Electronic Supplementary Information (ESI)

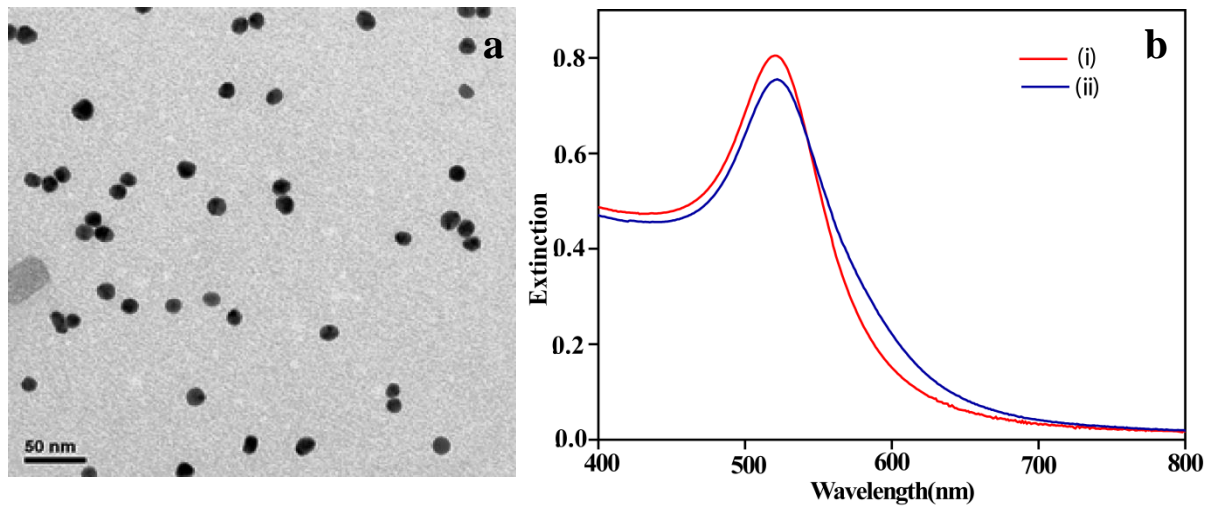# Effect of Temperature on the Aggregation Kinetics of

Partially Bare Gold Nanoparticles

*Anushree Dutta,[a] Anumita Paul[a]* and Arun Chattopadhyay[a,b]**

[a]Department of Chemistry and [b]Centre for Nanotechnology, Indian Institute of Technology

Guwahati, Guwahati, Assam, India -781039

*E-mail: arun@iitg.ernet.in, anumita@iitg.ernet.in

Fig. S1 (a) Representative TEM image of as-synthesized citrate stabilized gold nanoparticles (Cit-Au NPs) before dialysis. (b) The UV-Vis spectrum of (i) as-synthesized citrate stabilized gold nanoparticles (Cit-Au NPs) before dialysis and (ii) that of Au NPs (1.59 nM) recorded following dialysis for 270 min.
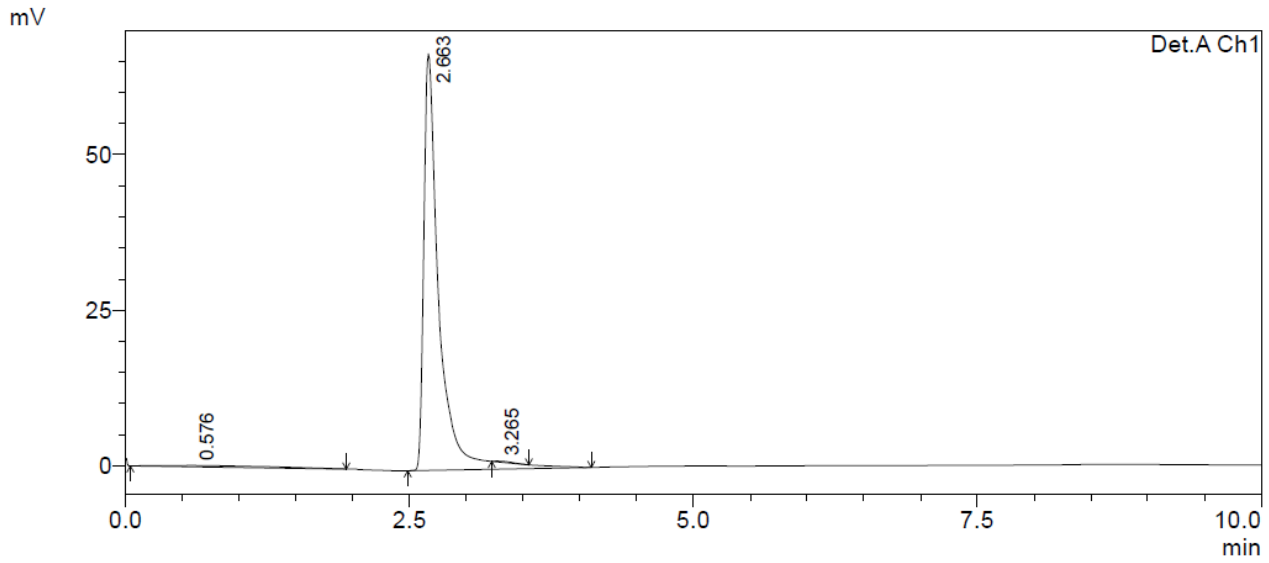
Fig. S2 A typical standard high performance liquid chromatogram of sodium citrate solution.
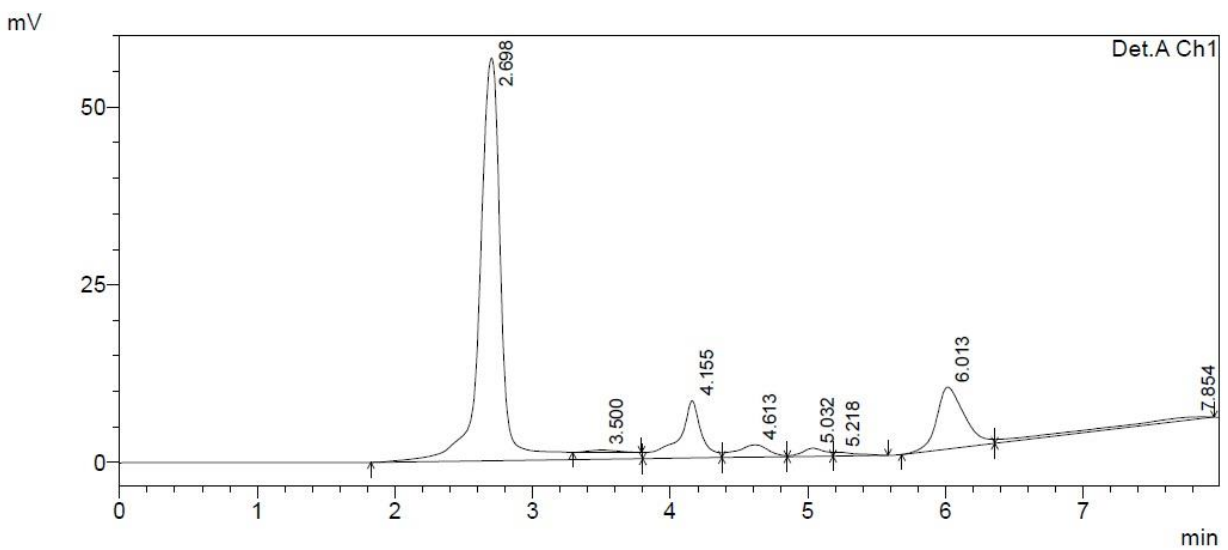
Fig. S3 A typical high performance liquid chromatogram obtained for citrate corresponding to 1.59 nM Au NP dispersion following dialysis (i.e., in the liquid medium outside the dialysis bag).

