

Collaborative Project: EiR: Understanding Interactions of Gold and Silver Nanoparticles with Proteins to Achieve Optimum Surface Plasmon Effect

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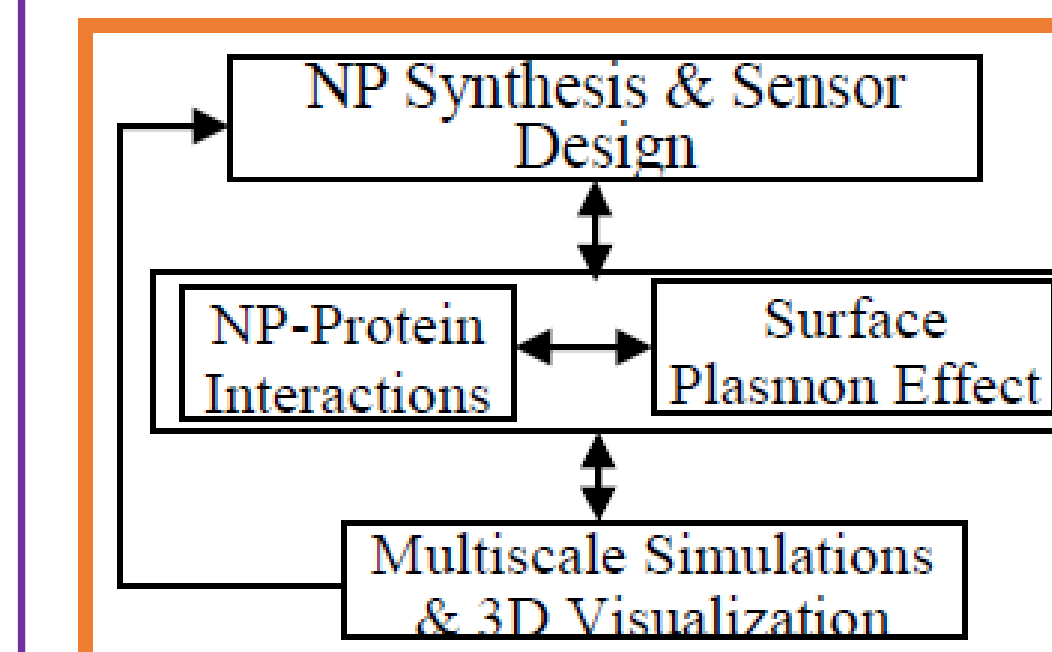


The overall goal: understand the fundamental plasmonic response of gold and silver nanoparticles (NPs) interacting with proteins, which is critical for disease detection using surface enhance Raman Spectroscopy (SERS).

The objectives include: (1) understanding the electronic properties and electromagnetic spectrum of structured Au and Ag NPs; (2) understanding Au and Ag NP-protein interactions in biochemical environments, including both physical interactions and chemical reactions; (3) understanding and determining the change in electromagnetic and plasmonic response, due to nanoparticle-protein interactions.

Educational goals: Promoting interest in STEM for undergraduates at Howard University and Winston-Salem State University and K-12 students, especially underrepresented minority students, through research, teaching, and outreach activities.

Methodology



Theoretical **multiscale simulations** (quantum, atomistic, molecular and macroscopic) combined with **3D virtual visualization (VR)** and **experiments** provide an understanding of protein-NP interactions from both **physical and chemical perspectives**.

Results

DFT and linear-response time-dependent DFT (LR-TDDFT) calculations^{1,2} are used to determine the electronic structure and explained the origin of the optical absorption spectrum.

