Supporting Information for

Silver Nanoparticle Detection in Real World Environments via Particle Impact Electrochemistry

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Section 1: Characterization of the carbon microdisc electrode

The size of the carbon microdisc electrode is determined by recording cyclic voltammetry of the ferrocenemethanol oxidation (Figure S1) based on the following equation:[1]

$$I_{ss} = 4r_e FDC$$

where I_{ss} is the steady state current (6.45 nA), D and C the diffusion coefficient (7.8×10^{-10} m^2 s^{-1})[2] and concentration (1 mol m^{-3}) of ferrocenemethanol, F is the Faraday constant (96485 C mol^{-1}). Accordingly, the radius of the microdisc electrode (r_e) is 21.4 μm.

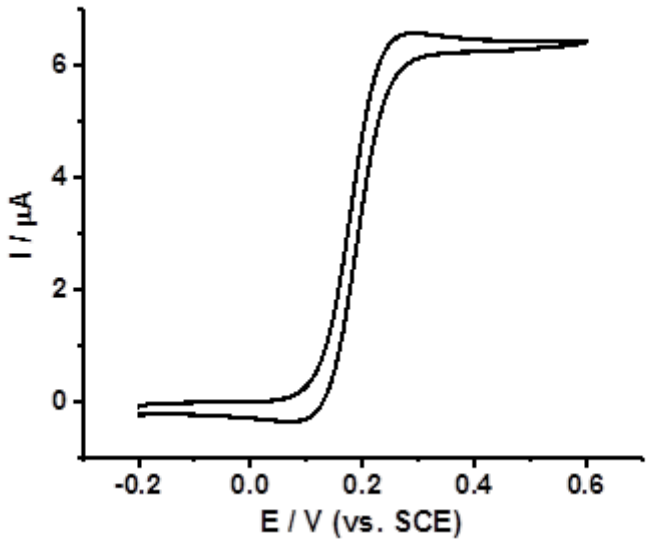

Figure S1. Cyclic voltammogram of 1.0 mM ferrocenemethanol oxidation in 0.1 M KCl at the carbon microdisc electrode at 25 °C.

Section 2: Diffusional weighting of the spike charge

The nano-impact measurements are inherently biased towards the detection of smaller nanoparticles due to their higher diffusion coefficients. Since the possibility of observing a NP is proportional to its diffusion coefficient (D) (assuming a steady-state flux) and $D \propto 1/Q^{1/3}$ according to the Stokes-Einstein equation, the electrochemically determined charge distribution can be corrected by weighting each nanoparticle impact with a factor of $Q^{1/3}$, where Q is the charge passed during a single impact event.[3] In 20mM KCl, the average spike charge becomes 41.8 ± 0.5 fC when diffusional weighting is taken into account.

