Coulomb blockade transport emerged in quasi one-dimensional PEDOT: PSS fiber

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Abstract. In organic materials, peculiar nonlinearity to current voltage appears, thought a general and comprehensive explanation of them is still controversial. Conductive segments in poorly conductive organic materials are expected to have a smaller electrical capacity, leading to a higher critical temperature for the blockade effect. Here we show an experimental evidence of Coulomb blockade taking place on quasi one-dimensional conductive polymer, PEDOT:PSS [poly (3, 4-ethylenedioxy-thiophene) doped with poly (styrene sulfonate) anions], fibers. The PEDOT:PSS wire grows through electro-polymerization, and bridges between electrodes immersed in EDOT monomer solution. Conducting measurement for the dried fibers shows clear nonlinear behaviour in the current-voltage characteristics as temperature decreases. The non-zero threshold voltage, which increased with decreasing temperature, appears in the current flows through a thinnest fiber. The effective percolative transport passes in thin fiber is able to consists of the connection of the Coulomb blockade islands. By considering both the charge blockade effect and the influence of structural disorder and dimensionality, it is hoped that a clear understanding of charge transport in organic materials can be achieved.

1. Introduction

Good organic conductors including the polymers and monomer materials often have a low-dimensional configuration, e.g., quasi-one-dimensional structures or two-dimensional (2D) layers. Nevertheless, a large number of fundamental questions remain to be answered regarding the charge transport mechanism, particularly in low-dimensional structures. One such question concerns the nonlinear behavior that is often observed in the current-voltage (I-V) characteristics of organic conductors. Even for materials that exhibit good linear I-V characteristics near room temperature (RT), nonlinearity can occur as the temperature is reduced. This effect has been interpreted using a variety of mechanisms, such as charge hopping, trapping, tunneling and emission, either within the organic material or at the interfaces. However, the observed nonlinearity cannot be fully explained using these conventional models or combinations of them.

Recently, it has been reported that the I-V characteristics obey a power-law relationship in low-dimensional organic materials such as polymer nanofibers [1], nanotubes [2,3] and films [4-6]. The observed power-law relationship for polymer materials was sometimes put forward as evidence for tunneling into a one-dimensional (1D) Luttinger liquid because of the quasi-1D structure of these materials [4]; however, power-law behavior was also observed for a three-dimensional (3D) organic films [5,6]. Meanwhile, in inorganic granular materials, the power-law dependence of the I-V characteristics has commonly been attributed to dissipative tunneling processes, such as that...
associated with a Coulomb blockade (CB) [7-11]. CB transport occurs in systems consisting of an array of small conductive islands connected by narrow junctions, provided the tunneling resistance between neighboring sites is significantly larger than the quantum resistance ($>\hbar/e^2$), the capacitance associated with each island is sufficiently small, and the energy corresponding to an additional electron charge at each site is large compared to $k_BT$. Here, $h$ is Planck's constant, $e$ is the charge of an electron, and $k_B$ is Boltzmann's constant.

We have reported that CB transport investigated in a 2D conjugated polymer monolayer exhibits nonlinear behavior in the current-voltage characteristics, and a non-zero threshold voltage appeared, which increased with decreasing temperature [12] as predicted by Middleton and Wingreen [13]. The CB effect has been confirmed during charge transport through a single molecule spanning adjacent electrodes, although it has rarely been suggested as the origin of nonlinear conduction in larger condensed organic conductor systems [5,14,15]. In this paper, we investigate charge transport through quasi one-dimensional conductive polymer, PEDOT:PSS [poly (3, 4-ethylenedioxy-thiophene) doped with poly (styrene sulfonate) anions], fibers. The polymer fibers with different diameter show different charge transport feature at lower temperature regime. The typical CB transport feature were observed for the thin polymer fiber with about110nm diameter, whereas the thicker fiber shows only conductance decrease as hopping conduction. We associate the percolative transport passes connecting the conductive segment with the origin of CB charge transport in the quasi one-dimensional conductive fibers.

2. Methods
2.1. Polymer fiber growth
Single and straight conducting polymer fiber grows between electrodes with sharp apex immersed in monomer solution when the gap distance is short and absolute bipolar square-wave AC voltage with a 50% duty cycle were applied [16]. We performe the wire grows of PEDOT:PSS in 0.135M EDOT and 0.02M PSS in acetonitrile and ultrapure water ratio of 1:1. Liquid EDOT and PSS solution were obtained from Sigma-Aldric. Electrodes were fabricated by conventional photo lithography technique. Cr (10 nm) and Au (190 nm) were deposited on a glass substrate by using EB1100 (Canon Anelva). A solution trough made of Polydimethylsiloxane (PDMS) was placed on the substrates with electrodes and filled with EDOT and PSS solution. Bipolar AC voltage with square shape are made by using waveform generator WF1973 (NF) connected to high speed bipolar amplifier HSA4101 (NF). The AC voltage, which frequency from 500kHz to 1MHz and peak-to-peak voltage ($V_{pp}$) of 8V, is applied to one side of electrode whereas an opposite electrode is connected to GND. After the wire growth connecting between electrodes, the wires are dried in ambient condition. Wire images are observed by scanning electron microscopy (SEM) S-4700 (Hitachi) after the current measurement.

