Supplementary Information (SI) for New Journal of Chemistry.

Electronic Supplementary Information

Towards Aromaticity: A Driving Force for the Formation of Gold Nanoparticles

N. Srinivasa Rao[a, b]⍰, Satish Bolloju[a, c]⍰, Sweta Agarwala,[a] Dinabandhu Patra,*[d] Kamatham Narayanaswamy,[d] and Balaji Gopalan*[a]

[a] Department of Chemistry, Birla Institute of Technology & Science (BITS) Pilani, Hyderabad Campus, Jawahar Nagar, Kapra Mandal, Hyderabad – 500078, Telangana, India

[b] Presently, ValleyOak Junior College, Shrikaplaza, Puppalaguda, Hyderabad – 500089, Telangana, India

[c] Presently, WMG, University of Warwick, Coventry, CV4 7AL, United Kingdom

[d] Department of Chemistry, Department of Chemistry, SRM University-AP, Amaravati, Mangalagiri-522240, Andhra Pradesh, India

Corresponding authors:

Dinabandhu Patra, e-mail: dinabandhupatra2015@gmail.com

Balaji Gopalan, e-mail: gbalaji@hyderabad.bits-pilani.ac.in

Table of Contents

Materials: Gold (III) chloride, 99% ($AuCl_3$), cycloheptatriene, 95% (C_7H_8) (CHTE), dodecanethiol, >98% (DDT) and mercaptosuccinic acid, 97% (MSA) were purchased from Sigma-Aldrich. Milli-Q water was used for the entire study. D_2O and $CDCl_3$ were purchased from Cambridge Isotope Laboratories, USA NMR study.

Synthesis of CHTE assisted gold nanoparticles: 70 mL of 0.8 mM $HAuCl_4$ aqueous solution was taken in the 100 mL round-bottom flask and vigorously stirred. Then 17.5 μL CHTE was added under continuous stirring. The reaction continued for 3 minutes.

Characterization details: UV-Visible spectra of the reaction solutions were recorded using JASCO V-670 spectrophotometer after 2 minutes of the end of the reaction. To collect time-resolved UV-Visible spectra, an Ocean Optics DH-Mini spectrometer was used. The UV-visible spectral data of the Au^{3+} reduction were recorded at a rate of 9 scans per second and the data after every ninth scan was used for analysis after the necessary background correction. The spectroscopic setup was placed on a magnetic stirrer for continuous mixing during UV-Vis measurements. For temperature-dependent studies, the UV cuvette was kept in a hot water bath on the stirrer. The time lag between removing the cuvette from water bath and spectra measurement was 10 s. The X-ray diffraction (XRD) pattern of the gold nanoparticles was recorded using Rigaku Ultima-IV in the range of 20°-90° at a scan speed of 2°/min. To record the XRD patterns of the gold particles formed, the reaction solution was centrifuged at 2000 rpm for 20 minutes. The precipitate was dried and submitted for the XRD measurement. The same precipitate was submitted for Transmission Electron Microscope (TEM) images. The TEM images were captured using FEI Technai G2 F20 STEM with 200 kV microscope. TEM images of colloidal Au solutions were obtained by sampling 5 μL of the solution under continuous stirring. The TEM grid was placed in a flat plastic container positioned on an ice bath to minimize particle growth. After depositing the Au solution onto the grid, the container was sealed. Once the colloidal solution had frozen, the container was transferred to a vacuum oven, where the grid was dried overnight at 60 °C. ^1H NMR spectra of CHTE and the reaction mixture were recorded using a Bruker Advance 500 MHz spectrometer. The reaction mixture was prepared by adding $AuCl_3$ and CHTE in a 1:3 molar ratio to 1 mL D_2O, followed by a 5-minute reaction. The mixture was then centrifuged, and the supernatant was used for NMR analysis. CHTE was dissolved in $CDCl_3$ for NMR measurement. SEM images were captured using an Apreo S, FEI microscope, with samples collected from the supernatant of the reaction. For SEM analysis, 5 μL of the Au solution was drop-cast onto a silicon wafer and dried overnight in a vacuum oven at 60 °C. All glassware, magnetic beads, and cuvettes were cleaned sequentially with soap solution, tap water, piranha solution (H_2O_2:H_2SO_4 = 3:7), and Milli-Q water, then dried in an oven overnight before use. A magnetic stirrer (Remi 2L Magnetic Stirrer and Hot Plate 2MLH) was used to stir the reaction mixture.

