

Seed free synthesis of polyethylene glycol stabilized gold nanoprism exploiting manganese metal at low pH

Kanika Bharti,^a Md Azimuddin Sk^a and Kalyan K. Sadhu*^a

Department of Chemistry, Indian Institution of Technology Roorkee, Roorkee 247667, Uttarakhand, India

Correspondence:

Kalyan K. Sadhu
sadhu@cy.iitr.ac.in

Table of Contents

1.	Figure S1-S3.....	2
2.	Figure S4-S6.....	3
3.	Figure S7-S9.....	4
4.	Figure S10-S12.....	5
5.	Figure S13-S14.....	6
6.	Figure S15-S16 and Table S1.....	7
7.	Figure S17-S19.....	8
8.	Figure S20-S21 and Table S2.....	9
9.	Figure S22-S24.....	10
10.	Figure S25-S27.....	11
11.	Figure S28-S29 and Table S3.....	12
12.	Figure S30-S31.....	13
13.	Figure S32.....	14
14.	Figure S33-S34 and Table S4.....	15
15.	Figure S35-S37.....	16
16.	Figure S38-S40.....	17

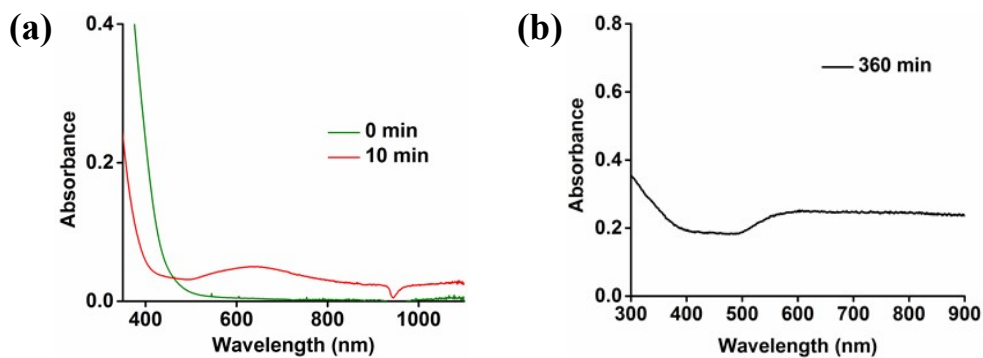


Figure S1: Time dependent absorbance spectra obtained using Au:PEG as 1:0.5 (a) 0- 10 min (b) after 360 min.

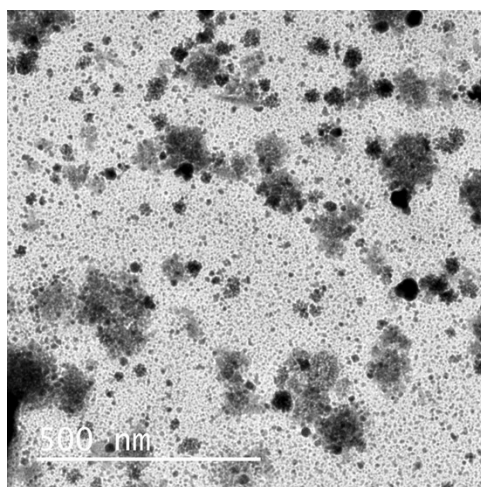


Figure S2: TEM image for reaction performed using Au:PEG as 1:0.5 after 10 min. The dark spots are due to gold nanoparticle and the lighter shade throughout the grid is due to excess PEG.

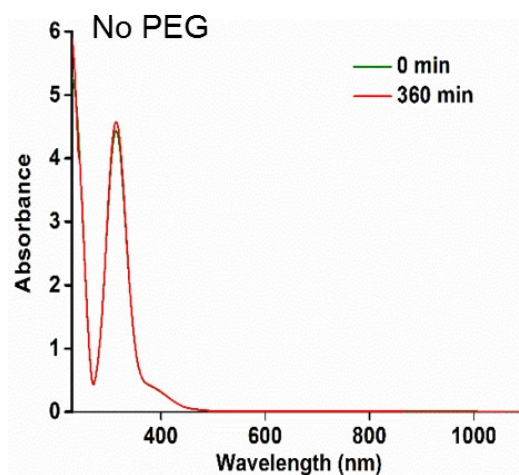


Figure S3: Time dependent absorbance spectra obtained using Au:Mn:HCl as 1:2:26.

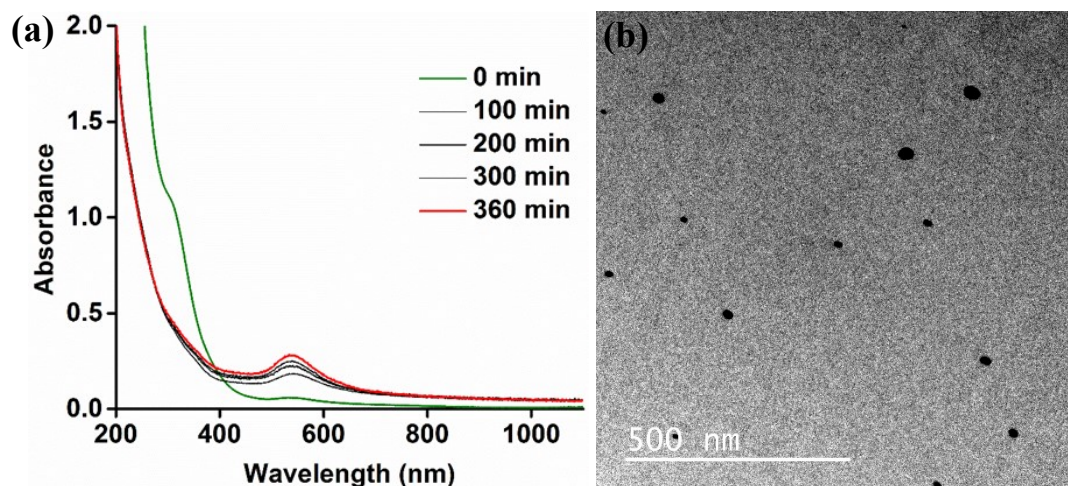


Figure S4: (a) Time dependent absorbance spectra obtained using Au:PEG:Mn as 1:0.5:2 (b)TEM image for reaction performed using Au:PEG:Mn as 1:0.5:2.

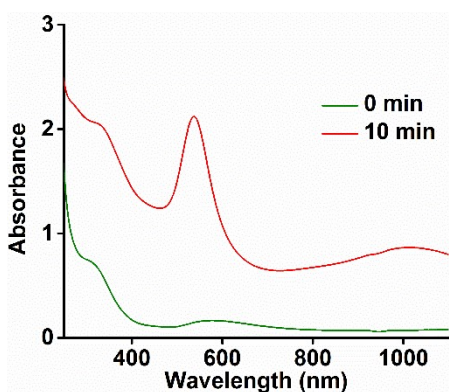


Figure S5: Time dependent absorbance spectra obtained using of Au:PEG:Mn:HCl as 1:0.5:2:10.

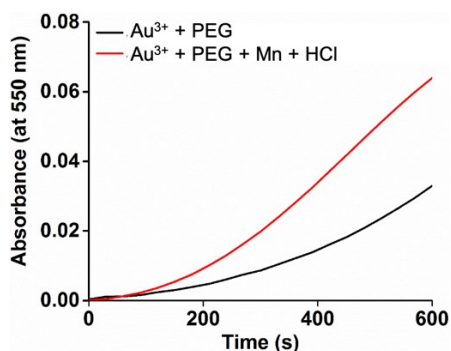


Figure S6: Time dependent absorption at 550 nm after the reduction of Au³⁺ (a) by PEG only and (b) by all three-reagent combination.

