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Review Research Paper

Structural, Electronic and Optical Properties of Gold Nanoparticles: Effects of Particle Size- A Review

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ABSTRACT

The review of Gold nanoparticles (AuNPs) has been done in this paper. The size of gold nanoparticles (AuNPs) demonstrates a radical change in structural, electronic and optical properties. The properties of AuNPs are size-dependent and enable this material to be particularly useful across catalysis and sensing to photonics and biomedicine. Here, we look at the study of the structural metrics (e.g., lattice spacing and crystallinity), electronic properties (e.g., quantum confinement and band structure effects), and optical properties (e.g., localized surface plasmon resonance) as the particle diameter is reduced between the bulk-like scales (>50 nm) and ultrasmall clusters (<3 nm). This review provides the in-depth discussion of size-dependent effects in AuNPs with references to theoretical models and experimental observations. It has been focused on atomic-scale structural evolution, quantization of the electronic density of states, change of the dielectric response, and localized surface plasmon resonance. The association of size of particle and functional applications is critically analysed.

1. Introduction

Nanoscience and nanotechnology have given gold nanoparticles (AuNPs) a very high level of attention because they are known to possess extraordinary body sizing, shape-related, physical, chemical and optical characteristics. AuNPs also support localized surface plasmon resonance (LSPR) unlike bulk gold, which forms as a result of collective oscillation of conduction electrons during electromagnetic excitation. The properties have allowed extensive use in fields like sensing, catalysis, photothermal therapy, drug delivery and nanoelectronics.

To comprehend the essential characteristics of AuNPs, it is necessary to have a more in-depth look at the way in which their behaviour changes at the nanoscale, when classical descriptions are usually not sufficient anymore. Although necessary, experimental methods are often restricted in their capacity to separate the effects of individual factors associated with the particle size, geometry, surface structure and the surrounding environment. Computational and theoretical methods are thus very important in this sense in giving an atom-level and electronic-level description which can be used to supplement experimental data and can be applied in the design of nanoparticles rationally.

Bulk gold is a noble metal that has a clear crystal structure of face-centered cubic (fcc), high electrical conductivity, and inertness. On a nanoscale (below 100 nm) however, the surface-volume ratios start to rise and quantum mechanics cannot be ignored anymore redefining fundamental properties. The behaviour of AuNPs is controlled by size, morphology, stabilizing ligands and the environmental conditions. It is a combination of these factors that control the optical and electronic performance of the particles, which, in most cases, differs substantially with bulk gold or even larger nanoparticles. Recent studies emphasize the fact that the size of particles per se can be used to tune lattice parameters, electronic state density, and frequencies of plasmon resonances, among other features with a significant impact on their potential to find application in technology and science. There are computational studies of AuNPs which cut across a range of theoretical frameworks based on the time scale and length of interest. Optical absorption, scattering and near-field

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enhancement properties have been commonly predicted using classical electromagnetic models, including Mie and Gan's models and their discrete approximations, e.g. finite-difference time-domain and discrete dipole approximation models. But in the case of ultrasmall nanoparticles and clusters quantum mechanical effects dominate and first-principles theories of electronic structure, charge distribution and excitation spectra are accessible using density functional theory (DFT) and time-dependent DFT (TD-DFT). Moreover, molecular dynamics (MD) simulations allow to explore structure of stability, thermal properties, and interactions of nanoparticles with the environment under real-life conditions. Notwithstanding the (large-scale) advances, there are still various issues in the computational modeling of AuNPs, which include high computational cost of quantum mechanical simulations of large systems, realistic representation of surface and ligand effects, as well as multiscale effects (electronic, optical, and thermal) in computational modeling. These are the challenges that must be addressed in order to come up with predictive models that can be depended upon to relate nanoscale structure to macroscopic functionality.

In this work, we report a computational study of gold nanoparticles with the aim of explaining their electronic, optical, structural properties using specific methods, e.g., DFT, MD, FDTD. Through a systematic study of the relationship between size, shape, surface functionalization, or environment], this paper aims to contribute to the theoretical knowledge on the behavior of the AuNP and give some insight based on their experimental implementation and technological use.

