Electron transport across capped Au nanoclusters adsorbed in different configurations on highly oriented pyrolytic graphite substrate using scanning tunneling microscopy / spectroscopy

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Abstract. Comparison of electron transport across dodecanethiol capped Au nanoclusters adsorbed in different locations viz. in an agglomeration, on isolated particle either on the terrace or at the step edge of highly oriented pyrolytic graphite using scanning tunneling microscopy / spectroscopy is carried out. Current-distance measurements on these different locations shows different regimes suggesting different mechanisms for electron transport. Current-voltage measurements at these locations have been carried out and the results are discussed in the light of orthodox theory for electron transport in double-barrier tunnel junction.

1. Introduction
Metallic and semi-conducting nanoparticles have drawn considerable attention in recent years due to their exciting size and shape dependent properties arising from quantum effects [1,2]. They are generally passivated with a layer of organic adsorbates that serves to stabilize the cores by protecting them from aggregation and sintering. Though several techniques are used to study such functionalized metal nanoparticles, Scanning tunneling microscopy (STM) / Spectroscopy (STS) is a powerful tool to look at the topographic and local electronic properties of these films [3]. STM images, current-voltage (I-V) characteristics and Coulomb blockade study of alkanethiol capped gold nanoclusters on different substrates have been reported by many groups [4,5,6,7,8] but there are no experiments on combined I-V and current-distance (I-s) measurements taken on capped gold nanoparticles adsorbed on different sites of the highly oriented pyrolytic graphite (HOPG) substrate.

In this paper we present a comparison of electron transport across dodecanethiol (DDT) capped Au nanoclusters adsorbed in different locations viz. in an agglomeration, on isolated particle either on the terrace or at the step edges of HOPG substrate. I-s spectroscopy measurements were carried out using STM to determine the barrier height ($\Phi$) at these different locations. The experimental I-Vs at these different locations have been analysed in the light of orthodox theory for double-barrier tunnel junction (DBTJ) by comparing the best fit of experimental data with theoretical ones [9,10].

2. Experimental Procedure
Synthesis of DDT capped Au nanoparticles was performed by modified Brust method [11] described elsewhere [7] and deposited on HOPG substrate using drop coating technique and subsequent drying for 5 minutes. STM / STS studies were carried out immediately (within 10 minutes) after the
deposition using chemically etched Pt-Ir tip with JSPM-5200. Tunneling spectroscopy (I-s and I-V) measurements was performed after locating the particle by positioning the tip in different locations mentioned above and measuring I-s and I-V characteristics. The dI/dV versus V characteristics was obtained by numerical differentiation of measured I-V curves. The slope of the plot of $\ln I$ versus distance ‘s’ at different sites gives the barrier height at these different locations.

![Image](image1)

**Figure 1.** (a) Constant current STM image of HOPG surface (Scan area: 20 x 20 Å$^2$, $I = 1.14$ nA, $V = 0.023$ V) (b) STM image of agglomeration of nanoclusters deposited on HOPG (Scan area: 1500 x 1500 Å$^2$, $I = 0.5$ nA, $V = 0.47$ V). (c) STM image of nanoparticles at the step edge deposited on HOPG (Scan area: 380 x 530 Å$^2$, $I = 0.5$nA, $V = 0.47$ V). (d) Line profile of the nanoparticles marked by a line in (b).

Figure 1(a) shows the STM image of bare HOPG substrate and figure 1(b) and figure 1(c) shows the drop coated film of DDT capped Au nanoparticles on HOPG substrate. The calculated size of nanoparticle from the line profile (shown in figure 1(d) ) comes out to be $\approx 6$ nm. As can be seen from the image in figure 1(b), there are some areas with isolated particles and some with agglomeration of particles. Figure 1(c) clearly shows the Au nanoparticles aligned along the step edges of HOPG substrate. I-s and I-V characteristics were taken on nanoparticles adsorbed in an agglomeration, isolated particle and particle at step edges of HOPG substrate.

3. Theoretical Section

According to Hanna and Tinkham [9] the tunneling current across nanoparticle in DBTJ is given by,

$$I(V) = \frac{1}{R_j C_\Sigma} \left[ -(n_0 e - Q_0) + C_1 V - \frac{e}{2} \text{sgn}(V) \right]$$

(1)

Where $R_j$ is the tunneling resistance of the $j^{th}$ junction, $n_0$ is the most probable number of electrons on the center electrode, $C_\Sigma = C_1 + C_2$ ($C_1$ and $C_2$ are the capacitance of the first and the second junction) and $Q_0$ is the fractional electron charge present on the particle. The $\text{sgn}(V)$ is the signum function of $V$ often used to define a function of real number, which is 1 for positive numbers, -1 for negative numbers and 0 for zero. In low bias free electron model [3]
\[ \frac{1}{R_j} \propto \frac{V}{s} \exp\left(-A\Phi^2 s\right) \]

where \( s \) is in Å, \( \Phi \) the average barrier height in eV and \( A = 1.025 \text{ (Å)}^{-1} \text{eV}^{-1/2} \). Since \( C_x \propto (1/s) \) for small distance where parallel plate capacitance formula is valid so the quantity \((1/(R_jC_x))\) of equation (1) is proportional to \(\exp(-A\Phi^2 s)\). Even if the parallel plate approximation is not valid, the distance dependence of prefactor in the expression of \( R_j \) [equation (2)] will be compensated by distance dependence of capacitance. The distance dependence of capacitance in two junction system in STM was investigated by Black et al. [12] who showed that the tip/grain capacitance increases as the tip is moved towards the sample, while grain/substrate capacitance indeed remained constant. Thus the plot of \( \ln I \) versus distance ‘s’ for DBTJ junction should be a straight line the slope of which yields \( \Phi \) in eV, the barrier height.

