Magneto-switchable single-electron charging of Au-nanoparticles using hydrophobic magnetic nanoparticles†

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Reversible magneto-switchable quantum charging of a Au nanoparticle array associated with a Au electrode is observed in the presence of hydrophobic magnetic nanoparticles attracted to the functionalized electrode surface.

The assembly of nanosized particles on electrodes and the study of the electrical and electron transfer properties of the nanoparticle systems attract substantial fundamental research with possible applications in nanoelectronics.[1] Within these efforts, the quantized (single electron) charging of metal nanoparticles (NPs) is a fundamental phenomenon. Single-electron charging of NPs at measurable potential steps, ΔE, is possible for small monodisperse metal nanoparticles provided that $\Delta Ee >> k_BT$, where $\Delta E = e/C_{NP}$ (k_B is the Boltzmann constant, C_{NP} is the capacitance of a single NP and e is the charge of an electron). The single-electron charging phenomenon was observed for gold clusters protected by hydrophobic monolayers and in organic solvents of low dielectric constants.[2] The single-electron charging of metal nanoclusters on surfaces was reported by the addressing of single NPs with a scanning tunneling microscopy tip,[3] or by the electrical charging of NP arrays,[4] consisting of small, monolayer-protected metal NPs such as Au or Ag. Different applications of the quantized charging of NPs in nano-electronic circuits were discussed, including the use of the systems as switches, single-electron transistors, memories and resonant tunneling diodes.[5] Magnetic NPs, Fe_3O_4, (*ca.* 5 nm) capped with a hydrophobic layer consisting of undecanoic acid in an aqueous electrolyte/toluene two-phase system, were recently introduced by us to control and switch the interfacial properties of electrode surfaces.[6] The magnetic attraction of the hydrophobic magnetic NPs to the electrode surface turned the electrode surface into a hydrophobic interface, while the removal of the magnetic NPs from the electrode to the toluene phase, by means of the external magnet, exposed the electrode to the aqueous electrolyte solution. By the cyclic attraction and removal of the magnetic NPs to and from the electrode surface, switchable and selective biorecognition processes on interfaces[7] and bioelectrocatalysis[8] were accomplished, and switchable directions of currents and photocurrents were reported.[9]

In the present study, we report on the use of hydrophobic magnetic NPs for the single-electron charging of a Au NP array. Previous studies[6–9] have demonstrated that the magnetic NPs attracted to the electrode support, by means of the external magnet, carry with them toluene molecules (*ca.* 410 toluene molecules per single magnetic NP). Thus, the hydrophobic layer capping of the magnetic NPs and co-adsorbed toluene molecules provide a microenvironment of low dielectric constant, and thus low capacitance of the Au NPs, allowing their quantized charging. We observe the phenomenon by linear sweep voltammetry that enables us to coulometrically assay the single voltammetric waves, and thus to quantify the charging events. Furthermore, the removal of the hydrophobic magnetic NPs from the electrode surface yields an aqueous environment, thus resulting in larger capacitance of the Au NPs. Under these conditions, quantum charging is not observed. Thus, the reversible attraction and retraction of the hydrophobic magnetic NPs to and from the modified interface provide a method for the magneto-switchable single-electron charging of a Au-NP array.

A monolayer of 11-mercaptoundecanoic acid was assembled on a Au electrode (0.78 cm^2 geometrical area, *ca.* 1.2 roughness factor) and the single amine-functionalized Au NPs (1.4 nm) were covalently linked to the monolayer (see the Electronic Supplementary Information†). The surface coverage of the Au NPs on the electrode support was determined separately by the analogous assembly of the Au NPs on a Au/quartz piezoelectric crystal. By following the frequency changes of the crystal, the surface concentrations of the 11-mercaptoundecanoic acid monolayer and of the Au NPs were estimated to be *ca.* 5×10^{-10} mol cm^{-2} and 3.5×10^{13} particles cm^{-2}, respectively. The surface coverage of 11-mercaptoundecanoic acid corresponds to a densely packed thiolate monolayer,[10] and *ca.* 12% carboxylic groups associated with the monolayer are covalently bound to the amine-functionalized Au NPs, while the other carboxylic groups remain free. The Au NP-modified electrode was horizontally positioned in the electrochemical cell and interacted with a two-phase system consisting of an aqueous electrolyte phase (0.1 M phosphate buffer, pH 7.0, 2 mL) in contact with the electrode and a toluene layer, 0.5 mL, that included the hydrophobic magnetic NPs, 1 mg mL^{-1}. The potential of zero-charge, E_{PZC}, of the modified electrode, being in contact with the aqueous electrolyte, was determined by impedance spectroscopy to be *ca.* 0.04 V (*vs.* SCE).

