Supplementary Information

Ag@Au bimetallic nanoparticles: an easy and highly reproducible synthetic approach for photocatalysis

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Table S1. Literature review of developed Ag-Au NP nanoparticles through several methods and compounds.

Au-Ag NPs type	Synthesis method	precursor	Capping agent	Size (nm)	ζ potential (mV)	Shape	SPR broadness	SPR λ max (nm)	Ref.
alloy	spark discharge	Ag and Au electrodes	-	11	-	Sphere	-	-	[1]
alloy	Chemical reduction	$AgNO_3$, and $HAuCl_4$	SDS, and Trp	10	-	Quasi sphere	Broad	427 (SDS) 578 (Trp)	[2]
alloy nanoclusters	Citrate reduction method	$AgNO_3$, and $HAuCl_4$	-	19.4 - 43.2	-	Quasi sphere	Broad	421 – 520 depending on metal ion concentration	[3]
Au@Ag Core-shell	microemulsion as nanoreactors	AuNP, and $AgNO_3$	Triton X-100	8.79 - 102.34	-	Sphere	Narrow Broad	322 nm 527 nm	[4]
alloy	Chemical reduction by dextran	Ag_2SO_4, and $HAuCl_4$	Dextran	20-40 nm (S7 and S5) 3-25 nm (S3)	-	Sphere	Broad	S7 = 518 nm S5 = 530 nm S3 = 542 nm	[5]
alloy	Galvanic replacement	Ag triangular plates, and $HAuCl_4$	-	284-289	-	Triangular nanoprisms	Broad	1100-1400 nm	[6]
Ag-Au alloy and core-shell types	Chemical reduction of silver nitrate and tetrachlorauratic acid ($AgNO_3$ and $HAuCl_4$) with amino acid tryptophan	$AgNO_3$, and $HAuCl_4$	Tryptophan	Ag-Au alloy 7-10 nm Au core Ag shell 10-25 nm Ag core Au shell 10-25 and 25-50 nm	-	Sphere	Broad	Ag-Au alloy 3:1 427 nm 1:1 466 nm 1:3 511 nm Au core Ag shell ~ 460 nm Ag core Au shell ~ 520 nm	[7]
Ag-Au alloy	Chemical reduction by tryptophan	$AgNO_3$, and $HAuCl_4$	Tryptophan	10 nm	-	-	Broad	3:1 = 435 nm 1:1 = 474 nm 1:3 = 497 nm	[8]

Ag-Au (Unspecified)	Chemical reduction	$AgNO_3$, and $HAuCl_4$	Tryptophan	> to 5 nm	-	-	-	-	[9]
Ag-Au alloy	Chemical reduction by dextran	$AgNO_3$, and $HAuCl_4$	Dextran T40	10-12 nm	-	Quasi spheres	Broad	520 nm	[10]
Ag-Au alloy	Galvanic replacement reaction	AgNP seeds Chloroauric acid (HAuCl4)	Glutathione	16 ± 5 nm	~ 20 mV	Sphere	Narrow	428 nm	[11]
Ag-Au alloy	Biosynthesized from marine red alga, Gracilaria sp.,	$AgNO_3$, and $HAuCl_4$	-	20nm for 1:1 24 nm for 1:3 22 nm for 3:1	-	Quasi Sphere	1:1 = 24 h (broad) to 96 h (narrow) 1:3 = 24 h (broad) to 96 h (narrow) 3:1 = 24 h (broad) to 96 h (broad)	1:1 = 504 nm 1:3 = 526 nm 3:1 = 501 nm	[12]
Ag@Au core@shell	Coating AgNP in a layer of gold through a reduction deposition process	AgNPs HAuCl4	Acrylate	17.5 ± 3.7 nm	-	Sphere	Narrow Broad Broad	Ag@Au NPs with 5% addition of Au = 410 nm Ag@Au NPs with 15% addition of Au (two main bands). The primary band at 422 nm and the second band at 600nm. Ag@Au NPs with 25% Au added = 610 nm.	[13]
Ag@Au core@shell	NaBH4 reduction	$AgNO_3$, and $HAuCl_4$	-	-	-	Sphere	Narrow (0.4:0) to broad	Ag@Au core@shell	[14]

