Synthesis of Ultra-stable and Bioconjugable Ag, Au and Bimetallic Ag_Au Nanoparticles Coated with Calix[4]arenes

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Table S1 Conditions tested to optimize the synthesis of AgNPs in the presence of calixarene C1. The term "monodisperse" describes nanoparticles that show, after synthesis and cleaning, a strong and intense LSPR band with a A.420nm/A.600nm ratio higher than 15. The term "ultra-stable" describes nanoparticles that can endure multiple pH variation cycles without degrading and exposure to 150 mM of KF for 45 minutes without loss of absorbance (i.e. 5% or less).

Solvent	Time (hours)	T (C°)	pH	Reducing agent (mM)	Calixarenes (mM)	$AgNO_3$ (mM)	Ultra-stable and monodisperse NPs
Water	2	60	7	Ascorbate (4)	1.2	1	NO
Water	4	60	7	Ascorbate (4)	1.2	1	NO
Water	6	60	7	Ascorbate (4)	1.2	1	NO
Water	16	20	7	Ascorbate (4)	1.2	1	NO
Water	16	40	7	Ascorbate (4)	1.2	1	NO
Water	16	60	7	Ascorbate (4)	1.2	1	YES
Water	16	80	7	Ascorbate (4)	1.2	1	NO
Water	16	60	3	Ascorbate (4)	1.2	1	NO
Water	16	60	4	Ascorbate (4)	1.2	1	NO
Water	16	60	5	Ascorbate (4)	1.2	1	NO
Water	16	60	6	Ascorbate (4)	1.2	1	NO
Water	16	60	8	Ascorbate (4)	1.2	1	YES
Water	16	60	9	Ascorbate (4)	1.2	1	YES
Water	16	60	12	Ascorbate (4)	1.2	1	NO
Water	16	60	7	Ascorbate (0)	1.2	1	NO
Water	16	60	7	Ascorbate (0.1)	1.2	1	NO
Water	16	60	7	Ascorbate (0.5)	1.2	1	NO
Water	16	60	7	Ascorbate (1)	1.2	1	NO
Water	16	60	7	Ascorbate (2)	1.2	1	NO
Water	16	60	7	Ascorbate (8)	1.2	1	NO
Water	16	60	7	Ascorbate (16)	1.2	1	NO
Water	16	60	7	Ascorbate (32)	1.2	1	NO
Water	16	60	7	Ascorbate (40)	1.2	1	NO
Water	16	60	7	Ascorbate (4)	0	1	NO
Water	16	60	7	Ascorbate (4)	0.3	1	NO
Water	16	60	7	Ascorbate (4)	0.6	1	NO
Water	16	60	7	Ascorbate (4)	2.4	1	NO
Water	16	60	7	Ascorbate (4)	1.2	0	NO
Water	16	60	7	Ascorbate (4)	1.2	0.5	YES
Water	16	60	7	Ascorbate (4)	1.2	2	NO
Water	16	60	7	Ascorbate (4)	1.2	4	NO
Water	16	60	7	Ascorbate (4)	1.2	8	NO
Water	16	60	7	Ascorbate (4)	1.2	16	NO
Water	16	0	7	$NaBH_4$ (4)	1.2	1	NO
Water	16	60	7	$NaBH_4$ (4)	1.2	1	YES
ACN	16	0	/	$NaBH_4$ (3)	0.6	1.25	NO

Table S2 Conditions tested to optimize the synthesis of AuNPs in the presence of calixarene C1. The term "monodisperse" describes nanoparticles that have, after synthesis and cleaning, their LSPR band strong and intense with a ratio A.520nm/A.700nm higher than 15. The term "ultra-stable" describes nanoparticles that can endure multiple pH variation cycles without degrading and exposure to 150 mM of KF for 45 minutes without loss of absorbance (i.e. 5% or less).

Solvent	Time (hours)	T (C°)	pH	Reducing agent (mM)	Calixarenes (mM)	$HAuCl_4$ (mM)	Ultra-stable and monodisperse NPs
Water	2	60	7	Ascorbate (4)	1.2	1	NO
Water	4	60	7	Ascorbate (4)	1.2	1	NO
Water	6	60	7	Ascorbate (4)	1.2	1	NO
Water	16	20	7	Ascorbate (4)	1.2	1	NO
Water	16	40	7	Ascorbate (4)	1.2	1	NO
Water	16	60	7	Ascorbate (4)	1.2	1	YES
Water	16	80	7	Ascorbate (4)	1.2	1	NO
Water	16	60	3	Ascorbate (4)	1.2	1	NO
Water	16	60	4	Ascorbate (4)	1.2	1	NO
Water	16	60	5	Ascorbate (4)	1.2	1	NO
Water	16	60	6	Ascorbate (4)	1.2	1	NO
Water	16	60	8	Ascorbate (4)	1.2	1	YES
Water	16	60	9	Ascorbate (4)	1.2	1	YES
Water	16	60	12	Ascorbate (0)	1.2	1	NO
Water	16	60	7	Ascorbate (0.1)	1.2	1	NO
Water	16	60	7	Ascorbate (0.5)	1.2	1	NO
Water	16	60	7	Ascorbate (1)	1.2	1	NO
Water	16	60	7	Ascorbate (2)	1.2	1	NO
Water	16	60	7	Ascorbate (8)	1.2	1	YES
Water	16	60	7	Ascorbate (16)	1.2	1	YES
Water	16	60	7	Ascorbate (32)	1.2	1	YES
Water	16	60	7	Ascorbate (40)	1.2	1	NO
Water	16	60	7	Ascorbate (4)	1.2	1	NO
Water	16	60	7	Ascorbate (4)	0	1	NO
Water	16	60	7	Ascorbate (4)	0.3	1	NO
Water	16	60	7	Ascorbate (4)	0.6	1	YES
Water	16	60	7	Ascorbate (4)	2.4	1	YES
Water	16	60	7	Ascorbate (4)	1.2	0	NO
Water	16	60	7	Ascorbate (4)	1.2	0.5	YES
Water	16	60	7	Ascorbate (4)	1.2	2	YES
Water	16	60	7	Ascorbate (4)	1.2	4	YES
Water	16	60	7	Ascorbate (4)	1.2	8	NO

