Supporting Information

Fouling Mitigation from Graphene Oxide, Reduced Graphene oxide

and Molybdenum Disulfide Polypyrrole Functionalized Surfaces

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Supporting Information:

1. Introduction

In this section, details on graphene oxide (GO) synthesis, characterization results of the nanomaterials and DLVO theory are provided. Raw data from EQCM-D are presented in the supporting information for better understanding of deposition and release studies. Moreover, interaction energy profile between BSA and GO/rGO/MoS₂ calculated from DLVO theory and mechanistic figure of BSA interactions with the GO and MoS₂ are provided in the supporting information.

2. Synthesis of GO and rGO-2hr

As discussed, a modified Hummer's was used to prepare GO. 2.9 115 ml concentrated sulfuric acid was placed in 2L beaker and cooled to 0°C using an ice water bath. 5 g of natural graphite flakes (3061 grade material from Asbury Graphite Mills) were added to acid followed by slow addition of 15g KMnO₄ with continuous stirring and cooling so that temperature did not exceed 20°C. Heating the mixture to 35°C, 230 mL of deionized (DI) water was added and the reaction was ended after the addition of 700 mL of DI water. Finally, 12.5 mL of 30% H₂O₂ solution was slowly added to the mixture. The mixture was treated subsequently by vacuum filtration and 1:10 HCL solution to remove as much as liquid and metal contaminants, respectively. After resuspension of the filtrate in 500 mL DI water, it was centrifuged for 12 h at 7500 rpm to sediment the GO, and the supernatant was decanted. After repeating the DI wash 6 times, the final solution resulted in a mixture with a pH of around 6. The mixture was further sonicated in stainless steel beakers via a Fisher Scientific Model 500 Sonic Dismembrator with a 1/2" tip for 1 hour at 50% amplitude (~55 W) while cooled in an ice water bath. Finally, any unoxidized graphite was removed by centrifugation at 5000 rpm for 10 min. The reduction of GO was performed by heating a purified GO suspension in N-methyl-2-pyrrolidone (NMP) to 150 °C

with constant stirring in a silicone oil bath, as described in previous study.³ The heat reflux was performed for 2 hr. After solvothermal reduction, the rGO was separated from the NMP using vacuum filtration with 0.1 μ m alumina filters (Millipore), rinsed heavily with DI water, and redispersed in DI water at an approximate concentration of 1 mg/mL.

3. Characterization of materials

3.1 Electrokinetic and Hydrodynamic Characterization

Hydrodynamic diameter (D_h) and zeta potential (ζ -potential) were measured using a Zeta Sizer Nano ZS (Malvern Instruments, Worcestershire, U.K.), described in previous articles.² ^{4, 5} ZetaSizer Nano ZS was equipped with a monochromatic coherent He-Ne laser with a fixed wavelength of 633 nm. ZetaSizer Nano ZS uses the Stokes–Einstein equation to calculate the intensity averaged (average size) hydrodynamic diameter (D_h). ⁶ Zeta potentials (ζ -potential) of the GO, MoS₂ and BSA were also measured using a ZetaSizer Nano ZS instrument, which employs phase analysis light scattering (PALS) to measure the electrophoretic mobility of charged particles. ⁷ ZetaSizer Nano ZS uses the Smoluchowski equation to calculate ζ -potential from electrophoretic mobility (EPM). ⁶

3.2 XPS analysis

Samples for XPS analysis were prepared using a procedure similar to previously published work.⁸ Approximately 5 mg of each materials were prepared by vacuum filtration of the material dispersions onto a PTFE membrane filter with a 0.1 µm pore size (Millipore). The film was allowed to settle for 15 minutes, rinsed with 30 mL DI water, and allowed to dry in air. XPS analysis was done using a Thermo Scientific ESCALAB 250Xi. XPS spectra were then corrected for background and fitted for peaks manually.



