Theoretical insights into the formation of thiolate-protected nanoparticles from gold (III) chloride*

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Reaction pathways for the formation of thiolate-gold nanoparticles are investigated by density functional theory (DFT) and a new mechanism upon solvent polarity and tetraalkylammonium is obtained. In solvents with high polarities, [Au(I)S*R*]$_n$ polymers can be formed as the precursor of metal ions prior to the addition of a reducing agent; while a product of [Cl···AuCl(HS*R*)] is identified as the precursor in solvents with low polarities, such as toluene and chloroform. In addition, tetraalkylammonium also has an obvious effect on the reactions when it is used as a phase transfer agent in the two-phase synthesis. These findings offer a systematic analysis on the pathways to thiolate-stabilized nanoparticles and give a favorable explanation by comparison with those in an experimental system.

Keywords: nanoparticle, Brust–Schiffrin method, mechanism, precursor

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1. Introduction

Metal nanoparticles have attracted great interest for their size-dependent electrochemistry[1] and their special optical properties.[2] The two-phase Brust–Schiffrin method[3] has been proved as an influential method for the preparation of small thiolate-stabilized AuNPs.[4] In this method, an aqueous solution of hydrogen tetrachloroaurate was mixed with a solution of tetraoctylammonium bromide (TOAB) in toluene and aqueous sodium borohydride ($NaBH_4$) was then added in the presence of dodecanethiol. The stepwise investigation on this method has been performed extensively[5–8] by many groups to obtain precise Au clusters.

However, the detailed mechanism, especially the form of the precursors of metal ions prior to the addition of reductant $NaBH_4$ remains controversial. A widely accepted assumption[9,10] on the precursors was that Au (III) was reduced to Au (I) by the thiol and formed [Au(I)S*R*]$_n$ species, while a recent NMR spectroscopy study[8] showed that the precursor was the tetraalkylammonium gold complex [TOA][$AuCl_2$]. Moreover, Raman spectroscopy[11] on Au–S bonds by Li *et al.* also demonstrated that no Au–S bonds were formed before adding $NaBH_4$. Most recently, we found that gold thiolate ([TOA][AuS*R*Cl] and [TOA][Au(S*R*)$_2$]) were also detectable as the precursors by NMR spectroscopy when increasing the concentration of reactants and [Au(I)S*R*]$_n$ could eventually form as precipitation.[12]

The two-phase Brust–Schiffrin method was improved in 1995[13] where the reaction was performed in a polar solution of methanol without the phase transfer agent TOAB. In this way, AuNPs could be obtained in a single-phase system and the introduction of TOAB impurities was avoided. From then on, a series of functional thiolate-stabilized AuNPs have been prepared using a modified single-phase method. For example, many kinds of solvents, such as tetrahydrofuran (THF)[6,14,15] and acetone,[16] have been used to replace methanol. In addition, other thiolate ligands[17–19] have also been used to synthesize functional AuNPs. In most cases, [Au(I)S*R*]$_n$ were formed as metal-ion precursors with a reduction of Au (III) to Au (I) in the single-phase system except when some highly electron-deficient thiols (such as Fluorinated thiols[17,20]) were present.

Despite the substantial effort in synthesizing thiolate-AuNPs, theoretical insights into the mechanism were limited. Until now, only Barngrover and coworkers[21] have examined the pathways for the formation of gold thiolate complexes from gold (III) chloride precursors $[AuCl_4]^-$ in a single-phase system (methanol solvent) with the density functional theory (DFT /BP86) method. Their results showed that a 2:1 ratio of thiol to gold could reduce Au (III) to Au (I), and a 3:1 ratio could lead to [Au(I)S*R*]$_n$ species.

In this work, we perform the stepwise reaction of thiol and gold (III) chloride $[AuCl_4]^-$ in different solvents to study their effects using the DFT method. Meanwhile, the actions of tetraalkylammonium in the two-phase synthesis are examined. A new detailed mechanism is obtained here and this leads to

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new insights into thiolate-gold nanoparticle synthesis. Most importantly, the form of the precursor species of metal ions which is critical for the subsequent growth of monodisper gold clusters is identified in this paper.

