Supplementary information

Polyethyleneimine for copper absorption: kinetics, selectivity and efficiency in artificial seawater

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S1. Experimental

Materials

All chemicals were purchased as analytical or reagent grade and used as received without further purification. Branched poly(ethyleneimine) (50 wt% in H_2O, Mn ~ 60,000 and MW ~ 750,000) was purchased from Sigma-Aldrich and stored under N_2. Glutaraldehyde (25 wt% in H_2O, Sigma-Aldrich) was used to prepare GA solution for cross-linking of PEI. $AlCl_3•6H_2O$, $Cd(NO_3)_2•4H_2O$, $CoCl_2•6H_2O$, $Cr(NO_3)_3•9H_2O$, $FeSO_4•7H_2O$, $MnSO_4•H_2O$, $Ni(NO_3)_2•6H_2O$, $MoNa_2O_4•2H_2O$, VCl_3, were all bought from Sigma-Aldrich. $Pb(NO_3)_2$ and $ZnCl_2$ were purchased from May & Baker Australia PTY LTD and Scharlau, Scharlab S.L respectively. $CuSO_4•5H_2O$, NaCl, KCl, Na_2SO_4, $MgCl_2•6H_2O$, NaOH pellet were all purchased from Chem-Supply (Pty Ltd, Australia) and $CaCl_2•2H_2O$ was purchased from Merck (Pty Limited, Australia). Ultrapure water with a resistivity of 18.2 MΩ cm was obtained using a Milli-Q® Advantage A10® water purification system.

Polyethyleneimine coating preparation

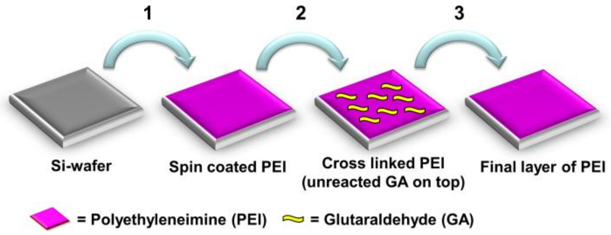

Fig. S1 Preparation of cross-linked PEI coatings.

The cross-linked PEI coatings were prepared in three steps (Fig. S1). First a thin layer of PEI was spin coated from a 0.05 % solution in ethanol on a ~ 1 cm^2 silicon wafer substrate (2000 rpm, 60 s). In the second step the sample was subsequently immersed in a 5 mL glutaraldehyde (GA) solution (0.5 % in H_20) for 30 minutes. After 30 minutes any unreacted GA was removed by dipping the sample in three solutions of 5 mL Milli-Q water. To avoid having any unreacted glutaraldehyde on the PEI surface the sample was immersed in a 5 mL 2 mg/mL solution of PEI in Milli-Q for 30 minutes. Then the sample was once again washed by dipping in three solutions of 5 mL Milli-Q water before finally being gently dried using N_2. The cross-linking method was adapted from Tong *et al.* [S1]

Solutions

Artificial seawater was prepared according to Fant et al.[S2] by mixing NaCl (24.615 g/L), KCl (0.783 g/L), Na_2SO_4 (4.105 g/L), $MgCl_2•6H_2O$ (11.06 g/L), $CaCl_2•2H_2O$ (1.558 g/L), and thereafter adjusting to pH 8 with NaOH solution (0.2 M). The pH of solutions was determined using an ION 700 meter equipped with a pH electrode (Eutech instruments, Singapore).

Copper sulphate ($CuSO_4$) in Milli-Q water was used for copper absorption studies. The volumes used for absorption studies were selected to contain more than ten times excess of copper ions relative to the estimated maximum copper uptake by the coatings. The maximum copper uptake was estimated using the following parameters: coating thickness = 15 nm, area of coating = 1 cm^2, maximum uptake ratio N/Cu[S3,4] = 4, film composition = 100 % PEI.

For the selectivity study a solution of artificial seawater was prepared as described previously.[S2] Metal ion solutions of 1mM concentration were prepared and added to the artificial seawater in order to achieve the same molar concentration of 3.25 µM, which corresponds to 200 ppb for Cu^{2+}.

For absorption studies samples were immersed for different times in the metal ion solutions. After immersion the samples were removed from solution, rinsed with Milli-Q water and dried with N_2 before further characterization. At each time point triplicate of samples were used.

