

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

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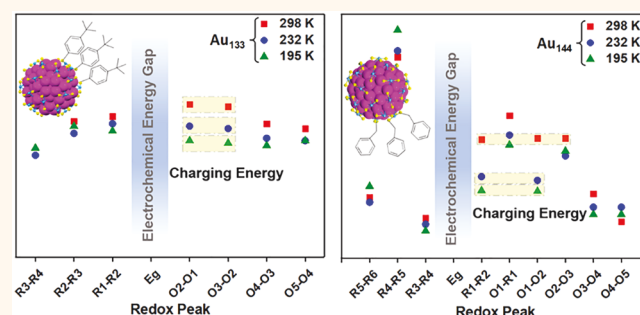
Supporting Information

ABSTRACT: 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 Au₁₃₃(TBBT)₅₂, Au₁₄₄(BM)₆₀, and Au₂₇₉(TBBT)₈₄ is analyzed to reveal the nonmetallic to metallic transitions (whereas TBBT is 4-*tert*-butylbenzenethiol and BM is benzyl mercaptan; abbreviated as Au₁₃₃, Au₁₄₄, and Au₂₇₉). Subhundred milli-eV energy differences are resolved among the “often-approximated uniform” peak spacings from multipairs of reversible redox peaks in voltammetric analysis, with single ETs as internal standards for calibration and under temperature variations. Cyclic and differential pulse voltammetry experiments reveal a 0.15 eV energy gap for Au₁₃₃ and a 0.17 eV gap for Au₁₄₄ at 298 K. Au₂₇₉ is confirmed metallic, displaying a “bulk-continuum” charging response without an energy gap. The energy gaps and double layer capacitances of Au₁₃₃ and Au₁₄₄ increase as the temperature decreases. The temperature dependences of charging energies and HOMO–LUMO gaps of Au₁₃₃ and Au₁₄₄ are attributed to the counterion permeation and the steric hindrance of ligand, as well as their molecular compositions. With the subtle energy differences resolved, spectroelectrochemistry features of Au₁₃₃ and Au₁₄₄ are compared with ultrafast spectroscopy to demonstrate a generalizable analysis approach to correlate steady-state and transient energy diagram for the energy-in processes. Electrochemiluminescence (ECL), one of the energy-out processes after the charge transfer reactions, is reported for the three samples. The ECL intensity of Au₂₇₉ is negligible, whereas the ECLs of Au₁₃₃ and Au₁₄₄ are relatively stronger and observable (but orders of magnitudes weaker than our recently reported bimetallic Au₁₂Ag₁₃). Results from these atomically precise nanoclusters also demonstrate that the combined voltammetric and spectroscopic analyses, together with temperature variations, are powerful tools to reveal subtle differences and gain insights otherwise inaccessible in other nanomaterials.

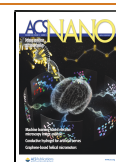
KEYWORDS: nanoclusters, quantized double layer (QDL) charging, spectroelectrochemistry, ultrafast, electrochemiluminescence (ECL), charging energy, energy gap

Metal nanoclusters (NCs) differ from regular nanoparticles with ultrasmall sizes and thus more prominent quantum effects, and with definitive atomic compositions and structures built on recent advances in the syntheses and characterizations.^{1,2} From the perspective of properties, one might argue that 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.^{3,4} Whether a band gap exists and how it is dependent on the composition/structure are fundamentally significant and have broad implications to various electro-

chemical, optical, and other properties. However, determining small energy differences and how the energy states change under reaction conditions, especially in the transition-size



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range from nanoclusters to larger nanomaterials, is challenging experimentally.

Electrochemical techniques are intrinsically suitable to measure charge transfers and related energy states/orbitals by direct oxidation or reduction at a specific orbital/energy state *via* electrode reactions. 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.^{5,6} The Au nanoclusters are the most studied prototype, also referred to as monolayer protected clusters (MPCs) in earlier literature, which are composed of an Au core stabilized by a monolayer of thiolate ligands.^{3,7,8} The QDL results from continuous or multiple one-electron transfer reactions (1e ETs) when the nanoclusters are considered as nanosized capacitors. With the capacitance in the atto-Farad range depending on the core and ligands, the charging energy needed for 1e ETs would be constant (at about hundred(s) of milli-eV) assuming that the capacitance remains constant, and thus display “uniformly spaced” peaks in current–potential plots.^{9–11} Although inhomogeneity in QDL peak spacing was noticed long ago, significant insight such as the existence of small energy gap(s) could not be determined due to the previously inevitable sample polydispersity, which causes the capacitance and thus the charging energy to vary.^{12–14} Therefore, atomically precise NCs are critically needed in order to gain insights into the fine features of QDL.

Unlike pure metals or naked clusters, ligand effects on the overall energy diagram can no longer be ignored especially when ligands are covalently attached to metal cores in nanoclusters.^{15–20} An exemplary case is the significant contributions from sulfur atomic orbitals to the energy states of Au-thiolate clusters revealed by superatom theory.^{20,21} In general, the energy gap increases with the decrease in size, though it also depends on atomic structures. Currently, discrepancies in the literature dispute such a trend of monotonous dependence in the nonmetal to metal transition range. Au₂₄₆(p-MBT)₈₀ is shown to be the largest nonmetallic nanocluster in the quantum size regime to date, whereas Au₃₂₉(PET)₈₄ is found to have no obvious electrochemical gap and being metallic.^{22–24} Furthermore, Au₂₇₉(TBBT)₈₄ is determined to be metallic by transient absorption spectroscopy but electrochemistry analysis is still absent.^{25,26} An abnormal case is the electrochemical properties of Au₁₃₃(TBBT)₅₂ reported by Dass and co-workers, in which no electrochemical energy gap in Au₁₃₃ was identified.²⁷ The same report analyzed Au₁₄₄(PET)₆₀ and showed a clear ~0.37 V peak spacing.^{27,28} Theoretical analyses on Au₁₄₄ and similar-sized Au₁₄₆ also showed small gaps.^{29,30} Further, the similar-sized Au₁₃₀ exhibits a clear ~0.45 and 0.50 V voltammetric peak spacing with monothiol ligands^{31,32} and ~0.35 V with mixed mono- and dithiol ligands in earlier work.³³ With the increasing availability of atomic structures and compositions of nanoclusters, density functional theory calculations provide energy diagrams with great detail; meanwhile, experimental probing and confirmation of theory would be highly desirable, ideally in both energy levels and density of states, at least semiquantitatively.^{34–36} Electrochemical characterizations at subhundred milli-eV, the energy range of electronic transitions overlapping with nuclear vibrations, remain scarce and challenging. The correlation and validation of energy diagram with structures in the nanocluster-to-nanoparticle transition regime would provide much needed

