Supporting Information

Mesoporous Silica Thin Films for Improved Electrochemical Detection of Paraquat

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Electrochemical methods for paraquat detection reported in the literature

Table SI1: Comparison of different electrochemical methods for detection of paraquat

Electrode material	Modification	Method	Linear range (mol L^{-1})	LOD (mol L^{-1})	Preconcentration	Reference
Mercury	--	SWV	5×10^{-8}-1×10^{-5}	1.5×10^{-8}	No	[1]
Boron doped diamond	--	SWV	8×10^{-7}-1.6×10^{-4}	7×10^{-8}	No	[2]
Boron doped diamond	--	SWV	5×10^{-9}- 1×10^{-6}	1.5×10^{-9}	No	[3]
Au-µE	--	SWV	No data	1.76×10^{-8}	No	[4]
Au-µE	--	SWV	5×10^{-7}-1×10^{-5}	8.2×10^{-8}	No	[5]
Cu	Bismuth film	DPV	0.1×10^{-6}-4.2×10^{-6}	1.2×10^{-8}	No	[6]
Cu	Bismuth Film	DPV	6.6×10^{-7}-4.8×10^{-5}	9.3×10^{-8}	No data	[7]
Au	Au NPs-DNA	SWV	5×10^{-6}-1×10^{-3}	1.9×10^{-6}	No data	[8]
CPE	Ag NP	SWV	1×10^{-7}-1×10^{-3}	2.01×10^{-8}	10 minutes	[9]
CPE	Sb NPs-Biochar	SWV	$0.2\text{-}2.9\times10^{-6}$	3.4×10^{-8}	2 minutes	[10]
Au	Au NPs-DNA	DPV	7×10^{-9}-1.5×10^{-6}	2×10^{-10}	No data	[11]
Graphene	(Ppy-g-NGE)	DPV	5×10^{-8}-2×10^{-6}	4.1×10^{-8}	5 minutes	[12]
GCE	Carbon nanotubes - DHP	SWV	5×10^{-8}-1.5×10^{-6}	1×10^{-8}	No data	[13]
GCE	PVP-GNs/Cu_2O	DPV	1×10^{-6}-2×10^{-4}	2.7×10^{-7}	No data	[14]
Pyrolytic graphite	Metallo-phthalocyanine	SWV	5×10^{-7}-2.9×10^{-5}	1.03×10^{-7}	10 minutes	[15]
CPE	Biochar	DPAdSV	3×10^{-8}-1×10^{-6}	7.5×10^{-9}	5 minutes	[16]
GCE	Nafion	CDPV	3.9×10^{-9}-3.9×10^{-7}	1.9×10^{-9}	3 minutes	[17]
GCE	Nafion - Clay	SWV	3.9×10^{-8}-2.7×10^{-7}	1.9×10^{-9}	4 minutes	[18]

CPE	Amberlite XAD-2 resin	CSV	4.2×10^{-6}	3.9×10^{-7}	3 minutes	[19]
CPE	Natural phosphate	SWV	2.3×10^{-8}-3×10^{-6}	7.8×10^{-10}	10 minutes	[20]
CPE	Hydroxyapatite	SWV	8×10^{-7}-2×10^{-5}	1.5×10^{-8}	30 minutes	[21]
GCE	Mesoporous silica	SWV	1×10^{-8}-5×10^{-8}	4×10^{-9}	3 minutes	This study

GCE: Glassy carbon electrode, CPE: Carbon paste electrode; AuNPs: Gold nanoparticles; PVP-GNs/Cu_2O-Polyvinyl pyrrolidone-graphene nanosheets/Cuprous oxide; Au-µE-Gold microelectrode; DHP: dihexadecylhydrogenophosphate; DPAdSV: Differential pulse adsorptive stripping voltammetry; DPV: Differential pulse voltammetry; SWV: Square wave voltammetry; CDPV: Cathodic differential pulse voltammetry; CSV: Cathodic stripping voltammetry.

