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Grafting zwitterionic polymer brushes via electrochemical surface initiated atomic transfer radical polymerization (e-SIATRP) for antifouling applications

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In the present work, the zwitterionic polymer brushes-sulfobetaine vinylimidazole were successfully grafted to silicon substrates via electrochemical surface initiated atomic transfer radical polymerization (e-SIATRP), which have exhibited excellent antifouling activities due to its two bactericidal functional groups- imidazolium and sulfonate. Various characterization techniques including Atomic Force Microscope, X-ray photoelectron spectroscopy and Quartz crystal microbalance were used to characterize polymer brushes modified silicon substrates. Subsequently, the anti-bacterial and anti-biofouling activities of zwitterionic polymer brushes - sulfobetaine vinylimidazole (pSBVI) based substrates have been evaluated. The experiment results show that the pSBVI can obviously resist adhesion of *Nannochloropsis maritima* and have a good anti-bacterial performance against *E. coli*. Moreover, comparing with polyvinylimidazole brushes (pVI) modified substrates and bare substrate, the pSBVI based materials have also exhibited excellent anti-adsorption performance against both bovine serum albumin (BSA) and Lysozyme.

Introduction

Marine biological can be defined as the undesirable settlement and metamorphosis of microorganisms and macroorganisms on artificial surfaces in sea water.[1-3] It is estimated that there are in excess of 4000 known marine fouling species including alga, polyps, barnacles and bivalves, all of which have the potentials to colonise submerged surfaces.[4,5] Biofouling is the attachment of organisms, bacteria, plants and animals onto materials surfaces (e.g., ship hull and pipelines) in contact with sea water for a period of time, which causes many serious problems, such as impairing the operational efficiency of a ship, excessive fuel consumption and corrosion, increased frequency of dry-docking and the introduction of invasive species.[6]

Furthermore, biofouling is also of great concerns in applications ranging from biosensors to biomedical implants and devices, and from food packaging to industrial and marine equipment. Many methods have been developed to solve the problems. Basically, these methods involve two strategies, either preventing biofoulants from attaching or degrading them via functionalizing with active ingredients, such as copper sheathing, antifouling paints, or (sub)nanometric thin self-assembled monolayers (SAMs).[7,8] Currently, copper and n-tributyltin (TBT) included coatings are widely used to avoid biofouling settlement.[6] Although they can effectively prevent the settlement of marine organisms, the prevalence of TBT and other tin based anti-fouling coatings on marine vessels is indeed a serious environmental problem due to heavy metals rapid enrichment in marine organisms.[9] Ederth et al. tested three different galactoside-terminated alkanethiol Self-Assembled Monolayers for their ability to resist adsorption of bacteria, barnacle cypris larvae and algal zoospores, and found that the exposed functional groups on the surface indirectly affect marine biofouling.[10] Chiag et al. studied the biofouling resistance of ultrafiltration membranes controlled by surface self-assembled coating with PEGylated copolymers and they found that the block copolymer had a higher BSA resistance.[11] However, SAMs are prone to have some drawback and poor durability.

Recently, polymer brushes have attracted considerable attention as an effective way to tailor the surface properties of materials owing to their higher mechanical, chemical robustness, and higher long-term stability.[12-14] Non-toxic functional polymer brushes have been used as non-releasing coatings to prevent the attachment of proteins, bacteria and marine organisms.[15] PEG and its derivatives have been widely designed for fabricating antifouling materials over the past decade due to the unique physical and biochemical properties, such as non-toxicity, non-immunogenesis, non-antigenicity and excellent biocompatibility, which exhibit good antifouling effects to a wide variety of proteins, suppress platelet adhesion, and reduce cell attachment and growth.[16-19] Although PEG-

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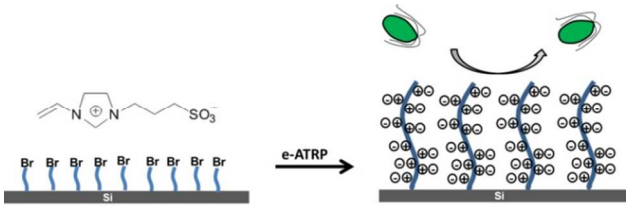
based materials have been common antifouling materials for many years, PEG has limitations especially for long term use due to the auto-oxidation in complex media. It is thus necessary to develop new antifouling polymers for a wide range of biological applications.