guidance on the design and development of the fast-growing atomically precise nanoclusters and other relevant materials.

In this report, well-defined Au₁₃₃, Au₁₄₄, and Au₂₇₉ NCs (atomic structures shown in Figure 1, steady-state UV–visible

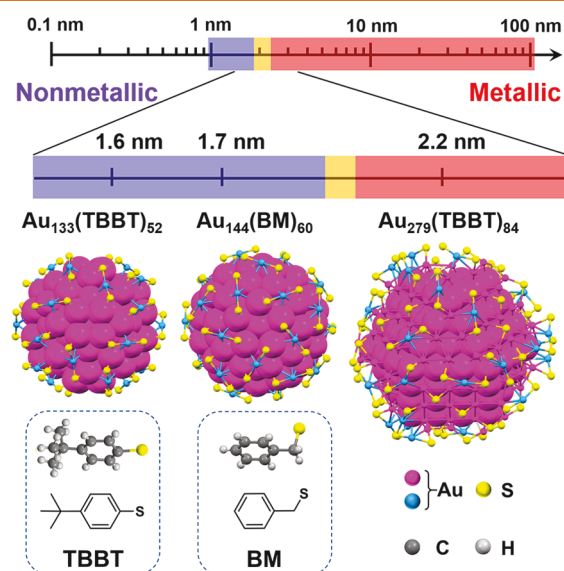


Figure 1. Structures of Au₁₃₃, Au₁₄₄, and Au₂₇₉ and size transition from nonmetallic molecule-like to metallic nanoparticles.

absorption spectra in Supporting Information Figure S1) are chosen to demonstrate how to achieve subhundred milli-eV resolution in electrochemical analysis, to reconcile the apparent discrepancy in the qualitative trend of the transition from molecular-like nanoclusters with discrete orbitals to larger nanoparticles with band structure, and to demonstrate a generalizable approach to correlate steady-state and transient spectroscopic features under related charge transfer conditions.

RESULTS AND DISCUSSION

Basic Voltammetry Features. Electrochemical properties of the Au₁₃₃, Au₁₄₄, and Au₂₇₉ NCs characterized by cyclic and differential pulse voltammetry (CV and DPV) are summarized in Figure 2. Twelve pairs of quantized double layer (QDL) charging peaks are identified in Au₁₃₃. The consistent 59 mV potential difference between each pair of reduction and oxidation QDL peaks indicate facile and reversible electron transfer (ET) for the core charging/discharging activities. In other words, the Au NCs are chemically stable and the corresponding energy states are not shifted upon the ET reaction. The ET reversibility is further confirmed by the independence of peak positions at higher scan rates shown in Figure S2. In Au₁₄₄, about 13 pairs of QDL redox peaks are observed in the mid-potential range. Toward more negative potentials, the cathodic CV current at above −1 V is much higher than the one-electron QDL current (about 8 times herein). Though under thorough purging and stringent controls for consistency in analyzing different samples, residual oxygen might still contribute to this current and affect the quantitation. Similar to the Au₁₃₃, the reversible ET of this QDL charging is confirmed by the consistent 60 mV peak separations of each redox pair that remain unchanged at higher scan rates (Figure S3). The CV of Au₂₇₉ is smooth and featureless, as opposed to the stepwise quantized one-electron QDL charging in the two smaller NCs. The two current

