Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information

Real-Time Detection of Copper Contaminants in Environmental Water using Porous Silicon Fabry–Pérot Interferometer

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# Equal contribution

Table S1. Environmental water analysis characterization by ICP-OES

Ion	Tap (ppm)	Ground (ppm)	Irrigation (ppm)
Ag	<0.0004	<0.0004	<0.0004
Al	0.018	0.007	0.005
As	<0.007	<0.007	<0.007
Ca	71.4	58.5	85.1
Cd	<0.0002	<0.0002	<0.0002
Cr	<0.003	<0.003	<0.003
Cu	0.001	0.001	0.001
Fe	0.027	0.039	0.012
Hg	<0.002	<0.002	<0.002
K	2.37	26.7	19.9
Mg	32.2	21.7	17.3
Na	37.0	107.1	102.9
Pb	<0.003	<0.003	<0.003
Zn	0.005	0.059	0.029

Table S2. Functionalization steps characterization through RIFTS measurements

Functionalization Steps	$_{eff}$OT (nm)	Intensity (a.u.)
p-SiO_2	15,183±58	17.0±0.2
APTS	15,901±43	20.8±0.4
GA	16,498±37	22.8±0.3
$(GA\text{-}PEI)_1$	16,734±46	24.8±0.3
$(GA\text{-}PEI)_1$-GA	17,238±31	26.7±0.2
$(GA\text{-}PEI)_2$	17,259±34	27.3±0.3

Data are reported as mean ± SD (n = 3).

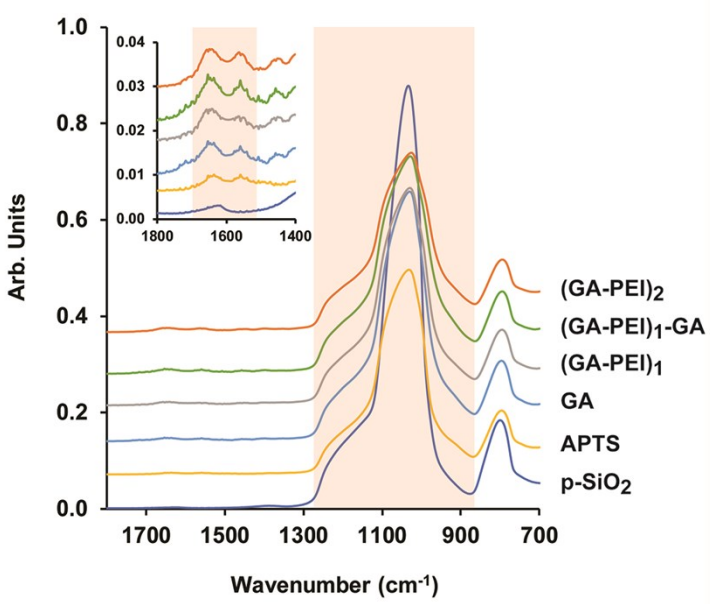

Figure S1. Representative ATR-FTIR analysis of two sequential PEI layers immobilization onto p-SiO_2 nanostructure. The modification steps include: unmodified p-SiO_2, APTS, GA, (GA-PEI)$_1$, (GA-PEI)$_1$-GA, (GA-PEI)$_2$. Inset: corresponding spectra magnification of the region of interest for clarity.