Among various types of anti-fouling polymer brushes, the zwitterionic polymers aroused many interests due to good chemical stability, low cost[20] and excellent antifouling properties, which are composed of a mixture of anionic and cationic terminal groups, and possess anti-adsorption of non-specific protein via a bound hydration layer from solvation of the charged terminal groups, in addition to hydrogen bonding.[21] Polymers incorporating zwitterionic molecules such as phosphorylcholine, sulfobetaine, and carboxybetaine, are promising as anti-biofouling surfaces. Zwitteration of dextran with carboxybetaine achieved via a one pot reaction highly resisted the settlement of bovine aortic endothelial cells (BAECs) and switched between cationic and zwitterionic states.[22] Poly(sulfobetaine methacrylate) brushes grafted onto the bifunctional tripeptide bromide-modified substrates through atom transfer radical polymerization (ATRP) exhibited long-term stability and excellent antifouling properties.[23-25] Liu et al. prepared the serine-based zwitterionic poly(serine methacrylate) (pSerMA)-grafted surfaces via a surface-initiated photoiniferter-mediated polymerization method which can be considered a good choice to the traditional ethylene glycol-based antifouling materials.[26] Therefore, it is reasonable to believe that the zwitterionic polymer-grafted surfaces can be highly resistant to protein adsorption when the surface density and chain length of the zwitterionic groups are well controlled.

Various surface modification methods were performed to obtain antifouling surfaces via chemical grafting, surface impregnation, or physical entrapment with antifouling polymer by comparison with the surface initiated polymerization (SIP) which is the most effectively grafting method and offer substrates with a higher mechanical and chemical robustness, even higher long-term stability. As a proof-of-concept, herein the zwitterionic polymer brushes - poly(sulfobetaine vinylimidazole) (pSBVI) [27] was grafted onto the silicon wafers via electrochemical surface initiated atomic transfer radical polymerization (e-SIATRP), as shown in Scheme 1. The e-SIATRP has been proved to be an attractive way to produce surface-grafted polymers with controlled thickness and architecture,[28] which is even better than the traditional ATRP because the reaction solution can be recycled. For comparison, polyvinylimidazole (pVI) brushes grafting Si-wafer was also prepared. The antibacterial and antifouling activities of the pVI and pSBVI functionalized surfaces were investigated. The zwitterionic polymer brushes pSBVI were found to be able to obviously resist the adhesion of *Nannochloropsis maritima*. Also, pSBVI had excellent anti-bacterial performance against *E. coli* and anti-adsorption ability of BSA and lysozyme protein, compared to PVI functionalized surfaces.



Scheme 1 Grafted zwitterionic polymer brushes with antifouling properties

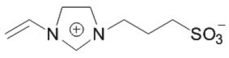
Experimental section

Materials

Vinylimidazole was distilled before use. Methanol (MeOH), Acetonitrile, Diethyl ether, $CuCl_2 \cdot 2H_2O$ were purchased from Chemical Reagent Company of Shanghai (Shanghai, China). 1,3-Propanesultone (99%) was purchased from the Chemical Reagent Co. of J&K Chemical Ltd (Beijing, China). 2,2'-Bipyridine was purchased from Sinopharm Chemical Reagent Co., Ltd. 3-(Trichlorosilyl)propyl-2-bromo-2-methylpropanoate was synthesized according to the publication.[29] Bovine Serum Albumin (BSA) was purchased from Aladdin. Lysozyme was purchased from Sigma Aldrich. Ultrapure water used in all experiments was obtained from a NANOpure Infinity system from Barnstead/Thermolyne Corporation. Nannochloropsis maritima were taken from Institute of Hydrobiology, Chinese Academy of Sciences. The Gram-negative bacterium Escherichia coli were obtained from Marine Culture Collection of China.

