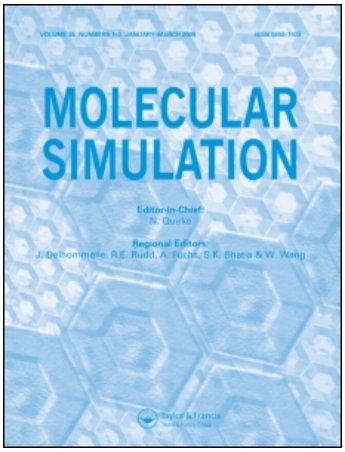

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Dissipative particle dynamics simulation of a gold nanoparticle system

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Dissipative particle dynamics (DPD) was carried out to study systems containing gold atoms, organic ether (oligohydroquinonyl ether terminated with a thiol group) and organic solvents. The components in the simulated system are very different in size and chemical nature. Our simulation showed that the reproduction of the macroscopic experimental phase separation, properly dividing the polymeric molecule into beads, selecting the size of gold bead, and choosing the appropriate interaction parameters between beads are crucial. In addition, the solvent effect was the dominant factor for the formation of spherical aggregates of Au atoms and organic ether molecules. We report the interaction strengths between the solvent and gold clusters. Our work has demonstrated that DPD methods can be applied to the study of complex meso-scale systems.

Keywords: Simulation; Molecular dynamics; Dissipative particle dynamics; Nanoparticle system

1. Introduction

In the current study, the dissipative particle dynamics (DPD) method was used to simulate a system containing gold atoms, thiol-terminated oligohydroquinonyl ether (abbreviated as TTOE) and organic solvents. Figure 1(a) shows the structure of the TTOE molecule. The TTOE-modified gold particles were synthesized by using a similar method developed by Brust and co-workers [1]. Au nanoparticles were grown in the presence of TTOE as stabilizer in toluene solvent. The particles were characterized by UV–visible, infrared and ^{1}H NMR spectroscopy as well as transmission electron microscopy (TEM). Figure 2(a) shows the high-resolution TEM image of these TTOE-modified Au-nanoparticles. The figure indicates that the average radius of these spherical particles is about 5 nm. TTOE forms a monolayer on the surface of Au-nanoparticles due to the strong interaction of the alkoxyl benzene of the oligohydroquinonyl ether chains to the Au atoms. Figure 2(b) shows the structure of this nanoparticle.

In addition to the experimental work, molecular dynamics (MD) was carried out to study this particular system [2]. In previous MD work, a nano-sized particle containing 169 Au atoms and 42 TTOE chains was simulated. The simulation showed that the inner Au cluster was very stable and had a crystal-like local order within 5 Å. The average dimension of the whole nanoparticle was about 5 nm. Detailed analysis was carried out for the orientations of TTOE molecules on the Au surface. The result showed that these TTOE molecules were very soft and had no long-range order. This MD simulation confirmed that the TTOE–Au nanoparticle was stable but no solvent effect was incorporated. In reality, different types of solvent and concentrations of the system will result in aggregates of different shapes and sizes. The interactions of molecules with solvents may serve as an important driving force and should be considered. The current simulation thus incorporates solvent into the TTOE–Au system. The DPD method is adopted to carry out such simulations [3]. This meso-scale simulation method is capable of studying systems containing million atoms in the nano-second time domain.

We have applied DPD to investigate self-assembled aggregation problem of ionic and non-ionic surfactants [4]. Using DPD method to study complex systems such as membrane, ionic surfactant and small biological system has been reported by a number of groups [5–8]. Although this simulation method was demonstrated to be very

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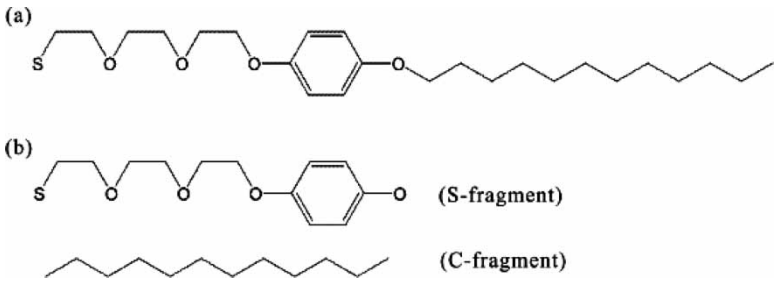

