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

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

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Organized assemblies of polysilsesquioxane having specific functional groups were used as template to synthesis 1D nano chains of Au having 1-2 nm gap silica peapod. The protonated amines in polysilsesquioxanes formed from N-[3-(trimethoxysilyl)propyl]-ethylene diamine binds with $AuCl_4^-$ leading to formation of mono dispersed Au nano-chain by auto reduction.

Self-assembly and chemical interaction of supra molecular assemblies with complex ions are used to form noble metal nano particles with polymer wrapping.[1-2] Self-assembly and transformation of nanoscale objects in various templates were extensively reviewed by S.Mann.[1] The forces that govern the self-assembly can be either electrostatic or by hydrophobic interactions.[3] Soft templates such as synthetic polymers, proteins, DNA or viruses possess distinct chemical structures and provide multiple well defined binding sites for the attachment of nano particles.[4,5] Bottom up synthesis of polymer enveloped gold nanoparticles chains using Poly acrylic acid based co-polymers were recently reported.[6] The well-known chemistry of hydrolysis and condensation of amino silanes to form siloxane network containing amine functionality have been advantageously exploited for the synthesis of noble metal nano sols of Au, Pt, Ag and Pd by Ovadia's group.[7] Attempts by Bharathi *et al.,* have revealed the stabilization of $AuCl_4^-$ in the amino siloxane network at acidic pHs.[8] The interaction of $AuCl_4^-$ with the protonated amine is attributed to the uniform dispersion of the Au colloid prepared by chemical reduction. Attempts to use N-[3-(trimethoxysilyl)propyl]-ethylenediamine (EDAS) instead of 3-aminopropyltrimethoxy silane (APTMS) have also shown to form stable gold sols on reduction with sodium borohydride. Recently, we have reported the use of the Au, Ag and Au-Ag alloy sols stabilized using EDAS for the chemical catalysis of p-Nitrophenol to p-Aminophenol. The detailed TEM analysis of these Au and Ag sols reveal that the Au and Ag nanoparticles formed were of poly-dispersed spherical particles.[9]

The formation of higher order nanostructured polysiloxanes was studied extensively by Kaneko *et al.,*[10] Preparation of ammonium group containing ladder-like Polysilsesquioxanes (PSQs) was reported first from 3-aminopropyltrimethoxy silane. The sol gel reactions of APTMS in the presence of hydrochloric acid (HCl) at elevated temperature were known to form PSQ with perfect ladder arrangements. Actual scheme for the formation of hexagonal phase formed by the arrangement of twisted PSQs were discussed in detail.[10] Similar synthesis of rod like PSQs having a diamine namely N-[3-(trimethoxysilyl)propyl]-ethylene diamine (EDAS) was described by the same research group.[11] The optical properties of the Au colloids can be tailored by coating their surfaces with uniform shells made of dielectric materials such as silica.[12] In principle, one can achieve a precise control over the optical properties of these core-shell colloids by fine-tuning the chemical composition, structure, and dimensions of the cores or shells.[13] Liz-Marzan *et al.,* have reported a three-step procedure that involved the use of an amine terminated silane coupling agent to render the gold with silica shells.[14] Hardikar *et al.,* later found that it was also possible to form uniform coatings of silica on silver nanoparticles without derivatizing their surfaces with any coupling agent.[15]

