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Supporting Information

Voltammetric Study of the Influence of Various Phosphate Anions on Silver Nanoparticle Oxidation

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Supporting information

Table S1 *Values of pH and equilibrium concentrations of the phosphate species in the studied solutions. (C - total phosphate concentration)*

Electrolyte	C, M	pH	$[PO_4^{3-}]$	$[HPO_4^{2-}]$	$[H_2PO_4^{-}]$
Na_3PO_4	0.0125	12.10	4.78×10^{-3}	7.72×10^{-3}	9.67×10^{-8}
	0.025	12.31	1.24×10^{-2}	1.26×10^{-2}	9.97×10^{-8}
	0.05	12.46	2.90×10^{-2}	2.10×10^{-2}	1.17×10^{-7}
	0.1	12.57	6.41×10^{-2}	3.59×10^{-2}	1.56×10^{-7}
	0.2	12.63	1.34×10^{-1}	6.56×10^{-2}	2.48×10^{-7}
	0.3	12.62	2.00×10^{-1}	1.00×10^{-1}	3.87×10^{-7}
Na_2HPO_4	0.1	9.47	1.41×10^{-4}	9.93×10^{-2}	5.43×10^{-4}
	0.2	9.37	2.23×10^{-4}	1.98×10^{-1}	1.37×10^{-3}
	0.3	9.31	2.91×10^{-4}	2.97×10^{-1}	2.35×10^{-3}
NaH_2PO_4	0.1	4.55	3.72×10^{-12}	2.19×10^{-4}	9.94×10^{-2}

Figure S1 *The cyclic voltammogram representing the oxidation of silver nanoparticles on a glassy carbon electrode at a scan rate of 0.05 V/s in 0.3 M Na_3PO_4. Black: 1st scan; Red: 2nd scan. The experiments consist of 3 repeats.*

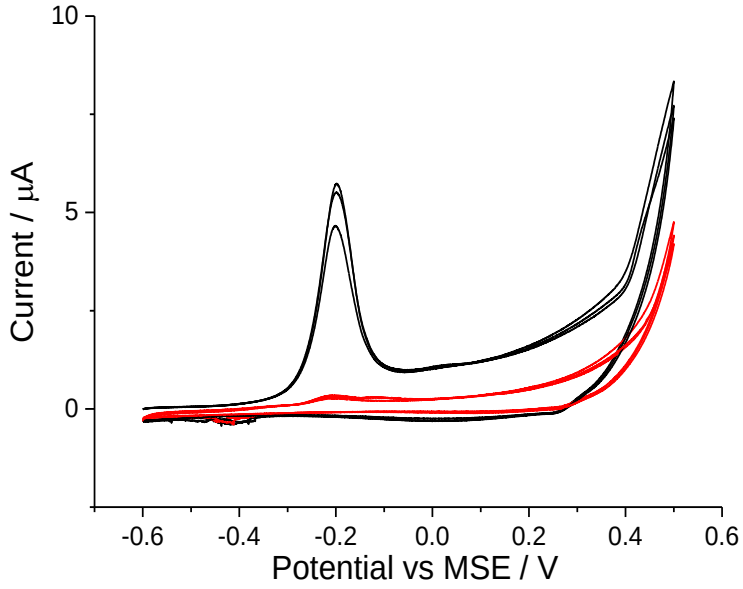
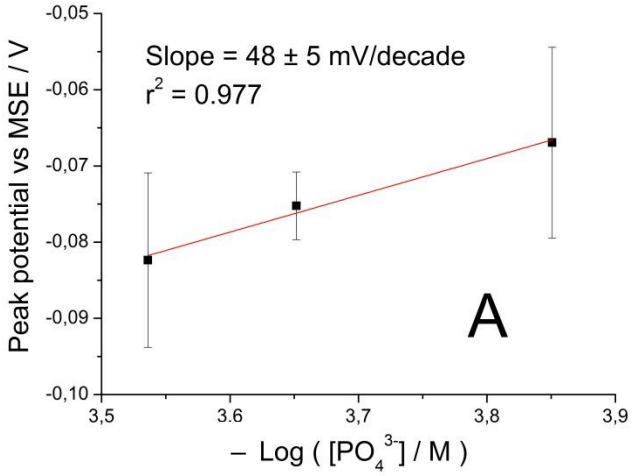
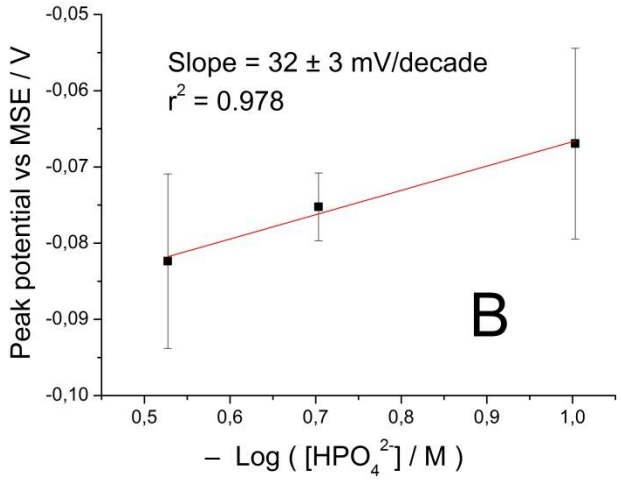


