

Supplementary Information

Eco-friendly polymer succinate capping on silver nano-particles for enhanced stability: a UV-Vis and electrochemical particle impact study

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S1 UV-Vis spectrophotometry

A solution of AgNO₃ and HPC-Suc was exposed to sunlight and the synthesis of the Ag NPs@suc in aqueous solution was monitored periodically (after an exposure time of 15 s, 30 s, 60 s, 90 s, 105 s, 120 s and 25 min) by recording the absorption spectra over a wavelength range of 300-800 nm. Upon exposure to sunlight during an initial period of 15 s to 25 min, the Ag⁺ was reduced to Ag Nps@suc and color of solution changed from light yellow to reddish brown. A single and broad LSPR peak was observed in the range 411-452 nm, confirming the synthesis of Ag Nps (Figure S1) (Mulvaney, 1996). This LSPR absorption peak showed a red shift in λ_{\max} and an increase in the intensity of absorption upon the increase of exposure time to sunlight, which suggests that the size of the Ag Nps@suc increases with an increase in exposure or reaction time (Abbas et al., 2015; Ding et al., 2017).

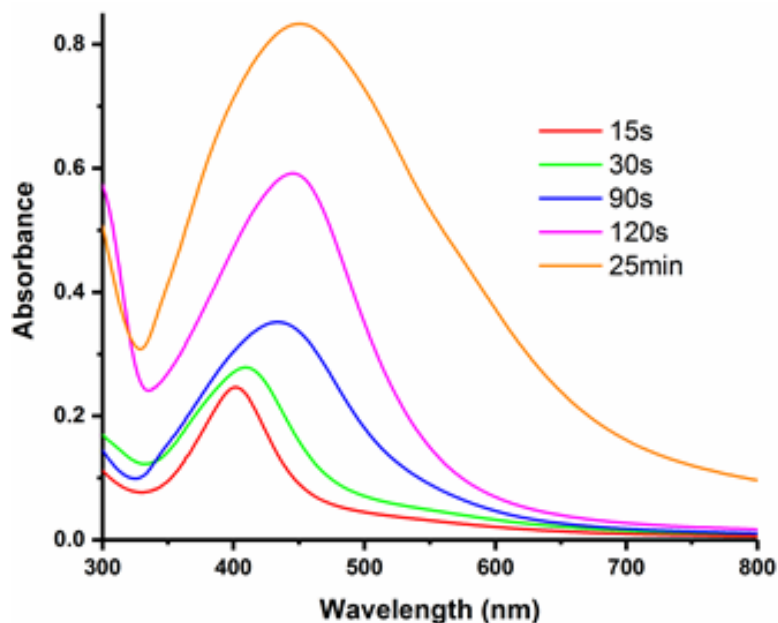


Figure S1. UV-Vis spectra of Ag Nps@suc showing a red shift and increase in absorption with exposure time to sunlight

S2 SEM-EDX measurement

The success of the synthesis of Ag Nps@suc was supported by the appearance of a signal in the silver region in the EDX spectrum (around 3 keV) (Kaviya et al., 2017) as shown by Figure S3. The EDX profile of Ag Nps@suc also shows signals for oxygen and carbon, which likely originates from the HPC-Suc capping agent or reduction product or from glassy carbon substrate. Elemental EDX mapping (Figure S2 E-G) of Ag Nps@suc shows that Ag Nps are randomly dispersed throughout the Ag Nps@suc sample. The EDX elemental analysis also showed the presence of the elements (Ag, C and O) expected to be present in the Ag Nps@suc.

