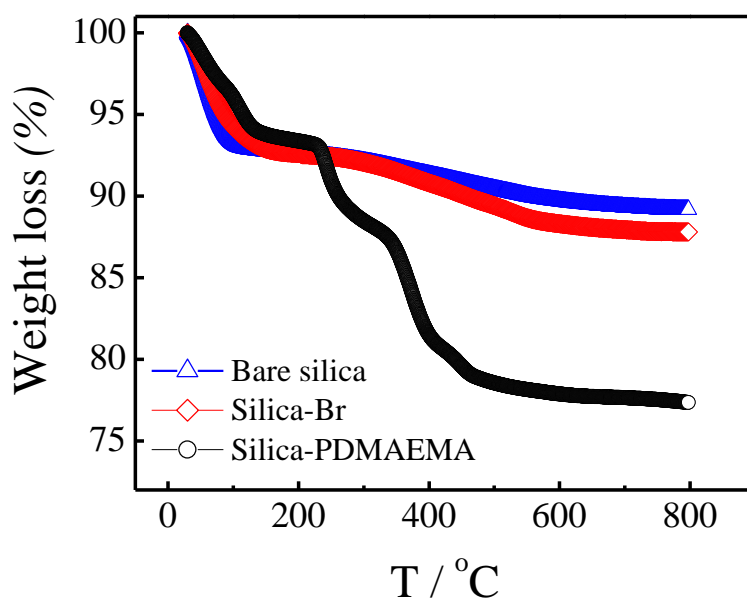


Fig. S4. TGA traces of bare silica nanoparticle, ATRP initiator modified silica nanoparticle (Silica-Br) and PDMAEMA modified silica nanoparticle (Silica-PDMAEMA).

Calculation of the dried PDMAEMA thickness on silica nanoparticles and its swelling ratio³

We have the following assumptions:

1. All the nanoparticles are ideal spheres;
2. Density of the PDMAEMA is: $\rho_{PDMAEMA} = 1.318 \text{ g/cm}^3$.

According to the LLS results, the radius of the bare silica nanoparticle is:

$$r_{silica} = 111.5 \text{ nm}$$

The radius of the PDMAEMA grafted silica nanoparticles (Silica-PDMAEMA) is:

$$r_{\text{Silica-PDMAEMA}} = 141.7 \text{ nm}$$

The swelled thickness of PDMAEMA in water:

$$r_{\text{PDMAEMA-Swelled}} = r_{\text{Silica-PDMAEMA}} - r_{\text{silica}} = 30.2 \text{ nm}$$

The density of bulk bare silica nanoparticles: $\rho_{\text{silica}} = 2.0 \text{ g/cm}^3$

Then we will get:

$$\text{Volume of a single bare silica nanoparticle: } V_{\text{silica}} = \frac{4\pi r_{\text{silica}}^3}{3} = 5.81 \times 10^{-3} \mu\text{m}^3$$

$$\text{Weight of a single bare silica nanoparticle: } W_{\text{silica}} = \rho_{\text{silica}} \times V_{\text{silica}} = 1.162 \times 10^{-14} \text{ g}$$

From the TGA traces, the residue weight at 800 °C:

$$\text{Silica-Br} = 88.07 \%$$

$$\text{Silica-PDMAEMA} = 78.09 \%$$

Hence, we will get:

$$\text{Bulk silica content for Silica-PDMAEMA} = 78.09 \%$$

$$\text{Bulk PDMAEMA content: } 88.07 \% - 78.09 \% = 10.98 \%$$

For 1 g of Silica-PDMAEMA, the polymer volume of one single silica particle:

$$V_{\text{PDMAEMA}} = (0.1098 \text{ g} \times W_{\text{silica}}) / (0.7809 \times \rho_{\text{PDMAEMA}}) = 1.24 \times 10^{-3} \mu\text{m}^3$$

For a single Silica-PDMAEMA particle,

$$\text{Total volume is: } V_T = V_{\text{silica}} + V_{\text{PDMAEMA}} = 7.05 \times 10^{-3} \mu\text{m}^3 = \frac{4\pi r_T^3}{3}$$

$$\text{Total radius is: } r_T = 118.95 \text{ nm}$$

Dried polymer thickness of PDMAEMA in Silica-PDAMEMA:

$$r_{\text{PDMAEMA-Dried}} = r_T - r_{\text{silica}} = 7.45 \text{ nm}$$

The swelling ratio of the PDMAEMA is:

$$R = r_{\text{PDMAEMA-Swelled}} / r_{\text{PDMAEMA-Dried}} = 4.05$$

Calculation of the initiator density on the silica nanoparticles

We have the following assumptions:

1. All the nanoparticles are ideal spheres;
2. Initiator molecule was grafted on the silica nanoparticles as a self-assembled monolayer.

Decomposed initiator BMTTP molecular weight is: $M_{initiator} = 209.8 \text{ g/mol}$

Silica particle radius: $r_{silica} = 111.5 \text{ nm}$

Bulk density of silica particles is: $\rho_{silica} = 2.0 \text{ g/cm}^3$

Thus, Surface area of one single silica nanoparticle: $S_{silica} = 4\pi r_{silica}^2 = 0.156 \mu\text{m}^2$

Volume of one single silica nanoparticle: $V_{silica} = 4\pi r_{silica}^3 / 3 = 5.81 \times 10^{-15} \text{ cm}^3$

Number of silica nanoparticle per mL: $N_v = 1 / V_{silica} = 1.72 \times 10^{14} \text{ cm}^{-3}$

Number of silica nanoparticle per gram: $N_w = N_v / \rho_{silica} = 8.6 \times 10^{13} \text{ g}^{-1}$

From the TGA traces, the residual weight at 800 °C:

Bare silica = 89.30 %

Silica-Br = 88.07 %

Hence,

Bulk silica content for Silica-Br = 88.07 %

Bulk initiator content = 89.30 % - 88.07 % = 1.23 %

The initiator density is:

$$\rho_{initiator} = \frac{0.0123 \text{ g Initiator}}{0.8807 \text{ g Silica}} \times \frac{1}{N_w} \times \frac{1}{S_{silica}} \times \frac{6.02 \times 10^{23} \text{ mol}^{-1}}{209.8 \text{ g/mol}} = 3.0 \text{ nm}^{-2}$$

References and Notes:

- (1) Wu, C.; Siddiq, M.; Woo, K. F. *Macromolecules* **1995**, 28, 4914.
- (2) Chu, B. *Laser Light Scattering*; 2nd ed.; Academic Press: New York, 1991.
- (3) Tan, K. Y.; Gautrot, J. E.; Huck, W. T. S. *Langmuir* **2011**, 27, 1251.