Figure 1. Chemical structure of (a) TTOE molecule; (b) S-fragment and C-fragment.

useful, some fundamental problems still remained unclear. To reproduce macroscopic experimental phase behavior in the simulation, the major difficulty lies in the determination of interaction parameters between DPD particles. Another central problem is the way to define so-called "DPD beads". No consistent protocol has been reported to determine these two important parameters. In this work, we simulated a complex system composed of simple Au atoms, organic polymeric molecules and solvents. These components are different in size and chemical nature. The determination of interaction parameters and the way to define DPD beads were discussed. Our simulation reproduced aggregation of Au and TTOE as observed experimentally. All simulations were performed with CERIUS^2 and MATERIALS STUDIO software packages [9].[†]

2. Computational methods

The description of the DPD model here is based on the work by Groot and Warren [3]. In the simulation, molecules are divided into beads. The motions of beads follow Newton's equations:

$$\frac{\mathrm{d}\vec{r}_i}{\mathrm{d}t} = \vec{v}_i \quad \frac{\mathrm{d}\vec{v}_i}{\mathrm{d}t} = \vec{f}_i \tag{1}$$

where $\vec{r}_i$, $\vec{v}_i$and $\vec{f}_i$ are the position vector, velocity and total force on the ith bead, respectively. For simplicity, the mass of each bead is set to unity. The total force exerted on bead i contains three parts, each of which is pair wise additive.

$$F_i = \sum_{i \neq j} (F_{ij}^{\mathrm{C}} + F_{ij}^{\mathrm{D}} + F_{ij}^{\mathrm{R}}) \tag{2}$$

where the sum is over index j with $i = j$ excluded, F_{ij}^{C} is the conservative force; F_{ij}^{D} and F_{ij}^{R} are the dissipative and random forces, respectively. The significance of these terms is investigated in detail elsewhere [3,10]. The conservative force F^{C} is a soft repulsive central force between bead i and j

$$F_{ij}^{\mathrm{C}} = \begin{cases} a_{ij}(1 - r_{ij})\hat{r}_{ij} & r_{ij} < 1 \\ 0 & r_{ij} > 1, \end{cases} \tag{3}$$

where a_{ij} is a maximum repulsive parameter between beads i and j; $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, $r_{ij} = |\vec{r}_{ij}|$ and $\hat{r}_{ij} = \vec{r}_{ij}/r_{ij}$, respectively. The Newtonian equations of positions and velocities of particles are solved by modified version of the velocity-Verlet algorithm [3]. The dynamic behaviors of beads are followed along trajectories through the phase space by integrating equations of motions. The equilibrium properties are then calculated by performing suitable averages along beads' trajectories.

To simulate a system, a set of interacting parameters a_{ij}'s between different types of beads must be determined. With these pre-determined parameters, the DPD simulation should reproduce correct phase behaviors as observed experimentally. There are several methods suggested in the literature to evaluate interaction parameters [11,12]. In compromising the accuracy and computation time, we adopted Monte Carlo method to evaluate the interaction parameters. The derivation of a_{AB} is based on Flory–Huggins mixing parameter χ_{AB}, where the subscript AB denotes type A and B beads [13]. This mixing parameter χ_{AB} represents the repulsive energy of an AB pair averaged over all possible configurations.

Following Ryikina *et al.* [14], the mean interaction energy between pairs of beads can be obtained from the calculation of mixing energy of two corresponding fragments by

$$E_{\mathrm{AB}}^{\mathrm{mix}} = \frac{1}{2}[Z_{\mathrm{AB}}\langle E_{\mathrm{AB}}(T)\rangle + Z_{\mathrm{BA}}\langle E_{\mathrm{BA}}(T)\rangle - Z_{\mathrm{AA}}\langle E_{\mathrm{AA}}(T)\rangle - Z_{\mathrm{BB}}\langle E_{\mathrm{BB}}(T)\rangle] \tag{4}$$

where Z's are the calculated values of the coordination numbers for each pair of fragments. The average pair-interaction energy $\langle E(T)\rangle$ can be obtained from Monte Carlo sampling over the most probable conformations on a pair of molecules in contact [15,16]

$$\langle E_{\mathrm{AB}}(T)\rangle = \frac{\int \mathrm{d}E_{\mathrm{AB}} P(E_{\mathrm{AB}}) E_{\mathrm{AB}} \exp(-E_{\mathrm{AB}}/k_{\mathrm{B}}T)}{\int \mathrm{d}E_{\mathrm{AB}} P(E_{\mathrm{AB}}) \exp(-E_{\mathrm{AB}}/k_{\mathrm{B}}T)} \tag{5}$$

where k_{B} is Boltzmann constant. The Flory–Huggins parameter $\chi_{\mathrm{AB}}(T)$ between particle pair A and B is related

[†]Program CERIUS^2 version, 4.8, Accelry Inc.

