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# **Spectacular oscillations in dark and photocurrent in thiol-capped CdS quantum dots embedded in PMMA matrix**

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### Abstract

In this work, experimental results of low frequency time dependent current oscillations (under both dark and photoexcitation) in the sample cells of thiol-capped CdS quantum dots (QDs) embedded in poly(methyl methacrylate) (PMMA) matrix have been presented. The dependence of the oscillatory behavior of dark and photo current have been studied under different conditions, such as sample cell temperature, the applied bias voltage across the electrodes and concentration of thiol-capped CdS QDs. The amplitude of oscillations gradually increases with the applied bias voltage at a particular temperature and also with the increasing sample cell temperature. The period of oscillation i.e. frequency can be tuned over a wide range either by changing the sample temperature, applied bias voltage or varying concentration of thiol-capped CdS QDs. Existing theories of current oscillations in semiconductors have failed to explain the observed low-frequency current oscillations in these semiconductors. Such current oscillations are possibly associated with some kind of the formation of charge density waves in the PMMA films embedded with thiol-capped CdS QDs.

## 1. Introduction

Research on polymer nanocomposites exhibiting interesting optical, electrical, mechanical or other properties has become a subject of extensive interest during the last many years<sup>1-13</sup>. From the previous studies it has been realized that the major obstacle<sup>3</sup> for the large scale production and commercialization of nanocomposites is the serious lack of cost effective methods for controlling the dispersion of nanocomposites in polymeric hosts. The absence of structure-property relationship is another obstacle<sup>3</sup> to the extensive use of nanocomposites. In fact, to resolve the above issues serious efforts are needed for the studies of various aspects of polymer nanocomposites.

It is known that PMMA is an insulator, but from our study<sup>13</sup> metallic behaviour of the nanocomposites of PMMA with single-walled carbon nanotubes (SWCNTs) has been noticed. The interactions of nanoparticles with polymers are mediated by the ligands attached to the nanoparticle and the ligands markedly influence particle behaviour and spatial distribution<sup>3</sup>. Studies on the synthesis and photophysical properties of the nanoparticles of CdS attached / capped with thiols as ligands have attracted much attention in the recent years<sup>14-16</sup>. Our earlier study<sup>10</sup> has shown bistable electrical conductivity i.e., conductance switching between two conducting states in the nanocomposites of PMMA with benzyl mercaptan (thiol)-capped CdS QDs.

Fluctuations in physical properties have been reported near the phase transition temperature in many cases<sup>17,18</sup>. On the basis of the switching<sup>10</sup>/ transition in electrical conductivity in thiol (BM1)-capped CdS QDs embedded PMMA thin films from one conduction state to another conduction state at a certain threshold bias voltage (different for forward and



reverse bias voltage sweeps in the current-voltage (I-V) characteristics; depending on the sample cell temperature and other experimental conditions), it was thought worthwhile to check the occurrence of the fluctuation in the electrical conductivity in thiol-capped CdS QDs embedded PMMA thin films under suitable experimental conditions. The electron correlation effects on the charge transport properties of a QD under the influence of an external potential have been studied in the recent past<sup>19</sup>. Because of the small dimension of the nanostructure device, a very small bias applied on the device can cause a very strong internal electric field. Thus, the carriers in the device in presence of a field can exist in a state far from the equilibrium state and cause current oscillations. A current oscillation is a very interesting phenomenon that was usually observed in weakly coupled compound semiconductor super lattices (SLs)<sup>20</sup>. Current oscillations in ferrocene and its some derivatives under vapor-adsorption had been studied in our laboratory<sup>21</sup>. Recently Majumder et al<sup>9</sup> have reported current instabilities in poly(methyl methacrylate) (PMMA) films with dispersed silver nanoparticles. Carrier relaxation dynamics in semiconductor quantum dots is important both for understanding the fundamental physics of nanoscale materials as well as for their incorporation into optoelectronic devices<sup>22</sup>. In the course of studies in the electrical conductivity of PMMA embedded with thiol capped-CdS QDs we have observed a bias voltage dependent self-sustained current oscillations or so-called current self-oscillations in thiol-capped CdS QDs embedded in PMMA matrix at room temperature and also at higher temperatures. The presence of thiol-capped CdS in PMMA matrix caused the observed current oscillations in presence of suitable bias voltage and interestingly without any thiol-capped CdS doping in the PMMA films, no such oscillations were observed under identical conditions. The experimental results have also shown that regular oscillations were noticed only at a certain temperature and with a particular bias voltage. At other temperatures and applied

voltages, the regularity of oscillations was not maintained. It is required to mention that between the two conduction switching events at different voltages in forward and reverse bias voltage sweeps in BM1-capped CdS QDs embedded PMMA thin films, the current-voltage characteristic curves exhibited hierarchy of hysteresis loop<sup>10</sup>. The threshold voltage and width of hysteresis loop were observed to decrease with increasing sample cell temperature in the range 303-333K. Ultimately the loop almost vanished around 333K and at this temperature, conduction switching was not clear. In fact, this temperature is near the glass transition temperature<sup>23</sup> of PMMA (isotactic). Therefore, to perform the experiment in the same phase of the polymer, the sample temperature was kept lower than this glass transition temperature for the studies of oscillatory behaviour of current. The experimental results of the dependence of current oscillations on several parameters such as sample cell temperature, bias voltage and concentration of thiol-capped CdS in the PMMA matrix are presented in this paper. The possible mechanism of such current oscillations has been discussed.

## 2. Experimental

Benzyl mercaptan (BM) capped CdS QDs were synthesized<sup>16</sup> by using the microwave irradiation method. For the preparation of BM-capped CdS nanocrystallites/ QDs, 50mM of each of cadmium acetate and thiourea and 30 mM of benzyl mercaptan (thiol) were taken<sup>16</sup>. The prepared BM-capped CdS QDs were designated as BM1 in our earlier paper<sup>16</sup>. The sizes (diameter: 2R) of the CdS QDs capped with BM1 were estimated<sup>16</sup> to be 2.734 nm. A measured amount of synthesized BM1-capped CdS QDs was dispersed into PMMA (MW 1, 20,000) matrix. The mixture was dissolved in chloroform (Spectroscopic grade, SRL India) solvent (100 mg/3mL) and sonicated for 1/2 h to obtain a homogeneous mixture of PMMA/BM1-capped CdS QDs. In the mixed solution, concentration of BM1-capped CdS QDs in

