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Current–Voltage Characteristics in Individual Polypyrrole Nanotube, Poly(3,4-ethylenedioxythiophene) Nanowire, Polyaniline Nanotube, and CdS Nanorope

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Abstract In this paper, we focus on current–voltage (*I–V*) characteristics in several kinds of quasi-one-dimensional (quasi-1D) nanofibers to investigate their electronic transport properties covering a wide temperature range from 300 down to 2 K. Since the complex structures composed of ordered conductive regions in series with disordered barriers in conducting polymer nanotubes/wires and CdS nanowires, all measured nonlinear *I–V* characteristics show temperature and field-dependent features and are well fitted to the extended fluctuation-induced tunneling and thermal excitation model (Kaiser expression). However, we find that there are surprisingly similar deviations emerged between the *I–V* data and fitting curves at the low bias voltages and low temperatures, which can be possibly ascribed to the electron–electron interaction in such quasi-1D systems with inhomogeneous nanostructures.

Keywords Conducting polymers · *I–V* characteristics · FIT model · Nanowires/tubes

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Introduction

Recently, low-dimensional materials especially nanowires and nanotubes have attracted considerable attention in view of their novel features and electronic device applications in future [1–3]. The unusual electronic transport properties in conducting chemically doped polymers have been widely investigated and reported owing to their unique structural features, which are known to be very inhomogeneous; namely, in some regions, the polymer chains are ordered, and in other regions, the chains are disordered [4–6]. This complex structure in disordered materials including doped polymer and inorganic nanofibers is generally considered as conduction regions or long conducting pathways separated by small insulating barriers. Especially, as a key indicator to electrical behavior, novel nonlinear current–voltage (*I–V*) characteristics with temperature and field-dependent features are observed in such quasi-one-dimensional (quasi-1D) inhomogeneous structures [7–13]. In particular, Kaiser et al. [11, 12] recently proposed a generic expression (extended fluctuation-induced tunneling (FIT) [13] and thermal excitation model) for the nonlinear *I–V* characteristics based on numerical calculations for metallic conduction interrupted by small barriers and showed that the expression can give a very good description to the temperature and field-dependent nonlinearities of *I–V* curves in polyacetylene nanofibers, vanadium pentoxide nanofibers, etc.

The electronic density of states (DOS) near the Fermi energy E_F is known as an important physical quantity for understanding the electronic transport mechanism in strongly localized systems [14] where the electron–electron interaction (EEI) is first showed with created depletion in DOS near E_F by Pollak [15] and Srinivasan [16]. Efros and Schklovskii [17, 18] called this depletion "Coulomb gap,"

which can strongly affect the transport properties. Furthermore, it is reported that the electron states in doped nanofibers are more localized by disorder at low temperature [7]. However, most of conduction electrons are considered as delocalized and free to move over a very large distance compared to atomic dimension in FIT regime [13], the EEI is not considered. Thus, if taking the EEI into account, is Kaiser expression still generic for nonlinear *I–V* characteristics of quasi-1D material? In this paper, the *I–V* characteristics of a series of doped polymer nanofibers and helically twisted CdS nanowire ropes are measured by a standard two-probe method covering a wide temperature range to investigate the transport behavior and figure out this open question. We find all these *I–V* characteristics show similar nonlinear features and are well fitted to Kaiser expression. However, the surprisingly similar deviations between the *I–V* data and fitting curves emerge in low-field region at low temperatures, which have not been reported and discussed before.

Experimental Details

8-Hydroxyquinoline-5-sulfonic acid doped polypyrrole (PPY-HQSA) nanotubes and camphor-sulfonic acid doped polyaniline (PANI-CSA) nanotubes were prepared by a template-free self-assembly method [6]. The tubular morphology of polypyrrole and polyaniline nanotubes was confirmed by a transmission electron microscopic (TEM) with outer diameters about 100–120 nm as shown in Figs. 1a and 4a, separately. Conducting poly(3, 4-ethylenedioxythiophene) (PEDOT) nanowires with diameters about 95 nm (as shown in Fig. 3a) were prepared by a hard template method described in Refs. [19–21]. As shown in Fig. 2a, helically twisted CdS nanowire ropes composed of nanowires with diameters about 6–10 nm were synthesized by aqueous chemical growth method [22, 23].