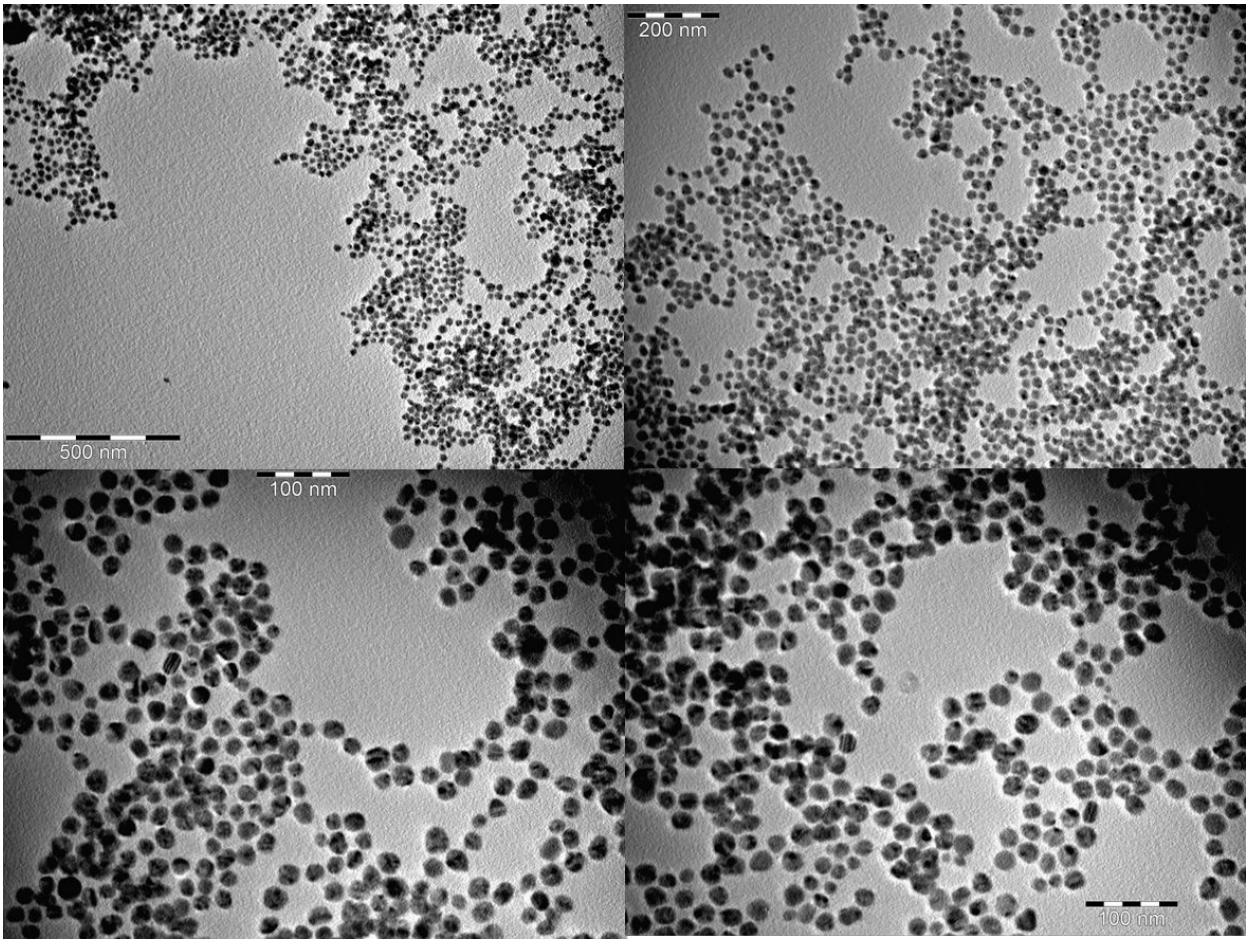

Figure S1. TEM images of AgNPs-C1.

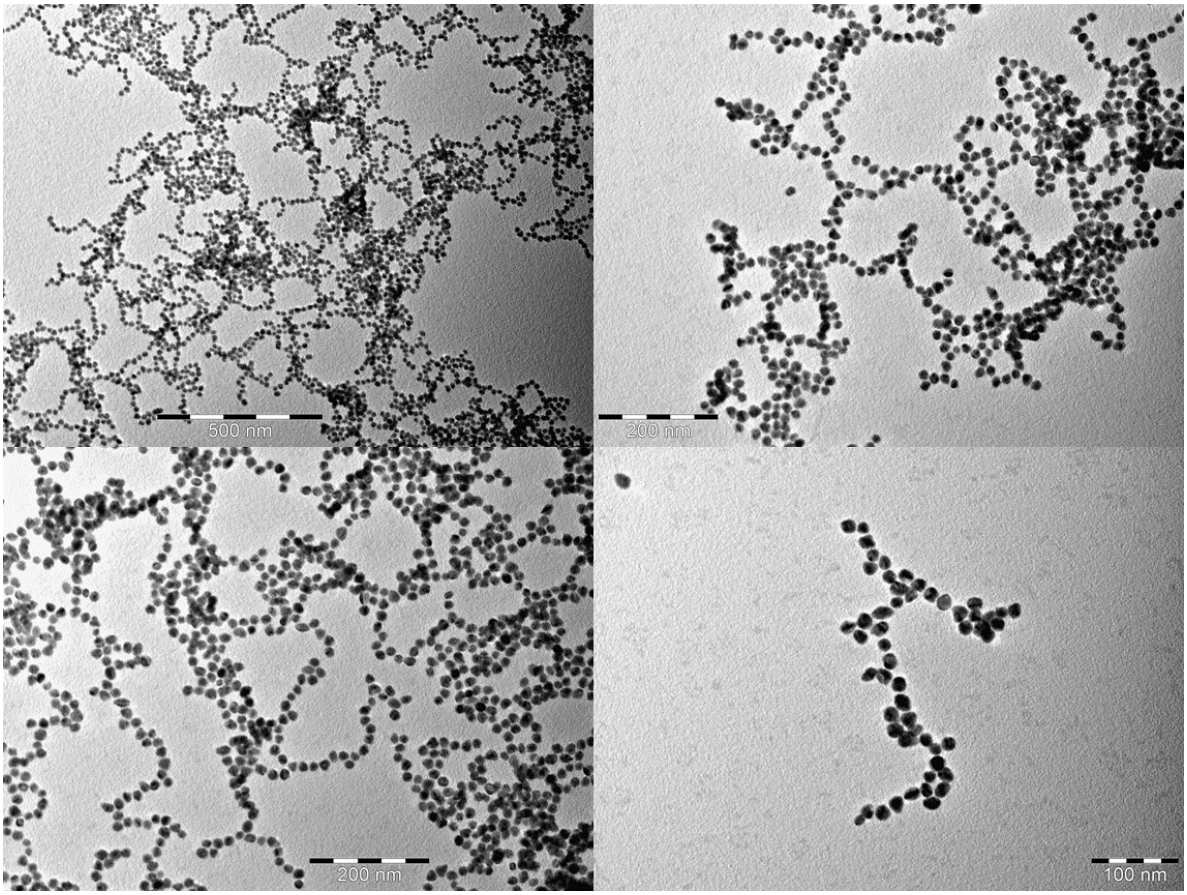

Figure S2. TEM images of AuNPs-C1.