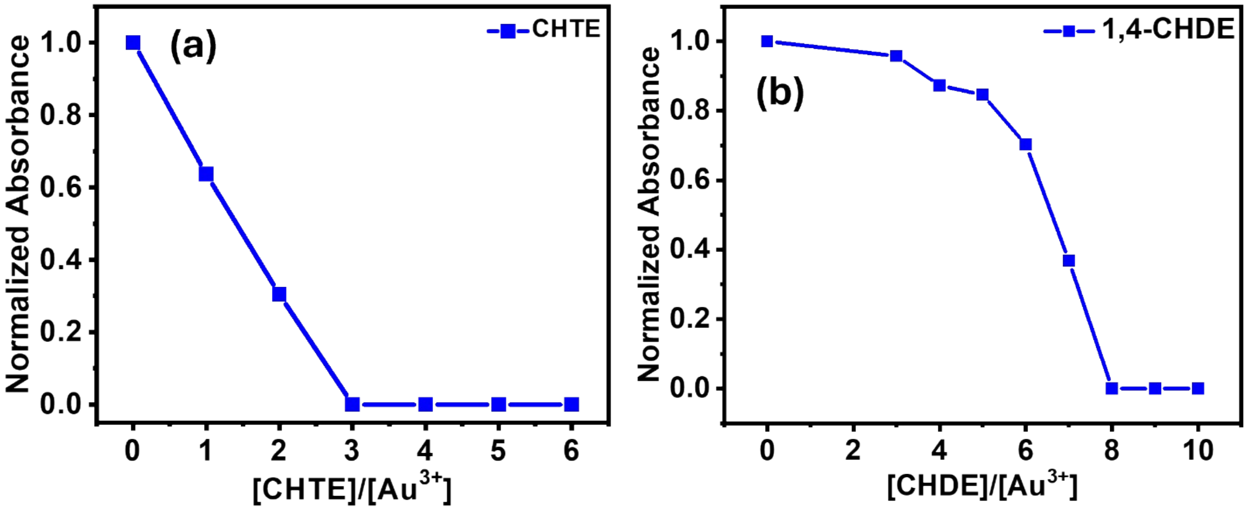

Fig. S1. Stoichiometric plot for gold nanoparticles synthesis using (a) CHTE, and (b) 1,4-CHDE. For both the reductants, Au^{3+} concentration was 1 mM. UV-Vis spectra were recorded after 3 min of the reaction for CHTE and after 8 min for 1,4-CHDE reductants, respectively for all initial Au^{3+} concentrations. The absorbance at the 300 nm peak corresponding to Au^{3+} was monitored to generate the above data.

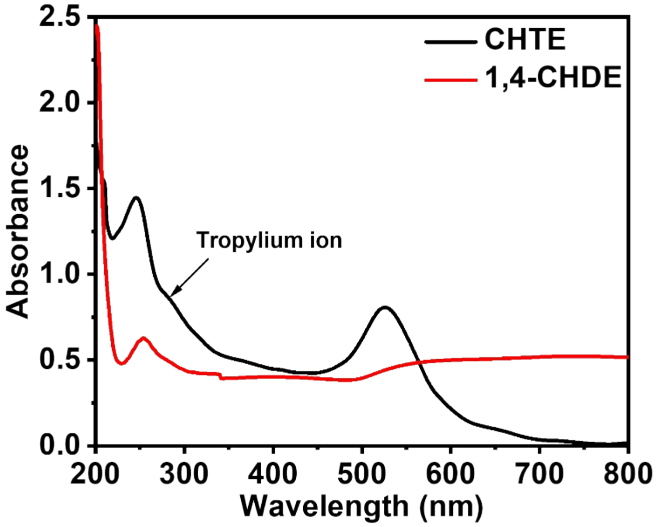

Fig. S2. UV-spectra for colloidal gold nanoparticles prepared by CHTE, 1,3-CHDE, and 1,4-CHDE reductants after 3 minutes of the reaction for CHTE (Au^{3+} = 1mM and Au^{3+}:CHTE = 1:3) and after 8 minutes for 1,4-CHDE (Au^{3+} = 1mM, Au^{3+}:1,4-CHDE = 1:8).