The Pt microleads attached on isolated nanofibers were fabricated by focused-ion beam deposition. The detailed procedure can be found in previous publications [6, 21–24]. The *I–V* characteristics of individual polypyrrole nanotube, helically twisted CdS nanowire rope, PEDOT nanowire and polyaniline nanotube were measured by scanning the voltage from −6 to 6 V with a step of 0.03 V using a Physical Property Measurement System from Quantum Design and a Keithley 6487 picoammeter/voltage source over a wide temperature range from 300 to 2 K. Here, it is noted that since the low-temperature resistance of the measured polypyrrole tube and CdS nanorope is very large, and thus, the corresponding current is very small (∼ pA), their *I–V* curves are only measured above 15 and 60 K, separately.

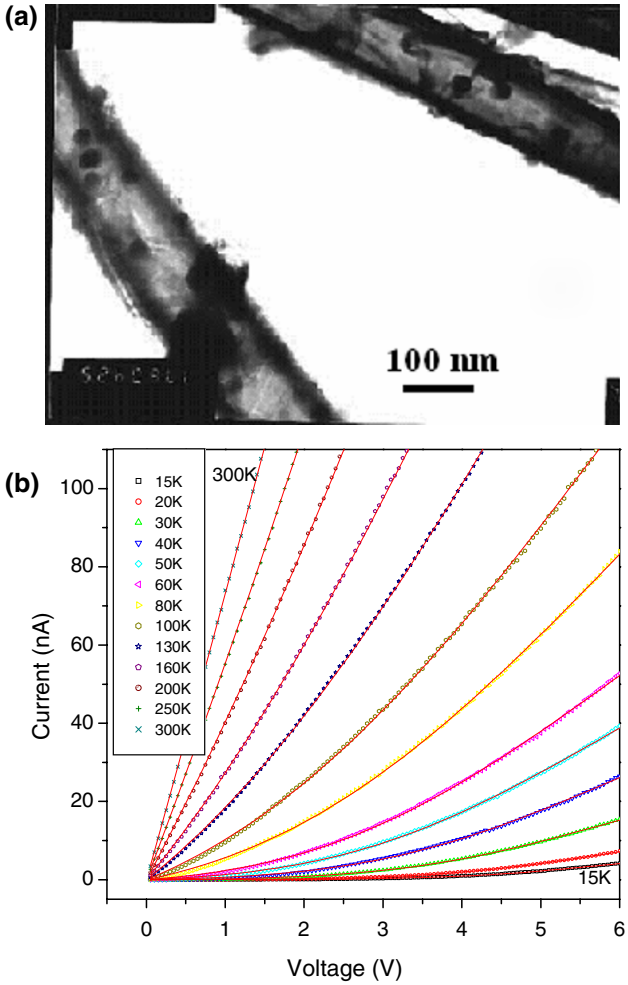

Fig. 1 **a** Typical TEM image of polypyrrole nanotubes and **b** the corresponding *I–V* characteristics with fitting curves to Eq. 3 measured from 300 down to 15 K

Kaiser Expression

Since the complex structure of disordered materials generally considered as conduction regions or long conducting pathways separated by small insulating barriers, the FIT conduction mechanism, proposed by Sheng [13], characterizes electrons transfer across the insulating barriers, which can be directly influenced by the voltage fluctuations in the conducting pathways. The mean current density through a barrier when a field E_a is applied across it is evaluated as

$$j(E_a) = \int_{-\infty}^{\infty} dE_T \, j(E_a + E_T) \, P(E_T) \quad (1)$$

where $P(E_T)$ is the probability that the fluctuation field across the junction has the value E_T (which may be in either direction). The tunnelling current $j(E)$ for a total field $E_b = (E_a + E_T)$ in the barrier is denoted as

