Electronic Supplementary Material (ESI) for Chemical Communications.

Support Information

Scalable Polyzwitterion-Polydopamine Coating for Regenerable Oil/Water Separation and Underwater Self-Cleaning of Stubborn Heavy Oil Fouling without Pre-Hydration

*Jiawen Zhang, Ling Zhang, Xinwei Cui, Lu Gong, Li Xiang, Chen Shi, Wenjihao Hu, Hongbo Zeng**

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, AB, T6G 1H9, Canada

** E-mail address: Hongbo.Zeng@ualberta.ca; Tel: +1 780-492-1044*

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1. Materials, synthesis and characterization

1.1 Materials. 3-[dimethyl(2-methacryloyloxyethyl)ammonio] propanesulfonate (MAPS), 2-(methacryloyloxy)ethyl trimethylammonium chloride (MTAC), dopamine hydrochloride, tris(hydroxymethyl)aminomethane, 4,4'- azobis(4-cyanopentanoic acid) (V501) and 3-sulfopropyl acrylate potassium (SPAK) were purchased from Sigma-Aldrich. The polyurethane (PU) sponge is commercially available. Sodium borohydride ($NaBH_4$) was purchased from Alfa Aesar. 4-Cyanopentanoic acid dithiobenzoate (reversible addition–fragmentation chain-transfer (RAFT) agent), and poly(3-[dimethyl(2-methacryloyloxyethyl) ammonium] propanesulfonate) (PMAPS), poly(2-(methacryloyloxy)ethyl trimethylammonium chloride) (PMTAC) and poly(3-sulfopropyl acrylate potassium (PSPAK) (mole ratio of monomer to RAFT agent equals to 50:1) were synthesized according to a previous report.[1] Milli-Q water was used for all the experiments.

1.2 Preparation of PDA coated silica/sponge substrates

Before coating, silica substrates were rinsed by ethanol and water repeatedly, and then dried by the compressed nitrogen gas followed by a treatment in the UV-Ozone cleaner for 15 min. To coat PDA on silica substrates, silica substrates were immersed in dopamine solution (2 mg mL^{-1}, pH 8.5, 10 mM tris buffer). After stirring for 24 h at room temperature, the substrates were taken out from the solution, rinsed by water and ethanol, and dried by the compressed nitrogen gas.

The PU sponges were cut into blocks (25 mg) and cleaned by water and ethanol repeatedly. And then PU sponges were immersed in dopamine solution (2 mg mL^{-1}, pH 8.5, 10 mM tris buffer) to prepare PDA coating on the PU sponges. After magnetic stirring for 24 h, the PDA coated sponges were taken out from the solution and washed by water and ethanol followed by drying in vacuum at room temperature.

1.3 Preparation of polyelectrolytes-PDA coated silica/sponge substrates

30 mg of each polyelectrolyte, i.e., PMAPS, PMTAC and PSPAK, were dissolved respectively into 15 mL pH 8.5 tris buffer. Then, reducing agent $NaBH_4$ (with mole ratio of 3: 1 to polyelectrolyte) was added into the solution and the solution was stirred for 1 h. After that, PDA coated silica substrates were put into the solution under stirring for 24 h to graft the polyelectrolytes on PDA surfaces. Then, polyelectrolytes-

PDA coated silica substrates were taken out from the solution, extensively rinsed by water and ethanol, followed by drying with compressed nitrogen gas.

Each type of polyelectrolytes (PMAPS, PMTAC and PSPAK, 120 mg) were dissolved into 40 mL tris buffer (pH 8.5), to which reducing agent $NaBH_4$ with mole of 3: 1 to polyelectrolyte was added. The stirring was kept for 1 h, and then PDA coated sponges were put into the solution. After stirring for 24 h, the polyelectrolytes-PDA coated sponges were taken out and extensively washed with water and ethanol.

1.4 Characterization

The morphologies of the coated silica substrates were obtained using a Dimension Icon atomic force microscope (AFM) (Bruker, Santa Barbara, CA) by tapping mode. A scanning electronic microscopy (SEM, Tescan Vega-3, Czech Republic) was used to characterize the morphologies of the coated sponges. X-ray photoelectron spectroscopy (XPS) was employed to characterize the chemical composition using a spectrometer (Kratos Axis Ultra, NY) with Al Kα radiation (12 mA, 14 kV). Water residues contents of water-in-oil (W/O) emulsion were measured by a Coulometric Karl Fischer titrator (Mettler Toledo, OH). The average molecular weight of the polyelectrolytes was characterized by a Viscotek model 250 dual detectors gel permeation chromatography (GPC) system (Malvern Panalytical, Nederland), using 0.5 M acetic acid and 0.5 M sodium acetate as eluent.