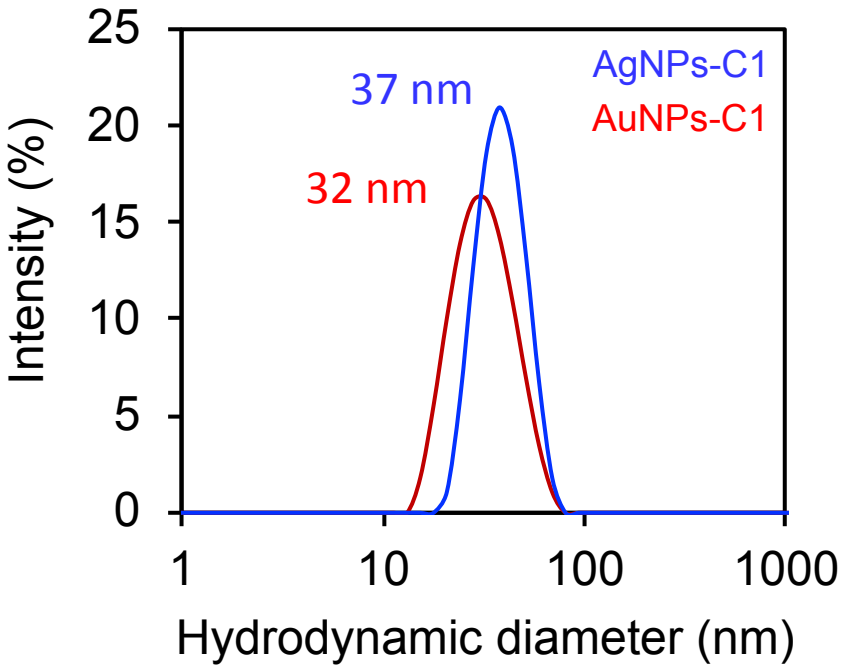

Figure S3. Average hydrodynamic diameters of AgNPs-C1 (blue) and AuNPs-C1 (red) measured by dynamic light scattering.

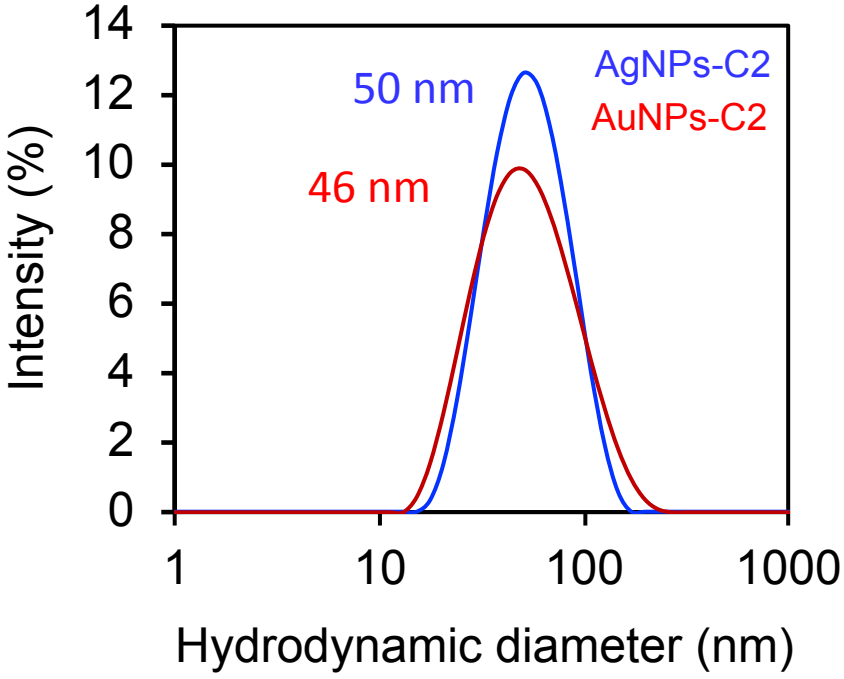

Figure S4. Average hydrodynamic diameters of AgNPs-C2 (blue) and AuNPs-C2 (red) measured by dynamic light scattering.

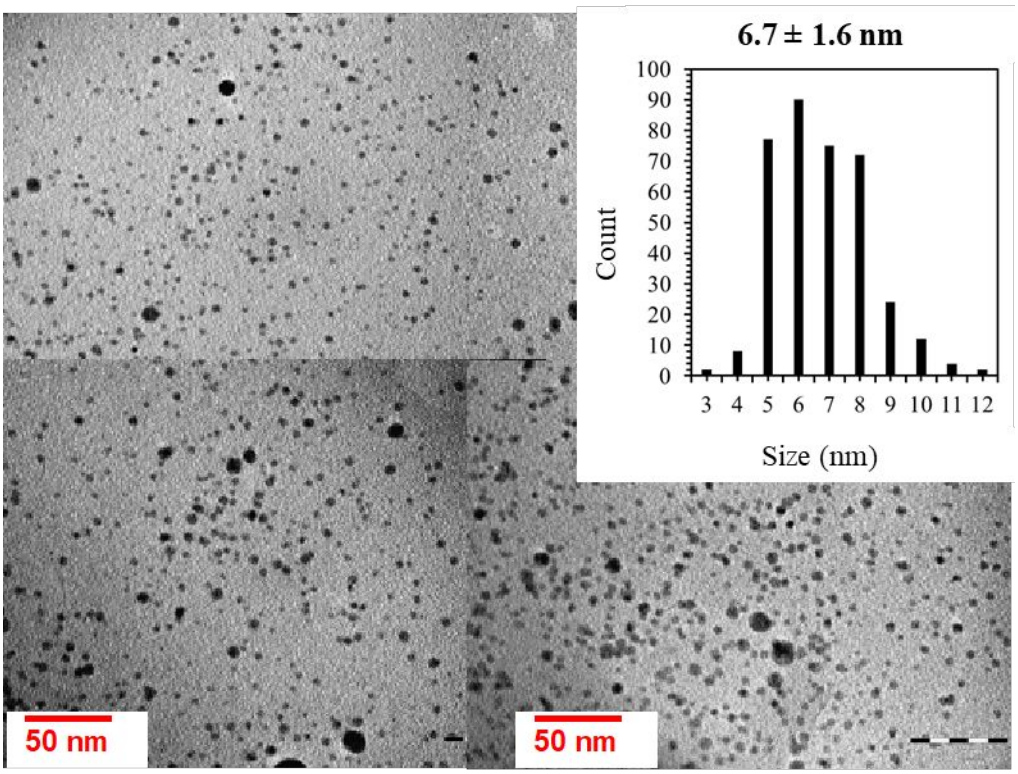

Figure S5. TEM images of AgNPs-C1 synthesized with $NaBH_4$.

