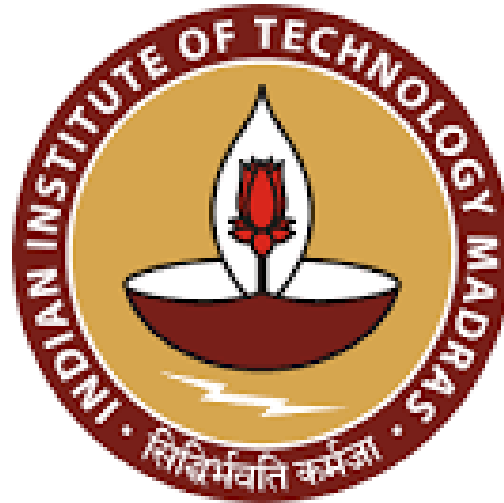


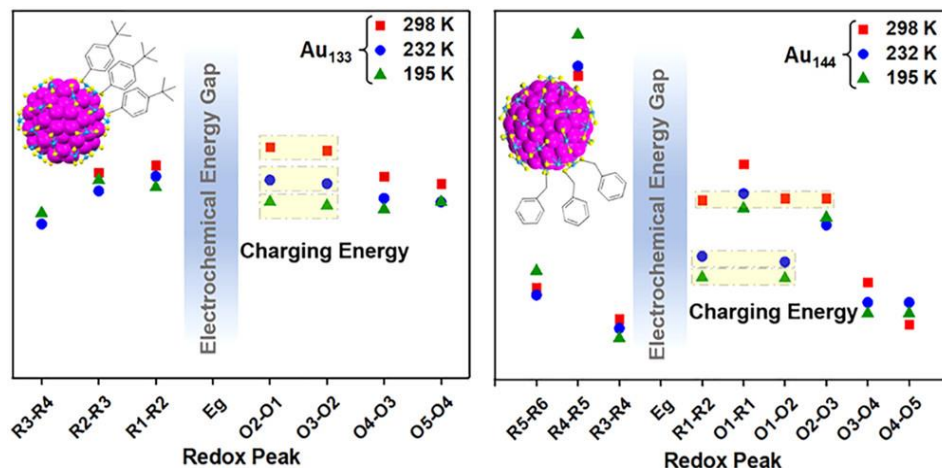
Paper Presentation



Sooraj B S
20-02-2021

Inhomogeneous Quantized Single-Electron Charging and Electrochemical–Optical Insights on Transition-Sized Atomically Precise Gold Nanoclusters

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Publication date: 10 Nov 2020

Why this paper?

- Small differences in electronic structures, such as an emerging energy band gaps or the splitting of degenerated orbitals, are very challenging to resolve but important for nanomaterials properties
- A signature electrochemical property called quantized double layer charging, i.e., “continuous” one electron transfers (1e, ETs), in atomically precise $\text{Au}_{133}(\text{TBBT})_{52}$, $\text{Au}_{144}(\text{BM})_{60}$ and $\text{Au}_{279}(\text{TBBT})_{84}$ are analysed to reveal the nonmetallic to metallic transitions
- This demonstrates an approach of combined electro spectroscopy analysis, together with temperature variations, as a powerful tools to reveal subtle differences and gain insights into nanomaterials.

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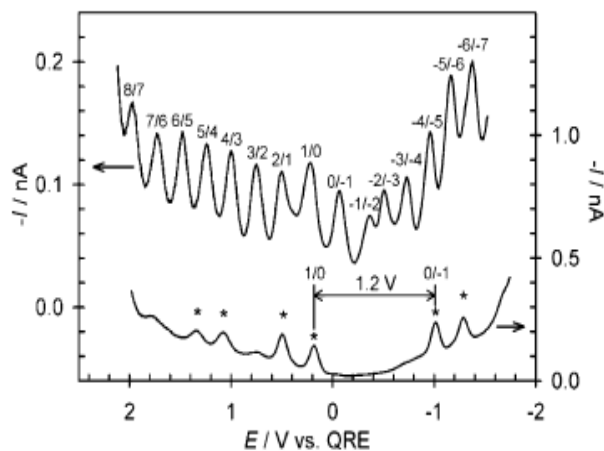
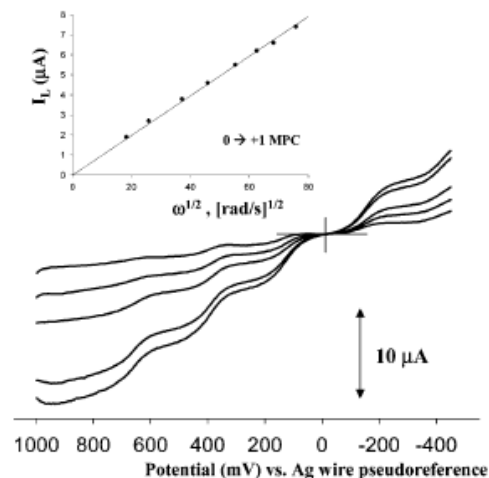
Published on Web 10/12/2002

