Electronic Supplementary Material (ESI) for RSC Advances

Electronic Supplementary Information

Surfactant less synthesis of anisotropic gold nanostructures: Can dicarboxylic acids alone act as shape directing agents?

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Oxalic acid to $HAuCl_4$ ratio	Colour	pH	
		Before adding oxalic acid to $HAuCl_4$ solution	After adding oxalic acid to $HAuCl_4$ solution
1:1	Bluish	2.86	2.73
2.5:1	Greenish	2.84	2.68
5:1	Bluish violet	2.83	2.61
10:1	Light blue	2.82	2.54
20:1	Faint blue	2.82	2.44

Table ESI-1: Colour of the colloidal dispersion and pH of the reaction mixture at different molar ratios of oxalic acid to $HAuCl_4$.

Dicarboxylic acid to $HAuCl_4$ molar ratio	COLOR				pH			
	Malonic acid	Succinic acid	Glutaric acid	Adipic acid	Malonic acid	Succinic acid	Glutaric acid	Adipic acid
1:1	No color	No color	No color	No color	2.99	3.01	2.99	2.85
2.5:1	No color	No color	No color	-	2.80	2.90	2.93	-
5:1	No color	Light purple	No color	-	2.72	2.86	2.89	-
10:1	Light brown	Bluish	No color	-	2.63	2.81	2.83	-
20:1	Brownish	Purple	No color	No color	2.58	2.73	2.74	2.77

Table ESI-2: Colour of the colloidal dispersion and pH of the reaction mixture at different molar ratios of dicarboxylic acids to $HAuCl_4$.

Name of the dicarboxylic acid	pKa[1]	Distance between the dicarboxylic groups (A°)[2]
Oxalic acid	1.23, 4.19	2.69
Malonic acid	2.83, 5.69	2.68
Succinic acid	4.19, 5.48	2.78
Glutaric acid	4.34, 5.42	3.26
Adipic acid	4.42, 5.41	2.87

Table ESI-3: pKa and distance between the carboxylic groups of different dicarboxylic acids used in the experiments.

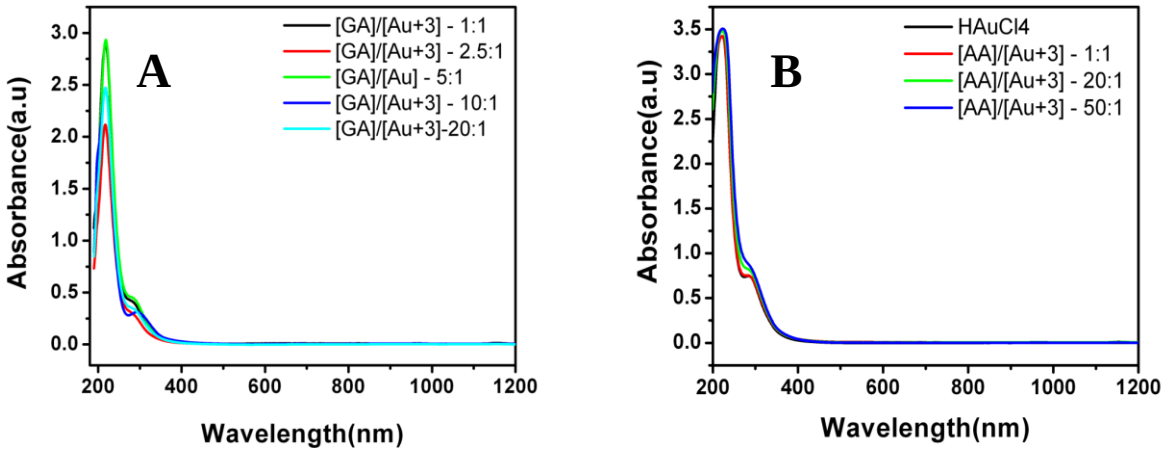

Figure ESI-4: UV-Vis- NIR of the samples synthesized using (A) glutaric acid and (B) adipic acid.