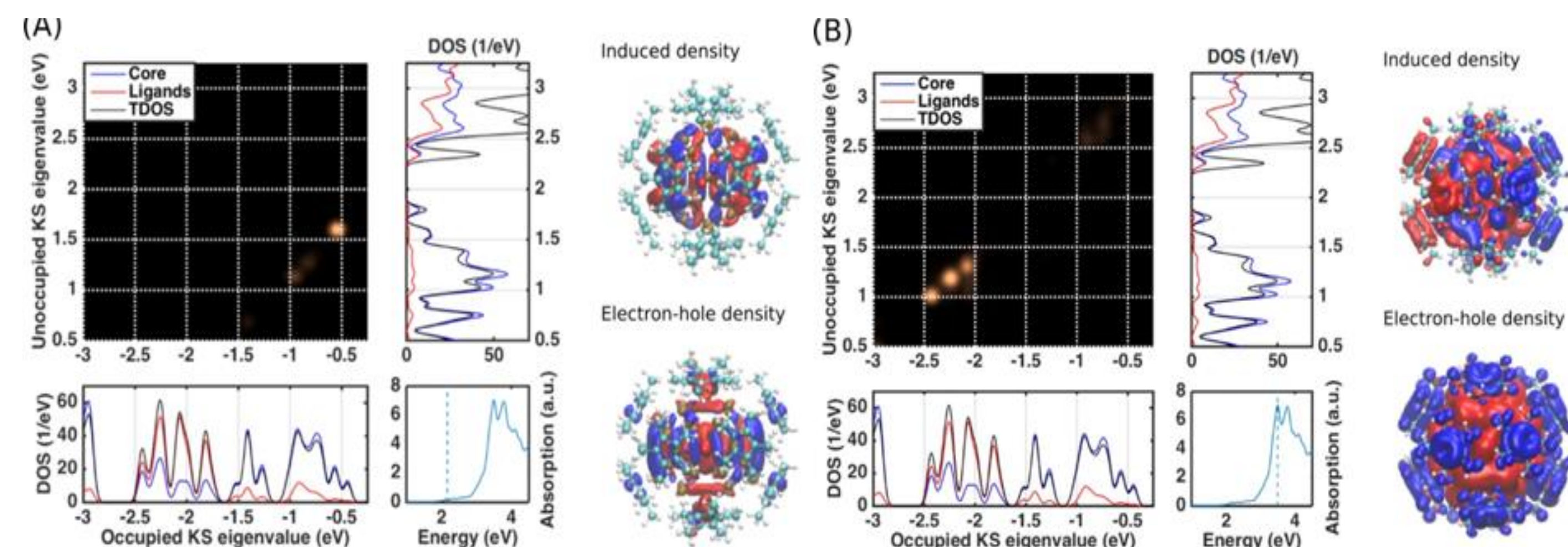


Fig. 1. Transition contribution map (TCM) for excitation at (A) 2.17 and (B) 3.50 eV for Al₅₀Cp₁₂.

➤ Al₅₀Cp₁₂ NPs exhibit optical transitions from metal core states to ligand states, metal core to metal core states, and to hybrid states, which were quite unique for metalloid NPs.¹