2. Structural Properties and Size Dependence

Nanoparticles differ from bulk in terms of surface atom fraction, lattice relaxation and possible strain effects. As the diameter of AuNPs decreases below approximately 10 nm, significant contraction in interatomic spacing have been observed experimentally and have been attributed to mostly finite size effects rather than any ligand induced distortion (ligand effects are secondary). Such a contraction is caused by the heightened stress of the surface and changes in the number of coordination of the surface atoms. Smaller particles are also likely to have wider X-ray diffraction (XRD) peaks (because of the smaller crystalline domain size and greater structural disorder) compared to larger particles (behafarid et al.).

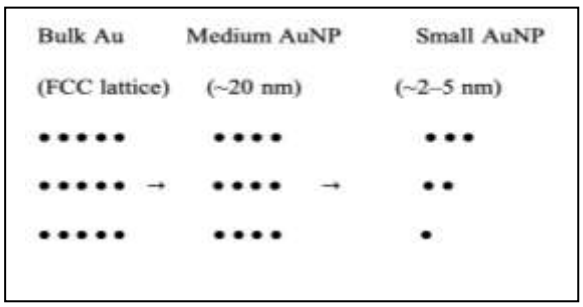

Fig. 1 Size-Dependent Structural Changes in Gold Nanoparticles

Structural stability is modulated by Ligand and support environments. Ultrasmall nanoparticles are stabilized by ligands like polystyrene derivatives and retain close similar interatomic distances to allow systematic examination of intrinsic size effects (e.g. lattice contraction) and not ligand induced deformations. Also, when the particle size is brought small enough, the properties switch to the molecular regimes where discrete atomic packing symmetry is used to determine the structural and physical behaviour. Computationally, this crossover has been developed with respect to cluster symmetry and the number of atoms.

Experimental investigations employing high-resolution transmission electron microscopy (HRTEM), synchrotron X-ray diffraction (XRD), and extended X-ray absorption fine structure (EXAFS) spectroscopy reveal pronounced size-dependent structural evolution in gold nanoparticles. As particle diameter decreases below approximately 10 nm, systematic contraction of the Au–Au bond length is observed, with values decreasing from the bulk distance of ~2.88 Å to ~2.75–2.82 Å for nanoparticles in the 2–5 nm range. XRD peak broadening and reduced coherent domain size confirm increasing lattice disorder, while EXAFS coordination numbers drop significantly, indicating a high fraction of under-coordinated surface atoms. Theoretical modeling and density functional theory (DFT) calculations consistently predict inward relaxation of surface atoms and nonuniform strain fields, with the largest distortions localized at edges and corners. For ultrasmall particles (<5 nm), both simulations and experiments report stabilization of non-fcc motifs such as icosahedral and decahedral structures, reflecting a competition between surface energy minimization and bulk crystalline ordering.

3. Electronic Properties: Quantum Confinement and Size Effects

At particle sizes that are close to the conduction electron mean free path (~40 nm) and beyond, electronic properties of AuNPs change significantly. In very small nanoparticles (under 2-3 nm) quantum confinement results in discrete energy states associated with the electronic structure of molecules, instead of a spectrum associated with bulk metals. Such quantization leads to size effects including variation of the density of states around the fermi level and new electronic gaps. Experimental results indicate that in the case of ligand-stabilized AuNP at approximately 1-4 nm interatomic distance contraction and cluster size is directly coupled with the electronic density profile and electronic structure which have a robust impact on electronic transitions irrespective of the surrounding.

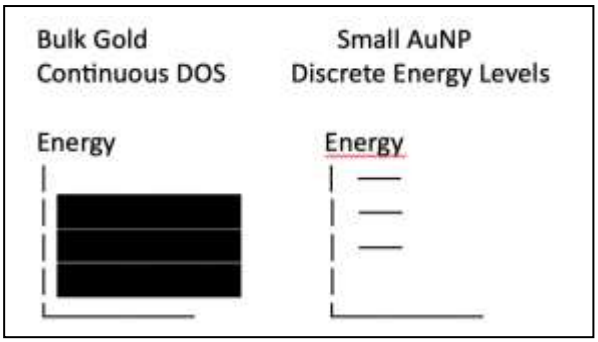

Fig 2. Comparison of electronic density of states (DOS) in bulk gold and ultrasmall gold nanoparticles. Reduction in particle size leads to quantum confinement, transforming continuous bands into discrete energy levels