Ag-Au alloy	method						(0.4:0.4) Broad	Ag:Au 0.4:0 ~390 nm 0.4:0.1 ~400 nm 0.4:0.2 ~510 nm 0.4:0.3 ~520 nm 0.4:0.4 ~525 nm Ag-Au alloy XAu=0 400 nm XAu=25 ~450 nm XAu=50 ~500 nm XAu=75 ~525 nm XAu=100 ~525 nm	
Ag-Au bimetallic janus	Galvanic exchange reactions	1-hexanethiolate-passivated silver (AgC6) NP Gold(I)-mercapto-propanediol (AuI-MPD) complex	-	5.36 nm ± 0.85	-	Sphere	Broad	472 nm	[15]
Au@Ag core@shell	Photochemical route with UV-A light using I-2959	AuNP, and $AgNO_3$	Aspartame	16.6 ± 4.7 nm	-	Sphere	Broad	510 nm and 405 nm	[16]
Ag core and Ag-Au alloyed shell	Overdeposition of Au over Ag seeds by the seed growth method								[17]
Au-Ag	Seeding-growth	AuNP, and	Citrate	75.2 nm (2	-31.5 mV (2 mL	Sphere	Broad	Au 450 nm	[18]

	technique	$AgNO_3$		mL of Au seed) 55.2 nm (5 mL of Au seed)	of Au seed) -20.9 mV (5 mL of Au seed)			Ag 435 nm	
Au@Ag core@shell	Electrochemical reduction of hydrogen peroxide (HP) and nitrobenzene (NB) Chemical reduction of AgNO3 followed by galvanic displacement of AuCl4-	AgNP and HAuCl4 AgNP and AuCl4-	Citrate	~16 nm	-	Sphere	Broad	482 nm	[19]
Au@Ag core@shell	Turkevich method	$AgNO_3$, and $HAuCl_4$	Citrate	50 ± 9 nm	-	Sphere	Broad	470 nm	[20]
Alloy NP	Two-phase reduction of AuCl4- and two-phase reduction of AuCl4- and AgBr2-	HAuCl4 and AgNO3 AgBr2- and AuCl4-	Decanethiol	2.4 ± 0.4 nm AuAg (1:4) 1.7 ± 0.2 nm AuAg (4:1)	-	Sphere	Broad	450 - 500 nm	[21]
Au@Ag core@shell	Chemical reduction	AuNP, and $AgNO_3$	Citrate	-	-	Sphere	Narrow	450 - 550 nm	[22]
Ag-Au alloys Ag 7.5 mm - Au 2.5 mm Ag 5 mm - Au 5 mm Ag 2.5 mm - Au 7.5 mm	Using a nanosecond-pulsed laser beam.	Ag/Au bilayer thin film	-	98 nm 102 nm 110 nm	-	Sphere	Broad	~400-450 nm ~450-500 nm ~500-550 nm	[23]

core@shell Au67Ag33 Au40Ag60 Au18Ag82 core@shell Ag67Au33 Ag40Au60 Ag18Au82	Microwave assisted synthesis	Seeds of Ag and Au	PVP	33 nm 60 nm 82 nm 33 nm 60 nm 82 nm	-	Sphere	Broad	core@shell Ag87Au18 ~525 nm Ag60Au40 ~450 nm Ag82Au18 ~425 nm	[24]
Ag@Au core@shell	One-vessel using simultaneous reduction of ions with rapid injection of NaBH4	HAuCl4 and AgClO4	PVP	1.6 ± 0.9 nm (Ag10Au90) 2.0 ± 0.6 nm (Ag20Au80) 2.1 ± 0.8 nm (Ag30Au70) 2.1 ± 1.8 nm (Ag50Au50)	-	Sphere	Broad	380 nm and 510 nm	[25]
Ag-Au alloy Au core - Ag shell	Co-reduction of HAuCl4 and AgNO3	-	Citrate	25-35 nm	-	-	-	-	[26]
Au core - Ag shell Ag core - Au shell Au-Ag with different molar ratio	Seeding growth method	-	-	45-50 nm	-	-	-	Au Au-Ag1 = 454 nm Au-Ag2 = 428 nm Au-Ag3 = 415 nm Au-Ag4 = 410 nm Au-Ag5 = 391, 500 nm Ag Ag-Au1 = 524 nm Au-Ag2 = 550	[27]