Scheme 1 depicts the magneto-switchable electrochemical functions of the modified electrode. When the magnetic NPs are confined to the toluene phase (Scheme 1(A)) linear sweep voltammograms corresponding to a Au NP system exposed to the aqueous electrolyte solution are obtained, as depicted in Fig. 1(A), inset, curve (a). These voltammograms are observed upon scanning of the potential from 0.04 to +0.56 V or from 0.04 V to −0.56 V. These voltammograms scanned to positive and

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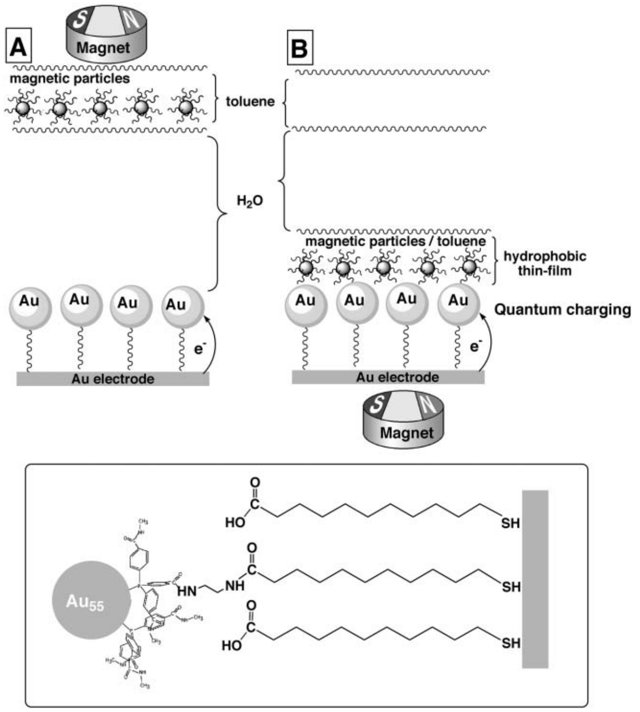

Scheme 1 Magneto-controlled quantum charging of the Au NP array associated with a Au electrode in the presence of hydrophobic magnetic NPs and two-phase liquid solution. (A) Magnetic NPs are retracted from the surface. (B) Magnetic NPs are attracted to the modified surface.

negative directions from the potential of zero-charge, E_{PZC}, reflect the capacitance current corresponding to the charging of the double-charged layer generated on the Au-NP/thiol monolayer-modified Au electrode exposed to the aqueous electrolyte solution. For comparison, Fig. 1(A), curve (c) shows the linear sweep voltammograms observed under similar conditions on the 11-mercaptoundecanoic acid-functionalized Au-electrode without attached Au NPs. The larger slope of the voltammogram measured in the presence of the Au NP-functionalized electrode reflects a capacitance increase of *ca.* 100-fold that originates from the positioning of the Au NPs on top of the thiol monolayer. Fig. 1(A), curve (b), shows the linear sweep voltammograms of the system upon the attraction of the hydrophobic magnetic NPs to the modified electrode surface, by means of the external magnet, Scheme 1(B). Eleven distinct charging waves (marked with stars) are observed, five upon the negative potential sweep and six upon the positive potential scan. The waves are equally separated, $\Delta E = 100 \pm 5$ mV, and the charge associated with each wave is almost identical, 6.4 ± 0.3 µC. Knowing the surface coverage of the Au NPs, and the total charge associated with each quantized charging step, we calculate that *ca.* 1 ± 0.05 electrons are charging each particle in the array in each of the cathodic quantized steps and *ca.* 1 ± 0.05 electrons are eliminated from each Au NP during the quantized anodic steps.

Thus, the analysis of the results provides clear evidence that the attraction of the hydrophobic magnetic NPs to the electrode surface allows the stepwise quantized charging of the Au NPs with electrons (or holes). According to the theoretical predictions,[2b,4c] eqn (1), the formal potential of a quantized charging peak, $E^\circ_{z,z-1}$, is linearly increased with the charge of the NP, z, upon the potential sweep in the negative or positive direction, Fig. 1(B).