PMMA varied between 1 to 15 wt%. The QDs were characterized through usual procedures, namely, using UV- Vis spectroscopy, FESEM (model: JSM-6700F, JEOL, Japan, operating voltage 5 kV), EDX analyses, SAED patterns, transmission electron microscopy (TEM) (Model: JEM-2010, JEOL, Japan, operating voltage 200 kV), HRTEM images and XRD etc. To make the thin films freshly prepared solution was used. Using this solution several almost identical thin films were prepared by spin coating (2000 rpm) method using programmable spin coater, SCU-2008C, Apex Instruments Co., Kolkata, India. Solutions were spun on glass/ quartz substrates at a speed of 2000 rpm for 60s. All these films were made in an ambient air with a relative humidity of 65-70%. To allow the evaporation of solvent from the films, the films were kept at room temperature for 24 hours. To study the electrical characteristics a sample cell with the film was placed in a specially designed brass conductivity chamber coated with Teflon<sup>9,24</sup>. Measurements were carried out at room temperature and also at higher temperatures. Silver paste was used for electrical contact. The area of each electrode was 2 x 9 mm<sup>2</sup>, and the separation gap between two electrodes was 4 mm in a surface-type cell configuration<sup>9,24</sup>. For the current-voltage measurement the sweeping direction of the applied bias was -ve → +ve → - ve. The voltage sweep was 500 mV for every set of reading after 2s resulting in a scan speed was 250mV/s. Temperature of the sample film was controlled by a PID temperature controller (model 2404, Eurotherm, UK). The current vs. time and current-voltage characteristics were recorded with a programmable electrometer (Model 6517A, Keithley Inst. Inc., USA). The photoexcitation was done by using a Xenon lamp source (Newport, Optical Instruments USA). A monochromator (Type-H-20-UV, Ins.SA, division Jobin Yvon, France) was used for obtaining monochromatic radiation of required wavelengths (200-800 nm) for the photoexcitations. Before measuring the conductivity the heating cooling treatments were also done. The rate of heating and cooling was

4<sup>0</sup>C/min and 2.5<sup>0</sup>C/min, respectively. All the measurements were performed in a vacuum chamber<sup>9,24</sup>. Between two successive measurements the sample was allowed to relax for at least 30 minutes. The instrument was interfaced with a computer.

### **3. Results and discussion**

#### **3.1 TEM and FESEM images of the composites of PMMA with BM1-capped CdS QDs.**

TEM image of the composites of PMMA with BM1-capped CdS QDs is shown in Fig.1a. Similar TEM image and corresponding histogram were presented in our earlier article<sup>10</sup>. For ready reference the histogram is shown in Fig.1b. The TEM image in Fig.1a shows that spherical and isolated particles are obtained. From the HRTEM analysis (Fig.1.b), the size distribution of the QDs is estimated to be nearly 3.35 nm. Clear crystalline lattices of the QDs were observed (shown in figure 1c), the spacing between two crystal planes was estimated to be nearly 2.3 Å. Fig.2 shows the FESEM images of BM1-capped CdS QDs embedded in PMMA matrix, having different concentrations of BM1-capped CdS QDs. With increasing concentration of BM1-capped CdS QDs in PMMA matrix, the size of the nanocrystallites/ particles increases. At higher concentration (15 wt%), aggregation of particles is noticed from Fig. 2e.

#### **3.2 Dependence of the current - voltage (I-V) characteristics on the amounts of BM1-capped CdS QDs in the nanocomposites with PMMA.**

The current vs. voltage (I-V) characteristics, in the voltage range -5V to +5V (at room temperature 303 K), of the sample cell of PMMA having different concentrations of BM1-capped CdS QDs embedded in it, is shown in Fig.3. During the forward direction of sweep (from negative to positive voltage), the current at a particular voltage is seen to be different (except for the two junction positions) from the reverse direction (from positive to negative

voltage) as demonstrated in Fig.3. The current in the cases of different concentrations under study shows hysteresis behavior (clockwise) with respect to the applied bias voltage. The hysteresis behavior presented in Fig.3 shows interesting dependence on the concentration of BM1-capped CdS QDs in the PMMA film. A drastic change in current was noticed for 20 and 50 wt % concentration (Fig. 3b). It is also noticed that the areas within the hysteresis loops (at room temperature) and the separation gaps between the forward and reverse currents at  $V = 0V$  increased almost linearly with increasing concentration of BM1-capped CdS QDs upto 15 wt % as shown in the inset of Fig.3a. It should be mentioned here that the separation gap increased abruptly for 20 and 50 wt% concentration (not shown). Also the separation gaps between the forward and reverse applied voltages corresponding to  $I = 0$  were observed to vary with the concentration of BM1-capped CdS QDs in the PMMA matrix and the variation in separation gap with the concentration was observed to be almost systematic at lower concentrations. The estimated separation gap for 1, 5, 7, 10 and 15 wt % concentration of BM1-capped CdS QDs embedded in PMMA was found to be 0.652, 0.88, 1.34, 1.52 and 1.02 V, respectively. From the observed results the role of the amount of BM1-capped CdS QDs in PMMA matrix for the occurrence of hysteresis behaviour is clearly established. The hysteresis in I-V characteristics may be caused by the mobile ions, rearrangement of the space charge, interfacial polarization, and crystal orientations<sup>25</sup>. The cause of variation in the observed currents (forward and reverse sweeps) might be due to the asymmetry in the density of production of charge carriers during the two sweeps. The asymmetric characteristics in the production of charge carriers during the forward and reverse sweeps seem repeatable as its effect is understood through the difference in current values during the two sweeps observed in each case. This observation reflects the intrinsic property of the contained material.

In the experiment<sup>24</sup> with thin films of pure (without doping) PMMA and using both the electrodes of same material (silver) in a surface type cell configuration, hysteresis behavior (clockwise) was noticed. That hysteresis did not depend on the starting position of the applied bias for the measurement of I-V characteristics which indicated that field-induced slow polarization in PMMA is not responsible for the observed hysteresis. Similarly in the present case also the observed hysteresis is not related to field-induced slow polarization in the system. Again, as the electrodes were of same material and the hysteresis loops were symmetric about current axis, the hysteresis behavior is not related to the tunneling of charge carriers from the electrodes.