Synthesis of the SBVI Monomer

In a three-neck round-bottom flask, 14.8 g (120 mmol) of sultone was dissolved in 125 mL of acetonitrile. To this solution, 9.4 g (100 mmol) of vinylimidazole was added and allowed to react for 2 days under nitrogen. The precipitate (Fig. 1) was separated and washed with ether and dried in vacuum. The product was used in the next step without purification, the yield was over 80%. ^{1}H NMR (400MHz, D_2O), (ppm): 9.00 (s, 1H), 7.64 (s, 1H), 7.49 (s, 1H), 7.02 (t, 1H), 5.68 (d, 1H), 5.30 (d, 1H), 4.38 (t, 2H), 2.85 (t, 2H), 2.36 (m, 2H).



SBVI

Fig. 1 The chemical structure of SBVI

Preparation of Polymer Brushes via Electrochemical surface initiated atomic transfer radical polymerization (e-SIATRP)

The silicon wafers were activated in an oxygen plasma chamber (Diener Electronic, Germany) at < 200 mTorr and 100 W for 180 s, and then modified with a monolayer of 3-(trichlorosilyl) propyl-2-bromo-2-methylpropanoate which was applied via vapor deposition for 15 min. Polymer brushes were grafted by using previously reported methods.[28,30,31] The e-SIATRP was carried out in an electrochemical cell equipped with platinum gauze working electrode, platinum wire counter electrode and saturated calomel electrode (SCE) reference electrode. In a typical experiment, initiator-modified substrates were placed in parallel to working electrodes and keep 360 μm away from working electrodes. When a negative potential was applied to reduce Cu^{II} to Cu^{I} on the working electrode, polymerization was locally initiated from electrode. Cyclic voltammetry of Cu^{II}/bipy complex exhibits a reversible peak couple and peak reduction potential (Epc) of -0.16 V for pSBVI and -0.35 V for pVI. Voltammogram (CV) measurement was carried out at a scan rate of 0.01 Vs^{-1} in 20 mL solution of H_2O/MeOH (2:1, v/v) containing monomer [SBVI] or [VI] = 1.75 M, supporting electrolyte [BBAC] = 0.5 M; [SBVI] or [VI] : [bipy] : [$CuCl_2$] = 50 : 2 : 1, monomer solution could be reused.

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Characterization

^{1}H NMR spectra were recorded on a 400 MHz spectrometer (Bruker AM-400) using D_2O as solvent. HRMS spectra were obtained on a Bruker Daltonics micoTOF-QIImass spectrometer.

The chemical composition was measured by X-ray photoelectron spectroscopy (XPS), which was carried on a PHI-5702 multifunctional spectrometer using Al Ka radiation (29.35 eV). The binding energy of C1s at 284.8 eV was used as the reference.

The thickness of the polymer layer was determined by a spectroscopic ellipsometer (Gaertner model L116E) equipped with a He–Ne laser source (λ = 632.8 nm) at a fixed angle of incidence of 50°. The refractive index of polymer film was 1.5, and the Cauchy model was used to calculate film thickness.

Sessile drop water contact angle values were acquired by using a DSA-100 optical contact angle meter (Kruss Company, Ltd, Germany) at ambient temperature (22 °C). 5μL deionized water was dropped on the samples using an automatically dispense controller, and the contact angles were determined automatically by using the Targent 1 fitting algorithm.

The optical micrographs of microalgae sitting on the substrate were acquired using an Olympus BX51 microscope.

Atomic force microscopy (AFM) measurements were performed on an Agilent Technologies 5500 AFM using a MacMode Pico SPM magnetically driven dynamic force microscope. Images were taken using commercially available type II MAC levers with a nominal force constant of 2.8 N/m at a driving frequency of 75 kHz in ambient condition.

The protein adsorption assay was acquired by Quartz Crystal Microbalance with dissipation measurements (QCM-D) at 25 °C. Commercially available (QSX-301, QSense) gold-coated quartz chips were used. The electrode was fixed in a special apparatus so that only one side of the electrode was in contact with the solutions. The decrease of the resonance frequency, Δf, was measured for each deposition step in PBS. The mass of the adhering layer is calculated by using the Sauerbrey relation:

$$\Delta m = -C\frac{1}{n}\Delta f$$

where Δf is the measured resonance frequency decrease (Hz), n is the fundamental crystal frequency (5 Hz), C is 17.7 ng Hz^{-1} cm^{-2} for a 5 MHz quartz crystal, and Δm is the mass change (ng/cm^2).

