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Supplementary Information

Anti-fouling and anti-bacterial polyethersulfone membranes quaternized from the additive of poly(*2*-dimethylamino ethyl methacrylate) grafted SiO_2 nanoparticles

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1. The details for the synthesis of SiO_2-*g*-PDMAEMA NPs via surface-initiated RAFT polymerization

(1) Synthesis of bare SiO_2 and amino-functionalized SiO_2 (SiO_2-NH_2) NPs

Bare SiO_2 NPs were prepared by classical sol-gel method. In brief, tetraethyl orthosilicate (TEOS, 0.14 M), ammonium hydroxide (25~28 wt%, 0.5 M), ultrapure water (2.5 M) and ethanol (16.2 M) were added into a round-bottom flask under stirring at 50 ^{o}C. After 5 h, (3-aminopropyl)triethoxysilane (3.0 g, 13.6 mmol) was dropped slowly and stirred for 12h at room temperature. The solid SiO_2-NH_2 NPs were isolated by centrifugation (10,000 rpm, 10 min) and washed with plenty of ethanol and pure water. The solid SiO_2-NH_2 NPs were obtained by freeze drying.

(2) Synthesis of RAFT agent anchored SiO_2 (SiO_2-CDP) NPs

The RAFT agent of 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl pentanoic acid (CDP) was synthesized according to the method in the literature.[1] The SiO_2-NH_2 NPs (8 g) were dispersed into dichloromethane (DMC, 500 ml) under ultrasonic dispersion. After 1 h, the RAFT agent CDP (4.04 g, 10 mM) was added into the mixture, and the amide reaction was happened under the catalysis of DCC/DMAP at room temperature for 48 h. These NPs were separated by centrifugation and purified by successive dispersion-centrifugation cycles in ethanol and ultrapure water. The white yellow SiO_2-CDP NPs were obtained by freeze-drying for 48h and used as the chain transfer agent (CTA) to regulate RAFT polymerization of DMAEMA to produce SiO_2-*g*-PDMAEMA NPs.

(3) Synthesis of SiO_2-*g*-PDMAEMA NPs via surface-initiated RAFT polymerization

SiO_2-CDP NPs (0.57 g, 62.6 μmol) were dispersed in DMAc (33g) under ultrasonication for

1 h. The mixture was degassed with N_2 for 1 h at room temperature. Then, DMAEMA (15.7 g, 100 mmol), AIBN (3.3 mg, 0.02 mmol) and free RAFT agent (CDP, 4.8 mg, 0.012 mmol) were added into the flask under stirring and degassed with N_2 for additional 1 h at room temperature. Then the mixture was transferred to an oil bath and the surface initiated RAFT polymerization was carried out at 70 ^{o}C under N_2 protection and stirring. After reaction for a predetermined time, the reaction was stopped by quenching in ice water. The raw product was separated through centrifuging (10,000 rpm, 30 min). In order to thoroughly dissolve and remove free PDMAEMA, the dispersion/centrifugation cycle was repeated at least five times. Furthermore, the raw SiO_2-*g*-PDMAEMA NPs were dialyzed against distilled water for 3 days. Finally, the loose SiO_2-*g*-PDMAEMA NPs were obtained via freeze-drying.

(4) Cleaving grafted PDMAEMA from the surface of SiO_2 NPs

The SiO_2-*g*-PDMAEMA NPs (100 mg) were dispersed in ultrapure water (4.0 ml) in a polymeric tube under stirring. Aqueous HF (1.0 ml, 49%) was added, and the mixture was stirred at room temperature over night. Then, the mixture was neutralized by adding Na_2HCO_3 aqueous solution. Finally, cleaved PDMAEMA was dialyzed against ultrapure water for 3 days and dried via freeze-drying.

2. The details for the structures and characters of the synthesized SiO_2-*g*-PDMAEMA NPs

FT-IR spectra for bare SiO_2, PDMAEMA and SiO_2-*g*-PDMAEMA NPs with polymerization time 12h were observed in **Fig. S1**. Compared with the bare SiO_2 NPs, the new obvious absorption band at 1730 cm^{-1} for purified SiO_2-*g*-PDMAEMA NPs was appeared which was attributed to the stretching vibration of carboxyl in ester groups from PDMAEMA. The absorption band at 1097 cm^{-1}, characteristic of the Si-O group of bare SiO_2 NPs, was also present in the SiO_2-*g*-

PDMAEMA NPs. Therefore, the FT-IR spectroscopic results indicated that PDMAEMA had been successfully grafted on the surface of SiO_2 NPs.

