WASHINGTON STATE UNIVERSITY

Application of External Voltage for the Release of Deposited Organic Foulant from PPy-Graphene Oxide and PPy-Molybdenum Disulfide Surfaces by NaCl Electrolysis

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Background

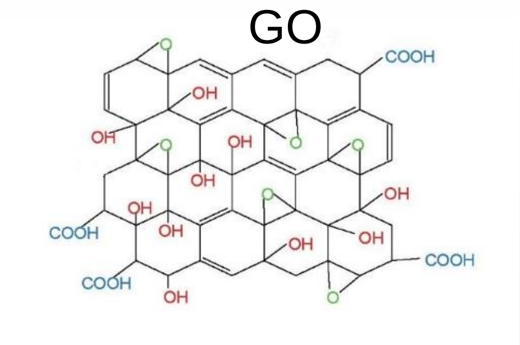
- ❑ Biofouling, organic fouling and scaling hinder efficient membrane application.

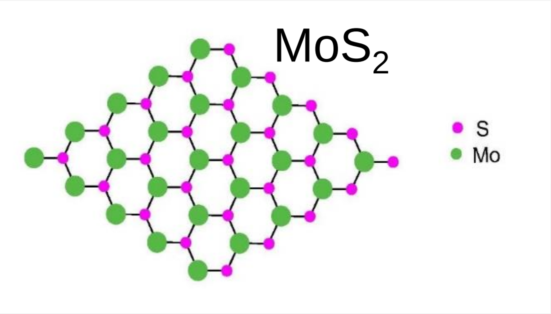
- ❑ Membrane fouling leads to
    - Low permeability
    - Low product water quality
    - Short membrane life
    - High maintenance cost
- ❑ Modification of polymeric membrane surfaces with nanomaterials

(Graham and Cady 2014)(Zodrow, Bar-Zeev et al. 2014)

Background

- Large lateral size and ultrathin thickness of 2D nanomaterials offer high specific surface area.
- GO and MoS_2 have also shown antibacterial property
- The presence of functional groups in GO induces hydrophilicity
- Transition metal dichalcogenides including MoS_2 and WS_2 have extremely low friction, low surface roughness.





(Chen, Peng et al. 2014)(Mejias Carpio, Santos et al. 2012)(Akhavan and Ghaderi 2010)(Le-Clech, Chen et al. 2006)

Background

- GO and MoS_2 have large negative zeta potential

- High energy barrier between foulants and GO/MoS_2 calculated using DLVO theory

Interaction Energy Profiles for BSA/SA in Na^+ and GO/MoS_2

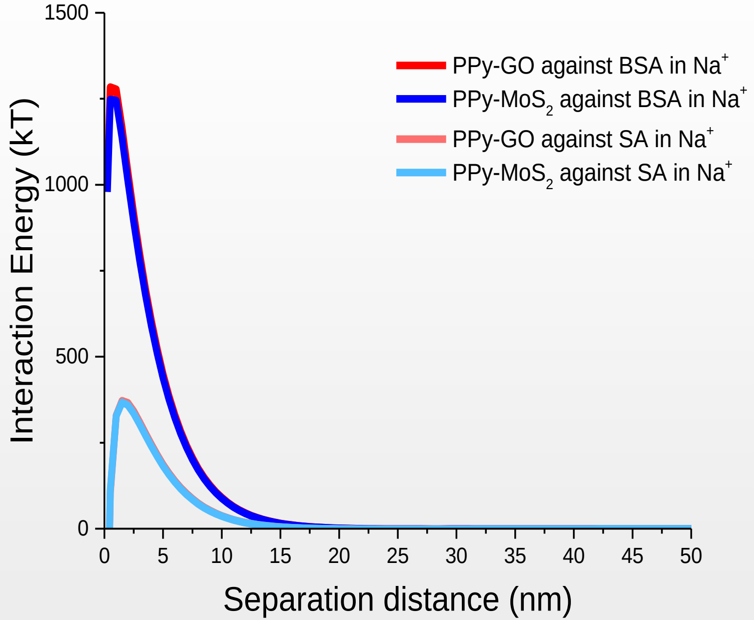


Fig: High energy barrier prevents the BSA/SA coming into true contact of GO and MoS_2

(Gregory 2005)(Hoek, Bhattacharjee et al. 2003)

