

ELECTRONIC SUPPORTING INFORMATION

Galvanic replacement based Cu_2O self-templating strategy for the synthesis and application of Cu_2O -Ag heterostructures, and hollow metallic (Ag, Au-Ag) mesocages

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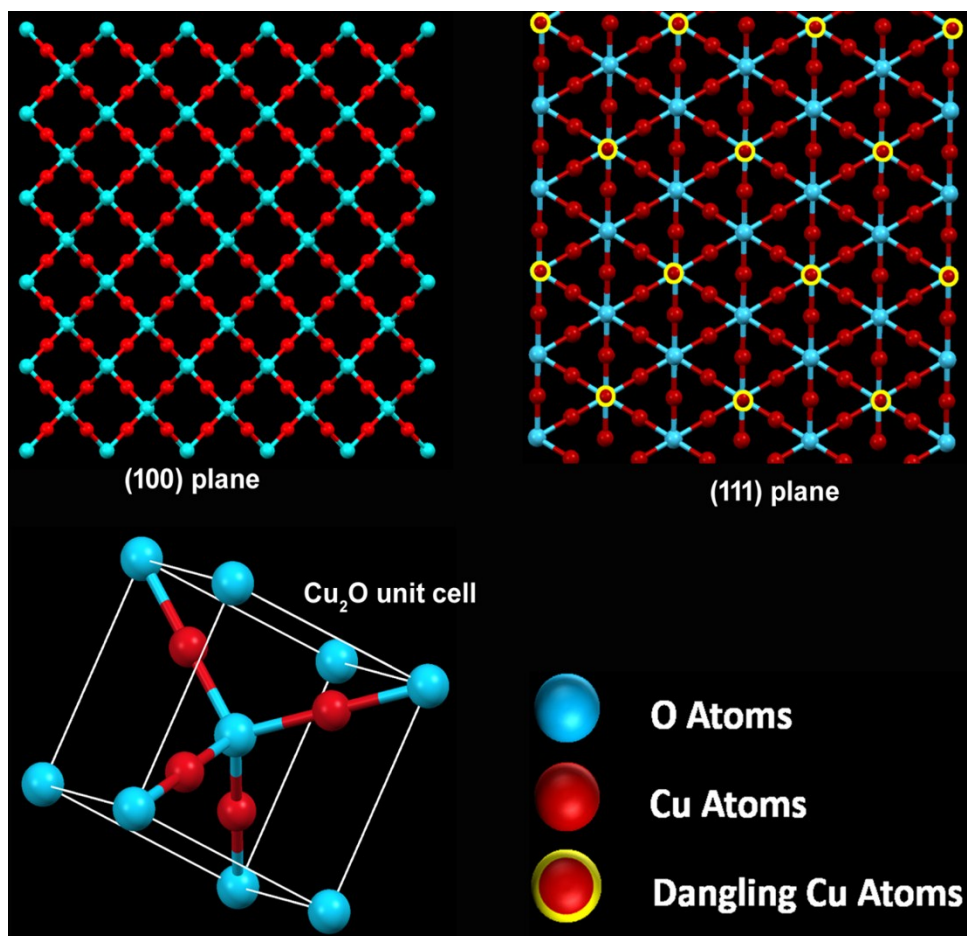


Figure S1: Crystal structure of Cu_2O with (100), (111) planes, and unit cell structure. The Cu atoms with dangling bonds are highlighted with yellow circles (All representations were obtained using Mercury 3.8 Software).