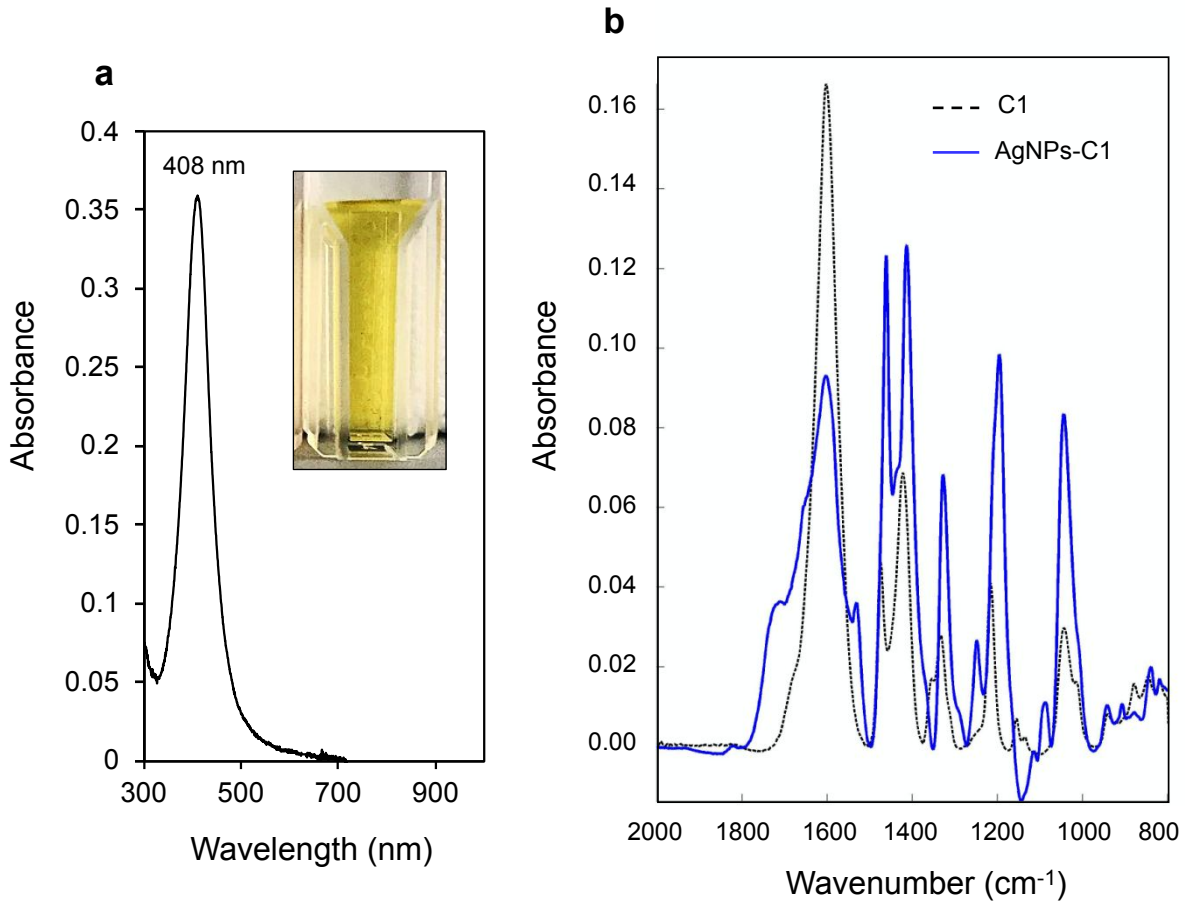

Figure S6. (a) UV-Vis and (b) ATR-FTIR spectra of AgNPs-C1 synthesized with $NaBH_4$. Insert shows the picture of the corresponding suspension.

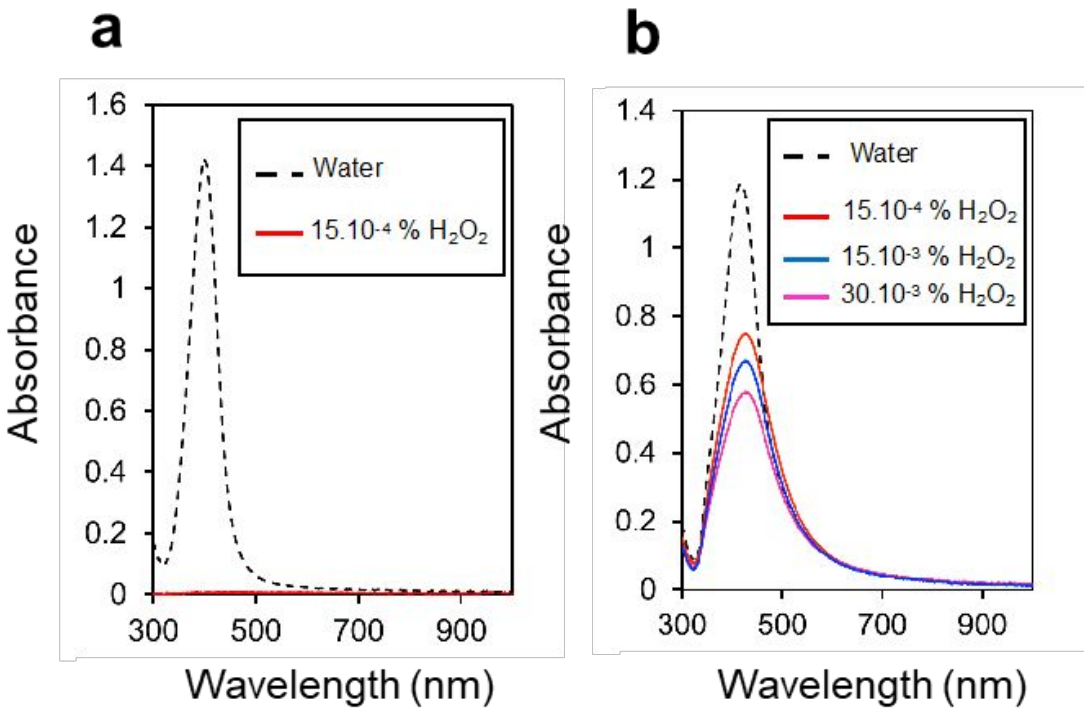

Figure S7. UV-Vis spectra of AgNPs-citrate (a) and AgNPs-C1 (b) before after addition of H_2O_2.

