

# Single electron tunneling in large scale nanojunction arrays with Bisferrocene-nanoparticle hybrids

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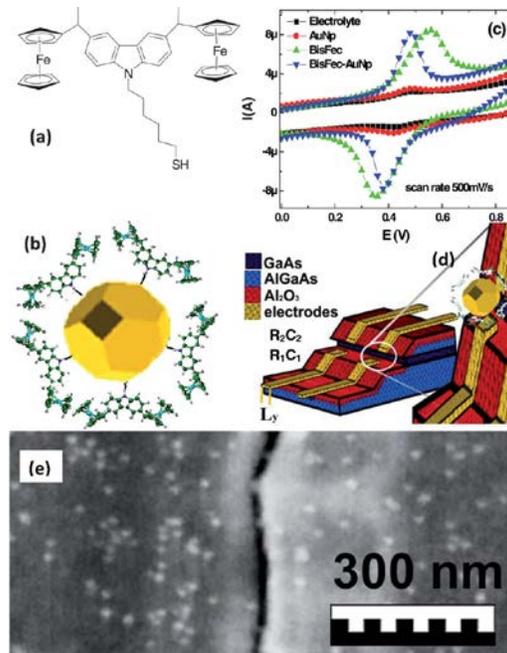
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Controlled single electron tunneling is useful for applications ranging from nanoelectronics to metrology and quantum computation [1, 2]. The precision and architecture of the nanoscale separation between the device elements, play a decisive role in controlling device response. Today, strategies for parallel processing have been researched for device integration. Recently, we demonstrated the fabrication of large-scale nanojunction arrays [3-5]. Here, we report on their application to single-electron devices based on bisferrocene molecule-gold nanoparticle, BFc-AuNP, hybrid systems (Fig.1(a-b)) [6], which are interesting for ON-OFF switching, bistable operations, molecular spintronics [7], etc. The use of metal NPs as a bridge between organic monolayers formed on metallic electrodes is also a smart approach to probe molecular conduction [8, 9].

The procedure for preparing the thiol ended BFc molecules [10], the hybrids [6] and the mesa nanojunctions [3-5] are described elsewhere. To confirm the formation of hybrids, electrochemical studies were performed and cyclic voltammograms are shown in Fig. 1(c). For both hybrids (blue triangles) and bisferrocenes (green triangles), clear forward anodic and return cathodic peaks could be observed with an average electrode potential value,  $E'_{av} = 0.429$  V and  $0.459$  V, respectively, which in both cases could be ascribed to a 2-electron process associated to the reversible oxidation of the two equivalent ferrocenyl moieties [11] with only a small shift in the position and reduction/oxidation peaks becoming closer after immobilization on gold nanoparticles. This undoubtedly confirms the formation of hybrids [12] since this signature is not present in the case of gold nanoparticles alone (red curve).

In order to immobilize the hybrids, the Au electrodes were first functionalized with hexane-1,6-dithiols (24 hours into a  $10^{-3}$  M ethanol solution). Then the nanojunctions were kept in

the hybrid solution of BFc-AuNP's for 24 hours and successively washed. Fig. 1e shows a typical SEM image of the mesa electrodes with self assembled BisFc-AuNP hybrids. Out of 198 prepared nanojunctions, around 35% showed hybrid attachment and hence conduction after immobilization. The typical resistance was in the order of T $\Omega$  before immobilization of the hybrids and then decreased in the range from few hundreds of k $\Omega$  to tens of M $\Omega$ . The final layer sequence in the device junction can be visualized as a double barrier tunneling junction. Transport measurements were carried out in a cryogen-free superconducting magnet in the temperature range from 1.5-300K.



**Figure 1.** (a) BFc molecule. (b) BFc-AuNP hybrid. (c) Cyclic voltammograms demonstrating the assembly of hybrids. (d-e) Schematic view and SEM image of mesa nanojunctions with BFc-AuNP hybrids in the gap.

In the weak coupling limit, transport through the

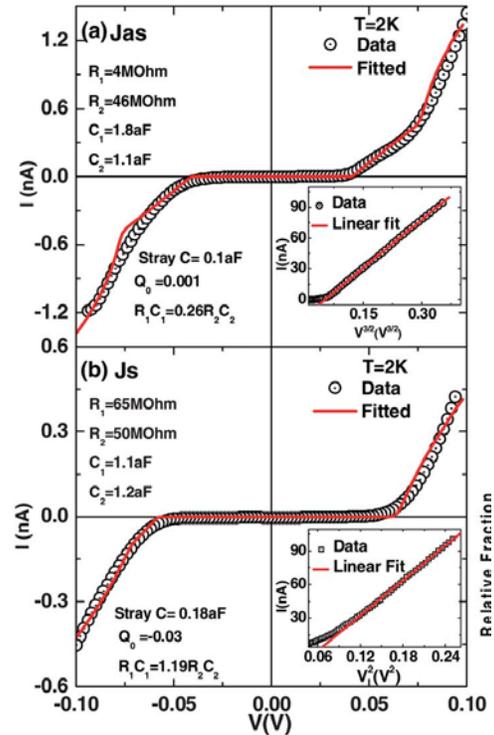
nanojunctions occurs through single electron charging of the conducting island and is determined by overall dynamics of this process and ultimately by the specific tunneling rates into and out the hybrid which define the tunneling regime (shell-tunneling or shell filling) [13-16] and are related to the resistances and capacitances of the first and the second electrodes ( $R_1$ ,  $C_1$  and  $R_2$ ,  $C_2$  respectively). A typical property of single-electron transport is the Coulomb staircase, the stepwise increase of electric current as a function of source–drain voltage, where each step corresponds to an addition/subtraction of one electron to/from the Coulomb island. According to the orthodox theory [16-19], the Coulomb staircase could be observed when the tunneling junctions are electrically asymmetric i.e.  $R_1C_1/R_2C_2 \gg 1$  or  $\ll 1$  (shell filling regime). This configuration is mostly satisfied in our nanojunctions due to the asymmetric positioning of the nanocrystals on the non planar gap. The hybrid particles are typically more strongly attached to the lower electrode (1) than to the upper one (2). As a result, we have observed Coulomb staircase like effect at low temperature in many devices using  $\sim 12.5$  nm hybrids (10 nm NP coated with a  $\sim 1.25$  nm molecular layer). If, however, symmetric junctions ( $R_1C_1 \approx R_2C_2$ ) were formed (which could occur when a hybrid is positioned at the same tunneling distances from both electrodes), a Coulomb blockade without a pronounced staircase was generally observed [20].

