Electronic Supplementary Information for:

Structure properties of polymer-brush-grafted gold nanoparticles at the oil-water interface: insights from coarse-grained simulations

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To validate the coarse-grained (CG) model of polymer-brush-grafted gold nanoparticles used in our study, for C1/N0 system, we choose the BA diblock polymer brush-functionalized gold nanoparticle as an example and investigate its phase transfer behaviour at the oil-water interface by all-atom molecular dynamics (MD) simulations. The methods and results are listed as follows.

1. Methods

1.1 System preparation

The gold core with a diameter of 2.0 nm was coated with 32 PEG-b-alkyl diblock brushes by using the Packmol software, which is similar to the CG model of BA polymer brush-grafted AuNP in the C1/N0 system (see Figure S1), but the chain length is much shorter for saving computational resources in the all-atom MD simulations. The decane-water interface was adopted to model the oil-water interface, which is the same as that used in Fan et al.'s work,[1] who investigated the phase behavior of amphiphilic silica nanoparticles at the decane-water interface by atomistic simulations.

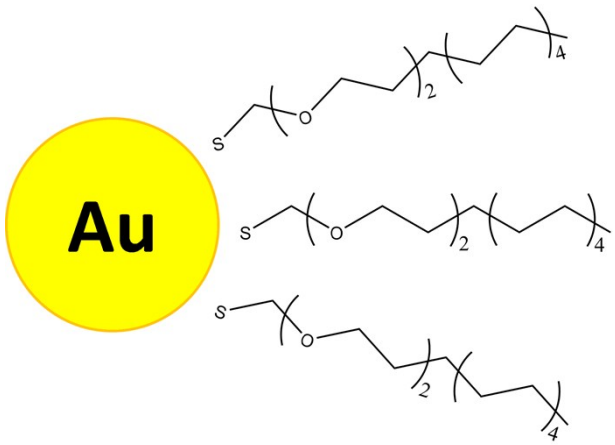

Figure S1. Schematic representation of the polymer brush-grafted gold nanoparticle

1.2 MD simulation details

The atomistic simulations were performed and analyzed by using the GROMACS 4.5.4 package with the Gromos53a6 force field,[2] and the SPC water model was used in this work. The same model has been adopted to study the pathway for insertion of amphiphilic gold nanoparticles into lipid bilayers.[3] The simulation box has a dimension of 9 nm × 9 nm × 18 nm and approximately has 80000 atoms, in which decane formed a 9 nm thick layer at the top. The polymer brush-modified AuNP was placed at the oil-water interface (Figure S2). First, the system was minimized by using the steepest descent method to remove inappropriate geometry or steric overlap. Then, a NPT equilibration with duration of 100 ps was performed to equilibrate the water and oil molecules around the NP. During this stage, the position of AuNP was restrained. After equilibration, the restrain was removed and the system went through a 40 ns MD simulation. The behaviour of grafted AuNP in the pure water was also investigated as a comparison. The simulation was carried out in a NPT ensemble under periodic boundary conditions. A simulation time step of 2 fs is used with all bond lengths constrained via the LINC algorithm. The system was coupled with Berendsen thermostat and barostat at 300 K and 1 bar. A switched potential was adopted to calculate the nonbonded interactions with a switching function between 9 and 10 Å. Electrostatic interactions were calculated by employing the particle mesh Ewald (PME) method. The cutoff distance of the electrostatic interactions was set to be 1.0 nm. The trajectories were visualized via the Visual Molecular Dynamics (VMD) program.

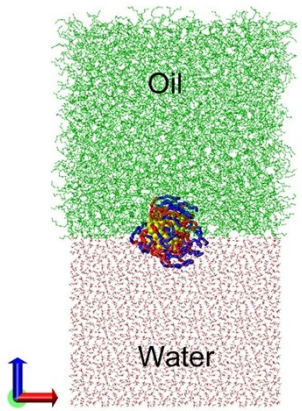

Figure S2. Schematic representation of the simulation box. Green, yellow, blue, red and pink balls represent oil, gold, alkyl, PEG and water, respectively.