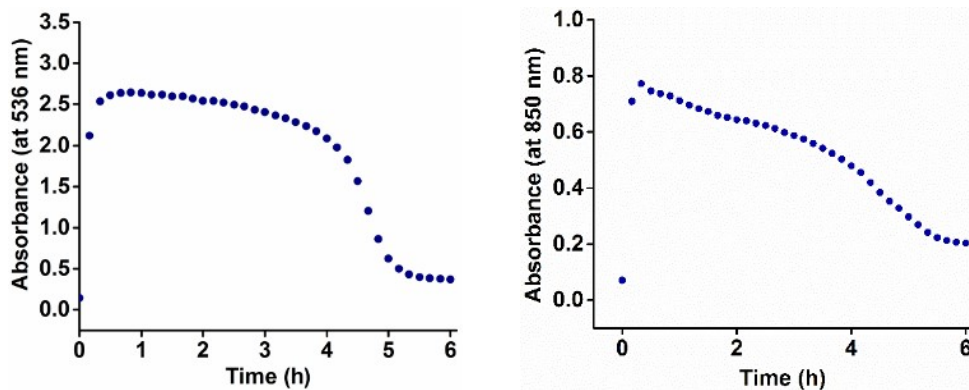


Figure S7: Time dependent absorbance plot at 536 and 850 nm obtained for reaction performed for 6 h using Au:PEG:Mn:HCl as 1:0.5:2:10

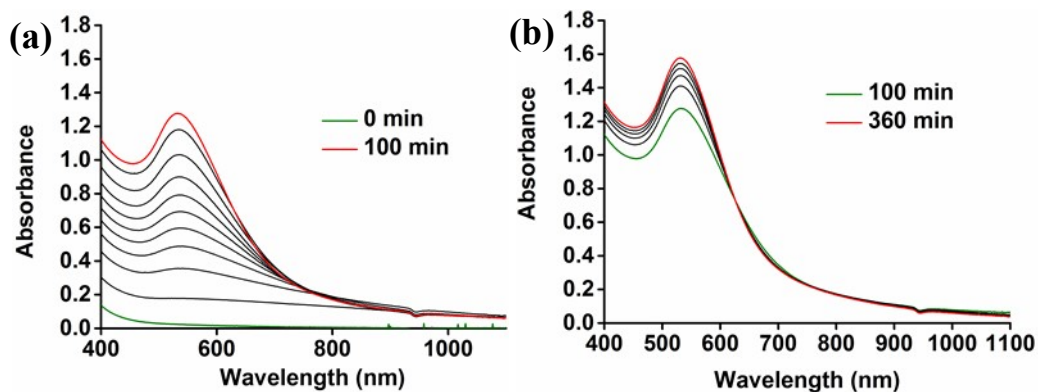


Figure S8: Time dependent absorbance spectra obtained using Au:PEG:Mn as 1:0.5:2 in 26 equivalent NaOH.

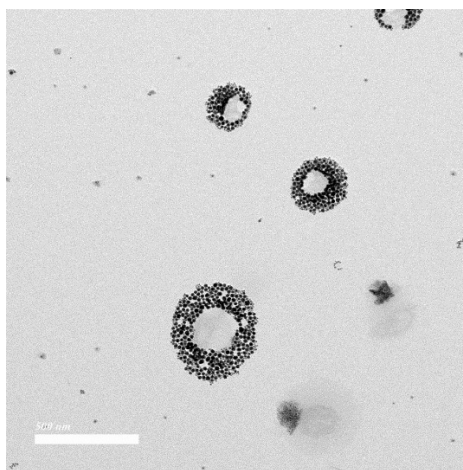


Figure S9: TEM image obtained using Au:PEG:Mn as 1:0.5:2 in 26 equivalent NaOH.

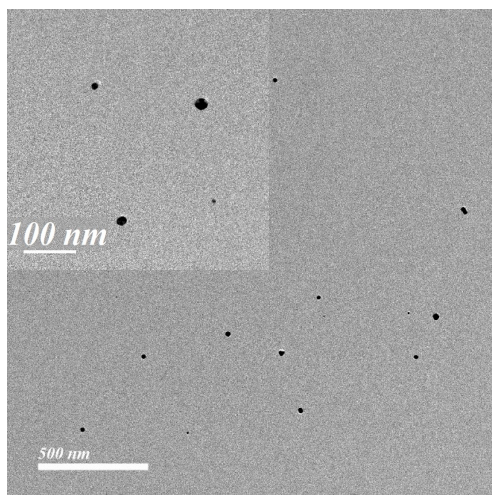


Figure S10: TEM image taken after 6 h of the reaction using Au:PEG:Mn:HCl as 1:0.5:2:10.

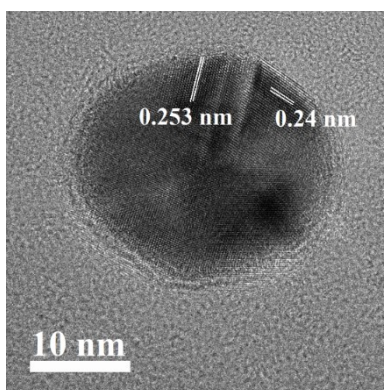


Figure S11: HRTEM image showing parallel twinning boundaries using Au:PEG:Mn:HCl as 1:0.5:2:10 for 6 h.

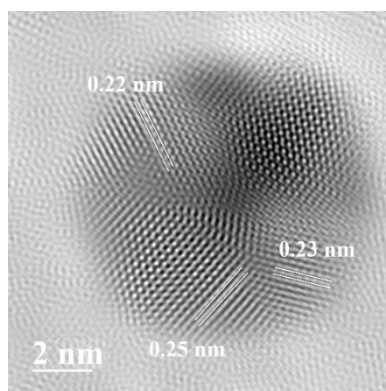


Figure S12: HRTEM image showing multiple packing defects using Au:PEG:Mn:HCl as 1:0.5:2:10 for 6 h.

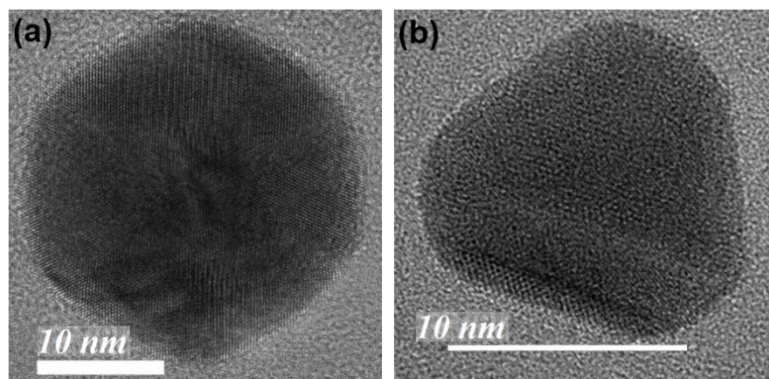


Figure S13: HRTEM images of gold nanostructures with (a) pentatwinned nanostructures and (b) nanoprism obtained from the reaction between Au:PEG:Mn:HCl as 1:0.5:2:20 for 6 h.

