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Influence of Polyethylene Glycol Passivation on the Surface Plasmon Resonance Induced Photothermal Properties of Gold Nanorods

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Molecular Models.

Three molecular models were created to study the thermal conductivity of the polyethene glycol (PEG) brushes. Each system was based on a five-layer slab of 1800 gold atoms with lateral dimensions of 5.075 × 5.274 nm^2. The upper and lower surfaces of the slab consisted of Au{111} crystal facets. The surfaces of the nanorods are expected to be more complex than flat fcc {111} facets; however, the simple Au{111} representation is likely sufficient for the goal of the simulations, namely calculating the thermal conductivity through the PEG brushes. Owing to periodic boundary conditions, the Au{111} surfaces were of effectively infinite in extent in the *xy* plane. Different numbers of thiolated PEG ($CH_3(OCH_2CH_2)_n$–SH) molecules of different lengths were added for each system as described below. Water molecules were added both sides of the slab, yielding system dimensions of about 17.8 nm along the *z*-axis.

System A contained only the gold slab and water, to mimicking the Raw AuNR system. Systems B and C were constructed to model the experiments involving thiolated PEG having molecular masses of 2 and 5 kDa, respectively. We placed thiolated PEG molecules, $CH_3(OCH_2CH_2)_n$–SH with $n = 45$ and 112, onto both the upper and lower gold surfaces. The areal density of thiolated PEG chains on the gold surfaces was calculated to approximately reproduce its value in the experiments. The specific surface area of the gold nanorods, $\sigma \approx 20.7\ \text{m}^2/\text{g}$, was estimated from their approximate dimensions (10 nm in diameter, 51 nm in length) and the density of solid gold at standard conditions. The approximate densities of PEG chains were calculated to be $N/A = 1.98$ and 0.86 nm^{-2} for the 2 and 5 kDa PEG systems using the formula $N/A = \alpha/[(1-\alpha)\sigma M]$, where α =12% and 12.7% were the mass fractions of PEG in the AuNR as determined by thermogravimetric analysis and M=2 and 5 kDa were the molecular masses of the PEG chains. The PEG molecules were initially oriented so that the thiol groups were only a few ångströms from the gold surface.

Molecular Dynamics Methods.

Interatomic interactions with the gold surface were represented according to the GolP-CHARMM force field,[1] which includes virtual surface atoms that favor atom adsorption atop the gold atoms and charged particles rigidly attached to gold atoms that endow polarizability.[2] The charge of the latter particles was 0.3*e*, while the gold atoms carried charges of −0.3*e.* PEG was represented according the carefully validated CHARMM model.[3] The force field parameters of the thiol group were obtained by applying the CHARMM General Force Field (CGenFF) version 3.0.1 web interface to a thiolated PEG molecule and integrating the resulting CGenFF parameters with the CHARMM PEG model.

Equilibration of the simulation systems was performed by the program NAMD 2.12,[4] using a 2 fs time step, rigid water molecules,[5] rigid covalent bonds involving hydrogen,[6] and particle-mesh Ewald electrostatics.[7] All atoms of gold remained fixed to their initial positions (an ideal fcc crystal), except for the polarization particles, which were able to rotate about the gold atom centers via rigid bonds. The mass of the polarization particles was set to 1.0 Da so that their bonds to the gold atoms would be kept rigid without modification of the NAMD source code. Lennard-Jones forces and direct Coulomb forces were smoothly truncated a distance of 9 to 10 Å. The temperature was maintained at 300 K by a Langevin thermostat. The pressure was maintained at 1.01325 bar by a Langevin piston,[8] which allowed only the z dimension of the simulation cell to fluctuate. The size of the system in the xy plane remained fixed, consistent with the size of the ideal Au{111} layers.

