Anisotropic Growth Mechanism of Au Nanorods Directed by CTA^+, Br^-, and Ag^+

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Gold Nanorods (Au NRs)

Gold nanorods are anisotropic gold nanoparticles with a rod-like shape, characterized by their tunable optical and electronic properties arising from localized surface plasmon resonance (LSPR).

They exhibit two plasmon bands: a transverse mode around 520 nm and a longitudinal mode that can be tuned from the visible to near-infrared region depending on their aspect ratio. These properties make Au NRs highly useful in photothermal therapy, sensing, and catalysis.

Growth Mechanisms of Au Nanorods

Gold nanorods are typically synthesized via a seed-mediated growth method in a CTAB-rich solution. Small spherical Au seeds are first formed by rapid reduction of $HAuCl_4$, then introduced into a growth solution containing additional $HAuCl_4$, CTAB, and $AgNO_3$.

The anisotropic growth occurs as silver ions selectively adsorb on certain crystal facets. During growth, the surfactant cetyltrimethylammonium (CTA^+) and silver ions (Ag^+) selectively adsorb onto specific gold facets, suppressing lateral growth while promoting elongation along the longitudinal direction of the nanorod.

In contrast, adsorption of CTA^+ together with bromide ions (Br^-) facilitates growth in the lateral direction. Thus, the balance between CTA–Ag and CTA–Br adsorption determines the anisotropic growth behavior and final aspect ratio of the nanorods.

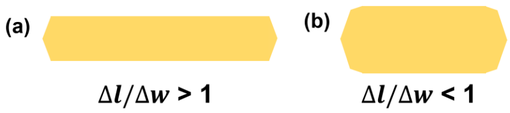


Figure 1. (a) Anisotropic growth in the lateral direction (b) Anisotropic growth in the longitudinal direction.

Optimization of FCC Au Lattice Parameter

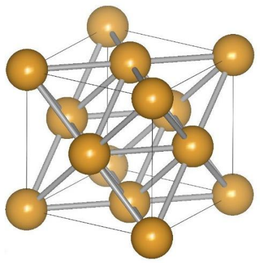


Figure 2. Face centered cubic structure of gold.

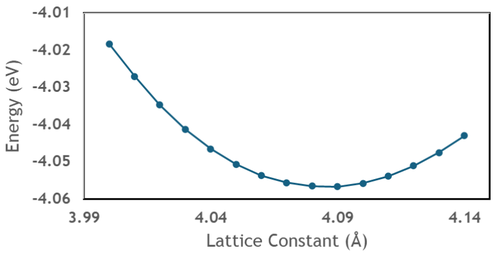


Figure 3. Cohesive energy vs. lattice parameter for Au in the FCC configuration.

The lattice parameter for FCC Au was determined by calculating the cohesive energy for various lattice parameters. The calculations indicate that Au in the FCC configuration exhibits an equilibrium lattice constant of approximately 4.09 Å, showing strong consistency with the experimental value of 4.08 Å. This calculation is essential for subsequent simulations involving gold surfaces.

Grand Canonical Monte Carlo Simulations

The Grand Canonical Monte Carlo (GCMC) method is a statistical simulation technique used to model systems in equilibrium with a particle reservoir at constant chemical potential (μ) and temperature. Unlike conventional Monte Carlo methods that keep the number of particles fixed, GCMC allows particles to be inserted or deleted during the simulation according to probabilistic rules derived from the grand canonical ensemble. This makes it particularly useful for studying adsorption and surface phenomena, where the number of molecules in a system can fluctuate.

GCMC simulations were performed in this study to model the adsorption behavior of Ag and Br atoms on the surfaces of gold nanorods. The investigated Au surfaces included the (100), (110), and (111) facets. In these simulations, the chemical potential of Ag ions was controlled to regulate adsorption, while specific atoms were designated as fixed or allowed to relax in order to accurately represent surface and subsurface interactions.

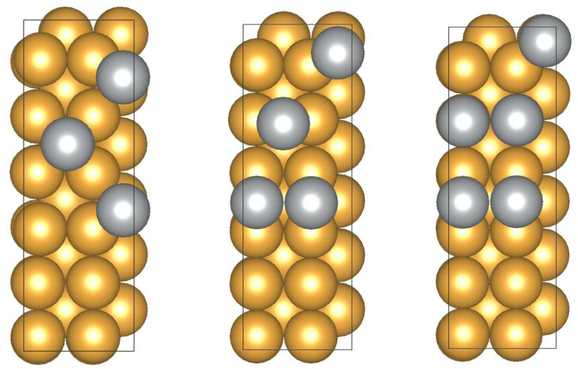
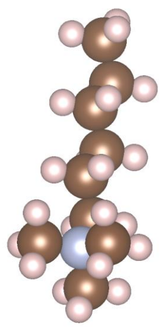


Figure 4. Grand Canonical Monte Carlo (GCMC) simulation results illustrating the adsorption configuration of Ag atoms on the Au (100) surface.