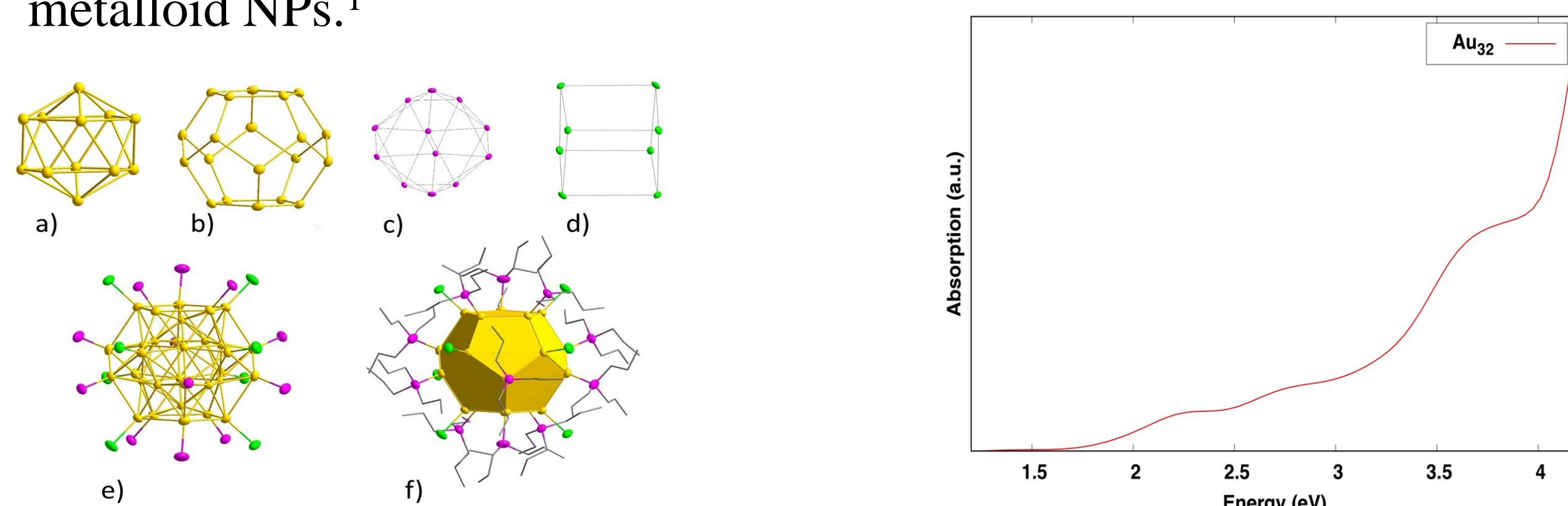


Fig. 2. Au₃₂(PR₃)₁₂Cl₈ geometry and optical properties: structure of **1**. a) inner Au₁₂ icosahedron; b) outer Au₂₀ dodecahedron; c) icosahedral arrangement of outer phosphorus atoms; d) cubic arrangement of outer chloride atoms; e) Au₃₂ kernel with peripheral chloride and phosphorus atoms, carbon and hydrogen atoms omitted for clarity; f) molecular structure of **1Pr**, P atoms, purple; Au atoms, gold; Cl atoms, green.

➤The geometry has inner Au₁₂ core with a Jahn-Teller distortion.. The outer Au₂₀ also exhibits a Jahn-Teller distortion. Both deviate from the typical icosahedral and dodecahedron symmetries.

➤The absorption spectra shows distinct features at 2.2 and 3.6 eV respectively. The transition at 2.2 eV is less intense, which indicate a core-core transition. The feature at 3.6 eV has multiple transitions that contribute to the intensity.

Coarse-grained, molecular dynamics (MD) simulations³ (conventional and Reactive forcefield) plus 3D VR⁴ are used to study peptide-NPs interactions: adsorption behavior, chemical reactions and quantum effects (polarization and charge transfer).