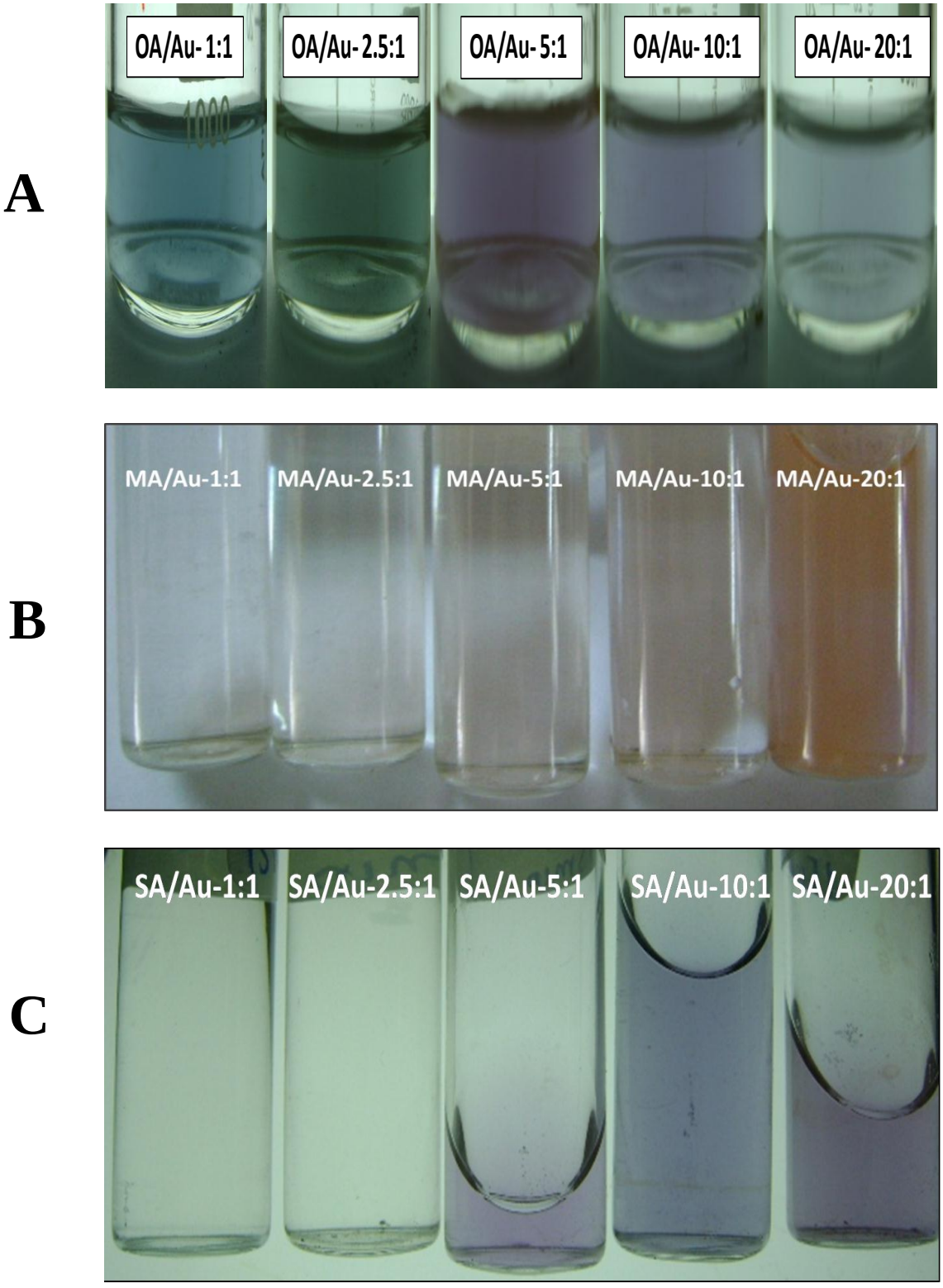

Figure ESI-5: Photographs of the samples synthesized at different molar ratios of (A) Oxalic acid, (B) malonic acid and (C) succinic acid to $HAuCl_4$.

