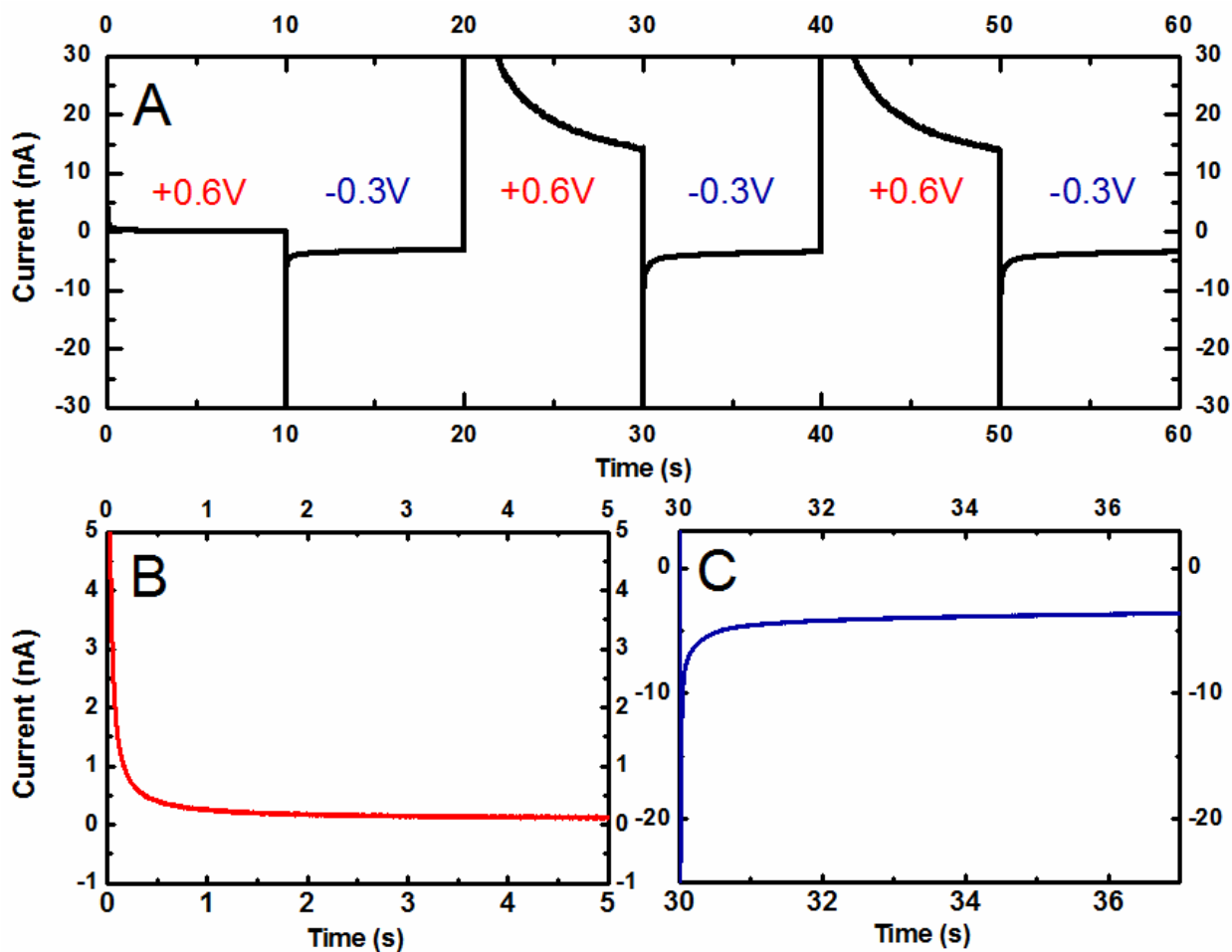


Supplementary information for

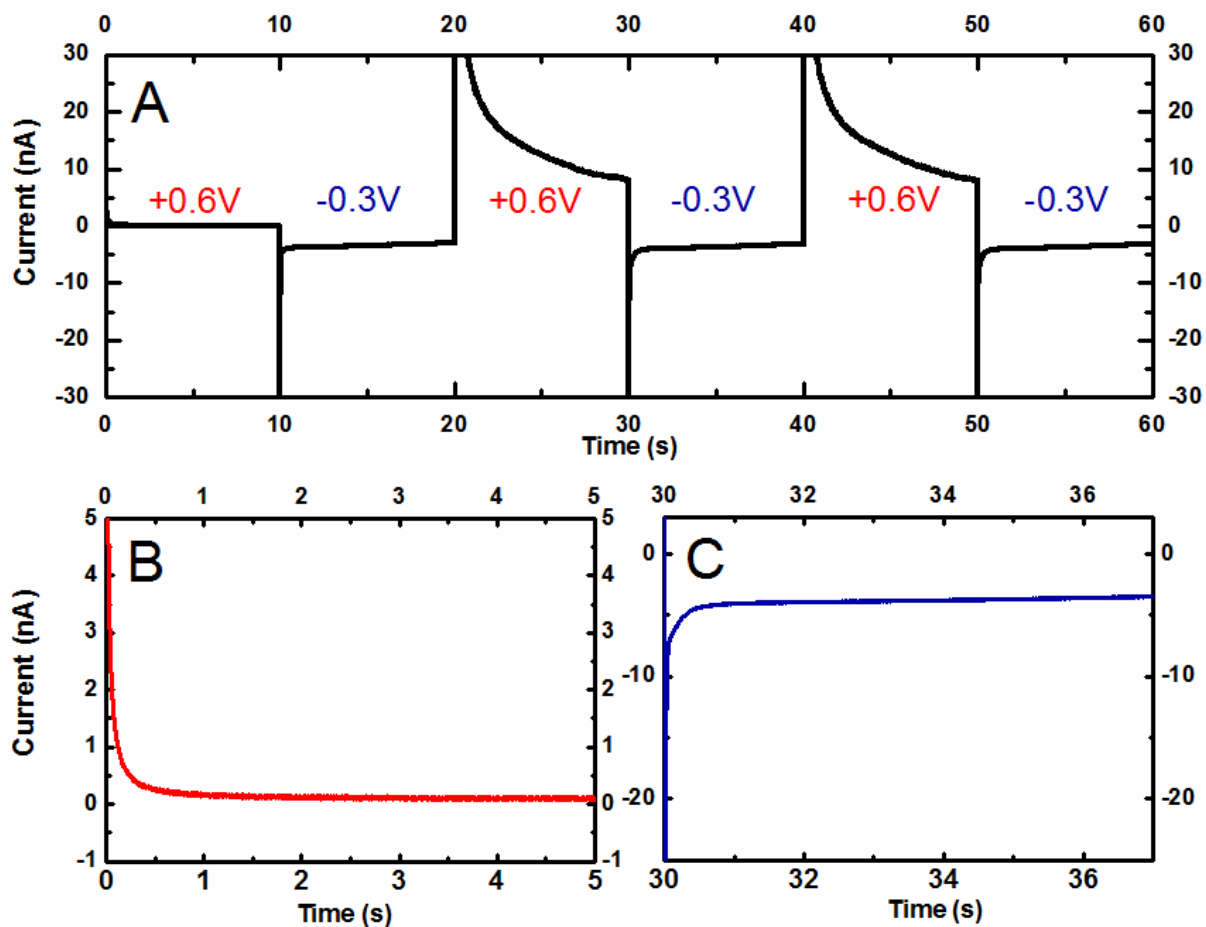
Electrochemical artifacts originating from nanoparticle contamination by Ag/AgCl quasi-reference electrodes

Alexey Yakushenko, Dirk Mayer, Johan Buitenhuis, Andreas Offenhäusser and Bernhard