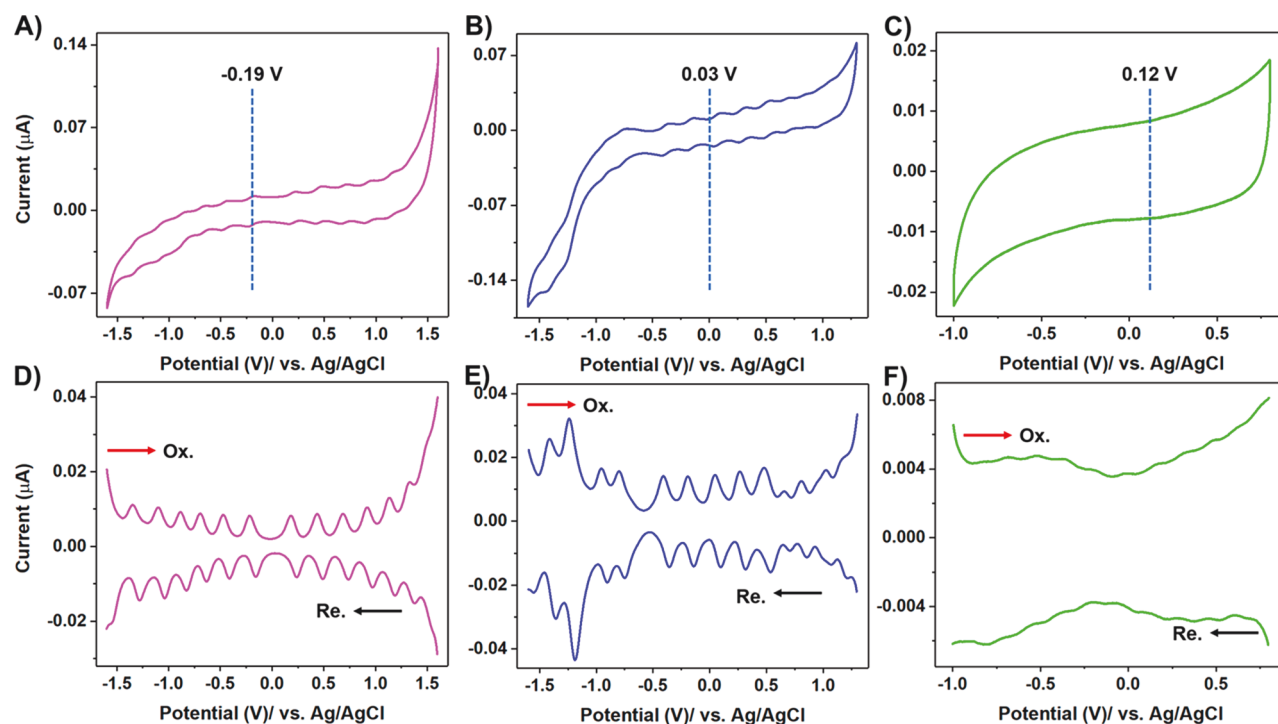


Figure 2. CVs (A–C) and DPVs (D–F) of Au₁₃₃ (A and D, pink lines), Au₁₄₄ (B and E, blue lines), and Au₂₇₉ (C and F, green lines). The concentration of Au NCs is *ca.* ~1 mM in DCM with 0.1 M TBAP (tetra-*n*-butylammonium perchlorate). The potential scan rate in CV is 0.1 V/s. All experiments were performed at 298 K except for the DPV of Au₂₇₉ that is at 232 K. Red arrows are oxidation scans, and black arrows are reduction scans in DPVs. The dashed lines indicate the rest potentials of Au₁₃₃, Au₁₄₄, and Au₂₇₉ at −0.19, 0.03, and 0.12 V, respectively.

branches are largely in parallel, which is characteristic of normal capacitive charging, or “bulk-continuum” (double layer) capacitor behaviors. The “bulk” nature of Au₂₇₉ is qualitatively consistent with the concentric sphere model in which a large core or capacitance would cause the peak spacing or charging energy to decrease, and thus harder to resolve experimentally. The stability of all three NCs during the voltammetric measurements is also supported by the insignificant changes in the UV–vis absorption spectra before and after the voltammetric measurements (Figure S4).

Differentiating Charging Energy from Different Energy States or Shift/Splitting. The peak positions and minor irregularities among the peak spacing (ΔV) are better resolved in the corresponding DPV results. The ΔV values determined from both oxidation and reduction DPVs are highly consistent (within about ± 4 mV) listed in Table S1. For Au₁₃₃, a much larger 0.40₀ V gap is clearly discernible, between the oxidation and reduction peaks at 0.184 V (O1) and −0.216 V (R1), among the otherwise more uniform peak spacings. As for Au₁₄₄, two pairs of cathodic peaks can be seen at around −1.2 and −0.8 V, separated by a 0.39₁ V gap from five highly uniform QDL peaks on the positive direction. QDL (10 pairs) features can only be resolved from the Au₂₇₉ at lower temperature (232 K) by DPV explained further below. The peak spacing ΔV s are highly uniform (ΔV s in the range of 0.16₄–0.17₄ V). Although single millivolt resolution can be read from the measured data, the subten mV difference is within the broadening by Boltzmann distribution and further limited by the pulse height (50 mV). In other words, the energy gap (if any) of Au₂₇₉ cannot be determined from these electrochemical analyses.

Next, we scrutinize the irregularities in the peaking spacing ΔV s to resolve different energy states. By identifying more

uniform ΔV or charging energy as internal standard, a resolution of lower tens milli-eV can be achieved to differentiate energy states/orbitals because thermal agitation and other measurement limitations are the same within a data set. The DPVs of Au₁₃₃ and Au₁₄₄ collected at different temperatures are analyzed in Figure 3. The subtle differences among ΔV s and their temperature dependence are revealed in panels B and D by excluding the much larger ΔV of 0.39–0.40 V. 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 (Figure 3B and Figure S5). The trend is consistent with the counterion permeation model in which permeation or intercalation of electrolyte ions would increase the relative permittivity of the ligand monolayer and thus the QDL compact capacitance ($C = 4\pi\epsilon_0\epsilon \frac{r(r+d)}{d}$, where ϵ is the dielectric constant or relative permittivity of the dielectric layer of a capacitor, *i.e.*, the ligand monolayer; ϵ_0 the permittivity of free space; and r the core radius and d the monolayer thickness).^{37,38} For one-electron transfer processes, the double layer capacitances (C_{CLU}) is correlated to the peak spacing ΔV and unit charge e by the equation: $\Delta V = e/C_{\text{CLU}}$.³ The smaller ΔV s at lower temperatures correspond to an increase in QDL capacitance which is explained by the increase in the ϵ of hydrocarbon monolayer (“oil”). Also shown in the individual temperature plots in Figure S5, the parabola shape flattens at lower temperature and can no longer be resolved at 195 K. The phenomenon is explained by the weakened ion/solvent

