Effects of surfactants on electrochemically prepared Ag nanostructures

Farkhondeh Fathi,^a Heinz-Bernhard Kraatz^{*a}



Fig. SI-1. Impedance spectra after cycling Ag in 0.1 M KOH: (a) with citrate (b), with PVP (c), with Tween-20 (d) and 0.01 M KOH: (e), with citrate (f), with PVP (g), with Tween-20 (h). Data points represent experimental results while solid lines correspond to spectra calculated for an equivalent circuit shown in Figure 1C. EIS were acquired at the potential of 0 V vs. Ag/AgCl at 10 mV amplitude and in the 0.01 Hz to 100 kHz range.

Solution	R_s/Ω	$C_{dl}\!/\mu F$	R_{ct}/Ω	$Q/mS.s^{-n}$	n	R_{f}/Ω	W/ mS.s ^{-0.5}
а	7.21±1.75	0.02 ± 0.00	85.51±9.80	0.32 ± 0.00	0.88 ± 0.00	15200.00±483.16	8.84±0.25
b	5.46 ± 0.10	0.03 ± 0.00	56.89±0.29	0.27 ± 0.03	0.86 ± 0.00	12776.67±155.03	2.21±0.10
с	9.61±0.28	0.02 ± 0.00	93.23±0.64	0.25 ± 0.04	0.85 ± 0.00	13210.00±1167.80	88.60±15.31
d	4.76±1.23	0.03 ± 0.00	94.34±1.54	0.08 ± 0.02	0.63 ± 0.03	22600.00±1456.64	0.02 ± 0.00
e	65.53 ± 2.08	-	735.50±2.40	0.09 ± 0.01	0.92 ± 0.00	14465.00 ± 403.05	0.56±0.29
f	13.53 ± 1.00	0.01 ± 0.00	146.05 ± 0.07	0.23 ± 0.04	0.88 ± 0.01	9155±811.76	2.92 ± 0.97
g	73.39±1.05	-	810.3±0.88	0.06 ± 0.00	0.91 ± 0.00	12903.33±657.29	10.10 ± 0.75
h	78.03±3.27	-	$1038.00{\pm}1.41$	0.08 ± 0.03	0.74 ± 0.06	2172±156.97	0.04 ± 0.01

Table SI-1. Impedance parameter values extracted from the fitting (Figure 1C) to the equivalent circuit for impedance spectra recorded in pure 0.1M KOH (a) and with citrate (b), PVP (c), Tween-20 (d) and in pure 0.01M KOH (e) and with citrate (f), PVP (g) and Tween-20 (h).



Fig. SI-2. Calibration curve of AgNO3 solution for GFAA measurements.



Fig. SI-3. The film thickness of formed deposited Ag NSs on the Ag surface after cycling Ag foil in the potential range of -0.4 to 0 V vs Ag/AgCl at a scan rate of 150 mVs⁻¹ in the 0.1 M KOH (a) and in the 0.1M KOH with citrate(b). There is a slightly thicker film of the nanostructured Ag film after addition of citrate due to the corrosion enhancement of the Ag leading to more dissolution and deposition of Ag at the same time window.

Electronic Supplementary Material (ESI) for Analyst This journal is $\ensuremath{\mathbb{C}}$ The Royal Society of Chemistry 2013



Electronic Supplementary Material (ESI) for Analyst This journal is $\ensuremath{\mathbb{C}}$ The Royal Society of Chemistry 2013



Electronic Supplementary Material (ESI) for Analyst This journal is The Royal Society of Chemistry 2013



Electronic Supplementary Material (ESI) for Analyst This journal is $\ensuremath{\mathbb{C}}$ The Royal Society of Chemistry 2013









Fig. SI-4. Mass spectra for 0.01M KOH (a-c) and 0.1M KOH with citrate (d-g) after exposure to Ag bulk and cycling at 150 mVs⁻¹ between 0.5 and 0.9 V vs. Ag/AgCl for 16 CV scans. The presence of $Ag(OH)_2H_2O$ ion (160.9076 and 162.9058 for two Ag isotopes) (a) and $[AgO(OH)_2H_2O[^{2-}$ ion (176.8823, 178.8806) (b) corroborate The dissolution of Ag in the alkaline solution. The presence of $[AgC_6H_5O_7(OH)_3(H_2O)_4]^{5-}$ (419.8582-422-3596 for isotopes), AgC12H11O13 ⁵⁻(471.5053-472.8393 for isotopes) and Ag (C₆H₇O₇)₂(H₂O)₄]⁵⁻ (572.7986-575.2987 for isotopes) (d-g), determined the presence of Ag citrate cluster formation in the solution after cycling Ag in the alkaline solution containing citrate.



Fig. SI-5. TEM images from the solution of 0.01 M KOH (a), 0.01M KOH with citrate (b), 0.01M KOH with PVP and 0.01M KOH with Tween-20 after cycling Ag for 16 times in the range of -0.5 to 0.9 V vs Ag/AgCl. The results show the presence of nano species in the solution which approved the release of Ag nanoparticles to the solution from the Ag NSs surfaces.



Fig. SI-6. Typical underpotential deposition (UPD) graph. Cadmium deposited on nanostructured-Ag surface from a solution of CdSO₄ (6×10^{-3} M) and Na₂SO₄ (0.1M) at pH=5. The CVs were recorded at a scan rate of 0.01 V.s^{-1} in the potential range of -1.2 and 0.2 V vs. Ag/AgCl.

Table SI-1. Results for real surface area of nanostructured Ag surfaces after cycling in 8M KOH. The surface area of polycrystalline Ag foil which is exposed to KOH solution is 0.063 cm^2 before roughening.

Number of cycles	1	5	10	15
Surface (cm ²)	4.93±0.32	5.90±0.10	4.12±0.72	5.09±0.23