Objective

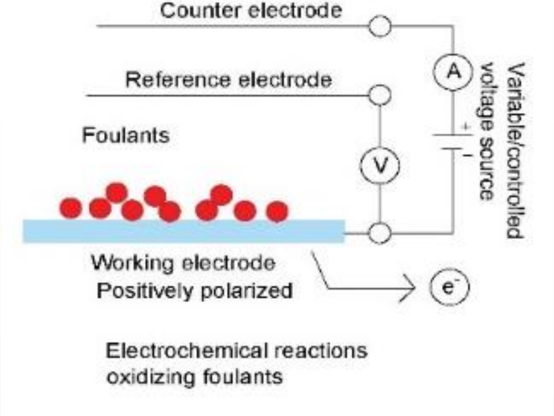
- Overall objective: To develop antifouling surfaces using two dimensional GO and MoS_2 nanomaterials for environmental applications

- Specific objective:
  Application of External Voltage for the Release of Deposited BSA from PPy- GO and PPy- MoS_2 Surfaces by NaCl Electrolysis

Hypothesis

- **Generation of biocides**

Formation of biocides (free Cl_2, $HOCl$, H_2O_2, $^{\cdot}OH$) and bubble formation during potential application



$Cl^- \rightarrow Cl_2 + 2e^-$ ($E° = +740\ mV_{Ag/AgCl}$)

$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$

$H_2O \rightarrow O_2 + 4e^- + 4H^+$ ($E° = +620\ mV_{Ag/AgCl}$)

$O_2 + 2H^+ + 2e^- = H_2O_2$ ($E° = +85\ mV_{Ag/AgCl}$)

$H_2O_2 + e^- = {}^{\cdot}OH + H_2O$ ($E° = +700\ mV_{Ag/AgCl}$)

(Gregory 2005)(Hoek, Bhattacharjee et al. 2003)(Bard and Faulkner 2000)(Vetter 1967)

Materials and Methods
(Nanomaterials preparation)

- Nanomaterials preparation

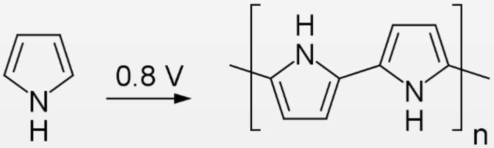
❑ Both the materials were prepared following the processes described in previous studies

GO: Modified Hummer's method ($KMnO_4$)

MoS_2: Mixture of bulk MoS_2 and butyllithium, utrasonication

- Polymer used

Electrochemical polymerization of Pyrrole :



Pyrrole to Polypyrrole (PPy)

- Foulant used

Bovine Serum Albumin (BSA) as protein foulant (M.W. 66 KDa, Sigma-Aldrich, St. Louis, MO)

(Chowdhury *et al.*, 2013; Lanphere *et al.*, 2015)

Materials and Methods
(Instrument used)

- Zeta Sizer Nano ZS (Malvern Instruments, Worcestershire, U.K.)

- Electrochemical Quartz crystal microbalance with dissipation monitoring (EQCM-D)
  - AC voltage pulsed across a quartz crystal causing it to oscillate in shear mode at its resonant frequency
  - A change in the mass of a film is directly proportional to a change in the resonant frequency of the crystal.

QCM-D

Potentiostat connected to QCM-D

Electro-chemistry module

Gold Sensor

Materials and Methods

Deposition kinetics study using QCM-D

Initial deposition and release rate:

$$r_f = \left| \left(\frac{d\Delta f_{(3)}}{dt} \right)_{t \to 0} \right|$$

Attachment efficiency:

$$\alpha_D = \frac{r_f}{(r_f)\text{bare polymer surface}} = \frac{\left| \left(\frac{d\Delta f_{(3)}}{dt} \right)_{t \to 0} \right|}{\left| \left(\frac{d\Delta f_{(3)}}{dt} \right)_{fav,\, t \to 0} \right|}$$