Quantized Double-Layer Charging of Highly Monodisperse Metal Nanoparticles

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Received July 16, 2002



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COMMUNICATIONS

Published on Web 05/10/2003

Electrochemical Resolution of 15 Oxidation States for Monolayer Protected Gold Nanoparticles

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Introduction

- Metal nanoclusters (NCs) differ from regular nanoparticles with ultras-small sizes and thus more prominent quantum effects.
- The existence of an energy band gap would be a more fundamental and quantitative descriptor for metal nanoclusters over larger nanomaterials of the same metal.
- The dependence of band gap on the composition or structure are fundamentally significant and have broad implications to various electrochemical, optical, and other properties.
- The determination of small energy differences and how the energy states change under reaction conditions, especially in the transition-size range from nanoclusters to larger nanomaterials, is challenging experimentally.
- Resolving small energy differences in transition-sized nanoclusters, however, is complicated by a signature electrochemical behavior called quantized double layer (QDL) charging initially observed from Au nanoclusters.

- The Au nanoclusters are the most studied prototype, which are composed of an Au core stabilized by a monolayer of thiolate ligands
- The QDL results from continuous or multiple one-electron transfer reactions (1e ETs) when the nanoclusters are considered as nanosized capacitors
- Depending on the core and ligands, the charging energy needed for 1e ETs would be constant assuming that the capacitance remains constant, and thus display “uniformly spaced” peaks in current–potential plots
- Polydispersity of sample, which causes the capacitance and thus the charging energy to vary
- Thus atomically precise NCs are critically needed in order to gain insights into the fine features of QDL.