2. Computational details

The DFT calculations are performed with the DMol^3 code.[22–24] According to the BP86 functional used by Li *et al.*, we employ the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE)[25] functional to describe exchange and correlation potential. A double numerical plus polarization (DNP) is used as the basis set. The all electron relativistic core treatment method is implemented for relativistic effects, which includes the core electrons and scalar relativistic effects. The convergence tolerance of the energy is 1×10^5 Ha (1 Ha = 27.21 eV), the maximum force and displacement are 0.002 Ha/Å and 0.005 Å, respectively. A smearing of 0.005 Ha to the orbital occupation is applied to achieve accurate electronic convergence. The spin-unrestricted method is used for all calculations. The solvents are simulated by means of the conductor-like screening model (COSMO),[26,27] which represents solvents by their dielectric constants. The COSMO is a continuum model in which the solute molecule forms a cavity within the dielectric continuum of permittivity. The charge distribution of the solute polarizes the dielectric medium. The response of the dielectric is described by the generation of screening charges on the cavity surface. The screening charges are determined from the boundary condition of the vanishing potential on the surface of a conductor. In our calculations, the four kinds of solvents are toluene, chloroform, ethanol, and methanol and their dielectric constants at room temperature are 2.40, 4.81, 24.30, and 32.63 respectively.

To investigate the minimum energy paths (MEPs) for the reactions, linear synchronous transit/quadratic synchronous transit (LST/QST) and nudged elastic band (NEB) tools are used here, which have been well validated to find a transition state.[28–30] In our paper, the –R group on the thiol is simplified to a methyl ($-CH_3$) to decrease the computational cost. Energies listed here include zero-point energy corrections, which are typically on the order of hundredths of an eV.

3. Results and discussion

3.1. Reaction pathways for formation of thiolate-Au nanoparticles

3.1.1. The first thiol addition

Theoretical reaction pathways for the thiol stepwise reaction with gold (III) chloride in methanol are given as an example here to explain the mechanism. For the first thiol addition (SI1), a chloride ion of $AuCl_4^-$ is substituted by the thiol through a bipyramidal transition state with a barrier energy of 0.34 eV, then it dissociates as a free ion with a reaction energy of -0.01 eV. These values are close to Barngrover's DFT/BP86 results[21] of 0.34 eV and -0.03 eV respectively. Subsequently, the free chloride ion reacts with the thiol proton and results in the formation of hydrogen chloride with a negative energy of -0.24 eV. Equations for the first thiol reaction with $AuCl_4^-$ can be summarized as below:

$$AuCl_4^- + HSCH_3 \rightarrow AuCl_3HSCH_3 + Cl^-, \quad (1a)$$

$$AuCl_3HSCH_3 + Cl^- \rightarrow AuCl_3SCH_3^- + HCL. \quad (1b)$$

3.1.2. The second thiol addition

When the second thiol is added, it reacts with the present mono-substituted gold (III) complex through another bipyramidal transition state to cause a second chloride to dissociate (SI1). The energy of the barrier and the reaction energy are 0.46 eV and 0.12 eV, respectively. Then, the free chloride ion reacts with the thiol proton resulting in the production of $[AuCl_2(SR)_2]^-$ and hydrogen chloride. At the same time, two internal electrons of $[AuCl_2(SR)_2]^-$ transfer from two RS^- (R = CH_3) to Au (III) instantaneously to cause the reduction of Au (III) to Au (I). Then, the two RS^- change into free radicals ($RS\cdot$) and form into a disulfide. This process has a negative energy of -0.07 eV and lowers the overall reaction energy. The equations can be written as follows:

$$AuCl_3SCH_3^- + HSCH_3 \rightarrow AuCl_2(HSCH_3)(SCH_3) + Cl^-, \quad (2a)$$

$$AuCl_2(HSCH_3)(SCH_3) + Cl^- \rightarrow AuCl_2(SCH_3)_2^- + HCl, \quad (2b)$$

$$AuCl_2(SCH_3)_2^- \rightarrow AuCl_2^- + CH_3S\cdot \rightarrow AuCl_2^- + (SCH_3)_2. \quad (2c)$$

Although this pathway is a little different from Barngrover's result, it is in agreement with the negative-ion electrospray ionization-mass spectroscopy (ESI-MS) results[31] that the reduction of auricyanide ($[Au(CN)_4]^-$) by glutathione (GSH) proceeded through two intermediates $[Au(CN)_3(SG)]^-$ and $[Au(CN)_2(SG)_2]^-$ respectively, and formed the disulfide GSSG as a byproduct via the reduction of gold (III) complex $[Au(CN)_2(SG)_2]^-$.