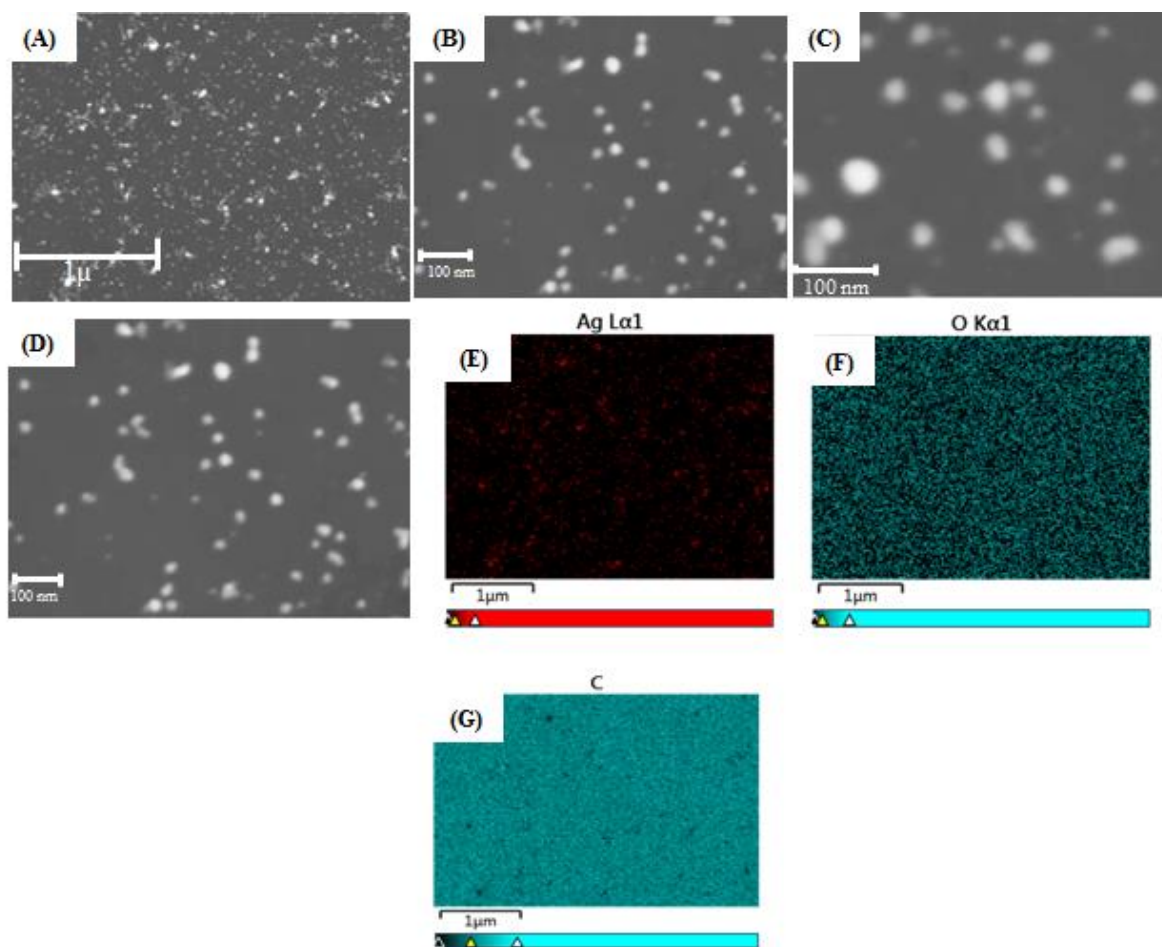


Figure S2. (A-D) SEM images of Ag Nps@suc synthesized by mixing aqueous solutions of HPC-Suc (1% w/v) and 50 mM Ag NO₃ followed by exposure to sunlight and (E-G) elemental mapping of Ag Nps@suc from EDX.