Results

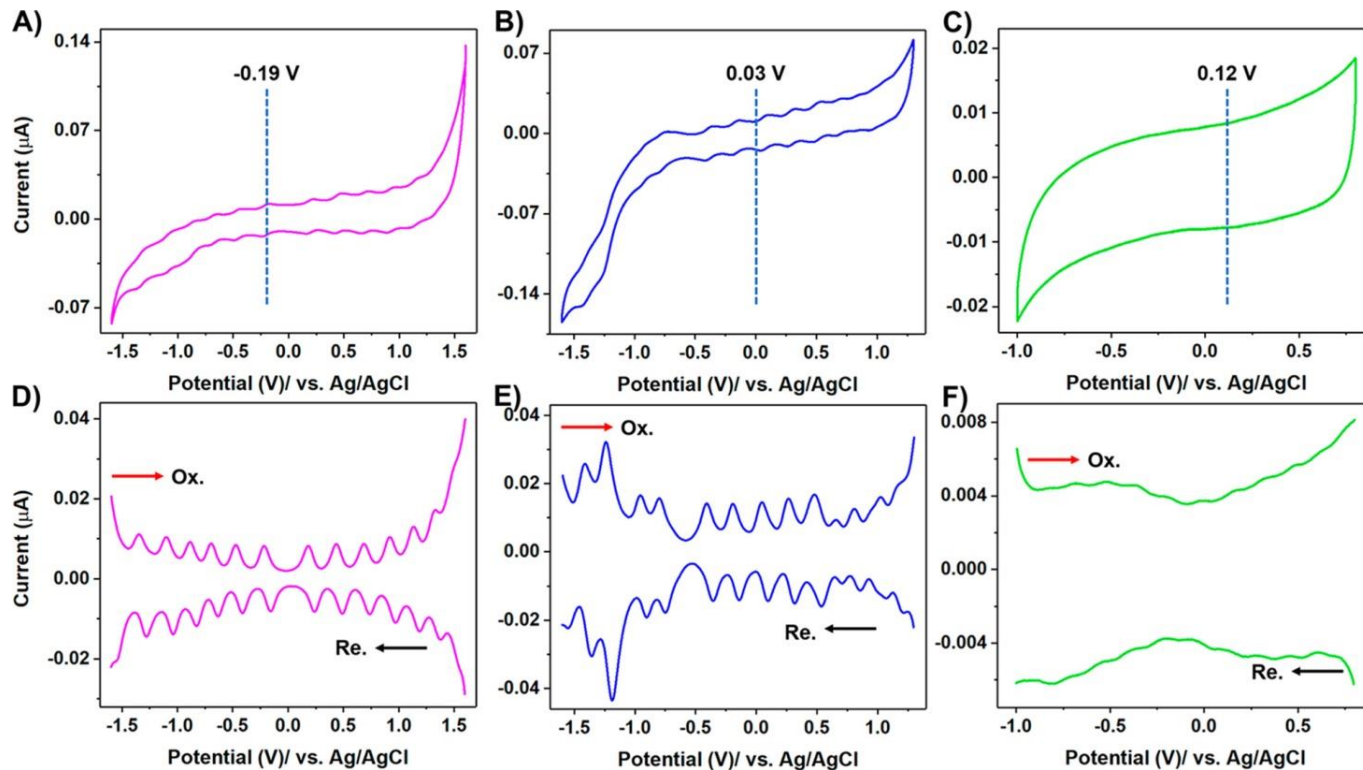


Fig. 1: CVs (A–C) and DPVs (D–F) of Au₁₃₃, Au₁₄₄, and Au₂₇₉. The potential scan rate in CV is 0.1 V/s. All experiments were performed at 298 K except for the DPV of Au₂₇₉ that is at 232 K.

- The CV of Au₂₇₉ is smooth and featureless, as opposed to the stepwise quantized one-electron QDL charging in the two smaller NCs
- The energy gap of Au₂₇₉ cannot be determined from these electrochemical analysis