We report the formation of Au nanochains using PSQ stabilizers derived from EDAS as template for the first time in what follows. To our surprise, on addition of $AuCl_4^-$ to aqueous EDAS at pH= 6.0, we have observed slow reduction of $AuCl_4^-$ to Au^0. This auto reduction was facilitated by pH above 5.0, sonication and increasing temperature. Though the APTMS or EDAS are known to form higher order PSQs under defined experimental conditions, we have not so far come across any attempt to use these higher order PSQ stablizers as templates for the synthesis of Au nanoparticles. To the EDAS solution, HCl was added to adjust the pH 6.0. The PSQ of higher order may be formed by heating the aqueous EDAS to 50-60 ºC for about 2 h.[11] The formation of ladder type PSQ from EDAS was confirmed by low angle peak at 5 ° in XRD as depicted in (Figure S3 †ESI). On addition of $AuCl_4^-$ in the above sol, auto reduction of $AuCl_4^-$ to Au^0 takes place as a function of time. The formation of Au colloid was identified by SPR band at 533 nm whose intensity does not show significant increase after 2-3 h. Au colloids prepared could be separated by centrifugation of the sol at 3000 rpm for 15-20 min. It is worth mentioning that the Au sols prepared using EDAS as stabilizer by chemical reduction with sodium borohydride could not be separated by centrifugation.[8] The separated particles could be re-dispersed in deionized water to give stable colloids of Au sol in pure water for at least one month. The Au sol re-dispersed in water also gave surface plasmon resonance (SPR) band exactly at 533 nm as seen from the (Figure S1 †ESI). It is important to point out that the Au or Ag sols prepared using APTMS and EDAS as stabilizers (and network formers) need at least 20 times excess silane for their stability. Similar experiments conducted at pH = 8.0 resulted in Au nano particles as aggregated assemblies. This may be perhaps due to the failure of $AuCl_4^-$ anion to interact with free amine group in EDAS at pH = 8.0.

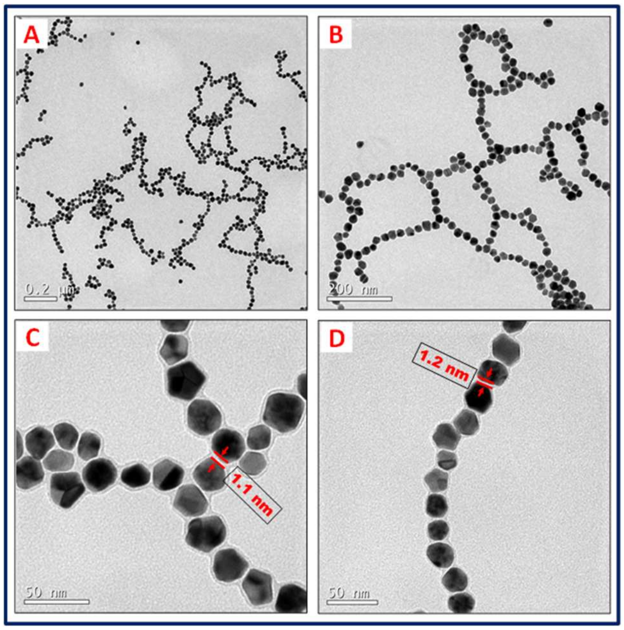


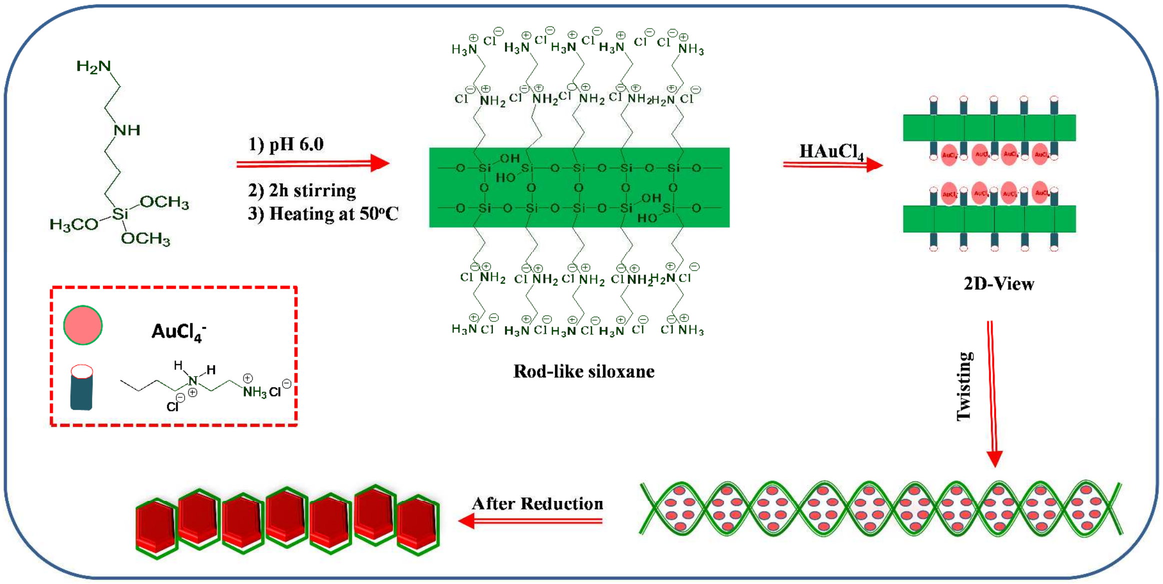
Figure 1. The transmission electron micrographs of the stabilized Au particles re-dispersed in water. Scale bars a) 0.2 µm, b) 200 nm, c) 50 nm, d) 50 nm.