Wolfrum



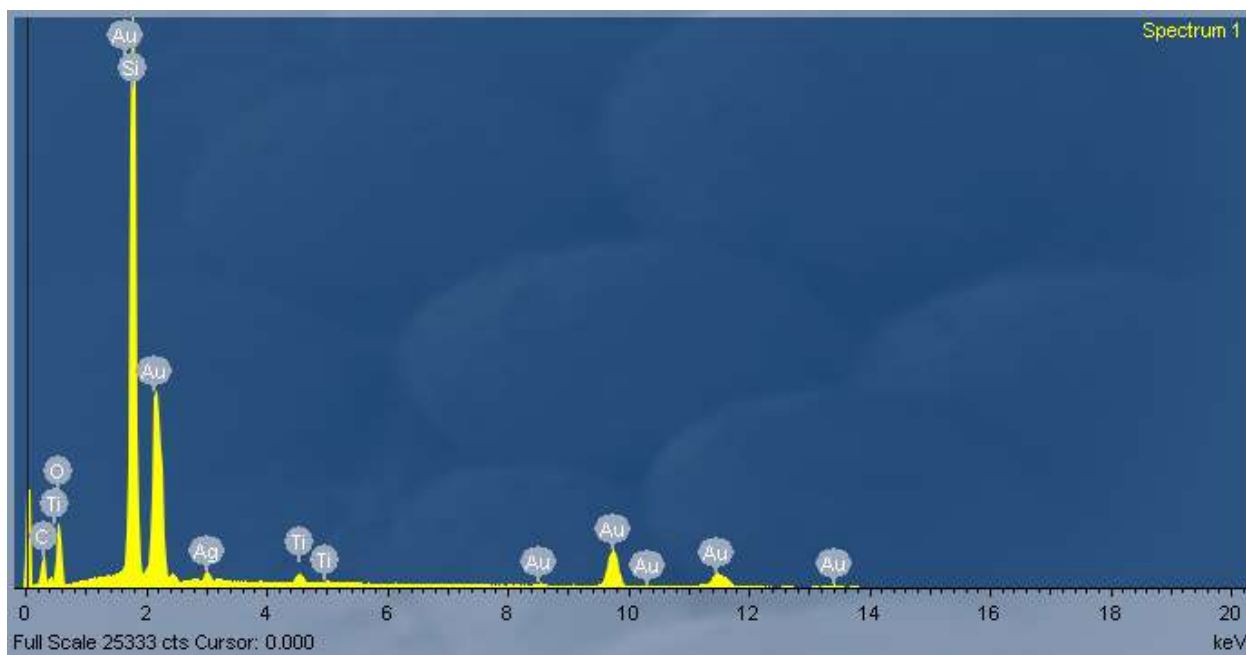
Supplementary Fig. S1 Amperometric measurement of an uncontaminated MEA, which had never been exposed to an Ag/AgCl wire, with a conventional Ag/AgCl reference electrode (RE-6, BASi, Kenilworth, United Kingdom). Switching between the anodic and cathodic potentials. A.) Trace with 3 anodic/cathodic cycles. B.) Zoom into the anodic part at +0.6 V. C.) Zoom into the cathodic part at -0.3 V.



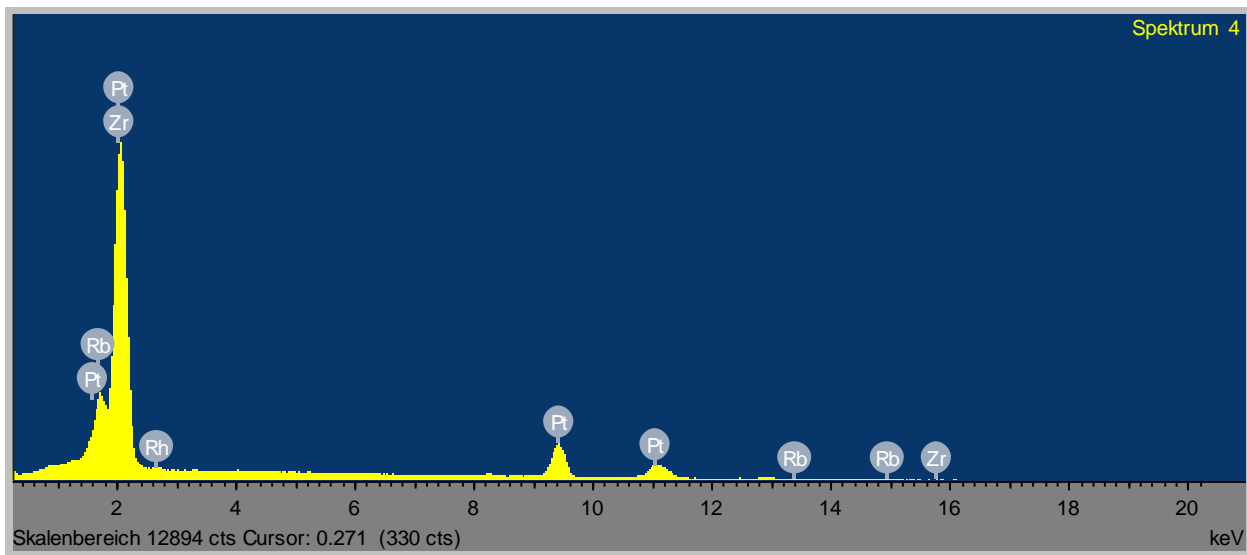
Supplementary Fig. S2 Amperometric measurement of an uncontaminated MEA, which had never been exposed to an Ag/AgCl wire, with a Calomel reference electrode (Schott B3510 Ch0 141 Kalomel, Schott AG Mainz, Germany). Switching between the anodic and cathodic potentials. A.) Trace with 3 anodic/cathodic cycles. B.) Zoom into the anodic part at +0.6 V. C.) Zoom into the cathodic part at -0.3 V.

