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Nanoparticles in Ionic Liquids

"Ligand-Free" Cluster Quantized Charging in an Ionic Liquid[**]

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Quantized charging of nanometer-sized metal particles has been the focus of intense research over the past decade, as it is expected to play a key role in future nanoelectronic devices,[1a] and efficient synthetic routes of such nanoparticles have become increasingly available.[1b,c] The most prominent examples are the so-called monolayer protected clusters (MPCs), as they are sufficiently robust to be purified to the narrow size dispersion required to resolve individual charge states.[2] There are only a few reports of quantized charging in ionic liquids, and all of these are concerned with MPCs.[3] For classical colloids, to our knowledge, only electrochemistry of considerably larger particles has been reported.[2b] As the capacitance of these particles is large, the electrostatic energy $e^2/2C$ (with electronic charge e and capacitance C) for their single-electron charging is well below $k_BT = 25.7$ meV at room temperature (with Boltzmann constant k_B and thermodynamic temperature T), leading to so-called bulk-continuum[2b] voltammetry.

In this study, we demonstrate for the first time that also "ligand-free" metal clusters can display quantized charging. Furthermore, this is the first report of quantized charging for particles dispersed in an ionic liquid, as previous work[3] has been concerned with particle films. The approximately 1.1 nm diameter Au clusters were generated directly in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim][BF_4]$) by thermal decomposition of $K[AuCl_4]$.[4a] In this context, the ionic liquid performs several functions: 1) its anion has been shown to serve as a template in the nanoparticle formation and controls through its size that of the resulting cluster,[4b] and 2) its supramolecular structure lends sufficient stability to the clusters without the need for strong ligands.[4c–h]

Figure 1 shows the differential pulse voltammogram for the as-prepared ligand-free Au clusters in $[C_4mim][BF_4]$, which can be deconvoluted in six Gaussian contributions. In keeping with the concepts of quantized charging,[2] the peaks correspond to electrochemical transitions between clusters with core charge states z (that is, the sign and number of elementary charges stored on the cluster core). The assignment of z was based on the potential of zero total charge of a polycrystalline gold electrode in the pure ionic liquid ($pztc = -0.15$ V versus Fc/Fc^+, Figure 1 ($Fc = [(\eta\text{-}C_5H_5)_2Fe]$), dotted vertical line and Supporting Information).

Following this assignment, values of z between -2 and $+4$ are experimentally accessible. The more remote from zero the charge state z, the broader the peaks observed. As the peaks delimit the regions where a certain charge state z prevails, cluster capacitances C_{CLU} as a function of z can be calculated from their spacing ΔE_z using $C_{CLU} = e/\Delta E_z$, and their values

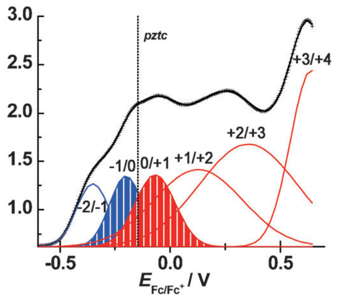

Figure 1. Differential pulse voltammogram of ligand-free Au clusters in $[C_4mim][BF_4]$. Black "+" markers: measurement; blue and red curves: Gaussian fits for electrochemical transitions between cluster charge states $z \leq 0$ and $z \geq 0$, as indicated; continuous black curve: sum of Gaussian fits. Cluster concentration 1.5 mM, pulse width 60 ms, pulse height 50 mV, period 200 ms, scan rate 20 mV s^{-1}, scan direction negative to positive. The dotted vertical line indicates the potential of zero total charge for a polycrystalline Au electrode in $[C_4mim][BF_4]$.

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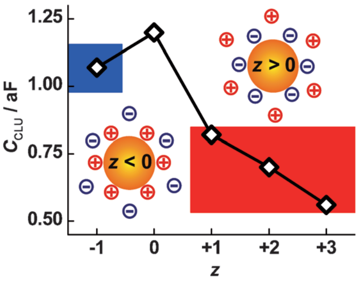

Figure 2. *z*-Plot indicating the experimental capacitance per cluster as a function of charge state, and associated polarity inversion of the cluster ionic shell. Data and color code (blue: $z<0$; red: $z>0$) from Figure 1.

are shown in Figure 2. Based on these data, the capacitance per cluster has a maximum at zero charge, and decreases as $|z|$ increases.

If we treat the ionic liquid as a dielectric medium in which the Au clusters are dispersed, the simplest expression of the capacitance is[5]

$$C_{\mathrm{CLU}} = 4\pi\varepsilon_0\,\varepsilon\, r \tag{1}$$

where C_{CLU} is the capacitance per cluster, ε_0 the permittivity in vacuum, ε the static dielectric constant of the ionic liquid, and r the radius of the gold core. In this model, the ionic liquid works as a polarizable medium that scales the capacitance of the bare metal sphere in vacuum ($4\pi\varepsilon_0 r$) by ε. With $r = (0.55 \pm 0.1)$ nm (from TEM, see Supporting Information) and $\varepsilon = (11.7 \pm 0.6)$,[6] we estimate a single-cluster capacitance $C_{\mathrm{CLU}} = 0.7$ aF, which is of the experimentally observed order.