The figure 1 shows that the uniformly sized (25-30 nm) Au nanoparticles are formed single chain like arrangements. Approximately equal size of Au nanoparticles in the chain impelled us to believe that the particles are formed by aggregation of Au atoms in a confined space in a micelle like assembly.

It is interesting to note that each particle is separated from the next particle by a coating of thickness 1-2 nm. The gold nanoparticles in the chain show surface plasmon resonance band at 533 nm (and absence of longitudinal peak upto 1100 nm) revealing that the SPR bands do not show any coupling effects by neighboring particles.[16] Noble metal nanostructures display unique and strongly enhanced optical properties due to the phenomenon namely localized 'surface plasmon resonance' (SPR). In noble metal nanostructures, plasmon oscillations on proximal particles can couple via their near-field interaction to neighboring particles, resulting in coupled plasmon resonance modes.[17,18] The absence of any such plasmonic coupling clearly indicates the presence of uniform dielectric silica layer of thickness (1-3 nm) on each gold nano crystals. The SPR band appeared at 533 nm in our experiments unequivocally proves that the Au particles in the nanochains behave as isolated particles. XPS studies (Figure S2 †ESI) and the X-ray diffraction studies[19] (Figure S4 †ESI) reveal that the thin coating on each gold particle is silica. Based on the knowledge of the formation of twisted rod PSQs reported in detail by Kaneko *et al.,*[10] and from the low angle XRD peak at above 5 ° characteristic of ladder type PSQs (Figure S3 †ESI), we have confirmed the formation of the nano-rods of siloxanes under our experimental conditions.

It is interesting to point out that in EDAS medium can form PSQs on heating under the conditions described under the 'experimental section'. $AuCl_4^-$ ions undergo auto reduction during heating at 50 °C of silane to form Au nano above pH = 5.0. This type of auto reduction was observed in APTMS at temperature above 100 °C.[20] The resulting oxidation of the R-PSQs (R = protonated alkyl diamine group, see scheme-1) after auto-reduction by interaction with $AuCl_4^-$ was investigated by ^{1}H NMR as depicted in (Figure S5 †ESI) the four protons in between two amine group in EDAS shown as'd' reduced to two protons. This may be attributed to the conversion of amine to imine functional group as shown in (Figure S5 (b) †ESI). The protons marked as 'a', 'b' and 'c' remain unchanged as seen from NMR data.

Scheme 1. Mechanism of nano gap polysilsesquioxanes wrapped gold nanoparticle chain formation



FT-IR spectra of poly-siloxane derived from EDAS and gold@polysiloxane nanoparticles were recorded by coating these materials on a glass plate, confirmed the formation of amine to imine. The FT-IR vibration peaks were tabulated in Table (S-T1 †ESI). The FT-IR and Raman spectra indicate the presence of imine functionality which clearly proves our claim (Figures S6&S7 †ESI). Based on the NMR and the FT-IR data, the formation of Au Nano chains were clearly explained by the scheme 1.

