

Supplementary information

Formation of Nanogap Au-Polysilsesquioxanes 1D chains for SERS application

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Materials and methods:

Chemicals: N-[3-(trimethoxysilyl)propyl]-ethylene diamine (EDAS), Tetra chloro auric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) and p-Mercaptabenzonic acid (p-MBA) were purchased from Sigma Aldrich. Milli-Q water (18 M Ω .cm) was used in all experiments.

Synthesis of Au-siloxane 1D chains: pH of an aqueous solution (10 ml) containing 50 mM of EDAS was adjusted to 6.0 using 0.1 M hydrochloric acid (HCl) and then this solution was stirred about 2 hours at room temperature. The mixture was heated to 50 °C in a water bath for about 30 min. 0.5 mM of tetra chloro auric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was added drop wise to the above solution with constant stirring to get wine red color for 2 h. Finally, the solution was cooled to room temperature; centrifuged (3000 rpm) to remove excess aminosilane present in the supernatant and then this viscous residue gold colloidal was washed three times using Milli-Q water. After washing, the AuNPs were re-dispersed in Milli-Q water for further characterization studies. Above colloid was stable for more than a month without showing any precipitation but the colloids prepared at pH-2 & pH-4 were not stable for more than a day as seen from black sediment settled down at bottom of the beaker on standing. The auto reduction of Au^{3+} to

metallic gold nanoparticle also was done by stirring the mixture about 20 hours at room temperature as well as by sonicating the mixture to about 2 hours.

Preparation of Samples for NMR, FT- IR, Raman and SERS, XPS, XRD and Instrument details are described below.

Characterization methods:

Au@poly-siloxane nanoparticle chain and networks were analyzed by TEM, UV-Visible, FT-IR, Raman, NMR, and zeta potential measurement. The pH adjustments were carried out using Elico LI 120 pH meter. TEM images were obtained using Philips CM 200 microscope (operating voltage is 200 keV) and UV-Vis spectra of colloidal AuNPs were recorded by Fiber optic SD-2000 spectrometer and DH-2000-BAL Light source (Ocean optics). FT-IR were analyzed by Thermo-Electron Nexus 670 model FT-IR spectrometer, Raman analysis were performed using Renishaw (Agilent Technologies) instrument (Ex. Source – helium Neon Laser; Ex. wavelength – 632.8 nm), NMR analysis were obtained by Bruker 400 MHZ instrument and Zeta potential measurement was carried out using Beckman Coulter Delsa™ Nano common with Flow cell. All samples were analyzed by the above mentioned experimental procedure except mentioned separately.

TEM sample preparation:

TEM samples were prepared by re-dispersing the sediment obtained by centrifugation of the colloidal gold nanoparticle at 3000 rpm and washed three times with Milli Q water to remove excess poly-siloxane. The re-dispersed solution were dropped on carbon coated copper grid and kept overnight for drying.

FT-IR sample preparation and ^1H NMR sample preparation:

For FT-IR analysis, the re-dispersed AuNPs chains were dropped on glass plate and dried at room temperature. The PSQ sample was taken before addition of tetra chloro auric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) i.e. after 2h stirring of pH adjusted EDAS room temperature; the solution was heated to $50\text{ }^\circ\text{C}$ about half an hour. Both poly-siloxane and Au@poly-siloxane samples were prepared using CDCl_3 inter-locked D_2O system.

SERS sample preparation:

For SERS activity measurement, the substrates were prepared by modifying the quartz plate with $30\text{ }\mu\text{L}$ of re-dispersed 1D gold nano chain (conditions: $\text{pH} = 6$, temperature $50\text{ }^\circ\text{C}$ & ratio of $(\text{Au}^{3+}):(\text{EDAS}) = 0.5: 50\text{ mM}$). After drying at room temperature, this modified quartz plate was coated with $30\text{ }\mu\text{L}$ of ethanolic solution of p-MBA with different concentrations (10^{-3} , 10^{-6} & 10^{-9} M) and allowed to dry at open environment. To get normal Raman signal, $30\text{ }\mu\text{L}$ of ethanolic solution of p-MBA were dropped on cleaned quartz plate and dried at room temperature.