Electrochemical impedance spectroscopy

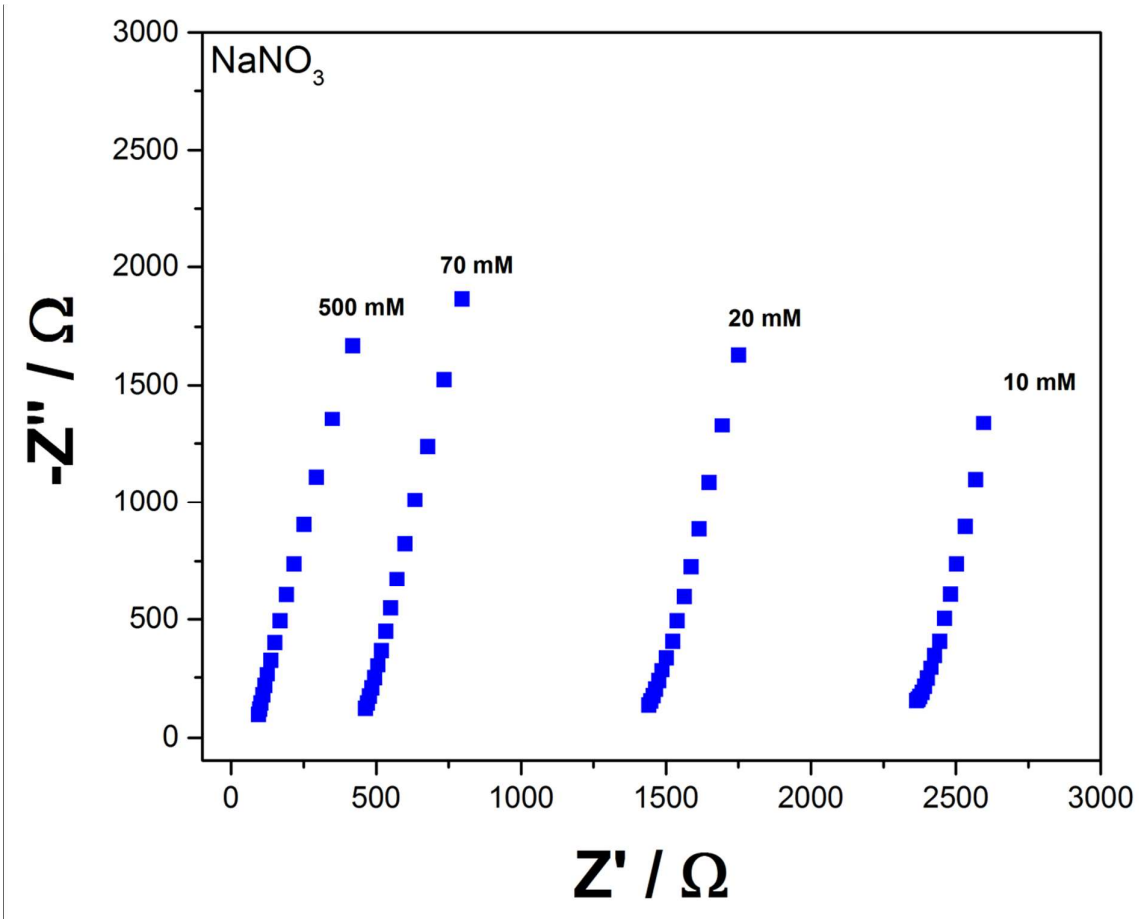

Figure SI1: Nyquist plot for the impedance measured at bare electrodes in solutions of different $NaNO_3$ concentrations (pH = 6). Frequencies were between 60 and 2000 Hz.