Supplementary Table S3 Inductively coupled plasma – mass-spectrometry analysis of the liquid from the chip (Ti/Pt/Ti) contaminated with Ag/AgCl nanoparticles chipped off the quasi-reference electrode.

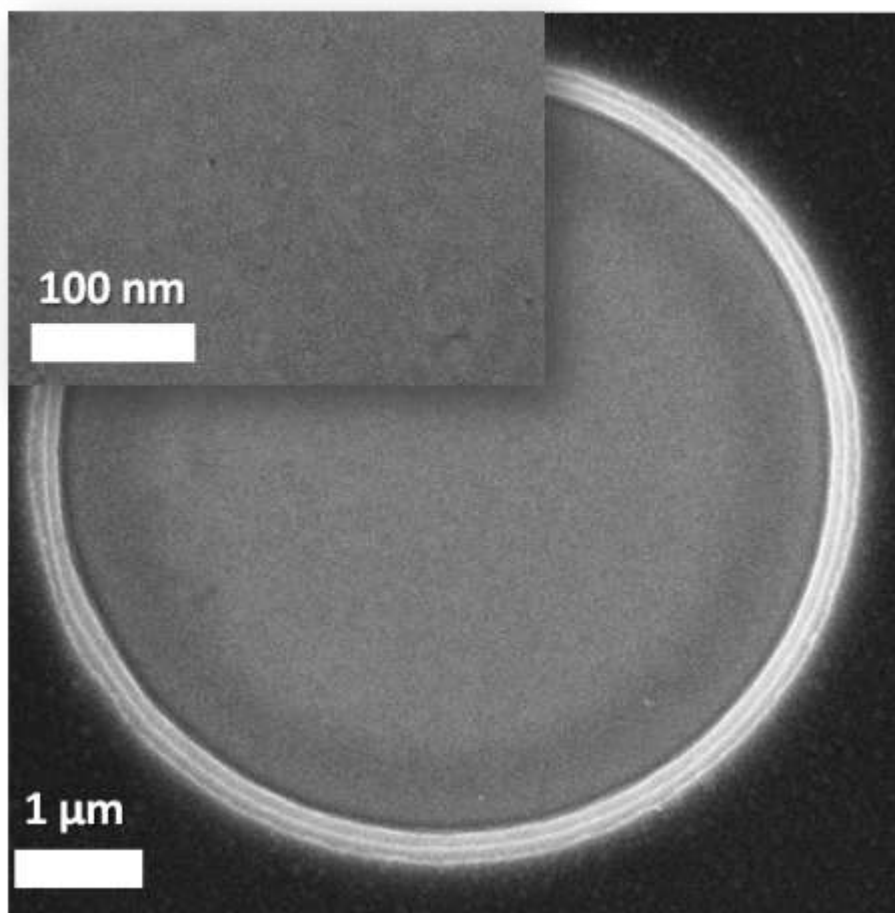
Element	Concentration in µg/L
Pt	465±36
Ag	141±2.6
Fe	87±9
Ti	62±3
Cu	44.8±4.3
Zn	44.3±1.5
Ni	11.2±0.1
Sn	11.1±1.5
Al	9.0±0.6
Hg	7.7±0.7
Mo	3.6±0.1
Cr	<3.3
Zr	2.2±0.2
Pb	1.7±0.1
Mn	0.65±0.05
Cd	0.25±0.01
Co	0.18±0.01
Au	<0.05



