SYNTHESIS AND CHARACTERIZATION OF LINEAR, BRANCHED AND NETWORK POLYSILANES AND THEIR REACTIVITY STUDIES TOWARDS Ag(I), Pd(II) AND Au(III) IONS

BY

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Submitted

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Dedicated to my parents

CERTIFICATE

This is to certify that the thesis entitled "***Synthesis and characterization of linear, branched and network polysilanes and their reactivity studies towards Ag(I), Pd(II) and Au(III) ions***" being submitted by Ms. Usharani Sahoo to the Department of Chemistry, Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy is a record of bonafide research work carried out by her.

Usharani Sahoo has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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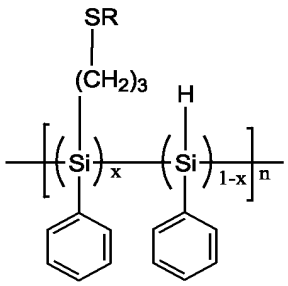
Usharani Sahoo

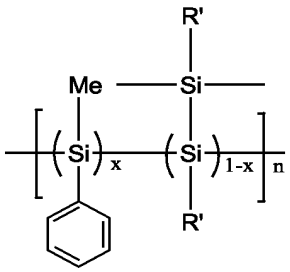
Abstract

The work embodied in the present thesis deals with synthesis and characterization of a few linear, branched and network polysilanes (chart 1) bearing sila-alkyl/thioether side chain groups.



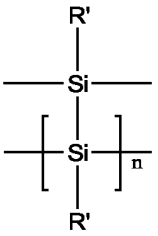
Linear polysilane

R = *n*-Dodecyl, *n*-Hex, *n*-Bu



Branched polysilane

R' = $Et_3Si(CH_2)_2$, 2-$FuMe_2Si(CH_2)_2$, $PhMe_2Si(CH_2)_2$



Network polysilane

Chart 1

Each class of polysilanes exhibits distinct electronic properties which are attributed to different structural frameworks comprising of catenated silicon atoms. A consideration of these intrinsic features has provided a basis to undertake a systematic study to explore potential applications of these functional polysilanes for the synthesis and *in situ* stabilization of noble metal nanoparticles within the organosilicon-based polymer matrices. A detailed account of the results obtained during the course of this work is presented in chapters III-V.

Chapter III – Synthesis and characterization of branched polysilanes and their application towards generation of fluorescent silver nanoparticles

The branched polysilanes, $[(PhMeSi)_x$-*co*-$(Et_3SiCH_2CH_2Si)_{1-x}]_n$ [x = 0.9 (**1**), 0.8 (**2**), 0.5 (**3**), 0.1 (**4**)] of varying compositions have been synthesized by dehalocondensation of a mixture of dichloromethylphenylsilane and the corresponding trichlorocarbosilane using sodium dispersion in refluxing toluene

(Wurtz coupling). Following a similar approach, analogous polysilanes, $[(PhMeSi)_x$-*co*-$(RSi)_{1-x}]_n$ [R = 2-$FuMe_2SiCH_2CH_2$ (**5**), *n*-Hex (**6**), Ph (**7**); x = 0.7-0.8] with different side chain substituents on the branched units (hereafter referred as polysilyne units) have been isolated by using dichloromethylphenylsilane and an appropriate chlorosilane, $RSiCl_3$. The GPC data reveal a monomodal molecular weight distribution in each case with M_w/PDI = 21.0-2.4 x 10^3/1.73-1.21. The $^{29}Si\{^1H\}$ NMR (CPMAS) spectrum of each polymer spans in two distinct chemical shift domains at δ -30 to -42 and -55 to -65 which are attributed to $[PhMeSi]_n$ (linear) and $[RSi]_n$ (branched) segments respectively. The polymers bearing sila-alkyl side chains reveal an additional sharp resonance at δ 7.80 to -9.18. The UV-vis and PL (λ_{exc} = 350 nm) spectral studies reveal the presence of two distinct chromophores associated with linear and branched segments [UV-vis (λ_{max}): 334-315 nm $(PhMeSi)_n$, 390-400 nm (tailing band) $(RSi)_n$; PL (λ_{max}): 363-360 $(PhMeSi)_n$, 407, 430 and 460 nm $(RSi)_n$]. The results corroborate well with cyclic voltammetric studies which exhibit two irreversible oxidation potentials (V_i) at 0.89-0.84 and 0.36 V (reference electrode: Hg/Hg_2Cl_2) associated with linear polysilane and polysilyne units respectively.