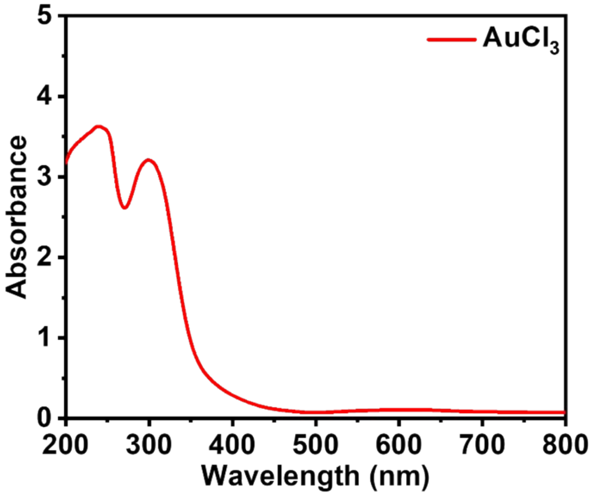

Fig. S3. UV-Vis spectrum of 2.5 mM aqueous AuCl$_3$ solution in milli-Q water.

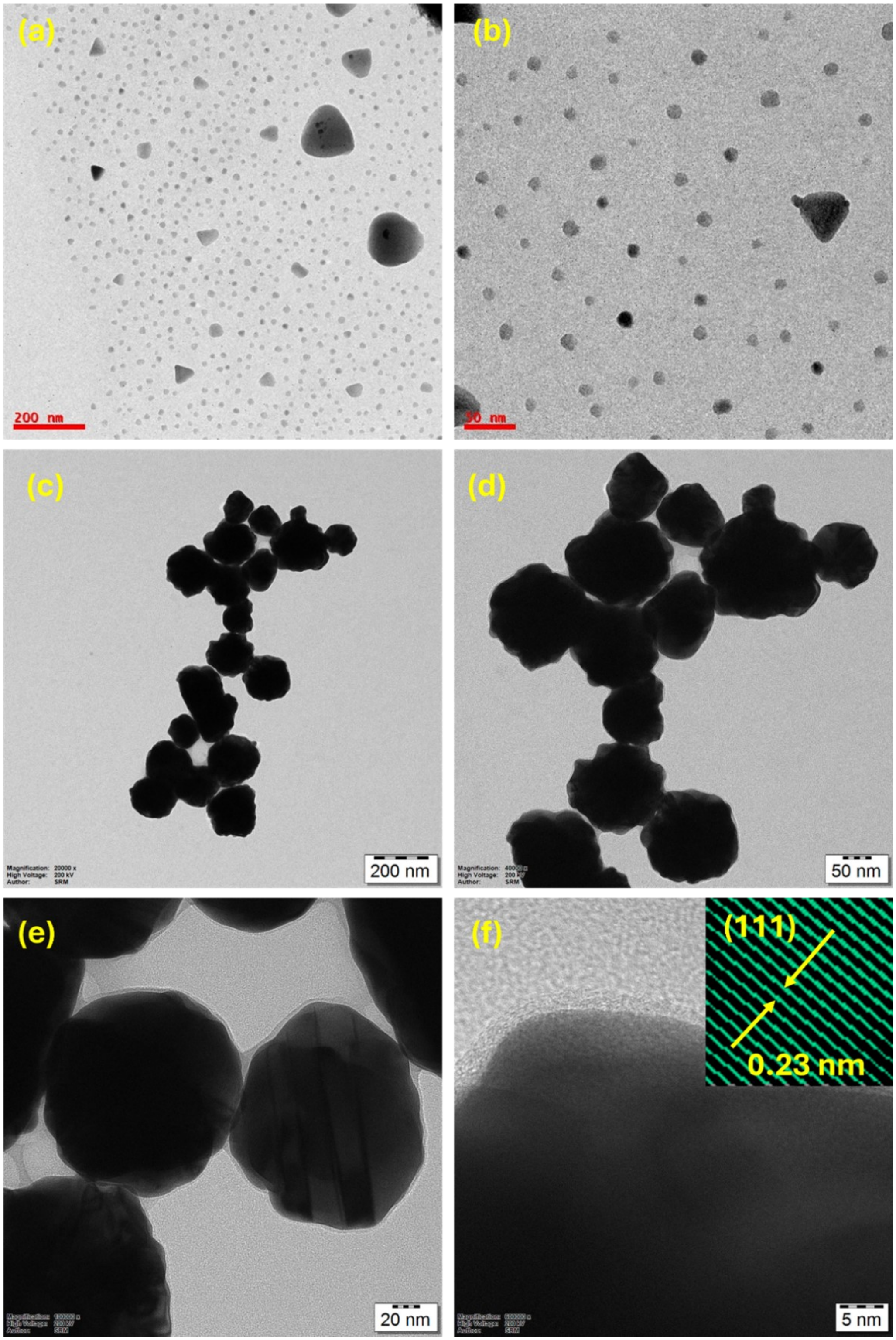

Fig. S4. TEM images of gold nanoparticles formed using (a) and (b) 1,3-CHDE, (c), (d), (e) and (f) for 1,4-CHDE, showing agglomeration. Inset at Fig. S4f shows the d-spacing value for (111) plane.

The inset of Fig. S4f is generated by applying reverse FFT to Fig. S4f using ImageJ software. For TEM images, gold solution was mounted on TEM grid after 8 minutes of the reaction.

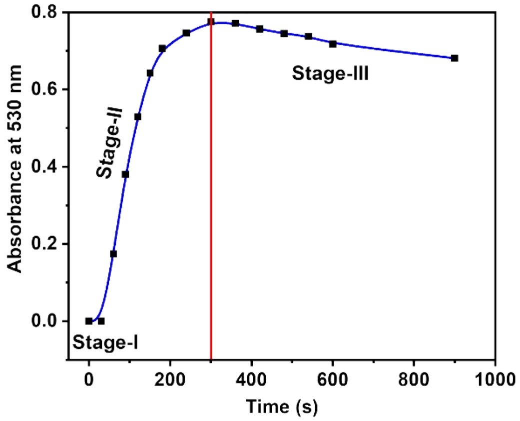