Section 3: Chronoamperomograms of AgNPs in different media

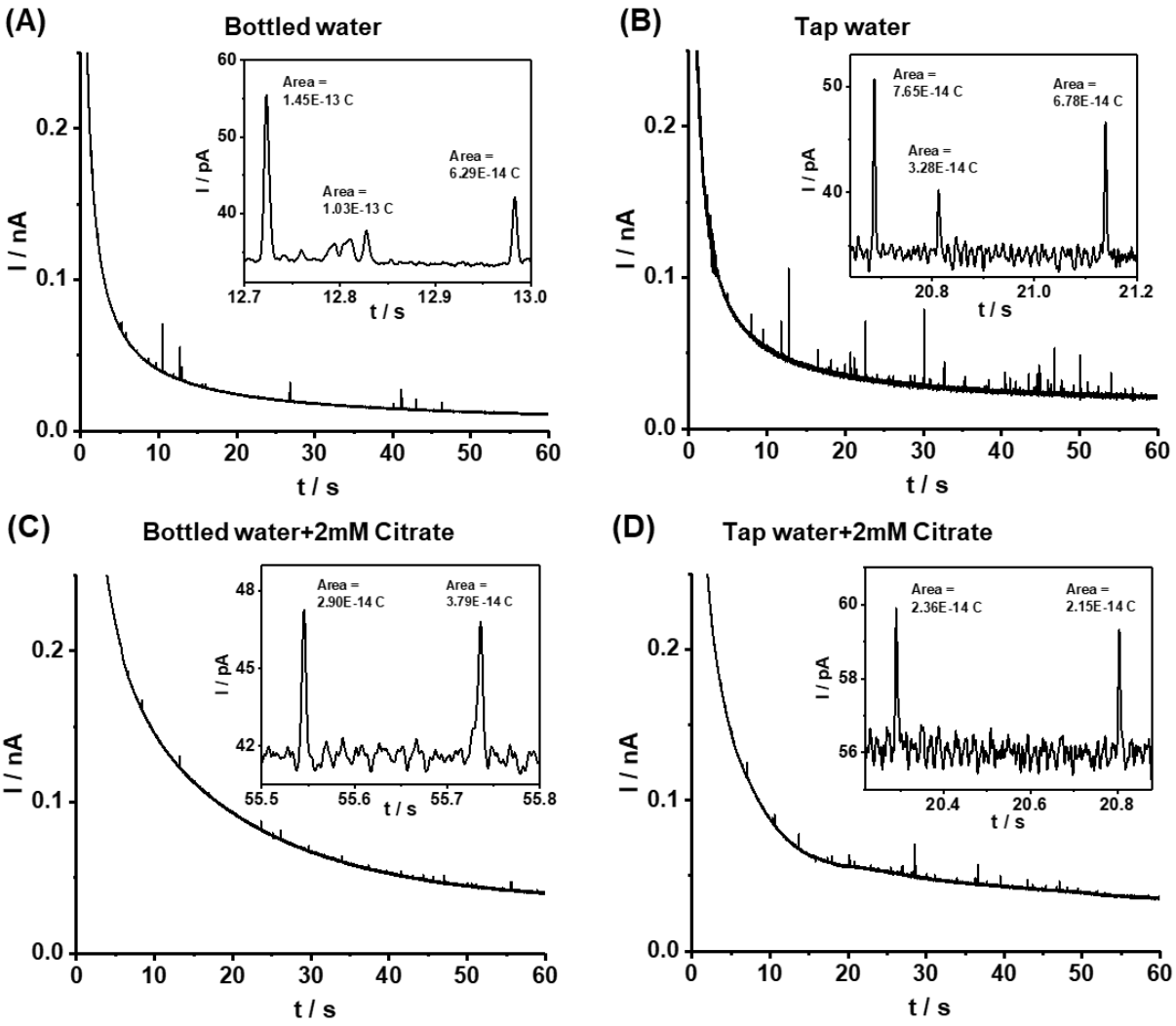

Figure S2. Representative chronoamperomograms of a carbon microdisc electrode (r = 21.4 μm) immersed in 12pM AgNP suspensions which were aged for 20 min in bottled mineral water (A), kitchen tap water (B), bottled mineral water containing 2mM citrate (C) and kitchen tap water containing 2mM citrate (D) respectively at 0.8V vs Ag/AgCl (3.4M KCl).

Section 4: Composition of the bottled mineral water

Ion	Concentration (mM)	mg/L
Calcium (Ca^{2+})	2.0	80
Magnesium (Mg^{2+})	1.1	26
Sodium (Na^{+})	0.28	6.5
Potassium (K^{+})	0.03	1.0
Bicarbonate (HCO_3^{-})	5.9	360
Chloride (Cl^{-})	0.28	10
Sulfate (SO_4^{2-})	0.15	14
Nitrate (NO_3^{-})	0.06	3.8

Table S1: Composition of Evian mineral water[4].