Table S1. Table summarizing the amount of citrate removed during dialysis, measured pH and ionic strength calculated for four different concentrations of Cit-Au NPs.

Concentration of Cit-Au NPs (nM)	pH of Cit-Au NP dispersion	Amount of citrate anion removed (mM) after 270 min. of dialysis (calculated with respect to Au NP dispersion inside the dialysis membrane)	% of citrate removed	Ionic Strength (mM), I
1.59	5.99	1.301	76.5	4.296
1.19	5.92	1.173	77.4	3.593
0.78	5.91	0.796	69.9	3.091
0.51	5.87	0.483	56.4	2.902

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Calculation of concentration of as synthesized Cit-Au NP :

Concentration of $HAuCl_4$ stock used = 1.72×10^{-2} M

Therefore, number of moles of $HAuCl_4$ in 1.0 mL $HAuCl_4$ stock solution

= Number of moles of $HAuCl_4$ in reaction mixture = 1.72×10^{-5}

Assuming complete reduction, we can write $[HAuCl_4] = [Au]$,

Total number of Au atoms in reaction mixture = $1.72 \times 10^{-5} \times N_A$ atoms.

For a spherical gold nanoparticle,

$$0.74 \times V_{NP} = n V_{atom}$$ (Considering packing density of 74.08 % in case of fcc structure)

$$\Rightarrow 0.74 \times \frac{4}{3}\pi R^3 = n\, \frac{4}{3}\pi r^3$$

where V_{NP} = volume of a nanoparticle,

V_{atom} = volume of a gold atom,

n = total number of Au atoms in a nanoparticle,

R= average radius of a gold NP as calculated from TEM measurement =7.5 nm,

r= radius of Au-atom = 0.144 nm.

Therefore, Total number of Au atoms in one NP, $n = 0.74 \times \left(\dfrac{R}{r}\right)^3$

Number of Au atoms in the nanoparticle dispersion = n×N

where, n= number of Au-atoms in one NP.

N= number of Au NPs in the reaction mixture.