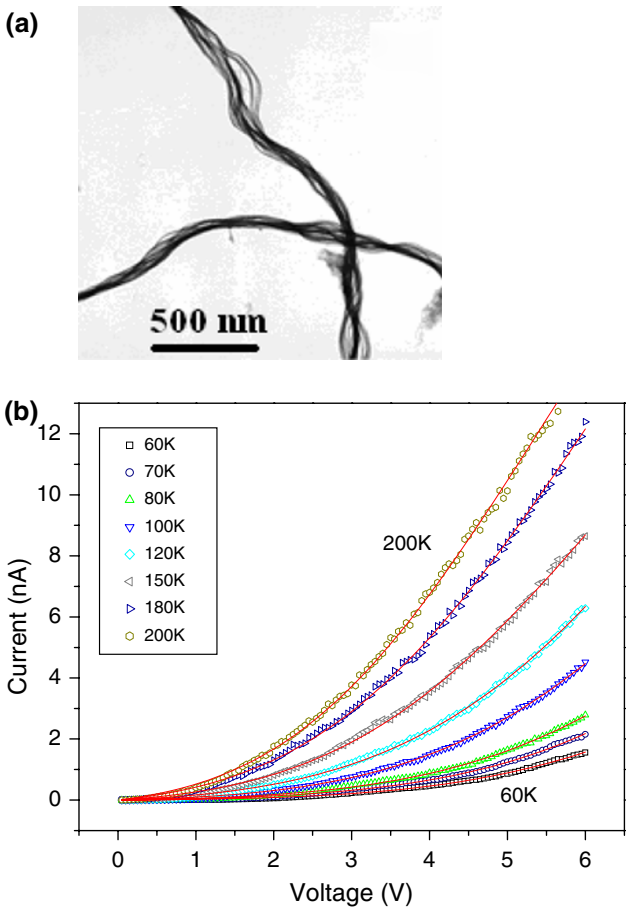

Fig. 2 **a** Typical TEM image of CdS nanowire ropes and **b** the corresponding *I–V* characteristics with fitting curves to Eq. 3 from 200 down to 60 K

$$j(E_b) = \frac{me}{8\pi^2\hbar^3} \int_{-\infty}^{\infty} d\varepsilon\, D(\varepsilon, E_b)\, \Theta(\varepsilon, E_b) \tag{2}$$

where m and ε are the carrier mass and energy, respectively. In terms of the structure features of quasi-1D disordered materials and the FIT model [13], Kaiser et al. [11, 12] proposed a generic expression, which can give a good description to the changing shape of nonlinear *I–V* characteristics in quasi-1D systems by performing numerical calculations of the current fluctuation-assisted tunnelling through conduction barriers and thermal activation over the barriers:

$$G = \frac{I}{V} = \frac{G_0 \exp(V/V_0)}{1 + h\,[\exp(V/V_0) - 1]} \tag{3}$$

where G_0, h, and V_0 are parameters. G_0 is the temperature-dependent low-field ($V \to 0$) conductance. The parameter $h = G_0/G_h$ ($h < 1$) yields a decrease of G below the exponential increase at higher voltages V (G_h is the saturated conductance at a high-field value). V_0 is a voltage scale factor, which gives an exponential increase in conductance as V increases depending strongly on the barrier energy. More details can be found in Refs. [11, 12].

Comparison with Experiment

Kaiser et al. [11, 12] has shown that the above expression can give a very good description to the observed nonlinearities in polyacetylene nanofibres, carbon nanotube networks, vanadium pentoxide nanofibres, and granular Sr_2FeMoO_6. In the present case, a series of *I–V* characteristics at different temperatures with fitting curves to Kaiser generic expression Eq. 3 are shown in Figs. 1(b), 2(b), 3(b), and 4(b). We note that all these *I–V* characteristics are essentially symmetric upon reversal of the voltage direction, so only positive voltages are used to show the fits more clearly.

