Control of Single-Electron Charging of Metallic Nanoparticles onto Amorphous Silicon Surface

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Sequential single-electron charging of iron oxide nanoparticles encapsulated in oleic acid/oleyl amine envelope and deposited by the Langmuir-Blodgett technique onto Pt electrode covered with undoped hydrogenated amorphous silicon film is reported. Single-electron charging (so-called quantized double-layer charging) of nanoparticles is detected by cyclic voltammetry as current peaks and the charging effect can be switched on/off by the electric field in the surface region induced by the excess of negative/positive charged defect states in the amorphous silicon layer. The particular charge states in amorphous silicon are created by the simultaneous application of a suitable bias voltage and illumination before the measurement. The influence of charged states on the electric field in the surface region is evaluated by the finite element method. The single-electron charging is analyzed by the standard quantized double layer model as well as two weak-link junctions model. Both approaches are in accordance with experiment and confirm single-electron charging by tunnelling process at room temperature. This experiment illustrates the possibility of the creation of a voltage-controlled capacitor for nanotechnology.

Keywords: Quantized Double-Layer Charging, Nanoparticles, Amorphous Silicon, Langmuir-Blodgett Layers, Voltammetry.

PUBLISHERS

1. INTRODUCTION

The preparation of novel nanostructured materials attracts much attention in materials research due to potential applications in electronics, optics, and magnetism. Physical properties of nanomaterials composed from nanoparticles are determined by three parameters: the size of particles, their composition, and topology of the system. The choice of technology used for organization of the system is thus important from the point of view of macroscopic properties. Preparation and processing of fine metallic nanoparticles (NPs) is motivated by the variety of applications, such as ferrofluids,^{1–2} data storage,^{3–5} or medicine and biosensors.^{6–10} Recently, with advances in colloidal nanocrystal synthesis, interest has grown in fabrication and

study of electro-optical properties of nanostructures for molecular electronics. $^{11}\,$

The small dimensions of NPs lead to small capacitance, which can be roughly calculated with a model of the concentric spherical capacitor using material parameters. The double-layer capacitance, $C_{\rm NP}$, of metallic NPs with an organic envelope is so small (subattofarad)¹² that the single electron charging to and from NPs occurs at apparent large potential steps $\Delta E_{\rm NP} \sim 100$ mV. This quantized double layer (QDL) charging¹³ has been observed in the voltammetry of gold NPs dissolved in the electrolyte solution and diffusing to the electrode,^{13–14} and in films of NPs attached to chemically modified electrodes.^{15–17} In this way, molecule-like characteristics of gold NPs^{18–19} was obtained and QDL charging up to 15 charged states²⁰ was measured. The QDL effect was reported for NPs with various organic envelopes. There have been used

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organics which consist from 6 up to 18 carbons in the chain. $^{15\matharrow17\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharrow21\matharow21\matharow21\matharow21\matharow21\ma$

This paper reports on the single-electron charging (also called QDL charging) of ordered NP arrays of iron oxides (ferrous, ferric) deposited onto undoped hydrogenated amorphous (a-Si:H) modified Pt electrode and measured by cyclic voltammetry. Recently it was shown that the distribution of charged gap states in a-Si:H layer of the a-Si:H modified Pt electrode can be changed with the simultaneous application of the bias voltage and the red light illumination.²⁴ This wavelength was chosen to obtain a uniform absorption of the light in the whole a-Si:H layer, thereby ensuring observation of bulk effects. Hence, the a-Si:H layer was choose for its potential of additional electric field generation in the surface region. Our approach in the QDL experiment is the deposition of a defined number of NP monolayers (layer-by-layer deposition) by means of the Langmuir-Blodgett technology and switching on/off the single-electron charging by means of the controlled creation of negative/positive charge states in a-Si:H. DADE