ESI-6 Texture Coefficient:

Degree of orientation of crystallographic plane can be characterized from texture coefficient, if it is greater than 1 for a particular plane indicates the preferred orientation of that specific plane.

For (hkl) plane the texture coefficient can be expressed as[3]

$$C_{(hkl)} = \frac{\frac{I_{(hkl)i}}{I_{o(hkl)i}}}{\frac{1}{n}\sum_n \frac{I_{(hkl)n}}{I_{(hkl)n}}}$$

$C_{(hkl)}$ is the texture coefficient of the facet {*hkl*}
$I_{(hkl)}$ is the intensity of the (*hkl*) reflection of the sample under analysis
$I_{o(hkl)}$ is the intensity of the (*hkl*) reflection of a polycrystalline bulk sample
'***n***' is the number of reflections taken into account

Di carboxylic acid to HAuCl4 molar ratio	Texture Coefficient of (111) plane		
	Oxalic acid	Malonic Acid	Succinic acid
1:1	1.90	--	
2.5:1	1.98	--	
5:1	1.964	--	1.678
10:1	1.956	--	1.664
20:1	1.961	2	1.605

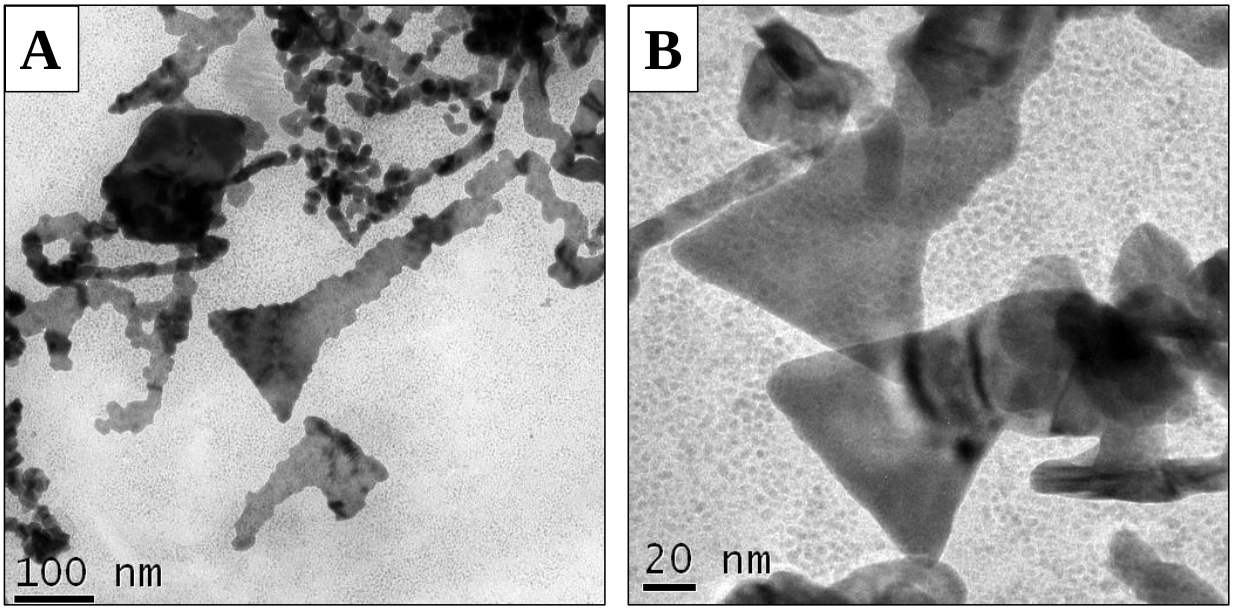

Figure ESI-7: TEM images of kite like Au nanostructures synthesized with oxalic acid using [OA]/[Au^{+3}] – 1:1.