The temperature-dependence of the steady-state dark current ( $I_d$ ) in the sample cells of organic and organometallic materials can be expressed by the relation<sup>10,24</sup>

$$I_d = I_0 \exp(-E_d/2kT) \quad (1)$$

where  $I_0$  is pre-exponential factor,  $E_d$  is the activation energy for dark conduction,  $k$  is the Boltzmann constant and  $T$  is the absolute temperature. The plots of  $\log I_d$  versus  $1/T$  are expected to be linear, following eqn.1. On the other hand, the electrical current  $I_d$  (dark condition) in polymers is known to be controlled by variable range hopping (VRH)<sup>10,24</sup>, which can be expressed as<sup>10,24</sup>

$$I_d = I_0 \exp[-(T_0/T)^{1/\gamma}] \quad (2)$$

where  $I_d$  is the value of the dark current at a temperature  $T$ ,  $I_0$  and  $T_0$  are constants and  $\gamma$  depends on the dimension of hopping;  $\gamma$  is 2, 3 and 4 for one, two and three dimensional hopping, respectively. We have discussed in a recent publication<sup>24</sup> the temperature-dependence of electrical conductivity (proportional to the measured current) for PMMA thin films prepared

from chloroform. It was noticed that the variation of  $\log I_d$  vs.  $1/T^{1/4}$  for bias voltage lower than a threshold voltage ( $V_{th}$ ) showed the best linear fitting (based on the values of regression coefficient of the linear plots) indicating the validity of VRH model. But the variation of  $\log I_d$  vs.  $1/T$  for bias voltage higher than  $V_{th}$  showed the best linear fitting. In the case of BM1-capped CdS embedded in PMMA, the validity of eqns. (1) or (2) was also checked as discussed in an earlier paper<sup>10</sup>. It was noticed that the variation of  $\log I_d$  vs.  $1/T^{1/4}$  for bias voltage lower than a threshold voltage ( $V_{th}$ ) showed the best linear fitting and the variation of  $\log I_d$  vs.  $1/T$  for bias voltage higher than  $V_{th}$  showed the best linear fitting. Thus the conduction mechanisms for the bias voltage lower and higher than  $V_{th}$  were observed to be significantly different. The value of  $V_{th}$  for BM1-capped CdS QDs studied<sup>10</sup> under dark condition and at room temperature was around 28 V. It should be mentioned here that the voltage range for the observation of hysteresis behaviour is lower than  $V_{th}$  which suggests the validity of VRH model in the present case.

Various physical and chemical characteristics<sup>26</sup> of polymers are determined by molecular movements, which depend on the sample temperature and other experimental conditions. The ester side-groups of PMMA is known<sup>27</sup> to have high electron density and possibly different conduction paths are activated<sup>10</sup> in the PMMA films through the ester side groups following different types of voltage/ electric field induced conformation changes during application of forward and reverse bias. It is known that PMMA can be electron donor<sup>28</sup>. The value of electron affinity of isotactic PMMA has been reported<sup>29</sup> to be 0.521 eV and that of CdS has been reported<sup>30</sup> as 4.5 eV. From the studies<sup>6</sup> of electric field induced absorption (E-A) and photoluminescence (E-PL) spectra of BM-capped CdS quantum dots embedded in a PMMA film it was suggested that BM-capped CdS QDs have a significant charge-transfer character in the emitting state, and the dipole moment of the QDs may be aligned along the applied electric field.

Also, field-assisted dissociation into hole and electron at the photoexcited state having a charge-separated character was indicated<sup>6</sup>. Hence, based on our experimental results, we propose charge transfer from polymer (PMMA) to BM1-capped CdS QDs under a high electric field for the electronic transition. At lower values of voltage, the concentration of free charge carriers is low, so that the device shows a low current. However, when the electrical field increases to a certain value, an electron on the highest occupied molecular orbital (HOMO) of PMMA<sup>31</sup> may gain enough energy to be transferred into the BM1-capped CdS QDs forming additional conduction paths. At present it is not possible to support the above statement with theoretical calculations and in future it may be done by other theoretical groups.

### **3.3 Temperature-dependent current-time (I-t) characteristics of the nanocomposites of PMMA with BM1- capped CdS QDs**

It has been stated<sup>32</sup> that the hysteresis phenomena may be related to oscillations in the system. The current vs. time (I-t) characteristics of BM1-capped CdS QDs embedded in the PMMA matrix (thin films) under dark conditions at different sample cell temperatures, with a constant bias voltage of 27 V, are shown in Fig.4a. In this figure, the profiles of the dark current as a function of time at different temperatures in the range of 303-328K reveal the strong temperature dependence of the oscillatory nature of current with the variation of frequency and amplitude. Fig. 4b shows the I-t curves for PMMA films, embedded with BM1-capped CdS QDs under photoexcitation having wavelength 555 nm, but other conditions remaining same as the experiment for Fig.4a. Observed currents under photoexcitation are lower than that for dark conditions. Fig.4c represents the magnified plot of curve3 of Fig.4a. At room temperature (303K), both in dark condition (Fig.4a) and under photoexcitation (Fig.4b) the oscillatory behaviour in current is not very clear. At temperature of 328K, the oscillatory behaviour in



current under photoexcitation (Fig.4b) is not so regular compared to that of the oscillatory behaviour in current measured in dark condition (Fig.4a). Plots of peak to peak height (peak height) and time interval between two consecutive currents peaks (peak interval) as a function of temperature are shown in Fig.5a and b, for under dark condition and photoexcitation respectively. In general an increase in peak height and decrease in peak interval with temperature were noticed for dark conditions as well as under photoexcitations.

### **3.4 Bias voltage-dependent current-time (I-t) characteristics of the nanocomposites of PMMA with BM1- capped CdS QDs**

To study the effect of bias voltage on the above- mentioned oscillatory behavior of the current, the current values were recorded at a fixed temperature as a function of time at different magnitude of bias voltage (in the range from about 5 V to 50 V) under dark conditions (Fig.6a) and also under photoexcitation with a wavelength of 555 nm (Fig. 6b). From the Fig.6a, curves 4 to 6, it is observed that the current- time profiles (oscillatory behaviour) for the bias voltages of 27 -50 V are significantly different from the current-time profiles corresponding to lower bias voltages (curves 2 and 3, Fig.6a). This observation is possibly related to occurrence of the voltage induced conductivity switching<sup>10</sup> (under dark condition) around 28 V in PMMA films embedded with BM1 capped CdS QDs. In contrast, the oscillatory behaviour in current under photoexcitation (Fig.6b, curves 1-5) is regular and also similar for bias voltage of 5-40 V and oscillatory behaviour in current for bias voltage of 50V (Fig.6b, curve 6) is different. The observation of regular oscillatory behaviour in current upto higher bias voltage under photoexcitation is related to the fact that voltage induced conductivity switching under photoexcitation occurs<sup>10</sup> at higher bias voltage in PMMA films embedded with BM1 capped CdS QDs. The variation in the current peak heights and the time interval between the two

consecutive current peaks (peak interval) with the increasing bias for both dark condition and under photoexcitation are shown in Figs.7a and b, respectively. With increasing bias voltage, peak height was observed to increase for both under dark condition as well as under photoexcitation. But the peak interval was found to increase upto 40 V and for higher voltage of 50V a decrease in peak interval was noticed for both dark condition and under photoexcitation. It has been discussed in earlier publications<sup>21,33</sup> that, if the frequency varies with field at all, it should increase, whereas it has been found in the present experiment that in general the frequency decreases with increasing field strength.