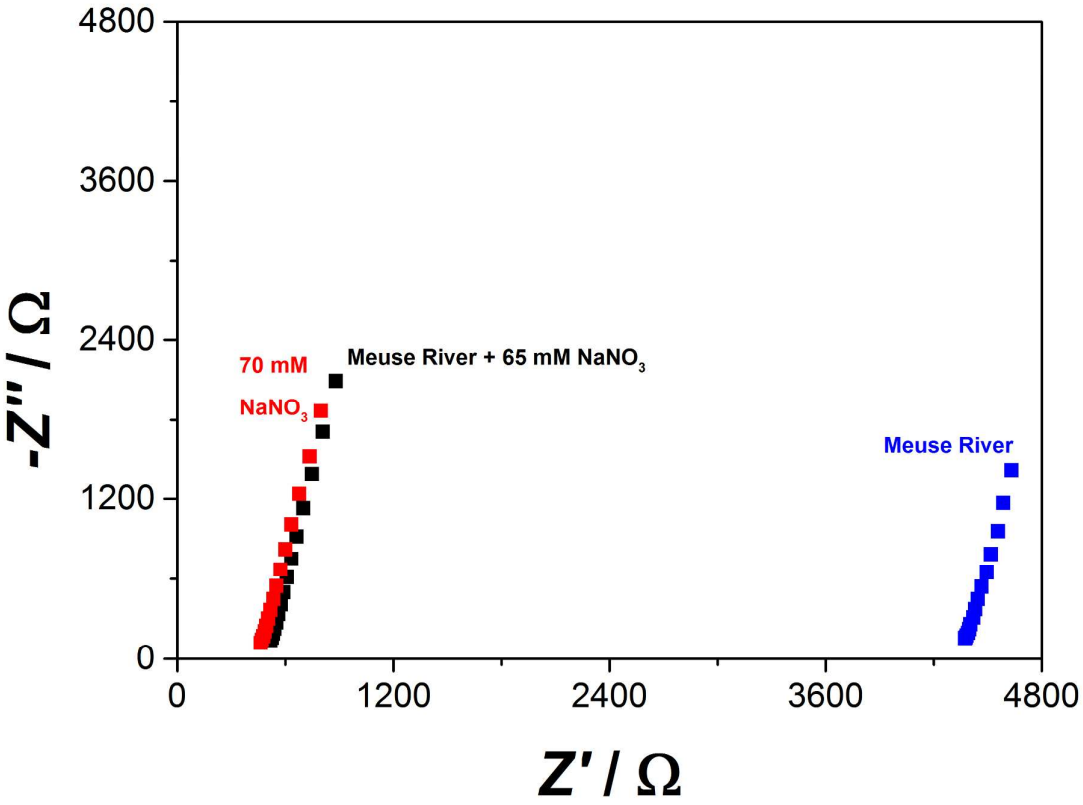

Figure SI2: Nyquist plot for the impedance measured in a laboratory solution of 70 mM $NaNO_3$ (red squares), in Meuse River sample before (blue squares) and after the additions of 65 mM $NaNO_3$ at a bare electrode.

Table SI2: Solution resistances obtained by electrochemical impedance spectroscopy

I / mM	R_s / Ω[a]
10	2344
20	1392
50	573
70	422
100	295
500	64
Real sample	4335
Real sample + 65mM $NaNO_3$	460

R_s : Solution resistance extracted from Nyquist plot obtained at the bare electrode. Same conditions as Figure SI1.