3.1.3. The third thiol addition

After the reduction of Au (III), a third thiol can also react with the gold (I) complex ($AuCl_2^-$) in methanol (SI1) to form a mono-substituted gold (I) complex with a barrier energy of 0.35 eV according to the following reaction:

$$AuCl_2^- + HSCH_3 \rightarrow AuCl(HSCH_3) + Cl^-. \quad (3)$$

The reaction energy for this process is 0.10 eV. The production of $AuCl(HSCH_3)$ here is very important because $[Au(I)SR]_n$ polymers can be further formed. After the dissociation of the thiol proton, the sulfur of $[AuCl(SCH_3)]^-$ will have two lone

pairs and can react with another gold. This leads to the dimerization of two $[AuCl(SCH_3)]^-$, then trimmers, tetramers,[21] and even cyclic or helical $[Au(I)SR]_n$ systems,[32–35] which is in agreement with the experimental results[36,37] that polymeric Au*SR* was obtained clearly with a 3:1 S/Au molar ratio. However, structures of the products in this step are different in some other solvents, such as toluene or chloroform. In these solvents, the chloride will not dissociate absolutely as a free ion, which makes it difficult to form $[Au(I)SR]_n$ polymers. This causes the reactions to follow two different pathways upon solvents. The solvent effects on the mechanisms are discussed in detail in the following section.

3.2. Solvent effects on the reactions

3.2.1. Effects on the reaction pathways

To better understand the solvent effects, we perform the stepwise reactions in three other kinds of solvents with different polarities (toluene, chloroform, and ethanol). Calculated results (SI2 and SI3) show that the reaction pathways in the three other solvents are the same as that in methanol at a 2:1 ratio of thiol to gold. However, two different pathways can be obtained when the third thiol is added. The whole mechanism is summarized in Fig. 1. When the third thiol reacts with $[AuCl_2]^-$ in solvents with low polarities (pathway (I)), such as toluene and chloroform, the chloride is imperfectly substituted by the thiol. Interestingly, it does not dissociate to a free ion as that in solvents with high polarities (ethanol and methanol) but binds to the gold to form a covalent bond. This product ([Cl···AuCl(HS*R*)]) is identified as the precursor species of metal ions in the two-phase Brust–Schiffrin synthesis method. While in pathway (II), $[AuCl(SR)]^-$ can be generated and further polymerize into $[Au(I)SR]_n$ species.

As shown in Fig. 2(a), the product [Cl···AuCl(HS*R*)] is obtained in toluene. The distance between the chloride and the gold is 2.664 Å where a covalent bond can be formed between them according to the electron density distribution (Fig. 3(a)). This strong interaction makes it difficult for chloride ions to dissociate as free ions. Thus the subsequent dissociation of protons and the polymerization of $[AuCl(SR)]^-$ to form $[Au(I)SR]_n$ polymers are not favored. This may be the reason why $[Au(I)SR]_n$ species were not observed experimentally.[8,12] In Fig. 3(b), similar facts are observed in chloroform that a covalent bond forms between the chloride and the gold. Interestingly, the bond length changes to 2.686 Å (Fig. 2(b)) which is a little larger than that in toluene. This suggests that the interaction between them changes weaker due to the higher polarity of chloroform and makes the bond angle between the other two bonds increase to 157.94°. When the reaction is performed in a polar solvent of ethanol (Fig. 2(c)), the reaction mechanism is the same as that in methanol. The thiol reacts with $[AuCl_2]^-$ to cause the chloride ion to dissociate as a free ion and the distance between the chloride ion and the gold is 3.226 Å, which is close to 3.227 Å in methanol. This value is obviously larger than that in toluene and chloroform. The electron density of the product in Fig. 3(c) confirms that no chemical bond forms between the chloride ion and the gold, thus the bond angle between the other two bonds is close to 180°. As a result, $[Au(I)SR]_n$ polymers are easy to form in solvents with high polarities.