Figure S2 *Variation in the peak potential for the oxidation of silver nanoparticles as a function of negative common logarithm of equilibrium concentration of PO_4^{3-} ion (A), HPO_4^{2-} ion (B) and $H_2PO_4^-$ ion (C) in Na_2HPO_4 solutions.*





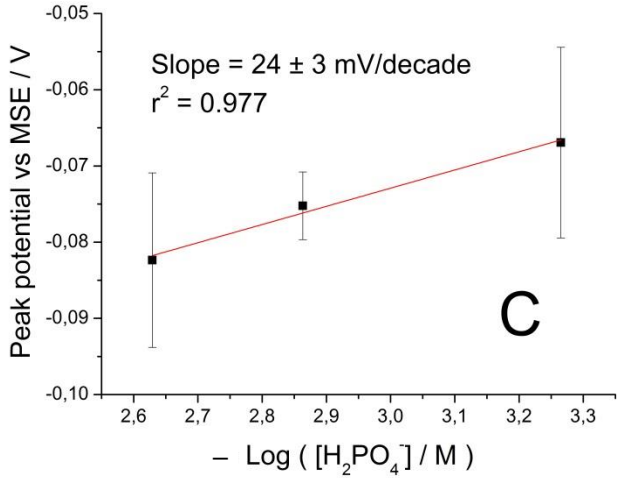
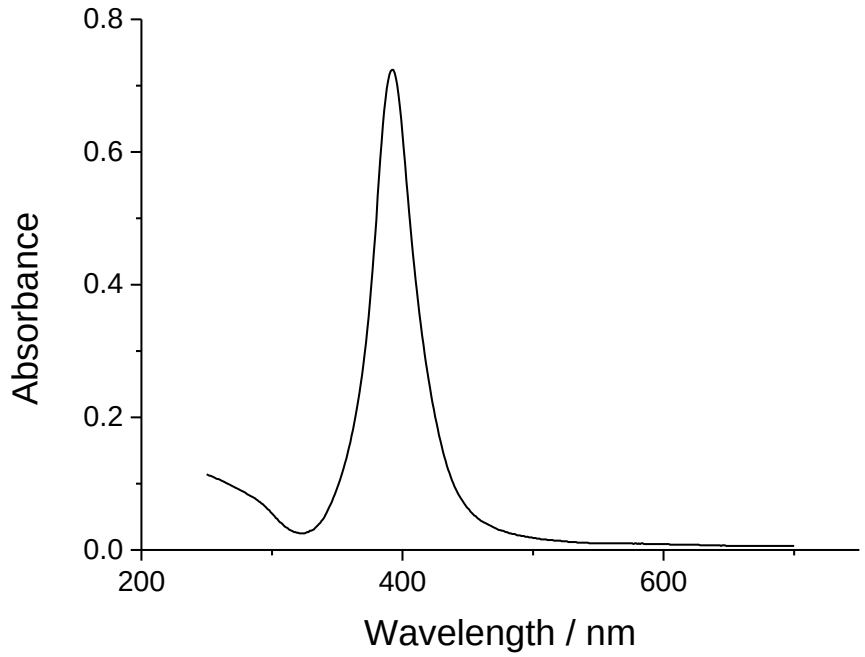


Table S2 *Comparison of oxidation peak potentials (E_{peak}) observed in solutions of approximately equal phosphate ions concentration.*

Approximate concentration	Ion	- E_{peak} ± Δ, mV
2 x 10^{-1} M	**[PO_4^{3-}]** = 2.00 x 10^{-1} M (in 0.3 M Na_3PO_4)	**200 ± 2**
	[HPO_4^{2-}] = 1.98 x 10^{-1} M (in 0.2 M Na_2HPO_4)	75 ± 4
1 x 10^{-1} M	**[PO_4^{3-}]** = 1.34 x 10^{-1} M (in 0.2 M Na_3PO_4)	**194 ± 22**
	[HPO_4^{2-}] = 1.00 x 10^{-1} M (in 0.3 M Na_3PO_4)	**200 ± 2**
	[$H_2PO_4^-$] = 9.94 x 10^{-2} M (in 0.1 M NaH_2PO_4)	16 ± 20
2 x 10^{-4} M	**[PO_4^{3-}]** = 2.23 x 10^{-4} M (in 0.2 M Na_2HPO_4)	**75 ± 4**
	[HPO_4^{2-}] = 2.19 x 10^{-4} M (in 0.1 M NaH_2PO_4)	16 ± 20