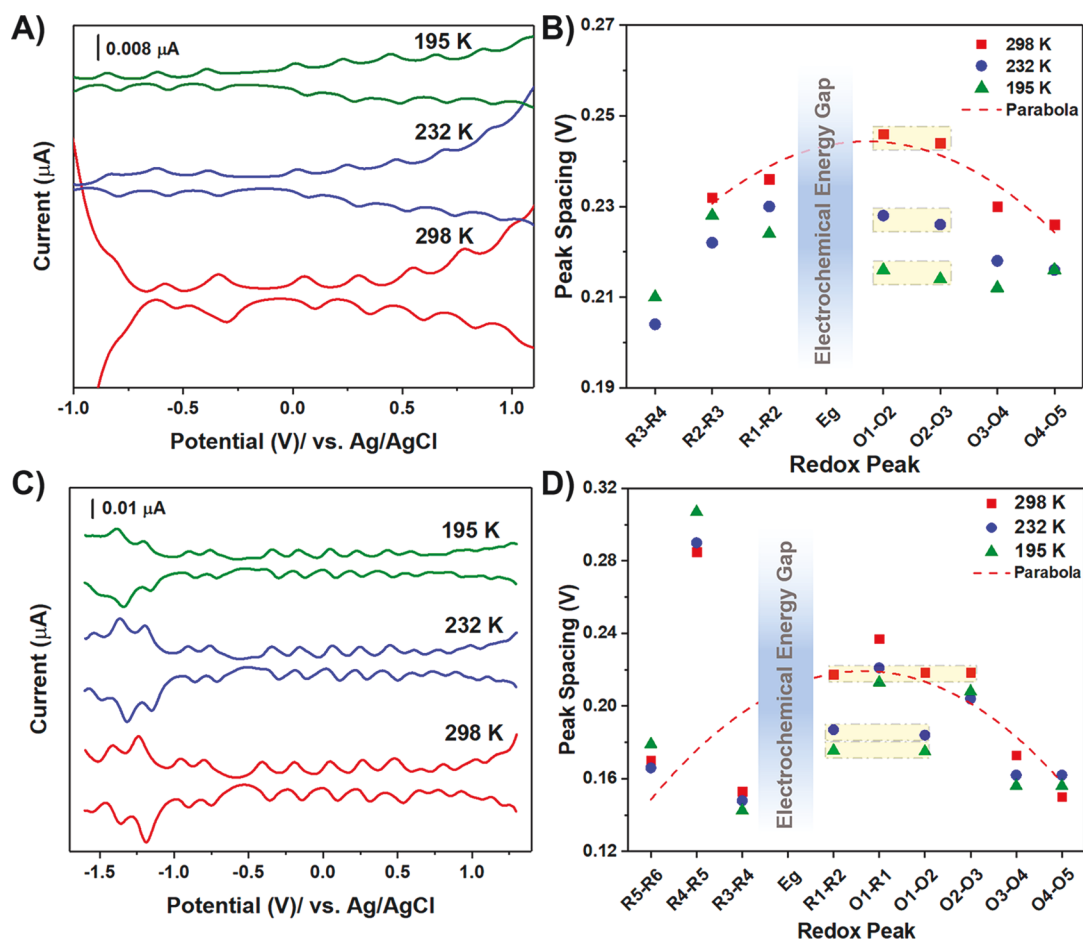


Figure 3. Temperature dependence of electrochemical properties of Au₁₃₃ and Au₁₄₄. The DPVs of (A) Au₁₃₃ and (C) Au₁₄₄ at 298, 232, and 195 K. Peak spacing ΔVs analyzed (B and D), respectively.

permeation, *i.e.*, decreased molecular motion at lower temperatures.

Interestingly, the charging energy is much less sensitive to temperature variations in the reduced states *versus* the oxidized Au₁₃₃ NCs. Given the ϵ of hydrocarbon monolayer being a function of ligand numbers, ligand molecular structures determining the conductivity and dielectric layer thickness (d), and ion/solvent permeation/intercalation *etc.*, we attribute the asymmetric response (oxidation *versus* reduction) to the steric hindrance on counterion permeation: the tetrabutylammonium cations are a lot bulkier than perchlorate anions to access the core stabilized by a bulky *tert*-butyl terminal functionality. The relatively larger decrease in charging energy of the oxidized NCs at lower temperatures is explained by the compact capacitance changes affected by different extent of solvent/counterion permeation accordingly. The leveling behavior of low oxidation states at lower temperatures (compared to higher oxidation states) seems to suggest a threshold for ion/solvent permeation, which is reasonably expected for a given monolayer “free volume”. With less counterion effects in reduced states, the weaker temperature dependence of the charging energy can arise from two factors: the ϵ of hydrocarbon monolayer or the diffuse layer capacitance.¹⁴ The results highlight that an accurate discrimination of different energy states at *ca.* sub-100 meV resolution should use the appropriate charging energy at the specific charge states and conditions, rather than the average values as widely adopted. Accordingly, the average ΔV from the points

near the energy gap (Figure 3B and Figure S5, highlighted by yellow rectangle) is adopted as charging energy for the analysis of energy band gap.

The benzyl mercaptan monolayer on Au₁₄₄ is thinner without the bulky *tert*-butyl portion and more flexible with the CH₂ group. With similar core diameter compared to Au₁₃₃, larger capacitance or smaller ΔVs are measured as expected. The peak spacing ΔVs 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. Besides the large gap at 0.39₁ eV, the next notable gap of 0.28–0.32 eV separates a pair of peaks above the energy gap, *i.e.*, “LUMO”, from higher energy states. The rest splitting between the highs to the next lows is about 0.04 eV or larger, with values listed in Table S1. The ΔVs at different temperatures display no clear pattern or difference between oxidation *versus* reduction, suggesting less discrimination against electrolyte ions of this thinner/leak monolayer.³⁷ Ignoring the oscillatory pattern and the two obvious gaps, a parabolic shape can still be argued centered at the rest potential (0.03 V), instead of between the energy gap in the case of Au₁₃₃ (Figure 3D and Figure S6). The results suggest two vacancies in the degenerated HOMO frontier orbital set. Following the trend established in Au₁₃₃ and in reference to the ΔVs at higher potentials (O3/O4, O4/O5, and R5/R6), the ΔV as highlighted is adopted to charging energy (Figure 3D and Figure S6, highlighted by yellow rectangle) to calculate the