Fig. 2(a) shows a typical IV curve from an asymmetric junction ( $J_{AS}$ ) demonstrating Coulomb staircase. The experimental data (open circles) agreed well with the simulated results [21] (red solid curve) using orthodox theory and DBTJ model with the following parameters:  $C_1 = 1.8$  aF,  $C_2 = 1.1$  aF,  $R_1 = 7$  M $\Omega$ ,  $R_2 = 43$  M $\Omega$  and  $Q_0 = -0.001e$ . This means that the hybrid particle is more strongly attached to side 1 than side 2 (Fig. 1(d)). On the other hand, in Fig. 2(b) an  $I$ - $V$  curve from a symmetric junction ( $J_S$ ) is reported with Coulomb blockade but no observable staircase. The corresponding simulated  $I$ - $V$  characteristics (red curve) were calculated with the following parameters:  $C_1 = 1.1$  aF,  $C_2 = 1.2$  aF,  $R_1 = 65$  M $\Omega$ ,  $R_2 = 50$  M $\Omega$  and  $Q_0 = -0.03e$ , showing that  $R_1C_1 \approx R_2C_2$  in this case. The non conducting voltage interval  $\Delta V_{DS}$  is  $\sim 108$  mV for  $J_S$  and  $\sim 80$  mV for  $J_{AS}$ . Accordingly to the orthodox theory, it is directly related to the total capacitance  $C_\Sigma$  and charging energy  $E_c$  required

to add one electron to the Coulomb island:

$$\Delta V_{DS} = 2e / C_\Sigma = 4E_c / e \quad (1)$$

This gives  $C_\Sigma$  (and  $E_c$ ) as  $\sim 2.96$  aF (27 meV) and 4 aF (20 meV) for  $J_S$  and  $J_{AS}$  respectively. The characteristic charging energy can also be calculated from the self capacitance value  $C_H \sim 2\pi\epsilon_0\epsilon d = 2.1$  aF for one isolated hybrid spherical particle of diameter  $d = 12.5$  nm using the expression  $E_c = e^2/2C_H$  giving  $E_c \sim 38$  meV, which is not too far from the experimental value, taking into account that other capacitances from electrodes were not considered for the calculation.



**Figure 2.** Current ( $I$ )–voltage ( $V$ ) characteristics of the typical (a) asymmetric junction,  $J_{AS}$ , and (b) symmetric junction,  $J_S$ , at 2 K. The parameters used for generating the simulated curves are indicated. Insets show the variation of junction current at higher bias voltages. Solid lines are fits to  $V^{3/2}$  and quadratic dependence for  $J_{AS}$  (inset (a)) and  $J_S$  (inset (b)).

Notably, a markedly difference in the high voltage-current behaviour for the symmetric and asymmetric junction was also observed (insets of Fig. 2). The asymmetric junction shows  $V^{3/2}$  voltage dependence at higher biases whereas the symmetric one exhibits a quadratic dependence [22] on the bias voltage,  $I \propto V^2$ . The red solid lines in Fig. 2 insets are the best fits to  $V^{3/2}$  and

$V^2$  dependence of junction current with bias voltage for  $J_{AS}$  and  $J_s$ , respectively. This deviation from linearity in I-V curves, outside the Coulomb blockade region indicates the presence of small multiple barriers in the surrounding BFc molecule capping the AuNP, which is suppressed at higher bias voltages [23]. The thermal dependence of the junction resistance was found to be mainly governed by Arrhenius dynamics. The value of the activation energy  $E_g$  calculated from the best fits with experimental data was found to be 7.12 meV ( $J_{as}$ ) and 8.24 meV ( $J_s$ ), which corresponds nicely with previous reports on monolayer alkanethiol coated AuNP's [24]. The observed difference between  $E_c$  and  $E_g$  ( $E_g \ll E_c$ ) might be due to cotunneling, barrier suppression phenomenon etc. However since the junction resistances were much larger than the quantum resistance ( $\sim 10^4$  Ohm); we discarded cotunneling to be responsible for this discrepancy [25]. Also, since small barrier suppression does not affect the coulomb blockade threshold voltage [26], we can neglect it too. This difference in energy scales might instead be ascribed to a voltage divider effect in the junction which takes into account the voltage drop in the BisFc layer capping the AuNP [3, 27]. In this scenario, only a fraction of total bias voltage actually gets applied to the AuNP and consequently larger bias voltages are required to charge the AuNP. From simple lever arm considerations [27], a rescaling factor around 1.5-1.7 can be estimated if a constant resistivity is assumed, but this value should reasonably increase considering that the metal NP is much more conductive than the molecular layer. So, a factor around 3 seems realistic and this would allow a good agreement among the different data. Hence, the values of  $E_g$  derived from the T dependence are considered to be more consistent, in this case. No sizeable magnetoresistance was observed increasing the magnetic field.

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