Computational Materials Science 141 (2018) 221–228

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Solvents induce phase separation for fabrication of Janus hybrid nanoparticles: A dissipative particle dynamics simulation

Yixuan Du, Xiaowei Zhang, Yunbo Li *

School of Materials Science & Engineering, Shanghai University, Shanghai 200444, China

ARTICLE INFO

Article history:
Received 24 July 2017
Received in revised form 17 September 2017
Accepted 20 September 2017

Keywords:
Janus nanoparticles
Polyacrylic acid
Dissipative particle dynamics
Gold nanoparticles
Molecular simulation

ABSTRACT

Polyacrylic acid-gold (PAA-Au) Janus nanoparticles (JNPs) show a broad application prospect in many fields. However, PAA-Au JNPs are difficult to prepare and characterize due to their specific structures and properties. In this work, the self-assembly of PAA-Au NPs was investigated by dissipative particle dynamics (DPD) simulation method. It was found that PAA-Au NPs had a structure transition with changing the volume ratio of different solvents according to DPD simulation. The morphology of PAA-Au NPs varied from core–shell structure to Janus structure when the volume ratio of isopropanol increased in the system, which was confirmed by experimental results. In addition, other solvents with different ratios were studied in DPD simulation system. The results indicated that isopropanol and ethanol were the proper solvents to form PAA-Au Janus nanoparticles because of their unique solubility parameters. Therefore, this study reveals an optimal mixed solvent for PAA-Au NPs Janus structure and the formation mechanisms of these Janus nanoparticles.

1. Introduction

Nanomaterials, known as the basic blocks of advanced materials in the future, are mainly due to their unique electronic, optical and mechanical properties [1–4]. Over the past few decades, Janus nanoparticles (JNPs) are unique among these nanomaterials because of asymmetry, which can impart drastically different chemical or physical properties [5]. These JNPs show a broad application prospect and are applied in many fields, such as functional surfactants [6], self-assembly and molecular recognition [7], photoelectric biosensors [8], multifunctional magnetic asymmetric materials [9,10], etc. Recently, polyacrylic acid-gold (PAA-Au) Janus nanoparticles are drawing lots of attention because they possess pH sensitivity and play a vital role in cancer therapy [11,12]. However, PAA-Au JNPs are difficult to characterize because of their tiny scales, specific structures and poor repeatability. In addition, the transmission electron microscope (TEM) operating voltages of PAA and Au are quite different because they are organics and inorganics respectively, which leads to an unclear image.

With rapid development of computers, theoretical models and simulation methods are applied to investigate the dynamical structures and properties of such polymer-inorganic composites in many advances [13]. Examples are thermodynamic simulation in a polymer and organics blends system [14], the simulated study of adsorption between copolymer and hydrophobic surface [15] and predictive science of supracolloidal architectures by design of patchy particles [16].

Over the past few years, the dissipative particle dynamics (DPD) method, a coarse-grained mesoscopic molecular simulation, is frequently applied in the polymer field to overcome weaknesses of experiments and practical characterization in a detailed molecular view. Comparing with conventional all-atom molecular dynamics (AAMD), the DPD method has the higher and faster computational capacity and is an interesting candidate to study complex fluids [17–20].

Stimuli-responsive polymers are those the conformational structures transformed when external conditions such as pH, temperature and salt concentration changed [21,22]. Luo et al. applied DPD simulation method to investigate the pH-sensitive polymer [23]. There are some reports of Janus structures by DPD simulation method. Luu and co-workers used DPD method to study the adsorption of Janus nanoparticles at the water–oil interface [24]. Guo et al. studied Janus micro phase structures of polymer blends through DPD method [25]. They reported that the polymer Janus structures had a transformation when the system temperature changed. Coarse-grained model was applied to investigate organo-functionalized inorganic Janus co-clusters by Yan and co-workers [26]. Moreover, Chen et al. added gold nanoparticles into PEO–PPO–PEO block copolymer system by DPD simulation, which

* Corresponding author.
E-mail addresses: liyunbo@shu.edu.cn, ybli@shu.edu.cn (Y. Li).

https://doi.org/10.1016/j.commatsci.2017.09.038
0927-0256/

offered a new method to study solid nanoparticles in DPD simulation [27].

In this work, we investigated PAA-Au nanoparticles (NPs) by the DPD method, which aimed to improve the current situation of difficult experimental preparation and characterization. The coarse-grained (CG) models were applied to study the self-assembly of PAA and Au NPs in a varied mixed solution. The effects of different solvent ratios on the morphology of PAA-Au NPs were scientifically investigated to guide JNPs' design by DPD simulation. The experimental morphology properties of PAA-Au JNPs were used to confirm the simulation results.

2. Simulation details

2.1. DPD method

Dissipative particle dynamics (DPD), a computational method for simulating dynamical and rheological properties, is applicable for mixed fluids, especially for complex systems. Hoogerbrugge and Koelman devised this stochastic simulation method firstly in 1992 [28], which was widely accepted by others. In addition, it was reformulated and mildly modified by Espanol for the appropriate thermal equilibrium system [29,30].