Each system was equilibrated for 100 ns to allow the PEG chains to relax. The PEG chains were initially in a grid arrangement. However, wishing to obtain realistic arrangements of the thiolated PEG chains, we did not covalently attached the thiols to the Au{111} surfaces, but simulated them in their reduced state, permitting slow diffusion of the thiol terminal groups across the surfaces. Nonetheless, all of the PEG chains remained adhered to the surface by a strong noncovalent thiol–gold interaction.[1] The resulting structures had disordered arrangements of PEG chains, presumably more realistic than the initial grid arrangement. The gold slabs were subsequently removed and filled in with additional water. The reason to remove the gold slab was to simplify the thermal conductivity calculations and remove the influence of the thermal conductivity of the gold model because it is unlikely that the fixed gold atoms of the GolP-CHARMM force field accurately represent heat conduction through gold. In all subsequent simulations, the sulfur atoms of the PEG molecules were restrained to their final positions before the gold slab was removed. Each system underwent energy minimization and a further 0.2 ns of equilibration after removal of gold slab.

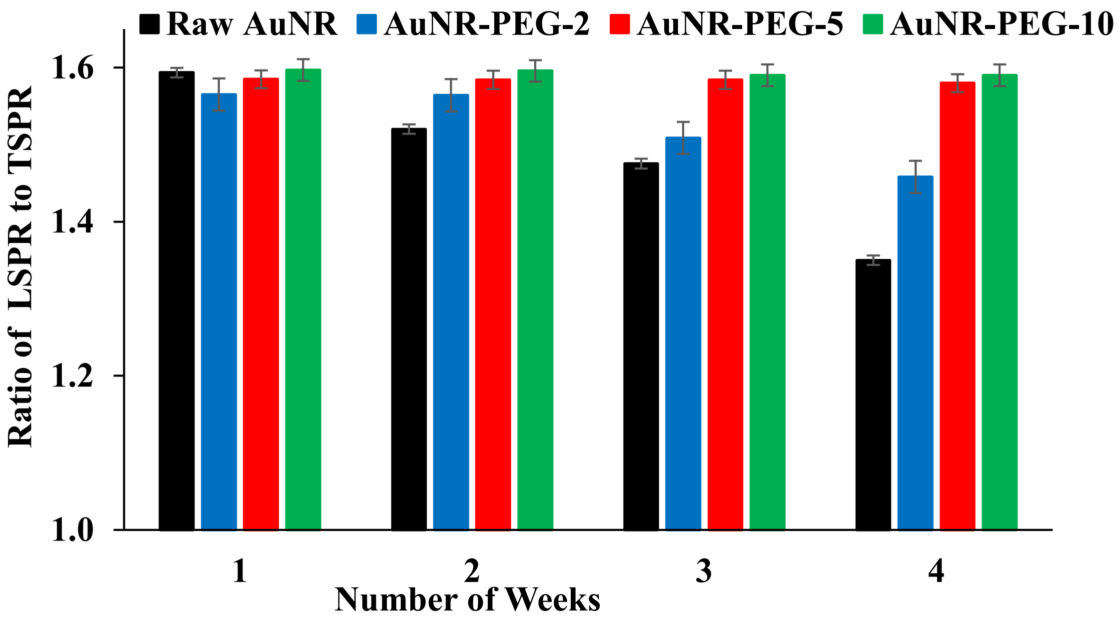

Figure S1. Stability of Raw and PEG-functionalized AuNRs at 4 °C. The ratio of maximum longitudinal surface plasmon resonance (LSPR) to the transverse surface plasmon resonance (TSPR) of both Raw and PEG-functionalized AuNRs was taken to calculate aspect ratio. The stability was observed while storing at 4°C and the surface plasmon resonance was measured by UV-Vis spectrum over the period. This graph shows higher stability of PEG functionalization of AuNRs as compared to that of Raw AuNR.