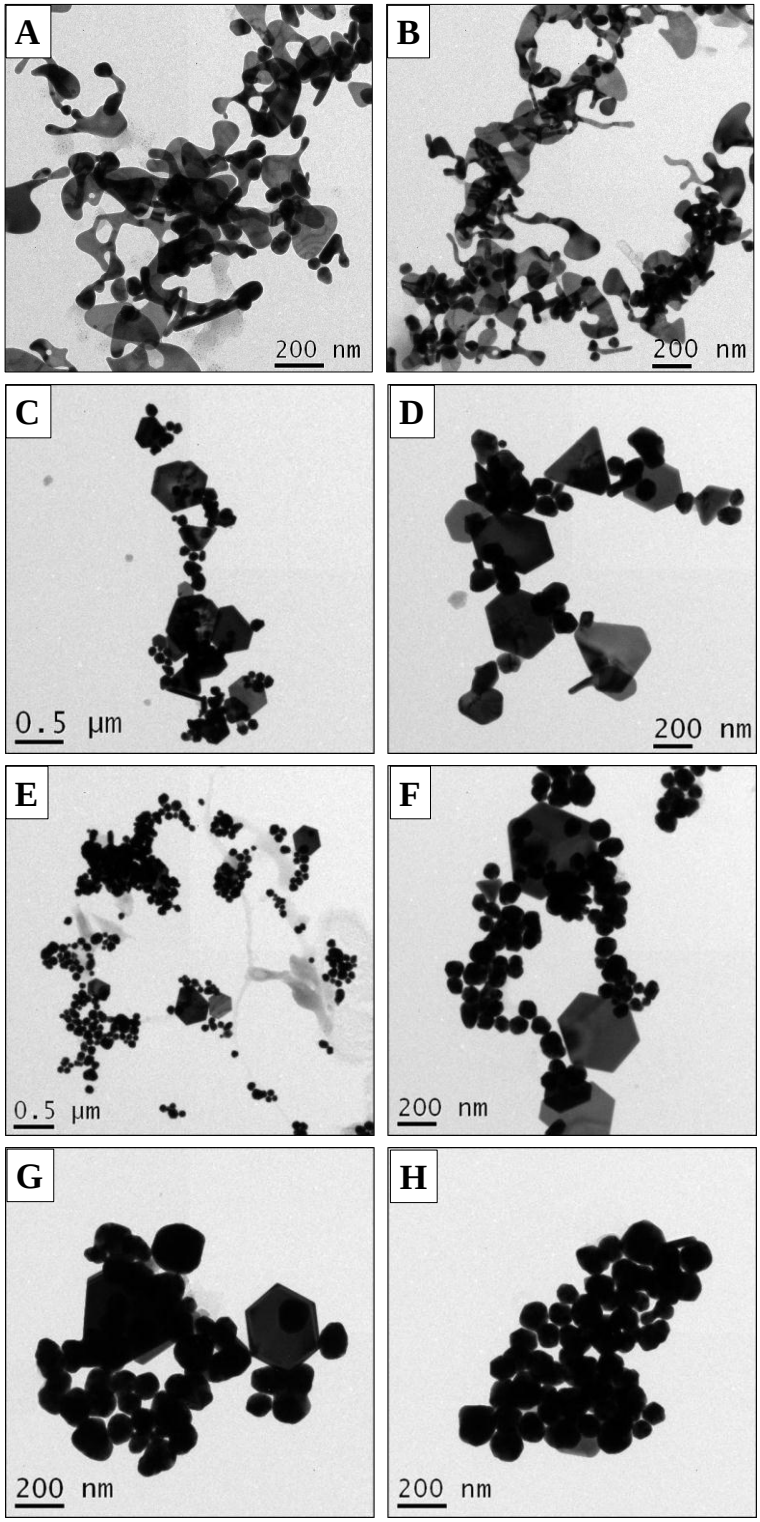

Figure ESI-8: Synthesis of Au nanostructures synthesized using oxalic acid at [OA]/[Au^{+3}] ratios (A-B) 2.5:1; (C-D) 5:1; (E-F) 10:1; and (G-H) at 20:1 respectively.