The reactivity behavior of polysilanes, $[(PhMeSi)_x$-*co*-$(RSi)_{1-x}]_n$ [R = $Et_3SiCH_2CH_2$ (**2**), 2-$FuMe_2SiCH_2CH_2$ (**5**), *n*-Hex (**6**), Ph (**7**); x = 0.7-0.8] as well as $[(PhMeSi)_{0.5}$-*co*-$(Et_3SiCH_2CH_2Si)_{0.5}]_n$ (**3**) towards Ag(I) ions has been examined under aerobic conditions. The choice of these polymers has been useful to study the influence of composition/side chain substituents on the stabilization of *in situ* generated silver nanoparticles. Synthesis of polymer-silver nanoassemblies involves slow addition of a solution of each polymer, **2, 5-7** in toluene separately into a stirred suspension of silver acetate (0.10 and 0.25 molar with respect to polymer repeat unit) in the same solvent. The reduction of Ag(I) to Ag(0) is readily accomplished by σ–delocalized

electrons of the polysilanes and does not require any external reducing agent. The polymer-silver nanoassemblies thus obtained are designated as **2a**, **5a-7a** (with 0.10 mole of Ag) and **2b**, **5b-7b** (with 0.25 mole of Ag) respectively. Transmission electron microscopy (TEM) reveals the formation of spherical silver nanoparticles in a quasi-monodispersed phase with an average diameter of 5-7 nm for **2a**, **5a-7a** and 8-11 nm for **2b**, **5b-7b**. Analysis of the crystal lattice shows Ag(1, 1, 1) with its characteristic 0.235-0.241 nm spacing and is in accord with the results reported earlier for silver nanoparticles. The UV-vis spectra of the nanoassemblies reveal surface plasmon resonance at 427-433 nm due to silver nanoparticles in addition to the absorption at 330 nm associated with σ-σ^* electronic transition of linear poly(methylphenylsilane) segment. A revealing feature of the PL spectra (λ_{exc} = 350 nm) is the appearance of a new band at 515-550 nm in lieu of the emission bands associated with the polysilyne units of the parent polymers (figure 1). The new emission is found to be independent of excitation wavelengths in the range of 350-430 nm, thereby suggesting that the obtained emission is a real luminescence from the relaxed state and not due to scattering effect. This emissive behavior of the nanoassemblies is corroborated by the observed green luminescence under UV light. The results obtained from photoluminescence spectra and fluorescent nature of each nanoassembly as green light emitter provide a strong basis to suggest the formation of silver nanoclusters in addition to the nanoparticles, as no plasmon emission is anticipated from bulk silver nanoparticles. Time-resolved fluorescence decay of the silver nanoassembly **2a** has been studied to substantiate the presence of silver nanoclusters. The decay phenomenon is monitored at 525 nm by using 340 nm lasers and the result can be fitted biexponentially with a fast component of 409 ps (55%) and

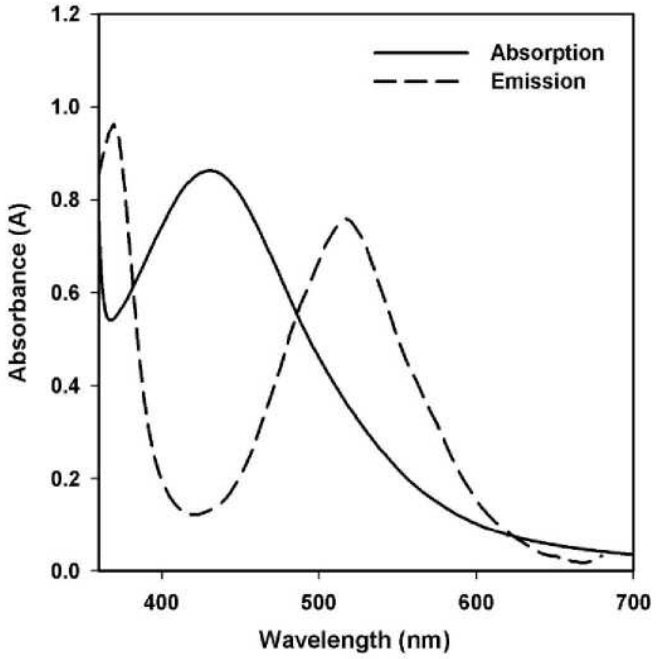


Figure 1: Absorption and emission spectra of polymer-silver nanoassembly 2a

a slow component of 2.84 ns (45%). The former value is assigned to the host polymer matrix and the latter with longer life time is consistent with a few recent reports on Ag_2 clusters which reveal fluorescence life time of 2-3 ns.