Figure 4 presents the most stable adsorption configurations of 3, 4, and 5 Ag atoms on the Au surface. Each configuration corresponds to the energetically favorable arrangement obtained from the simulations. These results provide a foundation for efficiently constructing various adsorption models, which will be used to investigate the adsorption behavior of Ag, Br, and CTA in subsequent analyses.

Cetyltrimethylammonium (CTA^+)



Cetyltrimethylammonium (CTA^+) is a cationic surfactant composed of a long hydrophobic alkyl chain and a quaternary ammonium head group, commonly used to stabilize and direct the growth of nanoparticles.

To reduce computational cost, the CTA^+ molecule was truncated by removing a portion of its alkyl chain, effectively modeling only half of the molecule.

Figure 5. Molecular structure of truncated CTA^+ used for simulations.

Adsorption of CTA, Ag, and Br on Au Surface

Various configurations of CTA, Ag, and Br were constructed for each Au surface. Density functional theory (DFT) simulations using VASP were then performed to investigate their adsorption behaviors. The results for the Au (100) surface indicate that the CTA–Ag complex exhibits a stronger affinity toward the gold surface compared to the CTA–Br complex.

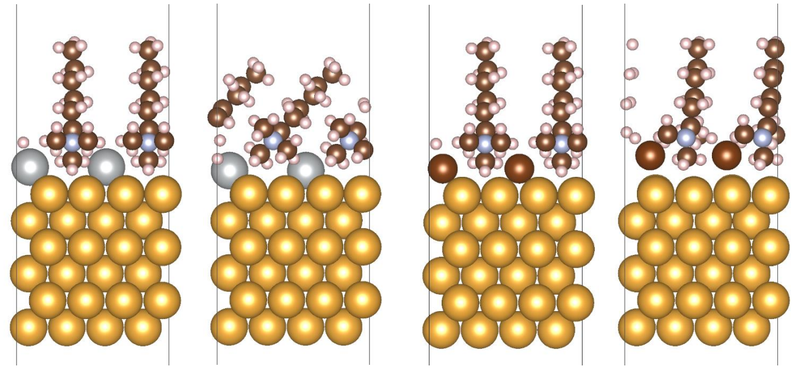


Figure 6. Configurations of CTA, Ag, and Br on the Au (100) surface. From left to right: CTA–Ag complex before and after structure optimization, CTA–Br complex before and after structure optimization. For both systems, one CTA molecule and one Ag (or Br) atom were placed on every four surface Au atoms.

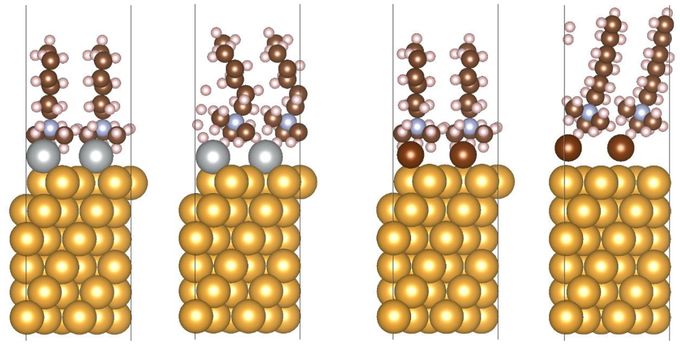


Figure 7. Configurations of CTA, Ag, and Br on the Au (111) surface. From left to right: CTA–Ag complex before and after structure optimization, CTA–Br complex before and after structure optimization. For both systems, one CTA molecule and one Ag (or Br) atom were placed on every three surface Au atoms.

The results for the Au (111) surface also indicate a strong affinity between Ag and Au. However, this interaction is more pronounced on the Au (100) surface. This behavior is likely due to the preferential adsorption of the CTA–Ag complex on the Au (100) surface, thereby suppressing growth along that facet.

References

[1] Zhu, J.; Lennox, R. B. Insight into the Role of Ag in the Seed-Mediated Growth of Gold Nanorods: Implications for Biomedical Applications. ACS Appl. Nano Mater. 2021, 4 (4), 3790-3798. DOI: 10.1021/acsanm.1c00230

[2] Hemmen, A.; Panagiotopoulos, A. Z.; Gross, J. Grand Canonical Monte Carlo Simulations Guided by an Analytic Equation of State—Transferable Anisotropic Mie Potentials for Ethers. J. Phys. Chem. B 2015, 119 (23), 7087–7099. DOI: 10.1021/acs.jpcb.5b01806

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