energy gap and to discriminate the splitting of orbitals/states. To further confirm the more complex patterns of the Au₁₄₄, the BM ligands were substituted with the bulky TBBM (TBBM is *P-tert-butyl benzyl mercaptan*) *via* ligand exchange, which is a nontrivial task. All main redox features are retained, including the two gaps and the oscillatory ΔV s (Figures S7–S9). The determined charging energy is about 30 meV higher consistently with the added *tert*-butyl layer at each temperature, which gives a larger monolayer thickness and thus smaller capacitance or slightly larger ΔV s. However, the discrimination of counterions, cations upon oxidation and anions upon reduction, was not as obvious compared to Au₁₃₃. Apparently the extra CH₂ group in TBBM made the monolayer more flexible and leakier than TBBT ones.

The highly uniform samples allow us to interpret the irregularities in the ΔV s at resolution. The broadening effects by Boltzmann distribution can be evaluated by the width of half-maximum ($W_{1/2}$) of DPV peaks following the equation for the one-electron process: $W_{1/2} = 3.52RT/F$, where R is the gas constant and F the Faraday constant. $W_{1/2}$ is predicted theoretically to be 90, 70, and 62 mV at 298, 232, and 195 K, respectively, though practical parameters such as pulse height (50 mV) can further broaden the redox peaks and lower the resolution. While baseline separation is not necessary in DPV to determine the peak positions, a value larger than one for the parameter of $\Delta V/2W_{1/2}$, that being the resolution between two neighboring peaks with comparable $W_{1/2}$, confirms the accurate determination of the peak spacings. From the experimentally measured $W_{1/2}$ at different temperatures (Table S2), any irregularities more than 20–30 mV can be resolved to reflect the properties of the sample.

Energy Gap between Frontier Orbitals/States. The values of charging energy used, the calculated capacitance, and energy gap are listed in Table 1. Those results at different

Table 1. Electrochemical Characterizations of Au₁₃₃ and Au₁₄₄ at 298, 232, and 195 K^a

Temp. (K)	ΔV (V)	C_{CLU} (aF)	$\ln C_{\text{CLU}}$	E_g (V)	HOMO–LUMO gap (eV)
Au ₁₃₃					
298	0.24 ₆	0.65	−0.43	0.40 ₀	0.15 ₄
232	0.22 ₈	0.70	−0.36	0.40 ₈	0.18 ₀
195	0.21 ₆	0.74	−0.30	0.40 ₈	0.19 ₂
Au ₁₄₄					
298	0.21 ₈	0.73	−0.31	0.39 ₁	0.17 ₃
232	0.18 ₅	0.86	−0.15	0.41 ₆	0.23 ₁
195	0.17 ₇	0.90	−0.11	0.41 ₄	0.23 ₇

^aThe single mV digit is listed to demonstrate the uncertainty of the calculated capacitance and band gap (one less significant figures). ΔV is the appropriate peak spacing determined from Figure 3, C_{CLU} is the double layer capacitance, and E_g is the electrochemical energy gap (HOMO–LUMO gap plus ΔV).

temperatures from the two samples, though not large, are statistically different. Of note, no electrochemical gap was resolved/claimed for the same Au₁₃₃ in the earlier report by Dass and co-workers, likely from either slight variation in sample quality or the less scrutinization on the inhomogeneous charging energy.²⁷ 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 or 45 meV at 195 K. Qualitatively speaking, larger Au cores would correspond to smaller band

gaps. In reference to other Au_{130/3} NCs and Au_{144/6} NCs,^{27,39–41} the hollow center in the core atomic structure of Au₁₄₄ is believed responsible for the larger HOMO–LUMO gap of Au₁₄₄.^{27,42,43} It is logical to perform similar analysis on Au₂₄₆, another nonmetallic NC and smaller than Au₂₇₉.^{22,23,25,26} DPV results at varied temperatures (Figure S10) confirm its nondetectable energy gap, as well as diminished yet distinguishable trends in charging energy such as (1) a parabolic shape with respect to the applied potential and (2) decrease and leveling at lower temperatures and higher potentials. No detectable energy gap or trends in charging energy were resolved from the larger Au₂₇₉ (results not shown).

The enthalpy and entropy portions in the Gibbs free energy changes associated with 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. In Figure 4, both the extrapolated intercept and the slope are

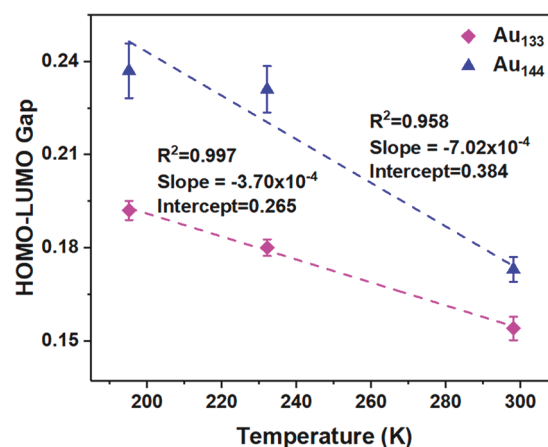


Figure 4. HOMO–LUMO gaps of Au₁₃₃ (pink) and Au₁₄₄ (blue) at 298, 232, and 195 K. Dashed lines are fitting. The error bar represents the standard deviation of the average charging energy highlighted in Figure 3.

larger for Au₁₄₄ over Au₁₃₃. The higher enthalpy is attributed to the structure differences in Au₁₄₄. The more sensitive temperature dependence indicates larger entropy which is explained by the more flexible monolayer: short flexible BM ligands without *tert*-butyl group and thus less steric effect, and slightly larger ligand-to-metal ratio (60/144 for Au₁₄₄ *versus* 52/133 for Au₁₃₃). It is important to mention that the ion/solvent permeation should be viewed as a dynamic exchange process between the bulk solution and the monolayer: both the extent/amount and the dynamics will contribute to the measured energy states/parameters and possible shift/splitting after the ET reactions. At lower temperatures, the motion of ligands can be more restricted with a reduced degree of freedom in certain vibration/rotation modes. The counterion/solvent permeation into the ligand monolayer will be less dynamic and correspondingly more constant relative permittivity of the dielectric layer and thus the capacitance. At higher charge states, similar reduction in the dynamics of counterions will arise due to the stronger electrostatics. The entropy factor will vary accordingly, which explains the lower linearity of the Au₁₄₄ results.