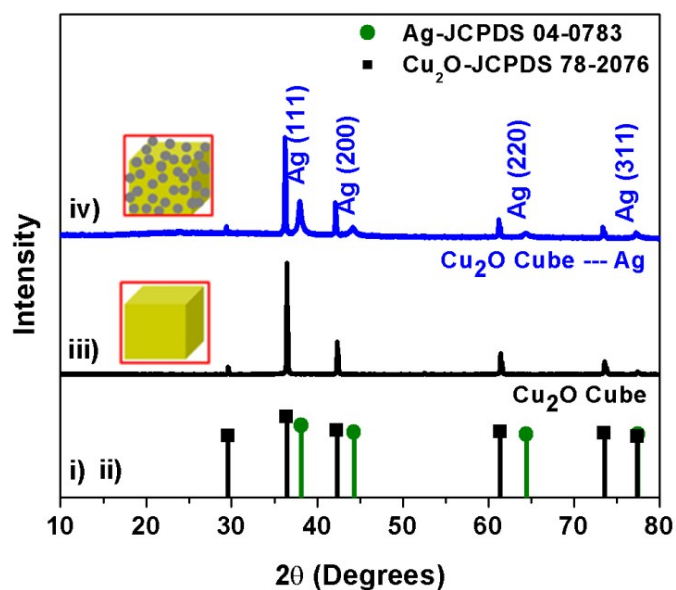


Figure S2: Powder XRD pattern of i) standard Cu_2O JCPDS file 78-2076, ii) standard Ag JCPDS file 04-0783, iii) Cubic Cu_2O particles, and iv) Cubic Cu_2O -Ag composite hetrostructure.

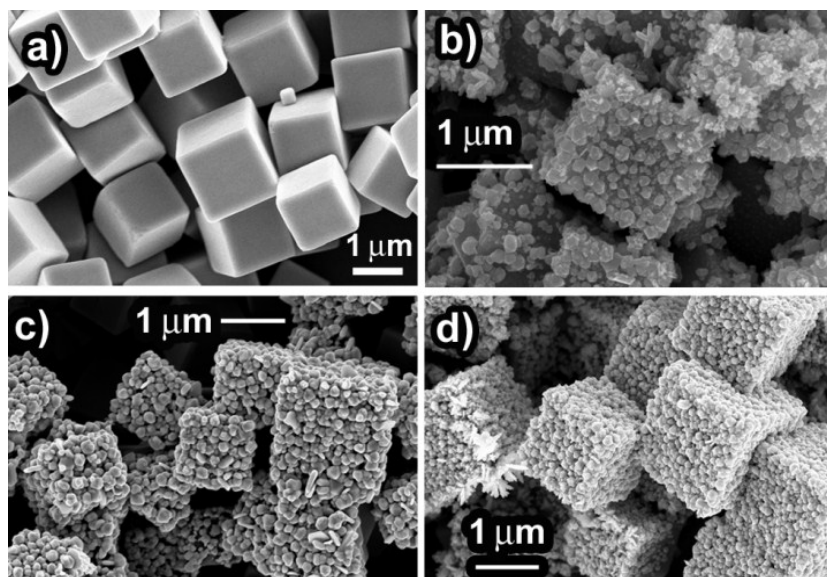


Figure S3: a) FESEM image of Cu_2O cube before GRR. b-d) FESEM image of cubic Cu_2O -Ag heterostructures after undergoing GRR with increasing $[\text{AgNO}_3]$ solution clearly showing increased loading density of Ag NPs decorating the cubic Cu_2O surface.

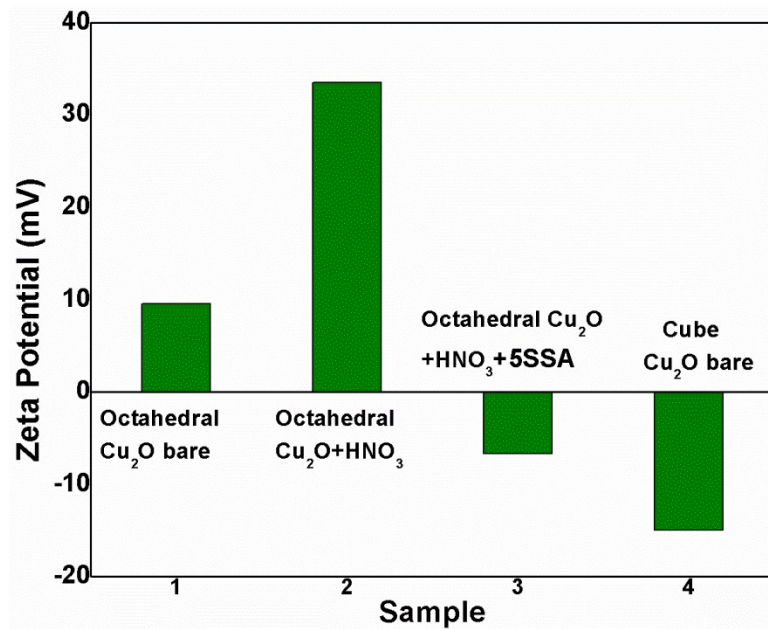


Figure S4: Zeta potential values measured for different samples under the experimental conditions.