In larger nanoparticles, although metallic conduction is maintained, the conduction electrons start to suffer increased surface scattering, which would cause size-dependent damping, enlarging electronic energy distributions and altering plasmonic responses. The finite size effects also change the electron mean free path, as well as influence electron-electron and plasmon-electron interaction of the particles and modify the optical and electrical behavior of the particle compared with bulk gold. These modifications are manifested in size-dependent dielectric functions which at higher energies and smaller radii do not follow classical Drude models. The electronic properties of gold nanoparticles exhibit a clear transition from bulk metallic behavior to quantum-confined, molecule-like states as particle size decreases. Scanning tunneling spectroscopy (STS), ultraviolet photoelectron spectroscopy (UPS), and transport measurements show that particles larger than ~20 nm retain a continuous density of states, while nanoparticles in the 3–10 nm range display broadened electronic bands due to enhanced surface scattering. For clusters smaller than ~3 nm, discrete electronic energy levels emerge, with experimentally measured HOMO–LUMO gaps ranging from 0.2 to 1.0 eV and pronounced Coulomb blockade effects in single-particle measurements. These trends are quantitatively consistent with quantum confinement models in which electronic level spacing scales inversely with the square of particle radius. DFT calculations further reveal size-dependent redistribution of charge toward surface atoms, a downward shift of the d-band center by up to ~0.5 eV, and a reduction in work function, all of which strongly influence adsorption energies, charge transfer processes, and catalytic activity at the nanoscale.

4. Optical Properties: Plasmonic and Size Tailoring

Localized surface plasmon resonance (LSPR) - coordinated oscillation of conduction electrons driven by light of a certain frequency is the most examined optical effect in AuNPs. LSPR predominates optical absorption and scattering in particles of the order of 10-100 nm, with very high extinction peaks in visible spectra, whose peak position and width highly depend on size, shape and local dielectric environment. Smaller diameters would also tend to peak plasmonically (blue/red), and widen as a result of the higher electron surface scattering and quantum effects and shorter coherent lifetimes of the electron oscillation. Size-dependent LSPR causes optical colour variations in colloidal solutions of AuNPs; e.g. colloids of < size of about 15-30 nm usually appear red due to strong absorption in the regime of around 520 nm, and alterations in diameter cause the resonance shifting the apparent colour. This tunability is utilized in imaging, optoelectronic and sensing applications. Gold nanoparticles exhibit strongly size-dependent optical properties governed primarily by localized surface plasmon resonance (LSPR). Experimental UV–visible absorption spectra show intense plasmon bands near ~520 nm for nanoparticles around 15–25 nm in diameter, with systematic red-shifting and broadening as particle size increases due to retardation and radiative damping effects. As particle size decreases below ~10 nm, plasmon intensity diminishes and linewidth broadening becomes pronounced, reflecting increased electron–surface scattering and reduced coherence length. Time-resolved spectroscopic studies further demonstrate a reduction in plasmon dephasing times with decreasing size. Classical Mie theory accurately describes the optical response of larger nanoparticles but fails in the ultrasmall regime. Time-dependent density functional theory (TDDFT) calculations show that for clusters smaller than ~3 nm, collective plasmon oscillations vanish and optical absorption spectra become dominated by discrete electronic transitions, marking a clear plasmon-to-molecular crossover that mirrors size-dependent changes in electronic structure

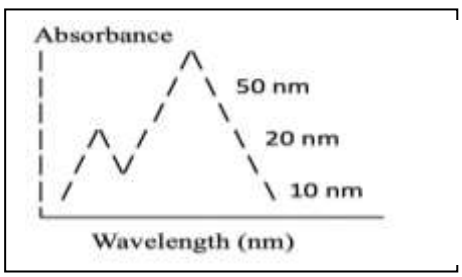

Fig. 3 Schematic UV–Vis absorption spectra of gold nanoparticles with different sizes. Increasing particle size enhances plasmon intensity and shifts the localized surface plasmon resonance (LSPR) peak due to collective oscillation of conduction electrons.