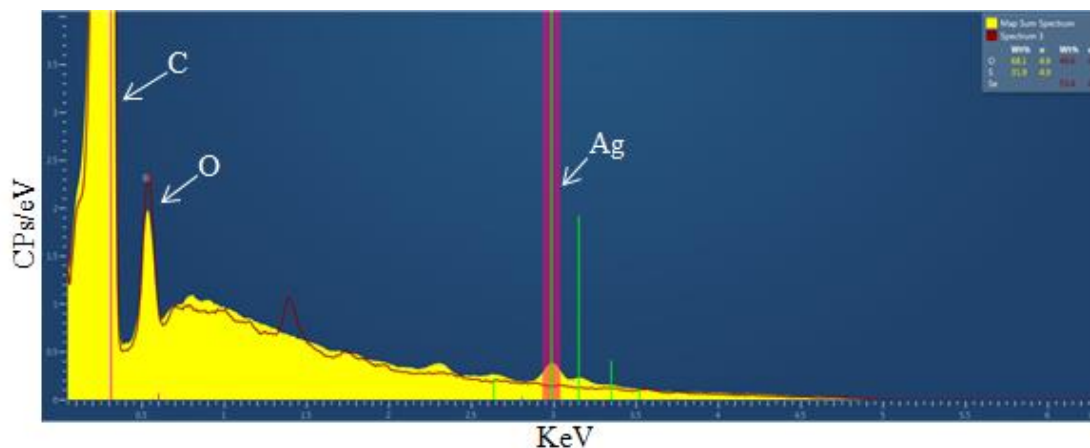


Figure S3. Representative EDX profile of corresponding area shown in Figure 3 of synthesized silver nanoparticles showing signals for C, O and Ag

S3 ATR-FTIR spectroscopic characterization

In order to identify various functional groups present in HPC-Suc and Ag Nps@suc ATR-FTIR spectra of HPC, HPC-Suc and Ag Nps@suc were recorded (Figure 4S). The ATR-FTIR spectrum of HPC shows absorption bands at 3433, 2902 and 1160-1057 cm^{-1} indicating the presence of $-\text{OH}$, $-\text{CH}_2-$ and C-O-H and C-O-C bonds, respectively. The appearance of absorption peaks in the FTIR spectrum of HPC-Suc at 1726, 1618, 1399, 1260 and 1140-1007 cm^{-1} due to C=O, COOH, C-O, C-O-H and C-O-C bonds, respectively is attributed to the successful esterification of HPC to form HPC-Suc. The FTIR spectrum of Ag Nps@suc showed bands closely similar to those in FTIR spectrum of HPC-Suc. Retention of all these signals with the expected slight shift of frequency, in the FTIR spectrum of Ag Nps@suc is a strong evidence that HPC-Suc is present as capping agent of Ag in this study.

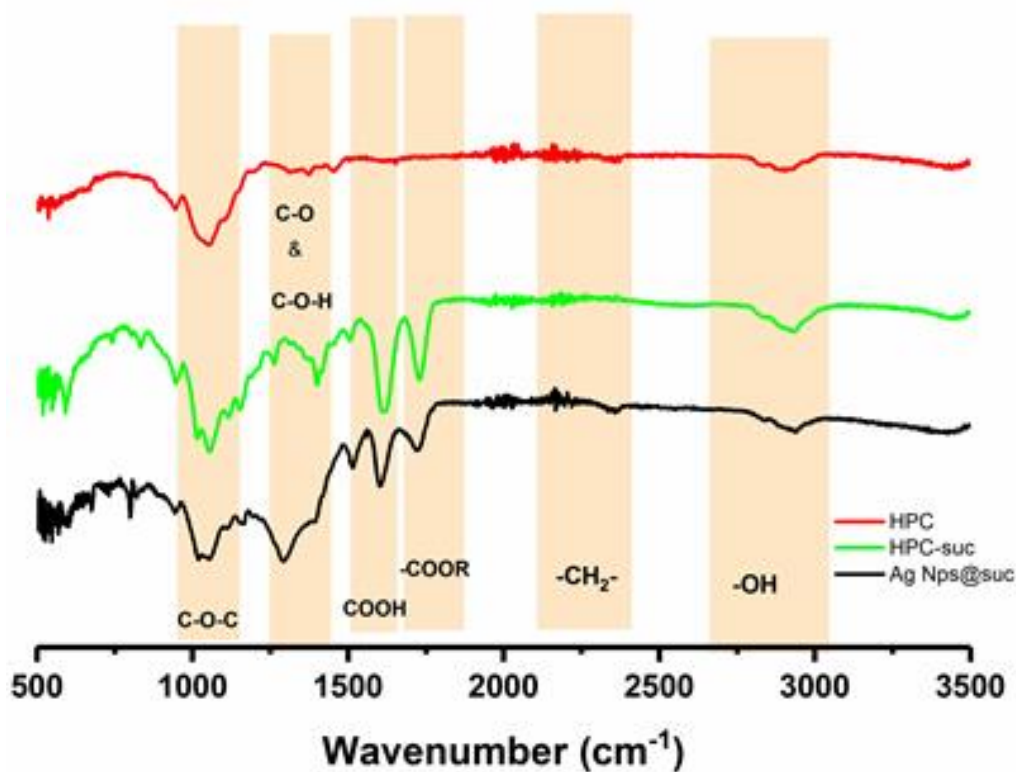


Figure S4. Overlay ATR-FTIR spectra of HPC (red), HPC-Suc (green) and Ag Nps@suc (black)