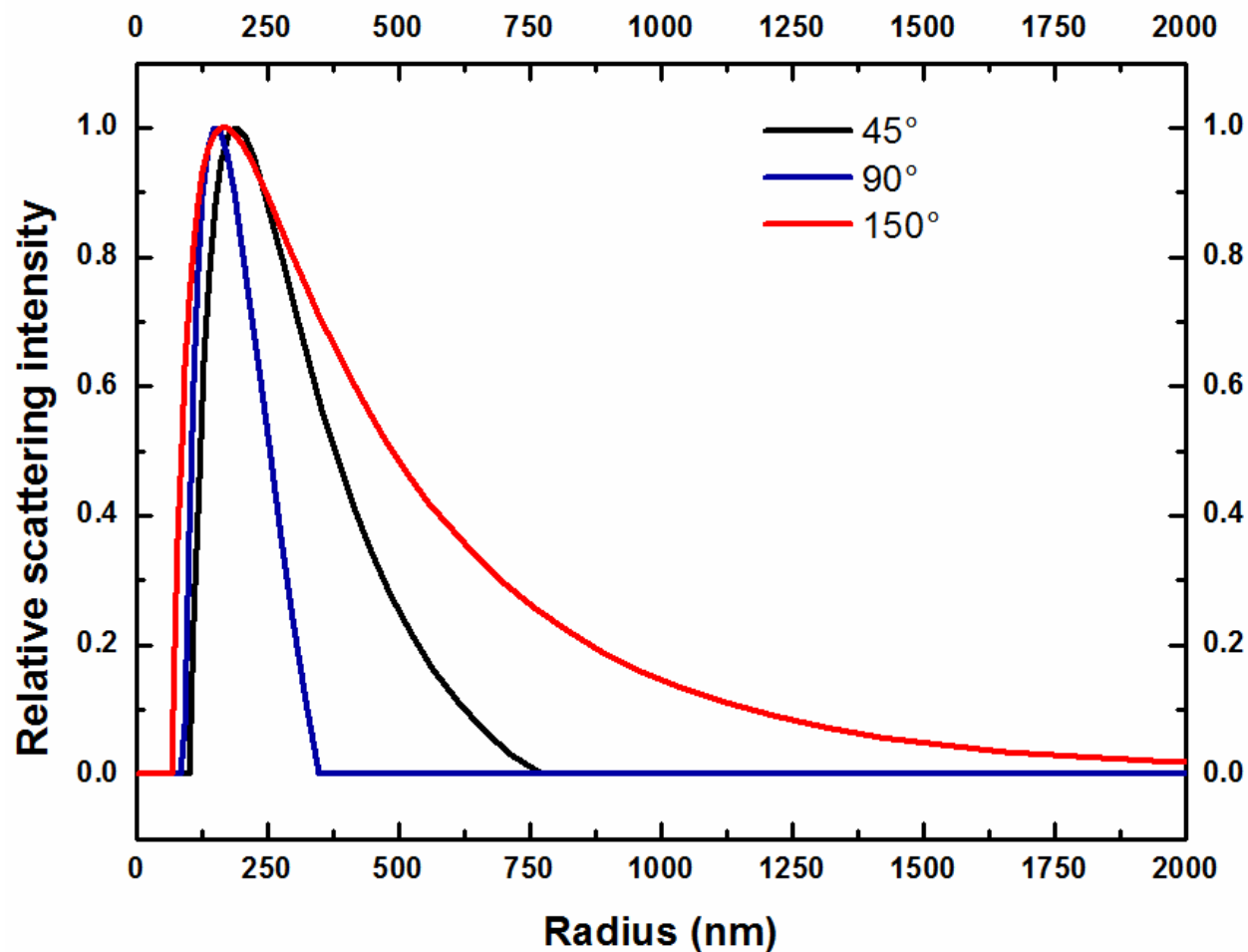
Supplementary Fig. S4 EDX-analysis of a MEA (Ti/Au/Ti, 10/150/10 nm) surface contaminated with Ag/AgCl wire. $V = 20$ kV, $I = 0.4$ nA. Element assignment: Au, Ti – electrode material and adhesion layers; O, Si, N – dielectric passivation layer; Ag – contamination from the Ag/AgCl quasi-reference electrode. The ratio of the weight percentage of the main electrode material – Au and Ag contaminants was ~ 20 to 1. The amount of Ag was higher than that of Ti adhesion layers.



Supplementary Fig. S5 EDX-analysis of a clean MEA (Ti/Pt/Ti, 10/150/10 nm) surface that has never been exposed to Ag/AgCl wire. $V = 20$ kV, $I = 0.4$ nA. Element assignment: Pt – electrode material.



Supplementary Fig. S6 SEM image of a single MEA microelectrode (Ti/Pt/Ti), which has never been exposed to an Ag/AgCl wire. Inlay: zoom onto the electrode surface.



Supplementary Fig. S7 Dynamic Light Scattering of Ag/AgCl nanoparticles in PBS. Examples of radii distributions for three angles (45° , 90° and 150°) are shown and the radius with the highest scattering intensity ranges from 148 to 190 nm depending on the angle. DLS measurements of a blank PBS solution resulted in negligible signals at least two orders of magnitude lower than a signal coming from a PBS solution exposed to an Ag/AgCl wire.