2. Results and discussion

The structure properties of PEG-b-alky diblock polymer brush-grafted AuNP at the decane-water interface were studied by all-atom MD simulations to validate the CG simulations based on the MARTINI force field. We analyzed the morphologies, density profiles and the processes of phase transfer of the functionalized AuNP, the results were compared with the corresponding CG simulations.

2.1 Equilibrated morphology of functionalized AuNP

As shown in Figure S3, the polymer brushes are bent on the gold NP surface in the pure water environment, the inner hydrophilic PEG blocks are exposed to the water phase. After the solvent has been changed from water to oil-water mixed phase, the functionalized AuNPs can break the interface region and move into the oil phase completely, as demonstrated by the density profiles shown in Figure S3, these results are in good agreement with those of CG simulations. (Figure 2, 2a-2c).

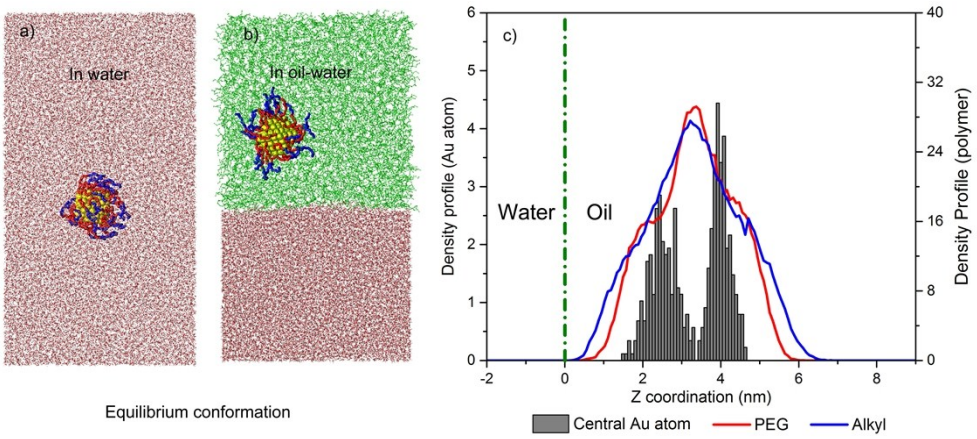

Figure S3. Equilibrium morphologies and density profiles of the functionalized AuNP brush. (a) equilibrium morphology in water; (b) equilibrium morphology in oil-water; (c) density profiles, the dashed green line represents the interface.

2.2 Phase transfer processes of functionalized AuNP

Four snapshots of the phase transfer of functionalized AuNP are presented in Figure S4. From these snapshots, we can see clearly that the whole processes of phase transfer can be divided into four stages, which is very similar to the corresponding CG simulation system (as shown in Figure 4). The conformational change of bent-to-straight of grafted ligands also shows highly consistency with experimental data[4, 5] and our previous [6] and present simulation works.

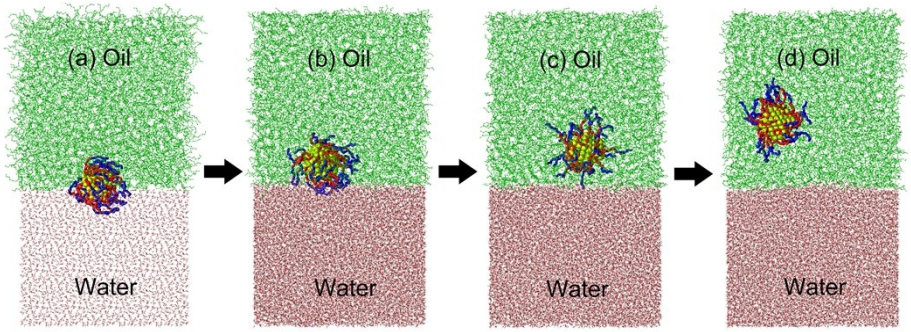

Figure S4. Phase transfer process of functionalized AuNP in all-atom molecular simulations. (a. brushes bend at the interface, 0 ns; b. brushes start to stretch and leave the interface, 0.24 ns; c. more brushes stretch and the NP just leaves the interface, 12 ns; d. the NP completely leaves the interface, 20 ns.)

References

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