The shifting of the C=O signal to 1724 cm^{-1} , -COOH signal to 1602 cm^{-1} , C-O signal to 1293 cm^{-1} , C-O-H, C-O-C signal to $1020\text{-}1057\text{ cm}^{-1}$ and the appearance of a $527\text{-}569\text{ cm}^{-1}$ signal due to Ag---O weak interactions in FTIR spectrum of Ag Nps@suc shows successful capping of Ag Nps by HPC-Suc (Gupta et al., 2010; Shameli et al., 2012)

S4 DLS and ZP

The ZP value and the z-averag for Ag Nps@suc were also measured as shown in Figure S5 A and S5 B, respectively.

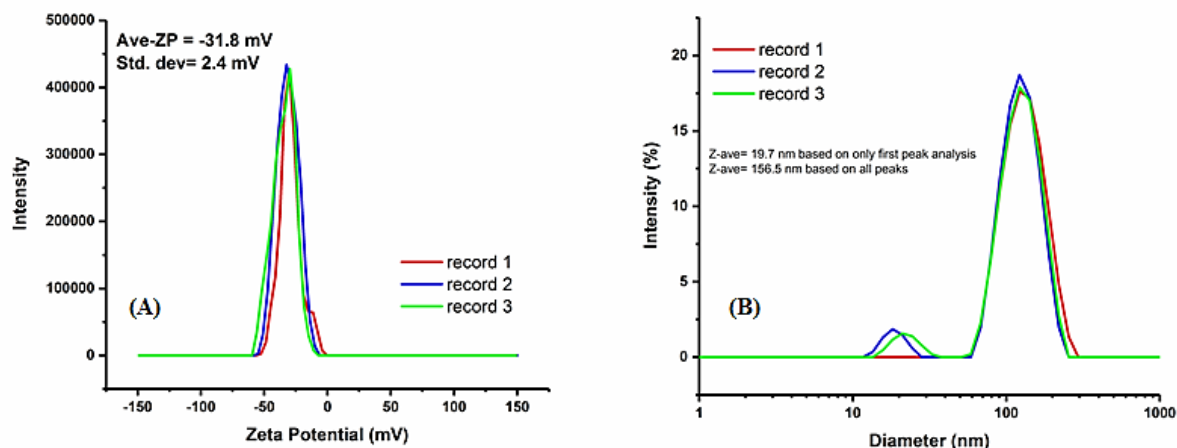


Figure S5. (A) Zeta-potential and (B) Z-averager of synthesized Ag Nps@suc

S5 Determination of the concentration of Ag Nps@suc in a suspension

The concentration of a Ag Nps suspension was estimated by UV-Vis using the procedure of Ngamchuea and co-workers (Ngamchuea et al., 2017a). Accordingly, first, the absorbance (A) of the suspension of Ag Nps@suc was determined and the molar extinction co-efficient (ϵ) for “one Ag atom” measured for citrate capped Ag Nps of size 20 nm was assumed to apply for Ag Nps@suc ($15500 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$). The concentration of suspension in terms of silver atoms was determined by $C=A/\epsilon l$, where l is the optical path length of the quartz cell used for UV-Vis measurement (10 mm). This concentration is divided by the number of silver atoms in one nanoparticle to convert it into concentration in terms of Ag Nps. The number of silver atoms in one silver nanoparticle can be determined by:

$$\text{Number of silver atoms in one nanoparticle} = (V_{Np} \times N_A \times \rho) / M \quad (1)$$

where V_{Np} is the volume of one nanoparticle, N_A is the Avogadro constant, ρ is the density of silver, M is the atomic mass of silver. The number of silver atoms in one average nanoparticle of Ag Nps@suc was calculated to be $(2.45 \pm 2.5) \times 10^5$. The concentration of Ag Nps was found to be $189 \pm 6.5 \text{ pM}$.