Addition of donor solvent such as THF into the polymer-silver nanoassemblies affords the isolation of host polymers. An examination of the GPC data reveal a perceptible decrease in molecular weights (M_w = 10.4-4.0 x 10^3/2.1-1.4) as compared to those of the corresponding parent polymers (M_w = 21.0-9.7 x 10^3/1.9-1.3) suggesting oxidative cleavage of the skeletal silicon backbone during the reduction of Ag(I) ions. UV-vis and photoluminescence (PL) spectra identify linear poly(methylphenylsilane) segment by characteristic absorption and emission bands at 330 and 360-365 nm respectively. The spectral profiles of the host polymer matrices derived from **2a, 5a-7a** exhibit the signatures of residual polysilyne fragments (λ_{max} ~ 400-450 nm) while those isolated from **2b, 5b-7b** are devoid of this characteristic emission. An important feature of the PL spectra is the absence of emission band at

~525 nm as observed in the polymer-silver nanoassemblies. These results provide a basis to draw a few important conclusions. (a) The absence of polysilyne framework in the host polymers derived from **2b, 5b-7b** clearly suggest that the branched units act as preferential sites for the reduction of Ag(I) ions to Ag(0) in comparison to linear poly(methylphenylsilane) segment. (b) The green emission at ~525 nm and associated fluorescence characteristics of the silver nanoassemblies are the attributes of silver nanoclusters and do not originate from the polymer matrices. (c) The structural framework of the host polymer in the nanoassemblies is comprised of linear poly(methylphenylsilane) with branching sites associated with siloxane units (IR: 1060-1080 cm^{-1}) which act as scaffolds for the stabilization of silver nanoparticles/nanoclusters in the nanoassemblies.

To better understand the unique property of branched polysilanes as scaffolds for silver nanoparticles/nanoclusters, the reaction of a mixture of homopolymers $[PhMeSi]_n$ and $[Et_3SiCH_2CH_2Si]_n$ (5:1 equivalents) with 0.10 equivalent of silver acetate has been performed under identical reaction conditions as described for the branched polymers. The nanoassembly thus formed does not exhibit fluorescent characteristics and is devoid of emission band at ~ 525 nm in a range of excitation wavelengths between 350 to 430 nm. These studies clearly suggest that the polymer matrix derived from physical blend of the homopolymers does not meet the structural requirements which are essential for the protection of *in situ* generated silver nanoclusters.

Chapter IV – Synthesis and characterization of network polysilanes and their application towards generation of silver and gold nanoparticles/nanoclusters

The trichlorocarbosilanes, $RR'_2Si(CH_2)_xSiCl_3$, [R = Ph, R' = Me; R = R' = Et; R = 2-Fu, R' = Me; x = 2, 3] have been chosen as precursors for dehalocondensation

reaction using classical Wurtz coupling (Na, toluene, 110 °C) approach. The synthetic method allows the isolation of high molecular weight polysilynes (table 1). However, the monomer, 2-$ThMe_2Si(CH_2)_2SiCl_3$ is found to be intolerant to harsh reaction conditions and invariably affords an insoluble solid which could not be characterized further. However, the monomer undergoes a smooth dehalocondensation reaction with sodium dispersion at room temperature conditions in THF to yield the polysilyne, $[2\text{-}ThMe_2Si(CH_2)_2Si]_n$. The validity of this method has been examined for the synthesis of polysilynes bearing phenyl and 2-furyl substituted sila-alkyl side chains. As shown in table 1, polysilynes obtained by the modified Wurtz coupling approach (Na, THF, RT) is advantageous since it allows the formation of high molecular weight polysilynes in improved yields as compared to those obtained from classical Wurtz coupling (Na, 110 °C) involving refluxing toluene as the medium.

