Citrate-hydrazine hydrogen-bonding driven single-step synthesis of tunable near-IR plasmonic, anisotropic silver nanocrystals: Implications in SERS spectroscopy of inorganic oxoanions

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Supplementary Information

1. Effect of concentration of reducing agent:

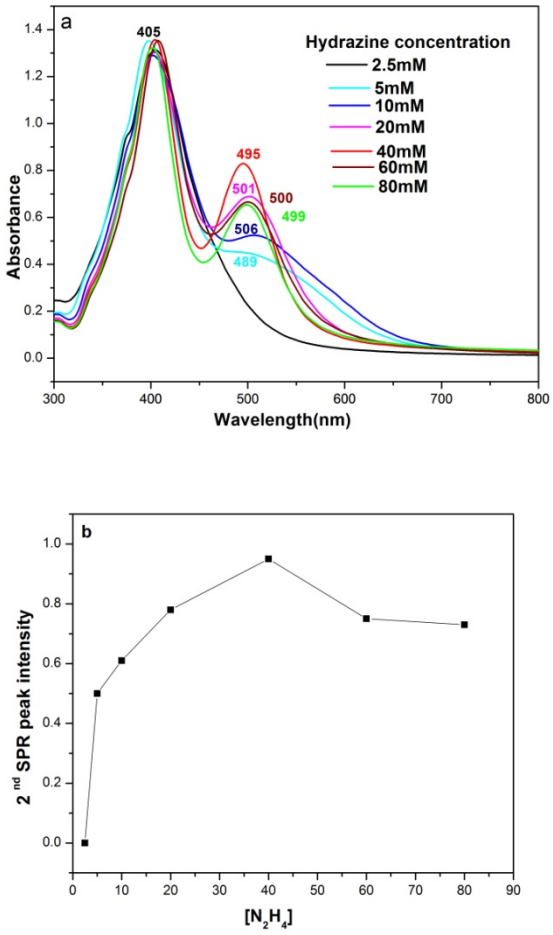

Figure S1. The effect of concentration of hydrazine hydrate on the UV-Vis absorption spectra of silver nanoparticles (pH 7, room temperature).

Concentration of reducing agent plays a crucial role in the formation and growth of anisotropic silver NCs. It was found that 5 mM hydrazine is the threshold concentration to initiate the directional growth. At this concentration of hydrazine, UV-vis absorption spectrum shows two SPR bands that consist of a strong band at 405 nm and a shoulder at about 489 nm. As the hydrazine concentration is increased to 10 mM, the absorption shoulder transforms into well-defined peak centred at 506 nm. With further increase in the

concentration to 20 and 40 mM, the plasmon peak moves to 501 and 495 nm respectively. This is accompanied by gradual rise in plasmon intensity and reduction in FWHM of the peaks.

3.Structural analysis by TEM images:

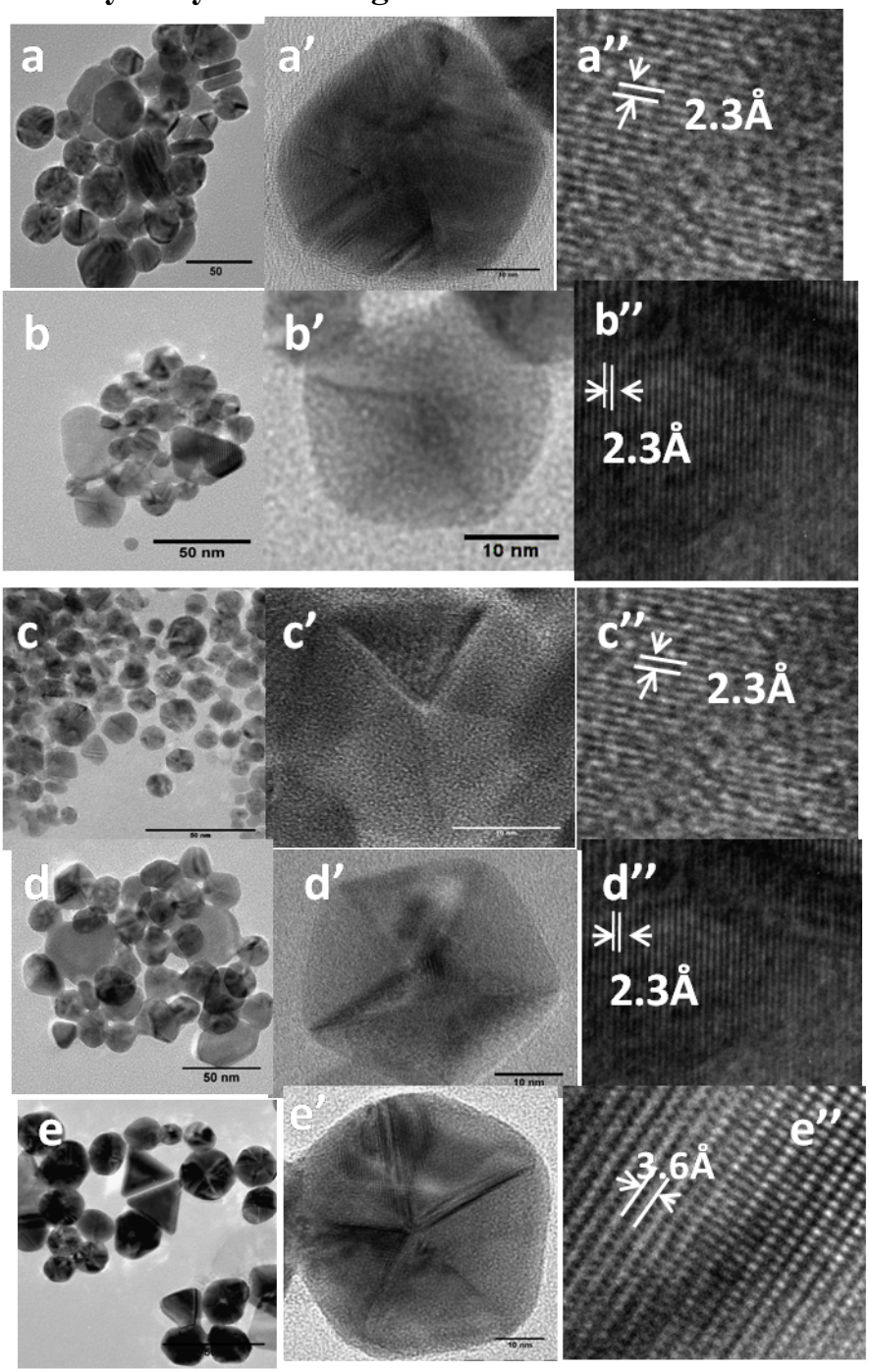

Figure S2. Low magnification and high resolution TEM images showing showing shape/size distribution and lattice fringes of anisotropic silver NCs (a) Ag-550, (b) Ag-700, (c) Ag-790, (d) Ag-900 and (e) Ag-1010.