The amino group in EDAS remains weekly protonated at pH 6.0. On heating the EDAS at 50–70 °C, a ladder type PSQ-R was formed as reported by Kaneko *et al.,* Weekly protonated siloxane having two amine group can interact with the tetrachloro aurate anion and undergo auto reduction. The $AuCl_4^-$ has week electrostatic interaction with the rod shaped PSQs with cationic centers which enable uniform assembly of $AuCl_4^-$ ions. The auto reduction takes place with time as monitored by the gradual growth of SPR band at 533 nm by the in situ UV-Vis spectral measurements (Figure 2). The formation of the Au nanoparticles was complete in 2-3 h. The amines to imine [21] changes as revealed from ^1H NMR spectra (FT-IR and Raman) are responsible for the reduction of Au^{3+} to Au^0. The gold chloride was electro-statically bound inside an alkyl chain. This assembly places the $AuCl_4^-$ anion in relatively high hydrophobic regions. Reduction of $AuCl_4^-$ to metallic gold using long chain aliphatic amines as reducing agent in organic and aqueous medium was reported.[22,23] Noble metal nanostructures display unique and strongly enhanced optical properties due to the phenomenon of localized surface plasmon resonance (SPR). In noble metal nanostructures, plasmon oscillations on adjacent particles can couple via their near-field interactions to neighboring particles, resulting in coupled plasmon resonance modes.[17] Such a plasmonic coupling by neighboring particles were absent in our case.

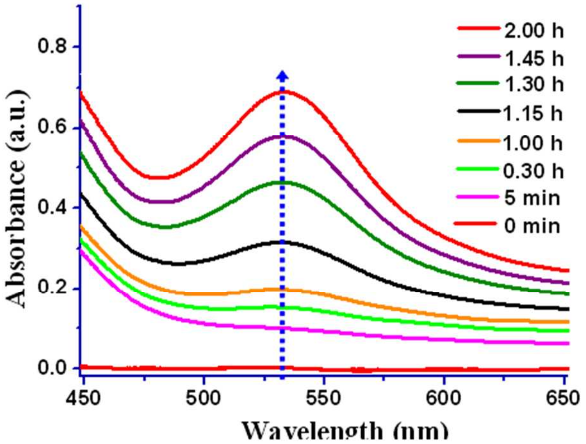


Figure 2. Time-dependent UV-Vis spectra of colloidal AuNP chain growth in EDAS with stirring measured at regular intervals up to 2 h at pH-6 (50 ºC).

Prashant K. Jain et al.,[24] have extensively discussed the electromagnetic (plasmonic) coupling in metal nanoparticle pairs based on discrete dipole approximation (DDA). They concluded that the dielectric constant of local surrounding medium, polarization directions of incident light, inter-particle distance, dipolar/quadrupolar interaction, nanoparticle size and shape are the factors involved in the determination of optical property of self-assembled metallic nanoparticles. The dielectric constant of pure SiO_2 is around 3.2. It is reasonable to assume that the defect free layers of polysilsesquioxane with non-hydrolysable propyl group might have higher dielectric constant. We believe that the absence of near field coupling between particles need further detailed investigations both theoretically and experimentally. This effect may be arising as due to the lower refractive index of the ordered polysilsesquioxane filled in the nanogap. A synthesis of Au nano chains utilizing templates such as biomolecules,[23] polymers,[25] etc were reported. A general problem of these methods is the lack of means to achieve close packing of the NPs in a chain and avoid irregular gaps. On the other hand, simple colloidal aggregation is advantageous in preparing NPs closely together, with short and regular gaps dictated by their ligand layers are reported rarely.[26] Many of these Au nano polygons have clear edges which can serve as hot junctions for the SERS signals.[27] Both SERS substrate and reference samples were prepared by drop casting the solution onto a cleaned quartz plate. The substrate for SERS measurement were prepared by drop casting 30 µL of redispersed gold nanoparticle chain onto the quartz plate and dried in open atmosphere. This modified film was coated with 30 µL of raman active molecule (p-MBA) and allowed to dry at room temperature overnight. The reference sample was prepared by drop casting 30 µL of p-MBA (1 mM) on quartz plate and dried at room temperature. The SERS spectra of p-Mercapto benzoic acid (p-MBA) adsorbed on poly-siloxane embedded gold metal surface was shown in Figure 3. The strong bands at 1076 and 1587 cm^{-1} are assigned to be aromatic ring vibrations of υ_{12} and υ_{8a} [28] respectively. The SH group of p-MBA attached on gold surface due to the well-known strong interaction between sulphur and gold atom.[29] The broad shoulder intense peak observed below 1400 cm^{-1} in Raman spectra is attributed by us (COO^-) of p-MBA.[28] This may due to surface bonded COO^- group on Au nanoparticles surface which containing ammonium ion on its surface. The positive zeta potential measurement was confirmed that the positively charged molecules present on re-dispersed Au@poly-siloxane nanoparticles in water (value of +26.67 mV). At the same time, we could observe the symmetric stretching peak at 1181 cm^{-1} of COO^- group in Fig 3.[27] The SERS spectra were measured by excitation laser source of 632.8 nm. The SERS enhancement factor of p-MBA was calculated using the formula which reported by Gupta and Wiemer [30] as:

$$\text{EF (Enhancement factor)} = (I_{Surf}/N_{surf}) \times (N_{Raman}/I_{Raman})$$