The Gram-negative bacterium Escherichia coli were used in the test. Plate counts were used to test the antibacterial properties of the modified silicon wafers. The bare silicon wafers and silicon wafers modified with polymer brushes were immersed in a bacterial suspension (5 mL) of 10^6 cells per mL in a sterile test tube after sterilization. Subsequently, *E. coli* bacterial suspensions were incubated at 37 °C for 24 h. After incubation, 15 mL bacteria suspensions were taken into petri dishes and were mixed with agar culture medium. After incubation of the petri dishes overnight at 37 °C, colony counting was used to determine the antimicrobial effect of the silicon wafers.

Cells of *Nannochloropsis maritima* were cultured in Erdschreiber medium contained in 250 mL conical flasks until cells reached the logarithmic growth phase, at 20 °C.[32] Three replicates of the samples were placed in Quadriperm dishes and filled with 10 mL of *Nannochloropsis maritima* culture suspension with a cell density of approximately 10^6 cells mL^{-1}. The *Nannochloropsis maritima* were cultivated on laboratory benches for 3 h, 9 h, 15 h and 21 h. Samples were rinsed by dipping each treatment in a new beaker of artificial seawater three times to remove unattached *Nannochloropsis maritima*; all the samples were briefly exposed to air during this dip-rinse process. Cells counted were obtained from 30 random fields of view on each of 3 replicate samples.

Results and discussion

Polymer brushes present large exclusion volumes to inhibit protein and bacterial adhesion, or possess bactericidal functional groups, which is thus of great importance in antifouling fields. It is a more environment-friendly method to manage marine and aquatic biofouling to grafting of non-releasing polymer brushes on material surfaces.[9] In the present work, for the proof-of-concept purpose, the zwitterionic pSBVI brushes were grafted from silicon wafer via e-SIATRP to investigate the anti-fouling properties. For comparison, pVI brushes were also prepared and investigated.

XPS measurements were made to monitor the surface chemical composition change of each reaction step. Fig. 2A displays the XPS full survey spectra of bare silicon wafers, initiator-modified silicon wafers, pVI-modified silicon wafers and pSBVI-modified silicon wafers. As shown in Fig. 2B, after 3 h e-SIATRP of the monomer vinylimidazole, pVI grafted silicon wafers exhibited N 1s signal at 401.7 eV, which were not detected in bare silicon wafers, indicating the successful grafting of the pVI brushes. And we have also grafted pSBVI brushes on silicon wafers by the same method. In Fig. 2C and D, pSBVI grafted silicon wafers exhibited N1s signal at 401.1 eV and the strong S 2p signal at 167.0 eV. This provided obvious evidence that the silicon wafers were successfully modified with the polymer brushes via e-SIATRP.

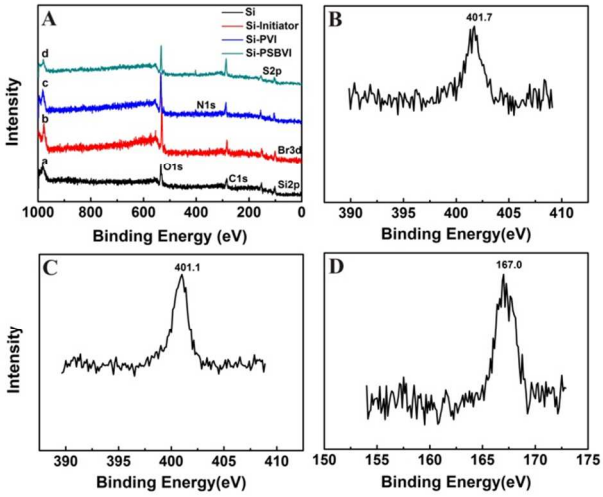

Fig. 2 (A) XPS survey spectra of bare silicon wafers, initiator-modified silicon wafers, pVI-modified silicon wafers and pSBVI-modified silicon wafers. N 1s XPS spectra of pVI-modified silicon wafers (B) and pSBVI-modified silicon wafers (C). (D) S 2p XPS spectra of pSBVI-modified silicon wafers.