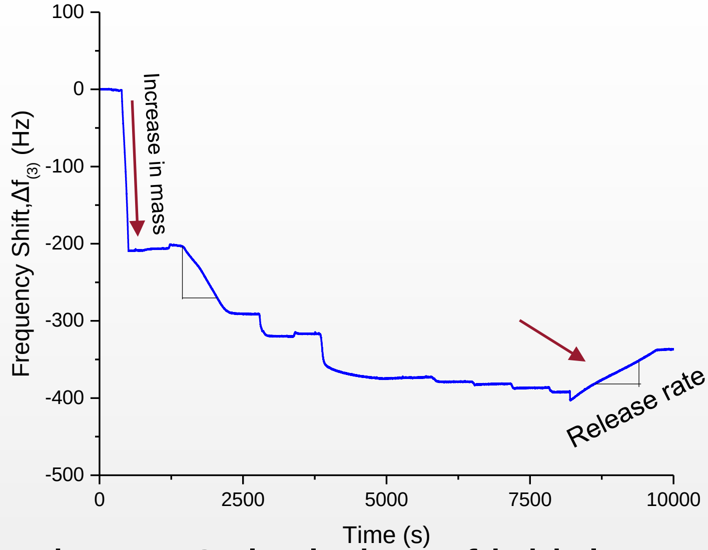


Figure: Calculation of initial deposition rate from frequency shift slope

Results and discussion
(Zeta Potential measurement)

Characterization of GO, MoS_2 and foulants:

Table: Zeta potential of materials and foulants under experimental condition

Sample name	pH	average zeta potential (mV)
GO in mili-Q water	4.51	-41.33±0.5
MoS_2 in mili-Q water	4.32	-40.34±0.76
BSA in 10 mM NaCl	6.5	-37.97±12.27

Interaction of BSA with bare PPy, PPy-GO and PPy-MoS_2

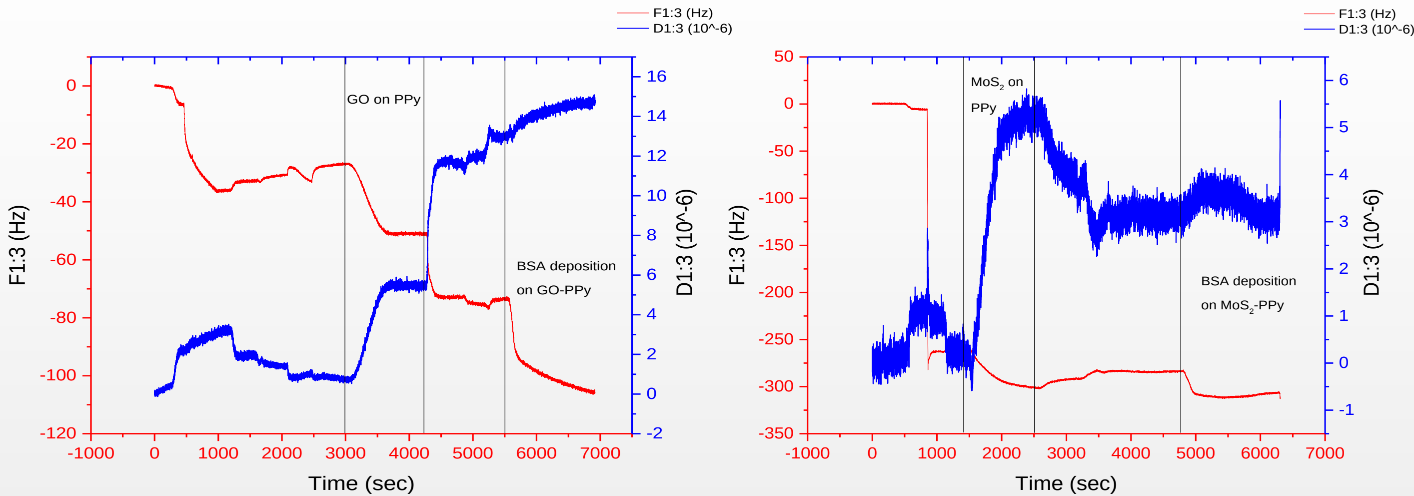
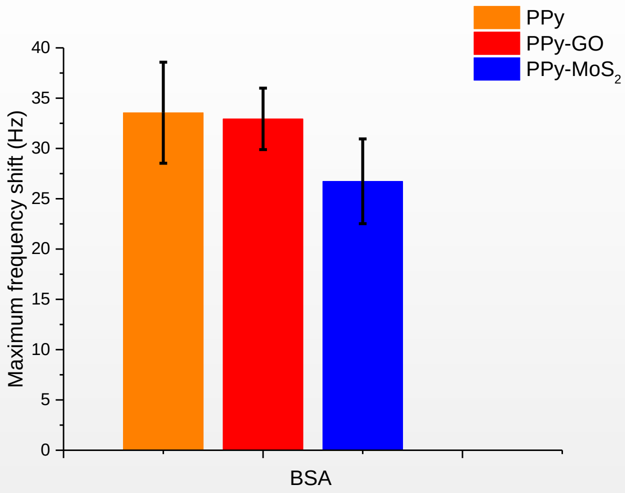