S2. Calculation of relative copper concentration in coatings

The coating volume was approximated from Equation 1, where the thickness of the coating is $h_{coating}$ and the area is $A_{coating}$.

$$V_{coating} = h_{coating} \cdot A_{coating} \tag{1}$$

The volume fraction attributed to the cross-linking was estimated by Equation 2, where $h_{after\ cross\text{-}linking}$ and $h_{before\ cross\text{-}linking}$ is the coating thickness after and before the cross-linking respectively.

$$Vf_{CL} = \frac{h_{after\ cross-linking} \cdot A_{coating} - h_{before\ cross-linking} \cdot A_{coating}}{h_{after\ cross-linking} \cdot A_{coating}} \tag{2}$$

To make sure that the copper concentration was not overestimated (in fact, it was underestimated) it was assumed that there were no nitrogens (no PEI) in the volume derived from the cross-linking. This gave an estimated volume of PEI with nitrogens available for copper binding according to Equation 3:

$$V_{PEI} = (1 - Vf_{CL}) \cdot V_{coating} \tag{3}$$

Assuming that the repeating unit is ethyleneimine where there is one nitrogen per repeating unit and that the molecular weight of the repeating unit is 43g/mol, the amount of nitrogens available for copper chelation was estimated by Equation 4. Where ρ_{PEI} is the density of PEI assumed to be 1g/cm^3, V_{PEI} is the volume of PEI, m_{PEI} is the mass of PEI and $M_{Ethyleneimine}$ is the molecular weight of a repeating unit of PEI.

$$N_{N\ available\ in\ coating} = \frac{\rho_{PEI} \cdot V_{PEI}}{M_{Ethyleneimine}} = \frac{m_{PEI}}{M_{Ethyleneimine}} \tag{4}$$

By using the copper to nitrogen ratio (Cu/N) acquired by X-ray photoelectron spectroscopy it was possible to estimate the amount of copper in the coating from Equation 5. Note, since the amount of nitrogens available for copper chelation was estimated from a volume where the volume increase from the cross-linking had been subtracted, the amount of copper in the coating would be somewhat underestimated.

$$N_{Cu\ in\ coating} = \frac{Cu}{N} \cdot N_{N\ available\ in\ coating} \tag{5}$$

Now the mass of copper in the coating was calculated:

$$m_{Cu\ in\ coating} = N_{Cu\ in\ coating} \cdot M_{Cu} \tag{6}$$

Finally the weight percent of copper relative to the total mass of the coating could be estimated as:

$$wt\%_{Cu\ relative\ mass\ of\ coating} = \frac{m_{Cu\ in\ coating}}{V_{coating} \cdot \rho_{PEI} + m_{Cu\ in\ coating}} \cdot 100 \tag{7}$$

Example using equilibrium copper uptake: The copper sorption from 200, 20 and 2 ppb Cu in artificial seawater reached equilibrium after about 4, 12 and 36 hours respectively. At equilibrium the copper to nitrogen ratio was approximately 0.13, 0.08 and 0.04 correspondingly. Using the values in Table S1 to estimate the weight percentages of copper relative to the total estimated mass of the coating gave ~13, 8 and 5 wt% for the different concentrations in decreasing order.

Table S1 Parameters used in calculations of relative wt% of copper in coating

Parameter	**Assumed Value**
$h_{coating}$	7.9 nm
$A_{coating}$	1 cm^2
$h_{before\ cross\text{-}linking}$	6.2 nm
$h_{after\ cross\text{-}linking}$	7.9 nm
ρ_{PEI}	$1*10^6$ g/m^3
$M_{Ethyleneimine}$	43 g/mol
M_{Cu}	63.546 g/mol

S3. Estimation of PEI coating material required for copper recovering in a marina

To estimate the feasibility of recovering copper in a marina we have chosen PIER 32 Marina (P32M) in southeastern San Diego Bay as an example of a copper contaminated marina.[S5] The water quality criteria, according to California Toxics Rule, for dissolved copper in seawater are less than 3.1 µg L^{-1} for chronic exposure (>4 days) and less than 4.8 µg L^{-1} for acute exposure (<1 h).[S5] Hence, a desired concentration of dissolved copper was assumed to be 2 µg L^{-1}. The highest concentration in individual samples of dissolved copper was 22.3 µg L^{-1}.[S5] Thus a mass of copper that needs to be removed was estimated to ~ 6354 g according to Equation 8, where the total volume of seawater in the marina (V_{P32M}) was 313000 m^3 ($3.13*10^8$ L)[S5].