Figure 1b shows the typical nonlinear *I–V* characteristics of single polypyrrole nanotube with diameter about 100 nm. With increasing temperature and voltage, the nonlinearity decreases and the ohmic component become dominant. The nonlinear *I–V* characteristics can be well fitted to Eq. 3 and the fitting parameters at some selected temperatures are shown in Table 1 In this case, the low-field conductance G_0 increases substantially from 0.0071 to 52.932 nS as temperature increases from 15 to 250 K. The parameter h increases from 0.0065 to 0.6805 with increasing temperature corresponding to a decrease of G below the exponential increase at higher voltages as shown in Fig. 1b. The voltage scale factor V_0 also increase from 1.0685 V at T = 15 K to 6.9725 V at T = 250 K, indicating a lessening of nonlinearity in the *I–V* characteristics as temperature increases. It is about 160 K where linear component becomes dominant in this case.

The similar highly nonlinear *I–V* characteristics of CdS nanorope are shown in Fig. 2b. Although the nonlinearity decreases with increasing temperature, the plot is still highly nonlinear even at T = 200 K. In this case, the nonlinearities at higher temperatures indicate larger barrier energies than that for the polypyrrole nanotube. It can be seen from the fits in Fig. 2b that Kaiser expression can give a good account to the temperature and field-dependent nonlinearities. The fitting parameters are shown in Table 2 The low-field conductance G_0 shows weaker increase with temperature than that for the polypyrrole case. h has smaller values indicating a higher exponential increase in G with increasing temperature (h = 0.1052 at T = 200 K). The voltage scale parameter V_0 also varies in a small range from 1.838 V at T = 60 K to 1.8558 at T = 200 K than that for the polypyrrole tube, reflecting the smaller change in nonlinearities of *I–V* characteristics.

As shown in Fig. 3b, the measured *I–V* characteristics of single PEDOT nanowire from 80 down to 2 K show a

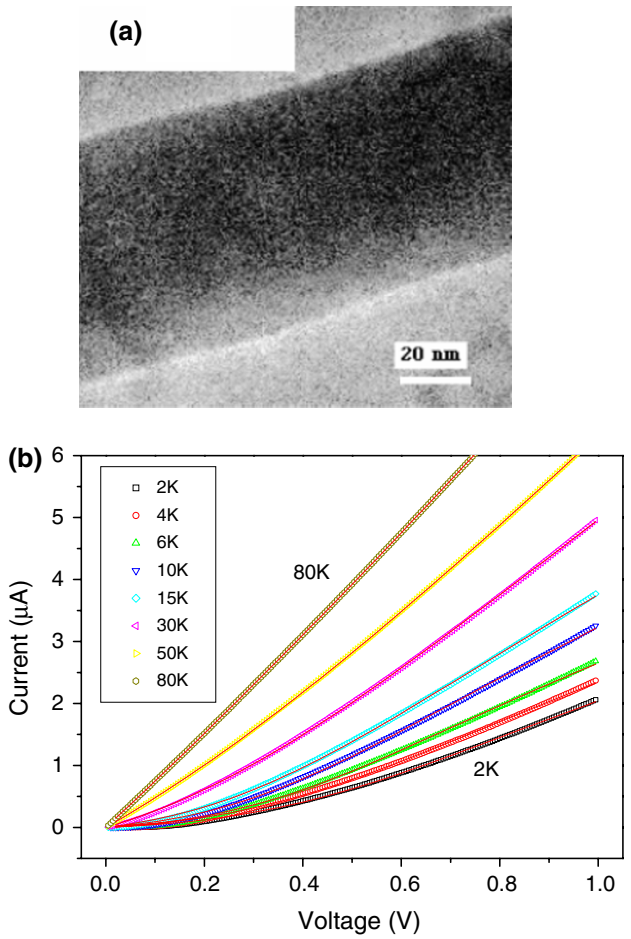

Fig. 3 **a** Typical TEM image of single PEDOT nanowire and **b** the corresponding *I–V* characteristics with fitting curves to Eq. 3 from 80 down to 2 K