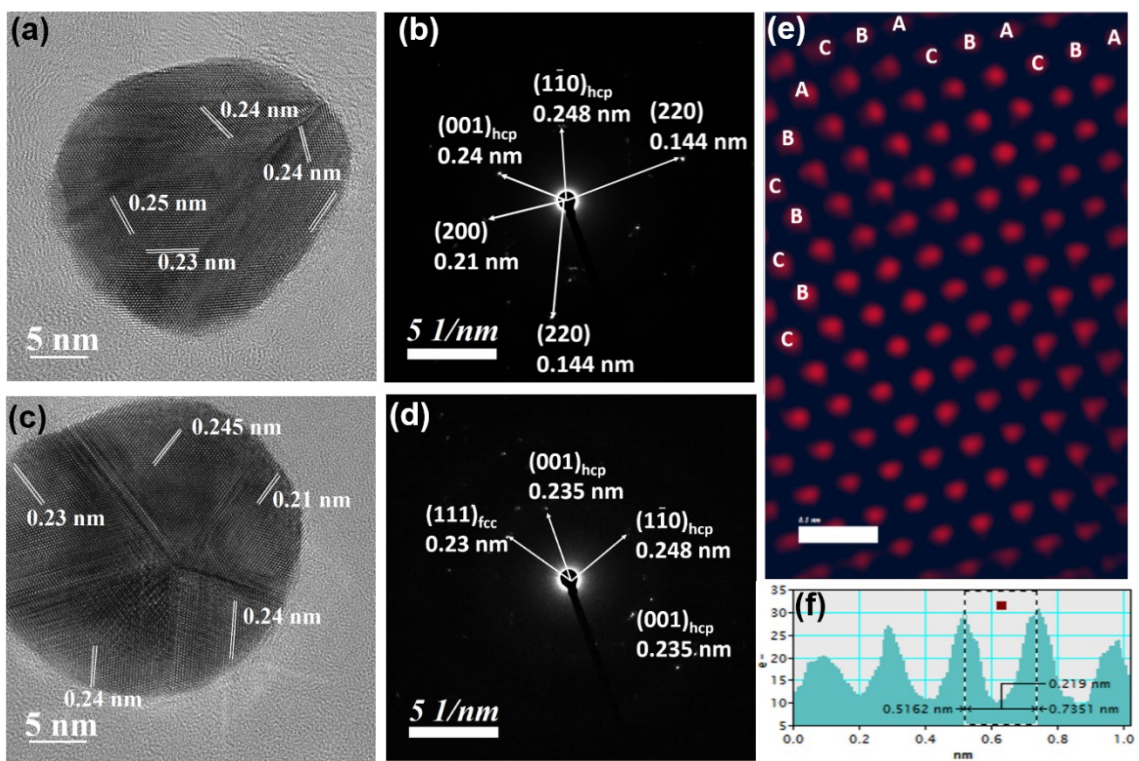


Figure S14: HRTEM images of gold nanostructures with (a) truncated nanoprism, (b) SAED analysis of truncated nanoprism, (c) pentatwinned nanostructures (d) SAED analysis of pentatwinned nanostructures, (e) HAADF image showing ABC-ABC (*fcc*) type and BC-BC-BC (*hcp* (2H)) type packing and (f) distance of fringe lines in truncated nanoprism using Au:PEG:Mn:HCl as 1:0.5:2:24 for 6 h.

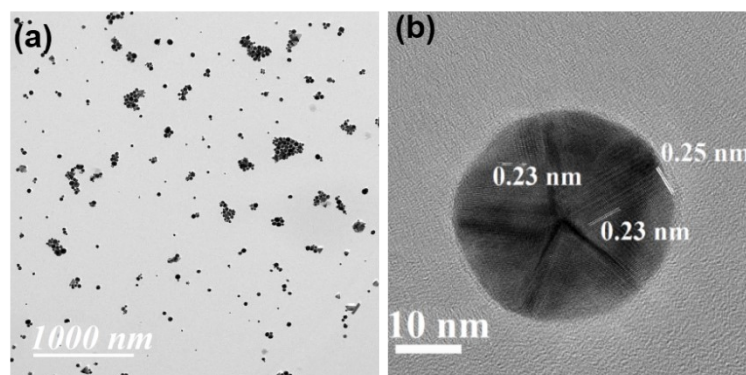


Figure S15: HRTEM images of (a) gold nanostructures with mostly (b) pentatwinned nanostructures using Au:PEG:Mn:HCl as 1:0.5:2:32 for 6 h.

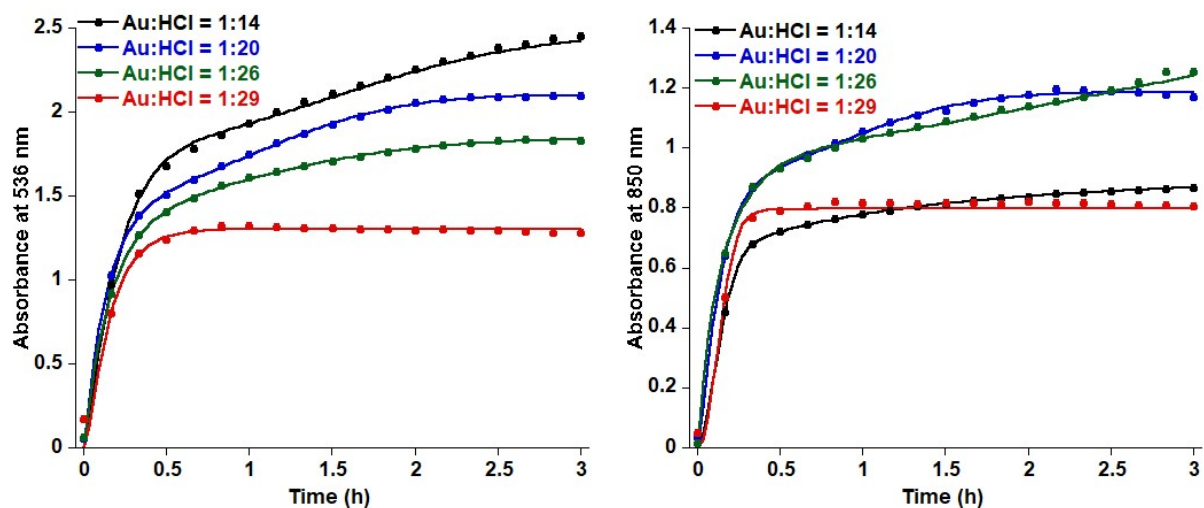


Figure S16: Fitting of time dependent data at 536 nm and 850 nm in presence of HCl variation using equation (1).