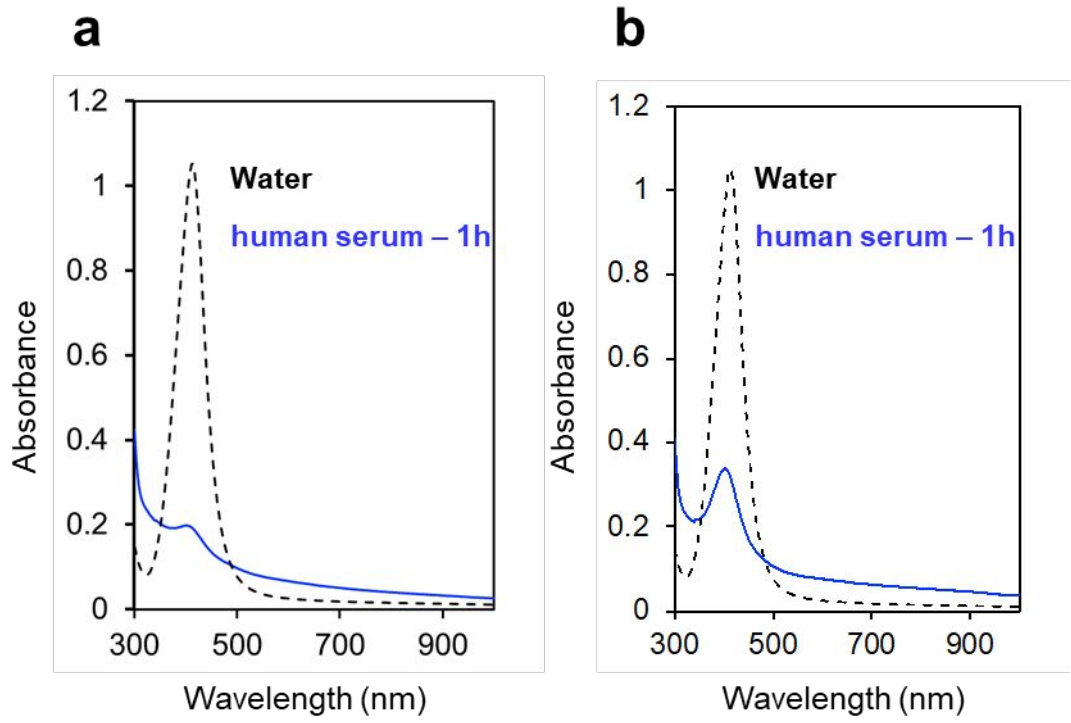

Figure S8. UV-Vis spectra of (a) AgNPs-citrate and (b) AgNPs-S-PEG3000 dispersed either in water (black dashed line) or in human serum for one hour, centrifuged and resuspended in water.

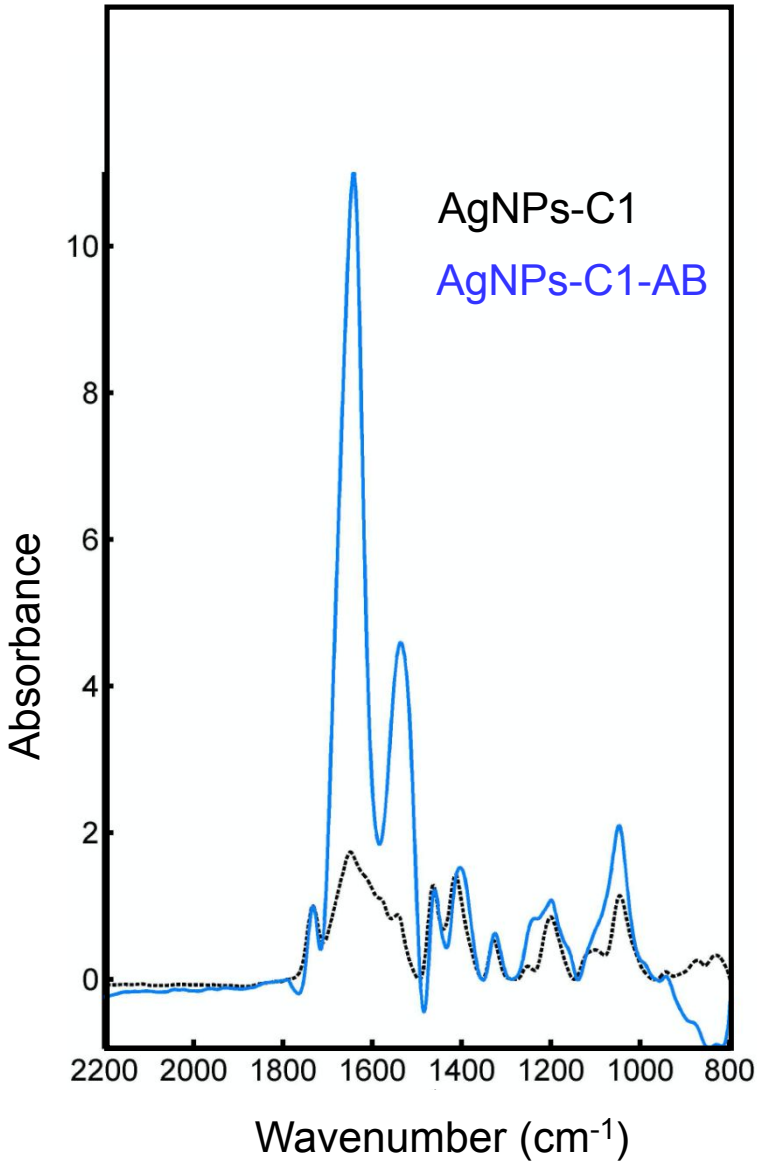

Figure S9. ATR-FTIR spectra of AgNPs-C1 before (black dashed line) and after the coupling via EDC/NHS procedure to human antibodies (blue plain line).

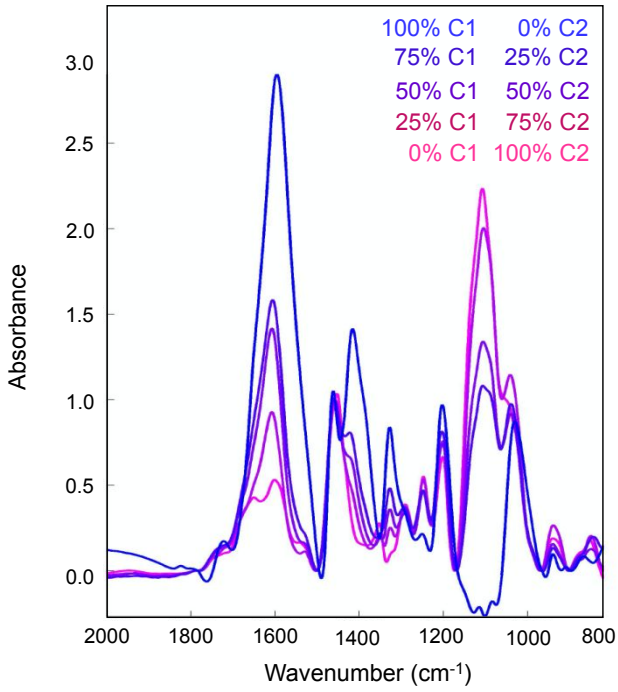

Figure S10. Normalized ATR-FTIR spectra of AuNPs-C1/C2 synthesized with different proportions of C1 and C2.