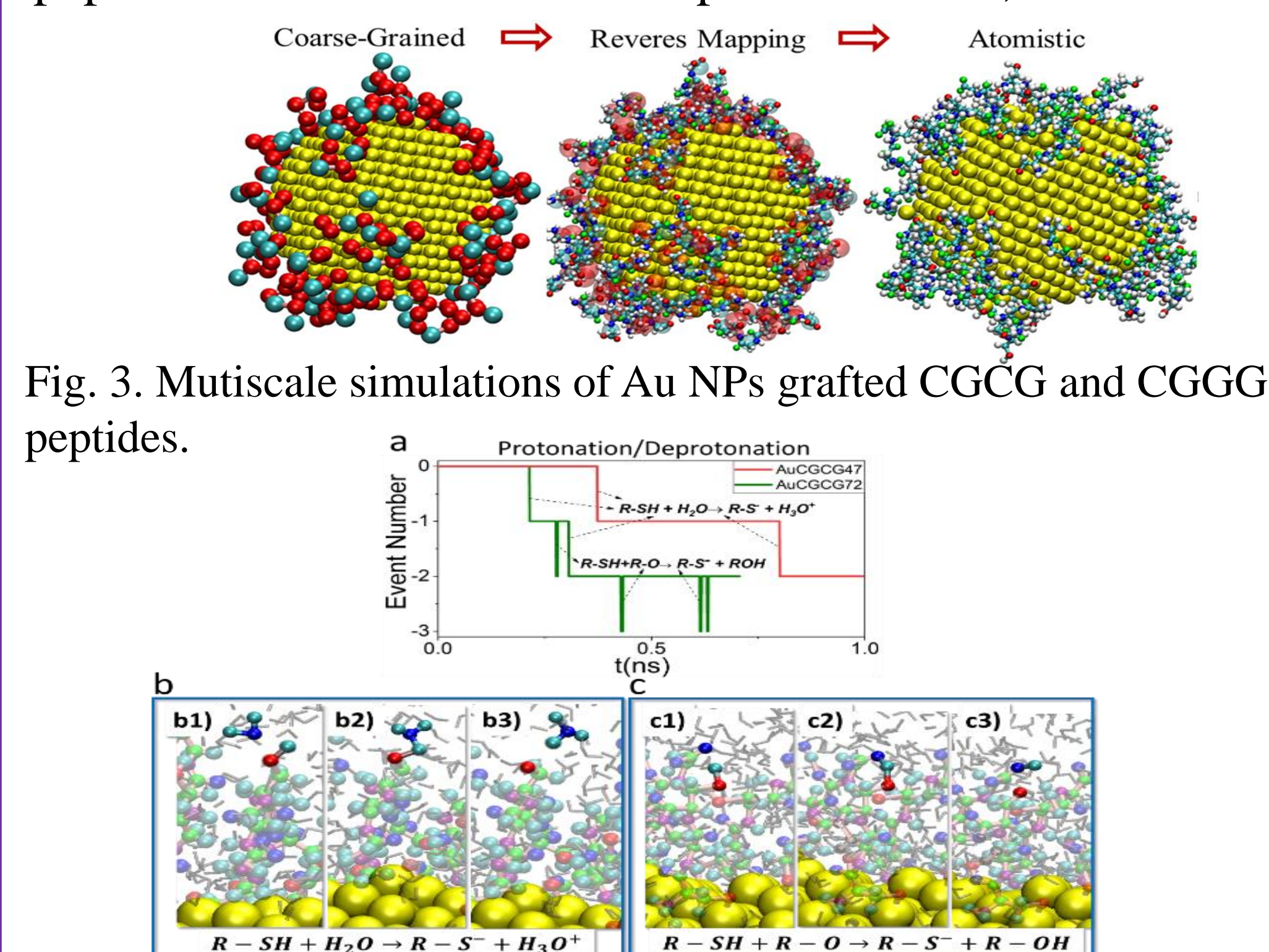


Fig. 3. Mutiscale simulations of Au NPs grafted CGCG and CGGG peptides.

➤Proton transfer from thiol groups of cysteine to water or carboxyl groups were detected.³