Figure S3 *UV-vis spectroscopy of the produced silver nanoparticle suspension.*



Anodic particle coulometry

Before every experiment, the electrochemical cell was soaked in aqua regia (3 HCl: 1 HNO3) for at least 30 minutes and sonicated in ultrapure water for 15 minutes to avoid any contamination by rogue nanoparticles. The silver nanoparticle suspension was diluted with 20 mM trisodium citrate solution to give a solution of 665 pM of silver nanoparticles. Fifty second long chronoamperometry with a sampling time of 0.0005 s were recorded at the potential of +0.3 V vs MSE. Figure 3 depicts the 'spikes' observed as the silver nanoparticle impacted the micro carbon electrode surface (BaSi, West Lafayette, USA). The charge under each 'spikes' was resolved and converted into nanoparticle size through the equation as below:[1]

$$R_{NP} = \sqrt[3]{\frac{3QA_r}{4\pi F\rho}}$$

where R_{NP} is the nanoparticle radius, Q is the total charge passed under a single 'spike', A_r is the atomic molecular mass of silver of 107.9 g mol^{-1}, F is the Faraday constant and ρ is the density of silver of 10.5 x 106 g m^{-3}. SignalCounter developed by Dr. Dario Omanović from Division for Marine and Environmental Research, Ruđer Bošković Institutue, Zagreb, Croatia was used to aid in the analysis.[2-3] The size distribution of the nanoparticles is plotted in Figure S4 where the nanoparticles are sized to be 10.9 ± 1.9 nm.

Figure S4 *Fifty seconds chronoamperomogram for a carbon fibre microelectrode (r = 4.9 µm) immersed in 20 mM trisodium citrate measured at + 0.3 V (vs MSE) in presence of 665 pM silver nanoparticles. Inset: A close up of individual signals observed.*

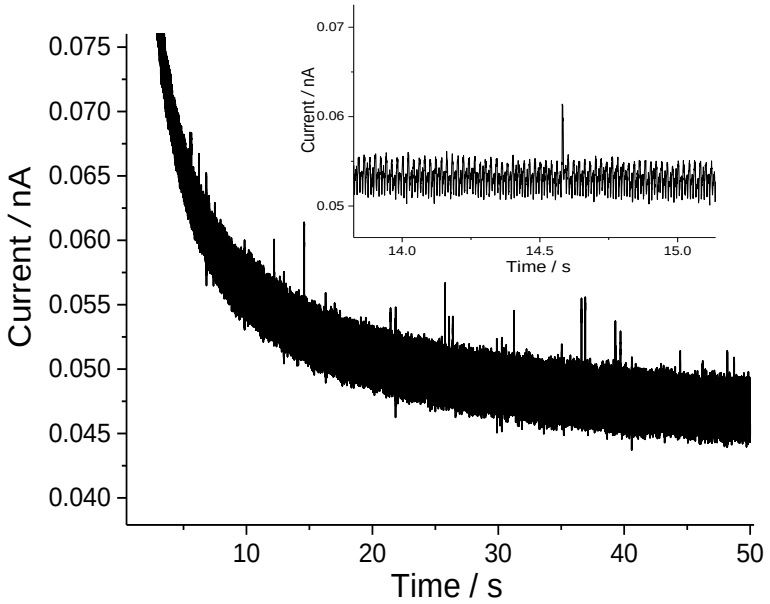
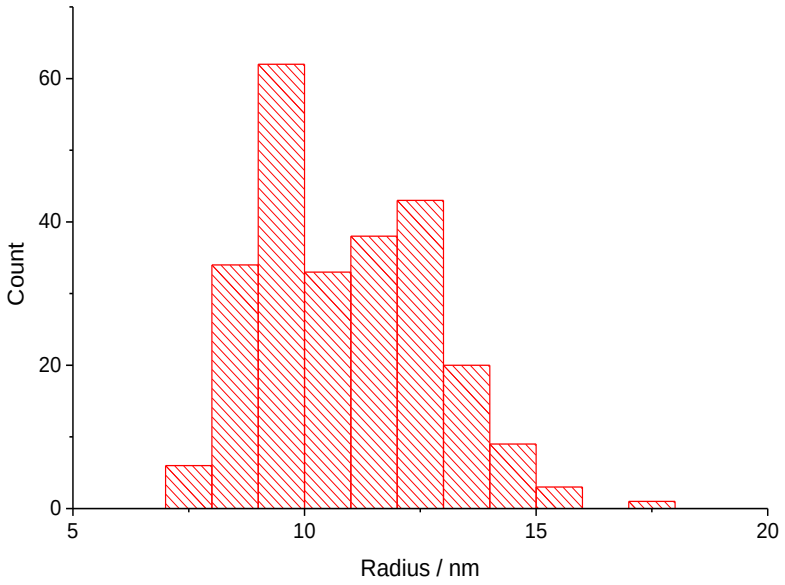


Figure S5 *Size distribution of the produced silver nanoparticle suspension.*



References

[1] Y.-G. Zhou, N. V. Rees, R. G. Compton, *Angew Chem Int Ed* **2011**, *50*, 4219-4221.

[2] J. Ellison, K. Tschulik, E. J. Stuart, K. Jurkschat, D. Omanović, M. Uhlemann, A. Crossley, R. G. Compton, *ChemistryOpen* **2013**, *2*, 69-75.

[3] E. J. E. Stuart, K. Tschulik, D. Omanovic, J. T. Cullen, K. Jurkschat, A. Crossley, R. G. Compton, *Nanotechnology* **2013**, *24*, 444002.