The topography of surfaces modified by different substances was examined through tapping AFM. The AFM topographic images in Fig. 3 reveal the morphology of the surfaces modified by initiator, pVI brushes and pSBVI brushes. Compared with the initiator-modified silicon wafers, bare silicon wafers are very smooth in Fig. 3A, and. After polymer modification (Fig. 3C and D), the rms roughness of Si-pVI and Si-pSBVI incresaed to 0.256 nm and 0.367 nm, and the entire

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surface was uniformly covered by a polymer brushes. The thickness of polymer layer (pSBVI) was about 16 nm via this e-SIATRP method, and the thickness of pVI was about 14 nm with ellipsometry measurements.

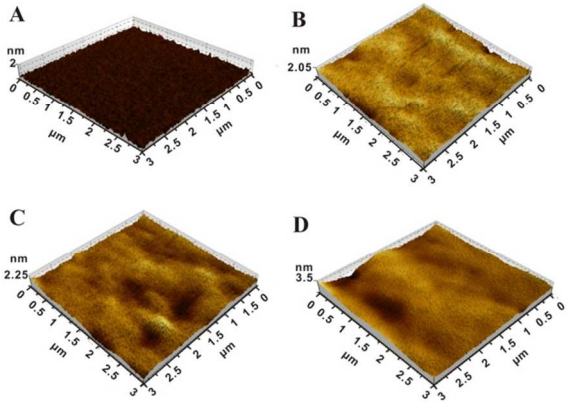

Fig. 3 3 μm × 3 μm AFM 3D images of bare Si before (A) and after modification with (B) initiator, (C) pVI and (D) pSBVI.

After successful functionalization of the silicon wafers, the static water contact angles of different surfaces were measured. In Fig. 4 the static water contact angle of pSBVI-modified silicon wafers was 27°, which is less than that of bare Si (82°) and pVI (70°). The zwitterionic polymer brushes pSBVI exhibited good water affinity with the introduction of sulfonic acid groups.

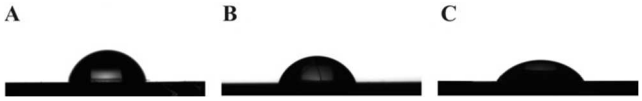

Fig. 4 Digital photographs of water droplets on different surfaces. (A) bare Si, (B) pVI-modified silicon wafers and (C) pSBVI-modified silicon wafers.

Protein adsorption and fouling are closely related to surface wettability and charge.[9] The protein resistance of different surfaces was tested by exposure to bovine serum albumin (BSA) and Lysozyme in PBS buffer (2 mg/mL and pH 7.4). The changes of frequency (Δf) is related to the mass of adsorbed film on quartz chip for rigid and thin film. We have investigated the adsorption amounts of bovine serum albumin (BSA, negatively charged at pH 7.4) and Lysozyme (positively charged at pH 7.4) adsorbed onto quartz chips. All chips were washed with PBS buffer, sequentially injecting 2mg/mL BSA solution (or 2mg/mL Lysozyme solution) and then washing with PBS buffer when the protein adsorption reach the upmost saturation, the change in frequency (Δf) was attributed to the adsorption of protein. Fig. 5A and C shows the changes in frequency and adsorbing capacity of bare quartz chip, pVI brushes and pSBVI coated quartz chip. When the quartz chips were exposed to BSA, the mass of the adhering layer for Au, Au-pVI and Au-pSBVI, were 56.64 ng/cm^2, 113.28 ng/cm^2 and 3.54 ng/cm^2. When exposed to Lysozyme, the mass of the adhering layer for Au, Au-pVI and Au-pSBVI were 162.06 ng/cm^2, 237.18 ng/cm^2 and 7.08 ng/cm^2, respectively. The protein adsorption curves on different surfaces are shown in Fig. 5B and D, the eventual frequency decrease (Δf) indicates that protein adsorption capacity increased as the order of Au-pVI > Au> Au-pSBVI. PSBVI exhibited better performance of resistance to nonspecific adsorption for each model protein at room temperature, on the contrary, hydrophobic pVI showed high protein adsorption against to BSA and Lysozyme, It is due to electrostatic interactions and hydration. Vinylimidazole that has a lot of positively charged imidazole group[33] at pH = 7.4 has strong ability of absorbing BSA which was negatively charged in artificial sea water. Since the hydrophobic of vinyl imidazole, pVI brushes also have a strong adsorption for hydrophobic segments of Lysozyme. PSBVI brushes display a very hydrophilic surface with a water contact angle of about 27°, therefore, pSBVI brushes form a hydration surface due to the introduction of sulfonic acid group,[34] which will enhance the capability of resisting protein adsorption.