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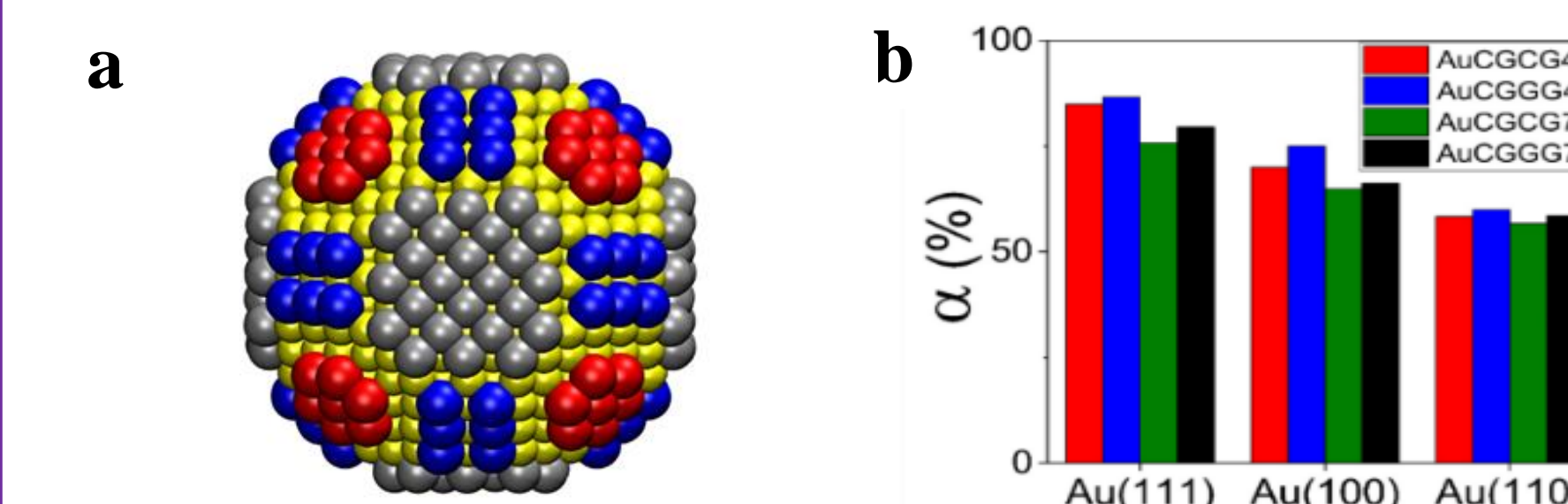
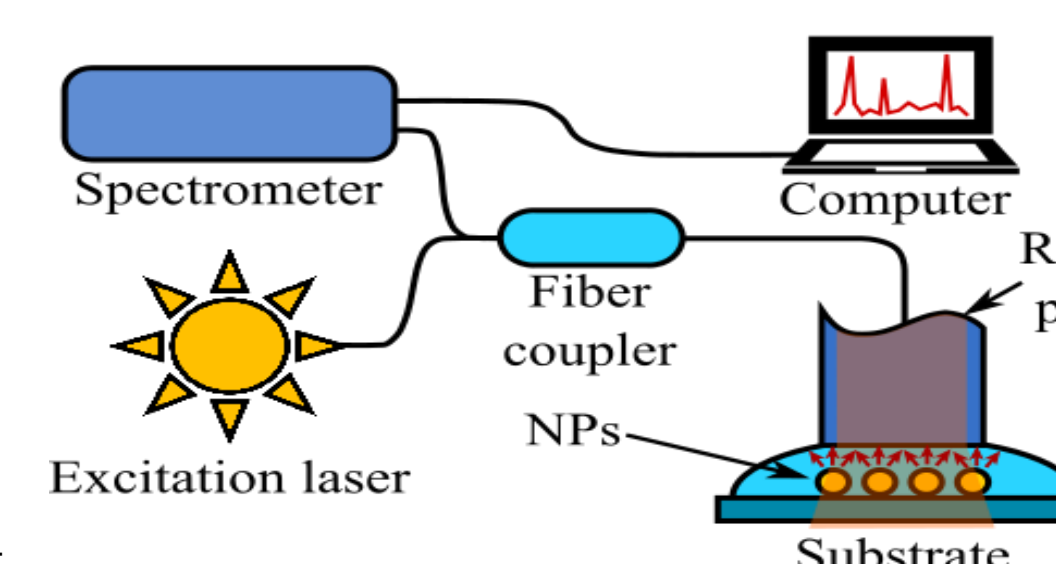


Fig. 5. (a) Au NP core (red: the outlayer of (111) facet, silver: the outlayer of (100) facet, blue: the outlayer of (110), yellow: inner Au layers) (b) normalized surface coverages (α) for facets for AuCGCG.

➤ Slight facet-dependent adsorption detected.³

Future Work



- Simulations of protein-NP interactions.
- Experimental development of SERS.