### **3.5 Dependence of the I-t characteristics on the amounts of BM1-capped CdS QDs in the nanocomposites with PMMA**

The oscillatory behaviour of current in the BM1-capped CdS QDs embedded PMMA thin film in dark and under photoexcitation with a wavelength of 555 nm is shown in Fig.8a and b, respectively for different concentration of BM1-capped CdS QDs. The changes in peak height and peak interval with concentration of BM1-capped CdS QDs are clearly observed from Fig.8. It is remarkable to note that the current self-oscillations occur even at lower concentration of BM1-capped CdS QDs in the PMMA matrix. However, at higher concentrations, the current–time profiles for these PMMA films embedded with BM1-capped CdS QDs exhibit discontinuities on the sequential current oscillations and show a series of saw tooth or plateau like behavior. In our experimental results the stability of current oscillations was quite high e.g. wave form oscillations show no observable change in the time span of more than 25 min. In Fig.9a and b the changes in peak height and peak interval with concentration of BM1-capped CdS QDs are shown. Both the peak height and peak interval, in general increases with the increasing concentration of BM1-capped CdS QDs in the PMMA films and ultimately trends

towards saturation or attains saturation. From the nature of systematic variation in current oscillations as a function of various parameters e.g., sample temperature, bias voltage, concentration of BM1-capped CdS QDs etc., it is clear that such current oscillations must have a physical basis.

### 3.6 Discussion on relevant models for current oscillations in semiconductors

In the past oscillatory behaviour of current has been reported in many semiconductors<sup>33-38</sup>. In some reported experiments, in addition to electric field, external illumination and/ or an external magnetic field was applied to the semiconductors to obtain the current oscillations. A large number of semiconductors have shown oscillatory behaviour in electric current as a result of an inherent specific negative resistance as observed in the case of GaAs<sup>34</sup>. In contrast, in the present experiment, oscillatory behaviour in current has been noticed by application of electric field only and without external illumination or an external magnetic field and the system has shown positive resistance. Oscillatory behaviour of current in the positive resistance region has been reported without application of external illumination and / or external magnetic field in the case of cobalt (or gold) -compensated n-type silicon<sup>35</sup> and iodine -doped polyethylene<sup>36</sup>. In these cases<sup>35,36</sup> propagation of low field domains and perturbation across the sample, respectively, have been proposed. A theory of domain formation and propagation based on the difference in capture times for electrons and holes by traps was proposed by Konstantinov and Perel<sup>33</sup>. The theory of Konstantinov and Perel<sup>33</sup> predicts that, if the frequency of oscillations varies with the electric field at all, it should increase with increasing field. But the reverse result has been found in the present experiment which confirms that the theory is not valid for the present case. The frequency range of semiconductor instabilities generally extends from few Hz to GHz<sup>35,36,38</sup>. In the present experiment the frequency of current oscillations is very low. The phenomenon of

current oscillations with a low frequency as observed in the present case is relatively rare<sup>21,37</sup> and poorly understood. Kispeter et al<sup>37</sup> reported low frequency oscillations in photocurrent in the polycrystalline selenium sample. In this material the frequency of oscillations in photocurrent was observed to increase with increasing bias voltage. But in the present case the frequency of current oscillations decreases with increasing bias voltages as mentioned earlier. Thus the modified barrier model in the case of selenium<sup>37</sup> is not applicable in the present study. It should be mentioned here that low- frequency current oscillations have been reported<sup>21</sup> in the sample cells of ferrocene and its some derivatives with adsorbed vapours and the frequency of current oscillations was found to decrease with increasing bias voltages. In these cases the current oscillations were thought to be originated due to the adsorption -induced phase transition in the system.

As mentioned earlier fluctuations in physical properties have been reported near the phase transition temperature in many cases<sup>17,18,21</sup>. The switching in electrical conductivity in BM1-capped CdS QDs embedded PMMA thin films has been reported<sup>10</sup> and transition from one conduction state to another conduction state was discussed. The observed current oscillation in BM1-capped CdS QDs embedded PMMA films, under various experimental conditions as discussed in this article, is expected to be related to the conductivity switching reported in our earlier paper<sup>10</sup>. Recently instability in current vs. time profile was reported<sup>9</sup> in silver nanoparticles dispersed PMMA thin films. Such instability in current vs. time profiles was explained in terms of the formation of charge density waves (CDWs) in the nanocomposite films of dispersed silver nanoparticles in PMMA films. The versatile polymer PMMA has been observed to manifest charge density waves<sup>39</sup>. The current oscillation reported in this article is possibly related to the formation of charge density waves in the PMMA films embedded with

BM1-capped CdS QDs. Such nanocomposites are expected to be useful for various nanotechnology-based devices.

#### 4. Conclusions

The observation of periodic current oscillations in the current vs. time characteristics of BM1-capped CdS QDs embedded PMMA thin films is related to the voltage induced conductivity switching in this material. The systematic variations of the current peak height and the time interval between the two consecutive current peaks (peak interval) with various parameters like sample cell temperature, bias voltage and concentration of BM1-capped CdS QDs embedded in PMMA thin films indicate that the oscillations in current must have some physical basis. The period of oscillation i.e. frequency can be tuned over a wide range either by changing the sample temperature, applied bias voltage or varying concentration of BM1-capped CdS QDs. Current oscillations reported in this paper are possibly related to the formation of charge density waves in the PMMA films embedded with BM1-capped CdS QDs. The hysteresis phenomenon is related to the current oscillations in the system. Such polymer nanocomposites are expected to be useful for various nanotechnology-based devices.