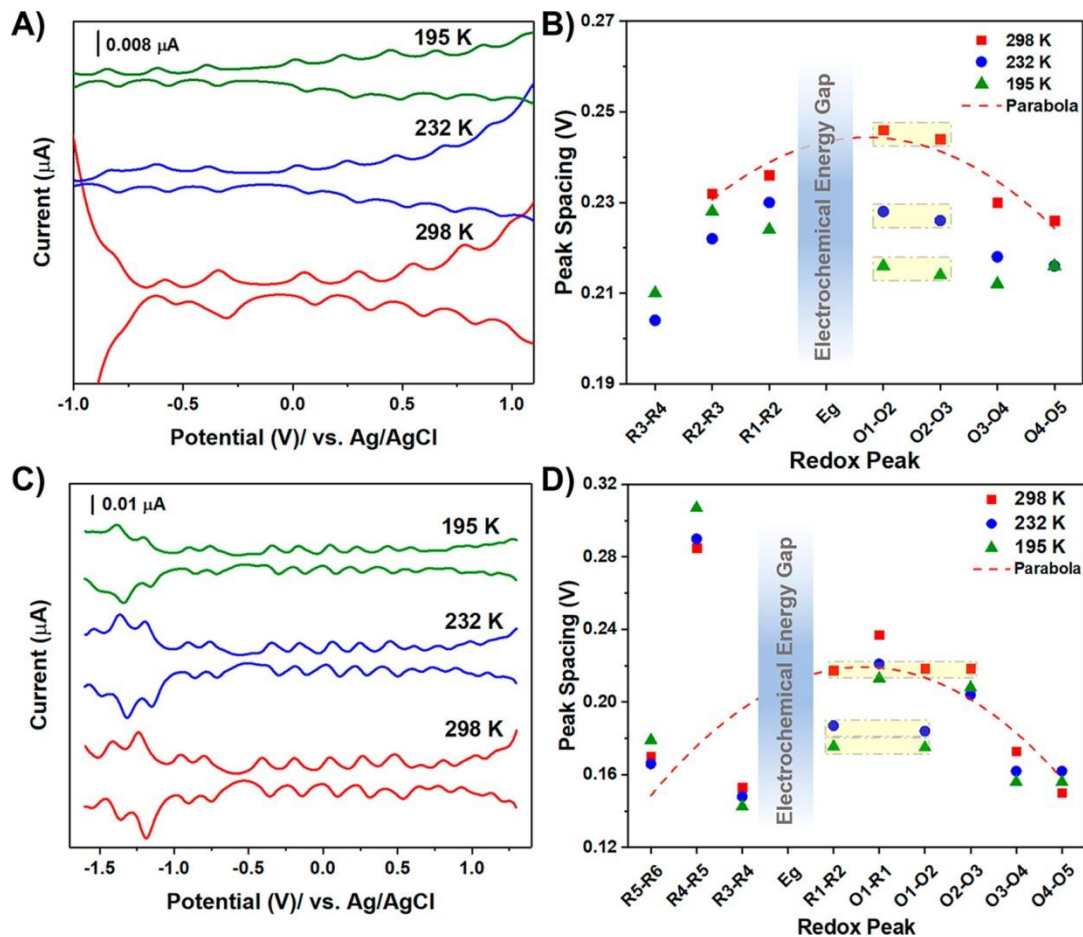


Fig. 2: Temperature dependence of electrochemical properties of Au₁₃₃ and Au₁₄₄. The DPVs of (A) Au₁₃₃ and (C) Au₁₄₄ at 298, 232, and 195 K.

➤ The subtle differences among ΔV s and their temperature dependence are revealed in panels B and D. This electrochemical gap is attributed to the energy gap between “HOMO–LUMO” frontier states plus charging energy

➤ In Au₁₃₃, the peak spacing ΔV displays a parabolic shape from the energy gap toward higher potentials (positive and negative), corresponding to the gradual and slight decrease in charging energy in more oxidized/reduced states

➤ In Au₁₄₄ peak spacing ΔV s vary almost in an alternative high–low manner, corresponding to consecutive pairs of redox peaks. The oscillatory pattern suggests small splitting of degenerated orbitals/energy states assuming the charging energy remains constant

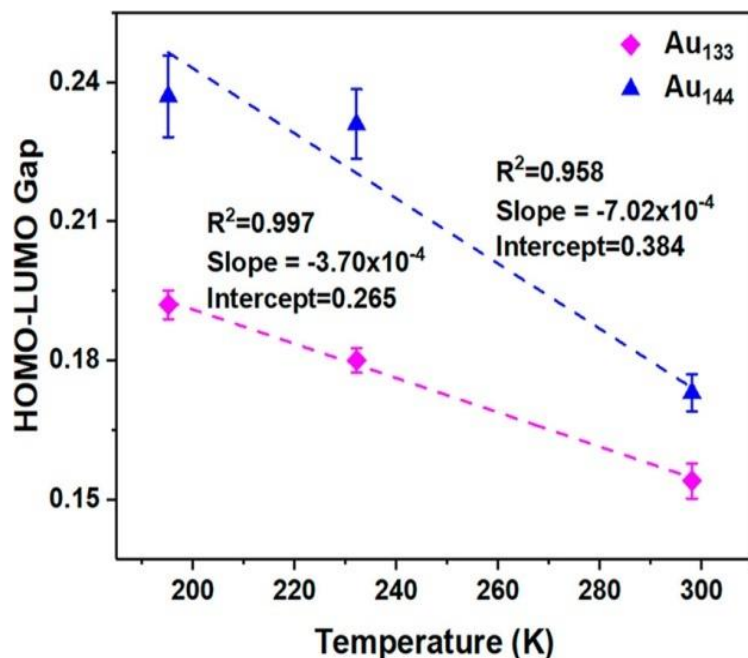


Fig. 3: HOMO–LUMO gaps of Au₁₃₃ (pink) and Au₁₄₄ (blue) at 298, 232, and 195 K. Dashed lines are fitting. The error bar represents the standard deviation of the average charging energy.

➤ The HOMO–LUMO gap of Au₁₄₄ is larger than that of Au₁₃₃, 0.173 eV versus 0.154 eV at room temperature

➤ The difference increases at lower temperatures, to 0.237 eV versus 0.192 eV at 195 K. The hollow center in the core atomic structure of Au₁₄₄ is believed responsible for the larger HOMO–LUMO gap of Au₁₄₄

➤ The enthalpy and entropy portions in the Gibbs free energy changes of the electron transfer reaction of Au₁₃₃ and Au₁₄₄ can be estimated from the intercept and slope of the linear fitting of HOMO–LUMO gap at different temperatures

➤ The higher enthalpy is attributed to the structure differences in Au₁₄₄. The larger entropy is explained by the short and more flexible ligands