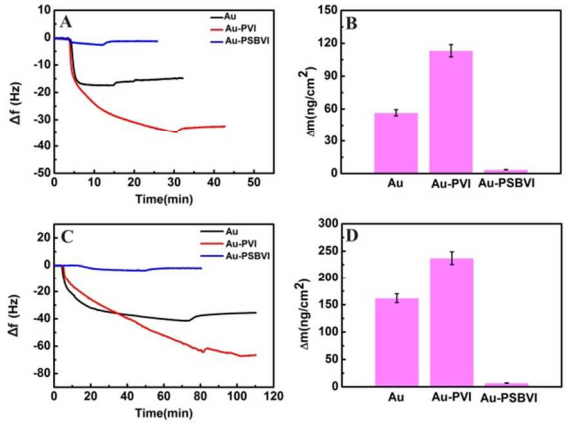

Fig. 5 The adsorption curves of bare QCM chips, QCM chips modified with pVI and pSBVI brushes in the presence of BSA (A) and lysozyme (C) solutions. The adsorption masses of bare QCM chips, QCM chips modified with pVI and pSBVI brushes in the presence of BSA (B) and Lysozyme (D) solutions.

In the present work, settlement of *Nannochloropsis maritima* was used to evaluate the antifouling capability of the functionalized surfaces. Fig. 6 shows the settlement data of the microalgae in static artificial sea water. After 3 h, 9 h, 15 h and 21 h exposed to the medium, the cell intensity of the *Nannochloropsis maritime* settled on bare silicon wafers were 331/mm^2, 345/mm^2, 579/mm^2 and 648/mm^2. The cell intensity of the *Nannochloropsis maritime* settled on pVI-modified silicon wafers were 172/mm^2, 433/mm^2, 233/mm^2 and 58/mm^2. And the cell intensity of the *Nannochloropsis maritime* settled on pSBVI-modified silicon wafers were 102/mm^2, 129/mm^2, 85/mm^2 and 25/mm^2. In Fig. 6D, after 15h exposed to artificial seawater, the cell intensity of the *Nannochloropsis maritima* settled on pVI-modified silicon wafers was significantly less than that of bare silicon. So imidazolium groups are of antifouling properties. It is obvious that zwitterionic polymer brushes with sulfonate groups can inhibit the settlement of *Nannochloropsis maritime* more efficiently compared with bare silicon wafers and pVI. It is in conformity to the result of protein adsorption. The zwitterionic polymer brushes (pSBVI) composed of a mixture of anionic and cationic terminal groups, the surfaces with terminal sulfate groups were most effective in reducing bacterial attachment.[19,34] Sulfate groups have a tendency to strongly bind water molecules to form a bound hydration layer from solvation of the charged terminal groups to prevent alga adsorption.