Therefore,

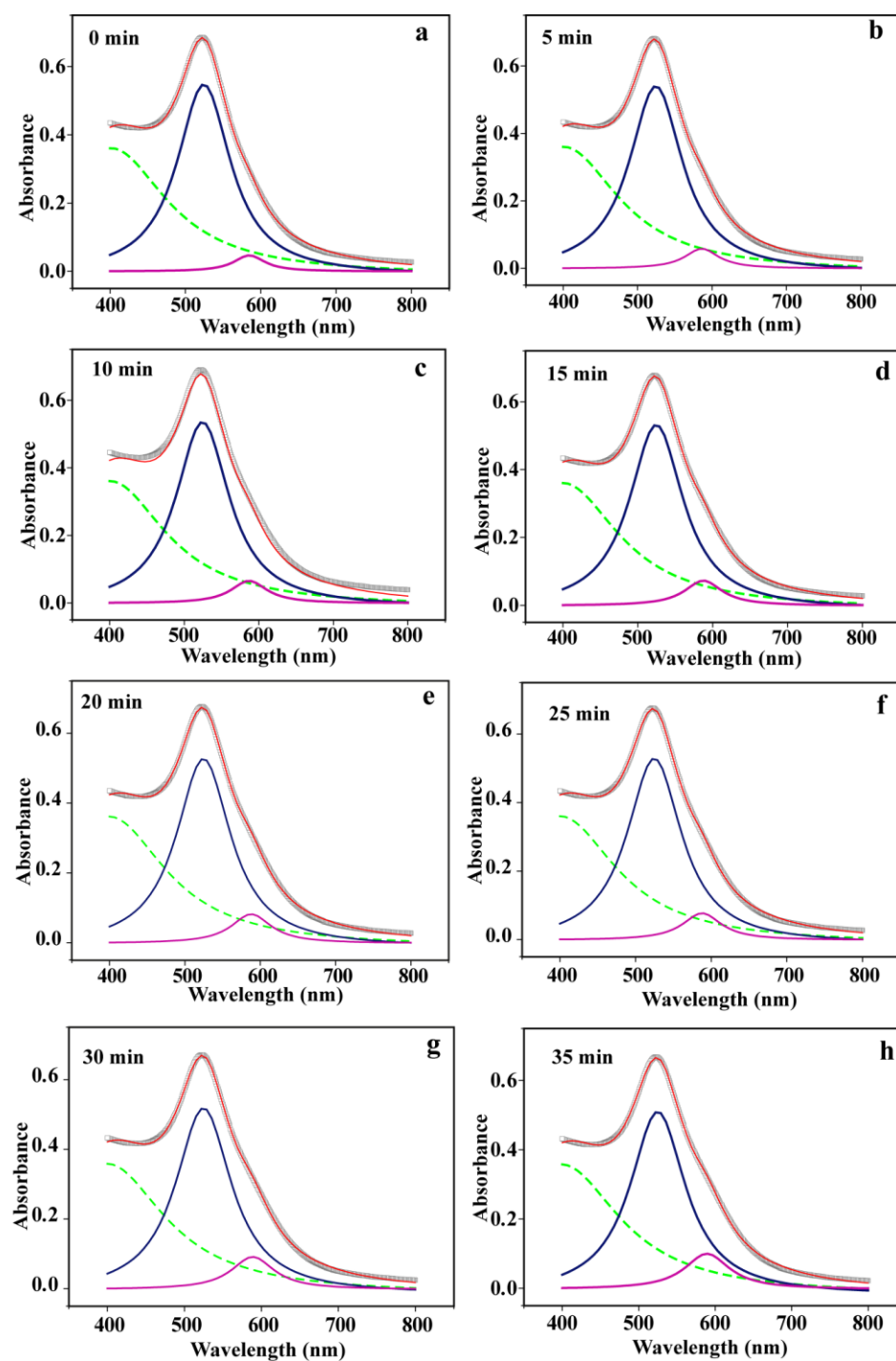$$N = \frac{N_A \times 1.72 \times 10^{-5}}{0.74 \times \left(\dfrac{R}{r}\right)^3} = 9908622 \times 10^9$$

Therefore, concentration of as synthesized gold nanoparticle was obtained as follows:

$$[Au\,NP] = \frac{N}{N_A} = \frac{9.9086 \times 10^{13}}{6.023 \times 10^{23}} = 1.64 \times 10^{-10}\,moles$$

Hence, final concentration of Cit-Au NP was = $\dfrac{1.64 \times 10^{-10}}{100} \times 1000$