We also find that [Cl···AuCl(HS*R*)] can subsequently change to $[AuCl(SR)]^-$ and Cl^- when the polarity of the solvent is increased. As seen in Fig. 4, the relationship between the structure of [Cl···AuCl(HS*R*)] and the dielectric constant (ε) is examined. Here, ε can represent the polarity of the solvent to a large extent. It is obvious that the bond length between Cl^- and Au in [Cl···AuCl(HS*R*)] changes larger with ε increasing. Subsequently, no bond can form and the chloride dissociates as a free ion. Then $[Au(I)SR]_n$ polymers can eventually be formed. This is identified as the reason why M (I) thiolate

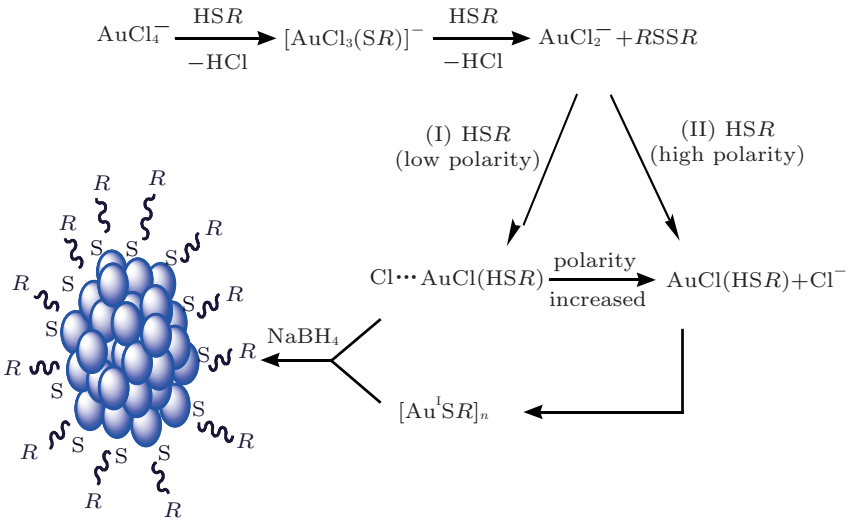


Fig. 1. (color online) Reaction pathways upon solvents for the formation of thiolate-AuNPs.

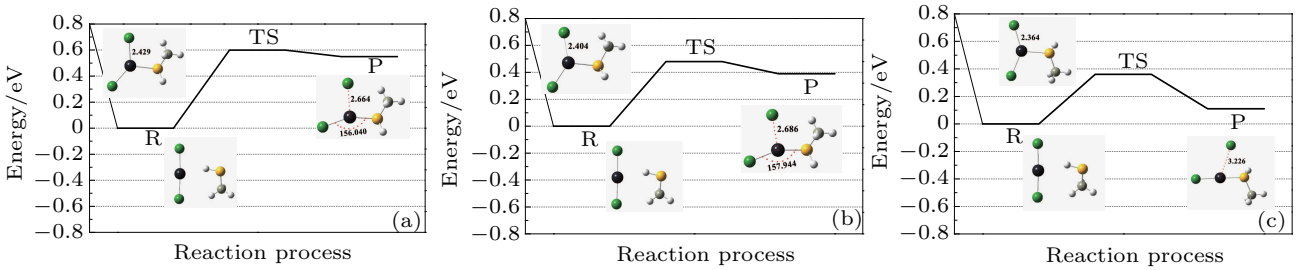


Fig. 2. (color online) Reaction pathways for the third thiol addition in different solvents. (a) Toluene; (b) chloroform; (c) ethanol. R: reactants; TS: transition state; P: products; Au: black; Cl: green: S: yellow; C: grey; H: white; N: blue.

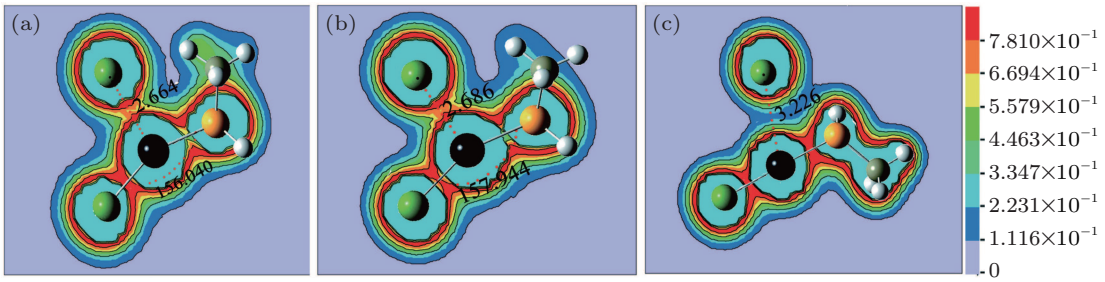


Fig. 3. (color online) Panels (a)–(c) plot the electron density distribution of the products in Figs. 2(a)–2(c), respectively.