#### Acknowledgements

One of the authors, Bipul Biswas thanks the Council of Scientific and Industrial Research (CSIR), New Delhi, India, for providing the financial assistances in the form of NET CSIR fellowship (file no.:09/080(0628)/2008/EMR-I). For this work the TEM facility of the Nanoscience Project (DST) of IACS was used.

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## Figure captions

**Figure 1.** (a) TEM image of CdS quantum dots embedded in PMMA matrix. (b) Histogram for the particle distribution. (c) HRTEM image of BM1-capped CdS QDs.

**Figure 2.** FESEM images of BM1-capped CdS QDs embedded in PMMA matrix with different concentration of BM1-capped CdS QDs : (a) 1, (b) 5, (c) 7, (d) 10 and (e) 15 Wt%, respectively.

**Figure 3.** Current –Voltage (I-V) characteristics of BM1-capped CdS QDs embedded in PMMA matrix (thin film) measured at room temperature (303 K) under dark condition with different amount of BM1-capped CdS QDs : **a** (1) 0, (2) 1, (3) 5, (4) 7, (5) 10 and (6) 15 wt%, respectively. The arrows indicate the direction of voltage sweeps. Inset represents the plot of separation gap at  $V=0$  V bias as a function of BM1-capped CdS QDs content in PMMA thin film. **b** (7) 20 and (8) 50 wt%, respectively.

**Figure 4.** Plots of (a) dark and (b) photocurrent (bias 27 V) vs. time profile for BM1-capped CdS QDs (amount: 1wt %) embedded in PMMA matrix (thin films), measured at different temperatures 1)303, 2) 308, 3) 313, 4) 318, 5) 323 and 6) 328 K, respectively. (c) Represent the curve 3 of Fig.4a. in a magnified scale.

**Figure 5.** (a) Plots of peak height and (b) the time interval between the two consecutive current peaks (peak interval) versus sample cell temperature for BM1-capped CdS QDs embedded in PMMA matrix (thin films) in the case of the surface type cell configuration (at 303 K), curves (1) dark, (2) under photoexcitation at wavelength 555 nm.

**Figure.6.** Current vs time profile for BM1-capped CdS QDs (amount: 1 wt %) embedded in PMMA matrix (thin film) measured at 313K under (a) dark, (b) under photoexcitation at wavelength of 555 nm for different bias voltages: 1) 5, 2) 10, 3) 20, 4) 27, 5) 40 and 6) 50 V, respectively.

**Figure 7.** Plots of (a) peak height and (b) the time interval between the two consecutive current peaks (peak interval) versus bias voltage for BM1-capped CdS QDs embedded in PMMA matrix (thin film) in the case of the surface type cell configuration (at 313 K), curves (1) under dark, (2) under photoexcitation at wavelength of 555 nm.

**Figure 8.** Current vs time profile measured at a fixed bias voltage of 10V for BM1-capped CdS QDs embedded in PMMA matrix (thin film) measured at 313K, (a) under dark, (b) under photoexcitation at wavelength of 555 nm with different concentration of BM1-capped CdS QDs: 1) 1, 2) 5, 3) 7, 4) 10 and 5) 15 wt%, respectively.

**Figure 9.** (a) Plots of peak height and (b) the average time interval between the two consecutive current peaks versus amounts of BM1-capped CdS QDs content in PMMA matrix (thin film) in the case of surface type cell configuration, (1) under dark, (2) under photoexcitation at wavelength of 555 nm.