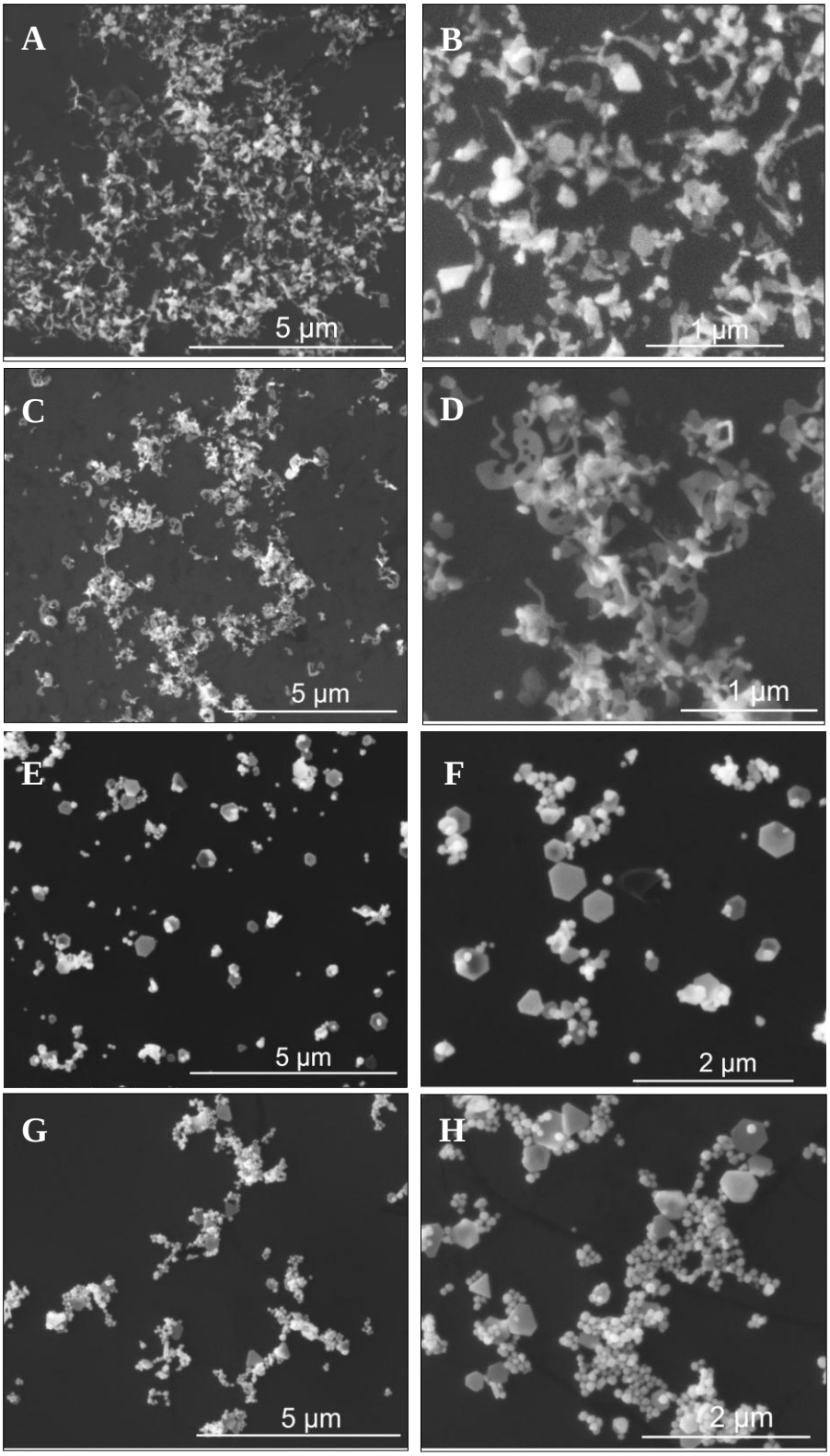

Figure ESI-9: SEM images of Au nanostructures synthesized using oxalic acid at [OA]/[Au^{+3}] - 1:1(figure A& B); [OA]/[Au^{+3}] -2.5:1 (Figure C &D); [OA]/[Au^{+3}] -5:1 (Figure E &F); [OA]/[Au^{+3}] - 10:1(figure G & H) respectively.