species form as a precipitate when the precursor solution was exposed to water[38] or toluene was removed.[8] In addition, our recent experimental results[12] found that [TOA][AuS*R*Cl] and [TOA][Au(S*R*)$_2$] were also detectable when increasing the concentration of reactants in the two-phase synthesis and [Au(I)S*R*]$_n$ could eventually form as precipitation. This is also due to the increase of polarity when the concentration of reactants was increased.

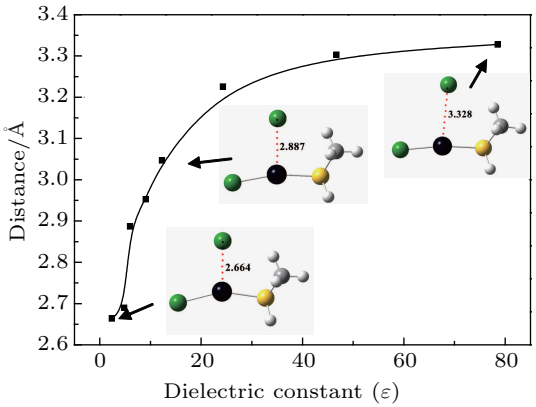


Fig. 4. (color online) Structures of [Cl···AuCl(HS*R*)] with the increasing of dielectric constant.

3.2.2. Effects on reaction energy and energy of barrier

It is no doubt that the polarity of the solvent has obvious effects on the reaction energy and energy of the barrier according to Fig. 5. For each step of thiol addition in Fig. 5(a), the largest barrier energy is in toluene, and it changes upon the solvent polarity. This implies that each step of the reaction occurs faster in highly polar solvents. Similar changes for the reaction energy are found in Fig. 5(b). As a result, these reactions are

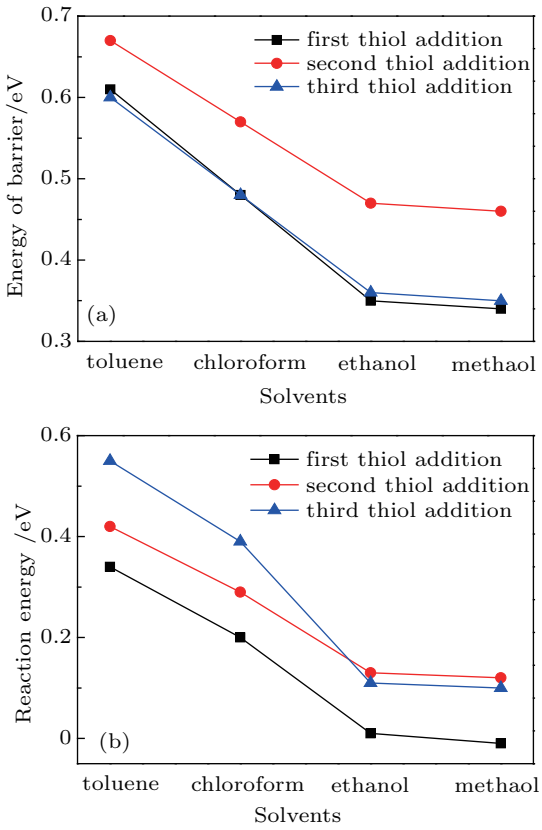


Fig. 5. (color online) Comparisons of energy of barrier (a) and reaction energy (b) for thiol stepwise addition in different solvents.

favored thermodynamically in the solvent with high polarity. The proton of HAuCl$_4$ may be a reason for this. In highly polar solvents, such as methanol and ethanol, HAuCl$_4$ can be dissociated as a proton and [AuCl$_4$]$^-$ easily and then [AuCl$_4$]$^-$ freely reacts with thiols. Meanwhile, the dissociation of the

proton improves the polarity of the solvent, which makes $HAuCl_4$ further dissociate. However, in solvents with low polarities, such as chloroform and toluene, the proton of $HAuCl_4$ is difficult to dissociate. This prevents $[AuCl_4]^-$ from reacting with thiols freely.