2.2. Current measurement
Measurements are carried out using a variable temperature probe (TPP-4, Lakeshore Co., Ltd.) and a semiconductor characterization system (Keithley 4200) in a vacuum of about $1\times10^{-5}$ Pa under dark conditions. Temperature is controlled by the cryogenic system with liquid helium flow from room temperature (RT) to 4.2 K. The $I-V$ characteristics are obtained from high to low temperatures keeping restrictive temperatures.

3. Results and discussion
3.1. Polymer fibers
It has been reported that PEDOT grows in wire shape through electro-polymerization by applying bipolar AC voltage between electrodes immersed in EDOT solution. The previously reported wire’s diameter was ranging from sub to few micrometres, thus they were observed by optical microscopy usually. We tried to fabricate single PEDOT wire connecting between electrodes with thinner dimeter to confirm the low dimensional structural effect on the charge transport feature. Figure 1 shows SEM images for two types of fabricated PEDOT:PSS wire. An AC voltage was applied for 0.1s for (a) and for 10s for (b), respectively. The wire diameter and number of bridging wires depends on the both frequency and time span of the applied voltage.
3.2. I-V measurement

The current flows through the PEDOT wire was measured at temperatures from RT to 4.2 K. Figure 2(a) and (b) shows the I-V characteristics observed for the thin and thick wires shown in Fig. 1(a) and (b). Both temperature depending I-V characteristics shows similar rapid current decreases with temperature decreases, Subtle nonlinearity, which is typical characteristic feature observed for organic materials frequently, are seen in the I-Vs observed in all temperature range. The nonlinearity can be emphasised in a double logarithmic plot as shown in Fig. 1(c) and (d). The solid black lines, which are overlapped on the data at low voltage region, have gradient 1 in the double logarithmic plot, whereas the data at higher region deviate from the black line to have higher gradient. This means that the I-Vs have power law dependence with higher exponent at higher voltage region, thought it has linear relationship at low voltage region.

There is a conductance difference of about 10 times at RT between these fibers, which is a reasonable value based on the cross-section area ratio. Although, the range of current decrease as temperature decrease is more than four order of magnitude for thin wire (Fig. 1(c)), whereas the conductance decrease only in two order for thick wire (Fig. 1(d)). The I-Vs at the lower temperature in Fig. 1(c) show the blockaded region with null current and subsequent power law current increase as voltage increase, which is a typical feature of CB charge transport. It is generally accepted that the thermal hopping transport in organic materials is origin of monotonical temperature dependence of conductance and subtle I-V nonlinearity as the features seen in Fig. 1(d). However, the power low with threshold observed at low temperatures in Fig. 1(c) never be explained by using the thermal hopping model.

Our previous study suggested that the percolative charge transport pass explained well the emergence of CB charge transport in low-dimensional organic materials. The charge blockade effect, i.e., the difficulty of charge injection from one conducting segment into another, becomes significant, when the temperature is low and the conducting segment has poor electrical capacity. If the hopping barrier is enough low and the charge transport pass only consists of the high capacitive conductive segments, charges will easily hop into subsequent segment. In the thick wire and three-dimensional PEDOT:PSS wire, such hopping transport passes survives even at lower temperatures. However, in quasi one-dimensional thin fiber, the electrical capacitive conductive segments might be basically poor and also the multiplicity of the pass would be low. Thus, the thermal activated hopping conduction vanishes and CB charge transport emerges at lower temperature in the thin fiber. By such considering both the charge blockade effect and the influence of structural disorder, it is hoped that a clear understanding of charge transport in organic materials can be achieved. Fitting by CB model.
Figure 2. $I-V$ characteristics observed for (a) thin wire and (b) thick wire from RT to 4.2 K. (c) and (d) $I-V$ curves of (a) and (b) shown on log-log scale, respectively. The solid black lines indicate linear conductance increase at lower voltage region.