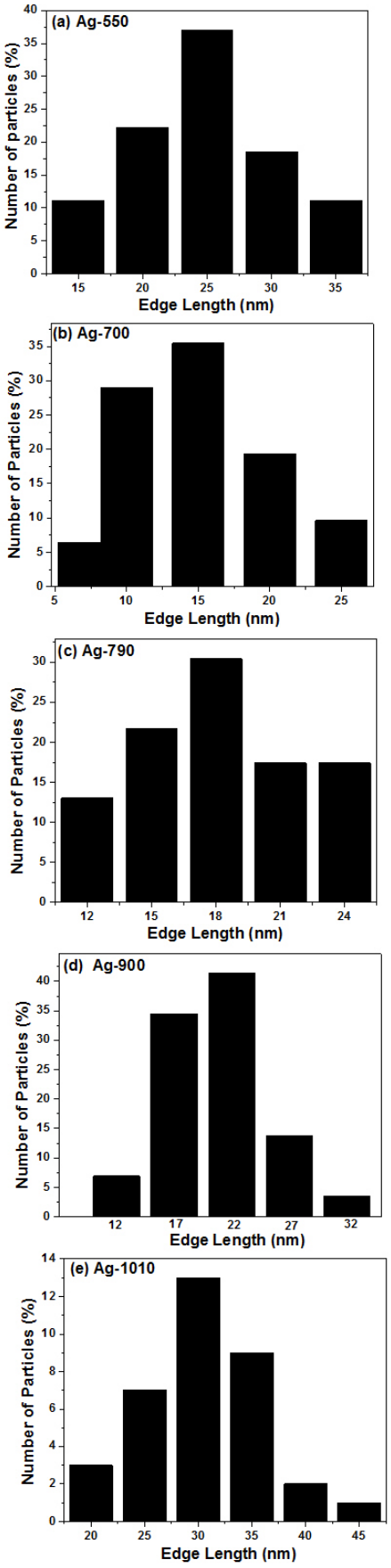

Figure S3. Size distribution histogram derived from TEM images: (a) Ag-550, (b) Ag-700, (c) Ag-790, (d) Ag-900 and (e) Ag-1010. (size is described in terms of the edge length of the anisotropic nanocrystals)

4. FTIR spectroscopy

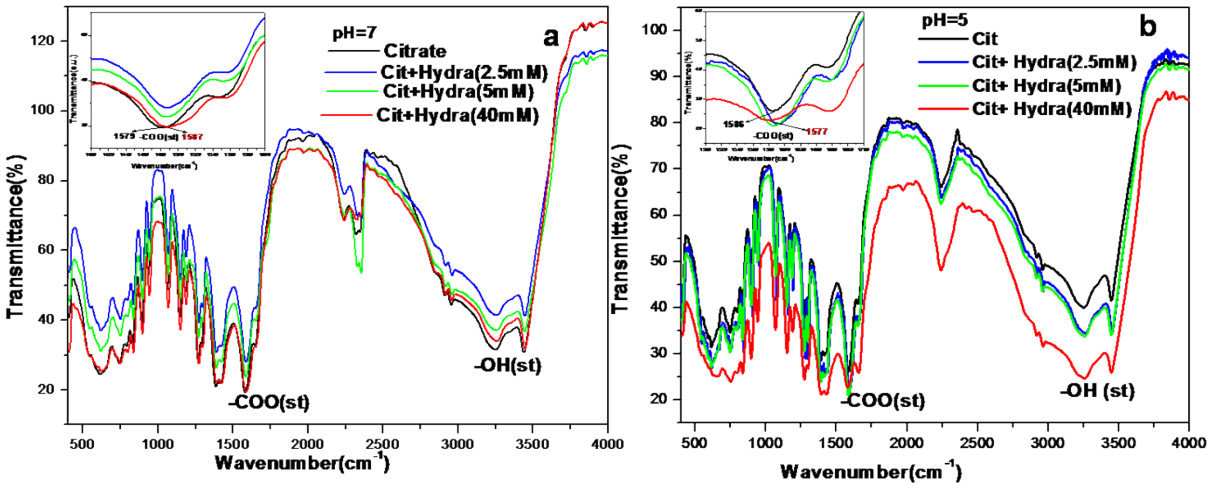

Figure S4. FTIR spectra of solid pure citrate and same amount citrate being combined with 2.5 mM, 5 mM and 40 mM hydrazine. inset: zoomed-in view of the 1500-1700 cm^{-1} region.