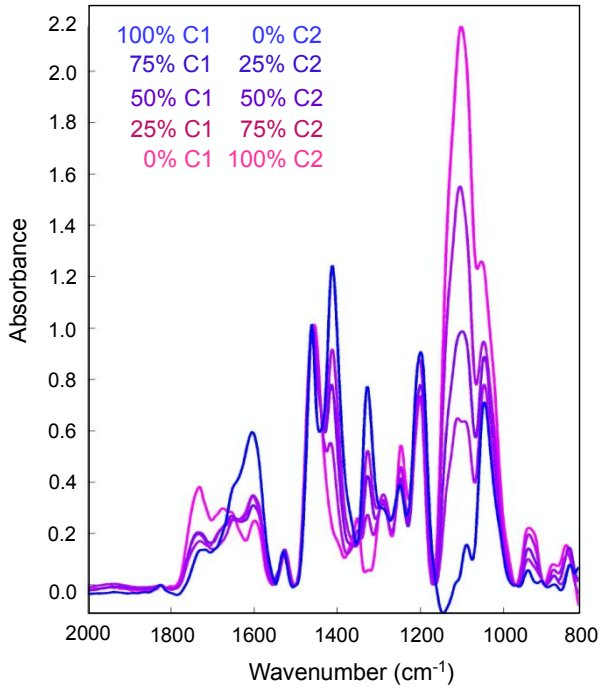

Figure S11. Normalized ATR-FTIR spectra of AgNPs-C1/C2 synthesized with different proportions of C1 and C2.

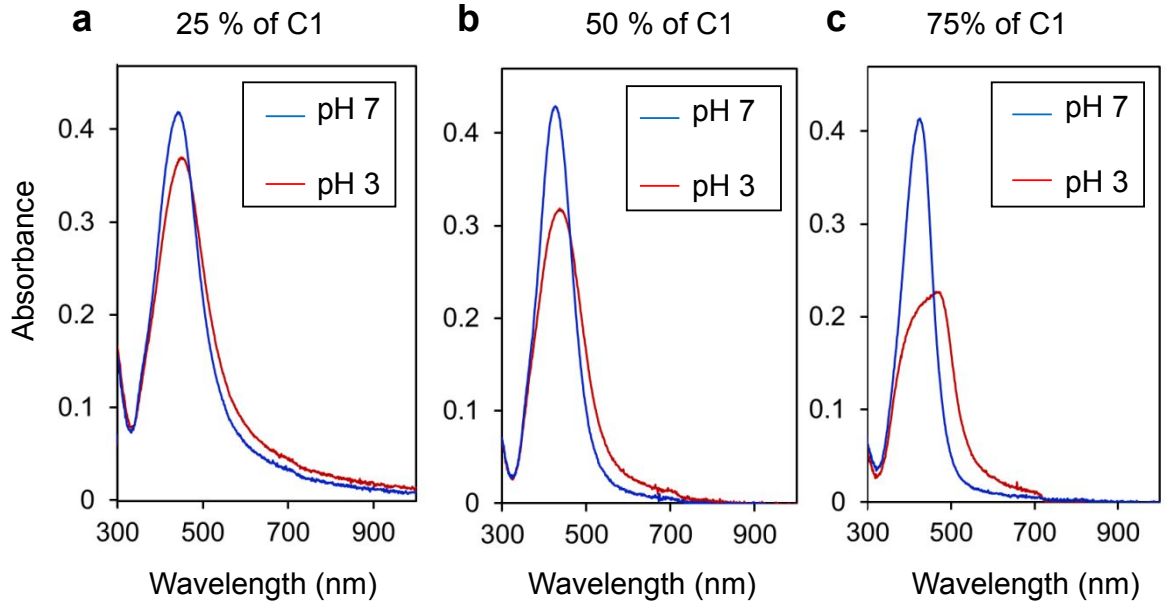

Figure S12. UV-Vis spectra of AgNPs-C1/C2 synthesized with mixture of C1 and C2 containing 25% of C1 (a) or 50% of C1 (b) or 75% of C1 (c) at pH7 (blue) then pH 3 (red).

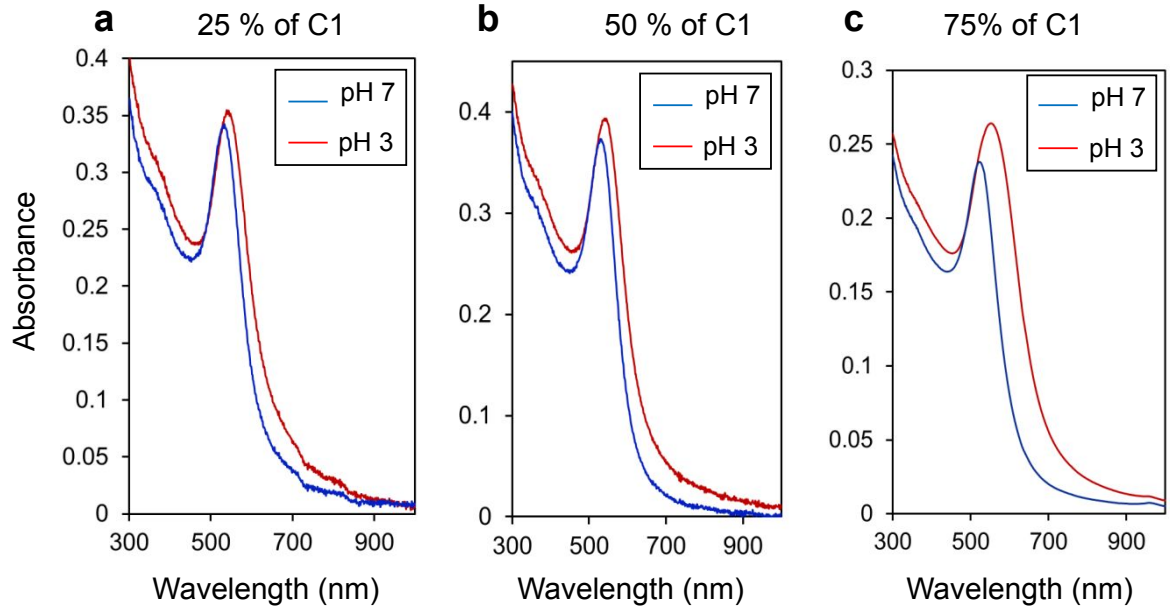

Figure S13. UV-Vis spectra of AuNPs-C1/C2 synthesized with mixture of C1 and C2 containing 25% of C1 (a) or 50% of C1 (b) or 75% of C1 (c) at pH7 (blue) then pH 3 (red).