Table 1: Molecular weight and isolable yield of polysilynes 8-13

Polysilynes	Formula	Yields[a] (%)	M_w[b]	PDI[c]
8	$[PhMe_2SiCH_2CH_2Si]_n$	15.7 (35.6)	5791 (10504)	1.3 (2.2)
9	$[PhMe_2SiCH_2CH_2CH_2Si]_n$	16.8	3500	1.4
10	$[Et_3SiCH_2CH_2Si]_n$	15.5	4546	1.5
11	$[Et_3SiCH_2CH_2CH_2Si]_n$	14.8	2900	1.3
12	$[2\text{-}ThMe_2SiCH_2CH_2Si]_n$	(30.5)	(5028)	(1.7)
13	$[2\text{-}FuMe_2SiCH_2CH_2Si]_n$	12.5 (33.4)	3321 (9176)	1.5 (1.5)

The values in parenthesis show the yields and M_w values of the polysilynes isolated under room temperature condition. [a]Isolated yield of high molecular weight fraction. [b]M_w = Weight average molecular weight. [c]PDI = polydispersity index (M_w/M_n).

The $^{29}Si\{^1H\}$ NMR chemical shifts accord the presence of appended carbosilyl side chains [δ ^{29}Si = 8.36 to -3.52] and higher dimensional catenated silicon backbone [δ ^{29}Si = -58 to -67, br] comprising of $-Si(Si)_3$ skeletal framework. Cyclic voltammetric

studies of the polysilynes reveal an irreversible oxidation wave with onset of oxidation (V_i) at 0.34-0.36 V with respect to Hg/Hg_2Cl_2 reference electrode.

The electronic properties and structural features of the polysilynes are considered useful to explore their potential applications for the synthesis of silver and gold nanoparticles. The reactions of polysilynes, $[RMe_2SiCH_2CH_2Si]_n$ [R = Ph (**8**), R = 2-furyl (**13**)] with 0.2 mole of silver acetate/tetrachloroauric acid, $HAuCl_4.3H_2O$ in toluene afford the formation of stable silver (**8a, 13a**) and gold (**8b, 13b**) nanoassemblies. Transmission electron microscopy of the as prepared nanoassemblies reveal spherical, monodispersed metal nanoparticles of average diameter 4-5 nm (for Ag) and 5-8 nm (for Au). Characteristic surface plasmon resonances for silver and gold nanoparticles appear at 425-428 and 527-530 nm respectively (figure 2a). The silver nanoassemblies are found to be fluorescent in green light region when exposed to UV light. The emissive behavior is corroborated by the appearance of a new band at 525-528 nm (λ_{exc} = 360 nm) in photoluminescence (PL) spectra (figure 2b) and is attributed to the presence of silver nanoclusters in conjunction with silver nanoparticles, as no fluorescence is expected from the later. The results resemble closely with the nanoassemblies derived from branched polysilanes (chapter III). In case of polymer-gold nanoassemblies, the PL spectral profiles are dominated by the signatures of residual polysilynes (403, 430, 460 nm) only. The nanoassemblies are non fluorescent under UV light and thus rule out the possibility of the presence of gold nanoclusters.

A subject of considerable interest in the present study is to examine the interaction between nanoscale silver and Hg(II) ions and its implications in the modulation of plasmonic and emission intensities associated with silver nanoparticles/nanoclusters.