								nm Au-Ag3 = 570 nm Au-Ag4 = 590 nm	
Core-shell	Bioreduction using piper beetle leaf extract	$AgNO_3$, and $HAuCl_4$	-	-	-	Sphere	Narrow	430 nm Ag 555 nm Au	[28]
Au@Ag	Successive reduction of metal salts	$AgNO_3$, and $HAuCl_4$	-	-	-	Sphere	Broad	~ 400 nm Ag ~ 500 nm Au	[29]
Ag-Au bimetallic film	-	-	-	-	-	Quasi sphere	Broad	~ 400 nm ~ 600 nm	[30]
Au@Ag core@shell	Chemical reduction	AuNPs and silver nitrate	Citrate and ascorbic acid	64.3 nm	-	Sphere	Narrow	407.6 nm Ag 570 nm Au	[31]
Ag@Au Core@shell	Seed mediated growth method	AgNP and HAuCl4	PVP	7.9 nm	-	Sphere	Broad	~ 500 nm (using AgNP as the seeds) ~ 400 nm and ~ 500 nm (using AuNP as the seeds)	[32]
Ag-Au alloy with metal ion concentration 0.05 M and 0.1 M	W/O microemulsion containing tritonX-100 and cyclohexane	$AgNO_3$, and $HAuCl_4$	-	Au:Ag 0.05 M 0.01 M (38:62) 26 nm 27 nm (50:50) 23 nm 20 nm (62:38) 23 nm	-	-	Broad	Au:Ag 0.05 M 0.01 M (38:62) 462 nm 513 nm (50:50) 493 nm 528 nm (62:38) 503 nm	[33]

				25 nm				550 nm	
Ag@Au Concave Cuboctahedra	-Ag nanocubes: polyol method. -Ag Cuboctahedra: seeds method. -Ag@Au Cuboctahedra and Concave Cuboctahedra: titration aqueous method.	-Ag nanocubes: silver trifluoroacetate. -Ag Cuboctahedra: Ag nanocubes and AgNO3. -Ag@Au Cuboctahedra and Concave Cuboctahedra: Ag cuboctahedra and HAuCl4 3H2O.	PVP 29,000) or PVP 55,000	-Ag cubes of 40.5 ± 4.4 nm. -Ag cuboctahedra of 48.2 ± 3.2 nm	-	Cuboctahedral	-Ag cuboctahedra: 200 nm -Ag@Au cuboctahedra: 275 nm -Ag@Au concave cuboctahedra: 325 nm	-Ag cuboctahedra: 435 nm -Ag@Au cuboctahedra: 450 nm -Ag@Au concave cuboctahedra: 460 nm	[34]
Bimetallic Au–Ag NPs	-AgNPs irradiated with a UV lamp (15 W). -Ag-Au NPs: immersion of AgNPs in HAuCl4 aqueous solution.	-AgNPs: AgNO3. -Ag-AuNPs: AgNPs and HAuCl4.	TiO2	-Ag30Au2.5: 7.3 ± 0.8 nm -Ag30Au30: 6.2 ± 0.7 nm	-	Sphere			[35]

Table S2. Tested formulations during the present work.

Formulation	Reactive 1	Reactive 2	Reactive 3	Method of preparation	Observed result
1	$AgNO_3$ (200 µM)	I-2959 (200 µM)	Sodium citrate (0.1 M)	Photochemical	AgNP
2	$HAuCl_4$ (330 µM)	I-2959 (200 µM)	Sodium citrate (0.1 M)	Photochemical	AuNP
3	$AgNO_3$ (200 µM)	Ascorbic acid (0.1 M)	-	Chemical	No apparent results
4	$HAuCl_4$ (330 µM)	Ascorbic acid (0.1 M)	-	Chemical	AuNP unstable
5	$HAuCl_4$ (330 µM)	$AgNO_3$ (200 µM)	Ascorbic acid (0.1 M)	Chemical	Ag@AuNP unstable
6	AuNP (0.064 µM)	Ascorbic acid (0.1 M)	-	Chemical	AuNP without change
7	AgNP (0.0075 µM)	Ascorbic acid (0.1 M)	-	Chemical	AgNP loss stability over time
8	AuNP (0.064 µM)	AgNP (0.0075 µM)	Ascorbic acid (0.1 M)	Chemical	Ag@Au-NP
9	AuNP (0.064 µM)	$HAuCl_4$ (330 µM)	Ascorbic acid (0.1 M)	Chemical	[AuNP] increment
10	AgNP (0.0075 µM)	$AgNO_3$ (200 µM)	Ascorbic acid (0.1 M)	Chemical	[AgNP] increment
11	AuNP (0.064 µM)	$AgNO_3$ (200 µM)	Ascorbic acid (0.1 M)	Chemical	Ag@Au-$AgNO_3$
12	AgNP (0.0075 µM)	$HAuCl_4$ (330 µM)	Ascorbic acid (0.1 M)	Chemical	Ag@Au-$HAuCl_4$
13	AgNP (0.0075 µM)	AuNP (0.064 µM)	Different reducing agents*	Chemical	
14	AgNP (0.0075 µM)	AuNP (0.064 µM)	Ascorbic acid**	Chemical	