Figure: Real time data of the BSA & SA deposition on GO & MoS_2 surface on QCM-D.

Results and discussion
(Interaction of BSA with bare PPy, PPy-GO and PPy-MoS_2)



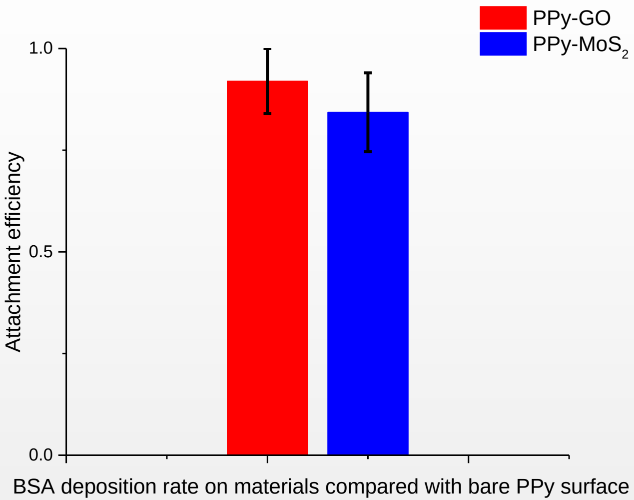


Figure: Maximum deposition (left) and attachment efficiency (right) of BSA on PPy, PPy-GO and PPy-MoS_2 surfaces without any potential.