The nonlinear CB current with a clear threshold voltage that shifts to higher values with decreasing temperature can be well fitted using a charge transport model based on a 2D CB array,

$$ I = \alpha(V - V_T)\xi $$

where $\alpha$ and exponent $\xi$ are coefficients, and $V_T$ is threshold voltage, where $V_T$ has the temperature dependence

$$ V_T(T) = V_T(0) \times (1 - \beta T) $$

The CB parameters $\xi$ and $V_T(0)$ can be estimated from the fitting results. In fact, curve fitting was carried out from low temperature to RT using the expression,

$$ I = aV^b + \alpha(V - V_T)\xi $$

where $a$ and exponent $b$ are coefficients also.

We perform data fitting by using Eq. (3) for all $I-V$s observed in the PEDOT:PSS fiber shown in Fig. 2(c). Through the fitting, the following conditions are applied:

A) $\xi$ should be independent of temperature;
B) $\alpha$ is better to be a constant especially at temperatures below $T*$;
C) Above $T*$, the coefficient $b$ should be 1,
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Figure 3. (a) Fitting curves for $I-V$ and (b) $V_T-T$ plot.

here the $T^*$ is critical temperature for the blockade effect. Figure 3 shows fitting curves overlayed on the $I-V$s and resulted $V_T-T$ plot. The fitting parameters are denoted in Table 1. This sample has $\xi$ of 2.2, which is smaller than that of polythiophene two-dimensional CB network [12]. We empirically know that the smaller value of $\xi$ is observed in better conductor, whereas the larger value is observed in material with lower conductance. The $V_T(0)$ of 0.16 and $T^*$ 51K are derived from the linear regression line in the $V_T-T$ plot as shown in Fig. 3(b). The relatively small values $\xi$ and $T^*$ suggest that the PEDOT:PSS is basically good conductor in an organic conductor.

| $T$ (K) | $a$         | $b$         | $\alpha$ | $V_T$ | $\xi$ |
|---------|-------------|-------------|-----------|-------|-------|
| 290     | $2.3 \times 10^{-9}$ | 1           | $1.4 \times 10^{-9}$ | -     | 2.2   |
| 280     | $2 \times 10^{-9}$    | 1           | $1.1 \times 10^{-9}$ | -     | 2.2   |
| 230     | $5.5 \times 10^{-10}$ | 1           | $5.3 \times 10^{-10}$ | -     | 2.2   |
| 180     | $1.5 \times 10^{-10}$ | 1           | $2.9 \times 10^{-10}$ | -     | 2.2   |
| 130     | $2.2 \times 10^{-11}$ | 1           | $1.1 \times 10^{-10}$ | -     | 2.2   |
| 80      | $2.8 \times 10^{-12}$ | 1           | $3.7 \times 10^{-11}$ | -     | 2.2   |
| 60      | $8 \times 10^{-13}$   | 1           | $2.3 \times 10^{-11}$ | -     | 2.2   |
| 40      | $4 \times 10^{-14}$   | 0.1         | $7.7 \times 10^{-12}$ | 0.04  | 2.2   |
| 30      | $2 \times 10^{-14}$   | 0.1         | $2.6 \times 10^{-12}$ | 0.07  | 2.2   |
| 20      | $5 \times 10^{-14}$   | 0.1         | $1.6 \times 10^{-12}$ | 0.1   | 2.2   |
| 4       | $3 \times 10^{-14}$   | 0.1         | $1.0 \times 10^{-12}$ | 0.16  | 2.2   |

In order to observe CB conduction in an inorganic system, it is necessary to prepare the quantum dots, which diameter almost less than 15 nm [11]. Meanwhile, conductive segments in poorly conductive organic materials are expected to have a smaller electrical capacity, leading to a higher $T^*$ for the blockade effect. Harnessing the nonlinear response in complex networking is now actively investigated in the exciting future challenge for physical implementation of informational processing [14]. The blockade effect emerges in the organic complex structure might be utilized in signal processing system interconnecting to the electrical circuit and biological systems, so on.
4. Conclusion

Charge transport through quasi one-dimensional conductive polymer, PEDOT:PSS fibers, were investigated. The typical CB transport feature were observed for the thin polymer fiber, whereas the thicker fiber showed only hopping conductance as we expected. It is demonstrated that the control of the structural dimensionality provides different charge transport regime. In 3D materials i.e., bulks and thicker films or thicker wires, CB transport should be difficult to be observed. Because due to its high variability of the conduction paths, the thermal activating hopping paths still keep its connection at low temperatures. Nevertheless, low-dimensional structure narrows down their conductive latitude, thus the hopping pass would be disconnected. Localization by disorder is a common cause of insulating behaviour of low-dimensional electron systems. The presence of disorder in organic materials will obscure the emergence of a distinguishable conduction threshold, although ironically, such disorder is a requirement for percolative transport. By considering both the charge blockade effect and the influence of structural disorder, it is hoped that a clear understanding of charge transport in organic materials and expanding to applications can be achieved.

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