The overall reaction energies for the three thiols reactions are presented in Table 1. The dielectric constants and dipole moments can represent the polarities of the solvents. In solvents with low polarities (toluene and chloroform), the reactions follow pathway (I). The reaction energies are positive with 0.27 eV and 0.14 eV respectively. Thus pathway (I) is not thermodynamically favored. While in ethanol and methanol polar solvents, the reactions follow pathway (II). The reaction energies change to negative with −0.09 eV and −0.10 eV respectively, thus pathway (II) is thermodynamically favored. In general, when the polarity of the solvent is increased, pathway (I) can change to pathway (II) and the reaction energy also decreases from positive to negative at the same time.

Table 1. Overall reaction energies for three thiols reaction in different solvents.

Solvents	(ε/F·m^{-1})[a)]	($\mu/10^{-30}$ C·m^{-1})[b)]	Reaction energy/eV
Toluene	2.40	1.33	0.27
Chloroform	4.81	3.83	0.14
Ethanol	24.30	5.63	−0.09
Methanol	32.63	5.67	−0.10

[a)] ε is the dielectric constant of the solvent.
[b)] μ is the dipole moment of the solvent.

3.3. Effects of tetraalkylammonium

In a real two-phase experiment, $[AuCl_4]^-$ was transferred from the aqueous solution to toluene using tetraoctylammonium bromide (TOAB) as the phase-transfer reagent.[3,8] Br^- can also replace Cl^- in $[AuCl_4]^-$ and then forms $[AuX_4]^-(X = Cl^-, Br^-)$.[8,11,12] Although the replacement affects the chemical reactions to some extent (the energy barrier and the reaction energy decrease after Br^- replacing Cl^-), the reaction mechanism is not changed. In this work, we choose $X = Cl^-$ for better analysis and comparison and $[N(CH_3)_4]^+$ is used as tetraalkylammonium to replace TOA^+ for computing efficiency. The stepwise reactions in toluene are performed in the presence of $[N(CH_3)_4]^+$ to study its functions.

3.3.1. Effects on the reaction pathways

When $[N(CH_3)_4]^+$ is present (SI4), Au (I) complex and disulfide are also obtained via the reduction of a gold (III) complex at an S/Au ratio of 2:1. Although the product of [Cl···AuCl(HS*R*)] is also obtained when the third thiol is added in the presence of $[N(CH_3)_4]^+$, its structure changes a little. As seen in Fig. 6, the bond length between the chloride and gold is 2.600 Å which is less than 2.664 Å when $[N(CH_3)_4]^+$is ignored (Fig. 2(a)). Obviously, the bond length becomes smaller in the presence of $[N(CH_3)_4]^+$ and the interaction between the two atoms increases. As a result, the bond angle between the other two bonds changes from 157.94° to 146.35°. These effects are attributed to the attractive effect from $[N(CH_3)_4]^+$. In short, the presence of tetraalkylammonium will hinder the dissociation of chloride ions and the further formation of $[Au(I)SR]_n$ polymers. This is considered to be the other reason why $[Au(I)SR]_n$ polymers were not generated in measurable quantities in toluene when tetraalkylammonium is used as the phase-transfer reagent.[8,11]

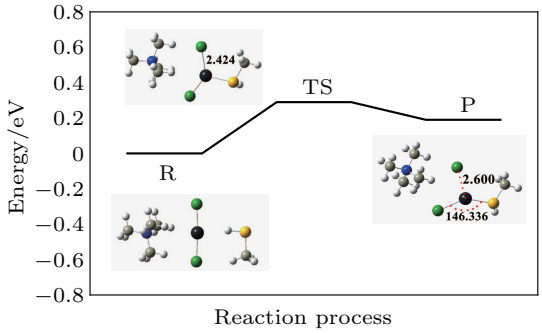


Fig. 6. (color online) Reaction pathways for the addition of the third thiol in toluene in the presence of tetraalkylammonium ($[N(CH_3)_4]^+$).