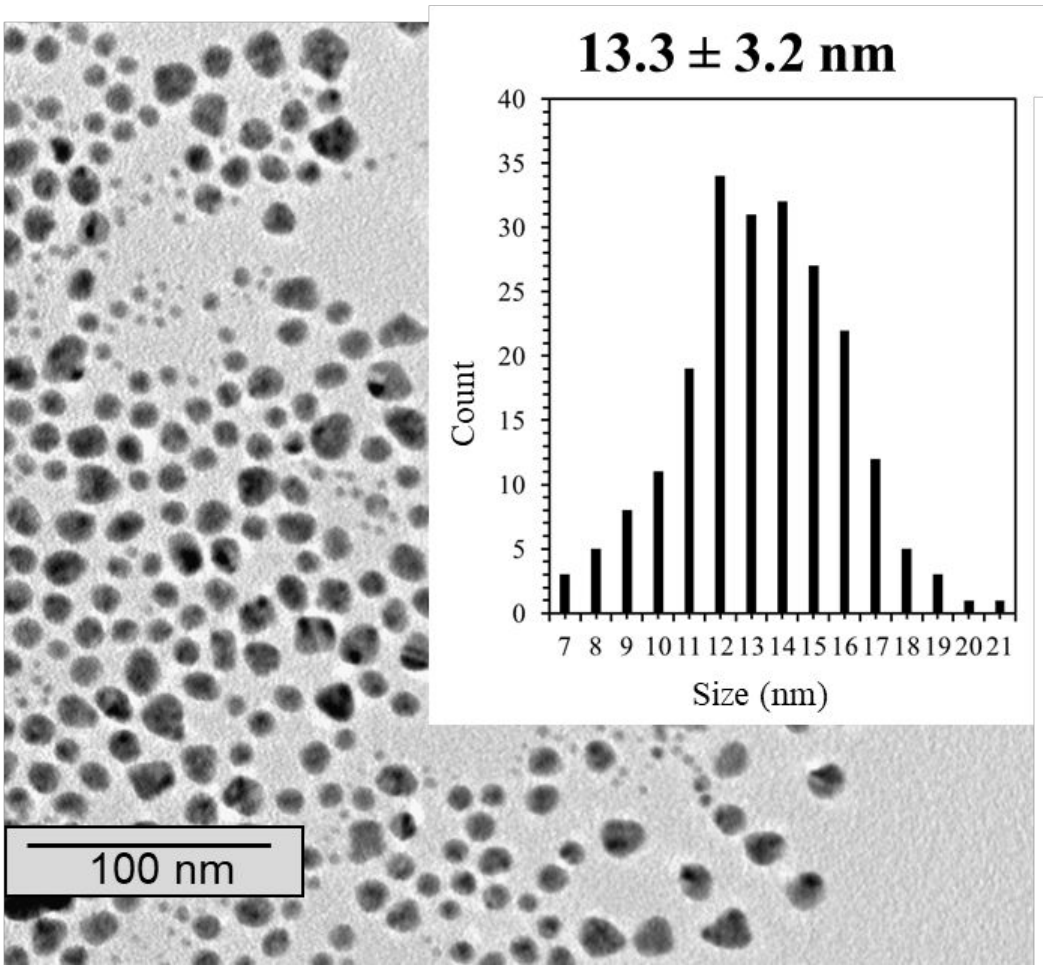

Figure S14. TEM pictures of Ag(50%)_Au(50%)NPs-C1.

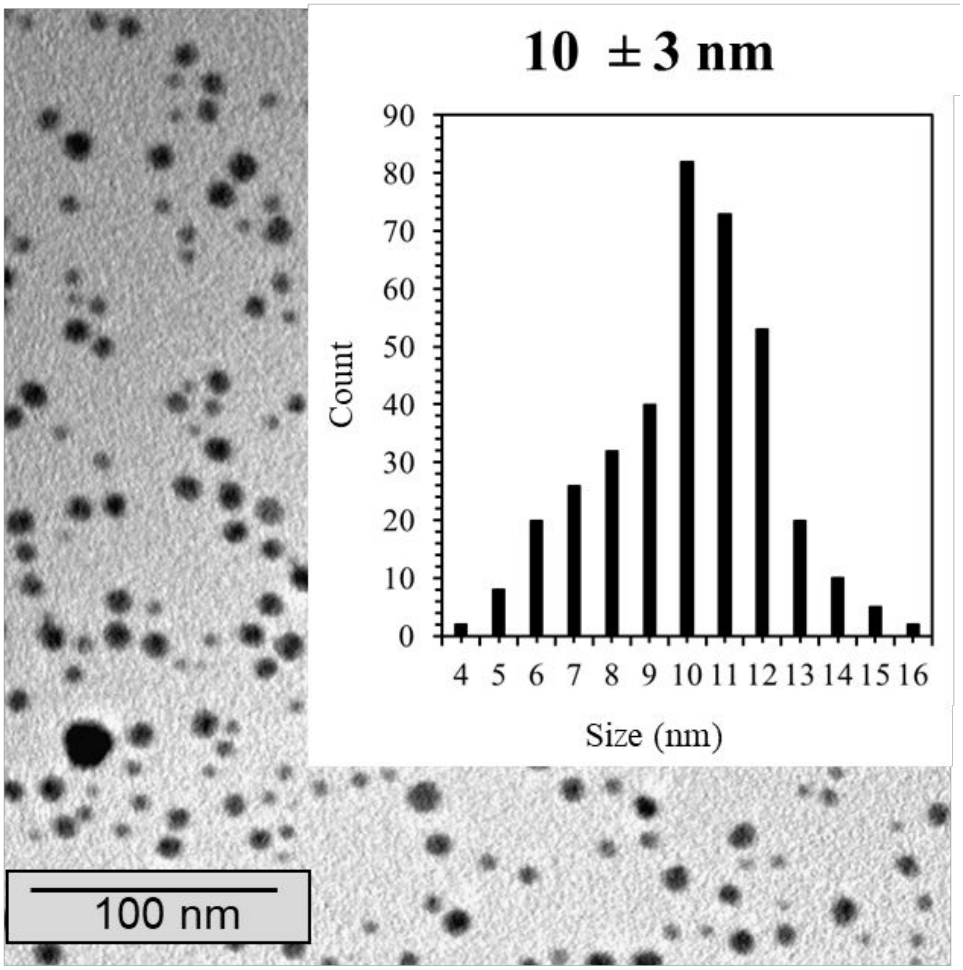

Figure S15. TEM pictures of Ag(50%)_Au(50%)NPs-C2.