Considering that the ligand-free Au clusters are stabilized directly by the ionic liquid itself, a polarity inversion of the ionic shell around the clusters may occur on changing the sign of z, Figure 2, as has been suggested for macroscopic electrodes around the zero-charge potential.[7] To test this assumption, we created an ab-initio model for the interaction of the gold clusters with the ionic liquid. Traditionally, the theoretical description of charged nanoparticles in electrolytes is based on classical solutions of the Poisson–Boltzmann equations and leads to a capacitive minimum around zero cluster charge.[8a] Extensions of this theory for charged surfaces allow for different behaviors of the capacitance ranging from a double peak to bell shapes, depending on the parameters.[8b–d] However, to our knowledge, a similar approach for the case of spherical nanoparticles has not yet been given.

Herein we adopt a different strategy, free of empirical parameters, in presenting results of ab-initio simulations of a small part of the system, namely the nanoparticle and up to eight ions treated in vacuum (i.e., $\varepsilon = 1$ in Equation (1) for the gold cluster in absence of the ions). The energetics in the model were described using electronic density functional theory (DFT) calculations[9a,b] in the projector augmented wave method on real space grids using the GPAW package[9c,d] and a gradient corrected functional.[9e]

In the first step, we studied the capacitance of a gold cluster of 39 atoms, extracted from the core of the structurally characterized cluster $\mathrm{Au}_{102}(p\mathrm{MBA})_{44}$.[10] This size corresponds to a radius of 0.54 nm and does not cause shell closing effects,[11] which is mirrored in our experiment by the absence of a recognizable band gap.

The charge dependent capacitance for a particle in the gas phase can be determined by the finite difference expression [Eq (2)][11b,12]

$$C[z] = e^2/(W[z+1] - 2\,W[z] + W[z-1]) \tag{2}$$

where $W[z]$ is the cluster's total energy at a given charge state z. For every value of z, the structures were allowed to relax without any symmetry restrictions, and the resulting capacitance is shown in Figure 3a. The neutral Au_{39} cluster has a capacitance of 65 zF which varies only slightly if z is changed, in excellent agreement with 66 zF for a related Au_{38} model cluster.[12] Along the lines of Equation (1), scaling with $\varepsilon = 11.7$ leads to a capacitance of 0.76 aF, in good agreement with the experimental mean value. However, the peak structure seen in Figure 2 remains unexplained at this point.

In the next step, we considered the presence of the ionic liquid, represented by four ion pairs in contact with the cluster, Figure 3a. The choice of ion pairs provides overall neutrality of the ionic-liquid part and represents the usual first step in the description of ionic liquids.[13] Different relative configurations of the ion pairs and the cluster were considered as sketched in Figure 3a, and their relative energies are summarized in Figure 3b (for details, see Supporting Information). As the energetic difference in all cases is at least 0.1 eV, which is well above room-temperature thermal energy, a clear preference for a single configuration exists.

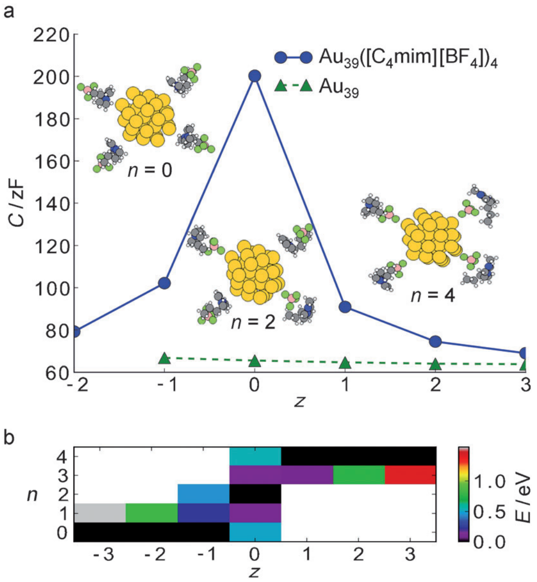

Figure 3. a) Charge dependent capacitance of the Au_{39} cluster in vacuum and in contact with 4 $[\mathrm{C}_4\mathrm{mim}][\mathrm{BF}_4]$ ion pairs. The configurations of the ion pairs relative to the Au_{39} cluster are shown (see text). Au yellow, F green, B pink, C black, N blue, H white. 1 zF $= 10^{-21}$ F. b) Energetic landscape for the configurations considered relative to the minimal energy at a given charge state z, as a function of the number of anions n next to the cluster.