Table S1. Calculated rate constants (k_1 and k_2) and Avrami constants (n_1 and n_2) from Absorbance data in Fig. S16

Equiv. of HCl	536 nm				850 nm			
	Spherical nanoparticle formation		Nanoprism formation		Aggregation of Spherical nanoparticle		Nanoprism formation	
	k_1 (h^{-2})	n_1	k_2 (h^{-1})	n_2	k_1 (h^{-2})	n_1	k_2 (h^{-1})	n_2
14	0.22	2.28	5.99	1.15	29.50	1.85	0.91	0.75
20	0.49	2.27	6.54	0.98	0.75	2.10	10.54	1.20
26	0.54	1.81	5.56	0.95	0.08	1.58	4.99	0.85
29	45.15	1.88	7.11	1.17	37.00	2.00	1.35	1.00

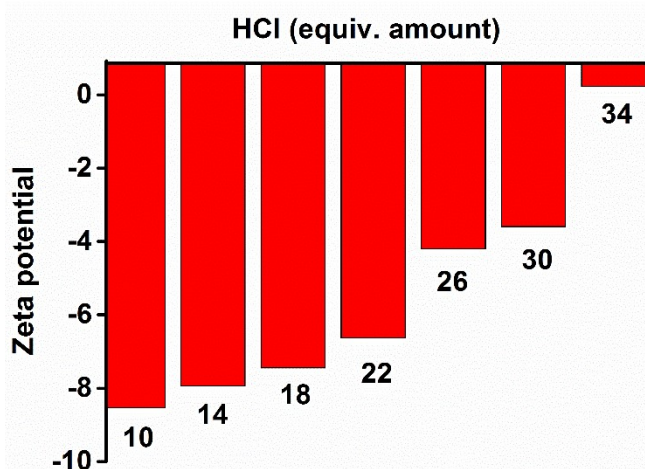


Figure S17: Variation in ζ potential of the synthesized particles while changing HCl amount from 10 equivalent to 32 equivalent.

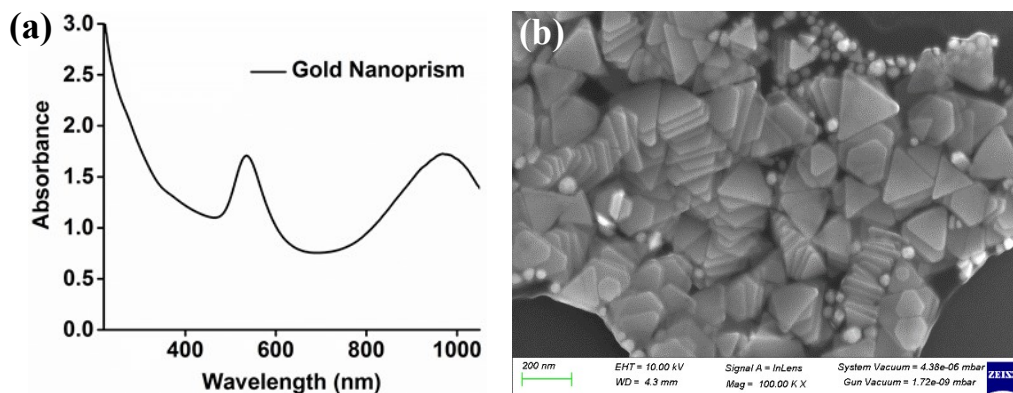


Figure S18: (a) Absorbance spectrum and (b) FESEM image of the gold nanoprism synthesis (Au:PEG:Mn:HCl as 1:0.5:2:26 for 30 min) on large scale after purification by centrifugation.

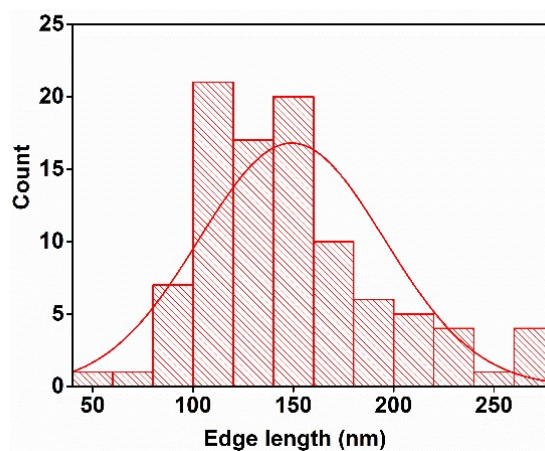


Figure S19: Histogram of nanoprisms after purification by centrifugation.

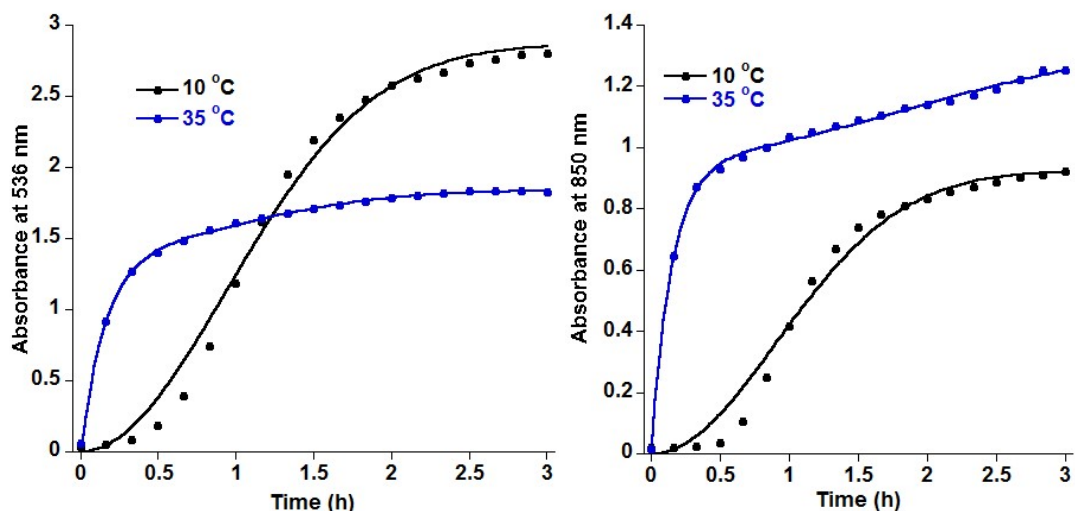


Figure S20: Fitting of time dependent data at 536 nm and 850 nm at different temperature using equation (2).

Table S2. Calculated rate constants (k_1 and k_2) and Avrami constants (n_1 and n_2) from Absorbance data in **Fig. S20**.

Temperature (°C)	536 nm		850 nm	
	Spherical nanoparticle formation	Nanoprism formation	Aggregation of spherical nanoparticle formation	Nanoprism formation
	k_1 (h ⁻²)	k_2 (h ⁻¹)	k_1 (h ⁻²)	k_2 (h ⁻¹)
10	0.57	0.0023	0.61	0.59
35	0.51	5.59	0.16	6.51