2. Experimental methods

2.1 Underwater self-cleaning performance tests

1000 ppm asphaltenes-in-toluene solution was used as the oil phase. Nitrogen-dried silica substrate, pure PDA coated silica substrate, and each type of polyelectrolytes (PMAPS, PMTAC and PSPAK)-PDA coated silica substrates were immersed separately in oil for 1 h. After that, the surfaces were taken out and washed in water for 1 min. Then, underwater oil contact angle measurements were carried out on these substrates. In the regeneration cycling test, after each contact angle measurement, the surfaces were dried by compressed nitrogen gas before the next cycle. The regeneration cycling tests were carried out for ten cycles for each type of polyelectrolytes-PDA coated silica substrates.

Oil contact angle in water (pH 2, adjusted by 0.1 M HCl; pH 5.6, natural pH; and pH 11, adjusted by

0.1 M NaOH) on each polyelectrolytes-PDA coated silica substrates were measured. The oil contact angle in water (pH 2, 5.6 and 11) were also measured after the substrates were being soaked in oil for 24 h without pre-hydration and washed in water (1 min) with the corresponding pH.

Contact angle measurements were carried out to characterize the oil contact angle in saline water (i.e., 100 mM NaCl solution, and 100 mM NaCl and 10 mM $CaCl_2$ solution) on PMAPS-PDA coated substrates after the substrates were soaked in oil for 24 h without pre-hydration and washed in corresponding saline solutions for 1 min.

2.2 Water residues removal performance tests

0.7 mL water was added into 10 mL 500 ppm asphaltenes-in-toluene solution and agitated to form a W/O emulsion solution. Different polyelectrolytes-PDA coated sponges were put into the W/O emulsion solution and shaken by hands for 10 seconds. The sponge was then manipulated by tweezer to access the water residues in the edge of container. After that, the sponge was taken out, washed thoroughly in clean water and dried for the next cycle. The water residues contents in the remnant oil were measured by the titrator.

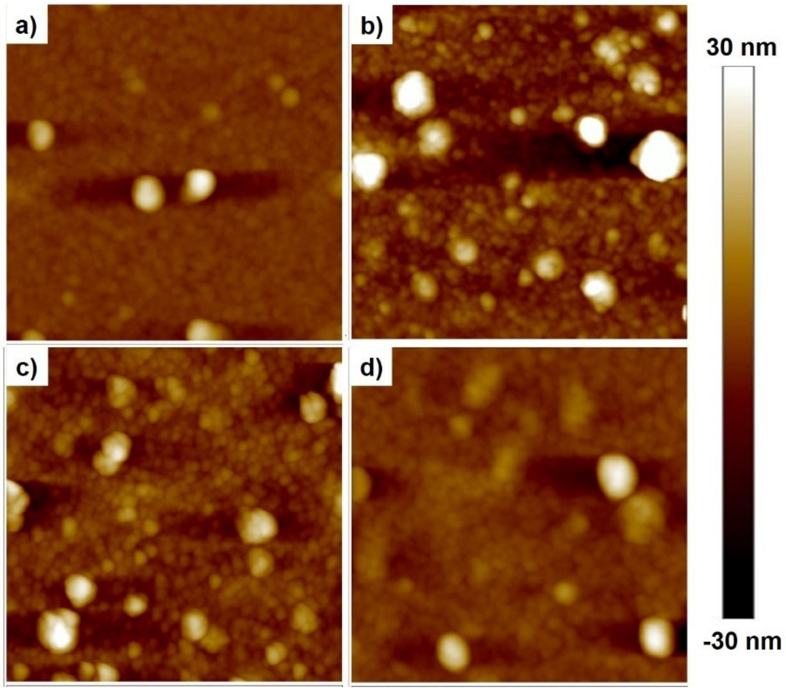

Fig. S1 Atomic force microscopy (AFM) images (1×1 μm) of a) pure polydopamine (PDA), b) poly(3-

[dimethyl(2-methacryloyloxyethyl) ammonium] propanesulfonate) (PMAPS)-PDA, c) poly(2-(methacryloyloxy)ethyl trimethylammonium chloride (PMTAC)-PDA and d) poly(3-sulfopropyl acrylate potassium (PSPAK)-PDA coated silica substrates.