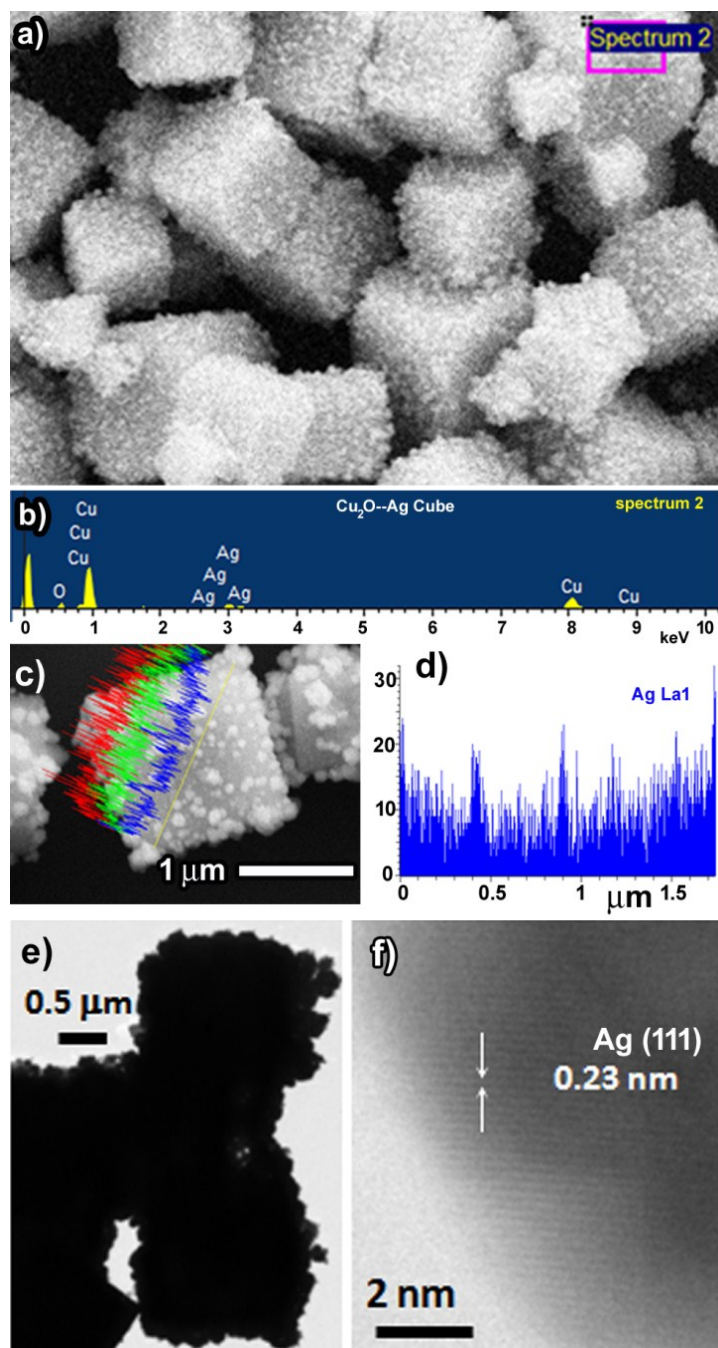


Figure S5: EDS spectrum of the (b) Cubic Cu_2O -Ag heterostructures from the highlighted region of the sample shown in (a) Line-scan EDS analysis of a (c-d) cubic Cu_2O -Ag heterostructure clearly identifying the Ag NPs decorating the surface of Cu_2O particles. TEM image of e) cubic Cu_2O -Ag heterostructure; f) observed lattice fringes from Ag NPs on the cubic Cu_2O -Ag heterostructure.

