Observation of random telegraphic noise in scanning tunneling microscopy of nanoparticles on highly oriented pyrolytic graphite

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Abstract. Random telegraphic noise in scanning tunneling microscopy of dodecane thiol capped Au nanoparticles on highly oriented pyrolytic graphite surface has been investigated. The presence of nanoparticles gives rise to random switching of tunneling current between two discrete levels. The experimental power spectra of these current fluctuations show $1/f^2$ dependence. Analysis of the behavior of the power spectrum indicates that observed noise originates from Brownian motion of the trapped nanoparticle. Statistical analysis of the fluctuations shows exponential behaviour with time width $\tau \approx 18$ ms. The results suggest a method of producing an electrostatic trap analogous to laser tweezer.

1. Introduction
Nanoparticles have received considerable attention over the last decade or so primarily due to their exciting application potential and the extraordinary physical, electrical and opto-electronic properties exhibited by them [1,2]. Among the various techniques to characterize the nanoparticles, scanning tunneling microscopy / spectroscopy (STM / STS) has the unique capability to resolve topographical and electronic structures at atomic level [3], have revolutionized the power of experimental techniques in high resolution imaging of surfaces. Recently we have shown that dodecane thiol capped Au (Au-DDT) nanoclusters of size $\sim 3.72$ nm exhibits Coulomb blockade [4].

In the present experiment, bursts of pulses with characteristic distribution which appeared unpredictably in STM tunneling current was observed for Au-DDT nanoclusters on DDT covered highly oriented pyrolytic graphite (HOPG) surface and this was totally different from random noise which was generally observed on adsorbate covered HOPG.

2. Experimental Section
The Au-DDT nanoparticles were prepared according to the modified method of Brust et al [5]. One of the most widely used test samples for STM is HOPG due to its reasonable flatness in sub-nanometer range and non-reacting nature. HOPG sample was dipped in spacer (DDT) solution for 24 hours and later in nanoparticle solution in toluene for 2 hours. A saturated layer of DDT provided an active surface which prevented agglomeration of nanoparticles on terraces or adsorption at the step edges of HOPG. Current-time (I-t) and STM studies were made on bare HOPG and Au-DDT nanoclusters on
DDT covered HOPG. The STM tips were prepared from 0.25 mm diameter polycrystalline Pt-Rh wire by mechanically cutting them at an angle to the axis of the wire.

**Figure 1.** Current-time graph for bare HOPG (upper trace) and Au-DDT nanoparticles adsorbed on DDT covered HOPG (lower trace) where I=0.5nA and V=100mV (The output of pre-amp is A.C. coupled to remove the D.C. part, I-t taken on bare HOPG is shifted upwards for clarity).

**Figure 2.** Power Spectra of Current-time graph for Au-DDT nanoparticles adsorbed on DDT covered HOPG in figure 1(lower trace). Dark solid line shows the linear fit with slope = -1.99 and intercept = 3.03. Right inset shows the 3D view of STM image of Au-DDT nanoparticles on HOPG substrate. Scan area= 130 x 130 nm², I=0.5 nA, V=0.47V. Left inset shows the plot of ln I versus ‘s’ for blank HOPG and Au-DDT nanoclusters on HOPG.
A home-built STM based on fine mechanical-screw-lever arrangement assembly [6] with a compact four-quadrant three dimensional scanner was used for this investigation [7]. With feedback loop suspended, I-t data for tunneling current was acquired for bare HOPG and for Au-DDT nanoclusters on DDT covered HOPG. The later shows a peculiar type of noise i.e. random telegraphic noise (RTN), for which amplitude remains constant and the duration of the pulse is random. Figure 1 shows a typical time-series plot of tunnel current for bare HOPG and Au-DDT nanoparticles on DDT covered HOPG. The high current spike (lower trace in figure 1) is presumably caused by diffusing nanoparticles touching the tip. The spectral density of these time-series data was then calculated using standard FFT routines [8]. In double logarithmic plot, the power spectra of these RTN in tunneling current for Au-DDT adsorbed on DDT covered HOPG consisted of $1/f^2$ behavior (shown in figure 2). Also from the statistical analysis of the fluctuations observed, the plot of the number of trapping events that have a residence time larger than a given duration as a function of time fits well with exponential curve with characteristics time $\tau \sim 18$ ms (shown in figure 3).