B)





Figure S1: XPS spectra of A) GO, B) rGO-2hr and C) MoS₂. Three convoluted peaks corresponding to C-C (~284.8 eV), C-O (~286.8 eV) and O-C=O (288.5 eV) in GO C1s spectra confirms presence of oxygen containing functional groups on GO structure. The peaks were also detected in rGO-2hr C1s spectra. However, decreased peak intensity of C-O suggests decrease in oxygenated functional groups in rGO structure. XPS spectra of MoS₂ did not show any indication of oxidation. The characteristic 3 peaks in the Mo3d scan corresponding to the Mo3d 3/2 (~232.5 eV), Mo3d 5/2 (~229 eV) and S2s (~226.5 eV) and the characteristic doublet peak in the S2p spectrum were found on XPS of MoS₂. (Fig. A & C are reproduced from Ref. 9 with permission from The Royal Society of Chemistry)

3.3 Contact angle measurement

25 μ L of GO, rGO and MoS₂ dispersions at a concentration of 0.02 mg mL⁻¹ was drop cast onto a clean SiO₂ wafer. A 5 μ L water droplet was placed onto the surface and the contact angle was measured within 30 seconds using a Krüss DSA100 Drop Size Analyzer. Error bars represent one standard deviation (n = 3).



Figure S2. Contact angle measurement of GO, rGO and MoS₂ on SiO₂ substrate.

3.4 Sheet resistance measurement

The sheet resistance of the GO, rGO and MoS_2 of used in the study was measured using a fourpoint method to investigate the electrical properties of the materials.¹⁰



Figure S3. Sheet resistance measurement of GO, rGO and MoS_2 indicating GO is highly resistive to current among the all three materials.

3.5 Deryagin, Landau, Verwey and Overbeek (DLVO) theory

From previous studies, it has been found that deposition and aggregation kinetics of natural organic matter (NOM) and other foulants on nanomaterials can be explained by colloidal theory including DLVO theory.^{11, 12} The DLVO theory explains the aggregation of aqueous dispersions quantitatively and describes the force between charged surfaces interacting in a liquid medium. It combines the effects of the van der Waals attraction and the electrostatic repulsion due to the so-called double layer of counter ions. When particles come too close to the surface, van der Waals attractions (V_A) become dominant and overcome the electrostatic repulsion (V_E) to come into true contact.¹² The attraction (van der Waals) energy between a sphere and a flat plate, at a separation distance of h, is:

$$VVDW in J = -\frac{Aa}{6h} \left[\frac{1}{1 + \frac{14h}{\lambda}} \right]$$
(5)

Where,

- A = Hamaker Constant, $5.8*10^{-21}$
- a = Colloid particle radius (m)
- λ = dielectric wavelength, 1*10⁻⁷ m

The interaction energy between sphere, with diameter d_1 , and a plate, and zeta potentials ζ_1 and ζ_2 , separated by a distance h, is given by the Deryagin method is as follows: ¹³

$$V_{EDL}in J = \pi a \varepsilon_o \varepsilon_r \left\{ 2\Psi_1 \Psi_2 ln \left(\frac{1 + e^{-\kappa h}}{1 - e^{-\kappa h}} \right) + \left(\Psi_1^2 + \Psi_2^2 \right) ln \left(1 - e^{-2\kappa h} \right) \right\}$$
(6)

Where,

 κ = debye length (m⁻¹)

- \mathcal{E}_{o} = permittivity of free space (C/Vm)
- \mathcal{E}_r = relative permittivity
- Ψ_1 = collector surface potential (V)
- Ψ_2 = colloid surface potential (V)

For calculation purposes, nanomaterials (collector) deposited on a gold surface were considered as a plate and BSA molecules (colloid) as spheres. The zeta potential of GO and MoS_2 were determined to be -41.33 mV and -40.34 mV, respectively. The hydrodynamic diameter of a BSA molecule was found to be 1567 nm.

Table S1. Conductivity of different salt solutions

olutionSalt solutions	Conductivity, μS/cm @ 23.5°C S/cm @ 23.5°C
1M NaCl	87700
500 mM NaCl	48500
100 mM NaCl	9650
10 mM NaCl	2110
SSW with 500 mM NaCl	52200



Figure S4: Electropolymerization of PPy onto the gold sensor by applying +0.8V. Dark brown color of the PPy (Right figure) after polymerization on top of the gold surface confirms the full coverage of the PPy.



Figure S5. Real time data of BSA deposition on PPy-MoS₂ surface in terms of frequency shift (Hz) on EQCM-D (Stage 2). Similarly, BSA also showed sharp frequency shift on GO- and rGO-PPy surfaces.