In ultrasmall (less than 3 nm) clusters where the individual plasmonic bands are not discernible, optical responses are controlled by discrete quantized electronic transitions but not by collective longitudinal electron oscillations. These clusters are capable of displaying molecule-like optical spectra with multiple absorption characteristics as opposed to the single broad plasmonic features, which represent the quantum confinement-based level structure. They are of central importance in applications where a high degree of control of electronic transitions is needed: in quantum dots, in nanoscale photonic devices, etc.

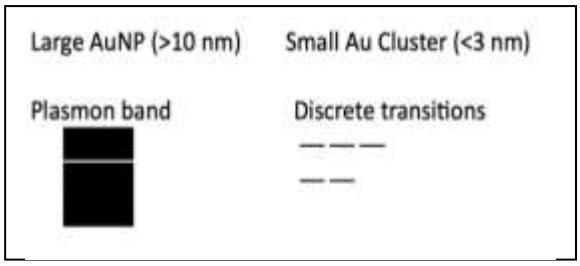

Fig 4. Plasmonic vs Molecular Optical Behavior. Transition from plasmonic behavior in larger gold nanoparticles to molecule-like optical absorption in ultrasmall gold nanoclusters. Below ~3 nm, collective electron oscillations vanish and discrete electronic transitions dominate.

5. Applications and Implications of Size-Dependent Properties

The size-tunable characteristics of AuNPs have been used in various ways:

- Sensing and spectroscopy Strong field enhancements at resonant frequencies in surface-enhanced Raman spectroscopy (SERS).
- Biomedical imaging and therapy: LSPR can be used to provide diagnostics and therapy with optical absorption and photothermal effects being targeted.
- Photovoltaics and optoelectronics: Nanoparticles of size tailoring can be incorporated into equipment to facilitate light collection and transporting of charges.
- Catalysis Catalytic pathways and activation energies in ultrasmall clusters are affected by the modulations of their electronic structures.

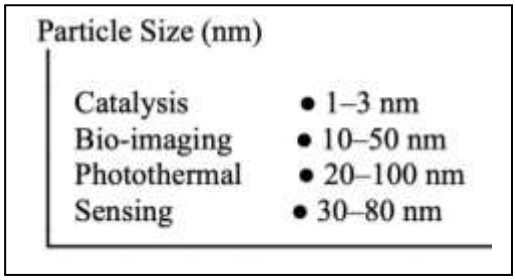

Fig. 5 Application Mapping Based on Particle Size. Different size regimes optimize catalytic activity, plasmonic sensing, imaging, and photothermal effects.

In each application, controlling nanoparticle size (and often shape) is a critical parameter for engineering desired functionality.

6. Conclusion

This review has demonstrated that particle size plays a decisive role in determining the structural, electronic, and optical properties of gold nanoparticles. Experimental studies using X-ray diffraction and high-resolution transmission electron microscopy consistently report lattice parameter contractions of approximately **0.1–1.0%** for particles smaller than **10 nm**, in agreement with density functional theory (DFT) predictions that attribute this contraction to increased surface stress and reduced atomic coordination. Additionally, theoretical calculations show a progressive discretization of electronic energy levels as particle sizes decrease below **~2 nm**, marking the transition from metallic to molecule-like behaviour. Size-dependent optical properties are particularly well documented. Experimentally, spherical gold nanoparticles with diameters of **~20–50 nm** exhibit a localized surface plasmon resonance (LSPR) peak near **520–530 nm**, while particles below **10 nm** show noticeable blue shifts and peak broadening due to enhanced surface damping. Classical Mie theory successfully describes the optical response of larger nanoparticles, whereas quantum-corrected models and time-dependent DFT calculations predict significant deviations for ultrasmall clusters, including reduced plasmon intensity and the emergence of interband-dominated absorption. Reported extinction coefficients and plasmon lifetimes decrease substantially for particles below **5 nm**, consistent with both experimental spectroscopy and theoretical simulations. The close agreement between experimental observations and theoretical models underscores the importance of particle size as a unifying parameter linking structure, electronic states, and optical response. Precise size control enables tuning of LSPR position, electronic density of states, and surface reactivity, which is crucial for applications in catalysis, biosensing, photothermal therapy, and optoelectronics. Nevertheless, challenges remain in achieving mono-