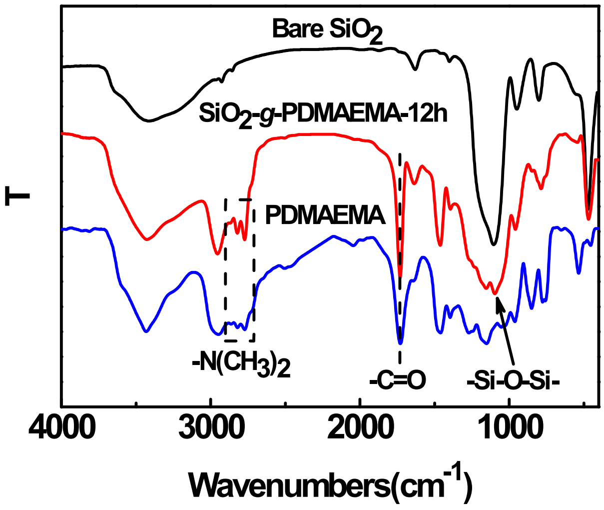

Fig. S1 FT-IR spectra for bare SiO_2, PDMAEMA and SiO_2-*g*-PDMAEMA NPs with a polymerazation time of 12h.

The cleaved PDMAEMA brushes were subjected to GPC analyses and the results were shown in **Fig. S2**. **Figure S2A** presented the evolution of the number-average molecular weight (*Mn*) and the polydispersity index (*PDI*) of the cleaved grafted PDMAEMA as a function of monomer conversion. It was found that the molecular weight *Mn* linear elevated along with the increasing of conversion. The molecular weight distributions *PDI* maintained about 2. Generally, in “living” polymerization, termination can occur in neighboring surface-grafted chains on the same silica and inter-molecular coupling of grafted chains from different silica cores, which lead to a broader PDI finally. **Figure S2B**, a pseudo-first-order kinetic plot for the surface initiate RAFT polymerization of PDMAEMA in the presence of the free RAFT agent CDP was depicted. This indicates a constant free radical concentration during the polymerization.

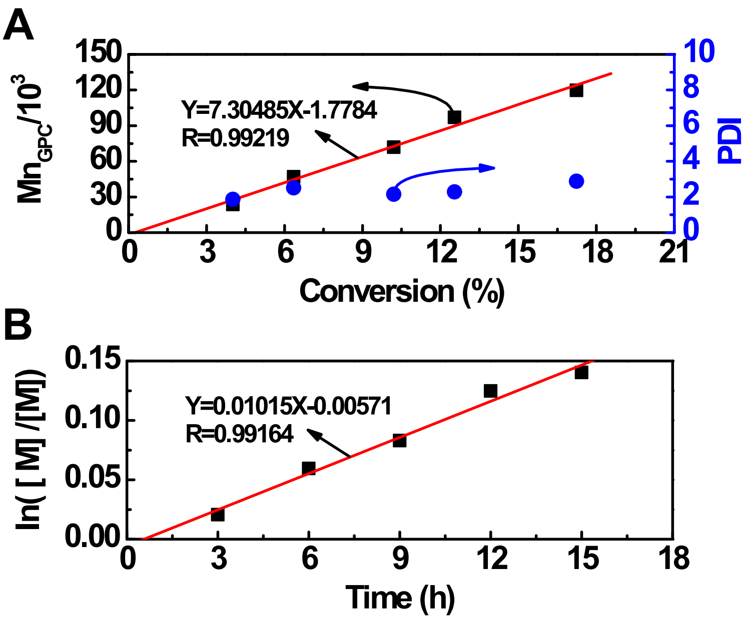

Fig. S2 Dependence of number-average molecular weight (Mn) and polydispersity (PDI=Mw/Mn) on conversion (A) and (B) pseudo-first-order kinetic plot of PDMAEMA chains cleaved from SiO_2-*g*-PDMAEMA NPs synthesized by surface-initiated RAFT polymerization ([DMAEMA]/[SiO_2-CDP]/[free CDP]/[AIBN] = 5000/3.2/0.6/1) in DMAc at 70 °C for a different polymerization time.

3. More supporting data for the PES/SiO_2-*g*-PDMAEMA hybrid membranes

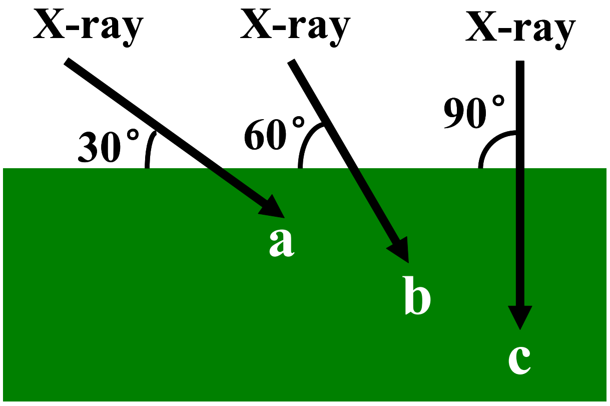

Fig. S3 The scheme for the analysis depth of XPS measurement by adjusting the take-off angle.

References

1 G. Moad, Y. K. Chong, A. Postma, E. Rizzardo and S. H. Thang, *Polymer*, 2005, **46**, 8458-8468.