Dual water-healable zwitterionic polymer coatings for anti-biofouling surfaces

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Experimental section

Materials: 4,4′-Azobis(4-cyanovaleric acid), (methacryloyloxy)ethyl] dimethyl-(3-sulfopropyl)ammonium hydroxide, cyano-4-(phenylcarbonothioylthio)pentanoic acid, and 2-methoxyethanol were received from Sigma-Aldrich and used as received. Ethyl acrylate was obtained from Sigma-Aldrich and filtered through a basic alumina column to remove inhibitors before utilizing it for polymerization. Alexa Fluor® 488 conjugate Albumin from Bovine Serum were purchased from Thermo Fisher Scientific. Acetone (Sigma-Aldrich, semiconductor grade VLSI PURANAL Honeywell 17617) and deionized water (resistivity 18.3 MΩ cm^{-1}) were used as received. Silicon wafers, with a 0.2° miscut angle along the ⟨112⟩ plane, were (111)-oriented, n-type, phosphorus-doped and with a specific resistance of 1−10 Ω cm^{-1} and purchased from Siltronix (France). Stoichiometric silicon nitride (Si_3N_4) surfaces

(1×1 cm^2) prepared by LPCVD deposition, were received from Lionix. All other chemicals were purchased from Sigma-Aldrich and used as received.

***Preparation of macro-RAFT reagent**:* In a 100 mL two-neck round-bottom flask that was filled with argon and magnetic stirrer bar, 0.032 g 4,4′-Azobis(4-cyanovaleric acid), 0.119 g 4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid, 5 mL ethyl acrylate and 20 mL THF were added to the flask. The mixture was purged with argon for 30 min and then the flask was put into an oil bath (70 ^{o}C; 16 h), and then cooled down to room temperature. The reaction solution was subsequently connected to a vacuum line to evaporate all the solvent. The resulting polymer melt was dissolved in 50 mL 2-methoxyethanol. The obtained polyethyl acrylate (PEA) solution was directly used for the next step polymerization.

Preparation of PEA-b-PMEDSAH: In a 100 mL two-neck round-bottom flask that was filled with argon and magnetic stirrer bar, 3.6 mg 4,4′-azobis(4-cyanovaleric acid), 0.15, 0.3 or 0.5 g [2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide, 5 mL PEA solution, and another 15 mL 2-methoxyethanol were added to the flask. The mixture was purged with argon for 30 min and then the flask was put into an oil bath (70 ^{o}C; 16 h), and then cooled down to room temperature. The obtained solution was directly used for characterization or preparation of the coatings. The samples were marked as PEA-b-PMEDSAH P1, P2 and P3, respectively.

Surface modification: The silicon/silicon nitride surface was sonicated in acetone for 5 min and subsequently cleaned using an air plasma (Harrick Scientific Products, Inc. Pleasantville, NY) for 5 min, and then quickly transferred to a one–necked flask, which was charged with 1 mL 3-aminopropyl triethoxysilane and 60 mL anhydrous toluene. The reaction mixture was heated to 80 °C for 16 h. The sample was then removed from the flask and extensively rinsed with CH_2Cl_2, sonicated for 5 min in CH_2Cl_2 to remove physisorbed molecules, and blown dry with a stream of dry argon. The surfaces were directly used for preparing ZPN coatings.

Preparation of ZPN coatings: The ZPN coatings were obtained by spin-coating or drop-casting the polymer solution onto cleaned surfaces, which were subsequently dried at 75 ^{o}C for 20 min, and subsequently at 120 ^{o}C for another 2 h.

***Fouling experiment*：** Clean and well-characterized ZPN coatings were covered by a drop of a 0.1 mg/mL Alexa Fluor 488-labled BSA solution for 10 min, and then washed five times by 10 mM PBS solution, and finally blown dry by argon. The well-cleaned surfaces examined by a confocal laser scanning microscope (Zeiss LSM 510 Meta; laser excitation wavelength: 488 nm). To allow a proper comparison of fluorescence images, the same settings were used in all measurements.