Real time data of the BSA release from PPy-GO surface on QCM-D

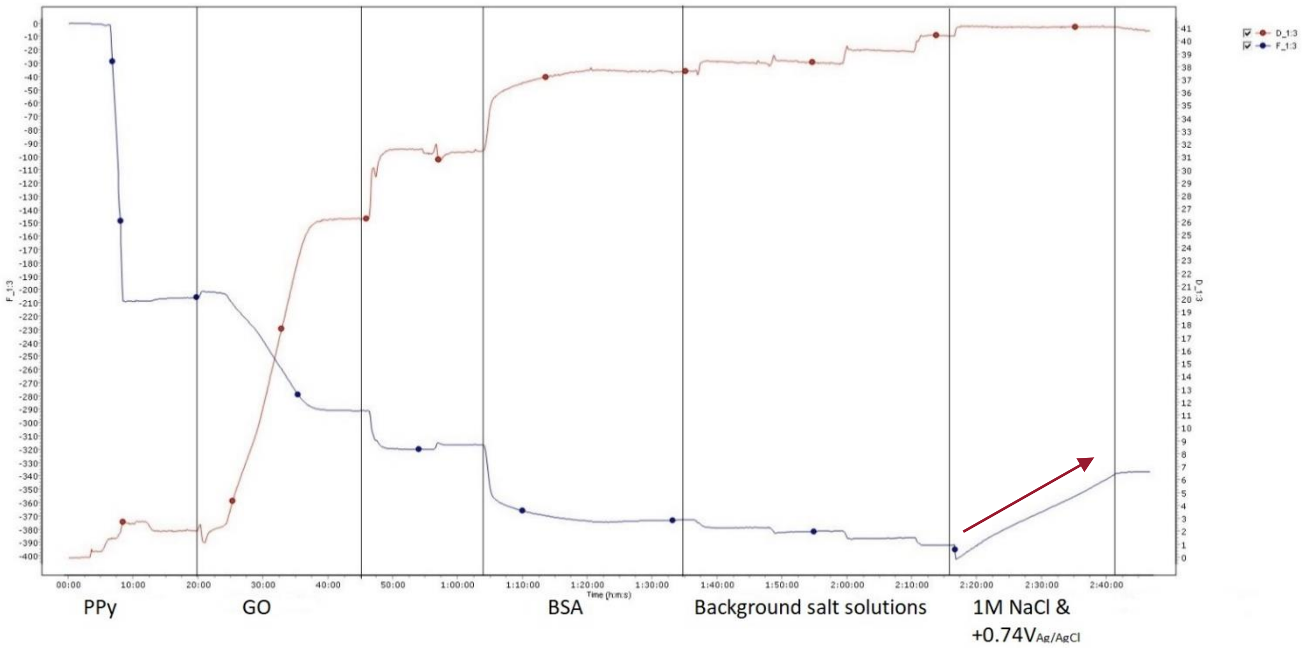


Figure: Removal of BSA from PPy-GO surface by 1M NaCl electrolysis under $+0.74V_{Ag/AgCl}$.

Real time data of the BSA release from PPy-GO surface on QCM-D

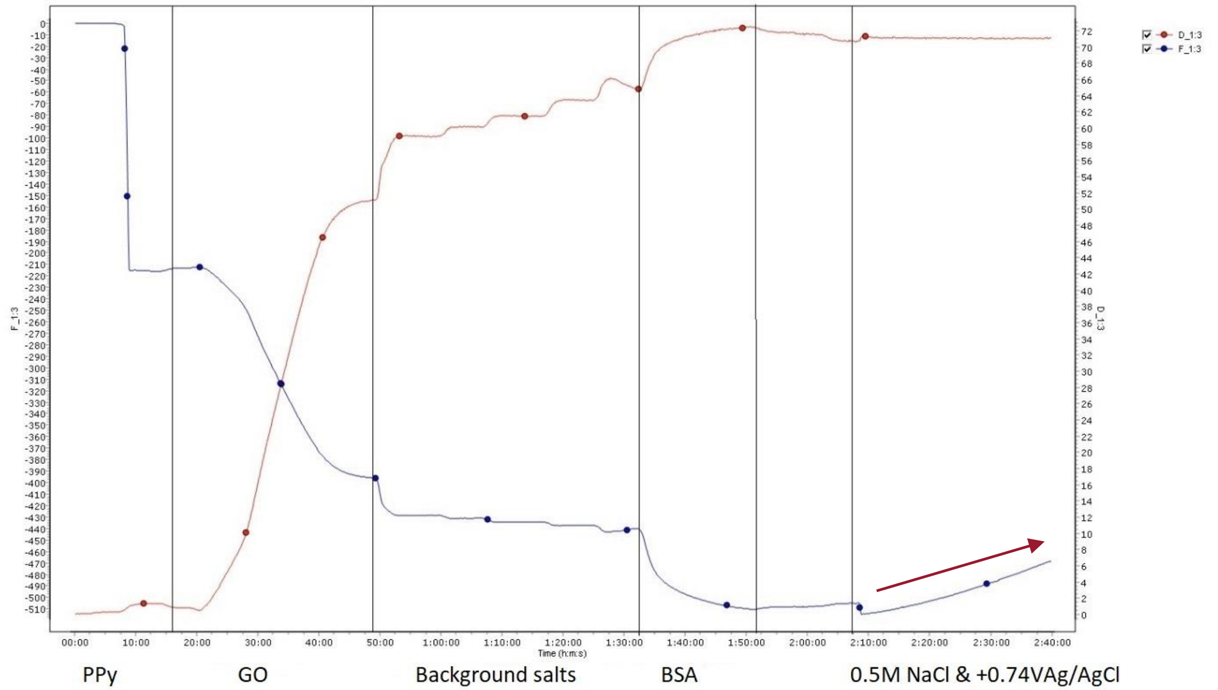


Figure: Removal of BSA from PPy-GO surface by 0.5M NaCl electrolysis under +0.74$V_{Ag/AgCl}$.