In which, I_{SERS} and I_{Raman} are the intensity of SERS signal and normal Raman signal respectively. Where, N_{surf} and N_{Raman} are the corresponding number of probe molecules which contribute to SERS and normal Raman signals. The EF value was determined for υ_{8a} aromatic ring vibration peak of 1587 cm^{-1} was given in table 1.

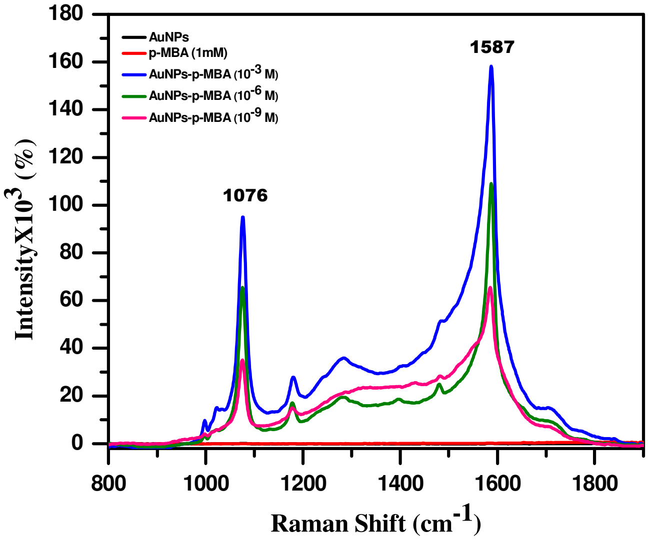


Figure 3. SERS spectra of p-MBA coated on gold nanoparticle chain recorded at different concentration of p-MBA molecule.

Table 1. EF values of different concentrations of p-MBA molecule.

S.No	Concentration of p-MBA	E.F Value
1	**1mM**	**7.561X10^3**
2	**1μM**	**5.197X10^6**
3	**1nM**	**6.221X10^{10}**

The high enhancement of SERS signal with p-MBA mainly depends on hot spots created in edges of Au nanoparticles covered by Polysilsesquioxanes. These periodic distances of average 1.5 nm have a pivotal role for electromagnetic enhancement of SERS signals even at low concentration of p-MBA. The contribution of chemical effects towards EF of SERS upto an order of 10^2.[31] The EF value of p-MBA depends on concentration of analyte. When we moved to low concentration the intensity of Raman signal decreased and at same time the EF value was increased up to the order of 10^{10}. Similar trend was followed in the work by Feng *et al.,*[29]

In summary, we report the formation of a uniform Au nano chains on functional Polysilsesquioxanes through self-assembly followed by auto reduction. The distance between the adjacent Au in the chain was 1-2 nm and was uniformly covered by silica layers. The nano gap chains do not show any plasmon coupling effects as seen from the invariant SPR peak at 533 nm. The Au chains cast on quartz were useful as SERS substrates. We expect that this kind of nano gap chains of Au particles separated by dielectric silica will possess interesting futuristic applications.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental details, XRD pattern for Au nano-chain, XPS for Au nano-chain, NMR spectrum for silane before and after Au reduction]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here.