2. EXPERIMENTAL DETAILS

Iron oxide NPs were synthesized by a high-temperature phase reaction of metal acetylacetonates solution (Fe(acac)3), with 1,2-hexadecanediol, oleic acid and oleylamine in phenyl ether.²⁶ For the NP synthesis the reactants (1.4 g Fe(acac)3, 5.2 g 1,2-hexadecanediol, 3.4 g oleic acid and 3.2 g oleylamine) were dissolved in diphenyl ether (40 ml) and magnetically stirred under an argon flow. In the argon ambient, the mixture was heated first up to 200 °C for 30 min, then up to 265 °C for another 30 min, and finally cooled down to room temperature. After adding ethanol, a black particulate product precipitated, which was diluted in toluene in the presence of surfactant (oleic acid and oleylamine). Afterwards, NPs were precipitated with ethanol, centrifuged to remove the solvent, and redispersed into chloroform.

Nearly monodisperse NPs of iron oxides (ferrous, ferric) encapsulated in an organic envelope were deposited onto a Pt round electrode with an area of about 3 mm² coated with a 400 nm thick a-Si:H film. The a-Si:H film on Pt was prepared by plasma-enhanced chemical vapour deposition from pure silane at the temperature of 190 °C. Figure 1 shows the NP size histogram obtained by measuring a diameter of about 600 particles using Transmission Electron Microscopy images of NP monolayer film on a carbon-coated copper grid. Obtained histogram was fitted assuming Gaussian curve and the NP mean size was estimated ~ 3.7 nm. In order to prepare defect free NP layers it was necessary to hydrophobize the surface of a-Si:H film by a monolayer of stearic acid (SA, purchased from Sigma-Aldrich). Both iron oxide NPs and SA were dissolved in chloroform at the concentration of 0.5 mg/mL and spread on the subphase using



Fig. 1. Histogram of the NP size populations as observed from transmission electron microscopy images (see inset) of monodisperse, oleic acid/oleylamine coated iron oxide nanoparticles deposited on a carbon-coated copper grid. Solid line represents Gaussian fit with NP mean size 3.7 nm AULO IF

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Fri, 21 Nov 20microsyringer (Hamilton, USA). The commercially available computer-controlled Langmuir-Blodgett (LB) trough (Type 611, Nima Technology, England) was used for transfer of SA and iron oxide LB layers on the a-Si:H modified Pt electrode. The surface pressure was measured by the Wilhelmy plate method to an accuracy of 0.05 mN/m. The water subphase (bidistilled, deionized, 15 M $\Omega \cdot cm$) was thermostated at the temperature of 17 °C. The layout of the a-Si:H modified Pt electrode with NPs is shown in Figure 2. The transfer of the SA monolayer onto a solid substrate was performed by vertical dipping in the LB trough at a surface pressure of 20 mN/m. This deposition leads to the creation of highly ordered solid-phase monolayer of SA. Subsequently, 16 monomolecular layers



Fig. 2. The cross-section of the working electrode with iron oxide nanoparticles (NPs) encapsulated in oleic acid/oleylamine envelope. The platinum substrate is covered with 400 nm thick layer of a-Si:H. The Langmuir-Blodgett technique was used for a modification of the a-Si:H surface with a stearic acid monolayer and the subsequent transfer of 16 monolayers of iron oxide NPs. The capacitances C_1 , C_2 and resistivity *R* characterize equivalent circuit of two weak-link junction model of quantized charging.



Fig. 3. Scanning electron microscopy image of the LB layers of iron oxide NPs on the surface of working electrode.

of iron oxide NPs were transferred onto the SA modified electrode at a surface pressure of 15 mN/m. The forma-by tion of ordered defect free NPs system was examined by E scanning electron microscopy (Fig. 3). IP : 143.10

Electrochemical experiments were performed in a two-20 electrode cell compartment with 1 mM solution of NaCl in redistilled water (pH = 6.4). The a-Si:H modified Pt electrode with NPs operated as the working electrode and the Ag/AgCl wire was used as the standard reference electrode. Cyclic voltammetry was carried out on this system using a homemade transient charge analyzer.²⁷ Experiments were conducted with a potential sweep rate of 100 mV/s at room temperature. Before the measurement the working electrode was simultaneously biased at a certain voltage and illuminated directly in the electrochemical cell by the red semiconductor laser (wavelength $\lambda = 670$ nm) with an incident power density of 1 W/cm². This wavelength was chosen to obtain a uniform absorption of the light in the whole a-Si:H layer. The positive (negative) potential applied during the light