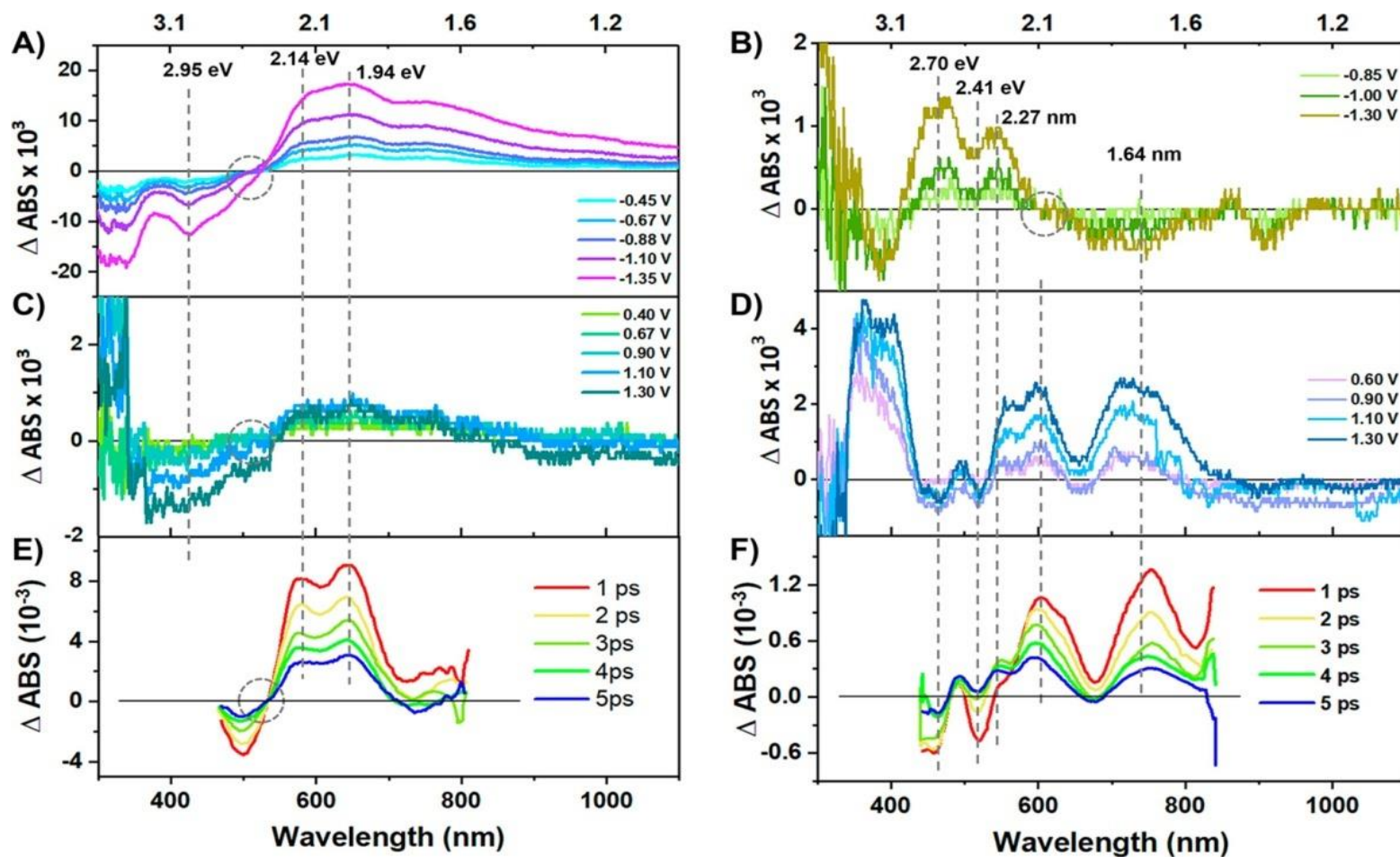


Fig. 4: Absorption changes of Au_{133} (left, A, C, and E) and Au_{144} (right, B, D, and F) in spectroelectrochemistry and ultrafast spectroscopy. ΔABS calculated by subtraction with the original spectrum. Panels A and B are after reductive electrolysis and panels C and D after oxidative electrolysis by spectroelectrochemistry. The denoted potentials are the valleys in DPV. Panels E and F are transit absorption spectra.