1. S. Mann, *Nat. Mater.*, 2009, **8**, 781–792.
2. F. Burlina and H. Fan, *Chem. Commun.*, 2008, 1383–1394.
3. J. M. Chem, H. Kitching, M. J. Shiers, A. J. Kenyon, and I. P. Parkin, *J. Mater. Chem. A*, 2013, **1**, 6985–6999.
4. E. Dujardin, C. Peet, G. Stubbs, J. N. Culver, and S. Mann, *Nano Lett.*, 2003, **3**, 413–417.
5. K. Böhm, H. Rösner, and E. Dinjus, *Adv. Mater.*, 2002, **14**, 1621–1625.
6. H. Wang, L. Chen, X. Shen, L. Zhu, J. He, and H. Chen, *Angew. Chem. Int. Ed. Engl.*, 2012, **51**, 8021–5.
7. S. Bharathi, M. Nogami, and O. Lev, *Langmuir*, 2001, **17**, 2602–2609.
8. S. Bharathi and O. Lev, *Chem. Commun.*, 1997, 2303–2304.
9. S. Harish, R. Sabarinathan, J. Joseph, and K. L. N. Phani, *Mater. Chem. Phys.*, 2011, **127**, 203–207.
10. Y. Kaneko, N. Iyi, K. Kurashima, and T. Matsumoto, *Chem. Mater.*, 2004, **16**, 3417–3423.
11. Y. Kaneko, N. Iyi, T. Matsumoto, and K. Kitamura, *Polymer*, 2005, **46**, 1828–1833.
12. R. Fernandes, M. Li, E. Dujardin, and A. G. Kanaras, *Chem. Commun.*, 2010, **46**, 7602–7604.
13. A. E. Neeves and M. H. Birnboim, *J. Opt. Soc. Am. B*, 1989, **6**, 787–796.
14. L. M. Liz-Marzan, M. Giersig, and P. Mulvaney, *Chem. Commun.*, 1996, **6**, 731–732.
15. V. V Hardikar and E. Matijević, *J. Colloid Interface Sci.*, 2000, **221**, 133–136.
16. Y. Lu, Y. Yin, Z. Li, and Y. Xia, *Nano Lett.*, 2002, **2**, 785–788.
17. S. Lin, M. Li, E. Dujardin, C. Girard, and S. Mann, *Adv. Mater.*, 2005, **17**, 2553–2559.
18. Z. Nie, A. Petukhova, and E. Kumacheva, *Nat. Nanotechnol.*, 2009, **5**, 15–25.
19. V. A. Online, C. Wu, Z. Lim, C. Zhou, W. G. Wang, S. Zhou, H. Yin, and Y. Zhu, *Chem. Commun.*, 2013, **49**, 3215–3217.
20. X. Sun and W. Wei, *Langmuir*, 2010, **26**, 6133–5.

21. F. Kretschmer, U. Mansfeld, S. Hoeppener, D. Hager, and U. S. Schubert, *Chem. Commun.*, 2014, **50**, 88–90.

22. X. Lu, M. S. Yavuz, H. Tuan, B. A. Korgel, and Y. Xia, *J. Am. Chem. Soc.*, 2008, **130**, 8900–8901.

23. M. Aslam, L. Fu, M. Su, K. Vijayamohanan, and V. P. Dravid, *J. Mater. Chem.*, 2004, **14**, 1795–1797.

24. P. K. Jain, W. Huang, and M. a. El-Sayed, *Nano Lett.*, 2007, **7**, 2080–2088.

25. S. Kinge, M. Crego-calama, and D. N. Reinhoudt, *chemphyschem.*, 2008, **9**, 20–42.

26. M. P. Pileni, *J. Phys. Chem. B*, 2001, **105**, 3358–3371.

27. V. T. Cong, E. Ganbold, J. K. Saha, J. Jang, J. Min, J. Choo, S. Kim, N. W. Song, S. J. Son, S. B. Lee, and S. Joo, *J. Am. Chem. Soc.*, 2014, **136**, 3833–3841.

28. A. Michota and J. Bukowska, *J. Raman Spectrosc.*, 2003, **34**, 21–25.

29. H. Feng, Y. Yang, Y. You, G. Li, J. Guo, and T. Yu, *Chem. Commun.*, 2009, 1984–1986.

30. R. Gupta and W. A. Weimer, *Chem. Phys. Lett.*, 2003, **374**, 302–306.

31. L. Polavarapu and Q. Xu, *Langmuir*, 2008, **24**, 10608–10611.

Table of Content

Synthesis of Au nanochains encapsulated silane peapods using functional polysilsequioxane as template, useful as SERS substrates were reported.