Fig. 4. Cyclic voltammetry of iron oxide NPs deposited on the a-Si:H layer. Blue and red lines represent measurements after excess creation of negative $D_{\rm e}$ and positive $D_{\rm h}$ charge states in a-Si:H, respectively. Potential sweep rate was 100 mV/s.

soaking pre-treatment leads to an excess of negative charge states, $D_{\rm e}$, (positive charge states, $D_{\rm h}$),^{24–25} hence to the creation of an excess of defect centres charged negatively (positively). The effect of these pre-treatments on the cyclic voltammetry signal of iron oxide NPs is shown in Figure 4. The QDL charging observed as fringes is measured only for the excess of $D_{\rm e}$ states during the cathodic scan. Anodic scan exhibits apparent redox reactions of iron ions without any recognizable QDL fringes. In the case of the excess of $D_{\rm h}$ states the measured voltammogram reflects only standard redox reactions in both the anodic and cathodic scans. Comparative experiments with NPs immobilized in the same way on the bare Pt electrode and a-Si:H modified Pt electrode without iron oxide NPs²⁴ do not show any QDL features.

3. DISCUSSION

Unlike the previous reports,^{11–23} QDL charging in our experiment is not reversible and is controlled by the distribution of charge states in the a-Si:H layer. This peculiar behaviour is determined by two specific experimental conditions: an additional electric field generating in a-Si:H interlayer and the use of non-noble metallic NPs. Experiment with iron oxide NPs deposited on the bare Pt electrode does not show the QDL signal. The absence of the QDL behaviour can be explained by the energy barrier arisen from the long chain of the used NP envelope. The effect of the barrier is influenced by the additional electric field of the charge defect states in a-Si:H interlaver. Variability of the defect-state distribution in a-Si:H allows controlling the QDL charging via preferential creation of positive (D_h) or negative (D_e) states. The experiment shows the QDL charging is not present for the excess of $D_{\rm h}$ states, which corresponds to a preferential electron capture on these states and increase of the tunnelling current barrier. The charge transitions due to the QDL charging are observed when the excess of D_e states is created. During the sweep from positive to negative potentials (cathodic scan) NPs are charged through a tunnelling current. Unlike previous QDL experiments with noble metal NPs¹¹⁻²³ for iron oxide NPs redox reactions are expected, too. When the potential is swept from negative to positive values (anodic scan) the accumulated electrons in NPs are released, enter into the above-mentioned redox reactions, and are envisioned as typical redox peaks in the voltammogram (Fig. 4).

The changes in electric field distributions for a given bias voltage applied to the designed structure against the reference electrode are depicted in Figure 5. The left and right columns show situations in the presence of D_e and D_h states, respectively. Deep states were modelled by the space charge in the amorphous silicon layer. Colour maps represent distribution of potential from negative (blue) to positive (red) values; arrows characterize vectors of



Fig. 5. The electric field distribution across the working electrode with iron oxide NPs. Calculations were performed for a given bias voltage E applied against the reference electrode. Colour maps represent distribution of potential (see colour legend); arrows characterize vectors of the electric strength field.

the electric strength field. The electric field distributions were calculated with the QuickField program.²⁸ Simulations were performed as 2D problem with real material parameters. Voltage drop in the water solution was not considered in consequence of solution with enough level of conductivity. Simulations were performed with. The calculation shows the influence of charged defect states on the current flow, what is directly related to the direction of vectors of the electric strength field. This effect is observed in the experiment (see Fig. 4) as the "current offset" of voltammogram for D_e and D_h states.

Two different models were used for the evaluation of the QDL charging experiment. Recently used QDL charging analysis based on spherical capacitor approximation^{12–23} is complemented for comparison with two weak-link junctions' model.