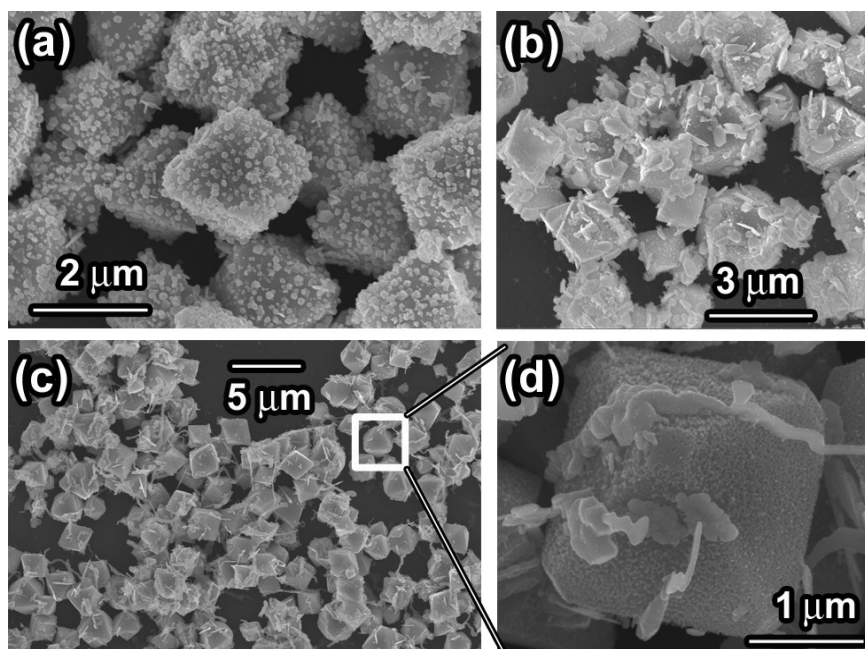


Figure S6: Effect of nitric acid and 5SSA on the morphology of the heterostructure: a) Cu_2O octahedra undergoing GRR with silver nitrate in presence of a) nitric acid and 5SSA; b) nitric acid only c) 5SSA only; d) magnified view of c).

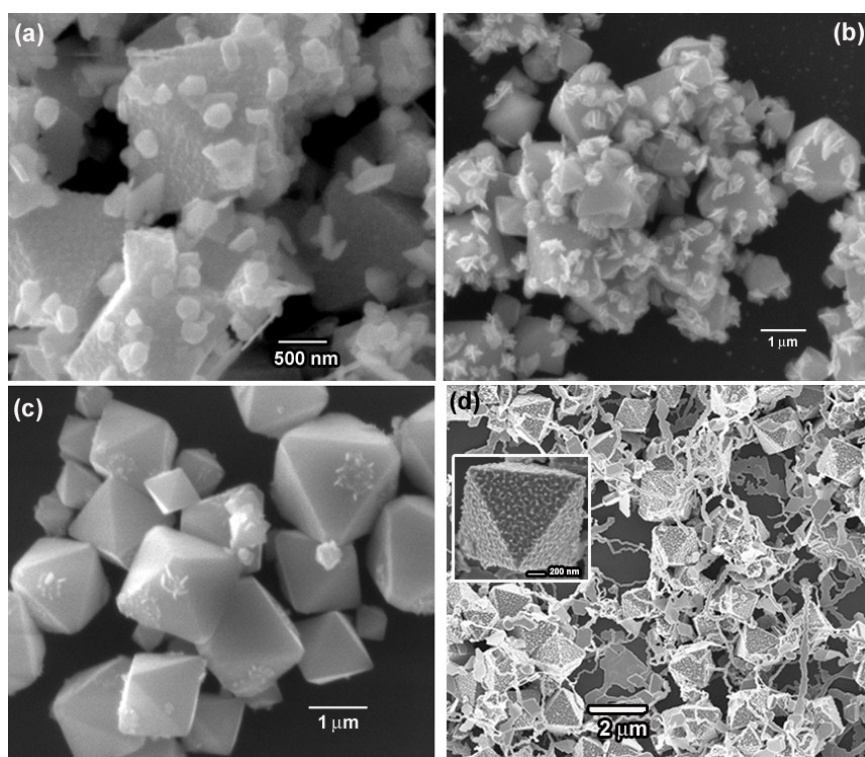


Figure S7: Effect of different surfactants on the morphology of the attained Cu_2O -Ag heterostructures : a) Oxalic acid, b) Citrate, c) SDS, d) PVP

Table S1: Peak frequencies (cm⁻¹) and their assignments for SERS/Raman spectra of p-MA.