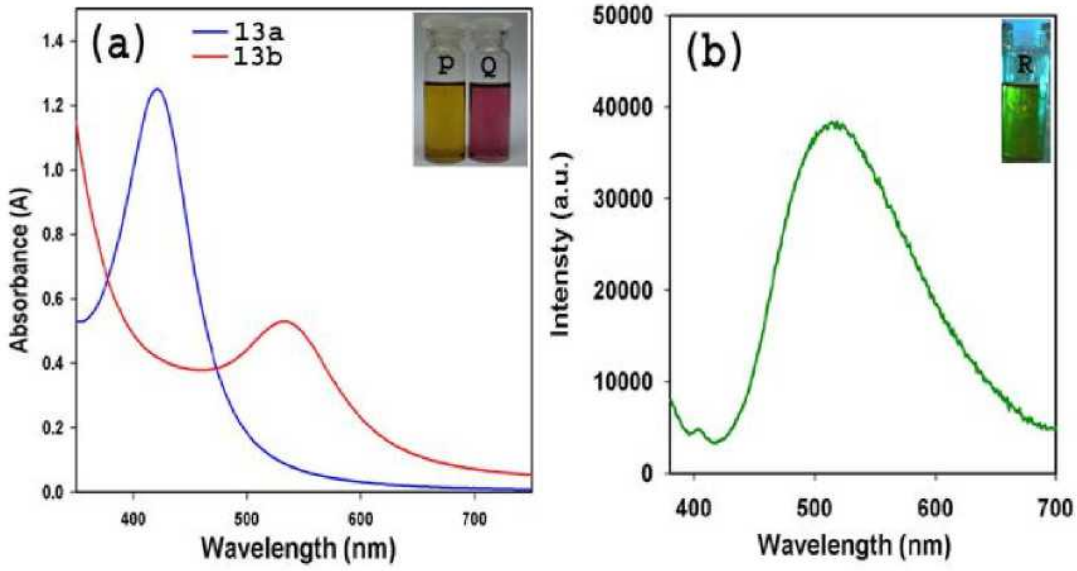


Figure 2: (a) UV-vis spectra of silver (13a) and gold (13b) nanoassemblies (b) PL emission spectrum of 13a (λ_{exc} = 360 nm, toluene, RT). The insets show the photographs of 13a (P), 13b (Q) under room light and 13a under UV light (R)

The solutions containing polymer-silver nanoassembly **8a** and varying concentrations of (10^{-12} to 10^{-4} M) of HgI_2 in toluene have been subjected to UV-vis and PL spectral studies. A progressive quenching of the plasmonic resonance (~ 430 nm) is distinctly observed with increasing concentration of Hg(II) ions (figure 3). By analogy with literature precedence, the quenching phenomenon is attributed to partial oxidation of silver nanoparticles in presence of Hg(II) ions, which brings about either surface coating of zero valent Hg on the nanoparticles or formation of amalgam like structure composed of metallic mercury and silver nanoparticles. The size domain/polydispersity [5-12 nm for 10^{-12} M Hg(II), 5-60 nm for 10^{-4} M Hg(II)] of chemically modified silver nanoparticles shows a perceptible increase in comparison to that of as prepared nanostructures (4-5 nm).

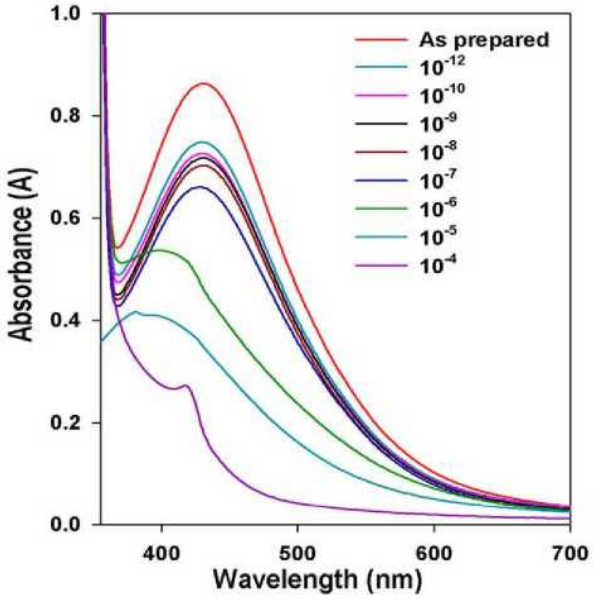


Figure 3: UV-vis absorption response of Ag nanoassembly 8a upon addition of HgI_2 in 10^{-12} to10^{-4} M concentration range

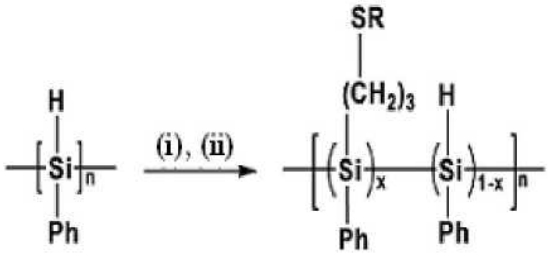
Time resolved fluorescence studies of the silver nanoassembly containing 10^{-12} M Hg(II) ions in toluene suggests the presence of silver nanoclusters (decay time = 3.87 ns) in the vicinity of modified Ag-Hg nanostructures. PL spectral studies of this solution reveal that the fluorescence intensity of ~ 530 nm band is enhanced by a factor of 1.3 in comparison to that of the parent nanoassembly. The enhancement factor decreases gradually upon increasing the concentration of Hg(II) ions till a limiting value of 10^{-7} M is reached in solution. After this threshold limit, the spectrum is dominated by the emission bands of residual polysilyne only with no PL signatures of silver nanoclusters. A plausible explanation of the observed modulations in the fluorescence intensity of silver nanoclusters has been put forth by considering coupling of surface plasmon energy of silver nanoparticles with the electronic transition of silver nanoclusters. The study represents a new step towards the development of chemical approaches to construct nanostructures which may prove to

be significant to understand the phenomena of fluorescent enhancement of silver nanoclusters in the vicinity of silver nanoparticles. In addition, the method offers both UV-vis as well as PL spectroscopic methods for the detection of Hg(II) ions at subnanomolar concentration limits.