5. Raman spectral analysis for hydrogen bonded network:

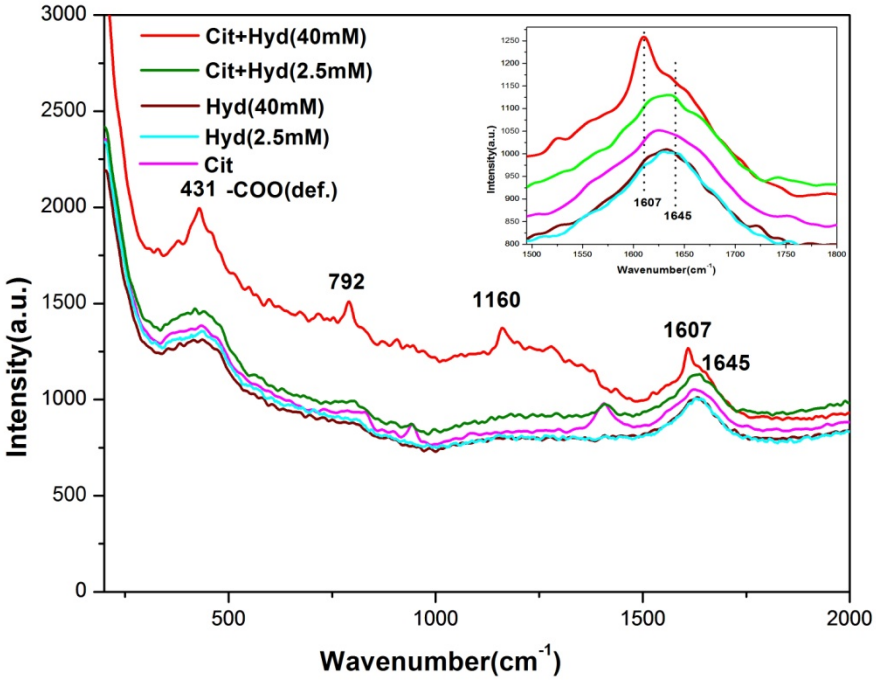

Figure S5. Solution phase Raman spectra of pure citrate, pure hydrazine (2.5 mM and 40 mM) and same amount citrate combined with hydrazine at aforementioned concentrations .

The analysis of the Raman spectra of pure citrate and the mixed solution of citrate and hydrazine corroborates our FTIR analysis with regard to hydrogen bonding interaction between the two species. The mixed solution having lower concentration of hydrazine, 2.5

mM, does not show any difference between the peak for carboxylic asymmetric stretch (1620 cm^{-1}) of pure citrate solution and citrate combined with 2.5 mM N_2H_4 solution. However, significant change can be seen in the Raman spectra of mixed solution having much higher concentration (40mM) of hydrazine. It can be easily seen that the carboxylic asymmetric stretch splits into two vibration modes, one at comparatively lower energy side (1607 cm^{-1}) and another at higher energy side (1645 cm^{-1}). The new peak at 1607 cm^{-1} could be attributed to H-bonding interaction between citrate and hydrazine. However, apart from the asymmetric stretching mode, some significant changes in the COO^- deformation band (431, 1160 cm^{-1}) of citrate have also been observed at high concentration of hydrazine (40mM) which could be attributed to strengthening of hydrogen bonded network.

6. Second Derivative FTIR analysis for hydrogen bonded network (pH 5)

Table S1: The position and area of the deconvoluted FTIR absorption peaks of mixed solution of citrate(pH 5) and hydrazine in the region of 1512-1739 cm^{-1}

Sample	**Deconvoluted Peaks** Position in cm^{-1} (% contribution to the total integrated intensity)			
	1,1'	2,2'	4,4'	5,5'
Cit	1577 (65%)	.....	.....	1651 (35%)
Cit+hyd (2.5 mM)	1580 (44%)	1602 (12%)	1660 (23%)	1673 (21%)
Cit+hyd (5 mM)	1581 (38%)	1602 (16%)	1660 (24%)	1674 (22%)
Cit+hyd (10 mM)	1581 (41%)	1604 (19%)	1657 (24%)	1676 (16%)
Cit+hyd (30 mM)	1575 (35%)	1599 (25%)	1655 (22%)	1671 (18%)
Cit+hyd (40 mM)	1577 (33%)	1600 (29%)	1655 (24%)	1673 (14%)