$$m_{Cu\ to\ remove} = \left(C_{Cu\ highest} - C_{Cu\ desired}\right) \cdot V_{P32M} \tag{8}$$

According to Equation 9 the mass fraction of copper that could be absorbed relative to the coating was estimated, where $m_{\text{Cu in coating}}$ is the mass of copper in the coating at equilibrium. Here the mass of copper absorbed after 36 hours in 2 ppb artificial seawater ($3.66*10^{-8}$ g) was used to obtain as good representation as possible of the sorption kinetics in the described system.

$$m_{f\,Cu\,relative\,coating} = \frac{m_{Cu\,in\,coating}}{V_{coating}\cdot\rho_{PEI}} = \frac{m_{Cu\,in\,coating}}{m_{PEI\,coating}} \tag{9}$$

Now the mass of coating needed for removal of the copper to achieve the desired concentration was estimated:

$$m_{coating\,needed} = \frac{m_{Cu\,to\,remove}}{m_{f\,Cu\,relative\,coating}} \tag{10}$$

By using values previously specified in S2 a PEI coating material with a total mass of approximately 137 kg is needed for the desired copper removal in the marina. Since the absorption kinetics for thicker coatings are unknown to the authors at present it is only fair to estimate the required surface area of support material for the current thickness. According to Equation 11 a surface area of ~ $1.7*10^7$ m^2 would be required, when the density of PEI is assumed to be 1 g/cm^3. As an example, this surface area would correspond to ~ 130 kg silica particles with a diameter of 20 nm and an assumed density of 2.3 g/cm^3.

$$A_{support\,material} = \frac{\frac{m_{coating\,needed}}{\rho_{PEI}}}{h_{coating}} = \frac{V_{coating\,needed}}{h_{coating}} \tag{11}$$

S4. Dry layer thicknesses determined using a Variable Angle Spectroscopic Ellipsometer (VASE)

Dry layer thicknesses were determined using a Variable Angle Spectroscopic Ellipsometer (VASE®) and WVASE32® software (J.A. Woollam Co., Inc.). Samples included thin film coatings on reflective substrate of silicon wafers. The coating thickness after the spin coating step was compared to the thickness after cross-linking and addition of the final PEI layer. The whole procedure lead to a 1.7 nm increase in thickness (Table S2). The coating thickness was shown to be easily tuned by changing the concentration of PEI in solution used in the spin coating process (Table S3). Furthermore, the effect of only the GA cross-linking on coating thickness was determined by analysing the thickness before and after the cross-linking step (Table S4). Here it was shown that the cross-linking with GA resulted in a thickness increase of approximately 0.6 nm.

Table S2 Dry layer thickness of PEI coating on silicon wafer, ± indicate one standard deviation (n=32).

After spin coating from 0.05 % in EtOH (nm)	After cross-linking procedure (nm)	Change in thickness (nm)

6.2 ± 0.7	7.9 ± 1.1	1.7 ± 0.8

Table S3 Effect of solution concentration during spin coating on coating thickness

Sample	Thickness (nm)	No. of measurements
PEI from 0.05% in EtOH	6.2 ± 0.7	32
PEI from 0.1% in EtOH	11.5 ± 0.5	30
PEI from 0.5% in EtOH	49.5 ± 1.9	5

Table S4 Effect of GA-mediated cross-linking on coating thickness, ± indicate one standard deviation (n=3).

Before cross-linking (nm)	After GA cross-linking step (nm)	Change in thickness (nm)
6.4 ± 0.3	7.0 ± 0.3	0.6 ± 0.1

S5. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) was used to examine the sample morphology. The samples had a very smooth surface, with the exception of regions where pinholes with a size of some hundreds of nanometres were observed. The pinholes seemingly penetrated down to the substrate allowing a second measure of the coating thickness that correlated with ellipsometry measurements (Fig. S2).