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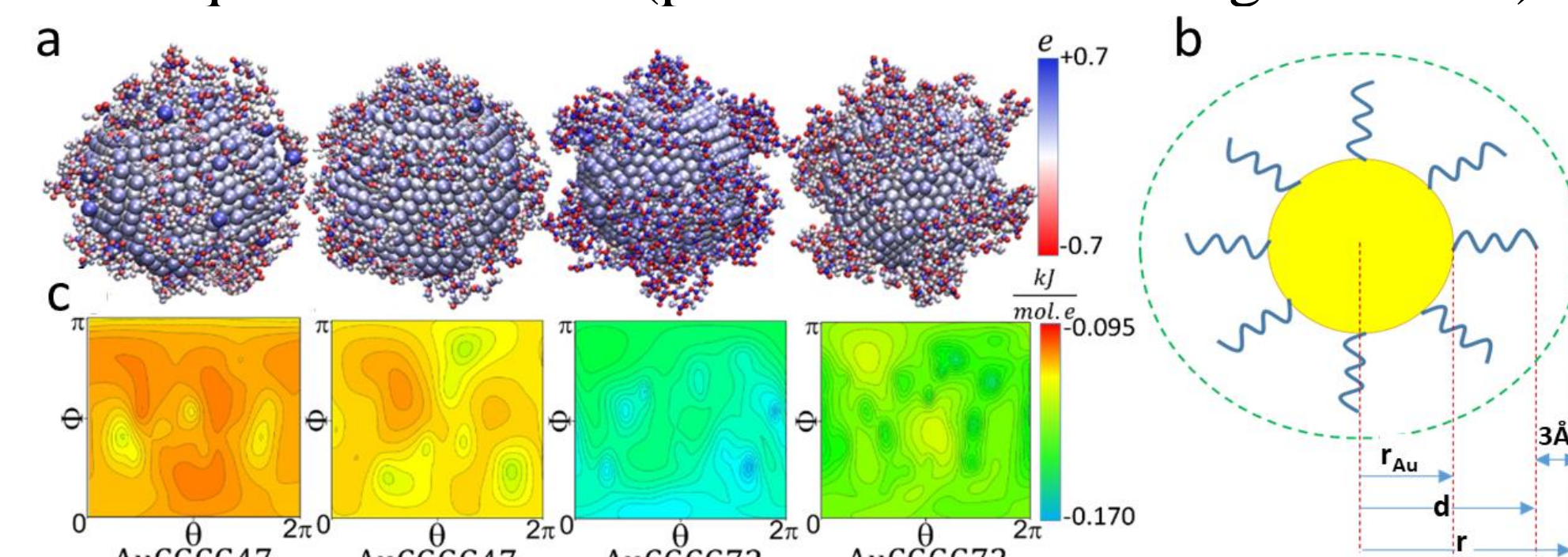


Fig. 6. (a) The charge distribution of functionalized AuNPs (1.46 peptides/nm² and 2.24 peptides/nm²); (b) Schematic graph (c) The contour of electrostatic potential, $\phi(\vec{r})$ as a function of spherical angles (ϕ and θ).

➤Functionalized Au NPs exhibit overall negative electrostatic potential due to the grafted peptides³.