$$= 1.64 \times 10^{-9}\,M$$

$$= 1.64\ nM$$

Fig. S4 Representative deconvoluted spectral band obtained from time-dependent UV-Vis spectra of samples monitored at 40 °C following dialysis of 1.59 nM Cit-Au NPs for 270 min. The curves in grey are the experimental curves, those in red are their Lorentzian fits; those in blue and pink are the primary and the secondary deconvoluted bands and the green (dotted) curves are the background spectra.
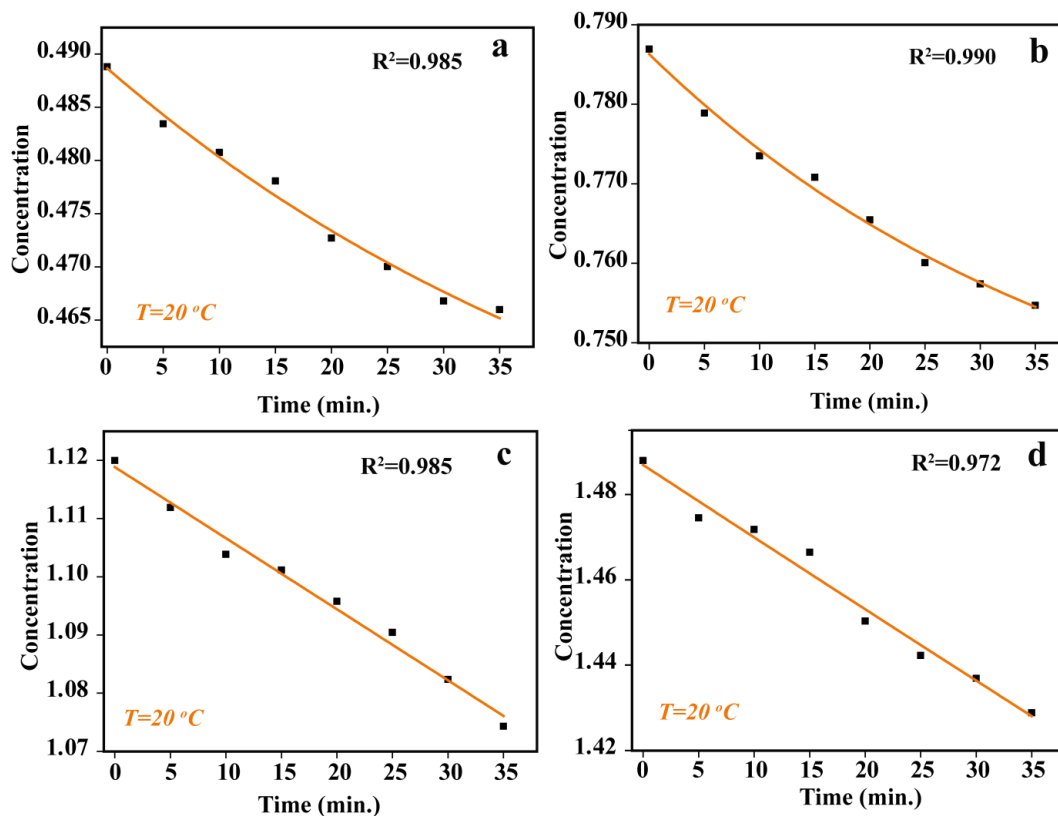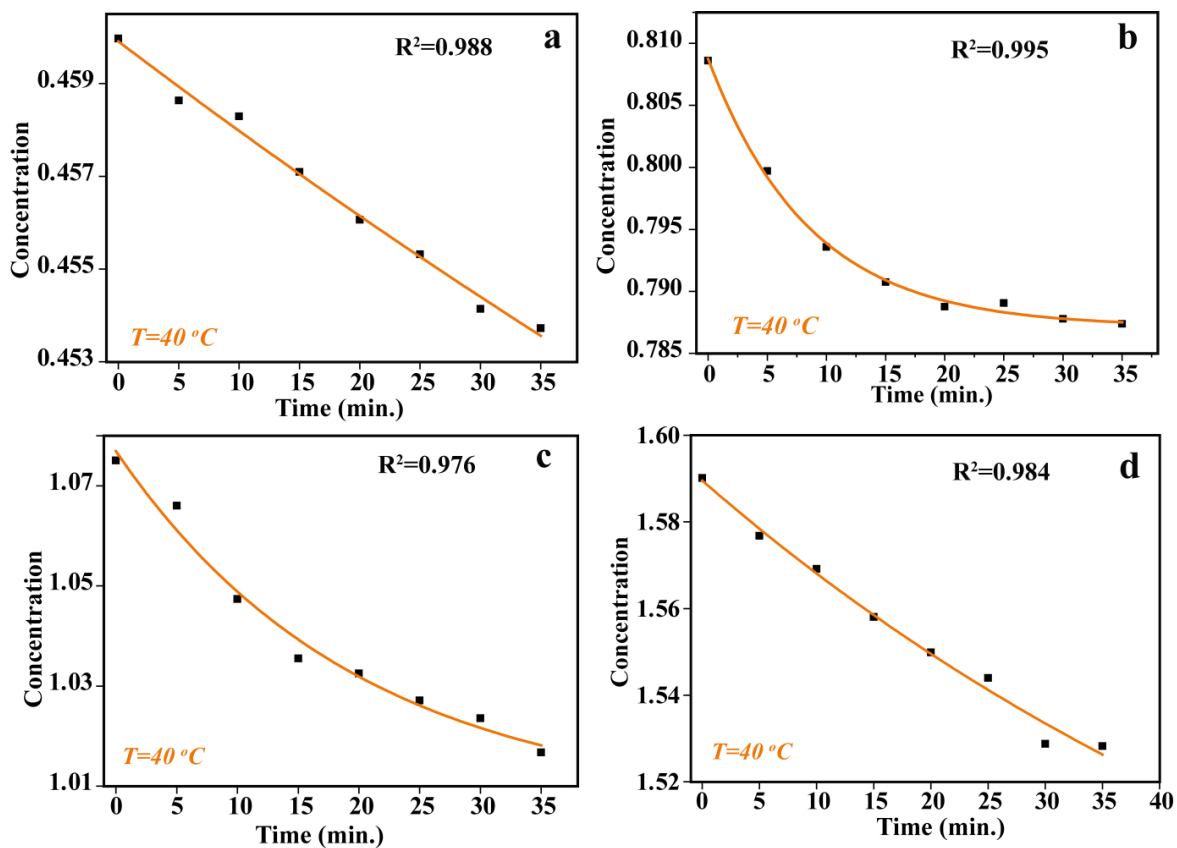
Fig. S5 Plots of concentration of Au NP (as obtained from the area under the primary deconvoluted band) monitored with time at T = 20 °C. The results were obtained from time-dependent study