



# 3-Aminopropyltrimethoxysilane mediated solvent induced synthesis of gold nanoparticles for biomedical applications

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## ABSTRACT

The effect of acetone on 3-aminopropyltrimethoxysilane (3-APTMS) mediated synthesis of gold nanoparticles (AuNPs) in polar protic, polar aprotic and non polar solvents specifically water, acetone and chloroform has been studied. The findings revealed that acetone promotes the formation of siloxane polymer in chloroform and acetone solvents, but not in water, while AuNPs are formed in all cases. The bifunctional nature of 3-APTMS  $[\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OMe})_3]$  controls the formation of siloxane polymer through hydrolysis and condensation of trimethoxysilyl group whereas the amine moieties are likely to form imine linkage, which are involved in the synthesis of gold nanoparticles. The siloxane polymer with imine linkage can be formed both in absence and the presence of gold precursor (i.e.  $\text{HAuCl}_4$ ). Accordingly, siloxane-gold nanoparticles can be made in different morphology, through control over the process, in three ways; (i) all precursors ( $\text{Au}^{3+}$ , 3-APTMS and acetone) mixed simultaneously yielding [(siloxane- $\text{Au}_{\text{sim}}$ )], (ii) polymer made first followed by sequential reduction of  $\text{Au}^{3+}$  in homogenous suspension forming ( $\text{Au-siloxane}_{\text{homo}}_{\text{seq}}$ ) and (iii) polymer made into thin film followed by sequential reduction of  $\text{Au}^{3+}$  in the heterogeneous system yielding ( $\text{Au-siloxane}_{\text{hetero}}_{\text{seq}}$ ). The AuNPs produced with the use of water as solvent is different from the three described above as discrete spherical AuNPs are formed as [(AuNPs)<sub>water</sub>] and in this case siloxane polymer is not formed. The results based on AFM and SEM characterizations revealed porous morphology of NPs fabricated in chloroform/acetone, due to the formation of siloxane polymer, and non-porous morphology for the same in water. The “( $\text{Au-siloxane}_{\text{hetero}}_{\text{seq}}$ )” efficiently promote the reduction of p-nitrophenol with good operational stability, justifying its interest for heterogeneous catalysis. On the other hand, (siloxane- $\text{Au}_{\text{sim}}$ ) and ( $\text{Au-siloxane}_{\text{homo}}_{\text{seq}}$ ) can be also deposited onto glassy carbon surfaces to yield polymer modified electrodes for subsequent electroanalytical applications. The cyclic voltammetry response of such modified electrodes to a redox probe (i.e.,  $\text{Fe}(\text{CN})_6^{3-/4-}$ ) was characteristic of diffusion controlled and thin-layer electrochemical behaviour respectively as a function of non-porous and porous nature of the polymer. The as made nanomaterial shows excellent biocatalyst for dopamine sensing based on peroxidase mimetic activity. The typical result on dopamine sensing is reported.

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## 1. Introduction

Due to their unusual properties, noble metal nanoparticles (NPs) like silver, gold, palladium and platinum are attracting a great deal of attention in many scientific and technological fields [1–5]. Accordingly different methods have been used to synthesize various functional metallic nanostructures [6,7]. NPs have been widely used for various catalytic applications however, due to the problem of recyclability their exploitation in suspension is limited. Besides, their use is also accompanied with the problem of residual metal impurities that are left in the final products [8]. Nowadays, green chemistry approach towards the use of catalyst (recyclable and reusable) is favoured more and more as it is

environment friendly. Further, semiconductor based photo catalysts have received substantial attention as they are non-toxic, cheap, easy to synthesize and environmental friendly [9–12]. Among all noble metal NPs, gold nanoparticles (AuNPs), have received greater attention due to their unique physicochemical features [13–14]. AuNPs are immobilized onto different supports like porous solids, membranes, fibres, functionalized clay [15–22] and various polymers for specific applications. Among polymers siloxanes are an important class of polymers that are used extensively in cosmetics, lithographic stamps and micro fluidic channels [23], to make biocompatible surfaces for immobilization of antibodies [24] and for fabricating super-hydrophobic surfaces [25–26]. Accordingly, the findings on the synthesis of siloxane-AuNPs hybrid have been one of prime attentions. Efforts have been made on these lines by Goyal et al. [27] involving the active role of octadecylsilane (ODS) to form a hybrid between AuNPs and siloxane