Comparisons of Spectroelectrochemistry and Ultrafast Spectroscopy Features. In spectroelectrochemistry, the

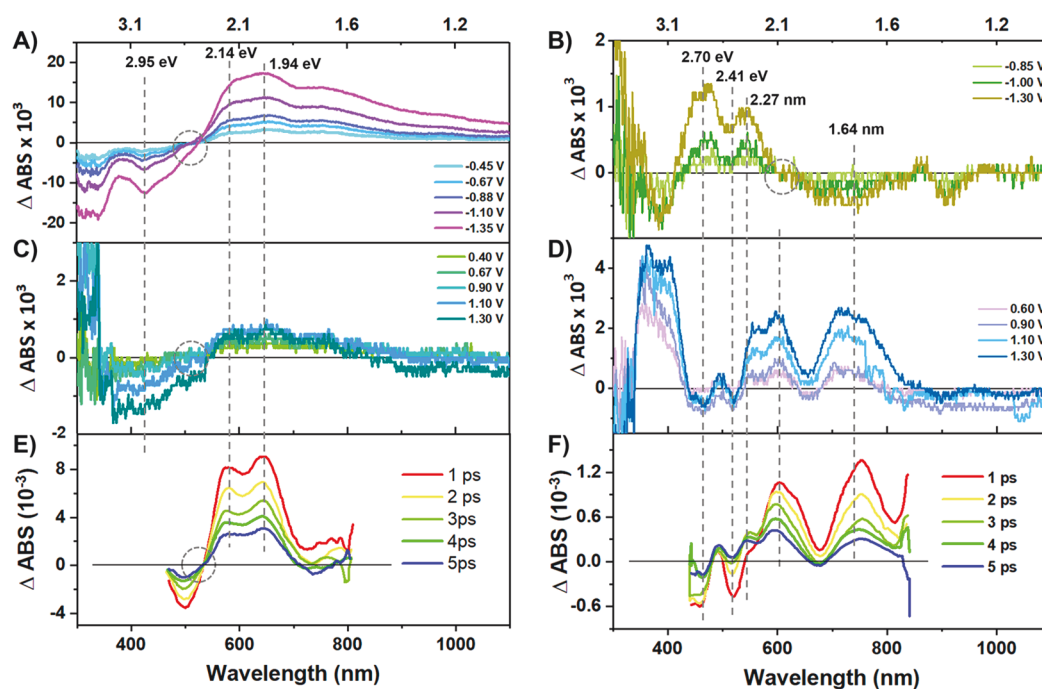


Figure 5. Absorption changes of Au_{133} (left, A, C, and E) and Au_{144} (right, B, D, and F) in spectroelectrochemistry and ultrafast spectroscopy. ΔABS calculated by the subtraction with the original spectrum. Panels A and B are after reductive electrolysis and panels C and D after oxidative electrolysis by spectroelectrochemistry. The denoted potentials are the valleys in DPV. Panels E and F are transit absorption spectra.^{34,42} The electronvolts listed above the dashed lines are the distinct absorption bands observed in original steady-state spectra. Additional lines are added to highlight the alignment of key features across different panels.

charge state of the sample is altered directly by addition/removal of an electron in a particular energy state *via* electrode ET reactions. The changes in the steady-state absorption spectrum are then collected. The charge states are unchanged in ultrafast spectroscopy; rather, the populations of electrons/holes in at least two orbitals or energy states are transiently adjusted by a laser and the dynamic changes in spectral features are recorded subsequently. The two techniques can provide complementary insights on energy states and related charge/energy transfer and relaxations, especially when the sample undergoes charge transfer with other entities, as in many applications. The concept and analysis approach are explained by aligning the spectroelectrochemistry results of the Au_{133} and Au_{144} NCs with previously reported ultrafast data^{34,42} in Figure 5. The corresponding original spectra are included in Figures S11–S14 for reference. NCs of these types have been extensively studied, so we defer detailed property discussion to earlier literature and only focus on key comparisons between the two techniques.

The first notion is that spectroelectrochemistry offers information over a much larger energy window (Figure 5, wavelength at the bottom axis and eV energy on the top) with great flexibility and convenience, but lacks dynamics. For example, the distinct 2.95 eV valley in Figure 5A (420 nm peak) and the >3 eV peak in Figure 5D from spectroelectrochemistry are inaccessible in ultrafast mode, which requires highly complex hardware.