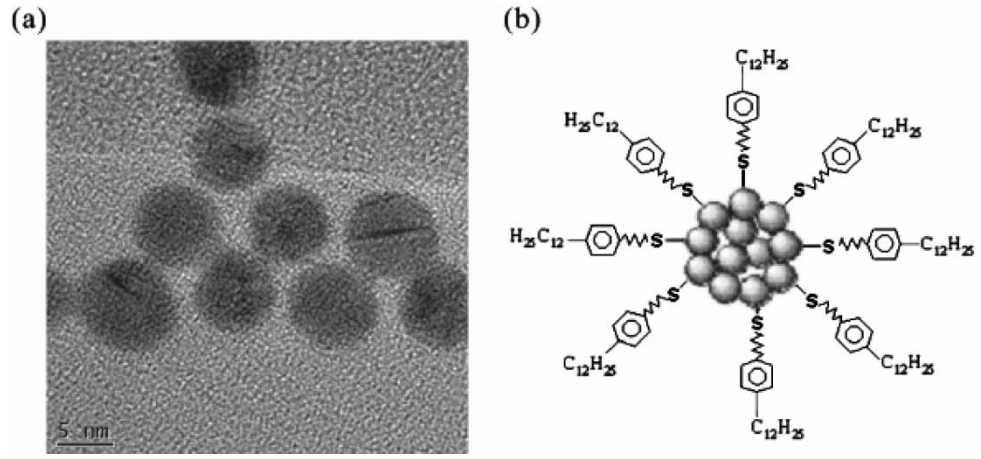

Figure 2. (a) TEM snapshot of the TTOE–Au nanoparticles at high magnification; (b) Structure of the TTOE–Au nanoparticles.

to the mixing energy by

$$\chi_{AB}(T) = E_{AB}^{mix}(T)/RT \quad (6)$$

The maximum repulsion a_{AB} is deduced from this χ parameter at a given particle density $\rho = N/V$, as suggested by Groot and Warren [3].

$$a_{AB}(T) = a_{AA} + 1.451\chi_{AB}(T) \quad \text{for} \quad \rho = 5 \quad (7)$$

The a_{AA} term is derived from the compressibility of pure component A ($a_{AA} = 75k_BT/\rho$) [3].

3. Results and discussion

To carry out DPD simulation, molecular fragments are usually treated as beads. There is no definitive way to divide the chain molecule into fragments. The general requirements are the sizes of fragments should be comparable and the types of beads should be as less as possible. In this work, we divided TTOE molecule into S- and C-fragments as shown in figure 1(b). In the S-fragment, the terminal proton was removed from TTOE and the whole fragment is negative charged. This differentiates the polarity of S- and C-fragments. S-fragment is very polar and C-fragment is almost non-polar. The structures of fragments were optimized with PCFF force field [17]. All atomic partial charges of fragments were obtained from quantum mechanical ZINDO method based on the optimized structures. Toluene solvent molecule was treated as another bead. In the first attempt, single Au atom was treated as a bead. The DPD simulation failed to reproduce aggregation behavior as observed experimentally. This was because the size of Au atom is too much smaller than those of S- and C-fragments and toluene. To generate Au-bead with its size comparable to the fragments of TTOE, a small Au cluster with unit cell crystal structure containing four Au atoms was adopted. The space group of this crystal is No. 225 with a lattice length of 4.0783 Å. Table 1 shows the calculated interaction parameters a_{ij}'s of TTOE fragments, Au-cluster and toluene. The molar ratio of Au to TTOE was set to 4:1 in all later simulation cases. All systems were simulated at the particle density $\rho = 5$. Various concentrations of the simulated systems were tested and found that Au-nanoparticle was formed at a molar ratio TTOE–Au–toluene = 1 : 4 : 8. Figure 3(a) shows a snapshot of the simulated system at this molar ratio. The size of the box is 10 × 10 × 10 DPD units. The figure shows that TTOE molecules and Au cluster tend to aggregate in the presence of toluene solvents at this molar ratio. This demonstrated that concentration of the solvent is an important factor to drive atoms (molecules) to form aggregates. Given in figure 3(b), (c) are snapshots of the simulated systems with box sizes of 15 × 15 × 15 and 20 × 20 × 20 DPD units at the fixed molar ratio TTOE–Au–toluene = 1 : 4 : 8. The number of particles was increased as the box size increases. The figures show that Au atoms aggregated in roughly spherical shapes at higher particle numbers. Table 2 summarizes the simulation results of TTOE–Au–toluene systems in various molar ratios and various box sizes. At box size of 15 × 15 × 15 DPD unit, we found that Au atoms formed spherical aggregates in two different sizes. The radius of the larger Au aggregate was estimated about 5 DPD units and that of the small aggregate was estimated about 2 DPD units. Using usual cutoff distance 10 Å as the length of DPD unit, we may conclude that the radius of these spherical nanoparticles are 5 and 2 nm, respectively. Further analysis of the arrays of TTOE molecules, we found that the S-fragments are close to the Au surface and the C-fragments are immersed in the toluene solvent. This picture agrees well with the experimental observation and our previous MD simulation.