The molecules are divided into a piece of DPD beads to represent a volume of fluid or a group of atoms in DPD method. In the simulation, every bead is followed by Newtonian motion under the action of force ($\mathbf{F}_i$) [31], as showed in Eq. (1):

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{F}_i \tag{1}$$

where $\mathbf{r}_i$, $\mathbf{v}_i$, and m_i denote the position, velocity and mass of bead i, respectively. $\mathbf{F}_i$ is the total force acted on bead i. The total force ($\mathbf{F}_i$) contains three components: the conservative force ($\mathbf{F}_{ij}^{C}$), dissipative force ($\mathbf{F}_{ij}^{D}$) and random force ($\mathbf{F}_{ij}^{R}$), each of which is pairwise additive [31–33].

$$\mathbf{F}_i = \sum_{j \neq i} (\mathbf{F}_{ij}^{C} + \mathbf{F}_{ij}^{D} + \mathbf{F}_{ij}^{R}) \tag{2}$$

The three types of forces: conservative force ($\mathbf{F}_{ij}^{C}$), dissipative force ($\mathbf{F}_{ij}^{D}$) and random force ($\mathbf{F}_{ij}^{R}$). are followed by [33]:

$$\mathbf{F}_{ij}^{D} = [-\gamma \omega^{D}(\mathbf{r}_{ij})(v_{ij}\hat{\mathbf{r}}_{ij})\hat{\mathbf{r}}_{ij}] \tag{3}$$

$$\mathbf{F}_{ij}^{R} = [\sigma \omega^{R}(\mathrm{r}_{ij})\xi_{ij}\hat{\mathbf{r}}_{ij}] \tag{4}$$

$$\mathbf{F}_{ij}^{C} = \begin{bmatrix} a_{ij}(1 - \mathrm{r}_{ij}/r_c)\hat{\mathrm{r}}_{ij} & (\mathrm{r}_{ij} < r_c) \\ 0 & (\mathrm{r}_{ij} \geqslant r_c) \end{bmatrix} \tag{5}$$

a_{ij} is the maximum repulsive force between bead i and bead j in last formula [33].

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j; \mathbf{r}_{ij} = \{\mathbf{r}_{ij}\}; \hat{r}_{ij} = r_{ij}/|r_{ij}| \tag{6}$$

The repulsive parameter between two beads, is related to the interaction among atoms. r_c is the cut-off radius between two beads in Eq. (5) and it could be calculated according to the following law [34]:

$$r_c = (\rho v)^{1/3} \tag{7}$$

where ρ is the bead density without dimension, v is the volume of one bead. The relationship between coefficient and temperature in the dissipative force and the random force is the following [35]:

$$\sigma^2 = 2\gamma k_B T \tag{8}$$

where σ is the standard deviation of random force; γ is coefficient of viscosity, k_B is the Boltzmann constant and T is absolute temperature.

For a complex system, the DPD method is applied to simulate in a longer time scale and larger spatial scale. At the same time, the inherent nature of system is not changed during the coarse granulation process. Instead of common molecular dynamics simulation and Brownian dynamics simulation, the DPD method adopts amended "Velocity-Verlet" method and flexible interaction potential, which allows for a larger time step to cost less time with a more satisfactory result [36].

2.2. Simulation system and parameters

2.2.1. Establishment of coarse-grained model

The DPD simulation, a mesoscopic method, was based on the construction of a coarse-grained model. In this mesoscopic system, the beads replace the molecules. There were five different beads in this work: polyacrylic acid (PAA), gold (Au), water (H_2O), isopropanol (IPA) and ammonia solution ($NH_3{\cdot}H_2O$). The five beads in this mesoscopic system were transformed into those coarse-grained models [37], as shown in Table 1. In this work, the average bead volume V_{ij} was set to 120 Å^3, which was equivalent to the volume of four water molecules and seven gold atoms in this table. Chain lengths were expressed in total number of DPD beads connected together in the chain [16]. A PAA (M_w = 3000) molecule contains 21 beads and seven gold atoms were consist of a bead in the simulation, so L(PAA) = 21 and L (Au) = 1/7 are set for the chain lengths, respectively.

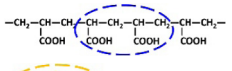
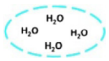
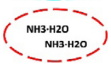
2.2.2. Calculation of repulsive force parameters

The coefficient a_{ij}, the vital factor, expressed the maximum repulsion between the ith and the jth bead in DPD simulation system. This parameter represents the complex interactions between atoms and molecules in real system. It can be obtained from the Flory–Huggins binary interaction parameter, χ_{ij}, through the following formula as shown in Ref. Groot and Warren's studies (1997) [38]:

$$a_{ij} = (a_{ii} + 3.27\chi_{ij})(k_B T/r_c) \tag{9}$$

where a_{ii} is the repulsion parameter for the same type beads. For the same beads, $\chi_{ij} \approx 0$, and a_{ii} is set to 25. T is the absolute temperature, k_B is the Boltzmann constant and r_c is the cut-off radius as mentioned before. The χ_{ij} will be interpreted detailedly in next part. This relationship is applied to a system, whose group density rangs from 3 to 5. If the system density is less than 3, it would lead to errors; but if it is applied to more than 5 of the system, it would cost a long time for the simulation. According to Groot's results [39], the density ρ is defined as 3 for the effective low-density simulation.

Table 1
Schematic description of the coarse-grained models in the system.

Molecule	Bead Type	Molecular structure	Coarse-grained model
PAA	P		
Au	A		
H_2O	W		
$NH_3{\cdot}H_2O$	N		
Orgnic Solvent	O