Second, the positive or negative ΔABS in spectroelectrochemistry can be correlated to the excited-state absorption (ESA, positive signals) or ground-state bleaching (GSB, negative signals) in ultrafast results but require deliberation. This is because at least two states (unfilled and occupied) are involved in the laser pumping, whereas the electrolysis changes

only one state directly, though indirect changes on other states are inevitable. Of note, a positive ΔABS means an increase in steady-state absorbance after the electrolysis and a negative for decrease. For example, the 2.14 and 1.94 eV peaks in Figure 5A in spectroelectrochemistry of Au_{133} match the ESA in ultrafast spectra, and 2.95 eV (420 nm) valley to GSB.⁴² For Au_{144} , the peak around the 1.64 eV absorption band in Figure 5D matches the onset of interband transition from 5d electrons, which will slightly shift due to the ligand effect.^{43–45} The 2.70, 2.41, and 2.27 eV absorption bands (panels B and D) can also find corresponding features in ultrafast spectra (panel F), which mainly originate from the core transitions on the basis of the fast decay. The transition from occupied states across the Fermi energy can contribute to these absorption bands.^{34,46,47}

Third, reduction and oxidation electrolysis modify the unoccupied and occupied orbitals respectively and would generate some symmetric/opposite spectral features.³³ While the peak/valley positions reveal the corresponding energy states and possible shifts, the intensity of $\pm\Delta\text{ABS}$ should reflect the accessible density of states (DOS): a lower DOS or number of degenerated orbitals will display stronger changes per one-electron oxidation/reduction. The reduction-induced changes of Au_{133} in Figure 5A display the most changes in ΔABS . Key transition features, such as (1) an isosbestic point (circular dotted line) at about 510 nm and (2) the 580 nm (2.14 eV) and 640 nm (1.94 eV) absorption bands, are consistently observed in both techniques. The oxidation-induced ΔABS in Figure 5C is too weak to be reliably interpreted, but the features are under further explorations.^{48–50} For Au_{144} , the ΔABS is stronger after oxidation electrolysis (unlike the stronger reduction ones in Au_{133}), suggesting stronger perturbation on the frontier occupied

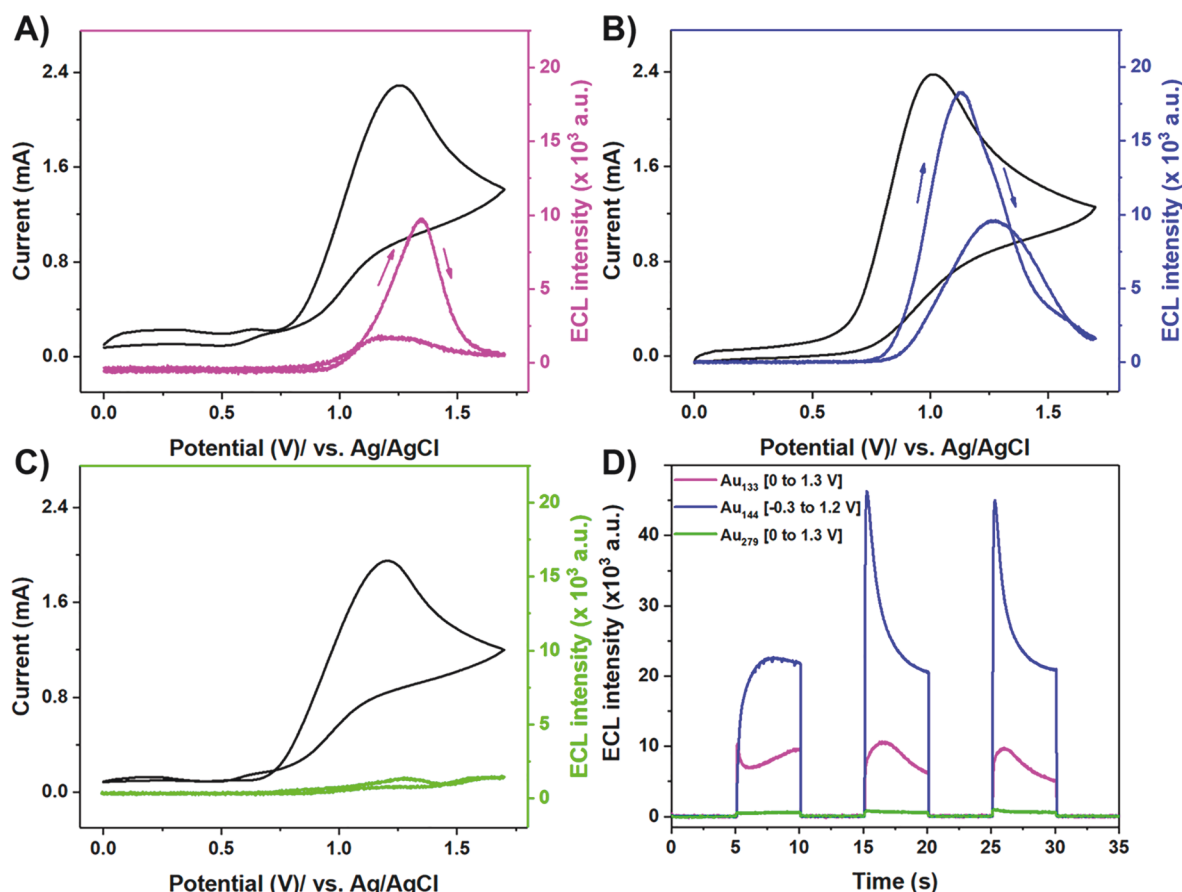


Figure 6. ECL of Au₁₃₃, Au₁₄₄, and Au₂₇₉ under potential scanning (A, Au₁₃₃; B, Au₁₄₄; C, Au₂₇₉) and potential step activations (D). The concentration of Au₁₃₃, Au₁₄₄, and Au₂₇₉ is $\sim 15 \mu\text{M}$ with 0.1 M TBAP electrolyte. The concentration of TPrA co-reactant is 10 mM. Potential scan rate is 0.1 V/s in CV-ECL. The electrode potential is held for 5 s in each step over three cycles at the denoted values.

orbitals. More consistent with previously reported spectroelectrochemistry features,^{32,33} oxidation/reduction panels (Figure 5D versus Figure 5B) largely mirror each other at respective wavelength ranges qualitatively.