\[ \text{Figure 2. (a) Plot of } \ln I \text{ (I in Amperes) versus distance ‘s’ (s in Angströms) on agglomeration of nanoclusters (marked by ‘o’) and on isolated nanocluster (marked by ‘Δ’). Inset (b) shows the plot of } \ln I \text{ (I in Amperes) versus distance ‘s’ (s in Angströms) for bare HOPG (marked by ‘o’) and nanocluster at the step edge (marked by ‘Δ’) to calculate the barrier height at different sites. Inset (c) shows I-V taken on bare HOPG.} \]

4. Results and Discussion

Figure 2 (a) and (b) shows plot of \( \ln I \) (I in Amperes) versus distance ‘s’ (s in Angströms) between tip and nanoparticle at various sites. It can be seen that all the plots except nanoparticle at the step edge exhibits two slopes with a change over point at around 7-10 Å. This is much smaller than the length of the DDT molecule i.e. 18.2 Å (reference [13]). It is known that DDT molecules on Au surfaces are tilted \( \sim 30° \) normal from the surface normal [14] to the substrate, in addition there may change in bond length after adsorption on gold surface. It is likely that tip would further compress the molecule before it penetrates [15]. We believe that this change over point at around 7-10 Å represents penetration of tip into the molecules leading low values of barrier heights. Table 1 summarizes the values of barrier heights obtained from \( \ln I-s \) plots where \( \Phi_1 \) and \( \Phi_2 \) are the slopes of two different regimes in figure 2 (a) and figure 2 (b). For nanoparticle at the step edge, there is a change in the slope.
in ln I-s plot at three different points so four different Φ has been observed which shows the presence of some complicated electron transport mechanism.

**Figure 3.** I-V taken on isolated nanoparticle (marked by ‘o’). Left inset shows I-V taken on nanocluster at the step edge (marked by ‘o’). Right inset shows the I-V taken on array of nanocluster (marked by ‘o’). Each curve is an average of eight runs. Dark solid line in all the three cases shows the theoretical fits based on orthodox theory for DBTJ.

**Table 1.** Comparison of barrier heights obtained from ln I-s plot and energy gaps obtained from I-V plot, conductance plot (dI/dV-V) and from DBTJ theory.

| Site of location of particle | Φ from ln I-s plot (eV) | E_g from I-V (eV) | E_g from conductance plot (eV) | E_g from DBTJ Theory (eV) |
|-------------------------------|-------------------------|------------------|-------------------------------|--------------------------|
| Bare HOPG                     | Φ₁=0.06                | –                | 1.97                          |                          |
|                               | Φ₂=0.26                |                  |                               |                          |
| Isolated                      | Φ₁=0.12                | 1.48             | 1.14                          | 0.32                     |
|                               | Φ₂=5.48                |                  |                               |                          |
| Agglomeration                 | Φ₁=0.20                | 0.97             | 0.624                         | 0.27                     |
|                               | Φ₂=2.76                |                  |                               |                          |
| At stepedge                   | Φ₁=0.2                 |                  |                               |                          |
|                               | Φ₂=0.03                | 1.69             | 1.41                          | 0.67                     |
|                               | Φ₃=0.37                |                  |                               |                          |
|                               | Φ₄=2.62                |                  |                               |                          |
It is also interesting to take I-V on these sites so it was carried out. Figure 3 shows I-V on array, on isolated particle and particle at the step edge respectively. Figure 2 (c) shows the I-V taken on bare HOPG substrate. It can be seen that I-V curves differ substantially on different locations. The data was fitted with the orthodox theory for DBTJ. We have performed curve fitting (from the program available in website) [16] of the I-V plots on Au nanoparticles capped with DDT based on the orthodox theory.

The Coulomb blockade energies (E_c) obtained from theoretical fits are 0.27eV (assembly), 0.32eV (isolated particle) and 0.67eV (particle at step edge). The results are discussed in the light of possible electron transport mechanism for DBTJ in STM configuration. Table 1 compares the barrier heights obtained from ln I-s plot and energy gaps obtained from I-V plot, conductance plot (dI/dV-V) and from DBTJ theory where E_c is the charging energy defined as $e^2/2C$ in orthodox theory for DBTJ [9] and E_g is the energy gap obtained from zero conduction regions in I-V and onset of conduction in dI/dV-V plots which are in some sense measure of barrier for tunneling. The low values of barrier heights both from orthodox theory for DBTJ as well as from onset voltage in the conduction plots (shown in Table 1) suggest that more complex mechanism is involved in the interpretation from I-V measurements of nanoparticles capped with molecular monolayers [17].

5. Conclusion
In conclusion, electron transport across DDT capped Au nanoparticles adsorbed in different configurations of HOPG has been investigated using STM/STS and the results have been analysed in the light of orthodox theory of DBTJ. In spite of the complicated I-s behaviour observed in the present work, the combination of I-s measurement with I-V spectroscopy appears to provide a better understanding of electron transport in self-assembled nanoparticles.

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