

Gold Nanorods Derivatized with CTAB and Hydroquinone or Ascorbic Acid: Spectroscopic Investigation of Anisotropic Nanoparticles of Different Shape and Size

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SUPPLEMENTARY INFORMATION

Table S1. Experimental conditions and plasmonic peaks for AuNRs. [AgNO₃] = 0.004 M, [CTAB] = 0.2 M, [AA] = 0.078 M, [HQ] = 0.1 M and [HAuCl₄] = 0.001 M.

*Conditions of samples used for spectroscopic characterizations in this work

ID	AgNO ₃ (mL)	Seed solution (mL)	Reducing agent (mL)	[HAuCl ₄] (mL)	CTAB (mL)	Plasmonic peaks (nm)	Size Ratios (with statistics from TEM measurements)
A	0.4	0.024	AA, 0.14	5	10	514-721	L = 44 ± 9 nm; W = 12 ± 8 nm; size ratio = 3.6
B	0.4	0.024	AA, 0.14	5	5	511-763	L = 42 ± 9 nm; W = 10 ± 3 nm; size ratio = 4.2
C*	0.4	0.024	AA, 0.07	5	5	511-768	L = 40 ± 6 nm, W = 10 ± 2 nm; size ratio = 4.0
D	0.4	0.024	HQ, 0.5	5	5	535-648	L = 95 ± 9 nm; W = 14 ± 9 nm; size ratio = 6.0
E	0.2	0.160	HQ, 0,5	5	5	536-703-997	L = 113 ± 9 nm; W = 15 ± 9 nm; size ratio = 7,5
F*	0.1	0.160	HQ, 0,5	5	5	535-720-1086	L = 100 ± 8 nm; W = 14 ± 4 nm size ratio = 7.1

Table S2. XPS results collected on AuNRs-AA and AuNRs-HQ (BE, FWHM, Atomic Percentage values and proposed assignments).

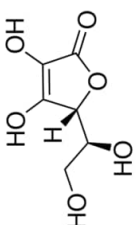
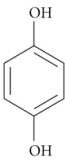
Sample	Signal	BE (eV)	FWHM (eV)	Atomic Percentage (%)	Assignment
AuNRs-AA 	C1s	285.00	1.34	86	C-C
		286.35		8	C-N/C-O CTAB+AA
		287.78		4	C=O AA+impurities
		289.15		2	COOH impurities
	N1s	398.93	1.68	12	C-N CTAB – AA electrostatic interactions
400.03	26	-N ⁺ terminal in “external” CTAB			
402.87	62	-N ⁺ in Ag(I) – Br ⁻ – CTA ⁺ complex			
Br3d _{5/2}	68.22	1.20	71	Br ⁻ counterions of CTAB	
	69.25		23	Br ⁻ in Ag(I) – Br ⁻ – CTA ⁺ complex	
	71.21		6	R-Br	
Ag3d _{5/2}	367.32	0.56	88	Ag(I)	
	368.07		12	Ag(0)	
Au4f	83.70	0.47	90	Au(0)	
	84.27		10	Au ^{δ+}	
AuNRs-HQ 	C1s	285.00	1.20	85	C-C alifatic + aromatic
		286.87		12	C-N/C-O CTAB+HQ
		288.12		2	C=O impurities
		288.84		1	COOH impurities
	N1s	399.60	1.62	42	-N ⁺ terminal in “external” CTAB
402.80	58	-N ⁺ in Ag(I) – Br ⁻ – CTA ⁺ complex			
Br3d _{5/2}	68.11	1.21	62	Br ⁻ counterions of CTAB	
	69.22		34	Br ⁻ in Ag(I) – Br ⁻ – CTA ⁺ complex	
	70.97		4	R-Br	
Ag3d _{5/2}	367.25	0.58	96	Ag(I)	
	367.85		4	Ag(0)	
Au4f	83.11	0.46	82	Au(0)	
	83.71		18	Au ^{δ+}	

Figure S1. EDX data collected on a) AuNRs-HQ; b) AuNRs-AA

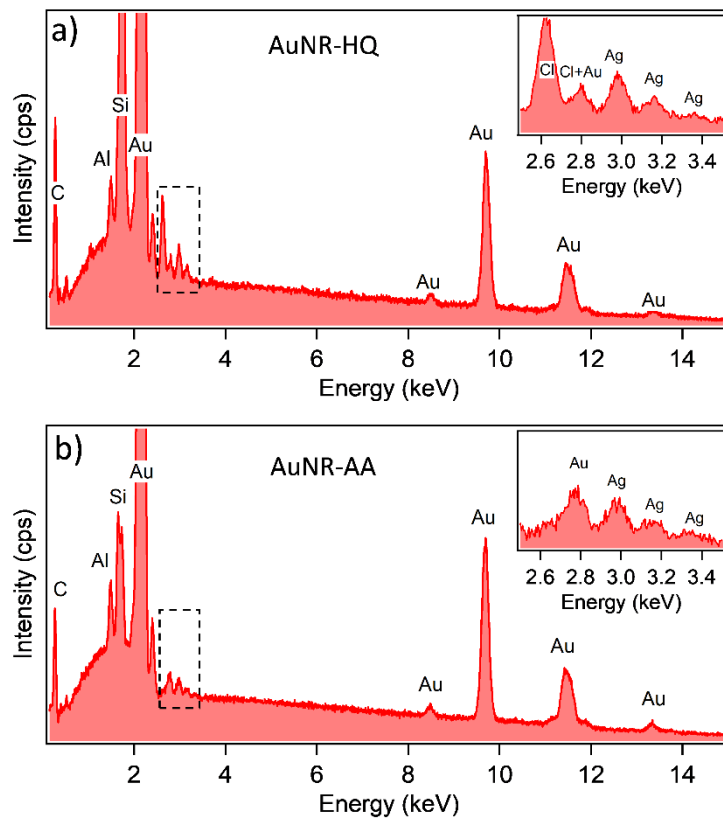


Figure S2. XPS spectra collected at C1s core-level on AuNRs-HQ and AuNRs-AA. C1s spectra of AuNRs-AA (a) and AuNRs-HQ (b) appear composite and at least four components can be individuated by following a peak-fitting procedure: the peak at lower BE (285.0 eV) is due to aliphatic C-C groups of CTAB and AA or, for AuNRs-HQ, C-C of CTAB superimposed to aromatic C of hydroquinone; the peaks at about 286.5 eV are due to C-N (CTAB) and C-O (AA, HQ) signals, that are impossible to deconvolute with the used resolution. The component at 287.8 eV in AuNRs-AA is attributed to the C=O functional group of AA, with a contribution attributed to adventitious carbon ($C_{adv} = O$) or amide groups arising by contaminants usually observed in samples prepared in wet environment, as also reported in the literature for CTAB-stabilized AuNRs [17: C. Oliveira et al., *J. materials res. technol.*, 2021, **15**, 768-776]. For AuNRs-HQ the entire 288eV spectral component arises from such impurities. Finally, the signal of extremely low intensity observed in both samples at 289.2 eV is due to carboxylic groups of contaminants ($C_{adv}OOH$), coherently with similar systems [26: V. Secchi et al., *ACS Biomater. Sci. Eng.*, 2019, **5**, 2190–2199.].