carried out for dialysed Au NPs with starting concentrations (a) 0.51 nM, (b) 0.78 nM, (c) 1.19 nM and (d) 1.59 nM. Data points were fitted to single exponential function for each concentration of Au NP dialysed. The initial rate was extracted from the slope of exponential fitting to the first four data points.
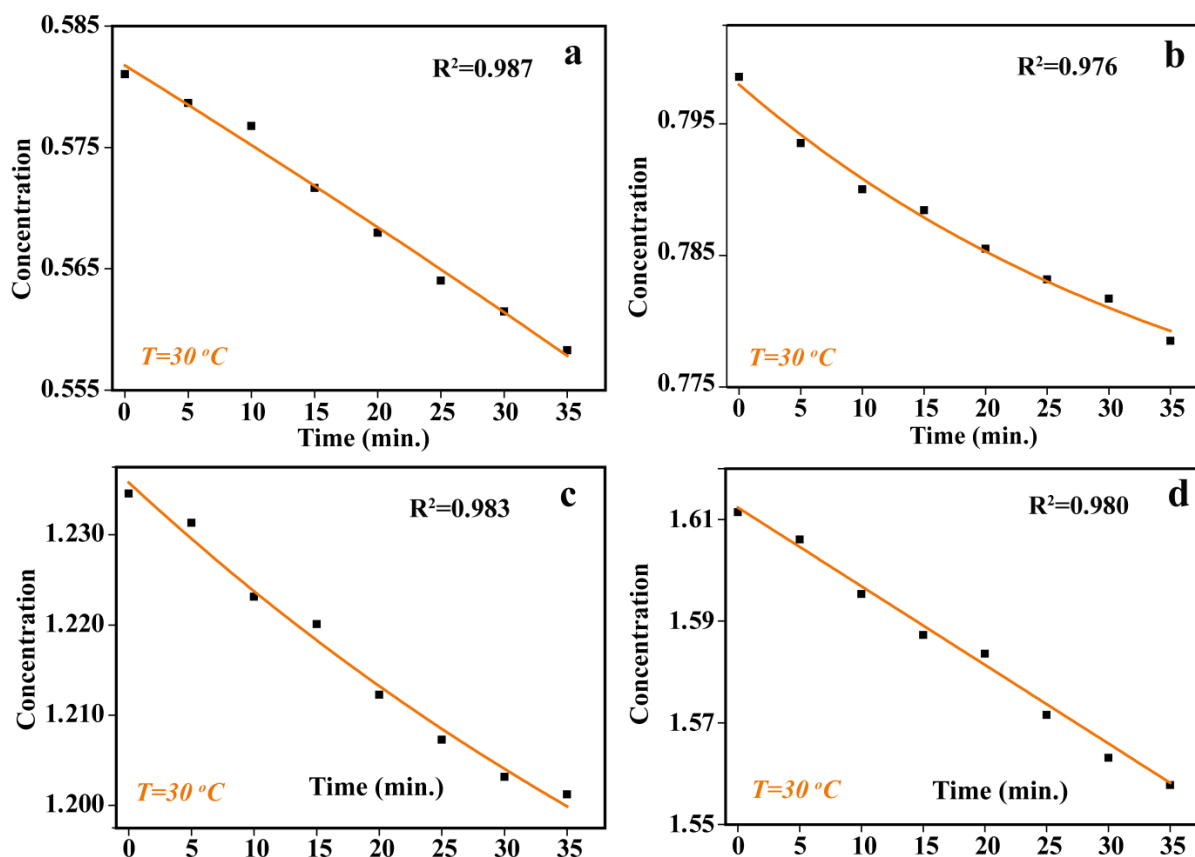
Fig. S6 Plots of concentration of Au NP (as obtained from the area under the primary deconvoluted band) monitored with time at T = 30 °C. The results were obtained from time-dependent study carried out for dialysed Au NPs with starting concentrations (a) 0.51 nM, (b) 0.78 nM (c) 1.19 nM and (d) 1.59 nM. Data points were fitted to single exponential function for each