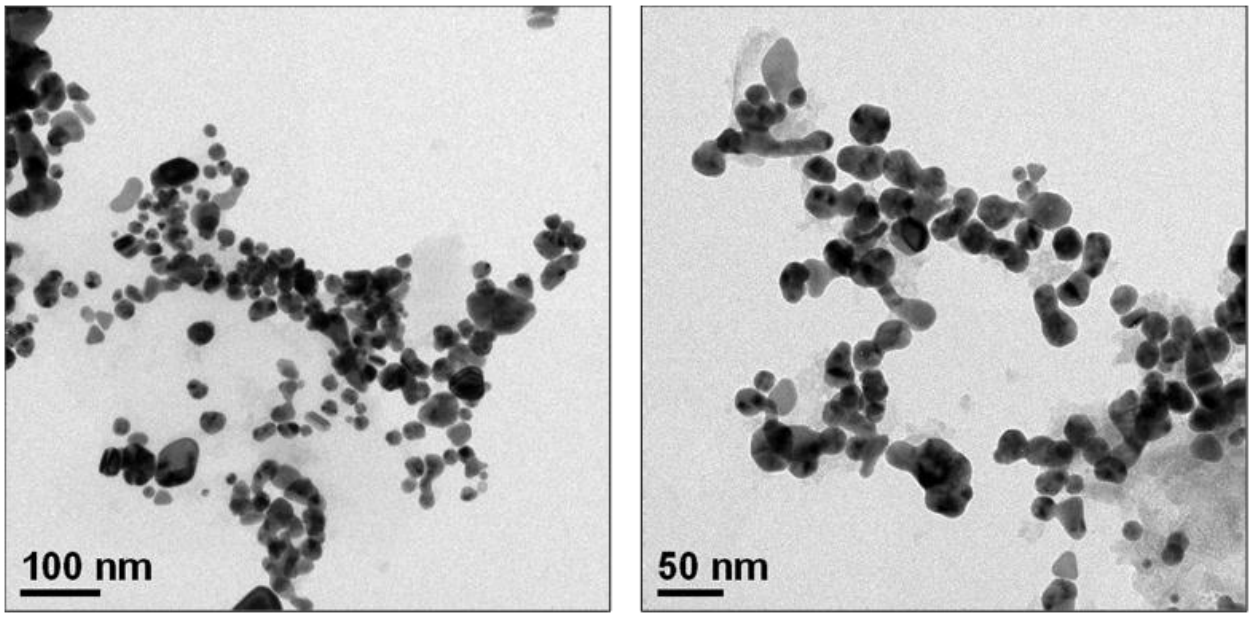

Figure ESI-10: TEM images of Au nanostructures synthesized using succinic acid at [SA]/[Au^{+3}] at 10:1.