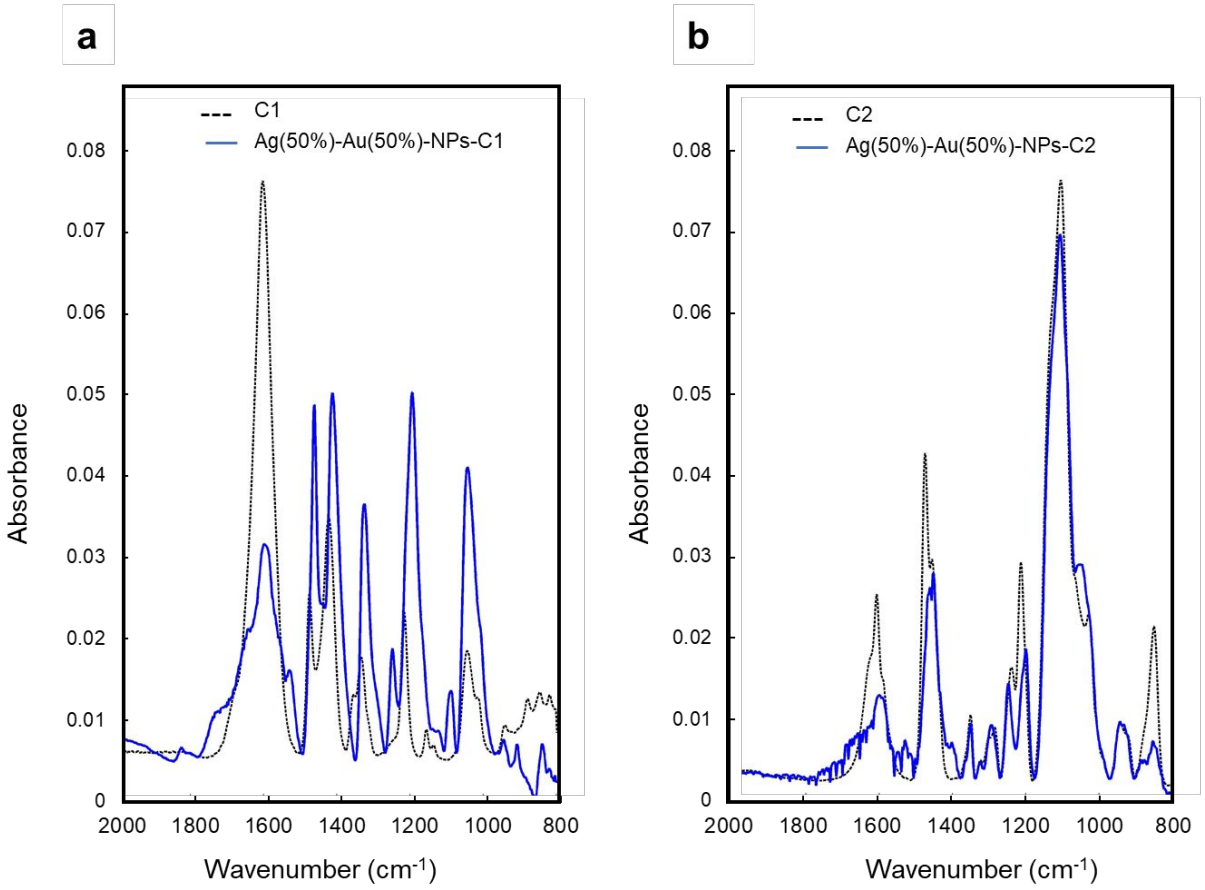

Figure S16. ATR-FTIR spectra of (a) C1 (black dashed line) and Ag(50%)_Au(50%)NPs-C1 (straight blue line) and (b) C2 (black dashed line) and Ag(50%)_Au(50%)NPs-C2 (straight blue line)

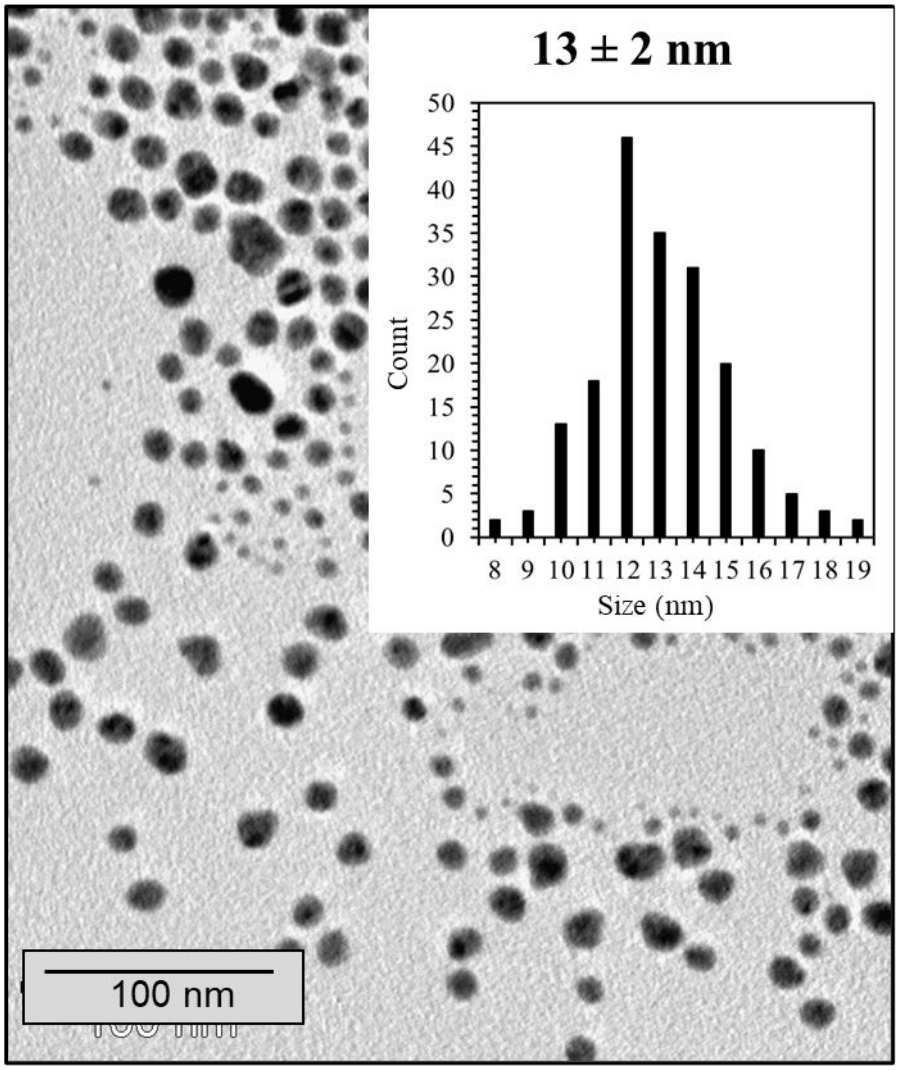

Figure S17. TEM images of Ag(50%)_Au(50%)NPs-C1(50%)/C2(50%).