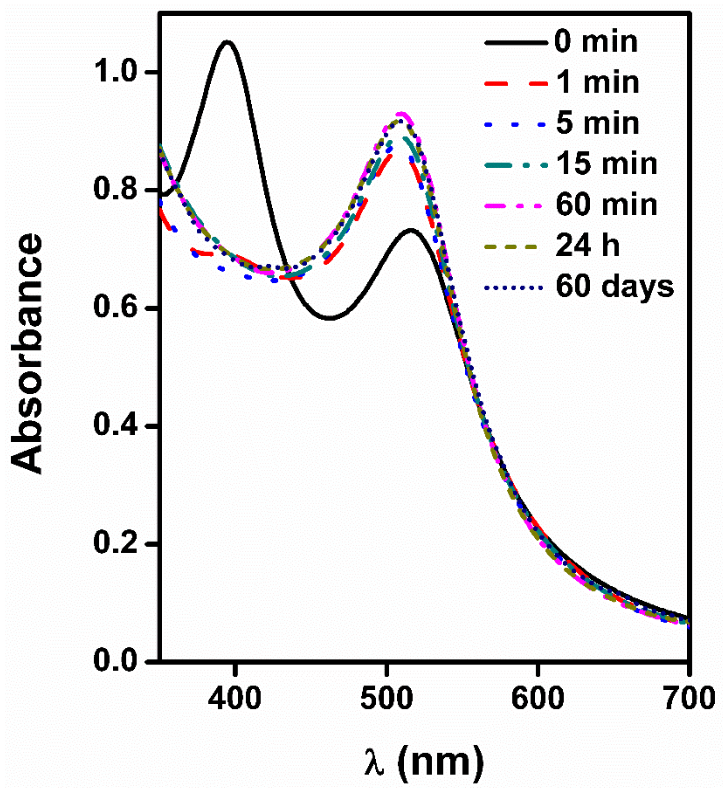

Figure S1. Ag-Au BNP formation on time following its SPR band. The experiment was carried out by mixing Ag and Au NPs with ascorbic acid (0.1 M) at room temperature and measured through UV-Vis spectroscopy.

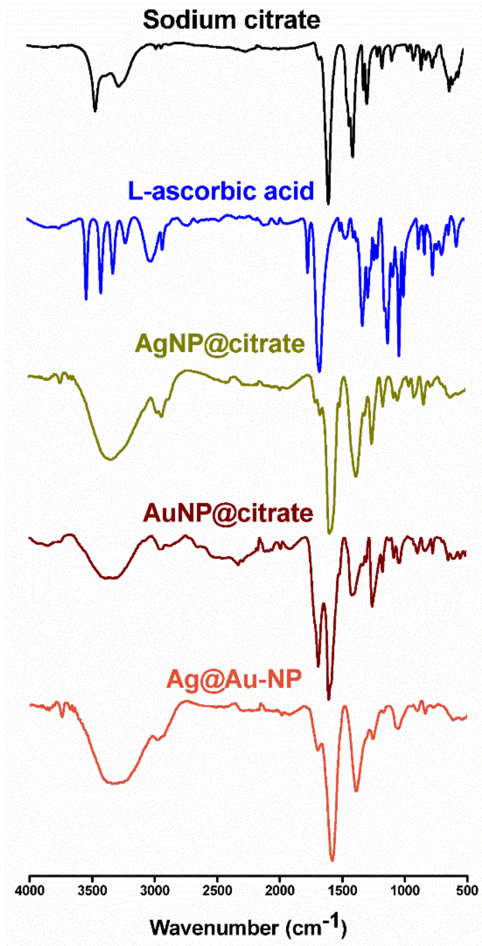

Figure S2. FT-IR spectra obtained from lyophilized samples. Samples codes are mentioned within the figure. A total of 64 runs were performed for each sample.