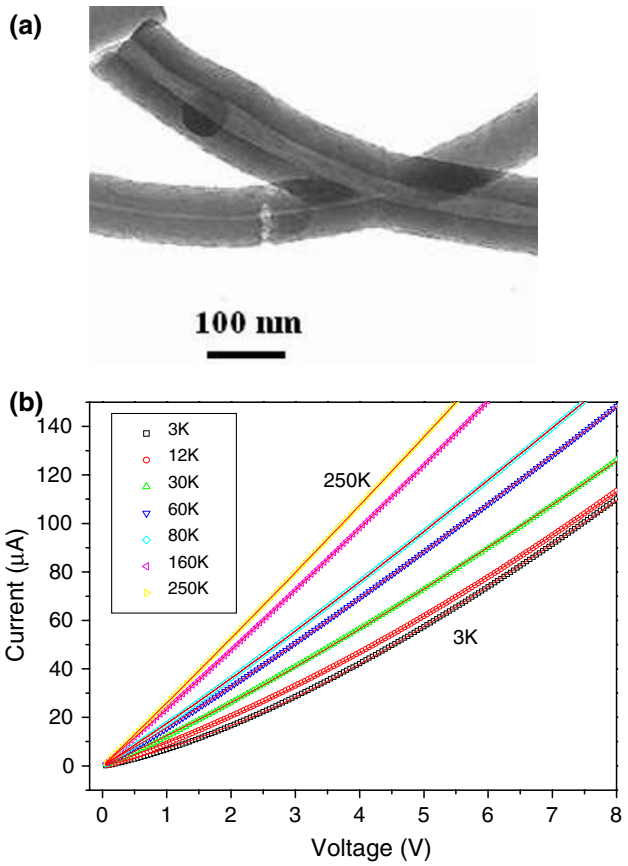

Fig. 4 **a** Typical TEM image of polyaniline nanotubes and **b** the corresponding *I–V* characteristics with fitting curves to Eq. 3 from 250 down to 3 K

much more linearity compared with that of polypyrrole nanotube in Fig. 1b and CdS nanorope in Fig. 2b. All these data for PEDOT nanowire can be well fitted to Eq. 3 (as shown in Fig. 3b) with fitting parameters given in Table 3 The low-field conductance G_0 shows higher values and increases substantially as temperature T increases. Linearity becomes dominant in *I–V* characteristics at a lower temperature about 50–80 K reflecting smaller barrier energy in the PEDOT nanowire. The more linear *I–V* characteristics than the foregoing two cases yield larger values in the fitting parameters h and smaller values in the voltage scale parameter V_0 as shown in Table 3. In addition, as shown in Fig. 4b, the similar *I–V* characteristics are also observed in single polyaniline nanotube with diameter about 120 nm with fitting parameters given in Table 4.

Thus, based on our experimental results as shown from Figs. 1, 2, 3, and 4, we conclude that the FIT model and Kaiser expression can give a very good explanation to the electronic transport properties and the nonlinear *I–V* characteristics in quasi-1D materials in accordance with previous reports [11, 12]. In FIT regime, most of delocalized and free conduction electrons compared to atomic dimension in disordered materials transfer across the insulating gaps in the conducting pathways [13]. In terms of Kaiser expression, considering the complex structures composed of ordered metallic regions in series with disordered conduction barriers in such quasi-1D systems, essentially, the nonlinear *I–V* behavior corresponds to tunneling through barriers with thermal fluctuations considerably smaller than the barrier height. As temperature increase, the thermal energy becomes comparable to the barrier height and linearity becomes dominant. Besides temperature, the nonlinearity also shows field-dependent feature. As the bias voltage increases, the difference in Fermi levels between two sides of barriers is comparable to the barrier energy, then the conductance will saturate at a value G_h and the *I–V* curves will become linear.