3.1. Quantized Double-Layer Charging Analysis

A model of QDL charging considers a nanoparticle as a concentric spherical capacitor. The capacitor formed by conducting metallic spheres with the radius, r, separated by a dielectric shell of the oleic acid/oleylamine monolayer with a thickness, d, and the static dielectric constant, $\varepsilon_0 \varepsilon_r$, has a capacitance, $C_{\rm NP}$ (Ref. [12]).

$$C_{\rm NP} = \frac{4\pi\varepsilon_0\varepsilon_r}{\frac{1}{r} - \frac{1}{r+d}} = 4\pi\varepsilon_0\varepsilon_r\frac{r(r+d)}{d} \tag{1}$$

The relative permittivity, ε_r for the organic envelope is 2.5 and the length of the chain d = 2 nm. An electric potential of the nanoparticle, $E_{\rm NP}$, depends on $C_{\rm NP}$, the number of electron charges on the particle, z, and the potential of zero charge of the nanoparticle, $E_{\rm PZC}$, (z = 0) via the relation.¹²

$$E_{\rm NP} = E_{\rm PZC} + \frac{ze}{C_{\rm NP}} \tag{2}$$

where e is the electron charge. The negative or positive sign of z corresponds to charging or discharging of

NPs, respectively. There are two basic requirements for the observation of the QDL charging of NPs. The first is the size of the NP core and dielectric shell, which determines its capacitance and thus a potential step between two charged states. Since the NP capacitance strongly depends on the metallic core radius, the second requirement commands that highly monodisperse NPs are essential.

Charge transitions in the cyclic voltammetry due to the quantized capacitance charging are marked in Figure 6(A) by arrows. The *z*-plot (Fig. 6(B)) shows that the dependence of potential steps can satisfactorily be fitted with the relation (2) (correlation coefficient 0.9973). The fitting procedure yields $E_{\text{PZC}} = -73$ mV and $\Delta E_{\text{NP}} = 167$ mV.



Fig. 6. (A) The electrochemical Coulomb staircase in the cyclic voltammetry of iron oxides nanoparticles is observed only with the excess of negative charge states, $D_{\rm e}$, in the a-Si:H layer and in the course of the sweep from positive to negative potential. Single-electron charging of individual iron oxides nanoparticles is marked by arrows. (B) Potential steps, $\Delta E_{\rm NP}$, (full dots) of the quantized capacitance charging of iron oxides nanoparticles between (z-1)/z charge states. Dashed line shows linear regression calculated according to Eq. (2) with the NP capacitance $C_{\rm NP} = 0.95$ aF and potential of zero charge $E_{\rm PZC} = -73$ mV.

The latter one corresponds to the NP core diameter of about 3.6 nm, the size of which is in a good accordance with the value from electron micrograph (Fig. 1). The capacitance of a nanoparticle determined according to formula (1) is $C_{\rm NP} = 0.95$ aF.

3.2. Two Weak-Link Junctions Model

To measure single-electron charging at room temperature two additional conditions must be fulfilled. The capacitor charging energy, $W = e^2/(2C_{\rm NP})$, from adding a single electron to a nanoparticle metallic core with dielectric (isolating) envelope characterized by capacitance $C_{\rm NP}$ must exceed the thermal energy $k_{\rm B}T$ (26 meV at temperature of 300 K). Otherwise, thermally activated electrons will overcome the Coulomb barrier and escape from the NP. Considering the capacitance of the nanoparticle experimentally $(C_{\rm NP} = 0.95 \text{ aF})$ the charging energy is 84 meV, i.e., thermally activated escape of electrons is suppressed at room temperature. The second condition is that tunnel resistance of electric contacts to the particles is to be larger than the quantum resistance, h/e^2 , to suppress quantum fluctuations Fr1, 21 Nov of the electron charge.