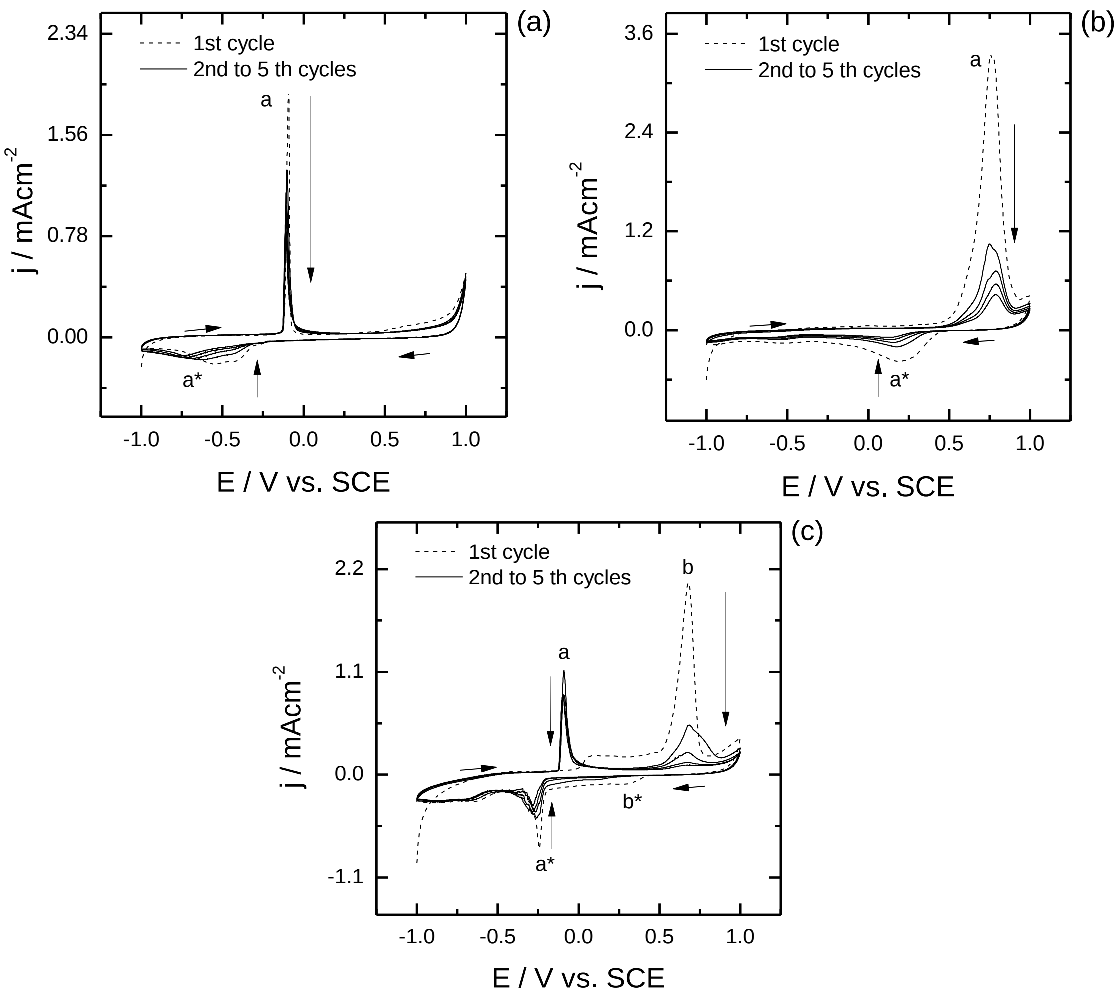

Figure S3. Cyclic voltamperometry of modified GC electrodes with a) AgNPs b) AuNPs; c) Ag@Au BNPs nanoparticles in a solution of PBS 10 mM at 25 °C.

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