No release of BSA in presence of 0.1M NaCl from PPy-GO surface on QCM-D

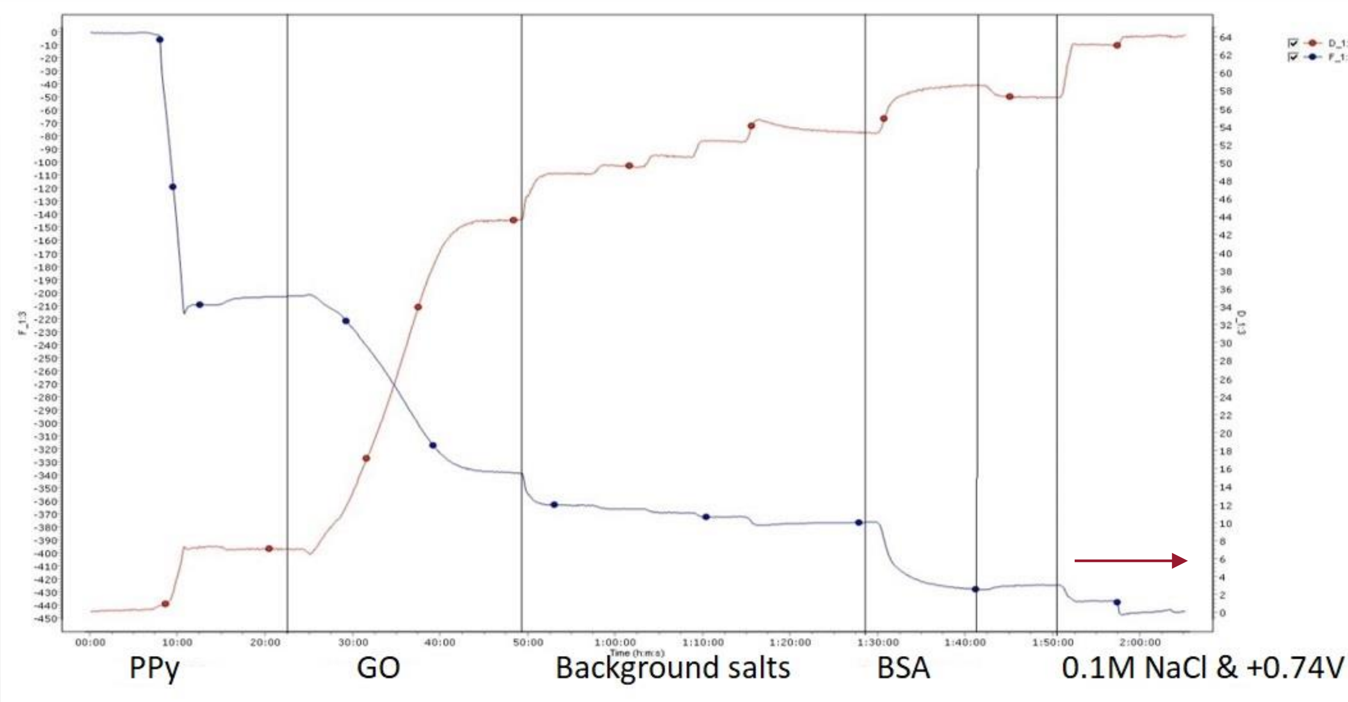


Figure: No release of BSA (No change in frequency shift) from PPy-GO surface by 0.1 M NaCl electrolysis under $+0.74V_{Ag/AgCl}$.

Release of BSA from PPy, PPy-GO & PPy-MoS_2 surfaces by NaCl and external voltage