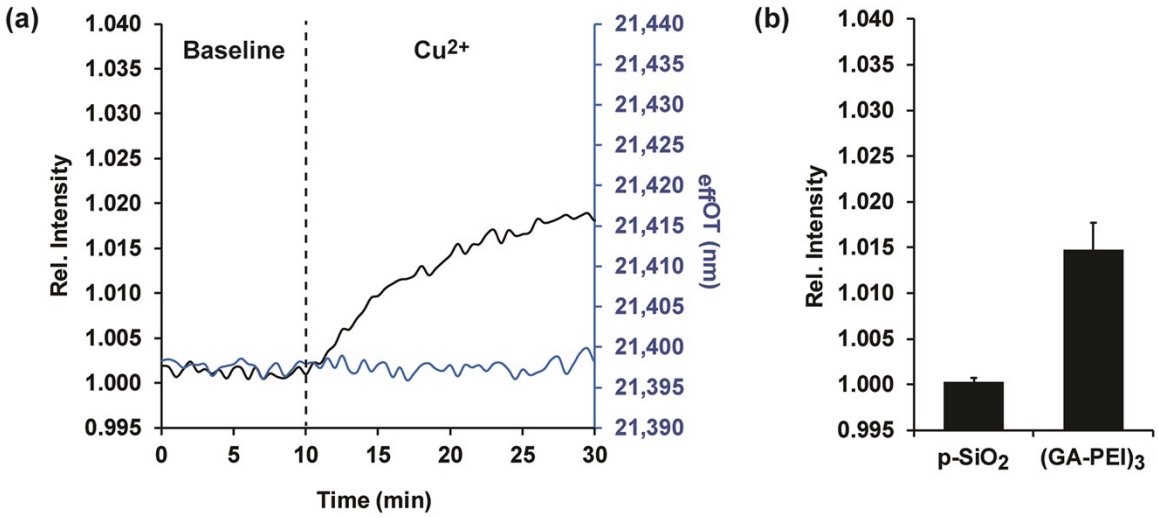

Figure S2. Reflective based response of (GA-PEI)$_3$ surface with copper ions. Both, relative intensity and $_{eff}$OT changes vs time are monitored. The optical transducer is first pretreated with ultrapure water (pH 6.5) to obtain a stable baseline, after which 1 ppm Cu^{2+} solution is injected at a constant flow rate of 200 µL min^{-1} using a peristaltic pump. (b) The corresponding averaged optical response of three PEI layers toward 1 ppm Cu^{2+} solution. Data are reported as mean ± SD (n = 3).

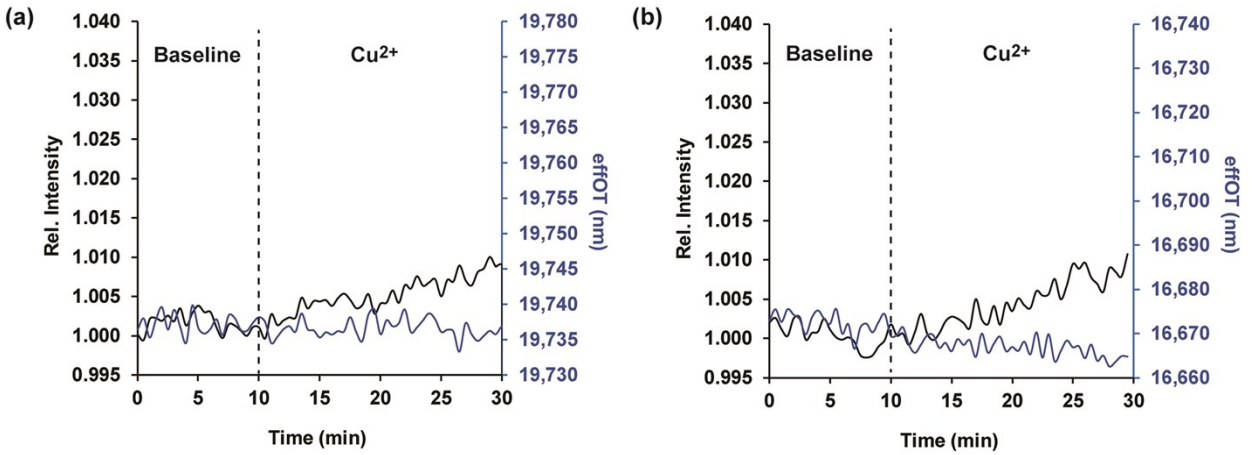

Figure S3. Reflective based response of the different surfaces (various pore sizes) modified with $(GA\text{-}PEI)_2$ toward copper ions. Both, relative intensity and $_{eff}OT$ changes vs time are monitored for pores diameter of (a) ~30-50 nm and (b) ~40-70 nm. Both anodization steps were performed under constant current densities of 231 mA cm^{-2} for 50 s and 385 mA cm^{-2} for 30 s, respectively. Each optical transducer is first pretreated with ultrapure water (pH 6.5) to obtain a stable baseline, after which 1 ppm Cu^{2+} solution is injected at a constant flow rate of 200 µL min^{-1} using a peristaltic pump.