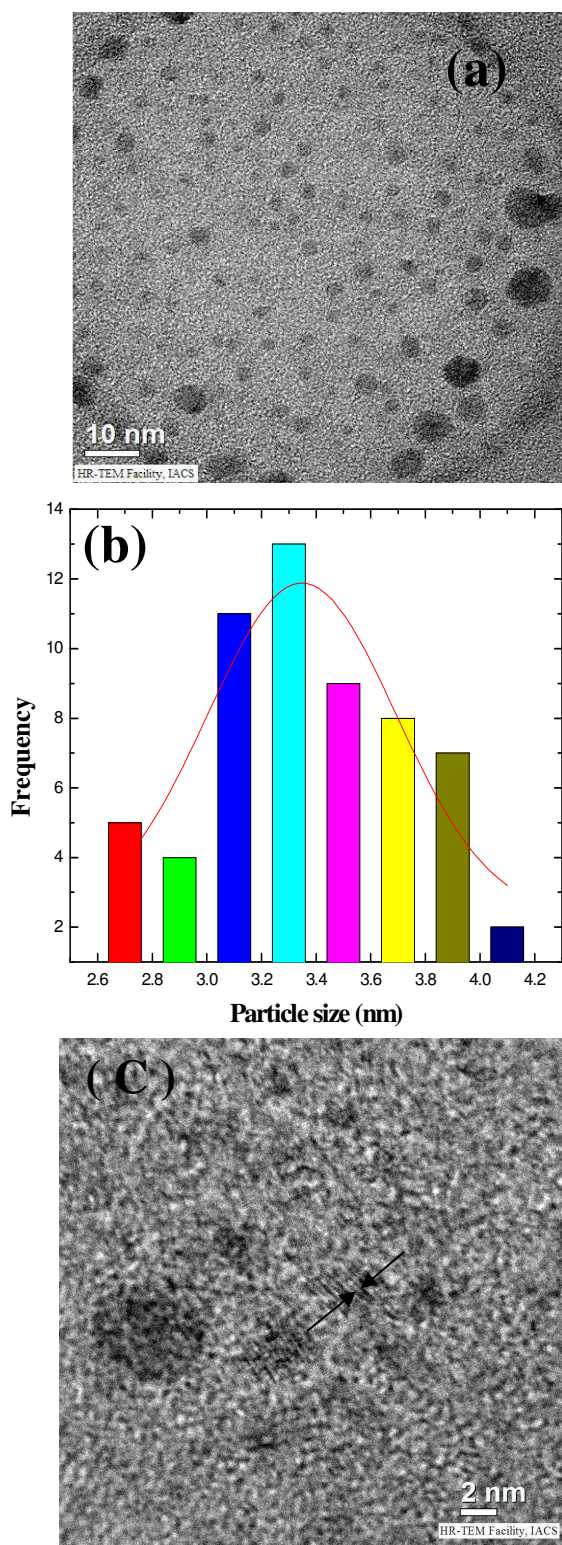


Figure 1

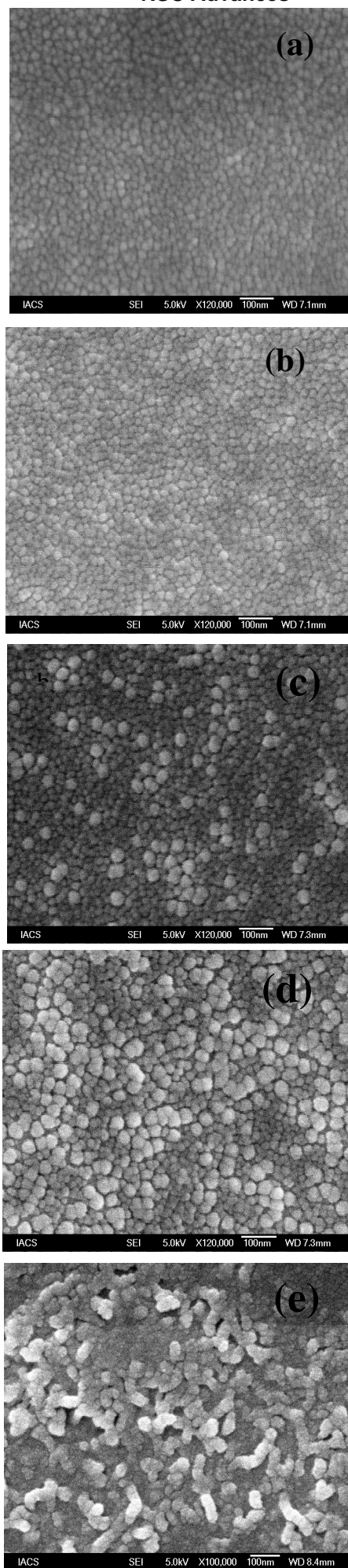


Figure 2

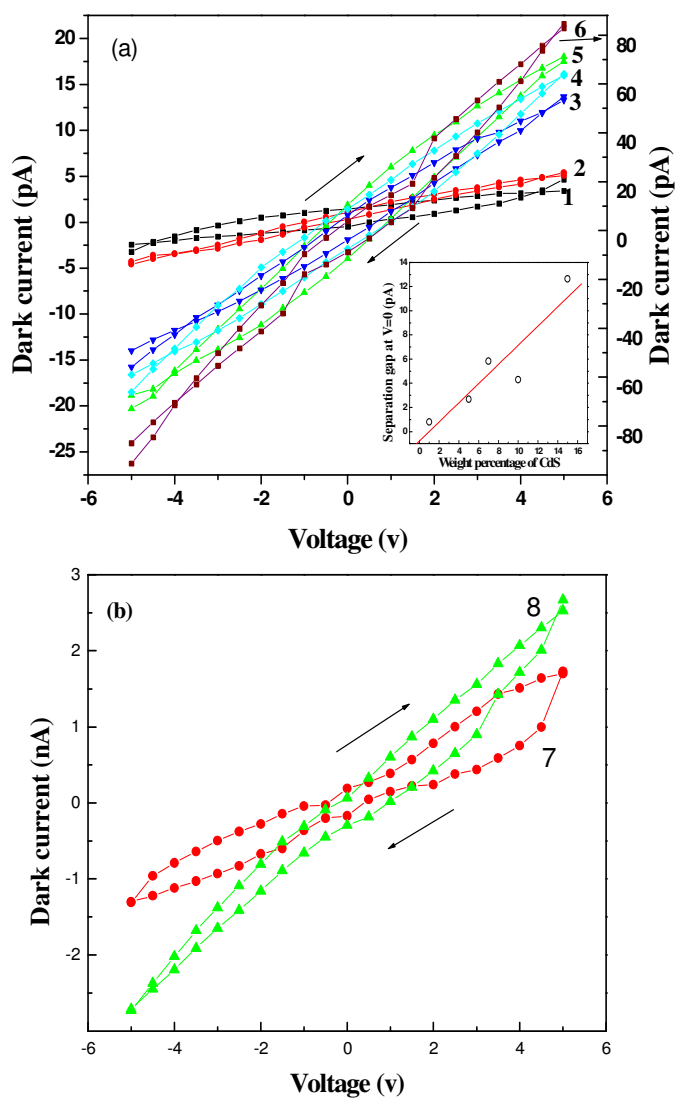


Figure 3

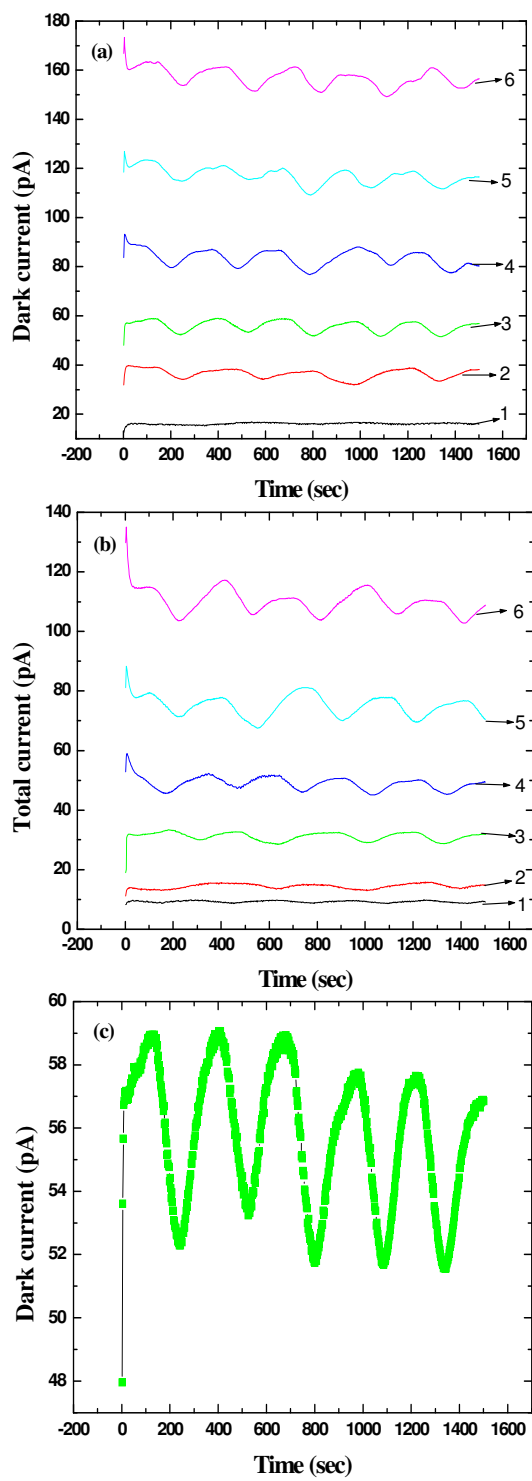


Figure 4

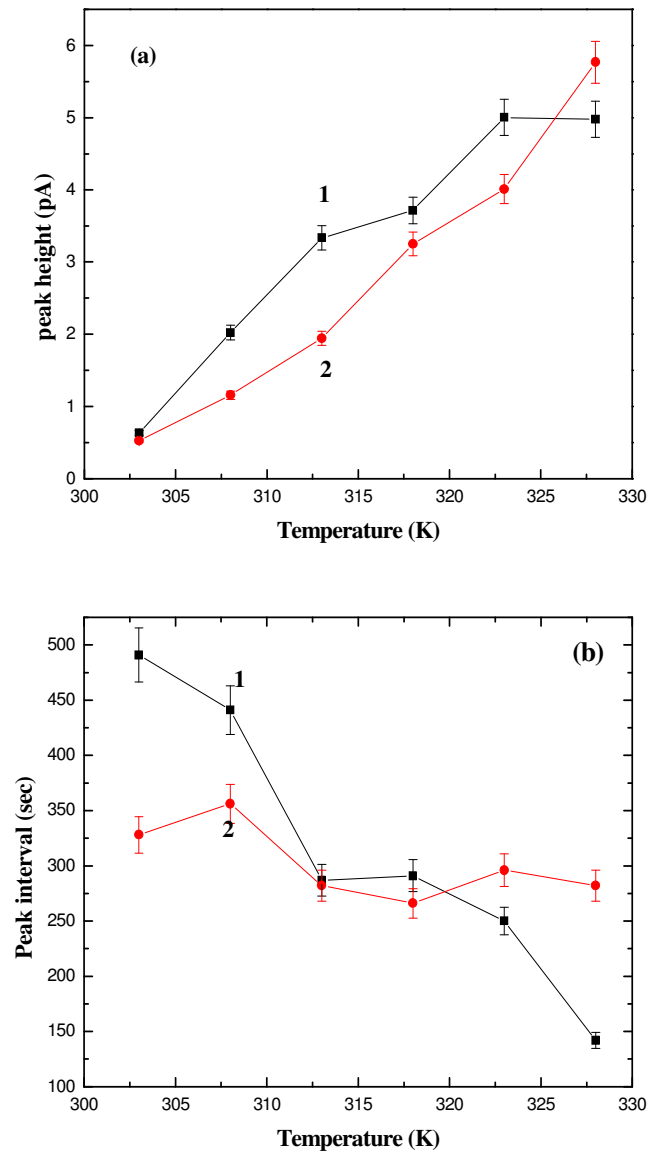


Figure 5