Static contact angle measurements: The static contact water angle (SWCA) measurements were conducted using a Krüss DSA 100 contact angle goniometer having an automated drop dispenser and image/video capture system. The SWCA were measured at three different places on a modified surface by dispensing three small droplets (3.0 μL volume of deionized water) with the help of an automated drop dispenser. The tangent 1 fitting model was implemented for SWCA measurements with an accuracy of ± 2°.

X-ray photoelectron spectroscopy (XPS): The X-ray photoelectron spectra at ambient temperature were obtained using a JPS-9200 photoelectron spectrometer (JEOL, Japan). A monochromatic Al Kα X-ray source (h_v = 1486.7 eV, 12 kV and 20 mA) with an analyzer pass energy of 10 eV was used. A base pressure of 3×10^{-7} Torr was maintained in the XPS chamber during measurements and the spectra were collected at room temperature. The X-ray incidence angle and the electron acceptance angle were both 10° to the surface normal. The intensity of the XPS core-level electron was measured as the peak area after standard background subtraction with a linear baseline correction. The takeoff angle φ (angle between sample and detector) of 80° is defined to a precision of 1°. The typical sample size was 1×1 cm^2. All XPS spectra were evaluated using the Casa XPS software (version 2.3.15).

Dynamic light scattering: The particles size is measured by using an ALV goniometer and correlator equipped with a 632.8 nm 22 mW Uniphase 1145P HeNe laser using avalanche photodetector (Exelitas Technologies). Measurements are performed at a fixed scattering angle of 150°. The measured decorrelation functions are fitted using the standard cumulant methods.