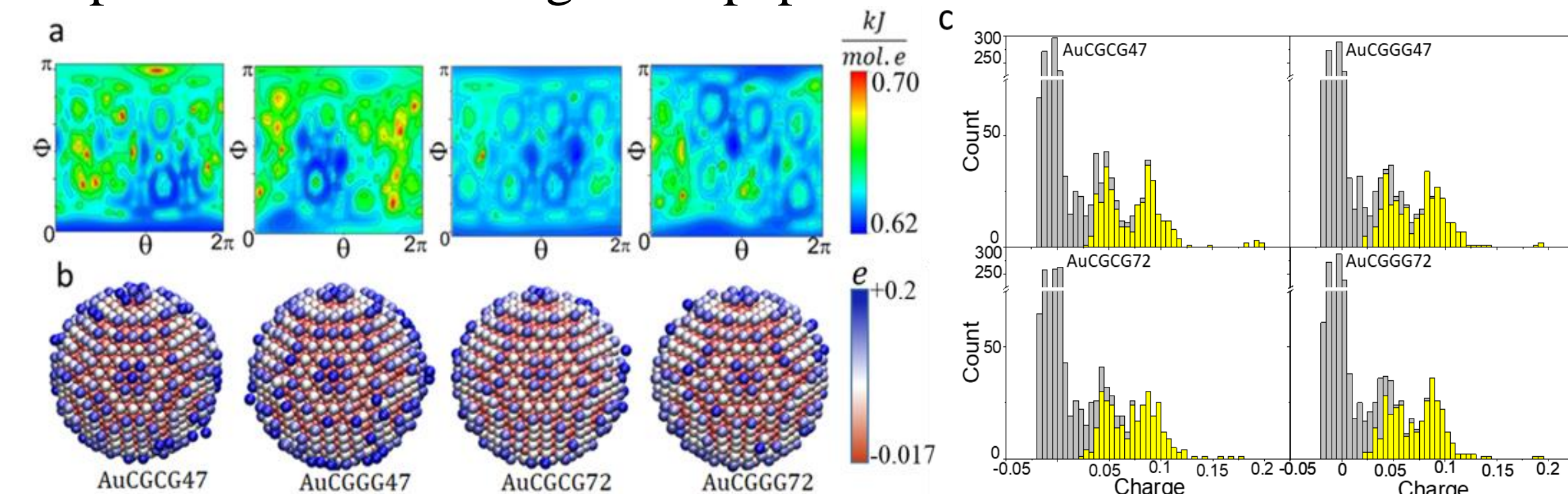


Fig. 7. The contour of ϕ as a function of ϕ and θ at $r=1.8$ nm; (b) The charge distribution on the AuNP core; (c) Histogram of the gold atoms' charges.

➤Due to the thiol-Au bonding and the strong binding of polarizable O and N atoms with Au surfaces, the outer surfaces of a AuNP core are polarized with positive electrostatic potentials and atoms of inner core are negatively charged.³

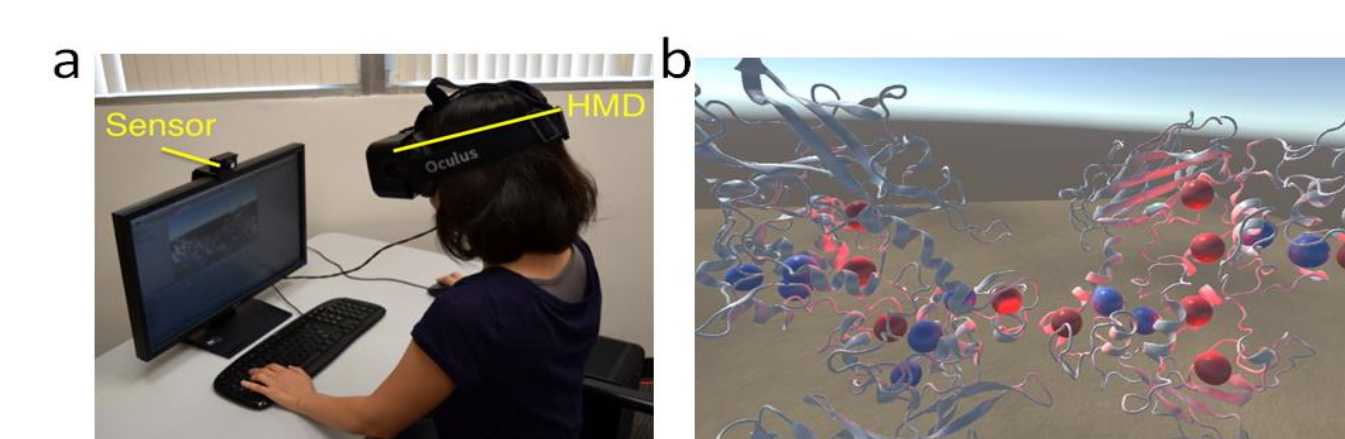


Fig. 7. In-house developed 3D VR technology⁴

1. O. Lopez-Acevedo, A. Z. Clayborne, H. Hakkinen, "Electronic structure of gold, aluminum, and gallium superatom complexes". *Phys. Rev. B* **2011**, 84, 035434.
2. S. Kenzler, F. Fetzer, C. Schrenk, N. Pollard, A.R. Frojd, A. Z. Clayborne, A. Schnepf, To be submitted **2018**.
3. M. Samieegohar, F. Sha, A. Z. Clayborne, T. Wei*, "ReaxFF MD Simulations of Peptide-grafted Gold Nanoparticles", submitted, **2018**.
4. C. M. Nakano, E. Moen, H. S. Byun, H. Ma, B. Newman, A. McDowell, T. Wei*, M. Y. El-Naggar*, "iBET: immersive visualization of biological electron-transfer dynamics", *J. Mol. Graph. Model.*, **2016**, 65, 94.