dispersity at the sub-5 nm scale and in fully reconciling discrepancies between idealized theoretical models and real experimental systems. Future research combining advanced synthesis techniques, in situ spectroscopic measurements, and multiscale theoretical approaches will be essential for refining quantitative structure–property relationships. Such efforts will further enhance the rational design of gold nanoparticles with tailored functionalities for next-generation nanotechnological applications.

References

Behafarid, Farzad, et al. "Structural and Electronic Properties of Micellar Au Nanoparticles: Size and Ligand Effects." ACS Nano, vol. 8, no. 7, 2014, pp. 6671–6681, doi:10.1021/nn406568b.

Govorov, Alexander O., et al. "Theory of Plasmonic Nanostructures: From Classical Electrodynamics to Quantum Effects." Chemical Reviews, vol. 115, no. 12, 2015, pp. 6056–6110, doi:10.1021/cr500395x.

Häkkinen, Hannu, et al. "Electronic Structure of Gold Clusters Au_n (n = 2–38)." Physical Review Letters, vol. 93, no. 9, 2004, p. 093401, doi:10.1103/PhysRevLett.93.093401.

Häkkinen, Hannu. "The Gold–Sulfur Interface at the Nanoscale." Nature Chemistry, vol. 4, 2012, pp. 443–455, doi:10.1038/nchem.1352.

Jain, Prashant K., et al. "Review of Some Interesting Surface Plasmon Resonance-Enhanced Properties of Noble Metal Nanoparticles and Their Applications." Chemical Physics Letters, vol. 487, no. 4–6, 2010, pp. 153–164, doi:10.1016/j.cplett.2010.01.062.

Kohn, Walter, and Lu Jeu Sham. "Self-Consistent Equations Including Exchange and Correlation Effects." Physical Review, vol. 140, no. 4A, 1965, pp. A1133–A1138, doi:10.1103/PhysRev.140.A1133.

Kreibig, Uwe, and Michael Vollmer. Optical Properties of Metal Clusters. Springer, 1995.

Link, Stephan, and Mostafa A. El-Sayed. "Size and Temperature Dependence of the Plasmon Absorption of Colloidal Gold Nanoparticles." Journal of Physical Chemistry B, vol. 103, no. 21, 1999, pp. 4212–4217, doi:10.1021/jp984796o.

NanoComposix. "Gold Nanoparticles: Optical Properties." NanoComposix, 2023, [www.nanocomposix.com/pages/gold-nanoparticles-optical-properties]

Negishi, Yuichi, et al. "Magic-Numbered Au_n Clusters Protected by Thiolate Ligands." Journal of the American Chemical Society, vol. 126, no. 21, 2004, pp. 6518–6519, doi:10.1021/ja048372m.

Perdew, John P., et al. "Generalized Gradient Approximation Made Simple." Physical Review Letters, vol. 77, no. 18, 1996, pp. 3865–3868, doi:10.1103/PhysRevLett.77.3865.

Scholl, Jonathan A., et al. "Quantum Plasmon Resonances of Individual Metallic Nanoparticles." Nature, vol. 483, 2012, pp. 421–427, doi:10.1038/nature10904.

Wilcoxon, Jess E., et al. "Optical Properties of Gold Nanoclusters." Journal of Chemical Physics, vol. 108, no. 21, 1998, pp. 9137–9143, doi:10.1063/1.476340.

Yoon, Bokwon, et al. "Charging Effects on Bonding and Catalyzed Oxidation of CO on Au_8 Clusters on MgO." Science, vol. 307, no. 5708, 2005, pp. 403–407, doi:10.1126/science.1104160.

Zuloaga, Jorge, et al. "Quantum Description of the Plasmon Resonances of a Nanoparticle Dimer." Nano Letters, vol. 9, no. 2, 2009, pp. 887–891, doi:10.1021/nl803843g.