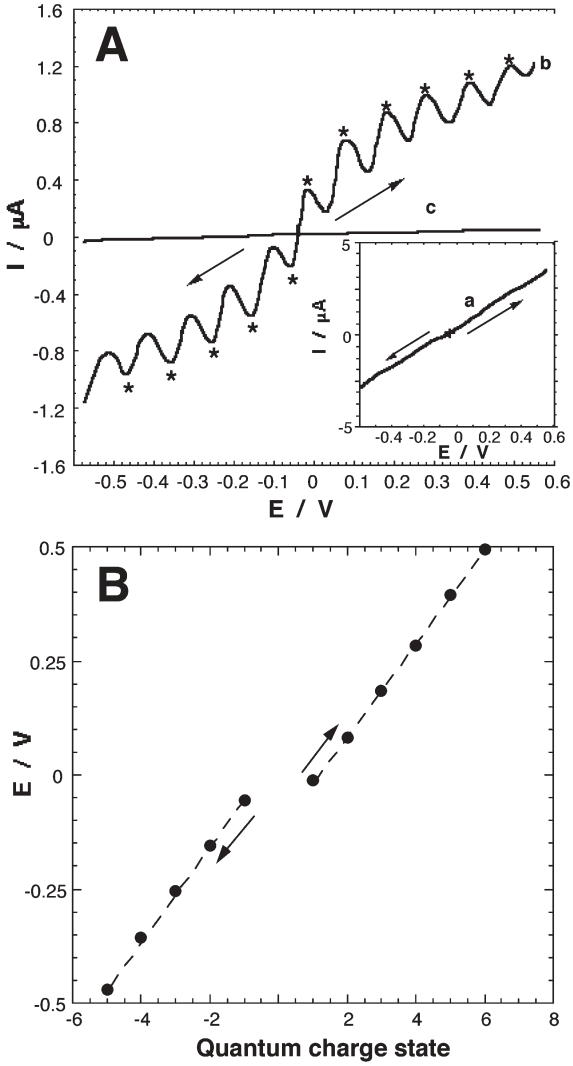

Fig. 1 (A) Linear sweep voltammograms recorded in the presence of: (a) magnetic NPs retracted from the Au NP/thiol monolayer-functionalized electrode (note the different current scale in the inset); (b) magnetic NPs attracted to the Au NP/thiol monolayer-functionalized electrodes (the quantized charging peaks are marked by stars); (c) magnetic NPs attracted to the thiol monolayer-modified electrode in the absence of Au NPs. The data were obtained under Ar in a biphase system consisting of 0.1 M phosphate buffer, pH 7.0, and toluene with the magnetic NPs, 0.5 mL, 1 mg mL^{-1}. Potential scan rate, 2 mV s^{-1}. Arrows show the direction of the potential sweep. (B) Plot of the variation of the formal charging potentials as a function of the Au NPs charging states (Z-plot) obtained from the linear sweep voltammogram shown in Fig. 1(A), curve (b).

$$E^\circ_{z,z-1} = E_{PZC} + (z - 1)e/C_{NP} \tag{1}$$

From the ΔE value, *ca.* 100 mV, the capacitance of the Au NP, C_{NP}, in the system that includes the magnetically attracted hydrophobic NPs is *ca.* 1.6×10^{-18} F. The effective value of the dielectric constant of the shell, ε, equal to *ca.* 9.5 was derived from C_{NP} assuming the concentric conductive sphere model of the capacitor,[2b] eqn (2), where r and d correspond to the radius of the Au NP and thickness of the organic shell, respectively.

$$C_{\mathrm{NP}} = 4\pi\varepsilon\varepsilon_0 r(r + d)/d \qquad (2)$$

The derived dielectric constant represents the effective value corresponding to the phosphine-capping layer in the presence of the hydrophobic magnetic NPs and the associated toluene solvent.

Upon removal of the magnetic NPs to the toluene phase by means of the external magnet, the linear sweep voltammograms without quantized charging waves are observed, Fig. 1(A), curve (a), and re-attraction of the magnetic NPs to the modified electrode surface restores the quantized charging of the Au NPs, Fig. 1(A), curve (b).

To conclude, the present study has introduced a method that enables the magneto-switchable quantized charging of a Au NP array associated with an electrode. The low dielectric properties of the hydrophobic magnetic NPs with the co-adsorbed toluene provide a microenvironment that yields Au NPs with low capacitance. The low capacitance of the Au NPs allows their quantized charging. The well separated and intense charging steps allowed the quantitative assay of the process and provided direct proof that each of the waves corresponded to the charging (or elimination) of each Au NP in the array by one electron. The single-electron charging of the Au NPs together with its switching on and off by means of the external magnet represent a new method to encode information and to erase it.

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