Fig. S5. The kinetic curve of SPR band at 520 nm during Au^{3+} reduction in presence of CHTE. Stage-I: initial Au^{3+} reduction (0-30 s), Stage-II: nucleation and growth of the particles (30-300 s), and Stage-III: particle coagulation (300 s-end of the process). Au^{3+} concentration was 0.5 mM Au^{3+}:CHTE = 1:3.

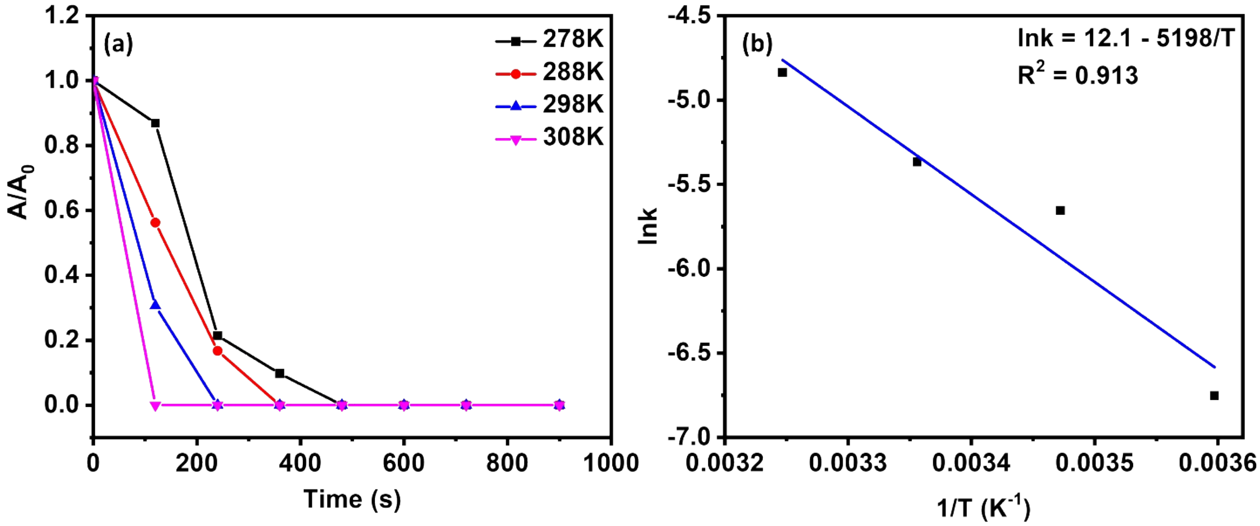

Fig. S6. Kinetic curve for (a) Au^{3+} reduction at different temperatures, Au^{3+} and CHTE concentrations were 0.5 mM and 1.5 mM, respectively, and (b) corresponding Arrhenius plot. The absorbance at the 300 nm peak corresponding to Au^{3+} was monitored to generate the above graphs.