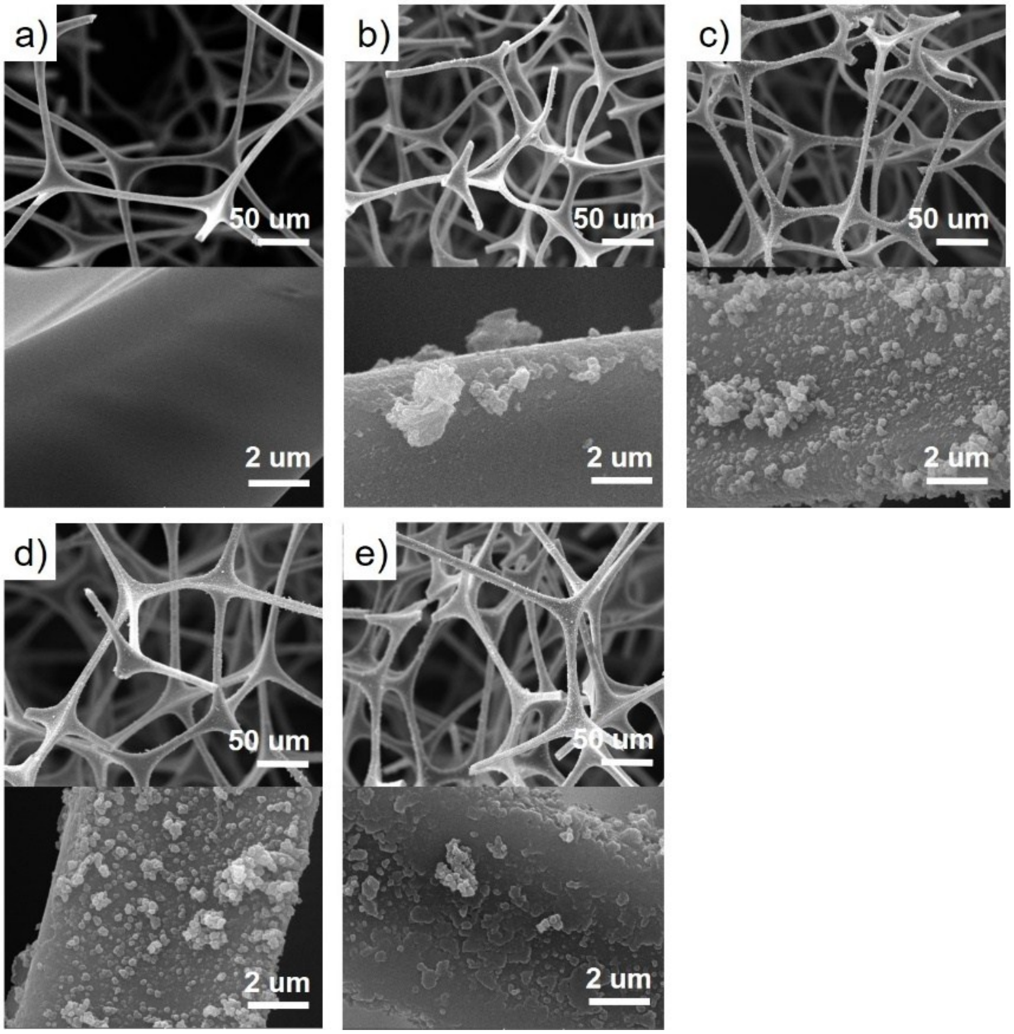

Fig. S2 Scanning electronic microscopy (SEM) images of a) blank polyurethane (PU) sponge, b) pure PDA, c) PMAPS-PDA, d) PMTAC-PDA and e) PSPAK-PDA coated PU sponges.