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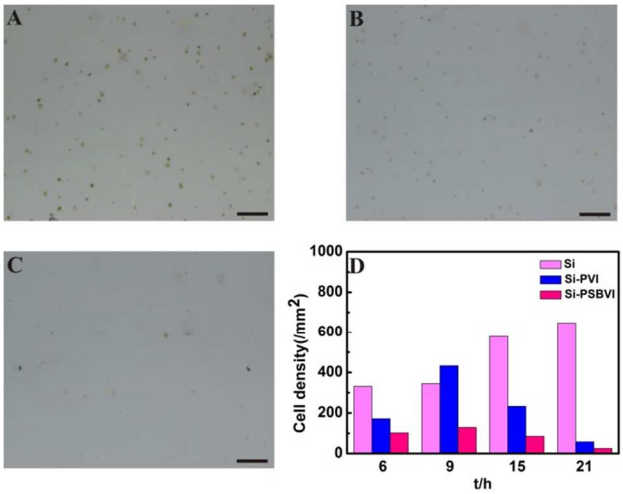

Fig. 6 Image of *Nannochloropsis maritima* settled on (A) bare Si, (B) Si-pVI and (C) Si-pSBVI after in the *Nannochloropsis maritima* culture suspension for 21 h (scale bars = 50μm). (D) The microalgae settlement data on bare Si surface, pVI and pSBVI brushes coating Si surfaces in different time.

To further evaluate the antibacterial efficacy of the polymer brushes coatings, the functionalized substrata were incubation at 37 °C for 24 h. Fig. 7 show that PSBVI brushes exhibited excellent antibacterial properties against *E. coli* (Fig. 7), and pVI brushes possess certain antibacterial activity which is less than pSBVI brushes. So the difference in bacterial adsorption on surfaces was due to the imidazole ring and sulfonic acid group. The zwitterionic polymers with good anti-bacteria effect derive from the high water content around the zwitterionic groups which possess stronger electrostatically induced hydration.[35] This work demonstrates that the pSBVI brushes not only suppress alga adsorption, but also resist protein and bacteria adhesion.

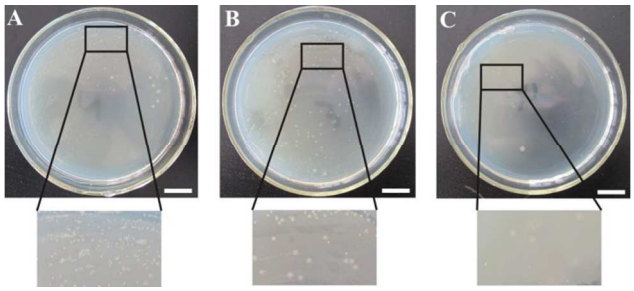

Fig. 7 Inhibitory effects against *E. coli* after 24 h of incubation without light irradiation condition. (A) bare Si, (B) Si-pVI and (C) Si-pSBVI (scale bars = 1 cm).

Conclusions

In this work, we demonstrated a facile and effective e-SIATRP approach to the zwitterionic polymer brushes (pSBVI) grafting surfaces. The resultant zwitterionic polymer functionalized substrates exhibited lower protein adsorption properties in PBS buffer and better anti-bacterial properties against *E. coli*, compared to pVI-modified surface. The excellent anti-fouling properties are attributed to the two bactericidal functional groups of zwitterionic polymer brushes. Moreover, the results showed that zwitterionic pSBVI is an effective and eco-friendly alternative for antifouling technologies.

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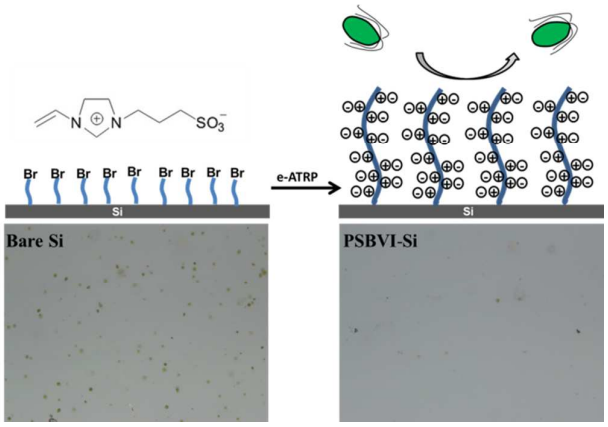

Grafting zwitterionic polymer brushes via electrochemically mediated-surface initiated atom transfer radical polymerization for antibacterial and antifouling applications.

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