Table 1. Interaction parameters of TTOE fragments, Au bead and toluene.

a_{ij}	*S-fragment*	*C-fragment*	*Au bead*	*Toluene*
S-fragment	15.000	7.627	63.406	9.371
C-fragment	7.627	15.000	190.577	0.000
Au bead	63.406	190.577	15.000	239.586
Toluene	9.371	0.000	239.586	15.000

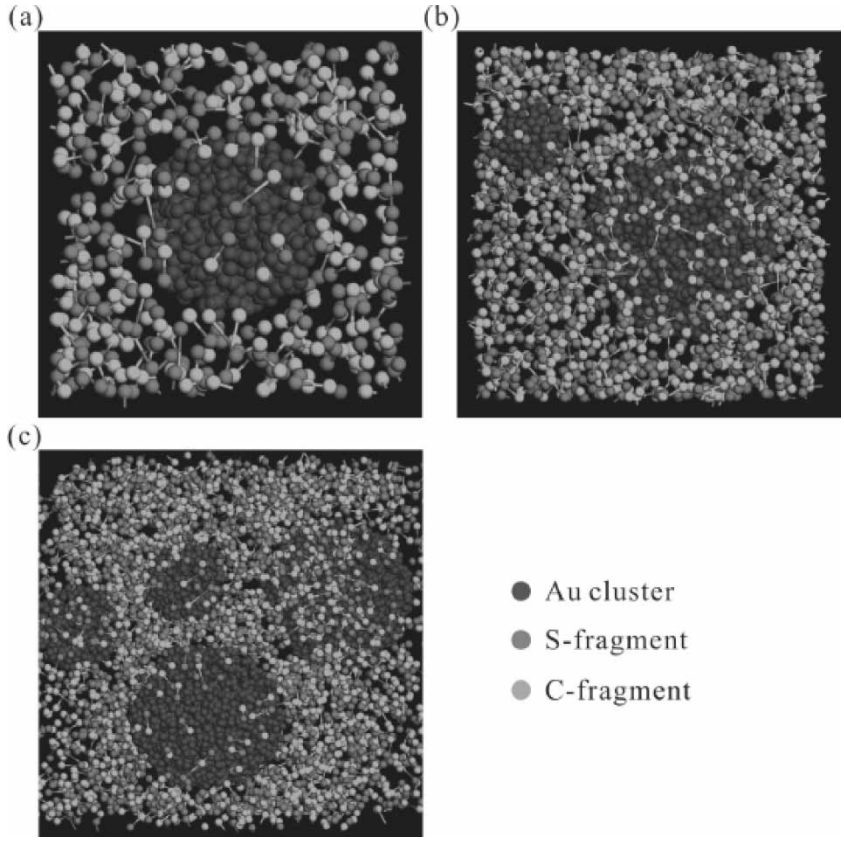

Figure 3. Simulation result of TTOE–Au–toluene system at box size of (a) 10 × 10 × 10 (b) 15 × 15 × 15 (c) 20 × 20 × 20 (in DPD unit).