![Figure 3](image3.png)

**Figure 3.** Plot of the No. of the trapping events with residence time larger than particular duration versus time (ms). Inset shows the STM image of DDT capped Au nanoparticles on DDT covered HOPG and its line profile. Scan area is $1000 \times 1000 \ \text{Å}^2$, $I = 0.2\text{nA} \ V = 160\text{mV}$.

### 3. Theoretical Section

There have been a number of observations related to RTN in electronic devices like metallic nanobridges [9], metal-insulator-metal (MIM) tunnel junctions [10], metal-oxide-semiconductor field effect transistors (MOSFETs) [11] etc. and it has been used to study the electronic conduction and dynamics of the disordered systems. In these cases random switching of the current, resistance or voltage takes place between two discrete values and the reason for RTN has been attributed to some processes like trapping and detrapping of electrons or defect mobility etc. A simple way to explain the origin of RTN in the present work would be to model nanoparticle trapped in tunnel junction as double barrier tunnel junction (DBTJ) [12] with two different time constants $\tau_1= R_1C_1$ and $\tau_2=R_2C_2$. For nanoparticles used in the present experiment, $\tau_1$ and $\tau_2$ were found [4] to be in nanosecond range and therefore RTN observed from this will not be detected by pre-amplifier with bandwidth of $\sim 10$ kHz. RTN in the tunnel current produced by shot noise has been predicted for an array of movable colloid particles by Monte Carlo and molecular dynamics calculations [13]. The electron transport is attributed to the shuttle mechanism where moving colloid particles carry charges. Shot noise that is uncorrelated with the colloid-particle motion causes transitions between the periodic and quasiperiodic vibration modes, resulting in random switching between the current levels corresponding to the vibration modes.
A comparison of power spectra in reference 13 shows that the frequencies of the peaks observed are much higher than that of the present work. However, these simulations are done at 0°K. It is possible that the spectra at high temperature are considerably modified. Secondly, the current-voltage (I-V) characteristics exhibit hysteresis. We could not take I-Vs during RTN due to instabilities and hence the presence or absence of hysteresis could not be verified. RTN has also been occasionally observed in STM in presence of water [14] or in extreme cases of sharp tips [15,16]. In this work, RTN observed only in the presence of nanoparticles is investigated and therefore refers to different situation. Another approach is to assume that the nanoparticles are trapped in the tunneling junction due to the electric field present around the area. The fact that the nanoparticles can be trapped electrostatically has been proved experimentally for planar tunnel junction [17,18,19].

![Figure 4](image)

**Figure 4.** Plot of Electric Field, $F(r)$ versus $r$ (It is the vector in the surface from origin directly under the tip apex in the plane) for metallic tip-sample combination (without spacer molecules and nanoclusters) where $r_t$ is the tip radius, $z_0$ is the distance between centre of spherical tip and plane (= $r_t + 10$ Å) and $V$ (= 0.1 V) is the applied voltage. Inset shows the schematic diagram of the model showing capped nanoparticle (NP) trapped in the tunnel junction.

In STM configuration, the electric field $F(r)$ for a tip above a plane surface is given by [20]

$$F(r) = F_0 \left[ 1 + \left( \frac{r}{z_0} \right)^2 \right]^{-\frac{3}{2}}; \quad F_0 = -V \frac{r_t(2z_0 - r_t)}{z_0^3 (z_0 - r_t)}$$  \hspace{1cm} (1)