Reference Raman	SERS	Peak Assignment
1598		vCC (a ₁)
1572	1576	vCC (b ₂)
1490	1475	vCC + δCH (a ₁)
1480		vCC + δCH (a ₁)
1445	1436	vCC + δCH (b ₂)
1403	1390	δCH + vCC (b ₂)
1310	1308	vCC + δCH (b ₂)
1266		vCH(a ₁)
1206		vCH(a ₁)
1173	1191	δCH(a ₁)
1142	1144	δCH (b ₂)
1118		δCH (b ₂)
1089	1078	vCS + vCC(a ₁)
1011	1007	γCC + γCCC (a ₁)
960	950	πCH(a ₂)
	921	πCH (b ₁)
820	820	πCH (b ₁)
	750	πCH (b ₂)
	723	πCH + πCS + πCC (b ₁)
633	634	γCCC (a ₁)

v-stretch; δ,γ-bend; π-wag; a₁, b₂: in plane mode; a₂, b₁: out of plane mode of benzene ring vibrations

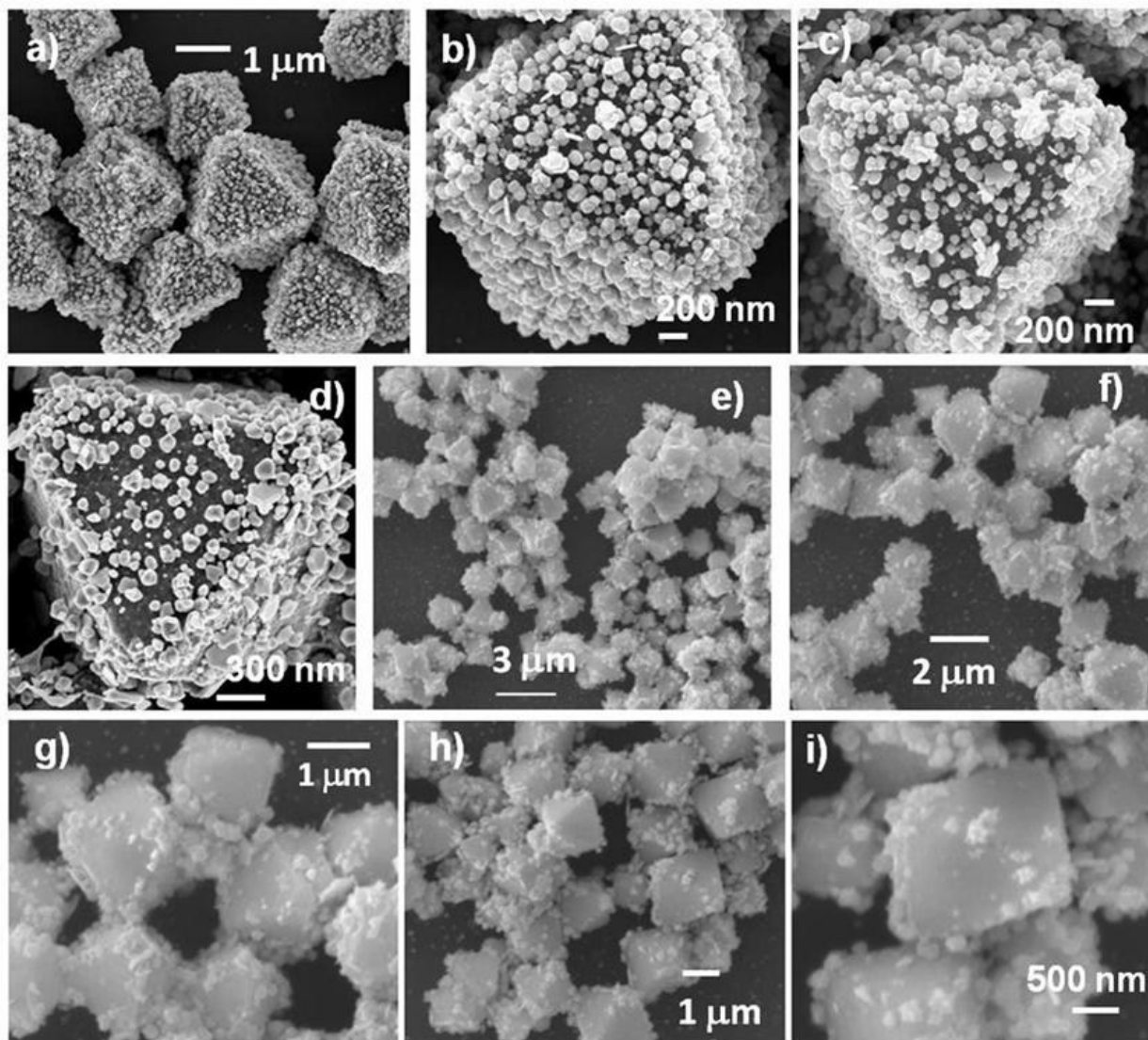