For a detail analysis of NPs single-electron charging through a tunnelling process the model based on two weak-link junctions (shown in Fig. 2) characterized by capacitances C_1 and C_2 is assumed. A positive bias voltage E_b will pull electrons onto the NP and a negative voltage will push electrons off the NP. The charge on the NP is related to the potential by the equation,

$$q = C_1 (E - E_b) + C_2 E$$
(3)

where E is the potential of the particle and q is its charge. Hence the potential of the particle is

$$E = \frac{q + C_1 E_{\rm b}}{C_1 + C_2}$$

The energy needed to add an infinitesimal charge dq to a NP is W = Edq. If the charge is added, then the potential of the NP is changed. To calculate the energy needed to add an electron to the NP, Edq must be integrated from 0 to -e,

$$\Delta W_{+}(z) = \int_{-ne+q_{0}}^{-(n+1)e+q_{0}} Edq$$

=
$$\int_{-ne+q_{0}}^{-(n+1)e+q_{0}} \frac{-ze+q_{0}+C_{1}E_{b}}{C_{1}+C_{2}}dq_{0}$$

=
$$-eE(z) + \frac{e^{2}}{2(C_{1}+C_{2})}$$
(5)

Here, the charge q has been written as the number of electrons z on the NP plus an offset charge, q_0 , and $q = -ne + q_0$, where e is the positive elementary charge. $\Delta W_+(z)$ is the energy needed to add one electron to the NP already occupied with z electrons and E(z) is the potential. The opposite sign for first term (i.e., eE(z)) represents

Fig. 7. Charge distributions versus applied potential during cyclic voltammetry (CV) calculated according Eq. (8). NPs parameters used for the calculation: $C_{\rm NP} = 0.95$ aF, T = 300 K. Stars represent experimentally observed charge transitions in CV.

the energy, ΔW_{-} , needed to remove one electron from the NP. The second term,

$$\Delta W_{\text{Charging}}(z) = \frac{e^2}{2(C_1 + C_2)} \tag{6}$$

is so-called the charging energy. The tunnel rates for electrons to tunnel onto/off the NP is

$$\Delta\Gamma_{\pm}(z) = \frac{\Delta W_{\pm}(z)}{e^2 R \left[\exp\left(\frac{\Delta W_{\pm}(z)}{k_B T}\right) - 1 \right]} \tag{7}$$

where R is the resistance of the tunnel weak-link junction (see Fig. 2). In a stationary state, the currents of electrons tunnelling onto/off the NP are equal to zero,

$$-e\Delta\Gamma_{+}(z)P(z) + e\Delta\Gamma_{+}(z-1)P(z-1) = 0$$
 (8)

P(z) stands for the probability that there are z electrons on the NP. We assume negligible capacitance C_2 . Thus the C_1 is equal to NPs capacitance $C_1 = C_{\rm NP} = 0.95$ aF and temperature T = 300 K. The result of this calculation is shown in Figure 7. Note agreement with experimental results (yellow stars in Fig. 7), where recorded transitions between charged states are confronted with calculated probability distribution. The observed single-electron charging argues that above-mentioned conditions are met as well and the internal electric field built up at the excess of $D_{\rm e}$ states is necessary to overcome the existing tunnel resistance.

4. CONCLUSION

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Iron oxide NPs were deposited onto a substrate by the LB technique and highly organized arrays of NPs was obtained. This is improvement in comparison with recently used techniques.^{29–30} The observed single-electron charging was controlled by additional electric field in the surface region, induced by the charge defect states in the a-Si:H layer which was deposited on the Pt electrode. Experiment was analyzed by recently used quantized double layer model and proposed two weak-link junctions' theory. Both approaches were in accordance with the experiment and confirm single-electron charging by tunnelling process at room temperature.

The LB technique demonstrates the viable way for the creation of homogenous large-scale NP multilayers of a defined number (layer-by-layer deposition) and the potential of electrochemistry for studying the charge transfer between NPs and external circuitry. Alternation of the electronic states in a-Si:H by light and bias voltage is an illustrative example for enhancing NP functionality. It provides applications of metal oxide NPs for memory devices as was already shown for silicon NPs.⁵ Hence, results show the opportunity for nanotechnology to control the single-electron charging by the applied voltage of the single-electron charging by the applications of the single-electron charging by the applications

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