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polymer (gold core-siloxane shell). Similarly Feng et al. [28], also reported the synthesis of gold nanowires (AuNWs) using trisopropylsilane (TIPS). It has been proved through experiments that TIPS is crucial for the formation of AuNWs. The use of different alkylsilanes for the fabrication of AuNPs justify the active role of –Si–H linkage. Similarly a report on the use trimethoxysilane [(OR)<sub>3</sub>SiH] for the reduction of Pd<sup>2+</sup> to Pd<sup>0</sup> has also been documented by our group [29]. However, the use of alkoxysilanes, to the best of our knowledge, which is less reactive and thus easy to handle compared to alkylsilanes have not been used for fashioning hybrid between AuNPs and siloxane. Thus, there is a need of suitable functional alkoxysilanes that allow the formation of stabilized AuNPs along with siloxane polymer and 3-APTMS appears to be a perfect choice for such synthesis as discussed below (Table 1).

We have used 3-APTMS for the controlled synthesis of monometallic, bimetallic and trimetallic noble metal nanoparticles involving a variety of organic reducing agents like 3-glycidoxypropyltrimethoxysilane, tetrahydrofuran hydroperoxide, cyclohexanone, formaldehyde, acetaldehyde, acetone and t-butyl methyl ketone [30–36]. The choice of reducing agent is very important as it has an impact on physical properties of NPs, like dispersibility in solvents, pH- and salt-tolerance etc. Further, the imine linkage, between 3-APTMS and few carbonyl moieties, have an impact on the catalytic activity as it also acts as a catalyst [33]. Further, functional alkoxysilanes under optimum ratio of hydrophobic and hydrophilic components leads to the formation of nanostructured network of organically modified silicates and has been used extensively for multiple applications, the synthesis of AuNPs is sought in porous matrix both in homogenous and heterogeneous systems.

Recently, in a report by Mazzei et al. [37], which was further revisited by Schraml et al. [38], acetone-induced polymerization of 3-APTMS in chloroform has been observed. Using <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR techniques they have proved that acetone reacts with the silane amino group to form an imine N-isopropylidene-3-aminopropyltrimethoxysilane/IPTMS/[(CH<sub>3</sub>)<sub>2</sub>C = N(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>]. The water that is released during the imine formation hydrolyzes the methoxysilane inducing thereby the formation of siloxane, Si–O–Si bridges. Further, the role of organic imine without alkoxy group during the synthesis of AuNPs has been documented by Wu et al. [39] However, the role of imine [(CH<sub>3</sub>)<sub>2</sub>C = N(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>], IPTMS formed from 3-APTMS and acetone as described above has not been explored during the synthesis of AuNPs, which might be useful in forming AuNPs and siloxane polymer simultaneously given the bifunctional nature of 3-APTMS. Corroborating these findings we have attempted the synthesis of spherical AuNPs utilizing the interaction between 3-APTMS and acetone under three different conditions viz. (i) all precursors (Au<sup>3+</sup>, 3-APTMS and acetone) mixed simultaneously, (siloxane-Au<sub>sim</sub>) (ii) polymer made first followed by sequential reduction of Au<sup>3+</sup> in homogeneous suspension, (Au-siloxane<sub>homo</sub>)<sub>seq</sub> and (iii) polymer made into thin film followed by sequential reduction of Au<sup>3+</sup>, in the heterogeneous system, (Au-siloxane<sub>hetero</sub>)<sub>seq</sub>. The same reagents in aqueous medium (water) allow the formation of AuNPs (AuNPs)<sub>water</sub> however, the growth of siloxane polymer was not detected in this case. The synthesis of nanomaterial using different solvent has been studied as it solvent

has an impact on the physicochemical properties of nanomaterial [40]. We have observed solvent-dependent morphological and catalytic behaviour of the AuNPs, due to the formation of porous siloxane matrix in the case of nanoparticles synthesis in organic solvents while the formation of such polymer has not been recorded when water is used as solvent. Also, the formation of porous siloxane matrix prompted us to synthesize and use the polymer, made from 3-APTMS and acetone, as scaffold for the synthesis of AuNPs over solid surface. The findings on these lines are reported in this manuscript.