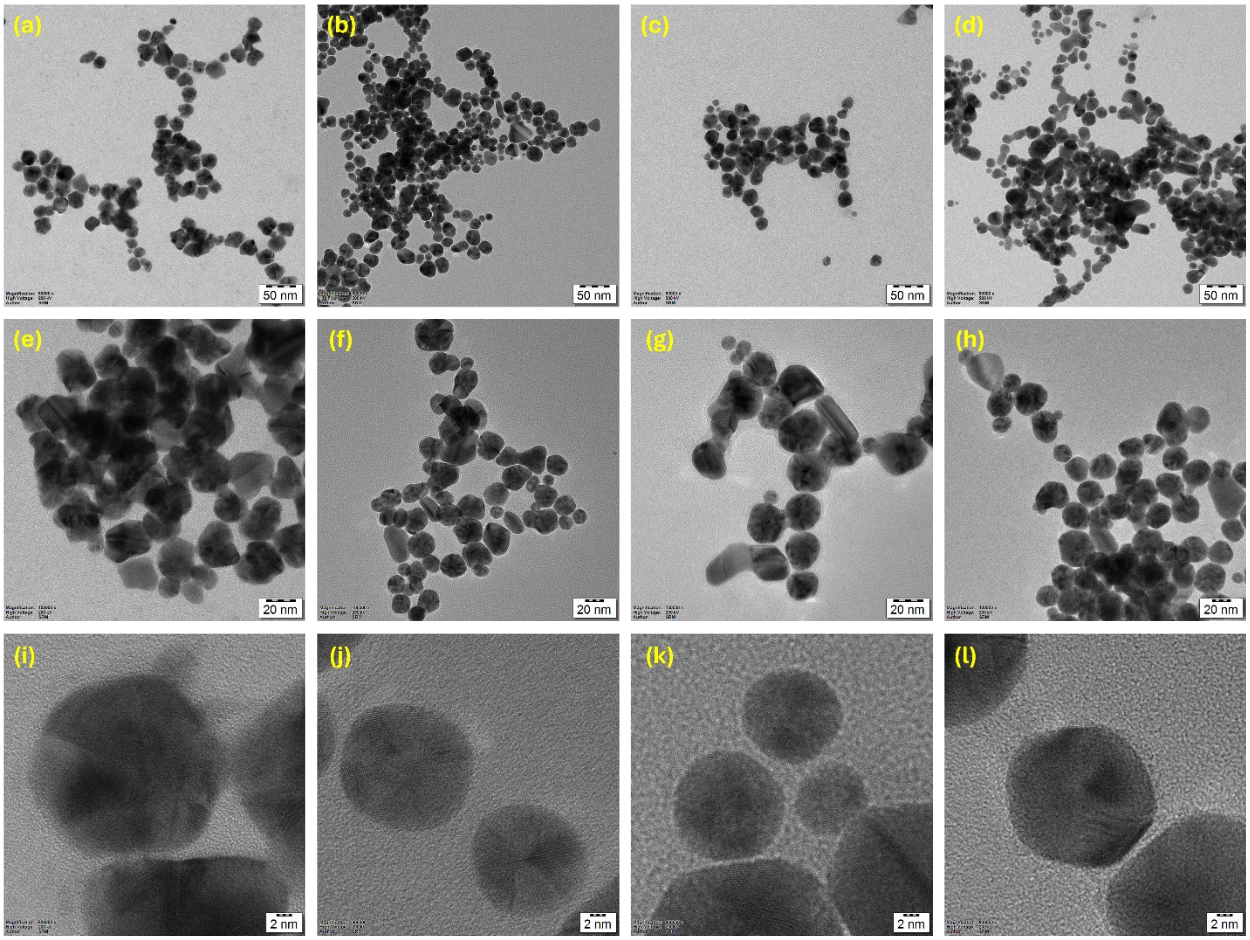

Fig. S7. TEM images of gold nanoparticles obtained from aqueous Au^{3+} solutions with concentrations of (a, e, i) 0.25 mM, (b, f, j) 0.5 mM, (c, g, k) 1 mM, and (d, h, l) 1.5 mM, maintaining an Au^{3+} to CHTE molar ratio of 1:3 in all cases. Gold solutions were taken after 60 s of reaction for TEM sample preparation.