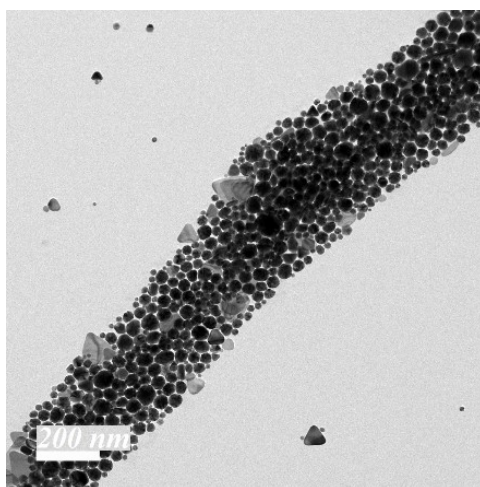


Figure S21: TEM image at 10 °C using 26 eq. HCl

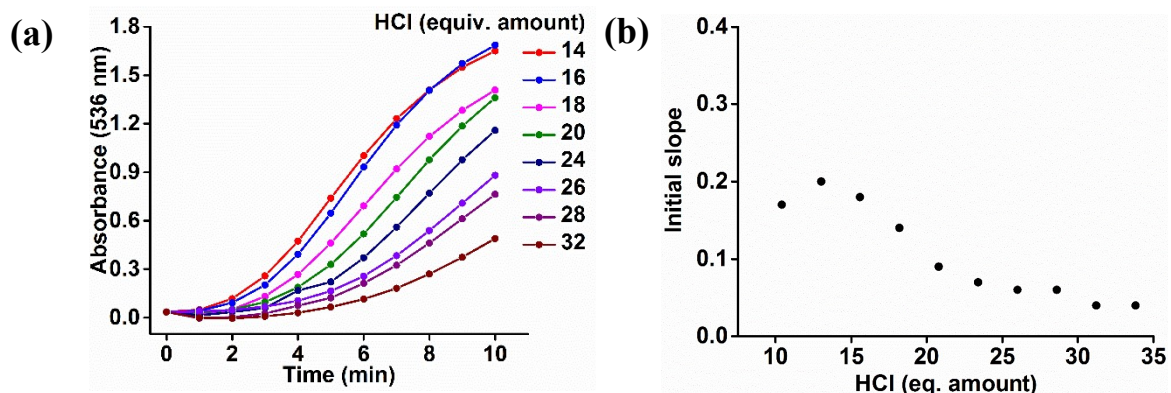


Figure S22: (a) Time dependent absorbance studies for 10 minutes and (b) change in the calculated initial slope with increasing HCl concentration.

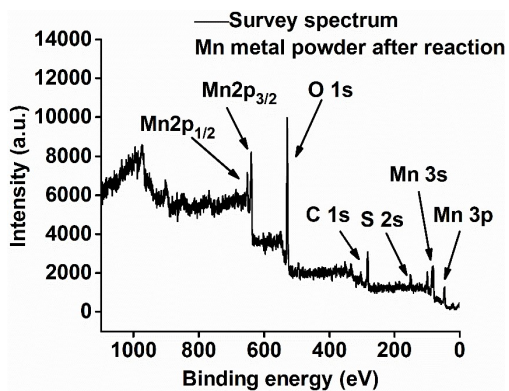


Figure S23: Survey scan of XPS confirms the presence of Mn and trace amount of PEG in the precipitate.

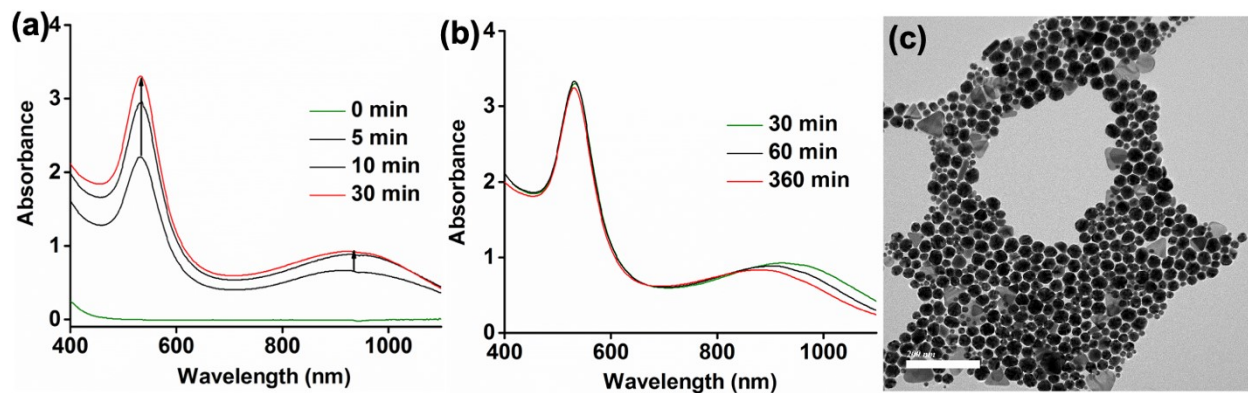


Figure S24: (a-b) Absorbance at different time intervals and (c) TEM image using 26 mM H₂SO₄.

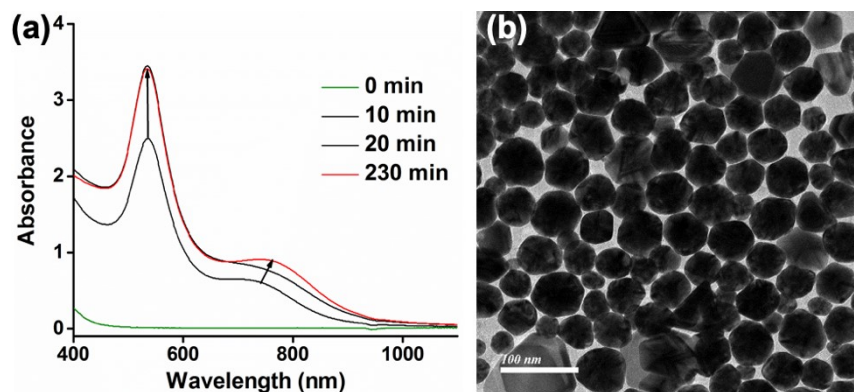


Figure S25: (a) Absorbance at different time intervals and (b) TEM image using 26 mM HNO₃.

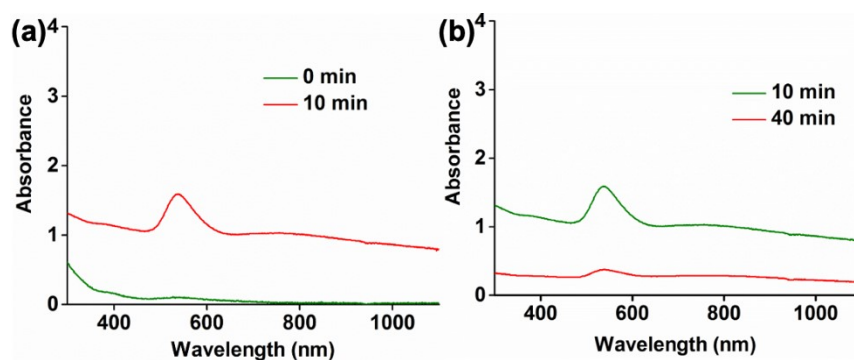


Figure S26: (a-b) Absorbance at different time intervals using 11 mM HBr.