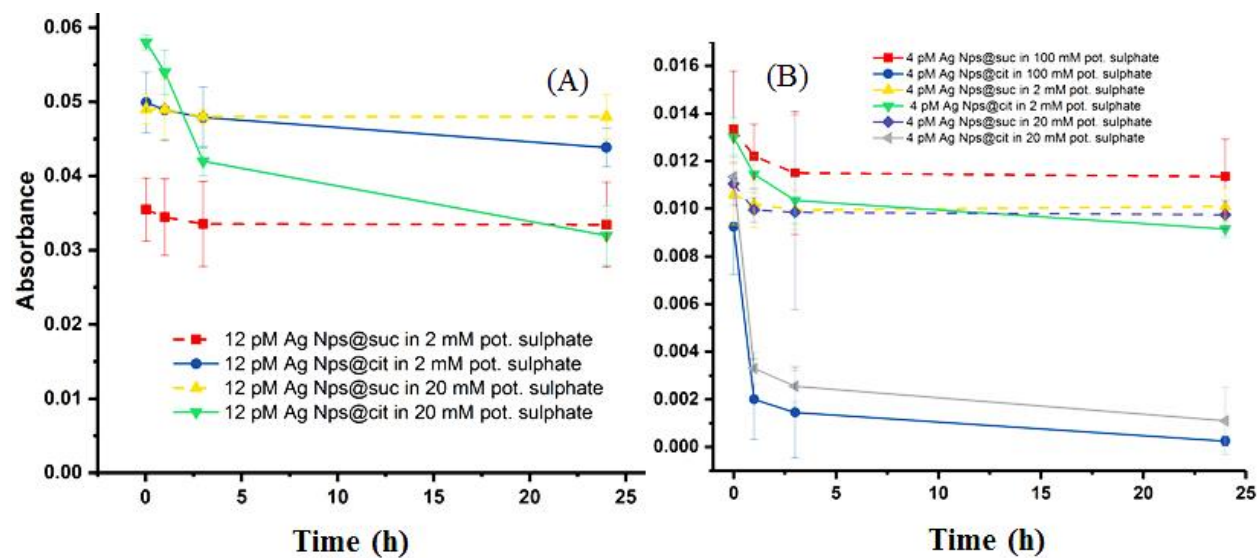


Figure S6. Absorbance as a function of time of Ag Nps@suc and Ag Nps@cit (A) 12 pM Ag Nps in 2 and 20 mM K₂SO₄ and (B) 4 pM Ag Nps in 2, 20 and 100 mM K₂SO₄