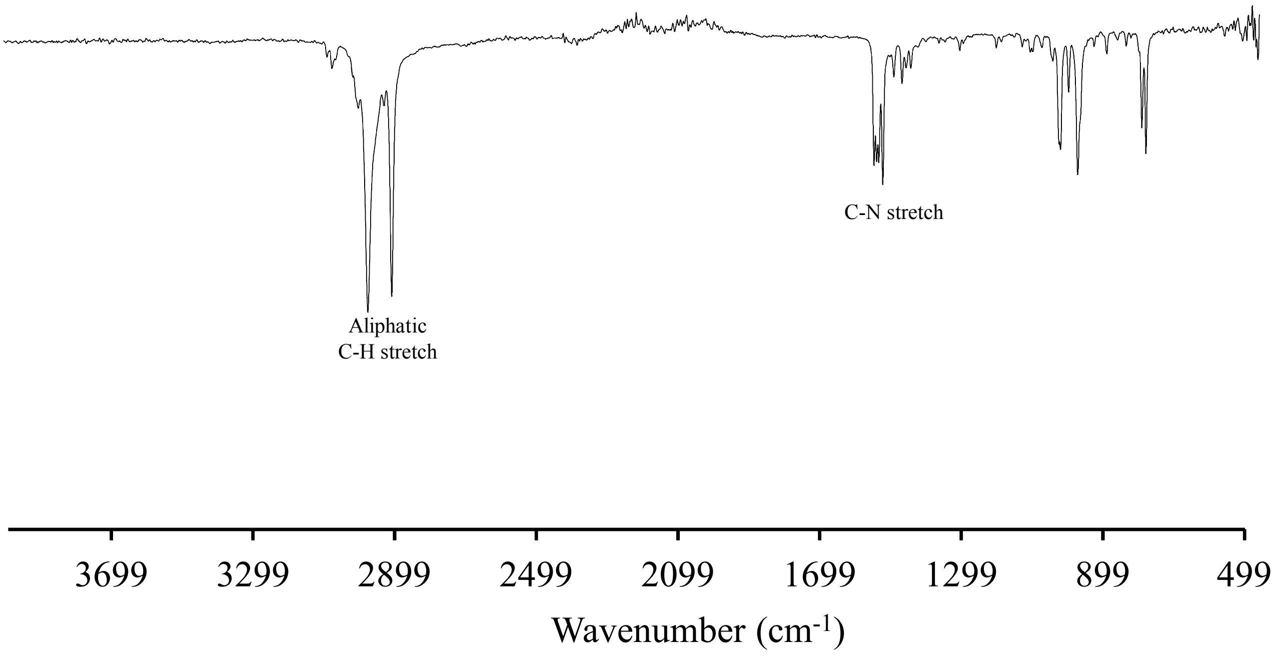

Figure S2. FT-IR spectrum of Cetyltrimethylammonium bromide (CTAB).

References

1 L. B. Wright, P. M. Rodger, S. Corni and T. R. Walsh, GolP-CHARMM, https://pubs.acs.org/doi/abs/10.1021/ct301018m, (accessed April 5, 2018).

2 Iori F. and Corni S., *J. Comput. Chem.*, 2008, **29**, 1656–1666.

3 K. Vanommeslaeghe, E. P. Raman and A. D. MacKerell, *J. Chem. Inf. Model.*, 2012, **52**, 3155–3168.

4 Phillips James C., Braun Rosemary, Wang Wei, Gumbart James, Tajkhorshid Emad, Villa Elizabeth, Chipot Christophe, Skeel Robert D., Kalé Laxmikant and Schulten Klaus, *J. Comput. Chem.*, 2005, **26**, 1781–1802.

5 Miyamoto Shuichi and Kollman Peter A., *J. Comput. Chem.*, 2004, **13**, 952–962.

6 H. C. Andersen, *J. Comput. Phys.*, 1983, **52**, 24–34.

7 T. Darden, D. York and L. Pedersen, *J. Chem. Phys.*, 1993, **98**, 10089–10092.

8 S. E. Feller, Y. Zhang, R. W. Pastor and B. R. Brooks, *J. Chem. Phys.*, 1995, **103**, 4613–621.