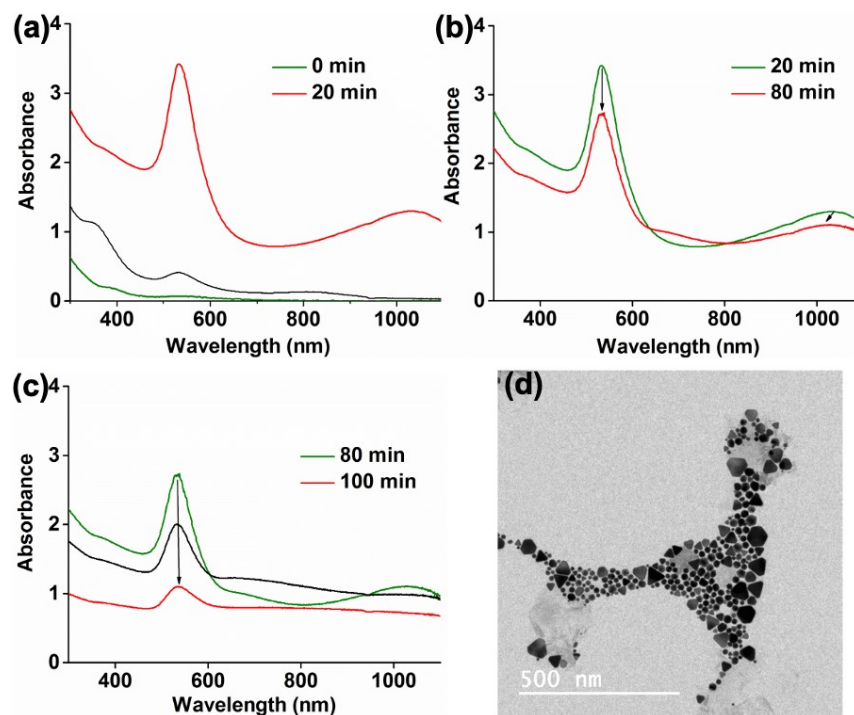


Figure S27: (a-c) Absorbance at different time intervals and (d) TEM imaging using 8 mM HBr.

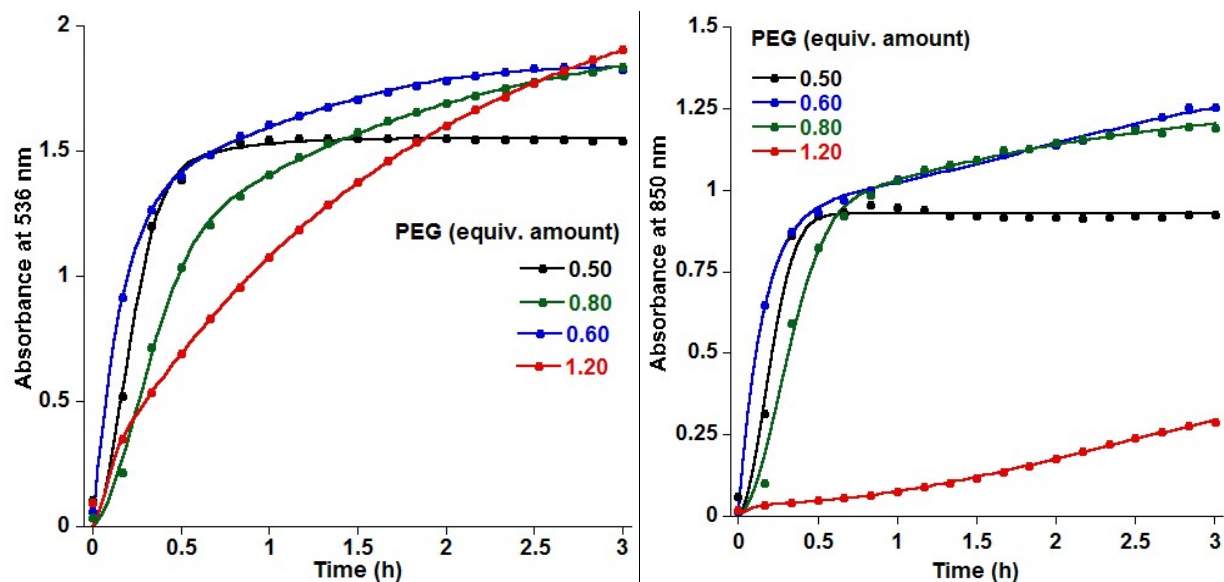


Figure S28: Fitting of time dependent data at 536 nm and 850 nm absorbance in presence of 0.5-1.2 equivalent PEG with respect to Au^{3+} amount using equation (2).

Table S3. Calculated rate constants (k_1 and k_2) from Absorbance data in **Fig. S28**.

Equiv. of PEG	536 nm		850 nm	
	Spherical nanoparticle formation	Nanoprism formation	Aggregation of spherical nanoparticle formation	Nanoprism formation
	k_1 (h^{-2})	k_2 (h^{-1})	k_1 (h^{-2})	k_2 (h^{-1})
0.50	14.72	2.82	16.65	8.15
0.60	0.51	5.59	0.16	6.51
0.80	6.97	0.63	7.28	0.51
1.20	85.94	0.54	0.09	13.18

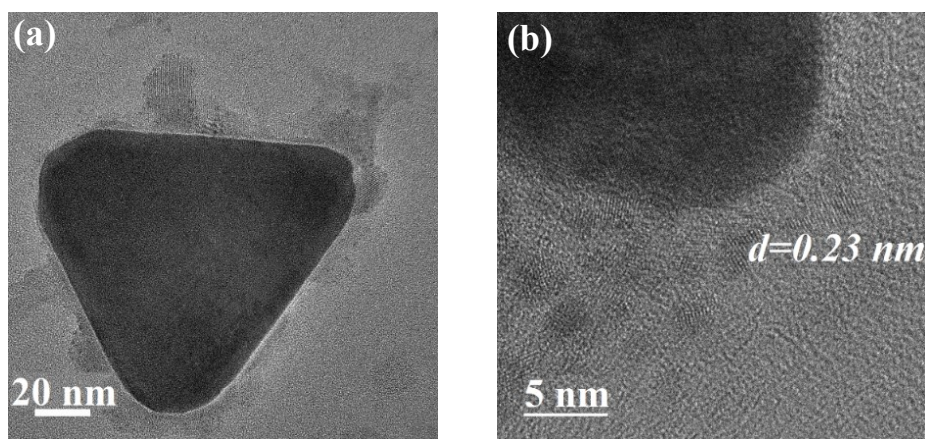


Figure S29: (a) TEM and (b) HRTEM images of gold nanoclusters observed on the surface of gold nanoprism using Au:PEG:Mn:HCl as 1:1.2:2:26 for 6 h.

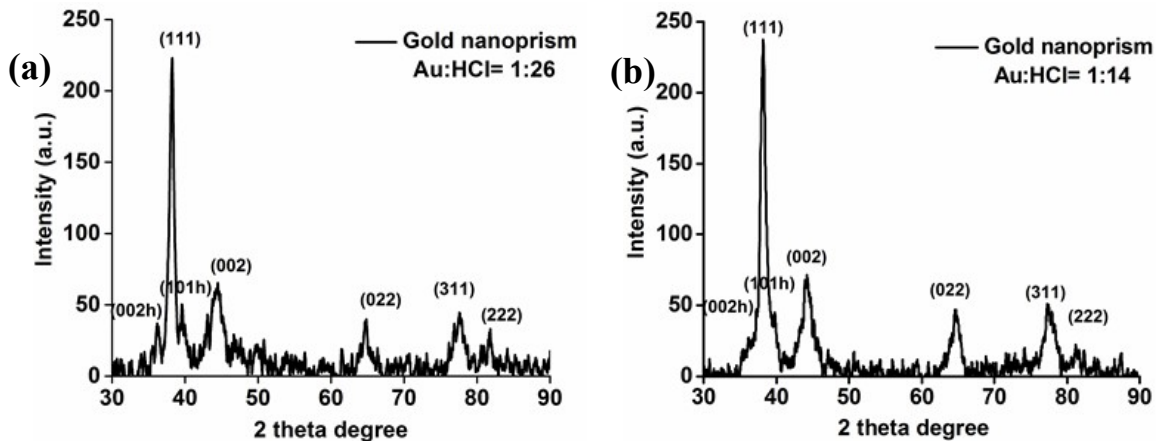


Figure S30: XRD pattern obtained with varying HCl concentration (a) Au:HCl= 1:26 (b) Au:HCl= 1:14.