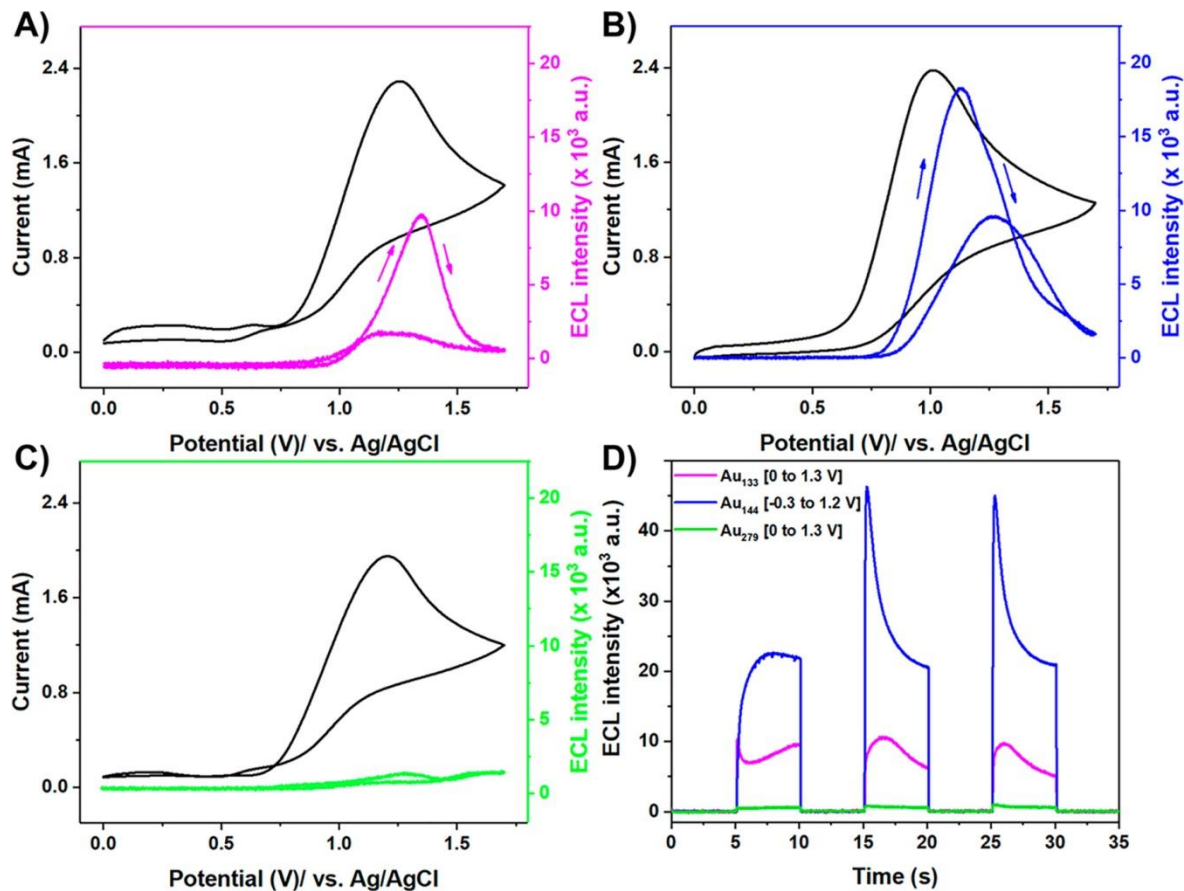


Fig. 5: ECL of Au₁₃₃, Au₁₄₄, and Au₂₇₉ under potential scanning A, Au₁₃₃, B, Au₁₄₄, C, Au₂₇₉; and potential step activations (D).

- Luminescence occurs when the excess energy, from either oxidation or reduction with optional following reactions, is released via radiative decay.
- The prominent current features such as the oxidation current peak of 1.2 V are dominated by the TPrA co-reactant
- While all are weak, the ECL from Au₂₇₉ is practically non-existent, which further confirms the continuous electronic energy state or innate metallic character.

Conclusions

- Energy differences at <0.1 eV resolution under charge transfer conditions are determined in three Au nanoclusters spanning the transition from molecular to metallic state
- Discrete energy states in Au₁₃₃ and Au₁₄₄ nanoclusters and more continuum redox behaviors of metallic Au₂₇₉ are revealed by scanning and pulse voltammetric analyses at different temperatures
- The more rigid and thicker ligand monolayer on Au₁₃₃ imposes stronger steric hindrance toward bulkier counterions, therefore less changes in relative permittivity and thus double layer capacitance or charging energy
- Spectroelectrochemistry is used to demonstrate a combined approach to analyze steady-state and transient spectral features under charge transfer conditions
- Such combined approach for combined electro spectroscopic understanding will help to explore the physicochemical properties on other nanoclusters