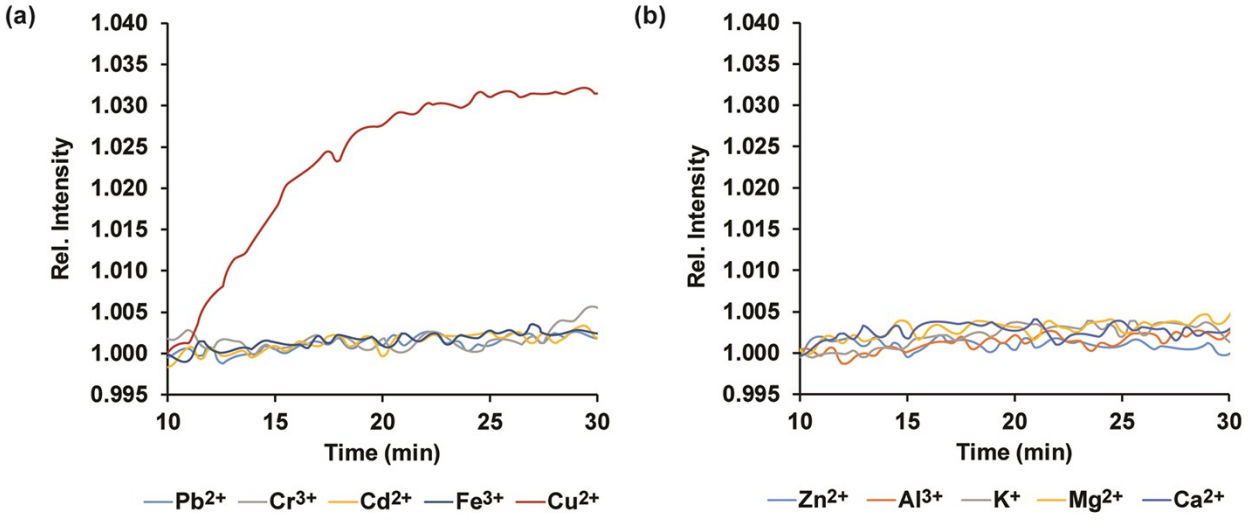

Figure S4. Relative intensity changes vs time of $(GA\text{-}PEI)_2$ surfaces throughout the optical experiments against five different cationic solutions (a) Pb^{2+}, Cr^{3+}, Cd^{2+}, Fe^{3+}, Cu^{2+} and (b), Zn^{2+}, Al^{3+}, K^{+}, Mg^{2+}, Ca^{2+}, 1 ppm each.

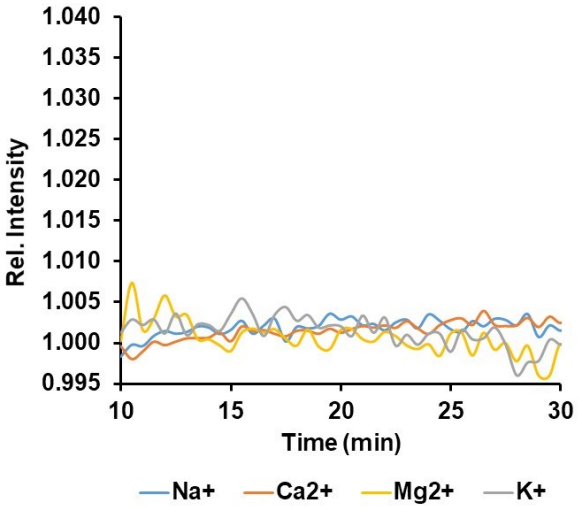

Figure S5. Relative intensity changes vs time of $(GA\text{-}PEI)_2$ surfaces throughout the optical experiments against four different cationic solutions simulating elevated concentrations as in real water samples. The inspected ions are Na^+, K^+, Mg^{2+} and Ca^{2+} (100 ppm each).

Table S3. Label-free copper ions detection techniques

Detection method	Recognition element	LoD (ppb)	Dynamic range (ppb)	Analysis time (min)	Portability for on-site	Ref.
ICP-OES	-	0.1	1-100,000	15	-	[1]
ICP-MS	-	0.007	0.05-50,000	15	-	[2]
Surface plasmon resonance	Cellulose-hexadecyltrimethyl-ammonium bromide	8	10-60,000	15	-	[3]
Photoluminescence	Me2Cyclen -GaAs	128	320-3,200	30	-	[4]
Colorimetry	Polyaniline/ polyamide	1	1-100,000	30	+	[5]
Optical fiber	Chitosan-EDTA	0.1	1-64,000	7	+	[6]
Refractometry	PEI modified Nanoporous Alumina	7	1,000-100,000	45	+	[7]
Refractometry	PEI modified PSi	53	200-2,000	20	+	This study

References

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