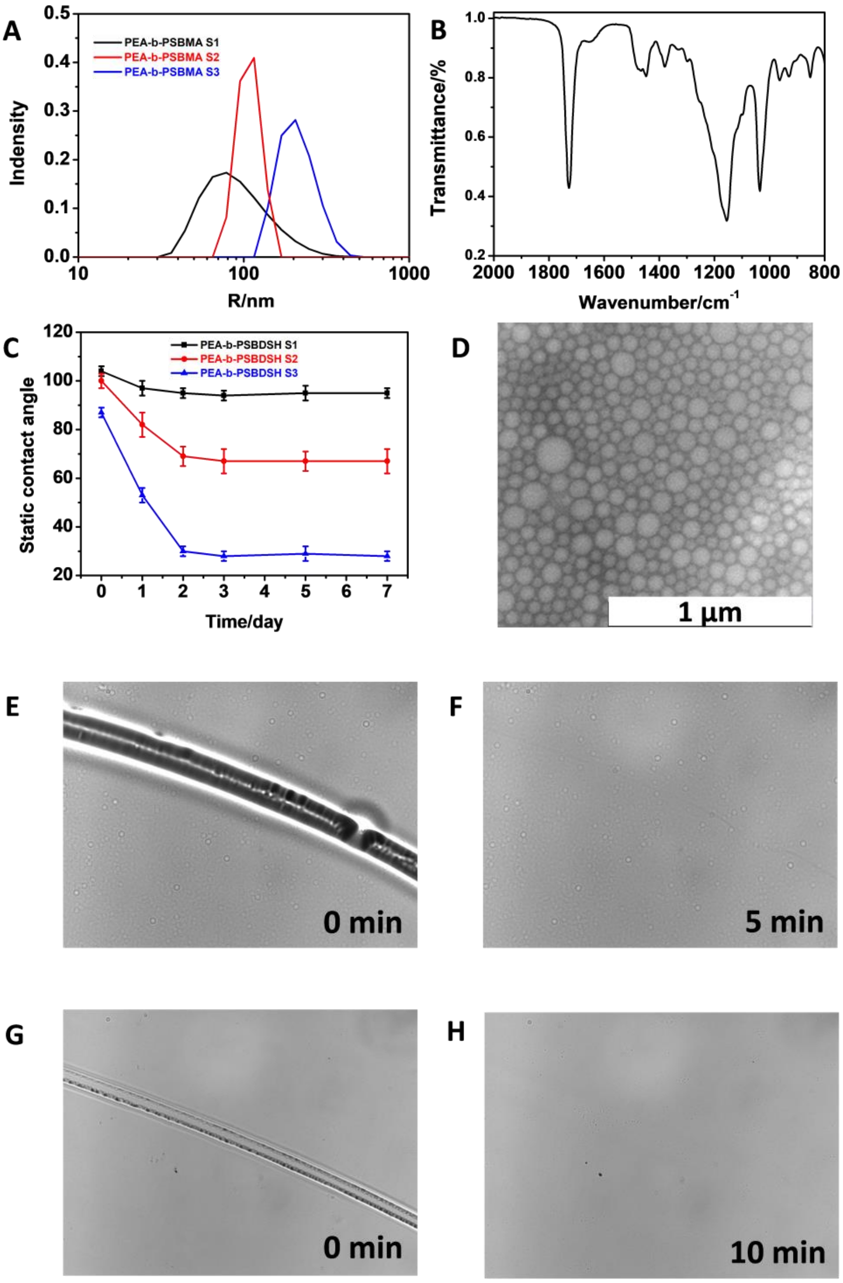

Figure S1. (A): The particle size distribution of PEA-b-PMEDSAH P1, P2 and P3 determined by DLS in NaCl solution; (B): The FTIR spectra of the PEA-b-PMEDSAH P3 ZPN coatings. (C): Contact angle change of the coatings formed by PEA-b-PSBDSH P1, P2, and P3 in 3 wt% NaCl solution for one week; (D): TEM images of PEA-b-PMEDSAH P3; (E-F): Optical images of a damaged ZPN coating formed from PEA-b-PMEDSAH P1 after immersion into 3 wt% NaCl for various durations; (G-H): Optical images of a damaged ZPN coating formed from PEA-b-PMEDSAH P2 by after immersion into 3 wt% NaCl for various durations.

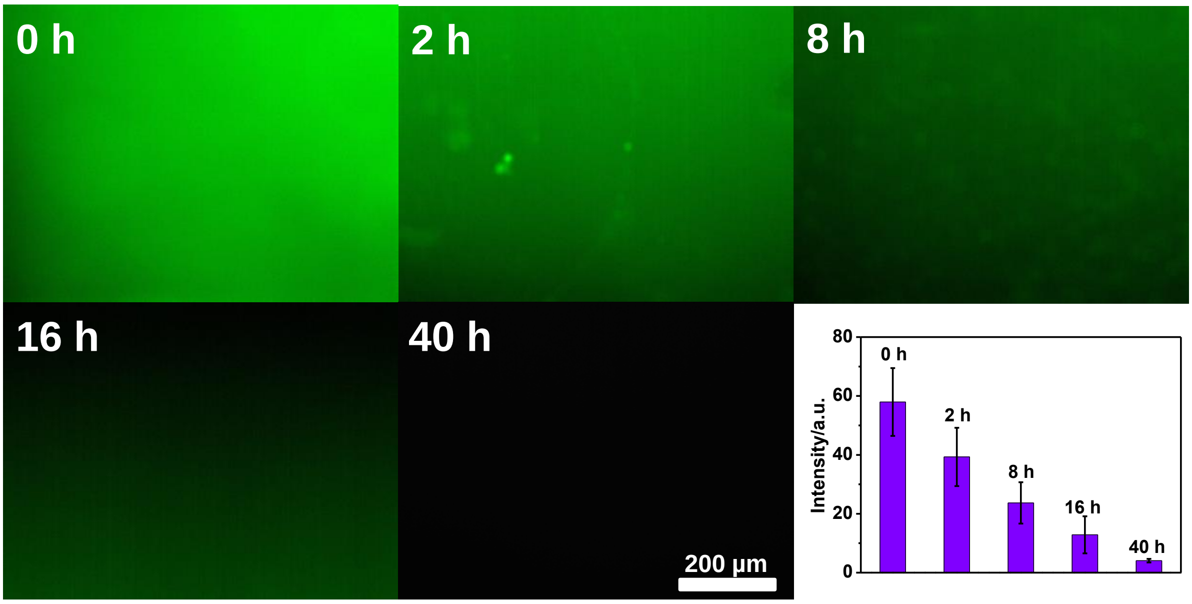

Figure S2. Effect of immersion times on antifouling properties. Fluorescence images and intensity of the ZPN coatings after immersing into 3.0 wt% NaCl for various times (from 0 to 40 h), followed by interaction with a Alexa Fluor 488-labled BSA solution for 10 min, rinsing clean, and subsequent examination by confocal fluorescence microscopy.