The reactions between the polymer-gold nanoassemblies (**8b, 13b)** and Hg(II) ions in 10^{-10} to 10^{-4} M concentration range in toluene have been studied by UV-vis spectroscopy. The results reveal that the absorption maxima as well as intensity of surface plasmon resonance of gold nanoparticles remain practically unaltered with the addition of Hg(II) ions, suggesting that redox reaction between zero valent gold nanoparticles and Hg(II) ions is not favored.

Chapter V – Synthesis and characterization of linear polysilanes with thioether side chain groups and their applications towards generation of silver and gold nanoparticles

The work described in this chapter relates to synthesis of new polysilanes bearing thioether groups as side chains. The synthetic protocol involves hydrosilylation reaction between poly(phenylsilane) and allyl-*n*-dodecyl/*n*-hexyl/*n*-butyl thioether using AIBN as the free radical catalyst (Scheme 1).



(i) CH_2=$CHCH_2SR$, (ii) AIBN R = n-Dodecyl, n-Hex, n-Bu

Scheme 1

The polysilanes, $[\{PhHSi\}_x\{Ph(RSCH_2CH_2CH_2)Si\}_{1-x}]_n$ [R = *n*-dodecyl (**14**), *n*-Hex (**15**) and *n*-Bu (**16**)] have been characterized by GPC [M_w/PDI = 4.8-3.5 x 10^3/1.27-1.17], IR and multinuclear NMR spectral studies. An examination of UV-vis spectra reveals a discernible red shift of the absorption maxima (λ_{max} = 327-324 nm) in comparison to that observed for the parent polysilane (~ 300 nm), suggesting a more extended trans conformation of the silicon backbone. A salient feature of $^{29}Si\{^1H\}$ NMR spectra is the appearance of new broad resonance at δ -25 to -35 due to SiC_2 backbone units along with a weak signal at δ -50 to -55 due to residual poly(phenylsilane).

The scope of these functional polysilanes as reducing agents towards Ag(I) and Au(III) ions and as stabilizing matrix for metal nanoparticles has been examined in detail. A suspension of $HAuCl_4.3H_2O$ in toluene upon treatment with polysilanes **14-16** (ten equivalents with respect to the repeat unit) separately reveals a gradual color change of the solutions from colorless to red within 3-4 hours, suggesting the formation of gold nanoparticles. The formation of gold nanoparticles in polysilane matrix is substantiated by the appearance of surface plasmon resonance at 530 nm in UV-vis spectrum. The polysilane bearing long dodecyl thioether groups is relative more effective for stabilization the gold nanoparticles which shows long shelf life stability in solution (ten months) when kept in the dark. The transmission electron microscopic studies reveal an ensemble of spherical, nearly monodispersed gold nanoparticles of average diameter 4.5 ± 1.9 nm (figure 4). Each particle in the assembled structure is well separated from the neighboring nanoparticles indicating that these are surface passivated well and stabilized by the polymer matrix.

The scope of polysilane-gold nanoassembly obtained above has been examined for the synthesis of Au-Pd bimetallic nanoparticles. The formation of bimetallic Au-Pd

nanoassemblies of varied compositions has been achieved by the addition of toluene solutions of palladium acetate (molar ratio, pure Au, 1:0, 0.8:0.2, 0.7:0.3, 0.6:0.4, 0.5:0.5, 0.8:0.2, pure Pd) separately into a stirred solution of preformed polymer-gold nanoassembly. The formation of bimetallic Au-Pd nanoparticles has been supported by examining the visual color change of the resulting solutions as well as changes in the plasmonic resonance associated with gold nanoparticles.