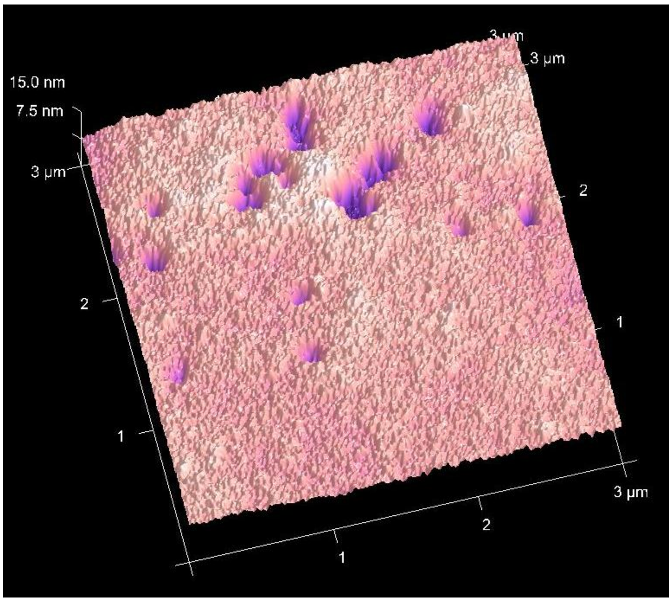

Fig. S2 Exemplifying 3D-image of a cross-linked PEI surface with regions of pinholes.

S6. X-ray Photoelectron Microscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was used to determine the relative elemental composition of elements from the top ~ 10 to 15 nm of the surface coatings. This technique allowed for the atomic percentages of copper and nitrogen, present in the films, to be determined. The XPS measurements were undertaken using monochromatized Al Kα X-rays (1486.7 eV) at a power of 225 W on a Kratos Axis-Ultra spectrometer (160 eV analyser pass energy for survey scans, 20 eV for high-resolution scans). The analysis spot size was ~ 300 x 700 µm. Core electron binding energies are given relative to an adventitious hydrocarbon C 1s binding energy of 284.8 eV. Atomic ratios of metal to nitrogen provided an evaluation of the coordination of the metals to nitrogens in the coating. Two different locations on every sample were analysed to calculate an average and standard deviation of the Me/N ratio for each sample.

XPS was further used to determine the oxidation state of the copper ions in the coatings (Fig. S3). To preserve the copper oxidation state in the coatings and minimize the photoreduction under vacuum and X-rays, samples needed to be cryogenically cooled down prior to, and during, analysis.[S6] The sample temperature was < -100 ^{o}C before transferring from introduction chamber to analysis chamber, and < -150 ^{o}C during analysis. The copper loaded coatings contained dominantly Cu(II) throughout the entire coating (Fig. S3 A). However, some Cu(I) could be seen at the surface (Fig. S3 B), as revealed by the more surface-sensitive analysis geometry. Presence of the small amount of superficial Cu(I) is most likely due to some unavoidable dehydration in the topmost film layers or, perhaps, imperfect reduction on adsorption due to limited coordination possibilities right at the coating surface. Fig. S3 C shows an example of extended exposure to the instrument X-rays, producing an increased contribution from Cu(I) due to photoreduction.