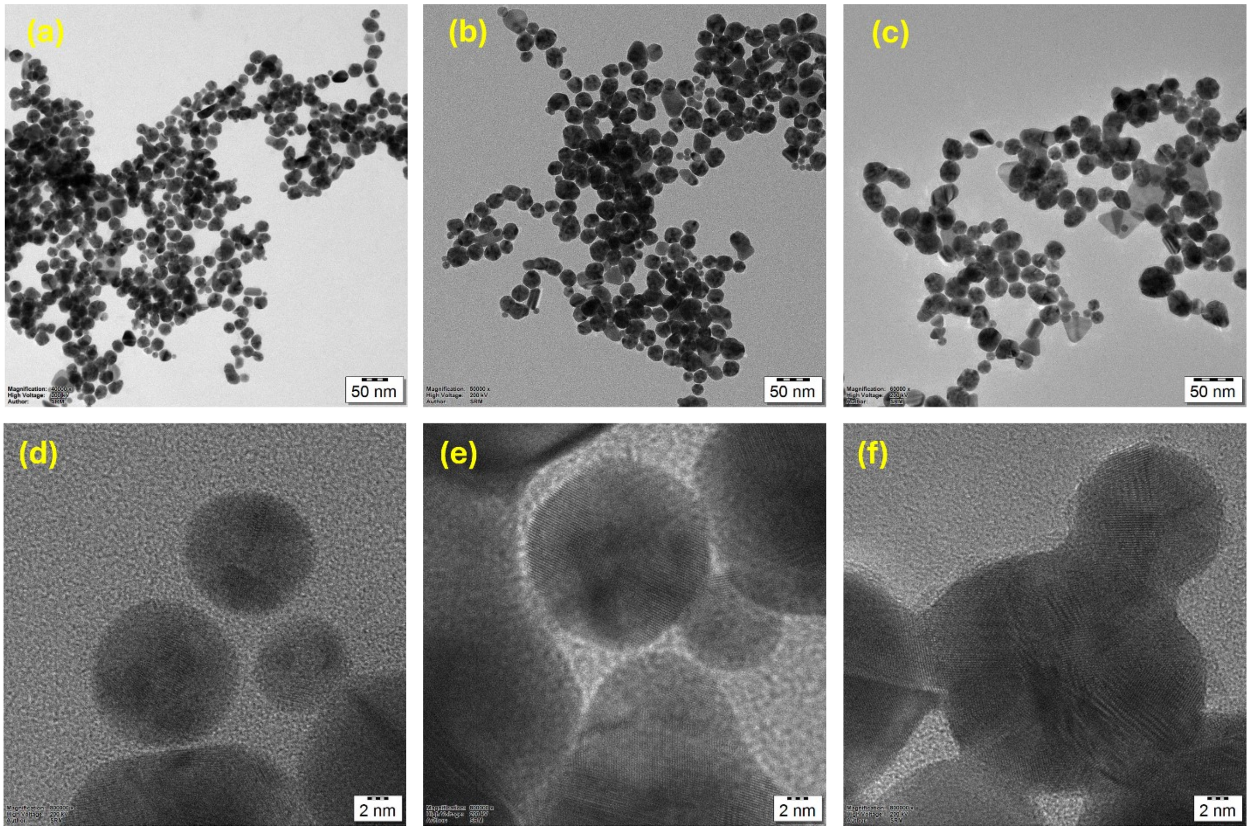

Fig. S8. TEM images of gold nanoparticles synthesized from a 1 mM aqueous Au^{3+} solution (with an Au^{3+} to CHTE molar ratio of 1:3 maintained for all concentrations) at different reaction times: (a) and (d) after 60 s, (b) and (e) after 180 s, and (c) and (f) after 900 s.

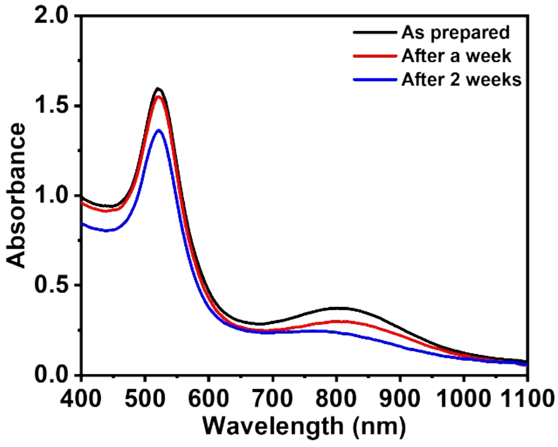

Fig. S9. UV–Vis spectra of gold nanoparticles prepared from a 0.5 mM Au^{3+} solution (Au^{3+}:CHTE = 1:3), recorded weekly to monitor their stability.