concentration of Au NP dialysed. The initial rate was extracted from the slope of exponential fitting to the first four data points.
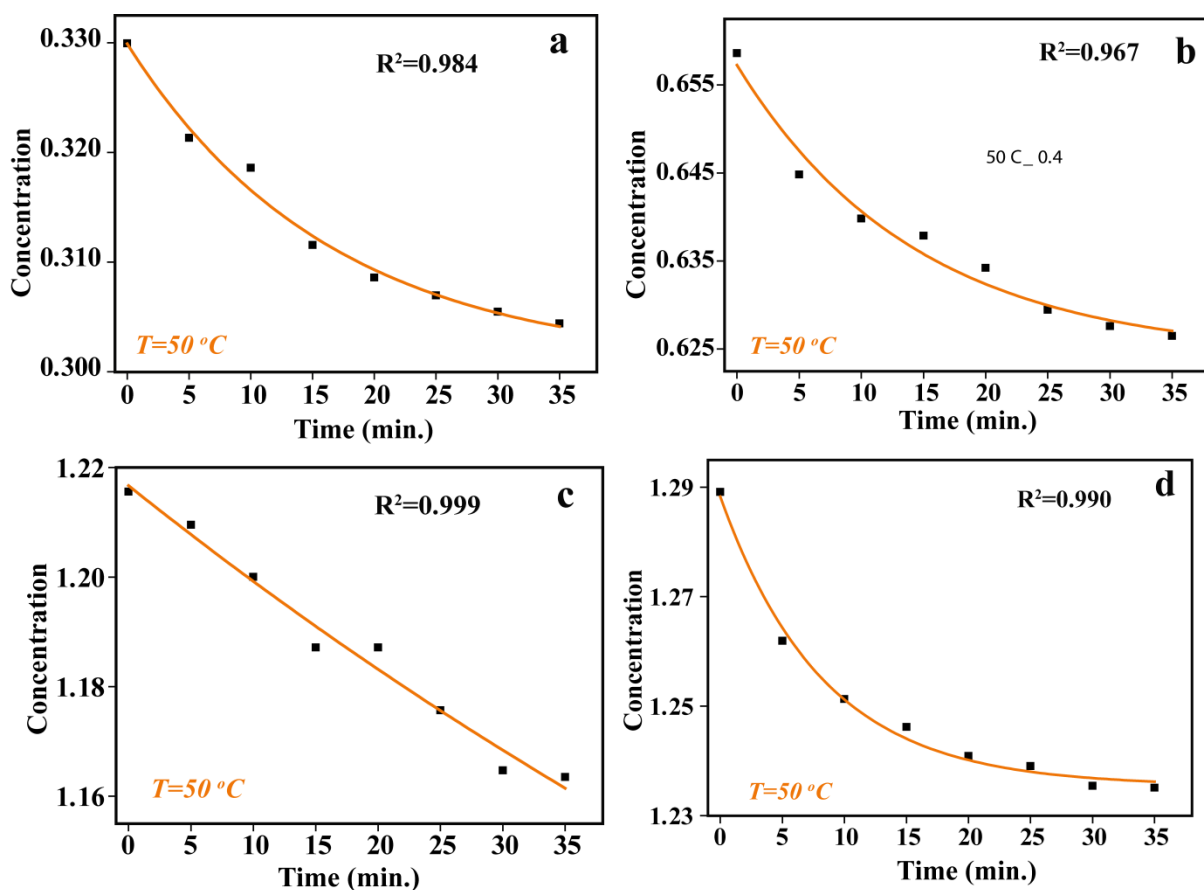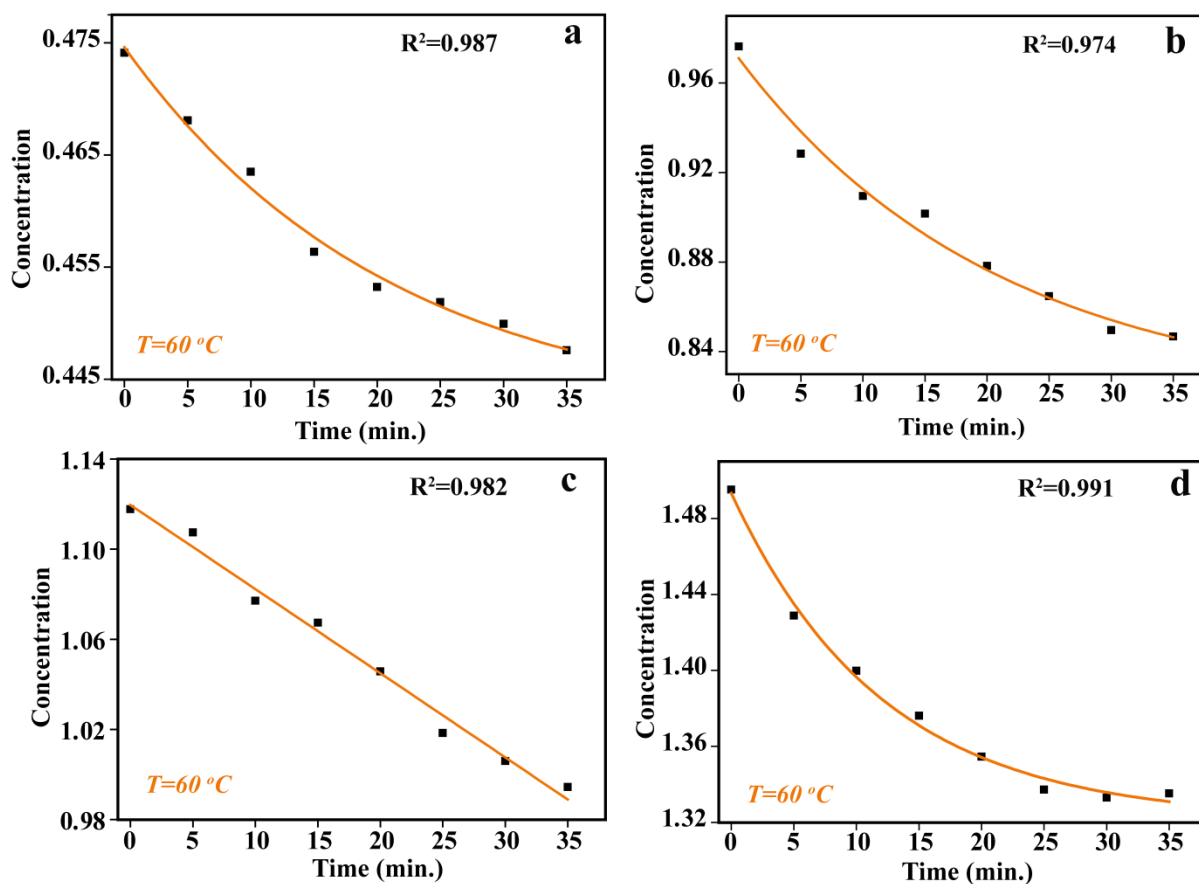
Fig. S7 Plots of concentration of Au NP (as obtained from the area under the primary deconvoluted band) monitored with time at T = 40 °C. The results were obtained from time-dependent study carried out for dialysed Au NPs with starting concentrations (a) 0.51 nM, (b) 0.78 nM, (c) 1.19 nM and (d) 1.59 nM. Data points were fitted to single exponential function for each concentration of Au NP dialysed. The initial rate was extracted from the slope of exponential fitting to the first four data points.