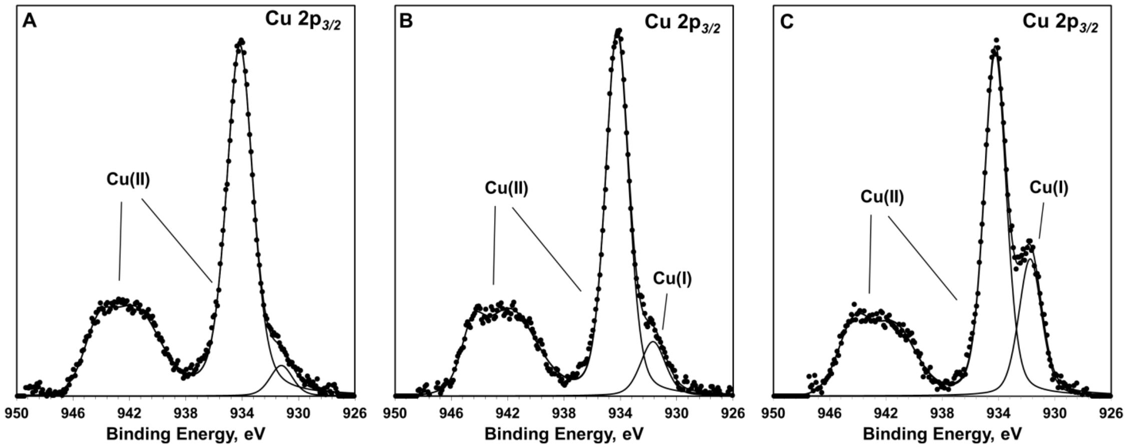

Fig. S3 XPS spectra of the Cu 2p3/2 peak collected at 90° take-off angle for 10 min (A), 20° take-off angle for 10 min (B) and 90° take-off angle for 2h10min (C) respectively. Samples where immersed in $CuSO_4$ (200 ppb), cooled with liquid N_2 both during the introduction into the spectrometer and in the analysis chamber during the 10 min experiment. The spectra have had the background subtracted and Cu(II) and Cu(I) contributions fitted.

Table S5 Contribution of Cu(I) and Cu(II) for each spectrum condition in Fig. S3 A-C.

Figure	Acquisition details	Contribution of Cu(I) (%)	Contribution of Cu(II) (%)
S4 A	90° Take-off angle, LN2, 10 min	5	96
S4 B	20° Take-off angle, LN2, 10 min	9	92
S4 C	90° Take-off angle, LN2, 2 h	21	79

S7. Stability of coatings after immersion in different solutions

To validate that the coatings were stable after immersion in different solutions the dry layer thickness was determined by ellipsometry (as described in S3) before and after immersion. The thickness did not change significantly after immersion in the different solutions (Table S6).

Table S6 Coating thickness before and after immersion in different solutions for 128 h, ± indicate one standard deviation (n=3).

Solution	Thickness before (nm)	Thickness after immersion (nm)
Milli-Q water 200 ppb $CuSO_4$	7.2 ± 0.9	6.7 ± 0.3
Artificial seawater 200 ppb $CuSO_4$	7.5 ± 0.5	8.2 ± 0.6
Artificial seawater 12 different ions	7.2 ± 0.5	8.1 ± 1.0

S8. Influence of shaking

To test if shaking had any effect on the copper absorption, the copper to nitrogen ratio of samples immersed in 20 ppb $CuSO_4$ with or without shaking were compared (Fig. S4). The result showed that the shaking did not have any significant effect on the copper absorption.

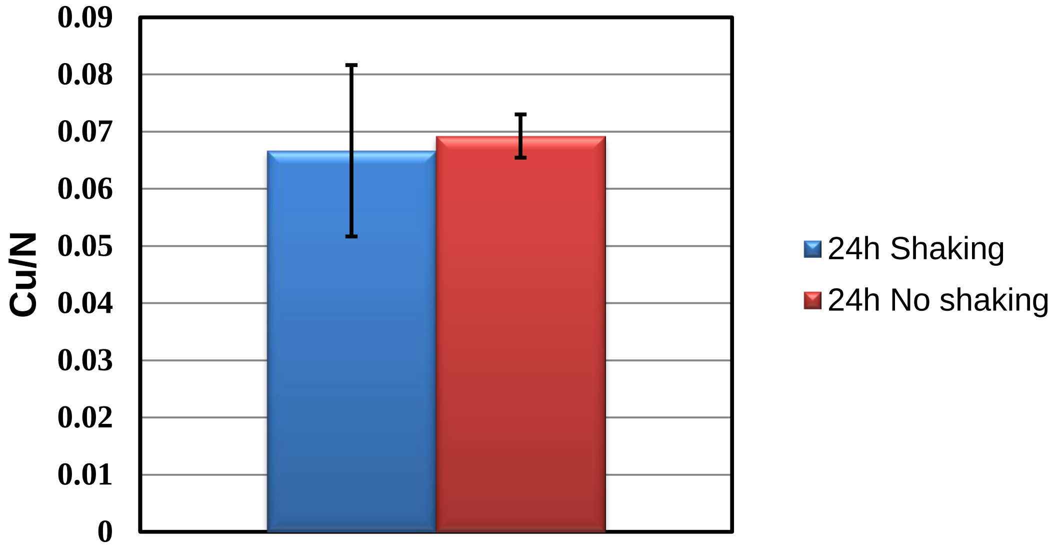

Fig. S4 Copper to nitrogen ratio of samples immersed in 20 ppb $CuSO_4$ for 24 hours. Error bars indicate one standard deviation (n=6).

References

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