Upon the discussion above, the polarity of the solvent and tetraalkylammonium are two main factors resulting in different precursors. The identification and quantification of the precursors are very important because they influence the dispersity of the products. For example, the formation of $[Au(I)SR]_n$ precursors is preferred to be avoided because they can lead to polydisper clusters or insoluble byproducts[39] in some cases. Therefore, we can modify the reactions by controlling the polarity of the solvent and the quantity of tetraalkylammonium.

3.3.2. Effects on barrier height and reaction energy

The presence of tetraalkylammonium has a great influence on the barrier height and reaction energy (Table 2). For the first thiol reaction, the barrier height changes from 0.61 eV to 0.26 eV when $[N(CH_3)_4]^+$ is present. This great decrease of the barrier height makes the reaction occur faster. For the second thiol reaction, the value decreases from 0.67 eV to 0.22 eV. Analogously, it decreases to 0.29 eV for the third thiol reaction. The overall reaction energy for three thiols addition in the presence of $[N(CH_3)_4]^+$ is also obtained with 0.02 eV compared with 0.27 eV when $[N(CH_3)_4]^+$ is ignored. As a result, the presence of tetraalkylammonium, which is used as the phase transfer reagent, will accelerate the reactions by decreasing the energy of the barrier and reaction energy when thiols react with $AuCl_4^-$ in toluene.

To further understand the effect of tetraalkylammonium, the electrostatic potentials of the reactants are calculated. As shown in Fig. 7, we take the reactant $[AuCl_2]^-$ as an example. It is clear that the value of the electronic potential decreases

sharply when $[N(CH_3)_4]^+$ is present. This is due to the electron withdrawing effect of tetraalkylammonium. Then the nucleophilic species (HS*R*) will attack the gold by overcoming a lower potential energy. Therefore, the reactions occur easily in the presence of tetraalkylammonium.

Table 2. Comparisons of energies for three thiols reaction in toluene with and without tetraalkylammonium.

	Energy of barrier/eV			Reaction energy/eV
	Step 1	Step 2	Step 3	
Without $[N(CH_3)_4]^+$	0.61	0.67	0.60	0.27
With $[N(CH_3)_4]^+$	0.26	0.22	0.29	0.02

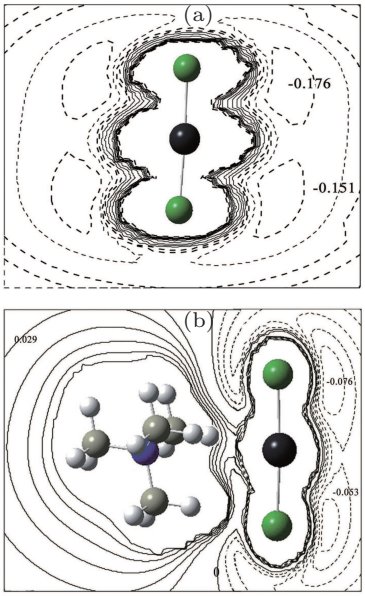


Fig. 7. (color online) Electronic potential for $AuCl_2^-$ (a) in the absence of $[N(CH_3)_4]^+$ and (b) in the presence of $[N(CH_3)_4]^+$.

4. Conclusion

In summary, a detailed mechanism upon solvents and tetraalkylammonium is obtained using the DFT method. Our results show that the disulfide *RSSR* and Au (I) complex can be obtained via the reduction of a gold (III) complex $[Au(Cl)_2(SR)_2]^-$ with an addition of 2 equiv of thiol; then the reactions follow two different pathways upon solvents with the addition of 3 equiv of thiol. The precursors of metal ions in the two pathways are also identified, which provides the key information for controlling the reactions. In addition, the presence of tetraalkylammonium ($[N(CH_3)_4]^+$) will hinder the formation of Au (I) thiolates by decreasing the distance between the chloride and gold in the product of [Cl···AuCl(HS*R*)]. Moreover, the reactions favor thermodynamically and occur faster in solvents with higher polarities and the presence of tetraalkylammonium can decrease the barrier height and reaction energy. These findings offer a systematic analysis on the pathways to thiolate-stabilized nanoparticles and give a favorable explanation by comparison with those in experimental systems.

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