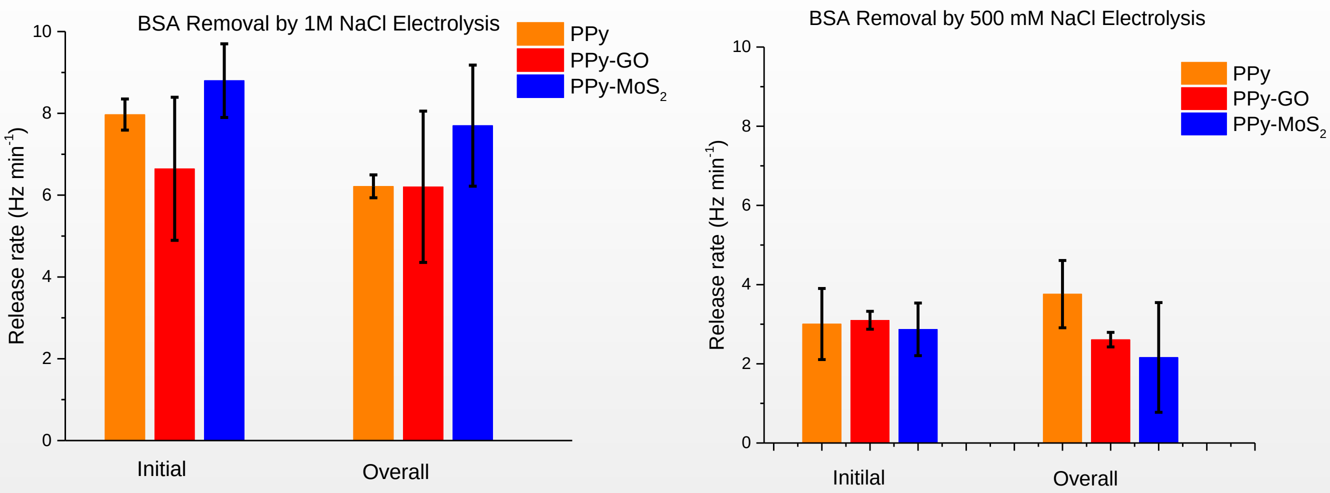


Figure: Release of BSA from PPy, PPy-GO and PPy-MoS_2 surfaces in presence of 1M NaCl (left) and 0.5M NaCl (right) under +0.74$V_{Ag/AgCl}$

Release of BSA from PPy, PPy-GO & PPy-MoS_2 surfaces by Synthetic Seawater (SSW)

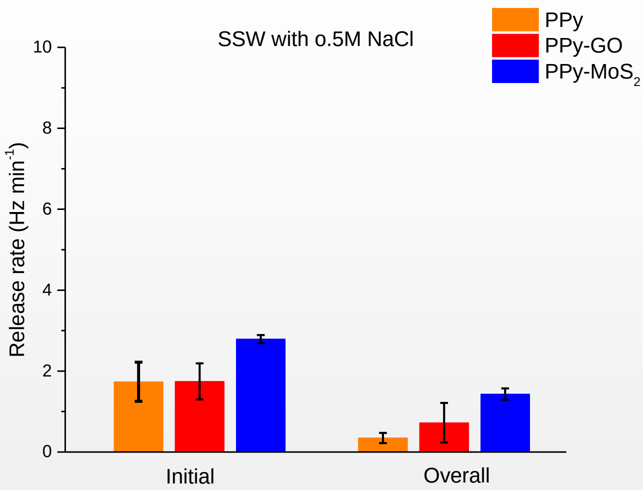


Figure: Release of BSA from PPy, PPy-GO and PPy-MoS_2 surfaces in presence of SSW under +0.74$V_{Ag/AgCl}$. To compare with previous release rate, the NaCl concentration was kept 0.5M.

Table: Synthetic seawater recipe

Salt	Concentration (g/L)
NaCl	29.22
$MgSO_4$	3.382
$MgCl_2$	2.504
$CaCl_2$	1.167
KCl	0.742
$NaHCO_3$	0.207
NaBr	0.085