Fig. S8 Plots of concentration of Au NP (as obtained from the area under the primary deconvoluted band) monitored with time at T = 50 °C. The results were obtained from time-dependent study carried out for dialysed Au NPs with starting concentrations (a) 0.51 nM, (b) 0.78 nM, (c) 1.19 nM and (d) 1.59 nM. Data points were fitted to single exponential function for each concentration of Au NP dialysed. The initial rate was extracted from the slope of exponential fitting to the first four data points.

Fig. S9 Plots of concentration of Au NP (as obtained from the area under the primary deconvoluted band) monitored with time at T = 60 °C. The results were obtained from time-dependent study carried out for dialysed Au NPs with starting concentrations (a) 0.51 nM, (b) 0.78 nM, (c) 1.19 nM and (d) 1.59 nM. Data points were fitted to single exponential function for each concentration of Au NP dialysed. The initial rate was extracted from the slope of exponential fitting to the first four data points.
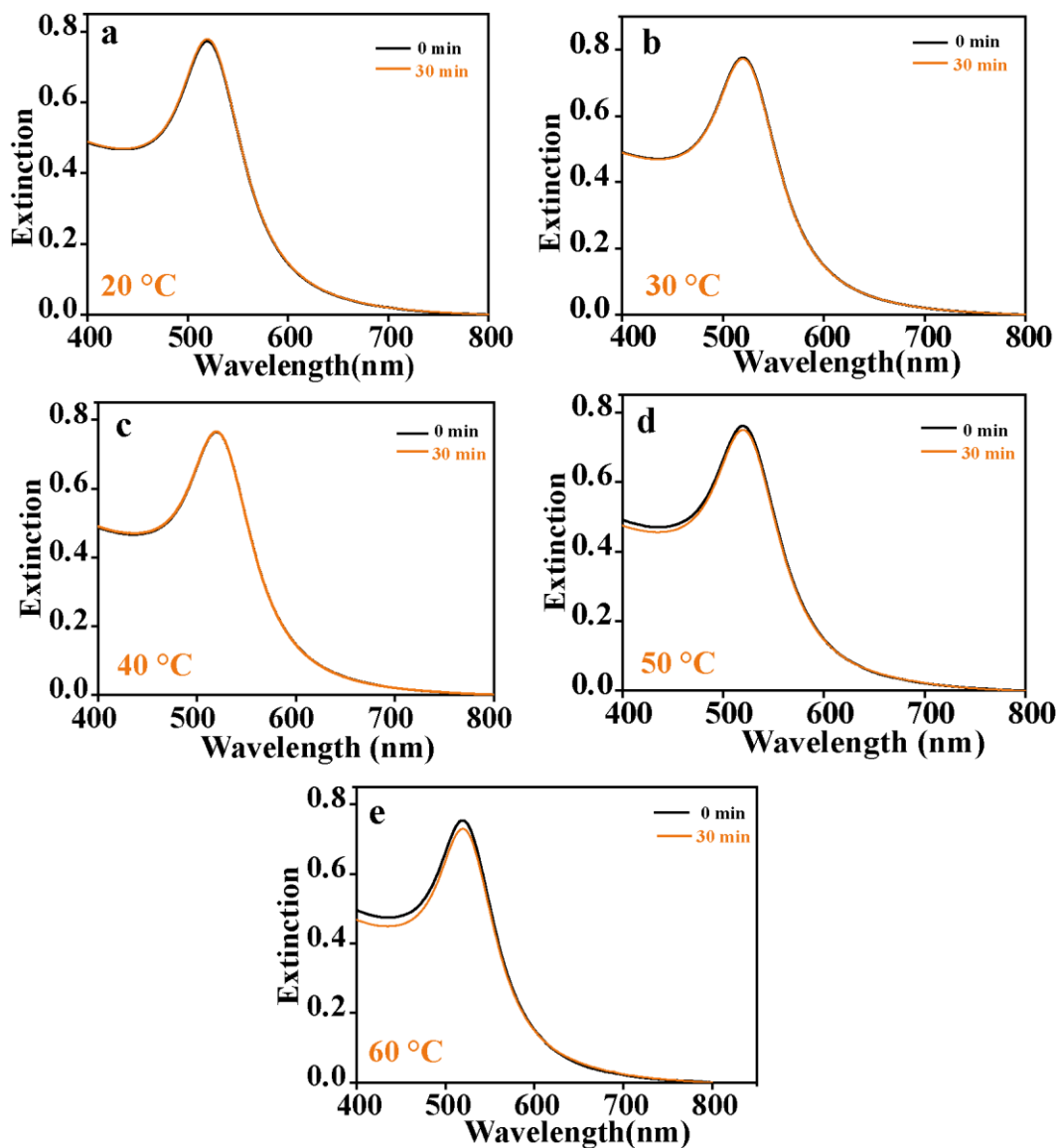
Fig. S10 Surface plasmon resonance extinction spectra of as synthesized Cit-Au NPs recorded at 0 and 30 min of incubation and at five different temperatures viz. (a) 20 °C, (b) 30 °C, (c) 40 °C, (d) 50 °C and (e) 60 °C.
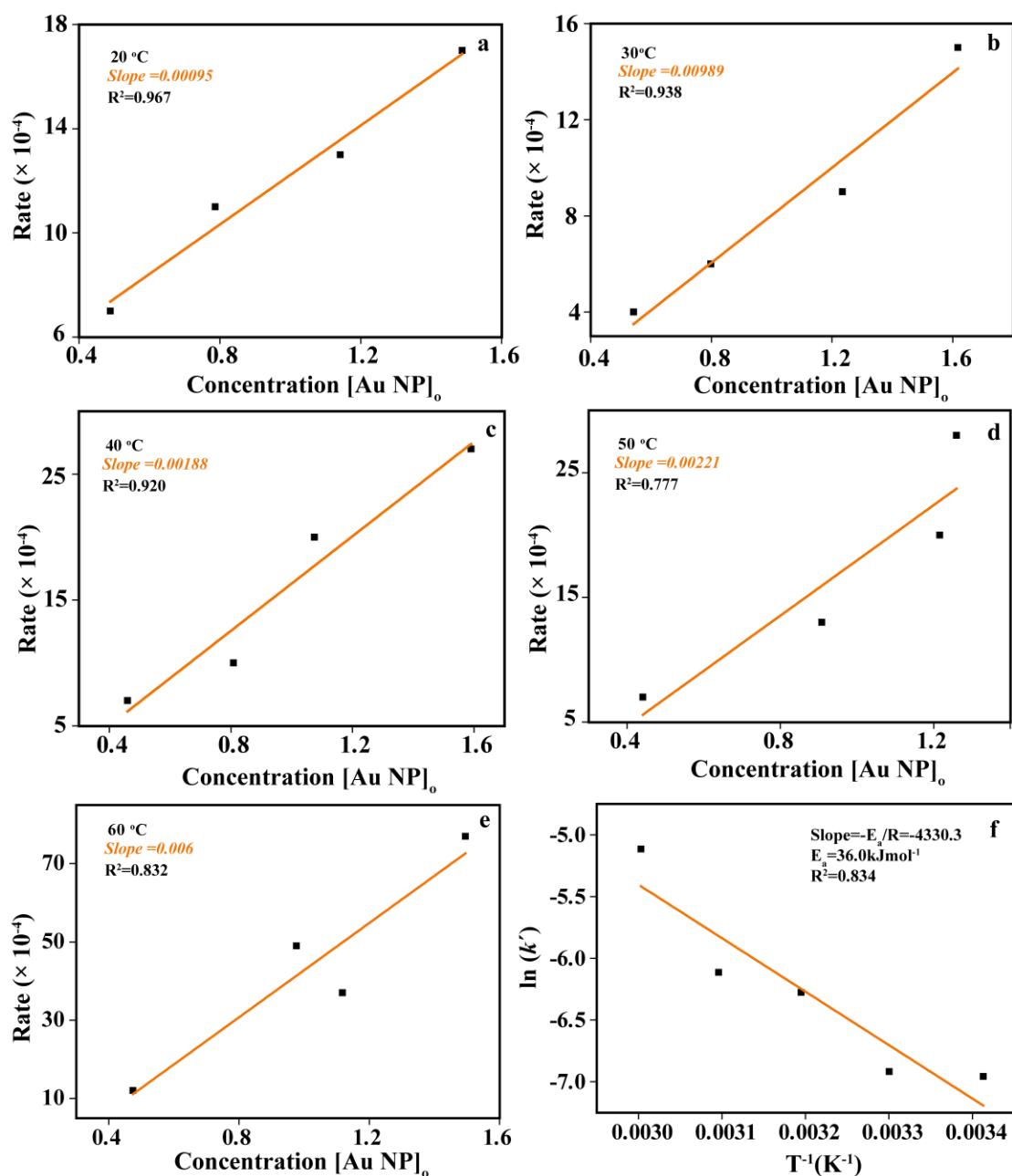
Fig. S11 Plot of *Initial rate versus concentration* (at t = 0 min) of dialysed Au NP at five different temperatures viz. (a) 20 °C, (b) 30 °C, (c) 40 °C, (d) 50 °C and (e) 60 °C. Data points were fitted to linear function and kinetic rate constant at the respective temperature was obtained from the slope of the linear fit. (f) Plot of *ln(k´) Vs T^{-1}* where *k´* represents the rate constant (obtained using initial rate method) and T represents temperature in Kelvin unit. Data points were fitted to linear function to obtain activation energy from the slope of the linear fit.