Figure S8: SEM images showing selective deposition of tips and edges, followed by facets for Cu_2O octahedral for 5SSA- Ag^+ system at increasing concentration. At low concentrations, tips and edges get preferentially decorated (e-i) with no deposition on the facets. At increased concentration, facets start progressively decorating ultimately leading to fully decorated octahedral (a-d) heterostructures. Utilized $[\text{AgNO}_3]$ are: h-i) 10mM; e-g) 20mM; d) 50mM; b-c) 75mM; a) 100mM respectively.

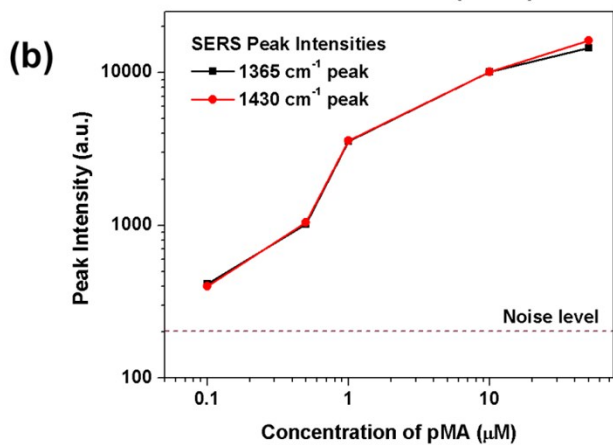
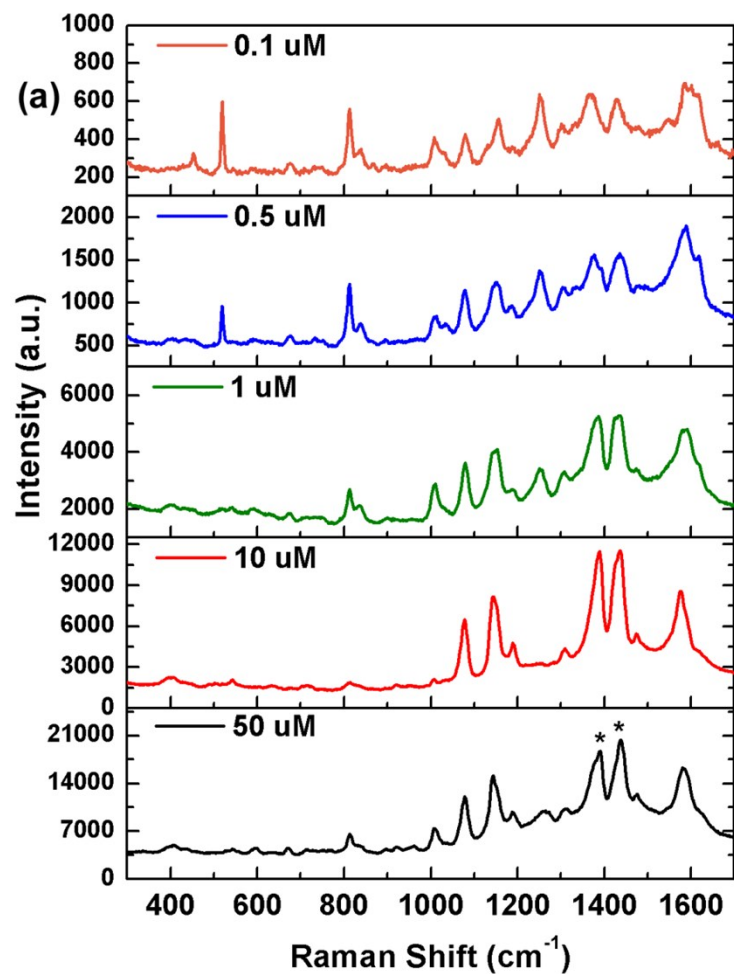


Figure S9: a) SERS spectra of p-MA at different concentrations showing the change in the SERS signal, b) Intensity of highlighted peaks ($1365, 1430 \text{ cm}^{-1}$) as a function of p-MA concentrations.