Figure S6. Actual mass of BSA deposited on PPy, GO-PPy, MoS₂-PPy and rGO-PPy surfaces. Sauerbrey equation was used to calculate the deposited BSA mass from the frequency shifts assuming BSA form a homogeneous rigid layer on the QCM-D crystals^{14, 15}:

$$\Delta m = -\frac{C\Delta f_n}{n}$$

where Δm is the deposited mass, Δf_n is the shift in overtone frequency, n is the overtone number (1, 3, 5, 7, ...), and C is the crystal constant (17.7 ng/Hz cm2 for the 5 MHz crystal).



Figure S7. Real time data of BSA deposition on PPy-MoS₂ surface in terms of frequency shift (Hz) on QCM-D under -0.5 $V_{Ag/AgCl}$. Like the PPy-GO surface, the frequency shift and rate of BSA deposition decreased when negative potential was applied (Stage 2). Also, BSA started to deposit more when the negative potential was withdrawn (Stage 3).



Figure S8. Real time data of BSA deposition on PPy-MoS₂ surface in terms of frequency shift (Hz) on QCM-D under +0.5 $V_{Ag/AgCl}$ (Stage 2).



Figure S9. Actual mass of BSA deposited on PPy, GO-PPy, MoS_2 -PPy and rGO-PPy surfaces under negative and positive voltage. Increased BSA deposition after withdrawal of $-0.5V_{Ag/AgCl}$ has been noticed.



Figure S10. Stage 1: MoS_2 deposition on PPy surface. Stage 2: BSA deposited on MoS_2 . Stage 3: Background NaCl solutions. Stage 4: 0.5 M NaCl was ran through the module without any voltage application. Stage 5: Release of BSA (increase in frequency shift) from PPy-MoS₂ surface by 0.5 M NaCl electrolysis under +0.74 V_{Ag/AgCl}.



Figure S11. Stage 1: MoS₂ deposition on PPy surface. Stage 2: BSA deposited on MoS₂. Stage 3: 0.1 M NaCl was ran through the module without any voltage application. Stage 4: No release of BSA (No change in frequency shift) from PPy-MoS₂ surface by 0.1 M NaCl electrolysis under +0.74 $V_{Ag/AgCl}$. Similarly, no release of BSA was detected from PPy-GO during 0.1 M NaCl electrolysis under the same voltage.



Figure S12. Stage 1: MoS_2 deposition on PPy surface. Stage 2: Background different NaCl solutions before passing BSA. Stage 3: BSA deposited on MoS_2 . Stage 4: SSW was ran through the module without any voltage application. Stage 5: Release of BSA (increase in frequency shift) from PPy-MoS₂ surface by SSW electrolysis under +0.74 V_{Ag/AgCl}.



Figure S13. Changes in the platinum counter electrode had been observed after seawater electrolysis (left: before electrolysis treatment, right: after treatment) in the three electrode system used in this study.



Figure S14. Higher electrical double layer interaction energy prevents the BSA from coming into true contact with GO, rGO and MoS_2 . Total interaction energy is higher in short range (<10 nm) in both cases, but it diminishes as the separation distance between BSA and materials slightly increases (>20 nm). In this range, other bonds form between BSA and materials to help foulant deposition on the surfaces.



Figure S15. Hydrogen bond, hydrophobic interactions, van der Waals, and π - π interactions between foulants and GO/MoS₂ surfaces help to overcome the high energy barrier and thus attachment of the foulants occurs at the material surfaces. At distances >15 nm, these interactions help the deposition of the foulants onto the material surfaces where the energy barrier falls significantly. rGO structure also interact with BSA like GO does. However, rGO has more hydrophobic interaction with BSA than GO.



Figure S16. Anodic current produced from the positive potential application on working electrode (PPy-MoS₂) for different salt concentrations. Generation of anodic current indicates the electrochemical reaction going on the working electrode when +0.74 $V_{Ag/AgCl}$ was applied.



Figure S17. Monitoring of the electrochemical stability of the PPy coated nanomaterials. A) Gold sensor before PPy polymerization and electrochemical study. B) Sensor after the electrochemical treatment by 1M NaCl for 30 min. It is clear that after the electrolysis treatment with 1M NaCl, some portion the PPy layer along with nanomaterials actually was released from the gold surface. C) PPy and nanomaterials were stable after the electrolysis treatment with 0.5M NaCl. D) No changes were observed in the coated layer after electrolysis treatment with SSW indicating stability of the nanomaterials and PPy layer.

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