## 2. Materials and methods

### 2.1. Materials and instrumentations

All reagents were used as received. Tetrachloroauric acid hydrate was purchased from HiMedia; 3-aminopropyltrimethoxysilane (3-APTMS) was obtained from Aldrich Chem. Co. All other chemicals employed were of analytical grade. Aqueous solutions were prepared by using doubly distilled-deionized water (Elga water purification system). The absorption spectra of nanoparticles were recorded using a Hitachi U-2900 Spectrophotometer. Transmission electron microscopy (TEM) images were recorded using Morgagni 268D (Fei Electron Optics) operating at 200 kV. Scanning Electron Microscopy (SEM) studies were performed with Kratos Analytical Instrument, Shimadzu group company, Amicus, UK. AFM was supplied from Bruker company.

### 2.2. Synthesis of AuNPs

The typical concentrations of the reagents i.e. 3-APTMS, Au<sup>3+</sup> and acetone used during siloxane-polymer supported AuNPs are shown in table-1 analogous to that reported earlier [34]. The experiments have been performed using 1 mM Au<sup>3+</sup> and 12 mM 3-APTMS and 9 M acetone in all co-solvents (except when acetone was used as single solvent). Table-1 gives the relative concentration of Au<sup>3+</sup>, 3-APTMS and acetone used during the synthesis of AuNPs in different solvents.

As shown in table-1 the synthesis of AuNPs was carried out in different solvents viz. Water, methanol, acetone and chloroform. In a typical process, to 1 mM solution of HAuCl<sub>4</sub> in either of the solvent (water, acetone and chloroform) was added 0.5 M (12 μl) of 3-APTMS so that its effective concentration is 12 mM. The solution is then stirred continuously for over a minute, followed by the addition of acetone as mild reducing at 50 °C. The suspension is then left undisturbed for over 6–12 h. The appearance of wine red color indicated the formation of AuNPs in various solvents. Stock solution of HAuCl<sub>4</sub> and 3-APTMS were prepared in acetone.

### 2.3. Sequential synthesis of AuNPs over polymer

3-APTMS solution in acetone using either chloroform or acetone as solvent was stirred continuously for 6–12 h at room temperature. The colorless solution turns to yellow indicating the polymer synthesis. To this medium was added the solution of Au<sup>3+</sup>. The sequential synthesis of AuNPs over polymer can be done in two ways (i) Liquid Phase synthesis by adding the solution of Au<sup>3+</sup> over polymer suspension, and (ii) Synthesis over Solid surface by first making a film of polymer over glass surface and then suspending it in the solution of Au<sup>3+</sup>.

### 2.4. Peroxidase mimetic like behaviour

The steady-state kinetics were performed by varying the concentration of DA (5 nM–1500 μM), at fixed concentration of H<sub>2</sub>O<sub>2</sub> (25 mM). The reaction was carried out in 2 ml phosphate buffer (0.1 M, pH 7.0) and the variation of absorbance for DA as substrate was monitored using a spectrophotometer (Hitachi U-2900) in time scan mode at 474 nm (ε = 3058 M<sup>-1</sup> cm<sup>-1</sup>). The kinetic parameters were calculated

**Table 1**  
Concentration of different constituents utilized during the synthesis of AuNPs in different solvent.

Solvent	Gold cations (mM)	3-APTMS (mM)	Acetone (M)
Water	1	12	9
Methanol	1	12	9
Acetone	1	12	>9
Chloroform	1	12	9

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