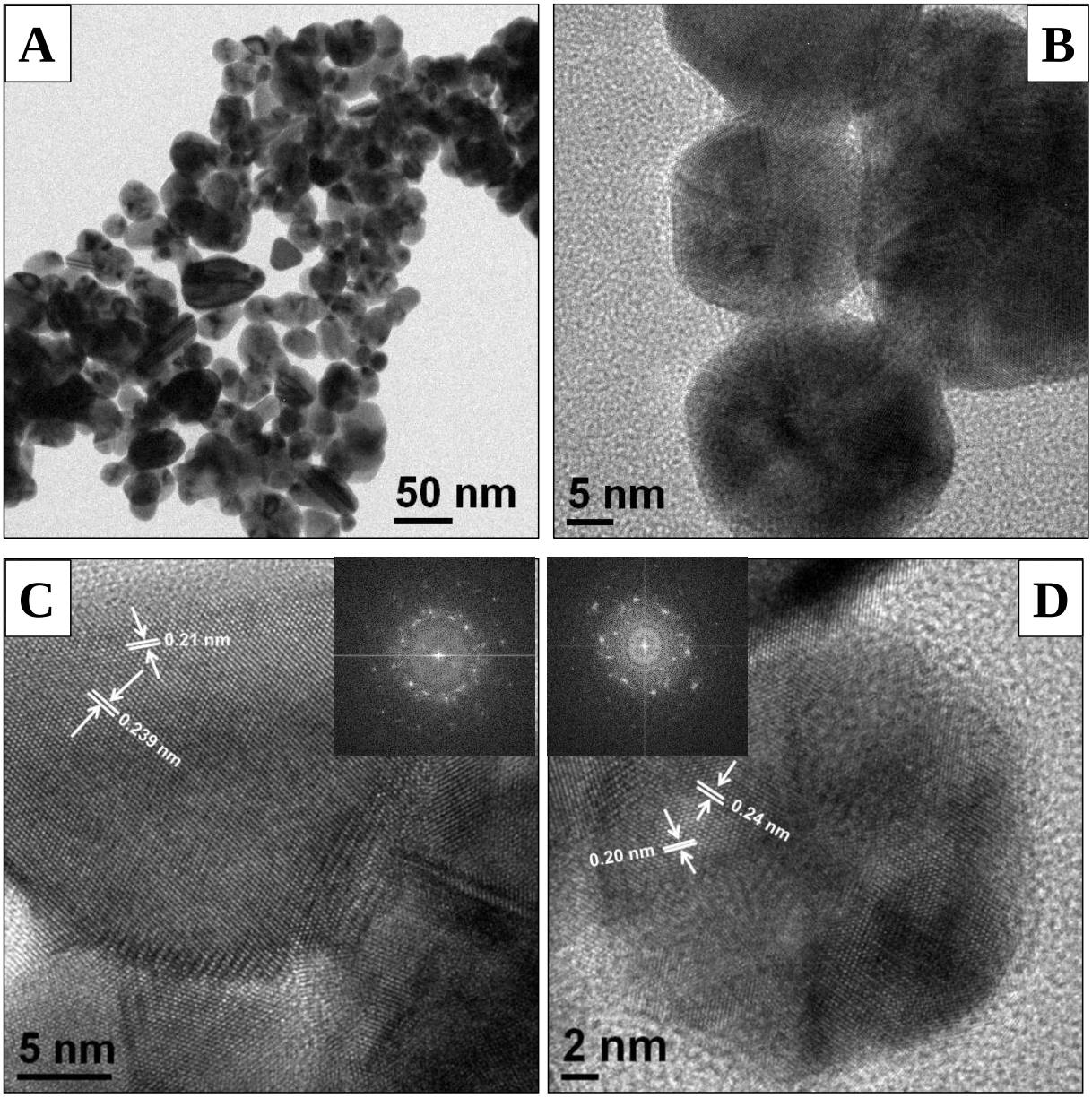

Figure ESI-11: (A) TEM image of Au nanostructures synthesized using succinic acid at [SA]/[Au^{+3}] at 20:1 (B-D) HRTEM images of twinned nanocrystals. Inset of C and D shows the FFT of corresponding nanocrystals.