Real time data of the BSA release from PPy-GO surface on QCM-D

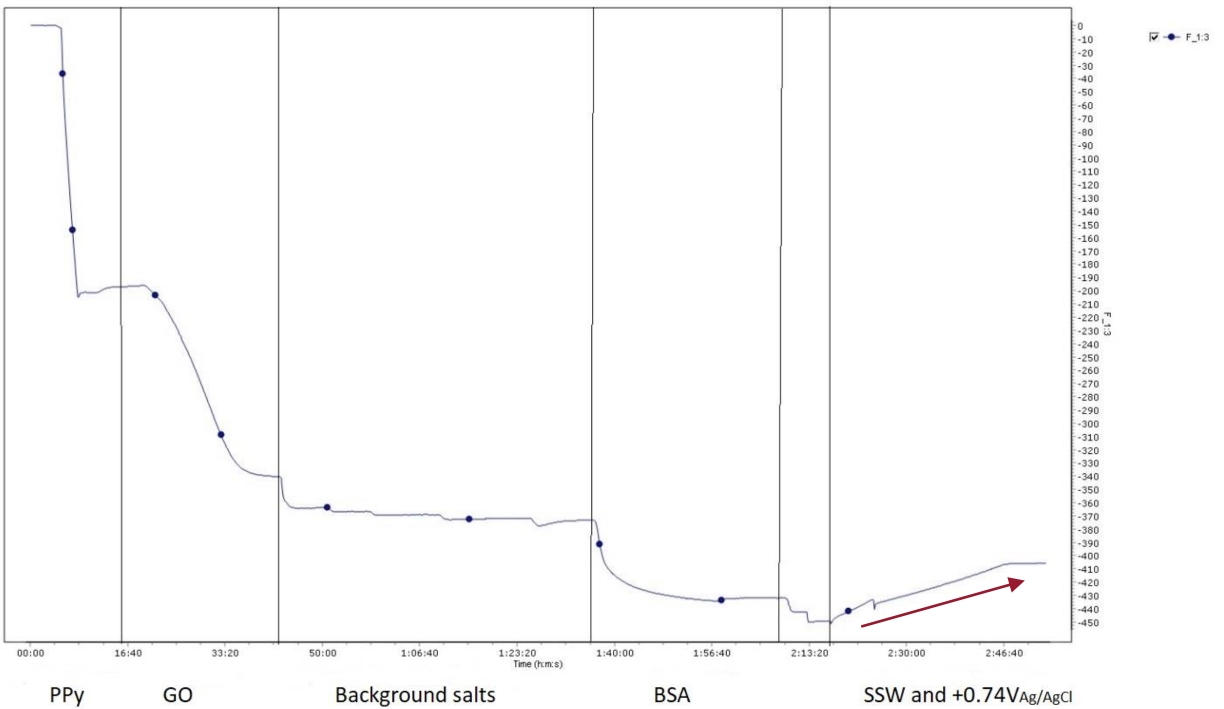


Figure: Removal of BSA from PPy-GO surface by SSW electrolysis under $+0.74V_{Ag/AgCl}$.

Generation of biocides by electrochemical reaction

- Generation of bubbles and biocides under +ve and –ve potential

$H_2O \rightarrow O_2 + 4e^- + 4H^+$ ($E° = +620\ mV_{Ag/AgCl}$)

$Cl^- \rightarrow Cl_2 + 2e^-$ ($E° = +740\ mV_{Ag/AgCl}$)

$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$

- Precipitation of solids during SSW electrolysis decrease the release performance:

$Mg^{2+} + 2\ OH^- \rightarrow Mg(OH)_2$ (s)

$Ca^{2+} + 2\ OH^- \rightarrow Ca(OH)_2$ (s)

$CO_3^{\ 2-} + Ca^{2+} \rightarrow CaCO_3$ (s)

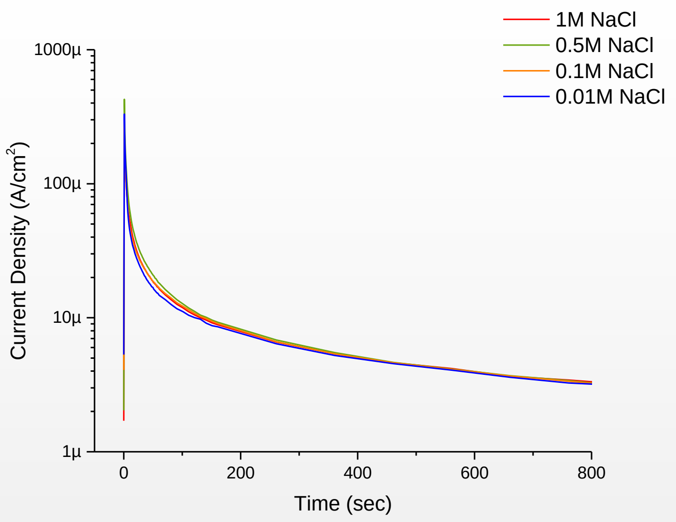


Figure: Generation of anodic current on material surfaces indicates the electrochemical reaction going on the working electrode when $+0.74V_{Ag/AgCl}$ was applied.

Conclusions and Recommendations

- Modification of polymer surface with GO and MoS_2 leads to less foulant attachment on the surface
- Electrochemical generation of free Cl_2, HOCl from seawater possible option for removing fouling layer
- External voltage to remove foulant layer during desalination
- The higher the NaCl concentration, the faster the foulants release
- Presence of different ions in seawater can decrease the release performance

Acknowledgements

Funding:
WSU New Faculty Award (Chowdhury)
National Science Foundation (Hersam)

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