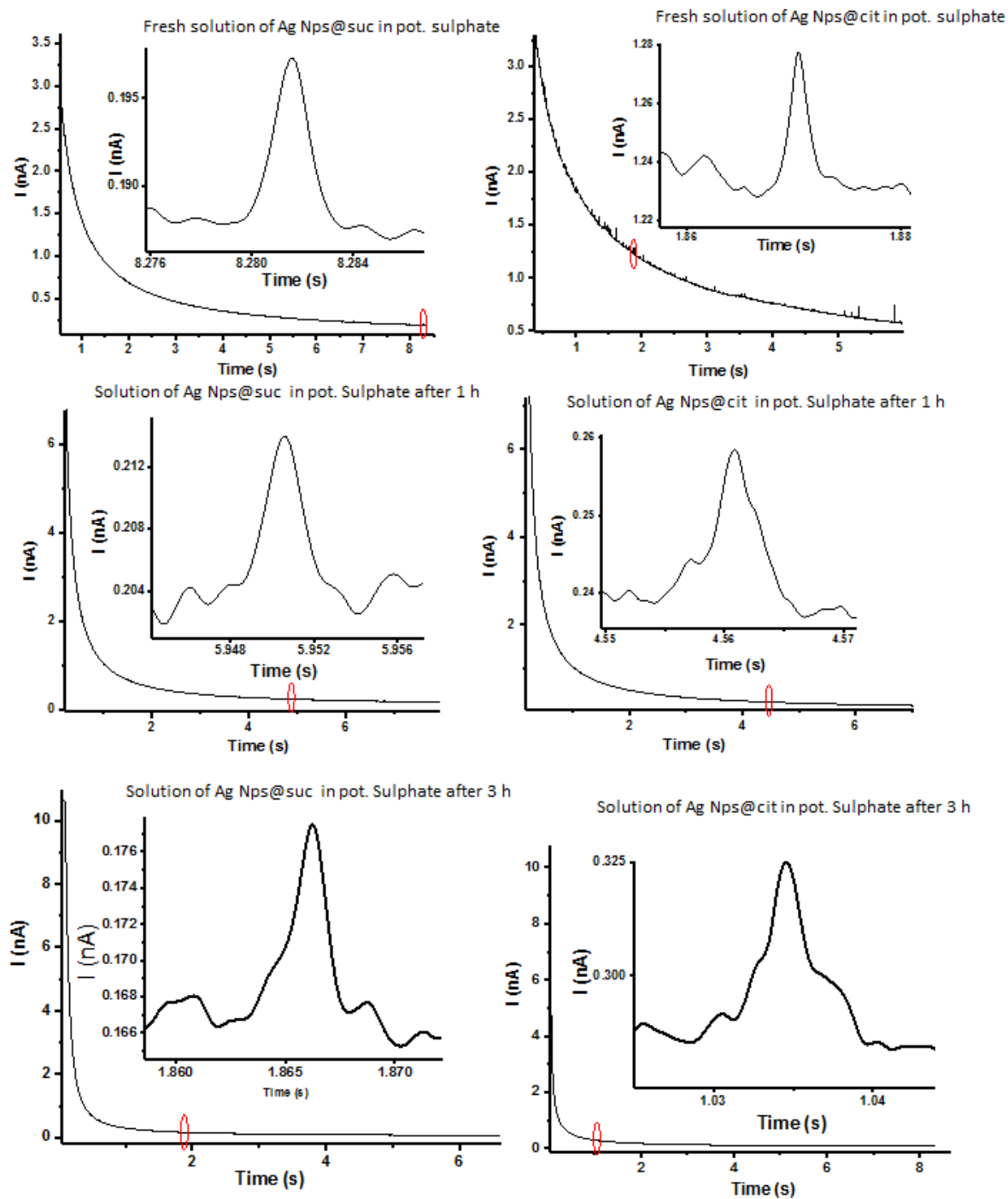


Figure S7. Chronoamperogram showing representative nano-impact spikes of 12 pM Ag Nps@suc and Ag Nps@cit in 100 mM K_2SO_4 using 33 μm carbon microdisc electrode, leakless Ag/AgCl reference electrode and platinum counter electrode in a fresh solution of silver nanoparticles and a solution kept in electrolyte for 1 h and 3 h (the inset depicts the enlarged chronoamperogram)