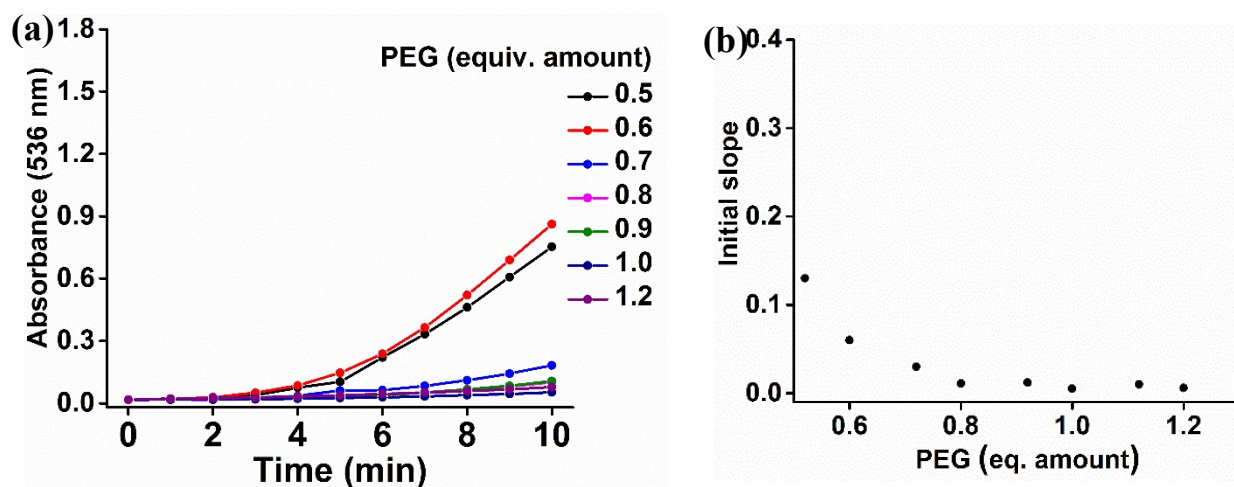


Figure S31: (a) Time dependent absorbance studies for 10 minutes and (b) changes in the calculated initial slope with increasing PEG amount.

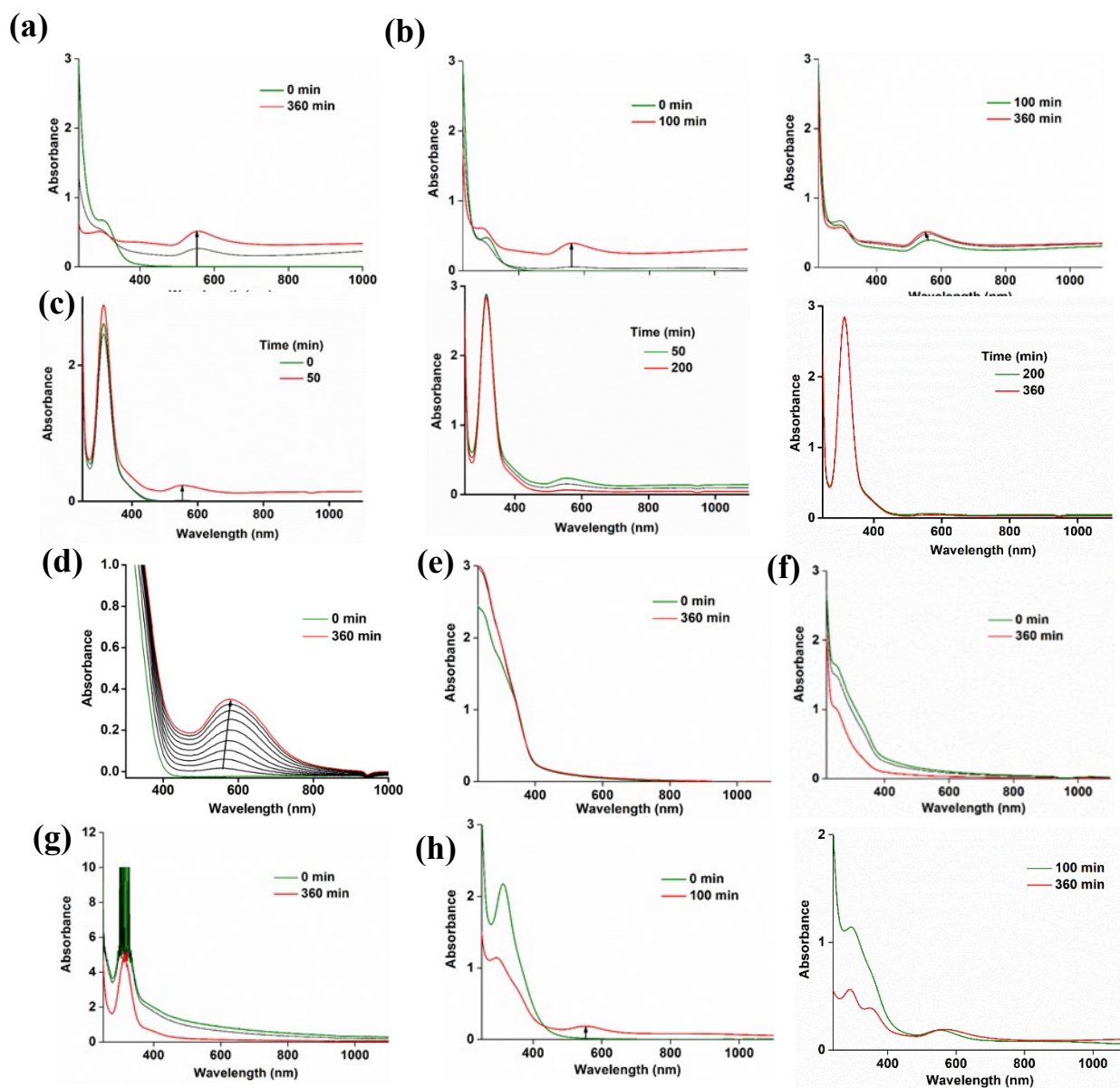


Figure S32: Absorbance spectra using (a) Reduced glutathione, (b) oxidized glutathione, (c) PEG-SH ($M_n=6000$), (d) PEG-SH ($M_n=800$), (e) 3-mercaptopropanoic acid, (f) 6-mercaptohexanoic acid, (g) polystyrene thiol terminated and (h) Lipoic acid.

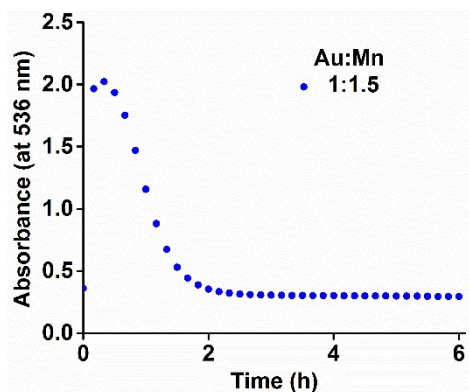


Figure S33: Time dependent absorbance at 536 nm using Au:PEG:Mn:HCl as 1:0.5:1.5:26 for 6 h.