Section 5: UV-vis spectra of AgNPs in different media over 60 min

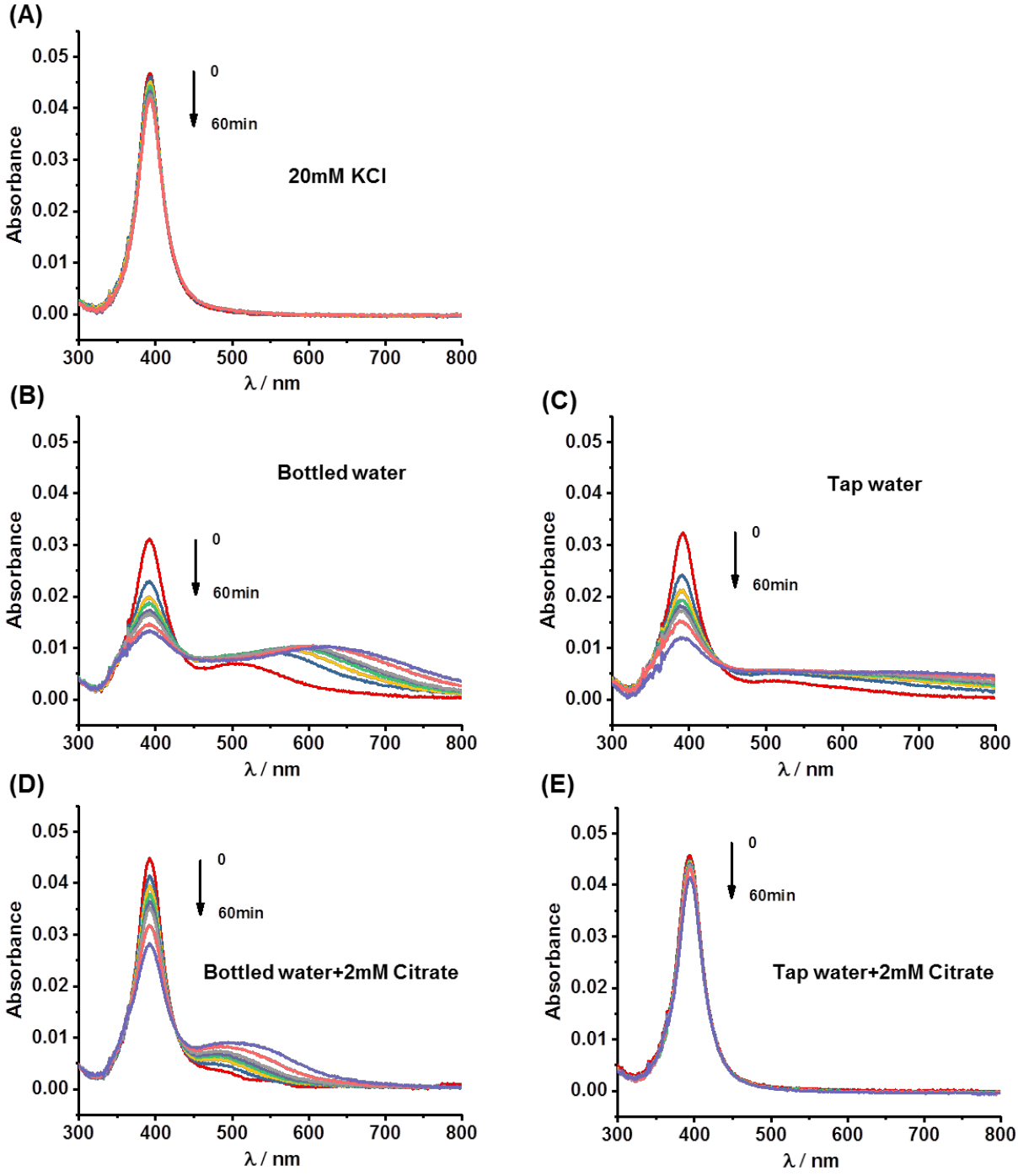

Figure S3. UV-vis spectra of 12pM AgNPs aged over a 60 min period in 20mM KCl (A), bottled mineral water (B), kitchen tap water (C), bottled mineral water containing 2mM citrate (D) and kitchen tap water containing 2mM citrate (E).

References

1. Bard, A. J.; Faulkner, L. R., *Electrochemical Methods: Fundamentals and Applications*; Wiley, 2000.
2. Sun, P.; Mirkin, M. V., Kinetics of Electron-Transfer Reactions at Nanoelectrodes. *Anal. Chem.* **2006**, *78*, 6526-6534.
3. Little, C. A.; Li, X.; Batchelor-McAuley, C.; Young, N. P.; Compton, R. G., Particle-Electrode Impacts: Evidencing Partial Versus Complete Oxidation Via Variable Temperature Studies. *J. Electroanal. Chem.* **2018**, *823*, 492-498.
4. As reported on the bottle and on the Evian website at time of submission https://www.evian.com/en_int/products