At the box size of 20 × 20 × 20 DPD unit, we found that several spherical nanoparticles were formed in the system. Two large size spherical nanoparticles with radius of 5 nm and two small size spherical nanoparticles with radius 3 nm were presented. The result showed that increasing the number of particles in the system (from box size of 15 × 15 × 15 to 20 × 20 × 20 DPD unit) did not further increase the size of nanoparticle. The limiting size of nanoparticle with radius 5 nm agrees well with the experimental result. Given in figure 4 is a snapshot of the simulated system without toluene solvent at box size of 20 × 20 × 20 DPD unit. The figure shows that the system formed layered structure and no nanoparticle aggregate was detected at this situation. The simulation clearly indicates that toluene solvent is the major driving force for forming the nano-sized aggregates. Referring to the interaction parameters in table 1, large a_{ij} value indicates strong repulsive interaction between beads i and j. Since Au has the largest repulsion to the toluene, these Au atoms tend to be away from toluene as much as possible. The consequence of this is that all Au atoms were in the interior part of the aggregates and the aggregate was wrapped by TTOE. The interaction parameter of the C-fragment is smaller than that of the S-fragment to toluene. Therefore, it is likely that these C-fragments of TTOE could mix with the toluene solvent and exposed outside of the aggregates. The S-fragment has larger repulsive interaction than that of C-fragment to toluene, but has very small repulsive interaction to Au. Therefore, these S-fragments were close to Au surface and tend to be away from the toluene. To further confirm the solvent effect on this particular system, we simulated Au atoms and TTOE molecules in other four solvents: acetone, ether, chloroform and dimethyl sulfoxide (DMSO). The simulation showed that TTOE–Au nanoparticles only formed in acetone and ether but not in chloroform and DMSO. The interaction parameters (which are not shown here) of acetone and ether to Au, S- and C-fragments of TTOE also indicate the same repulsive tendency as toluene. Figure 5(a), (b) are the snapshots of simulation Au–TTOE systems in ether and acetone solvent, respectively. In these two solvent systems, we found that Au atoms were aggregated into spherical

Table 2. Simulated structures of TTOE–Au–Toluene systems at various box sizes (in DPD units) and molar ratios.

Box size	*Molar ratio TTOE–Au–Toluene*	*Number of Au atoms in nanoparticle*	*Structure*
10 × 10 × 10	1:4:1.885		Layer
	1:4:2.166		Layer
	1:4:8	2060 atoms	Ellipse particle
15 × 15 × 15	1:4:8	580 atoms (2 nm)	Spherical particles
		6170 atoms (5 nm)	
20 × 20 × 20	1:4:8	1360 atoms (3 nm)	Spherical particles
		1360 atoms (3 nm)	
		6920 atoms (5 nm)	
		6920 atoms (5 nm)	
20 × 20 × 20	1:4:0		Layer

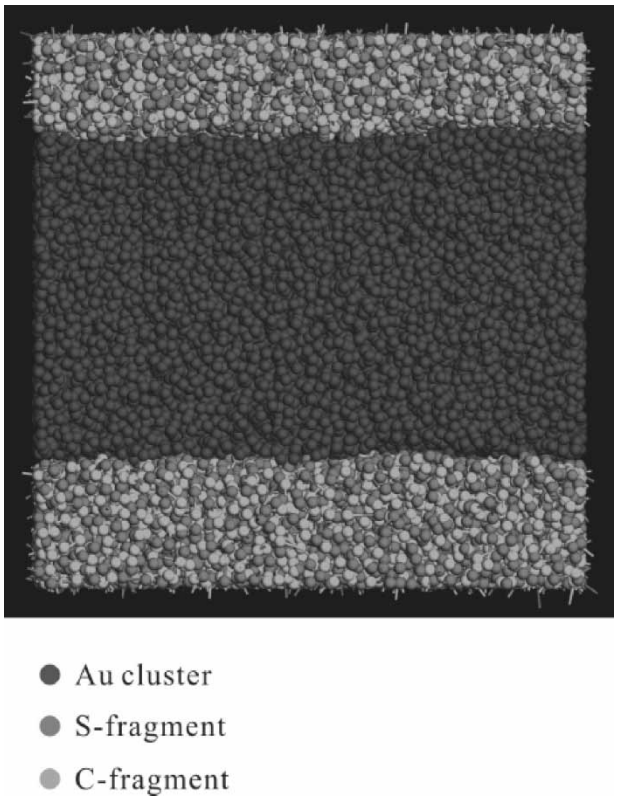

Figure 4. Simulation result of TTOE–Au system without any solvent at box size of 20 × 20 × 20 DPD unit.