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According to transition state theory, the enthalpy of activation, $\Delta H^{\ddagger}$ can be obtained by

means of Eyring plot, wherein a plot of gives $\ln\dfrac{k}{T}$ $vs\dfrac{1}{T}$ a straight line and slope of

the linear fit gives $\Delta H^{\ddagger} \sim$ 33.9 kJ mol^{-1}.[1]
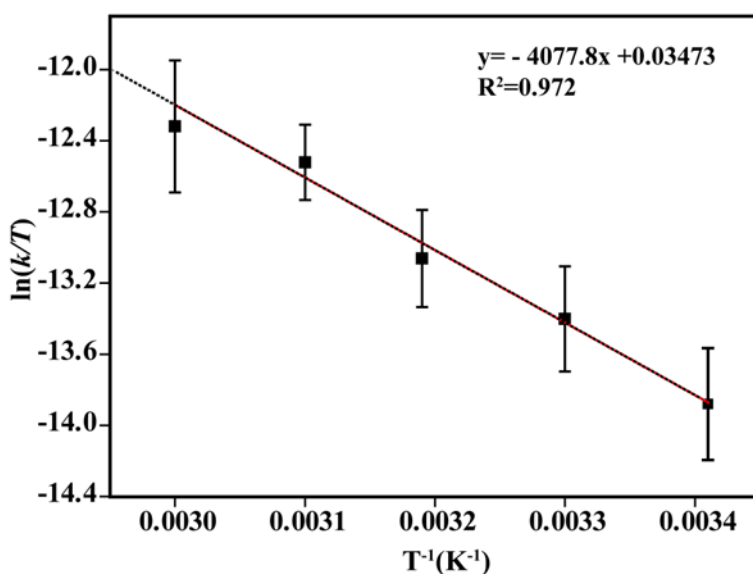
Fig. S12 Eyring plot of *ln (k/T) versus T^{1}* plot. Here, *k* refers to rate constant values extracted (following integrated rate method) from the time-dependent study carried out at five different temperature (20 °C, 30 °C, 40 °C, 50 °C and 60 °C) for dialysed 1.59 nM Au NP sample.

Reference

1. G. Lente, I. Fabiana, A. J. Poe, *New J . Chem*. **2005**, *29*, 759.