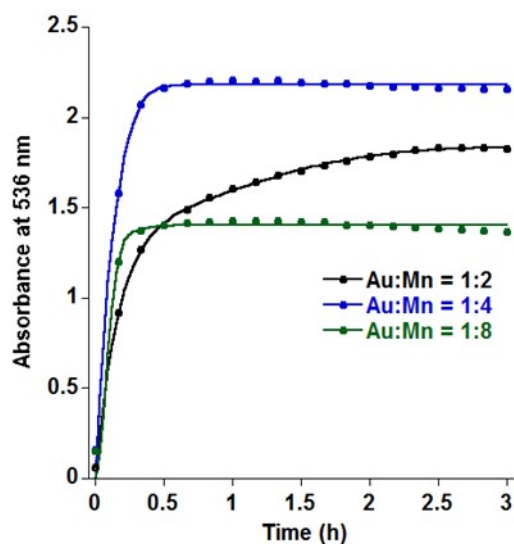


Figure S34: Fitting of time dependent data at 536 nm absorbance in presence of 2 to 8 equivalent of Mn with respect to Au^{3+} amount using equation (2).

Table S4. Calculated rate constants (k_1 and k_2) from Absorbance data in **Fig. S34**.

Equiv. of Mn	536 nm	
	Spherical nanoparticle formation	Nanoprism formation
	k_1 (h^{-2})	k_2 (h^{-1})
2.0	0.51	5.95
4.0	19.69	10.71
8.0	81.09	7.73

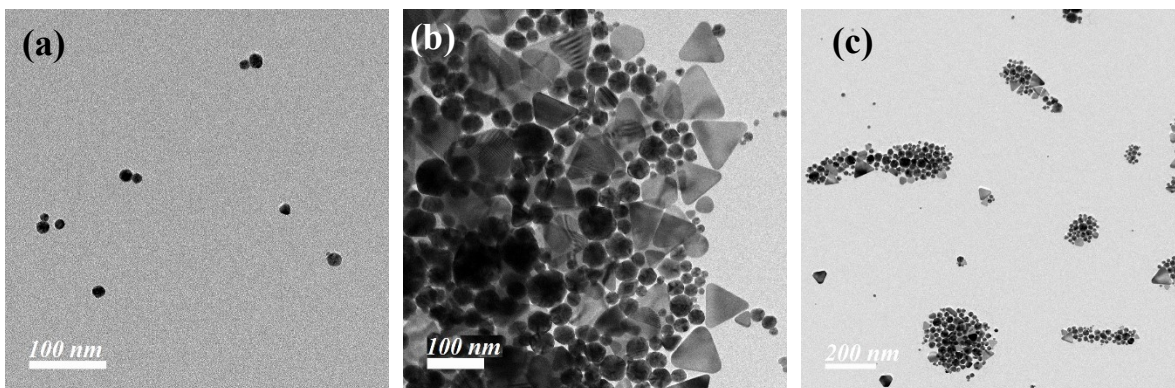


Figure S35: TEM images obtained by varying Au:Mn (a) 1:1.5 (b) 1:4 (c) 1:8.

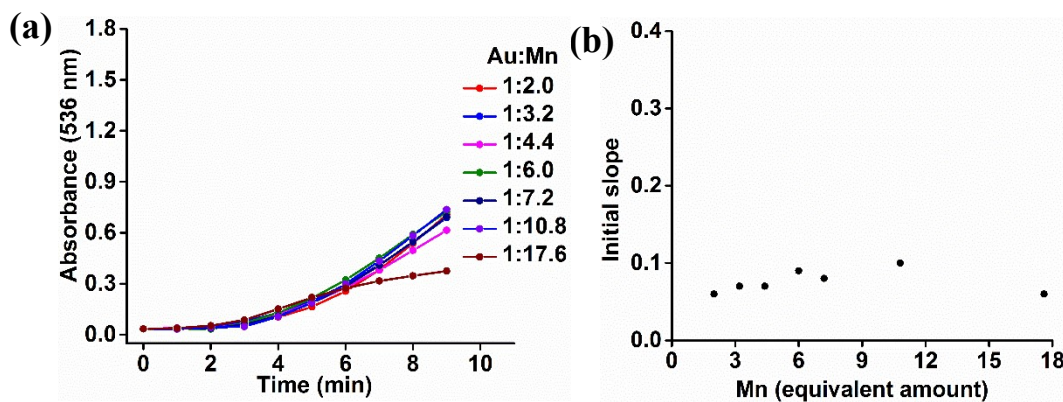


Figure S36: (a) Time dependent absorbance studies for 10 minutes and (b) changes in the calculated initial slope with increasing Mn amount.

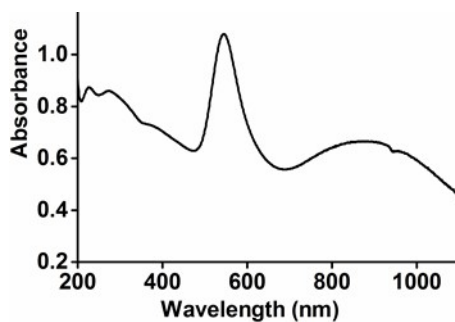


Figure S37: Absorbance spectrum of the nanoprism after growth in presence of amine modified single strand nucleic acid.

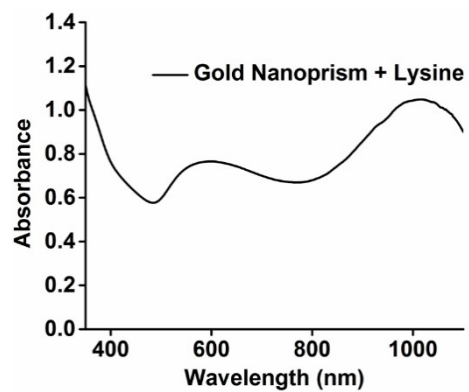


Figure S38: Absorbance spectrum of the nanoprism after growth in the presence of lysine.

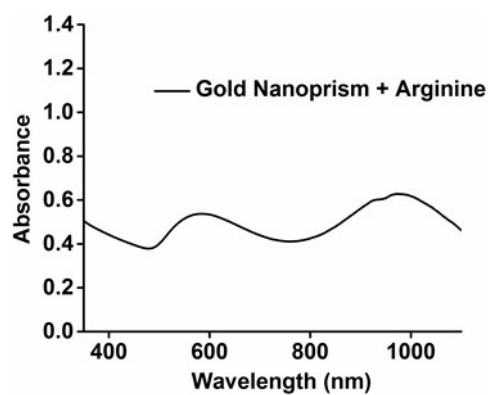


Figure S39: Absorbance spectrum of the nanoprism after growth in the presence of arginine.

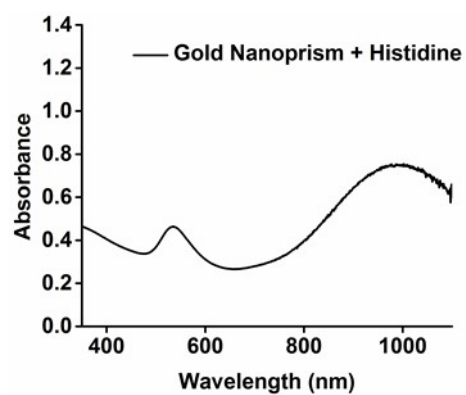


Figure S40: Absorbance spectrum of the nanoprism after growth in the presence of histidine.