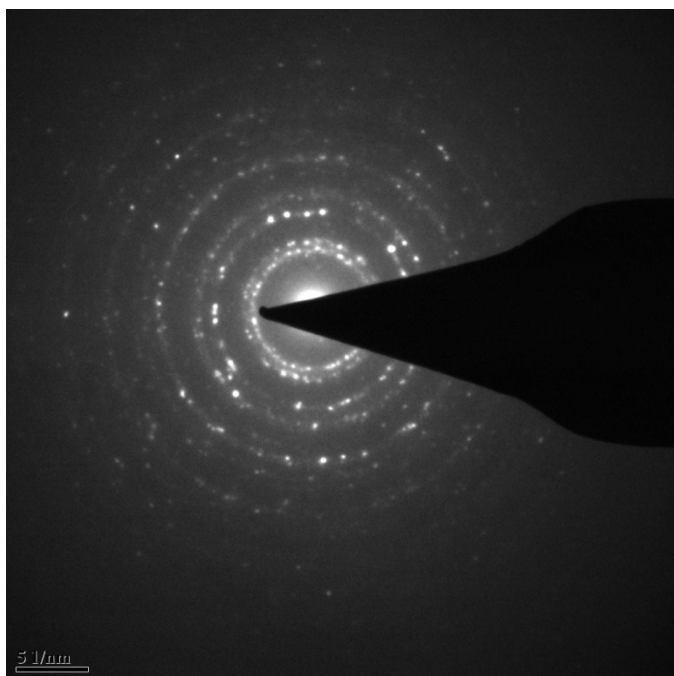


Figure S10: SAED pattern collected from a Au-Ag hollow mesocage showing the polycrystalline nature of the Au and Ag NPs comprising the mesocage.

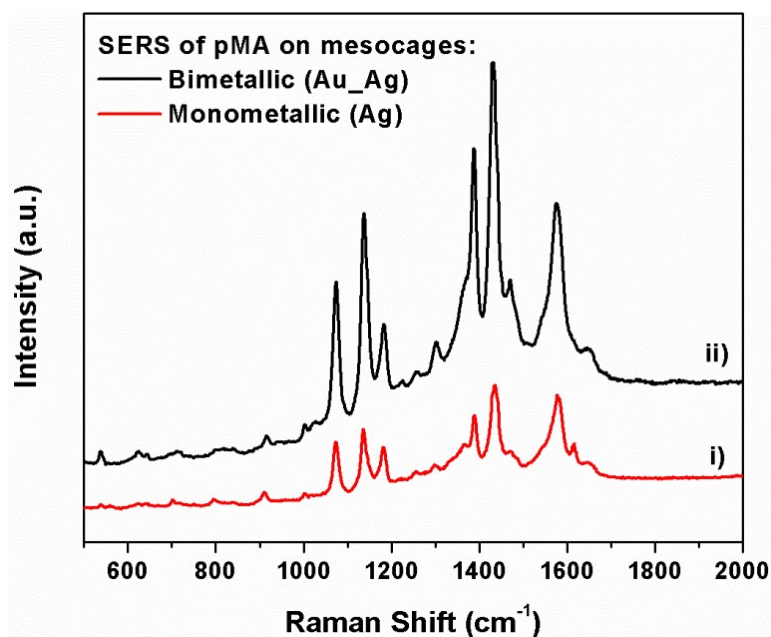


Figure S11: SERS spectra of pMA acquired using i) monometallic Ag and ii) bimetallic Ag-Au hollow mesocages as SERS substrate.

Table S2: Elemental concentrations as obtained using ICP-AES analysis

Au-Ag-Cu₂O heterostructure		
Cu(ppm)	Ag(PPM)	Au(ppm)
4119.04	114.62	8.69
Au-Ag hollow mesocages		
Cu(ppm)	Ag(ppm)	Au(ppm)
4.5	85.3	8.65