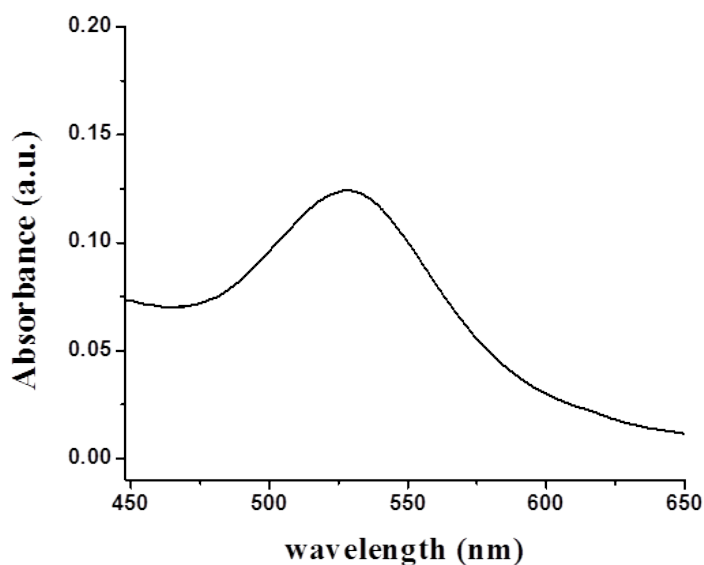


Fig. S1 UV-Vis spectra of re-dispersed AuNPs chain in water prepared at $\text{pH}=6.0$

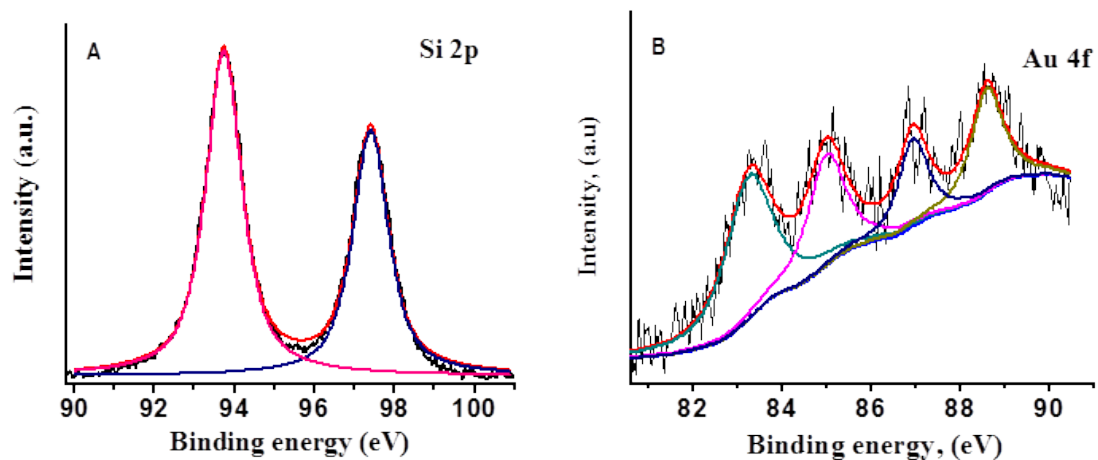


Fig. S2 XPS of a) 2p orbital of Si b) 4f orbital of gold nanoparticles.(Shift of B.E of Si -2p values to lower energy may indicate interactions of very thin siloxane films with surface states of Au nano particles)

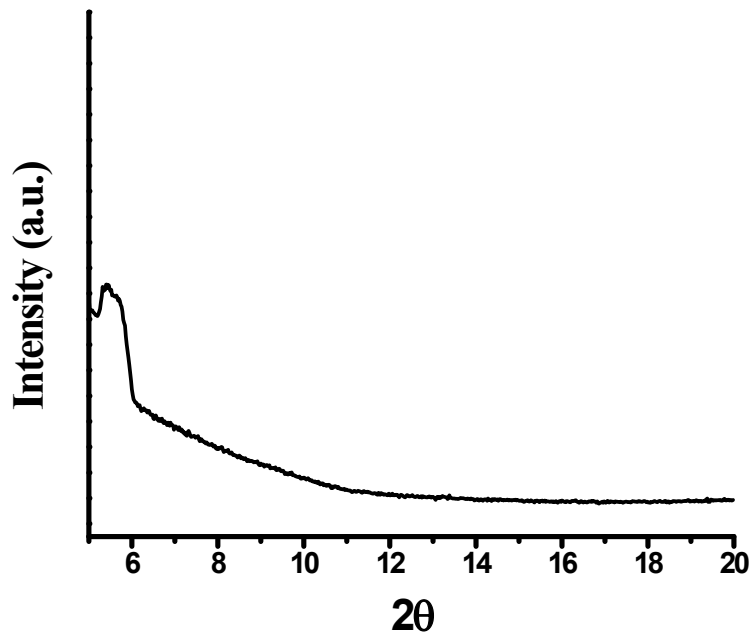


Fig. S3 XRD spectra of PSQ rods derived from EDAS before addition of gold chloride solution at pH = 6.0