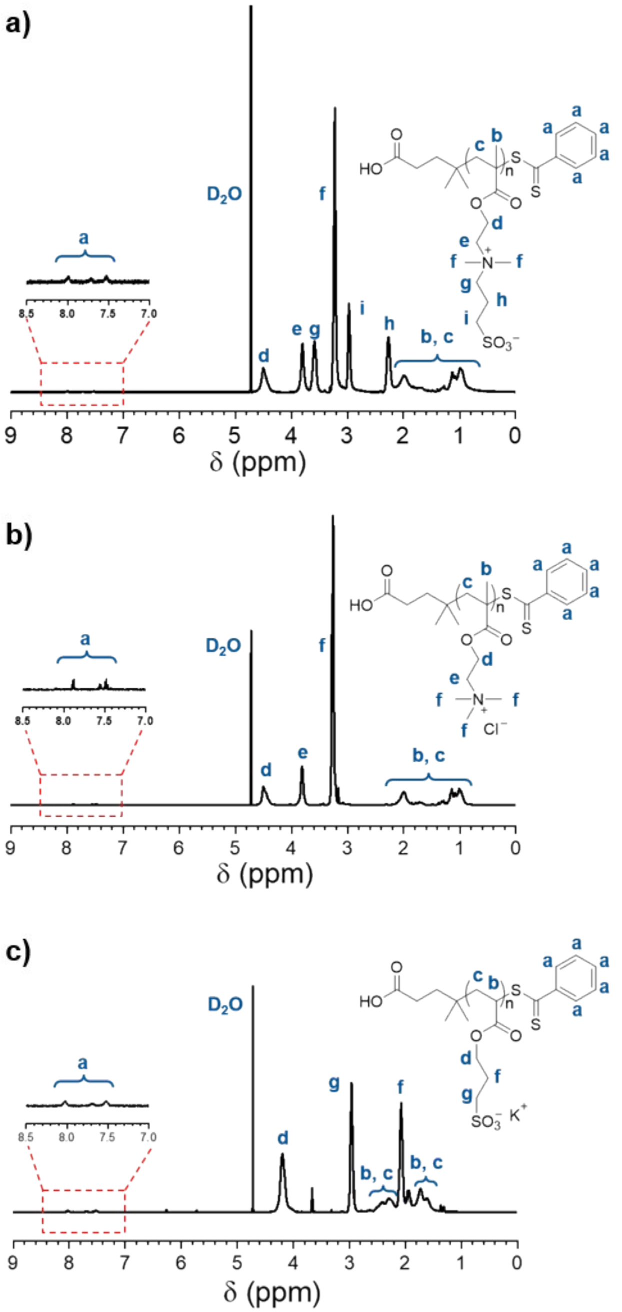

Fig. S3 ^{1}H NMR spectra of a) PMAPS, b) PMTAC and c) PSPAK.

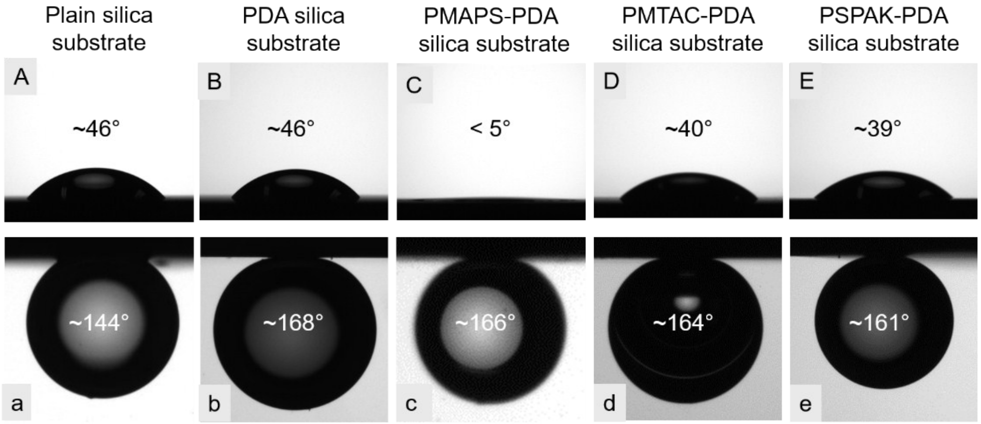

Fig. S4 Water contact angles in air (WCA-A) (A-E) and oil contact angles in water (OCA-W) (a-e) of different silica substrates.

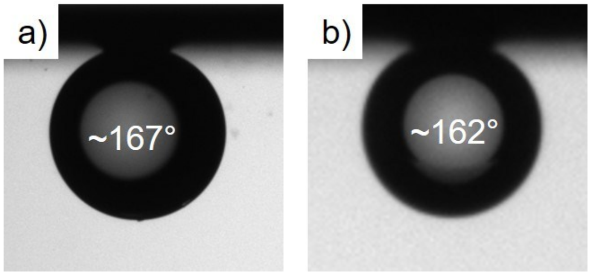

Fig. S5 OCA-W of zwitterionic PMAPS-PDA coated silica substrates after soaked in model heavy oil without pre-hydration and washed by various saline water: a) 100 mM NaCl solution, and b) 100 mM NaCl and 10 mM $CaCl_2$ solution, respectively.

Table S1. Average molecular weight of polyelectrolytes determined by GPC.

Polyelectrolyte	M_n (kDa)	M_w/M_n
PMAPS	13.6	1.35
PMTAC	10.7	1.26
PSPAK	9.5	1.20

Reference:

1. C. Shi, B. Yan, L. Xie, L. Zhang, J. Wang, A. Takahara and H. Zeng, *Angew. Chem. Int. Ed.*, 2016, **55**, 15017-15021.