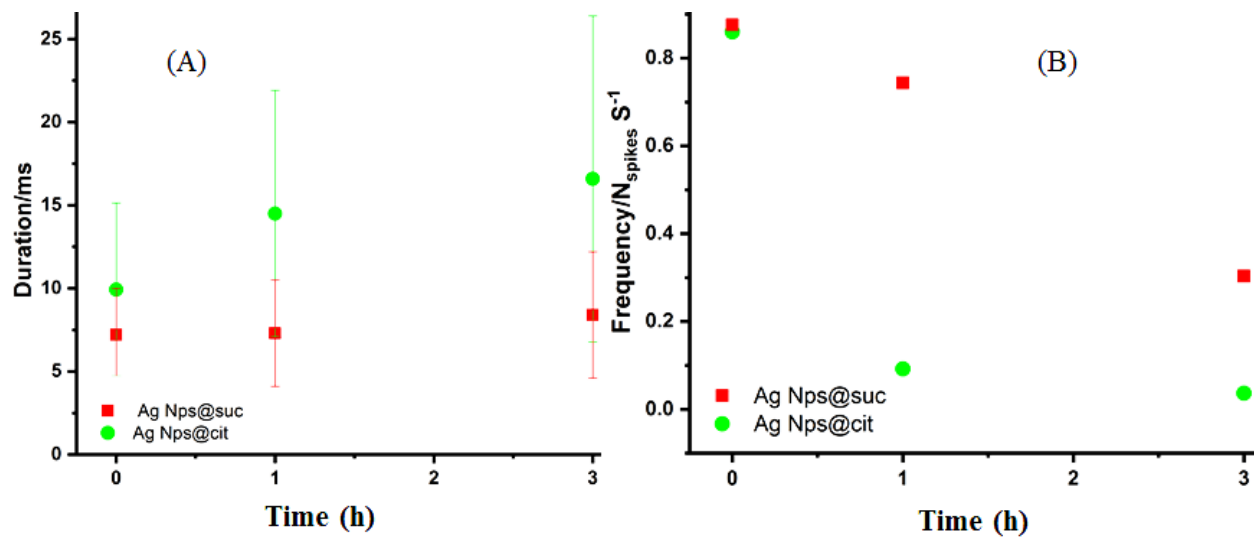


Figure S8. Duration (A) and frequency (B) of spikes of 12 pM Ag Nps@suc and Ag Nps@cit in 100 mM K_2SO_4 as a function of time

Table S1. Change in the relative absorbance for fresh solution 4 pM and 12 pM of Ag Nps in 2 mM, 20 mM and 100 mM of electrolyte K₂SO₄ with time as calculated from UV-Vis

Conc. of Ag Nps	Time (h)	AgNps@cit			AgNps@suc		
		(relative absorbance %)			(relative absorbance %)		
		100 mM K ₂ SO ₄	20 mM K ₂ SO ₄	2 mM K ₂ SO ₄	100 mM K ₂ SO ₄	20 mM K ₂ SO ₄	2 mM K ₂ SO ₄
12 pM	0	100	100	100	100	100	100
	0.02	47.3	87.8	87	99.8	99.8	98.8
	1	14.8	95.9	81	97.5	96.7	98.7
	3	11.4	94	63	94.5	94.2	97
	24	0.20	86	48	90.5	94.1	97
4 pM	0	100	100	100	100	100	100
	0.02	47.2	92.9	93.3	96.5	96.4	95.7
	1	10.3	82.2	17.8	87.8	92.3	86.2
	3	6.0	74	15	82.8	91.5	85
	24	0.1	66.1	10	82.8	91.4	84.5

Table S2. Change in relative absorbance for fresh solution of 4 pM and 12 pM Ag Nps in 2 mM, 20 mM and 100 mM of electrolyte (KCl, KBr and NaCl) with time as calculated from UV-Vis

Conc. of Ag Nps / Conc. of electrolyte	Time (h)	AgNps@cit (relative absorbance %)			AgNps@suc (relative absorbance %)		
		KCl	KBr	NaCl	KCl	KBr	NaCl
12 pM/100 mM	0	100	100	100	100	100	100
	1	21.2	9.9	15.9	64.6	87.8	50
	3	9.9	3.2	5	40.1	71.4	41
	24	0.9	0.01	0.001	10.1	16	5
4 pM/100 mM	0	100	100	100	100	100	100
	1	28.9	23.4	8	93.3	52.9	60.9
	3	15	0.001	0.001	42.9	14.8	29
	24	0.001	0.001	0.001	11.7	7.0	2.4
12 pM/20 mM	0	100	100	100	100	100	100
	1	94.3	91	81.1	111.5	99.9	114.4
	3	88.5	88.2	75	120	99.79	127
	24	38	5.8	58.5	127	34.3	108.3
4 pM/20 mM	0	100	100	100	100	100	100
	1	84.7	74.7	82.9	105.8	75	103.8
	3	74.4	54.9	64.3	101.9	64.1	91.3
	24	37.8	11.9	14.5	81.7	45.3	58.6
12 pM/2 mM	0	100	100	100	100	100	100
	1	98.4	95	99.1	106	111	105
	3	97.8	88.1	96.9	108	115	107
	24	96.7	42	81.6	107	40	99.6
4 pM/2 mM	0	100	100	100	100	100	100
	1	96.9	95.1	96.4	107.8	77.7	103.7
	3	95.1	95	92.6	115.4	76	109
	24	81.8	64	73	112.7	45.7	95.0