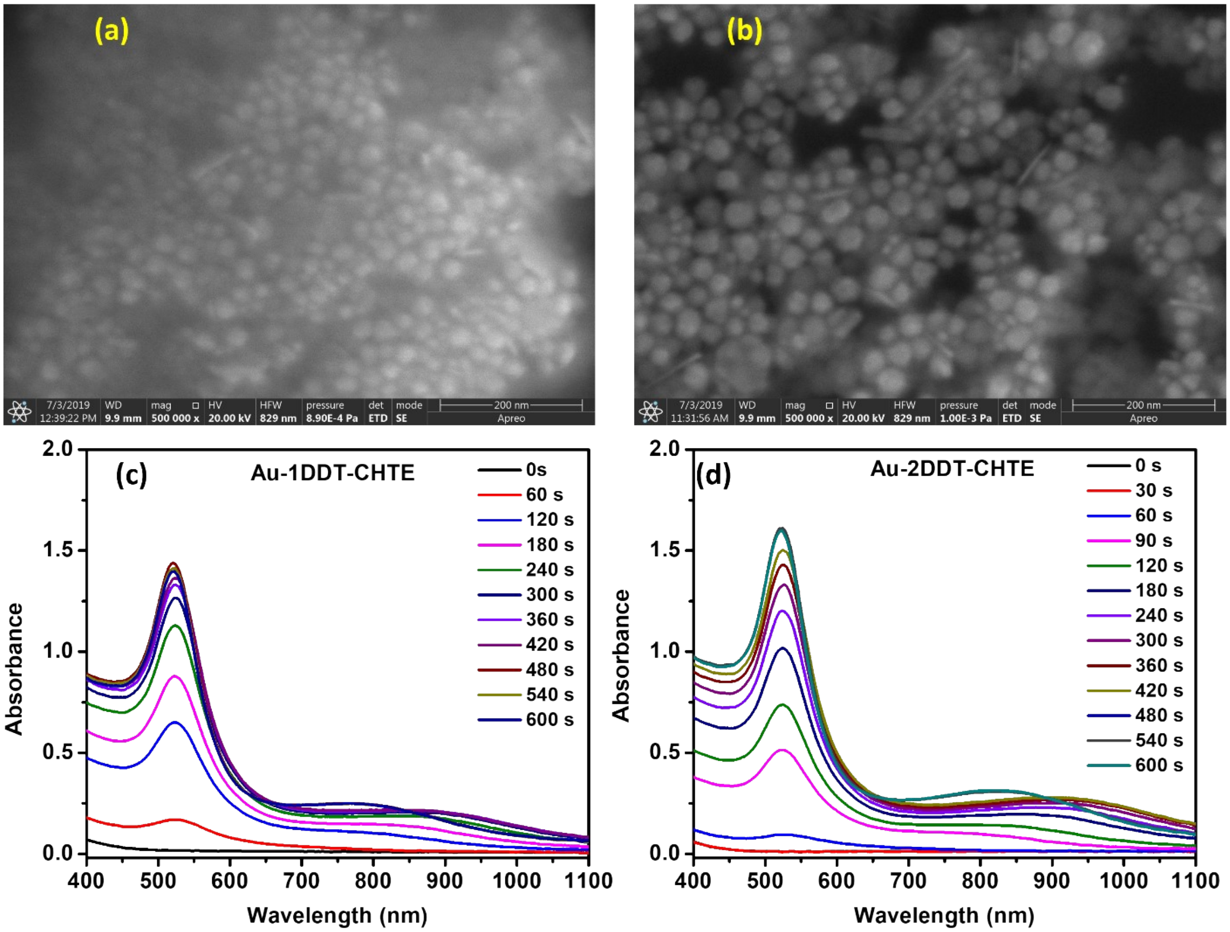

Fig. S10. Time-resolved UV-Vis spectra of Au nanoparticle formation using (a) 1 mM and (b) 2 mM DDT, and SEM images (c) 1 mM and (d) 2 mM DDT. Au^{3+} and CHTE concentrations were 0.5 mM and 1.5 mM, respectively.