Debye Length as a function of ionic strength

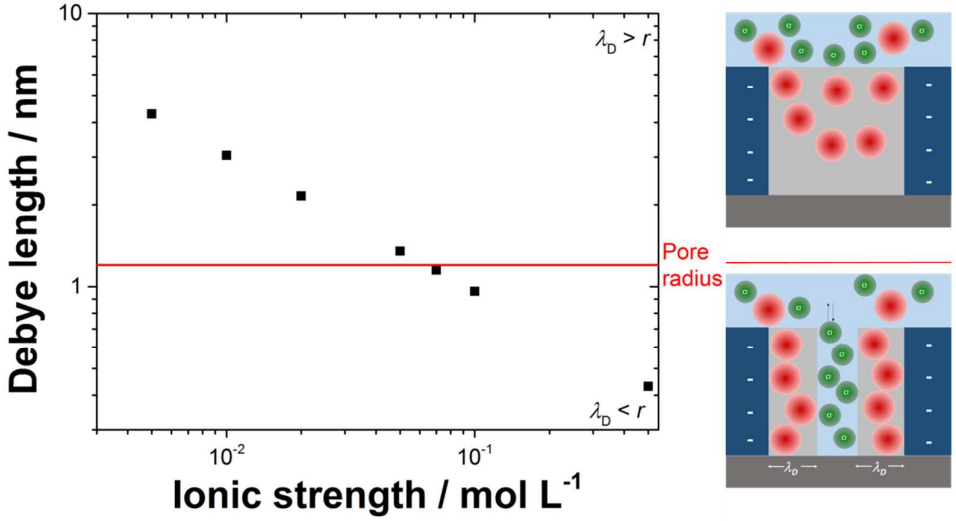

Figure SI3: Debye length as a function of the ionic strengths used in the SWV experiments. The red line symbolizes the value of the mesochannel radius. On the right, two schemes represent anion exclusion of the mesochannels (top) and the 'free' anion zone.

Electrochemical paraquat detection at three different kind of electrodes

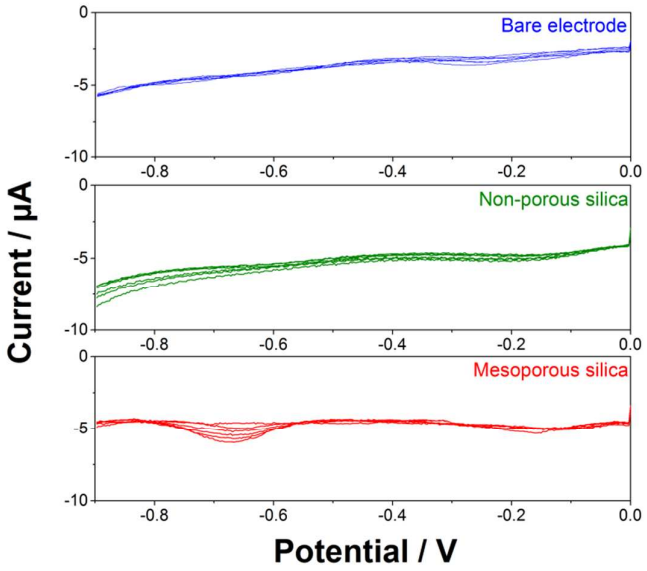

Figure SI4: Square wave voltammograms of 10 – 50 nM paraquat at a bare electrode (top graph, blue curves); a non-porous silica modified electrode (middle graph, green curves) and a mesoporous silica modified electrode (bottom graph, red curves) obtained in the optimal experimental conditions (i.e. 70 mM $NaNO_3$ and pH 6).

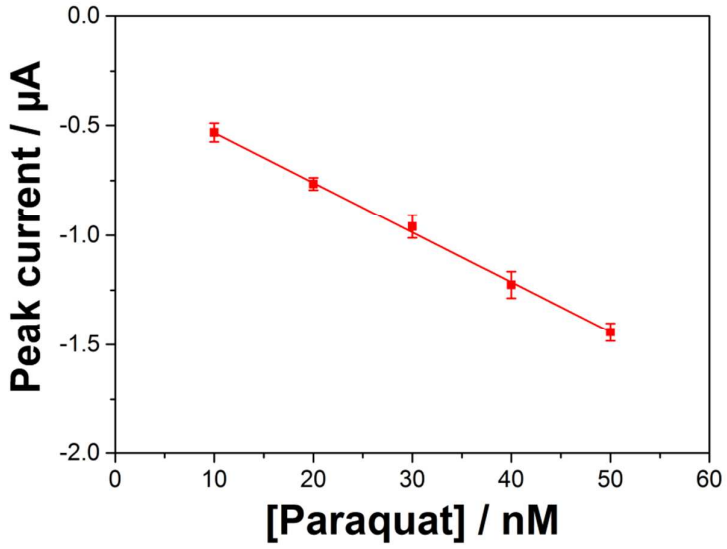

Figure SI5: Calibration curve for 10 – 50 nM paraquat at a mesoporous silica modified electrode obtained in the optimal experimental conditions (i.e. 70 mM $NaNO_3$ and pH 6).

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