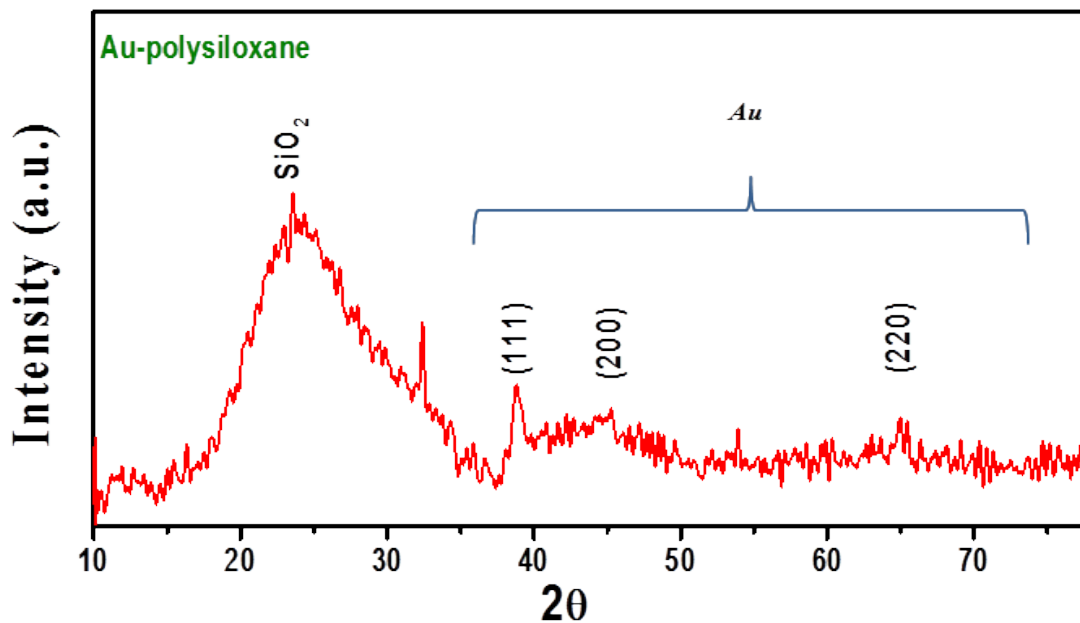


Fig. S4 XRD spectra of poly-siloxane enveloped gold nanoparticle prepared at pH = 6.0.

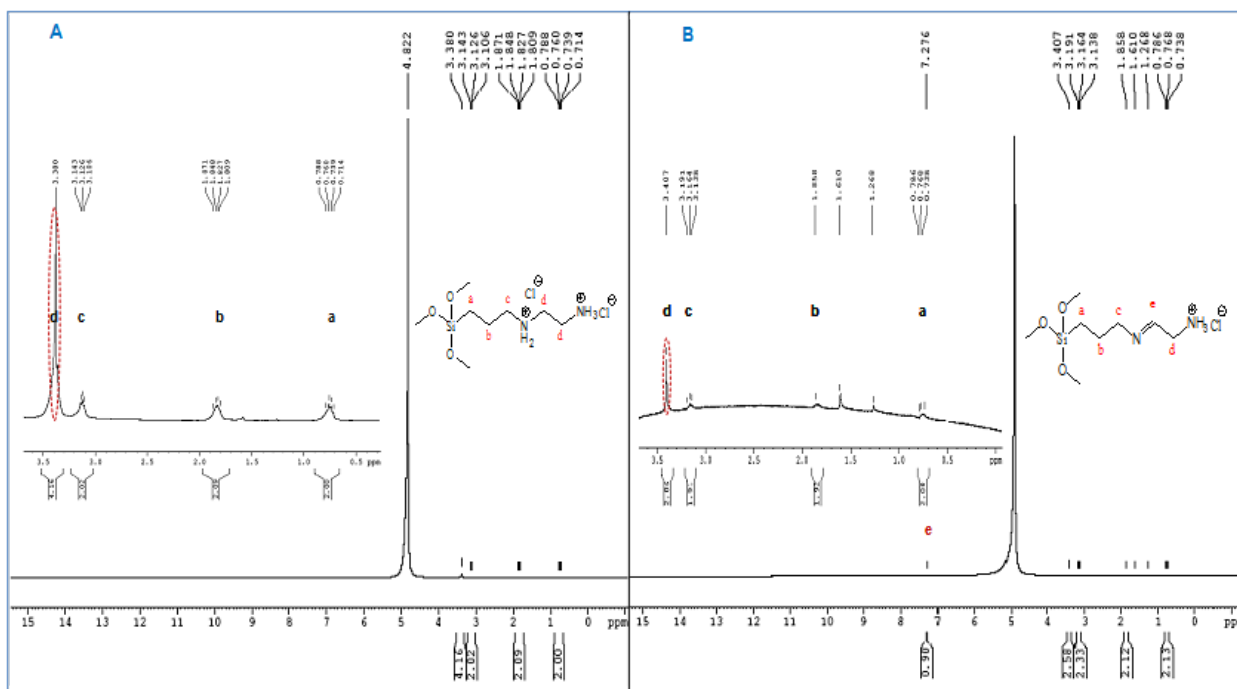


Fig. S5 ¹H NMR spectra of a) poly-siloxane derived from EDAS, b) poly-siloxane embedded Au nanoparticles [Chemical shift value of 4.8 (HOD), 1.6 (CDCl₃) and 1.2 (amine)].