7. The deconvolutions of plasmon peaks of growing Ag Nanocrystals

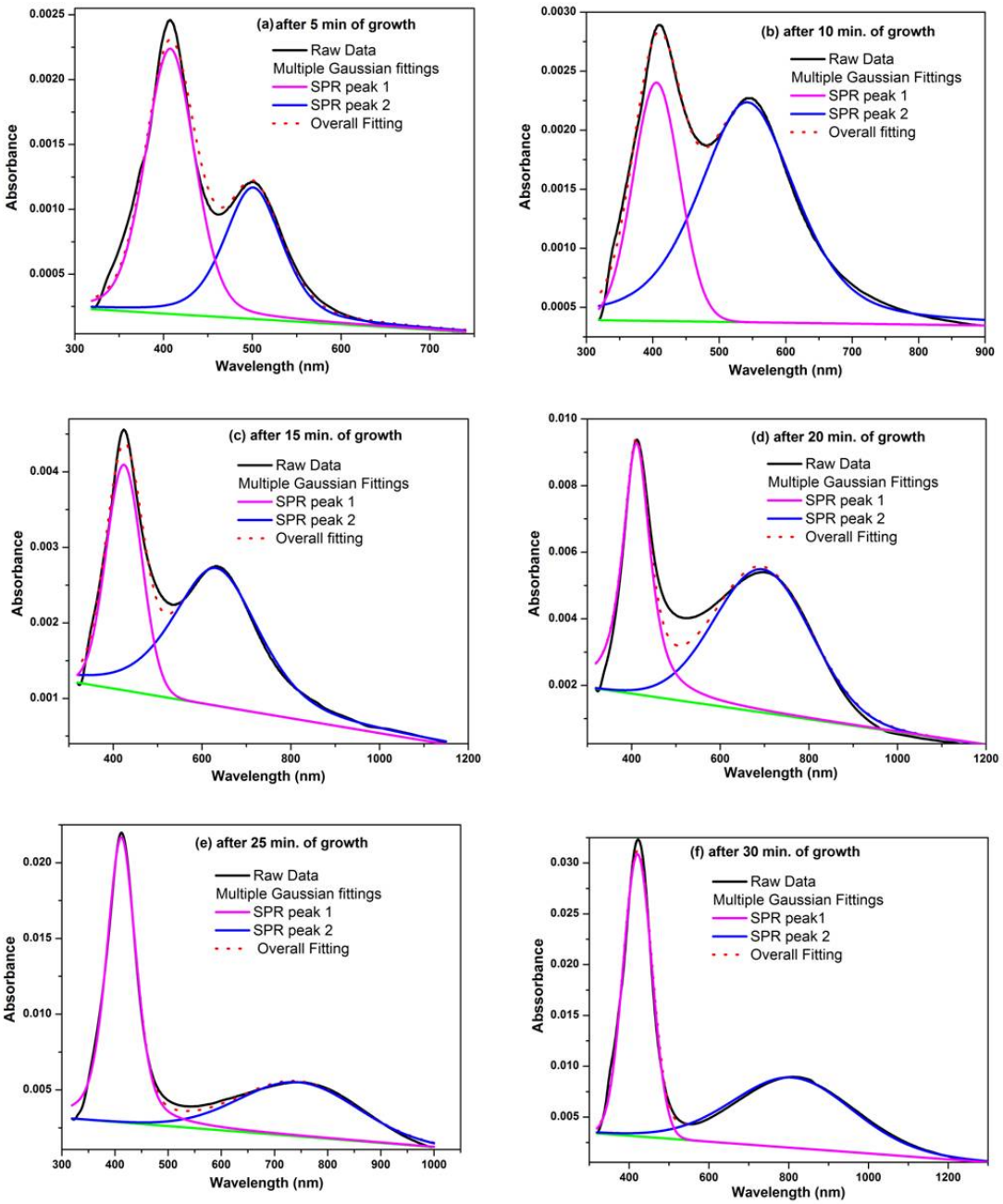

Figure S6. Deconvolution of plasmonic absorption of growing nanocrystals with Gaussian like functions

Table S2 Details of Gaussian deconvolutions for the plasmon peaks of growing anisotropic nanocrystals

*area under the deconvoluted peak

Time (min.)	SPR Peak 1			SPR Peak 2			Ratio of Plasmon intensities A_{SPR2}/A_{SPR1}
	Position (nm)	FWHM (nm)	Integrated intensity* A_{SPR1}	Position (nm)	FWHM (nm)	Integrated intensity* A_{SPR2}	
5	407	65	0.157	501	77	0.1	0.6369
10	410	86	0.189	545	157	0.408	2.1587
15	424	94	0.301	632	227	0.536	1.7807
20	411	72	0.780	696	256	1.172	1.5025
25	412	65	1.526	745	267	1.010	0.6618
30	420	84	2.603	809	352	2.576	0.9896