Lastly, irreversible chemical reactions or decomposition could occur in both measurements and affect the analysis. For example, the reduction at high potentials (-1.35 V for Au₁₃₃ and -1.30 V for Au₁₄₄) induces significant irreversible decompositions. Additional strong changes in absorbance such as the shift in isosbestic point in panel A of Figure 5 should be interpreted in reference to other more consistent features.

Electrogenerated Chemiluminescence or Electrochemiluminescence. In ECL, the excited species are generated by electrode reactions instead of light source. Luminescence occurs when the excess energy, from either oxidation or reduction with optional following reactions, is released via radiative decay. The energy/wavelength and intensity/efficiency of ECL depends on the energy diagram of the ECL reagents and the ECL reaction pathways (self-annihilation or co-reactants). Figure 6 shows the ECLs from Au₁₃₃, Au₁₄₄, and Au₂₇₉ under comparable conditions. Those ECL performances are seven orders of magnitude weaker compared to our recently reported bimetallic Au₁₂Ag₁₃ NCs and not worthy of further explorations. However, ECL is an energy-out measure and much more sensitive over spectroelectrochemistry which analyzes energy-in behaviors. Therefore, combined view of the energy diagram on these three

transition-sized nanoclusters–nanoparticles can be established. With high excess tripropylamine (TPrA) as co-reactants for oxidative–reduction ECL generation, the CV/ECL profiles (panels A–C) and potential step ECLs (D) are compared. 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. The trends/comparisons of the weak ECL from these samples are qualitatively comparable to their respective near IR photoluminescence (PL; PL results not shown).⁵¹ In other words, ECL and PL can be potentially used conveniently in a combined or cross-checking fashion to survey or predict high-performing luminophores among the fast-growing list of atomic precise nanoclusters or other materials.

CONCLUSION

In conclusion, energy differences at $<0.1 \text{ eV}$ 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 voltammetric peak spacing of consecutive one-electron transfer reactions, corresponding to the charging energy (eV), is shown inhomogeneous and depends on measurement conditions. Viewed as nanocapacitors described by concentric sphere model, major

differences in the charging energy (midtens of milli-eV) and the variations upon charge transfer reactions are explained by the changes in compact capacitance due to counterion permeation. 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. The discrimination of subtle energy differences is achieved by using appropriate charging energy under the respective conditions as internal standard. A 0.15₄ eV HOMO–LUMO gap in Au₁₃₃ is determined after the correction of 0.24₆ eV charging energy, while a 0.17₃ eV gap above the highest occupied frontier orbitals is observed in Au₁₄₄. The gaps and capacitance of Au₁₃₃ and Au₁₄₄ increase as the temperature decreases, which reveal the respective enthalpy and entropy contributions to the Gibbs free energy. Optical electronic transitions after electrolysis explored by spectroelectrochemistry are compared to ultrafast spectra. Similarities and differences between the two techniques are discussed to demonstrate a combined approach to analyze steady-state and transient spectral features under charge transfer conditions. ECL of these transition-sized nanoclusters is weak to be of direct practical use alone, but qualitative trends for strong ECL generation such as larger gap or less nonradiative decay pathways can be argued by comparing the ECLs from different nanoclusters. Approaches to resolve the subtle energy differences and density of states, and to gain combined electro spectroscopic understanding of the energy-in and energy-out processes under reaction conditions, are believed important to the explorations of the relative physicochemical properties on other nanoclusters or nanomaterials.

EXPERIMENTAL SECTION

Synthesis. The syntheses of transition-sized gold nanoparticles (i.e., Au₁₃₃, Au₁₄₄, Au₂₄₆, and Au₂₇₉) were based on size-focusing protocols following reported procedures (details in the [Supporting Information](#)). [Figure S1](#) shows the steady-state UV–visible absorption spectra of these three nanoparticles. Au₁₃₃ shows three peaks of 420, 510, and 700 nm (pink line). Au₁₄₄ exhibits 475, 515, and 715 nm absorption peaks (blue line). Au₂₇₉ displays a *ca.* 510 nm metallic surface plasmon resonance (SPR) absorption peak (green line). Those absorption features are highly consistent with the earlier reports, confirming the molecular purity needed for the detailed electrochemical analysis in this report.^{25,27,42,45}

Measurements. Cyclic and differential pulse voltammograms (CVs and DPVs) were recorded with a CHI Instrument (Model 750C). In general, the nanoclusters were dissolved in DCM at about 1 mM concentration with 0.1 M TBAP (tetra-*n*-butylammonium perchlorate) as supporting electrolyte. A Pt disk electrode (*d* ~ 0.5 mm) as working electrode, and an Ag/AgCl wire and Pt foil as reference and counter electrodes were used. A 20 min purging with argon processing was executed before each measurement. Dry ice in ACN and EtOH was used to maintain the test temperature at 232 and 195 K, respectively.

Spectroelectrochemistry and electrochemiluminescence experiments were performed with a three-electrodes system in a quartz cuvette. A Pt mesh working electrode and cuvette were aligned at a fixed position with respect to the detector/camera for consistency. An Ag/AgCl wire as reference electrode and a Pt foil as counter electrode were used (away from a light path). A Dropsens μ stat200 benchtop potentiostat and Shimadzu UV1700 UV–visible spectrometer were used for spectroelectrochemistry. The ECL emission intensity was recorded with an Andor iDUS CCD camera (Model DU401A-BR-DD). The camera was externally triggered by the potentiostat (Gamry R600) for synchronized light-current detection. The sample solution was purged for about 20 min with argon prior to the measurements.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.0c04914>.

Syntheses details; steady-state UV–vis absorption spectra; CVs at higher scan rates; data tables of voltammogram peak positions, peak spacing, and capacitance; original spectroelectrochemistry spectra (PDF)

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Notes

The authors declare no competing financial interest.

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