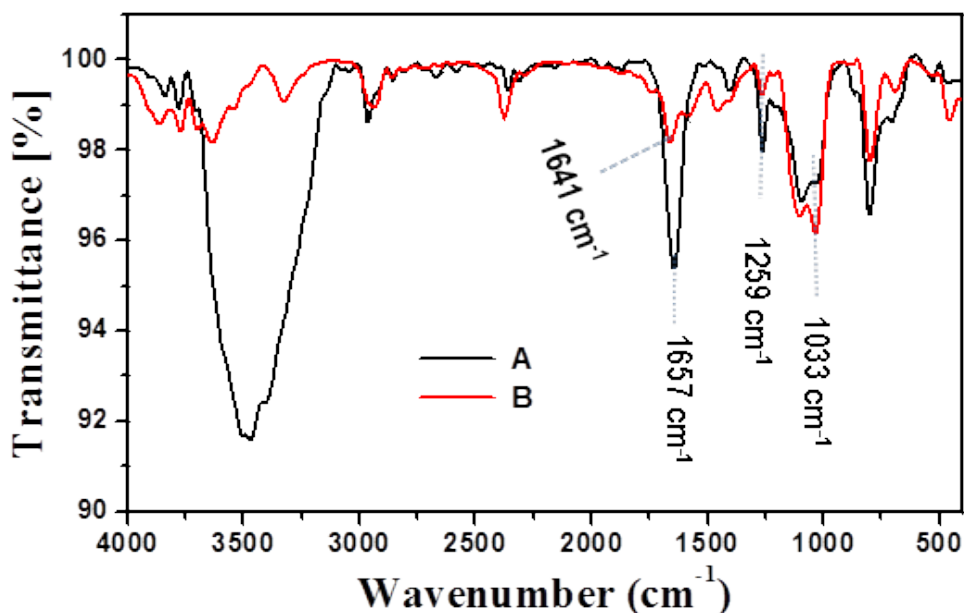


Fig. S6 FT-IR spectra of poly-siloxane of EDAS (black line A) and gold@PSQ nanoparticles (red line B) coated on glass plate.

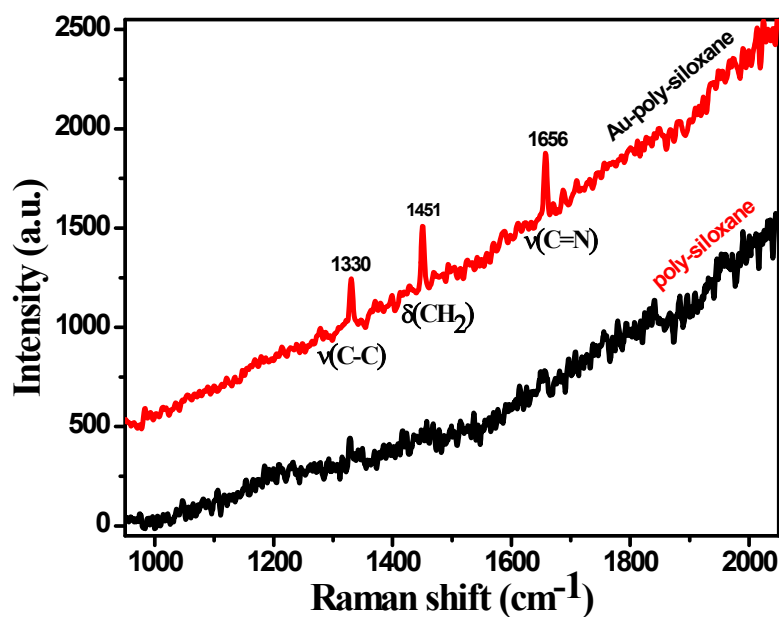


Fig. S7 Raman spectra of poly-siloxane (black line) and poly-siloxane enveloped AuNPs (red line) chain coated on glass plate.

Table S-T1. Vibrational peaks of FT-IR spectra

Poly-siloxane (cm ⁻¹)	Au-poly-siloxane (cm ⁻¹)
ν (1033) – Si-O-Si str	ν (1033) – Si-O-Si str
ν (1259) – Si-CH ₂ str	ν (1259) – Si-CH ₂ str
ν (1641) – OH bending	ν (1657) – C=N str