For the neutral cluster, the minimal energy configuration is found when a mixed orientation of the ion pairs prevails. As soon as a charge is added to the cluster, a complete structural change results—all the anions preferably point towards the cluster for $z > 0$ and for $z < 0$ all the cations point towards the cluster. $C[z]$ can be still evaluated by Equation (2), where now the energetic minimum at each z is relevant. The structural reorganization is seen to have a dramatic effect on the capacitance, Figure 3a. A pronounced maximum at $z = 0$ is observed, in nice qualitative agreement with the experimental finding in Figure 2. Scaling the theoretical capacitance by $\varepsilon = 11.7$, however, as was done for the naked Au_{39}, would enhance the peak too much compared to the experiment. This effect may be a consequence of the use of only four pairs to describe the ionic liquid around the cluster. It can also be expected that the orientational switching will not be immediate for a larger number of pairs. Indeed, we confirmed this effect for 7 ion pairs (see Supporting Information). Furthermore, part of the polarizability is already taken into account by the partial description of the surrounding liquid in our model, so that scaling with the full value of ε is no longer appropriate.

In conclusion, we have presented evidence that quantized charging of naked metal clusters in an electrolyte is feasible. Our system is an example of quantized charging of clusters dispersed in an ionic liquid, and demonstrates that the ionic-liquid environment imparts sufficient stability to the clusters to sustain the change in charge state of up to 4 elementary charges. The variation of the capacitance with the nanoparticle's charge can be attributed to rearrangements in the structure of the surrounding ionic liquid. Density functional theory simulations describe the effect and are in agreement with the experiment. Our findings open up perspectives of using naked metal clusters in molecular electronics in ionic-liquid environment.

Experimental Section

Materials: $K[AuCl_4]$ was obtained from STREM, *n*-butylimidazole (p.a.) from Aldrich and the ionic liquid (IL) *n*-butylmethylimidazolium tetrafluoroborate ($[C_4mim][BF_4]$) from IoLiTec (H_2O content < 100 ppm; Cl^- content < 50 ppm). All manipulations were carried out using Schlenk techniques under argon. $[C_4mim][BF_4]$ was dried under a high vacuum (10^{-3} mbar) for several days to avoid hydrolysis to HF.[14]

Cluster synthesis: The synthesis followed the procedure used by Redel et al.[4a] Thermal decompositions were carried out in a glass vessel which was connected to an oil bubbler. In a typical experiment, $K[AuCl_4]$ (0.058 g, 0.154 mmol) was dissolved/dispersed at room temperature in the presence of *n*-butylimidazole (1.5 equiv, 0.231 mmol) in $[C_4mim][BF_4]$ (3.0 g). The solution was slowly heated to 230 °C for 18 h under mechanical stirring to give the gold nanoparticle dispersion (containing 1 wt % Au or 0.03 g Au in 3.0 g $[C_4mim][BF_4]$). During the decomposition process, a white-yellow precipitate of *n*-butylimidazolium chloride was formed. After cooling to room temperature, this precipitate was separated by centrifugation (13 200 rpm for 5 min) and decantation of the supernatant dispersion. The precipitate was identified as *n*-butylimidazolium chloride (%): calculated C 52.34, H 8.16, N 17.44; found C 52.69, H 8.28, N 17.56; ^1H NMR (200 MHz, $(CD_3)_2CO$, 20 °C): $\delta = 9.02$ (br, 1 H; Aryl-*N*-CH-N), 8.6 (vbr, 1 H; Aryl-NH), 7.67 (t, $J = 1.5$, 1 H; Aryl-*N*-CH), 7.49 (t, $J = 1.5$, 1 H; Aryl-*N*-CH), 4.4 (t, $J = 7.3$, 2 H; NCH_2), 1.97 (m, $J = 7.4$, 2 H; CH_2), 1,41 (m, $J = 7.4$, 2 H; CH_2), 0.98 ppm (t, $J = 7.4$, 3 H; CH_3).

Electron microscopy: Transmission electron microscopy (TEM) was carried out on a Zeiss LEO 912 instrument operating at an accelerating voltage of 120 kV, and high resolution TEM (HRTEM) on a Jeol JEM FS2200 microscope equipped with an in-column filter operating at an accelerating voltage of 200 kV. The nanoparticle dispersion was applied directly to a carbon-coated copper or molybdenum grid.

Electrochemistry: Electrochemical measurements were carried out in a single compartment three-electrode cell with a working volume of 1 cm^3, containing a Pt coil counter electrode. The reference electrode (RE) was a non-aqueous $Ag|Ag^+$ electrode, in contact with the cell through a porous glass diaphragm. The liquid junction potential between the RE liquid phase and the ionic liquid was eliminated by calibration of the RE versus ferrocene (Fc).[15] All potentials herein are referenced against the Fc/Fc^+ formal potential. The working electrode was a polycrystalline Pt bead, cut in half and polished to mirror finish to expose a disk-shaped area of 3.5 mm^2. The potentiostat was a software controlled Autolab PGSTAT30 system (Eco Chemie BV, The Netherlands).

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