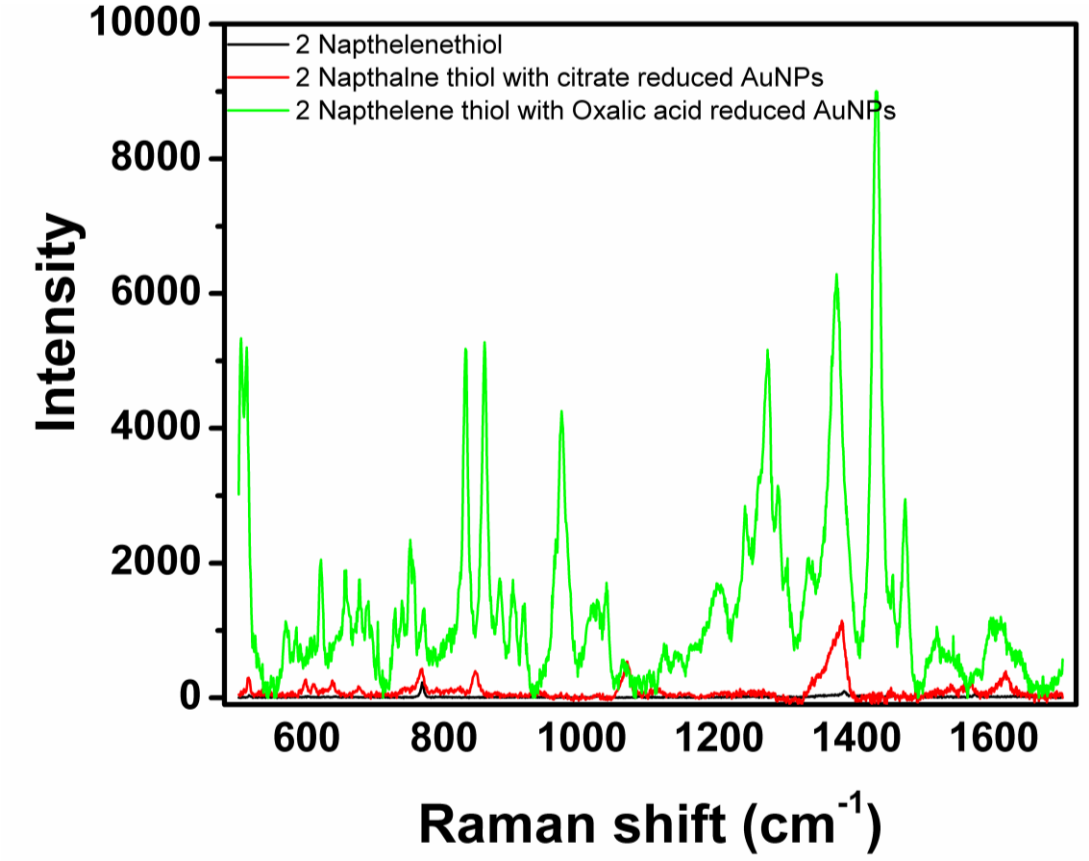

Figure ESI-12: SERS spectra of 2 Napthalenethiol (2 NAT) molecule with Au nanostructures synthesized from oxalic acid and trisodium citrate.

ESI -13: Analytical enhancement factor (AEF):

Analytical enhancement factor[4] of Au nanostructures synthesized from different carboxylic acids was calculated for the ring stretching Raman mode (at ~1428 cm^{-1}) of 2- Napthalenethiol molecule (1 µM) at excitation wavelength of 785 nm.

Analytical enhancement factor = (I_{SERS}/I_{Raman})* (C_{SERS}/C_{Raman})

Sample	**AEF**
[OA]/[Au^{+3}] – 1:1	7.4×10^9
[OA]/[Au^{+3}] – 5:1	1.26×10^9
[MA]/[Au^{+3}] – 20:1	2.9×10^8
[SA]/[Au^{+3}] – 5:1	2.6×10^7
[SA]/[Au^{+3}] – 20:1	6.4×10^6
Citrate reduced Au NP	5.5×10^6

References:

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2. Q. Zhang, N. Li, J. Goebl, Z. Lu, Y. Yin, *J. Am. Chem. Soc.* **2011,***133*, 18931-18939.
3. S. Karim, M.Toimil-Molares, F. Maurer, G. Miehe, W. Ensinger, J. Liu, T. Cornelius, R. Neumann, *App. Phys. A: Materials Science & Processing* **2006,** *84*, 403-407.

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