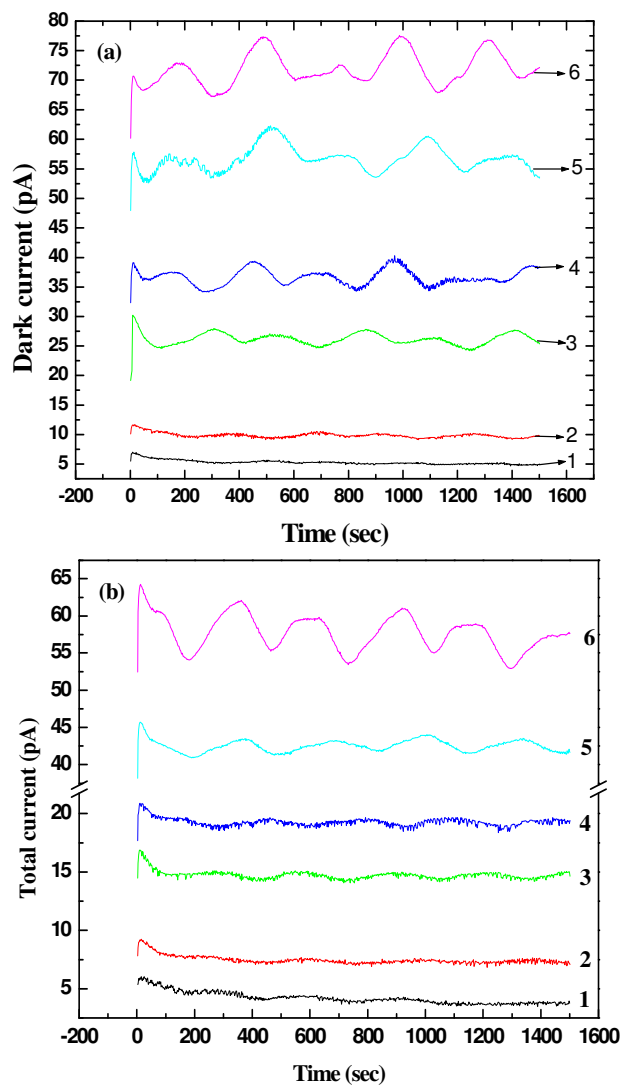


Figure 6



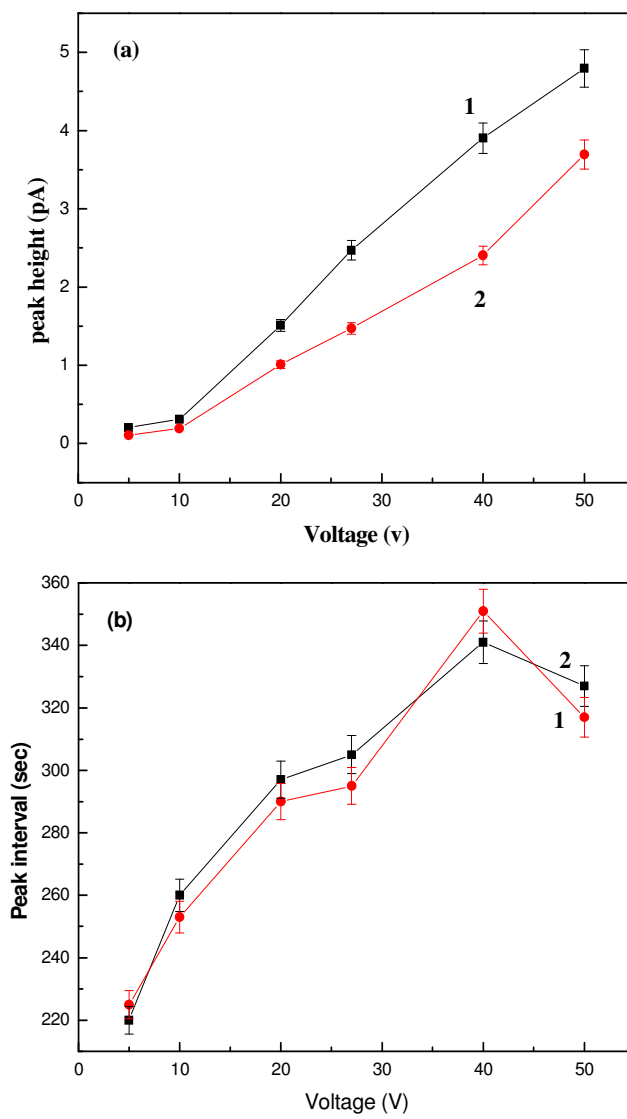


Figure 7

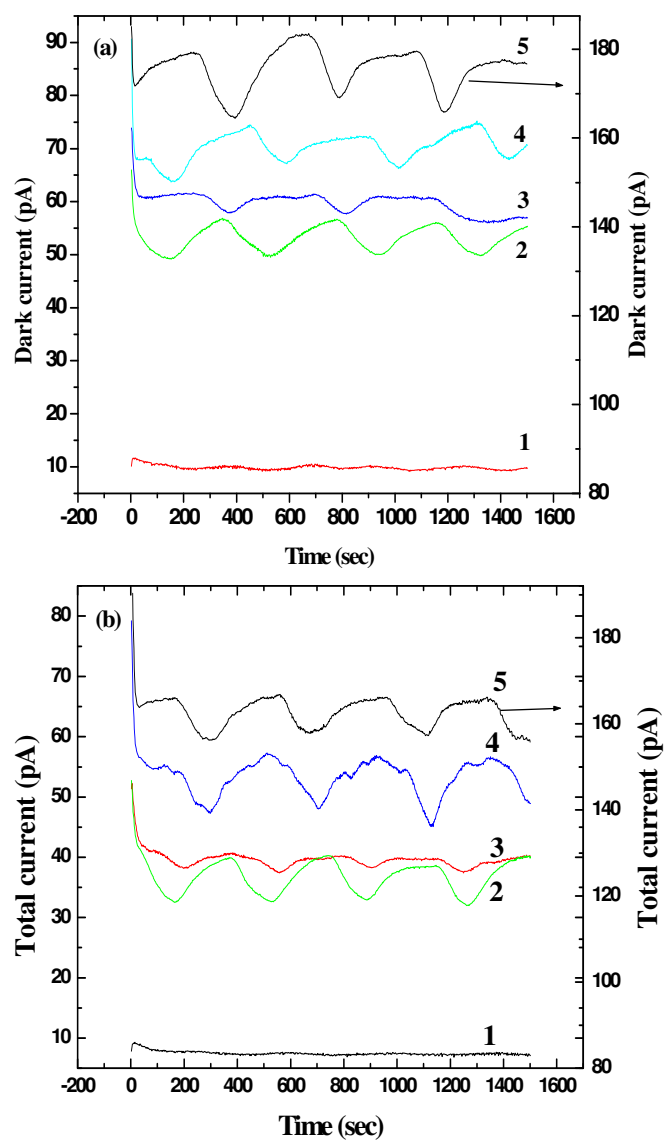


Figure 8

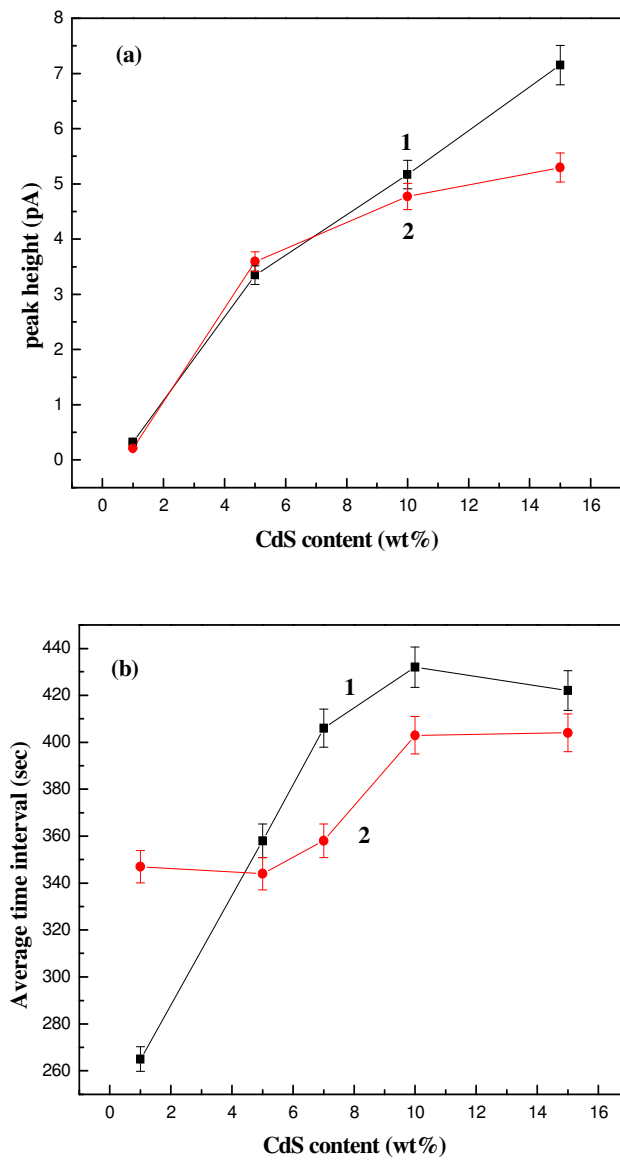


Figure 9

### Graphical Abstract

Oscillatory behaviour of current in thiol (benzyl mercaptan)-capped CdS QDs embedded PMMA matrix (thin films) under dark conditions at different sample cell temperatures: 1) 303, 2) 308, 3) 313, 4) 318, 5) 323 and 6) 328 K with a constant bias voltage of 27 V, is shown in Fig.a.