where $F_0$ is the field on the surface at $r = 0$, $r_t$ is the tip radius, $r$ is the vector in the surface from origin directly under the tip apex in the plane, $z_0$ is the distance between tip and plane and $V$ is the applied voltage. Figure 4 shows the plot of electric field $F(r)$ versus ‘r’ using above equation and it shows that for a tip of radius around 1000 Å, the electric field can influence the nanoparticles / molecules up to ~ 4000 Å on the surface [21]. The diffusing nanoparticles confined to the region of few thousand Å by polarization forces would repeatedly touch the tip due to Brownian motion and give rise to a sharp pulse (~100 nA in present case) in the tunnel current. The time for which a pulse lasts would then be a measure of residence time of the trapped particle. To verify this a separate experiment was performed in which current-distance (I-s) measurements were carried out on isolated Au-DDT nanoparticle on HOPG (shown in right inset of figure 2) and on blank HOPG surface. Left inset of figure 2 shows the
plot of \(\ln I\) versus distance ‘s’. At a distance of around 8-10 Å there is a change in slope indicating contact of tip to Au-DDT nanoparticle. Measured current of ~100 nA in I-s plot at this point further supports the view that current pulses observed in figure 1 are due to tip particle contact.

The STM imaging was carried out only after the fluctuations have died out, with optimum values of tunnel current (0.2 nA) and bias voltage (160mV) in constant current mode. Inset of figure 3 shows STM image (1000 x 1000 Å²) of Au-nanoparticles on DDT covered HOPG surface and its line profile. Several isolated particles could be identified. The particle size of 70-80 Å is estimated from STM image.

4. Conclusion
In conclusion, we observed RTN in STM of Au-DDT nanoparticles on DDT covered HOPG substrate. Although exact origin of RTN could not be determined unequivocally, the results suggest the combination of electrostatic trapping and Brownian motion of these nanoparticles give rise to RTN. These observations are similar to that observed for the beads trapped in optical trap and hence provide a feasibility of producing an electrostatic trap for nanoparticles [22].

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References
[1] Alivisatos A P 1996 Science 271 933
[2] Brus L E and Tranntman J K 1995 Phil. Trans. R. Soc. Land. A 353 313
[3] Dharmadhikari C V 2000 Encyclopedia of Analytical Chemistry: Instrumentation and Applications, ed Meyers R A (UK:Wiley) pp 9284
[4] Chaki N K, Singh P, Dharmadhikari C V and Vijayamohan K P 2004 Langmuir 20 10208
[5] Brust M, Walker M, Bethell D, Schiffrin D J and Whyman R 1994 J. Chem. Soc., Chem. Commun. 801
[6] Kaiser W J and Jaklevic R C 1987 Surf. Sci. 181 55
[7] Binnig G and Smith D P E 1986 Rev.Sci.Instrum. 57 1688
[8] Press W H, Teukolsky S A, Vetterling W T and Flannery B P 1992 Numerical Recipes in FORTRAN-The Art of Scientific Computing, 2nd Edition, Cambridge University Press
[9] Ralls K S and Buhrman R A 1988 Phys. Rev. Lett. 60 2434
[10] Rogers C T and Buhrman R A 1984 Phys. Rev. Lett. 53 1272
[11] Ralls K S, Skocpol W J, Jackel L D, Howard R E, Fetter L A, Epworth R W and Tennant D M 1984 Phys. Rev. Lett. 52 228
[12] Hanna A E and Tinkham M 1991 Phys. Rev. B 44 5919
[13] Nishiguchi N 2002 Phys. Rev. Lett. 89 066802
[14] Boussaad S, Xu B Q, Nagahara L A, Amlani I, Schmickler W, Tsui R and Tao N J 2003 J. Chem. Phys. 118 8891
[15] Sugita S, Mera Y and Maeda K 1996 J. Appl. Phys. 79 4166
[16] Grey F, Huang D and Aono M 1994 Philos. Mag. B 70 711
[17] Bezryadin A, Dekker C and Schmid G 1997 Appl.Phys.Lett. 71(9) 1273
[18] Amlani I, Rawlett A M, Nagahara L A and Tsui R K 2002 Appl.Phys.Lett. 80(15) 2761
[19] Sato T and Ahmed H 1997 Appl.Phys.Lett. 70 2759
[20] Gomer R 1986 Appl. Phys.A 39 1
[21] Although the formula is derived for metallic tip-sample combination, the presence of DDT layer on the surface will only change the magnitude by a factor of dielectric constant (\(\varepsilon \approx 3\) for DDT) and will not change the behavior of electric field distribution.
[22] Ashkin A 1978 Phys. Rev. Lett. 40 729