particles like that in toluene solvent but the particle sizes were different. For all aggregates the polar S-fragments of TTOE were close to Au interior and non-polar C-fragments pointed outside. In chloroform solvent, we found that C-fragment had large interaction parameter to chloroform. This repulsion disfavored the formation of C–S–Au type aggregate. In the DMSO solvent, we found very large interaction parameters of DMSO to both Au and S-fragment. These strong repulsive forces resulted in the mixing of Au and S-fragment. Therefore, the Au nanoparticle was not formed because of the interruption from S-fragments. On the basis of these simulation results we may conclude that the special type aggregation of Au atoms in organic solvents was due to the assistance of TTOE molecules. The polar and non-polar molecular nature of TTOE and the interaction strengths of its fragments to solvent and to Au induce the aggregation of Au atoms. In toluene solvent, the limiting size of nanoparticle is about 5 nm irrespective of the particle number.

4. Conclusion

DPD simulation was carried out to investigate the systems of Au atoms and TTOE molecules in various organic solvents. Our simulation results showed that Au atoms formed spherical nanoparticles in the presence of toluene solvent. The size of the nanoparticle depends on the presence of solvent and number of particles. The simulated maximum radius of Au-nanoparticle was about 5 nm irrespective of the increasing particle numbers. The simulated size of spherical Au nanoparticle agrees well with the experimental observation. The analyzed structure of Au nanoparticles showed that Au atoms were wrapped inside the particle by TTOE molecules with their S-terminals close to the Au surface, but C-terminals exposed in the solvents. The simulation showed that layered structure with no nanoparticle formed if no toluene solvent was present. We thus conclude that toluene is the major driving force leading to the formation of uniformly sized Au nanoparticles in the presence of TTOE molecules. The analysis of interaction strengths on Au, S- and C-fragments to various

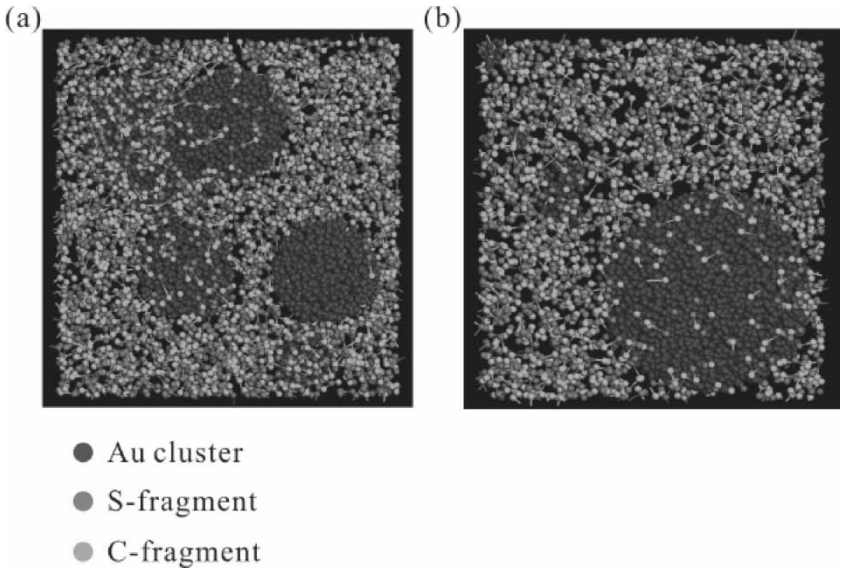

Figure 5. Simulation result of TTOE–Au system at box size of 20 × 20 × 20 DPD unit with solvent (a) ether (b) acetone.

solvents showed that the molecular nature of TTOE assisted the formation of Au nanoparticles.

In addition to the simulation reported here, a different force field (Universal, UFF) [18] besides PCFF and different ways to obtain atomic partial charges (Gasteiger) [19] were tested. Also, we have tested different ways to divide TTOE into fragments. In the evaluation of the interaction parameters between Au and molecules, we tested different sizes of Au clusters as beads. However, none of those tests gave satisfactory result as reported here. This shows the importance of choosing appropriate interaction parameters, fragmentation of chain molecules and also the proper selection on Au cluster size to ensure the success of simulation.

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