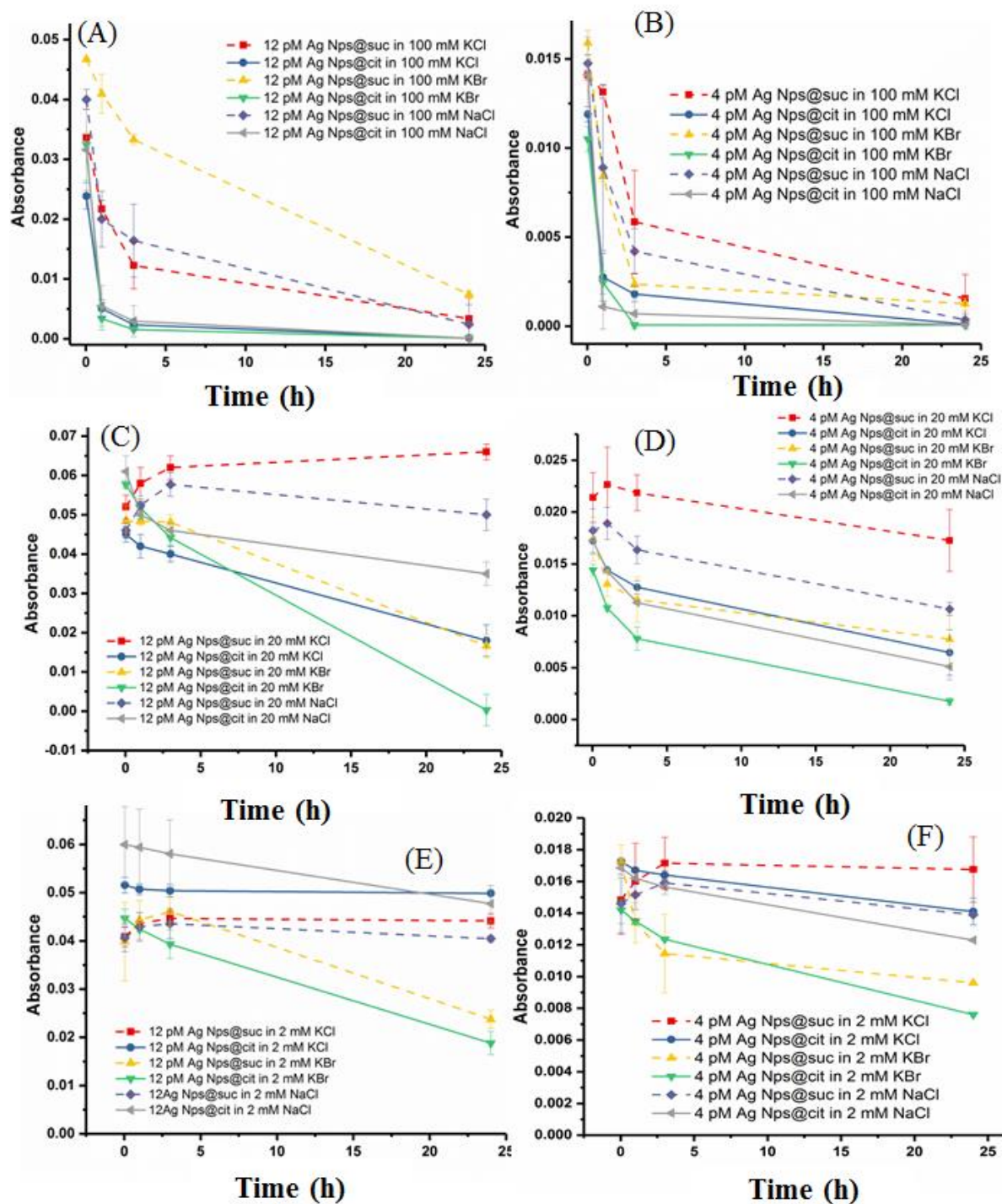


Figure S9. Absorbance as a function of time of Ag Nps@suc and Ag Nps@cit (A) 12 pM Ag Nps in 20 mM electrolyte, (B) 4 pM Ag Nps in 20 mM electrolyte, (C) 12 pM Ag Nps in 100 mM electrolyte, (D) 4 pM Ag Nps in 100 mM electrolyte, (E) 12 pM Ag Nps in 2 mM electrolyte and (F) 4 pM Ag Nps in 20 mM electrolyte

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