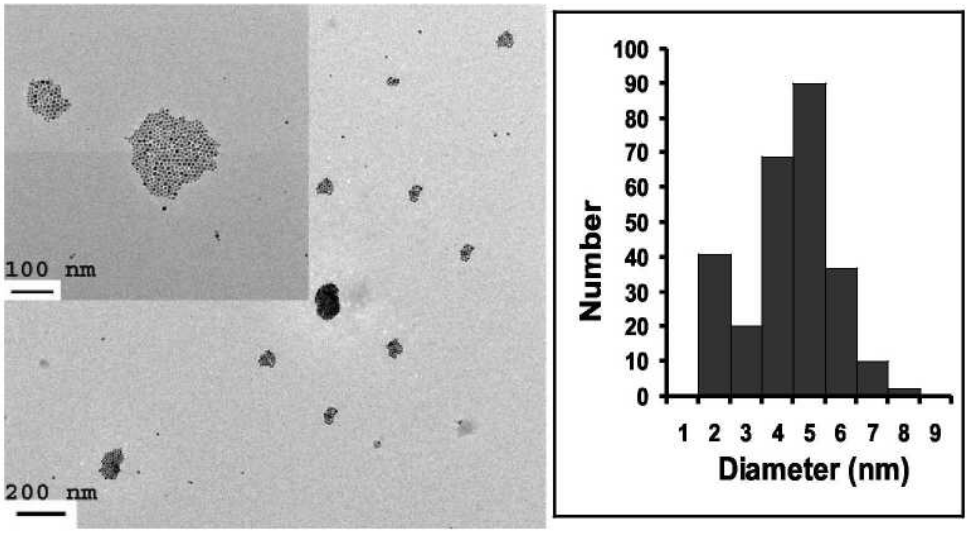


Figure 4: TEM image and particle size distribution of gold nanoparticles in polysilane 14 matrix

The original red color of the gold nanoparticles slowly fades as the concentration of Pd(II) ions is increased and ultimately turns dark brown. A concomitant decrease in intensity of the plasmonic band associated with pure gold nanoparticles is distinctly observed in the UV-vis spectral studies (figure 5). The plasmonic band of gold nanoparticles disappears completely when molar concentration of Au:Pd attains 0.2:0.8. The phenomena of dampening and disappearance of surface plasmon band of gold nanoparticles as a function of varying concentration of added Pd(II) ions is consistent with a few earlier reports on Au-Pd nanoparticles assemblies featuring

core-shell structure. A consequence of this modification is the observed increase in size/polydispersity of the resulting colloidal bimetallic nanoparticles (8-11 ± 5 nm),

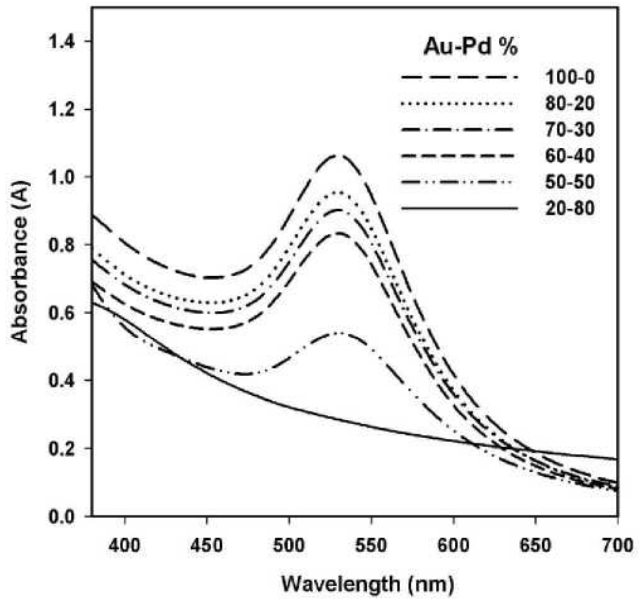


Figure 5: UV-vis spectra of Au-Pd nanoassemblies (toluene, RT)

as evident from TEM studies. The EDAX analysis of the bimetallic nanoparticles gives the peak of both palladium and gold suggesting the coexistence of Au and Pd in the nanoparticles.

The studies have been extended to construct silver nanoassembly with polysilane **14** as the reducing agent. The silver nanoparticles thus obtained are spherical in nature (6 ± 2.1 nm) and exhibit surface plasmon band at ~ 438 nm. The utility of this nanoassembly for the synthesis of Ag-Pd bimetallic nanoparticles is also demonstrated.

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