Further Discussion

Here, we should note that the *I–V* characteristics, which are linear–linear plotted in Figs. 1(b), 2(b), 3(b), and 4(b), as

Table 1 Fitting parameters to Eq. 3 for polypyrrole nanotube at different temperatures

T (K)	15 K	30 K	60 K	80 K	100 K	130 K	160 K	200 K	250 K
G_0 (nS)	0.0071	0.1125	1.5243	4.1920	8.2794	15.946	24.409	37.685	52.932
h	0.0065	0.0319	0.1379	0.2400	0.3437	0.4719	0.5753	0.6561	0.6805
V_0 (V)	1.0685	1.3740	1.9114	2.3964	2.8522	3.3231	3.4422	4.7180	6.9725

Table 2 Fitting parameters to Eq. 3 for CdS nanorope from 200 down to 60 K

T (K)	60 K	70 K	80 K	100 K	120 K	150 K	180 K	200 K
G_0 (nS)	0.01507	0.02728	0.06069	0.03608	0.10716	0.16697	0.26377	0.31185
h	0.02014	0.0176	0.03523	0.02557	0.04793	0.07768	0.09541	0.10523
V_0 (V)	1.838	2.11338	1.97387	2.0581	2.08389	1.87583	1.84095	1.85584

Table 3 Fitting parameters to Eq. 3 for PEDOT nanowire from 80 down to 2 K

T (K)	2 K	4 K	6 K	10 K	15 K	30 K	50 K	80 K
G_0 (μS)	0.3326	0.4488	0.4679	0.6709	0.9857	2.3406	4.5521	7.3941
h	0.1457	0.1754	0.1665	0.1964	0.2464	0.4330	0.6436	0.7953
V_0 (V)	0.2560	0.2531	0.2256	0.2343	0.2599	0.3713	0.6438	1.5196

Table 4 Fitting parameters to Eq. 3 for polyaniline nanotube from 250 down to 3 K

T (K)	3 K	12 K	30 K	60 K	80 K	160 K	250 K
G_0 (μS)	6.0844	8.7419	11.802	15.062	16.898	23.146	25.736
h	0.3806	0.4755	0.6586	0.7638	0.7900	0.7962	0.6675
V_0 (V)	3.5155	6.135	6.1051	5.1442	5.4773	12.736	29.749

well as in Refs. [11, 12], cannot show the low-field region clearly, so log-linear plots are adopted instead of linear-linear plots, which are shown in Fig. 5(a)–(d), separately. The surprisingly similar deviations between the I–V data and fitting curves emerge in low-field region at low temperatures, which have not been reported and discussed. According to the theory developed by Pollak, Efros, and Schklovskii and coworkers [15–18], the strong EEI creates a Coulomb gap in DOS near Fermi level in localized systems. By now, there have been a lot of experimental evidences in which hopping is indeed influenced by the presence of Coulomb gap at sufficiently low temperatures [6, 24–30]. For instance, the EEI can result in a smooth crossover from three-/two-dimensional Mott to Efros–Shklovskii variable-range hopping conduction [6, 25–28] and Coulomb gap-like structure in dI/dV curves [26–30]. In addition, our previous studies on conducting polyaniline, polypyrrole, and PEDOT nanotubes/wires have indicated that the quasi-1D nanostructures are composed of crystalline regions and amorphous regions [6, 31, 32], and the EEI may be enhanced and dominate the low-temperature electronic transport behavior [6, 24, 29]. Therefore, we suggest that the observed small deviations in Fig. 5(a)–(d) could be possibly due to the EEI, which has not been included in Kaiser expression or FIT model and should be taken into account especially at low temperatures in quasi-1D systems where electron states are more localized due to confinement effect or disorder. However, further theoretical and experimental investigations are needed to clarify this point.

Conclusions

In summary, the electronic transport properties in several kinds of individual polymer nanofibers and CdS nanoropes were measured and investigated covering a wide temperature range. All these quasi-1D materials show similar temperature and field-dependent I–V characteristics, which are well fitted to the extended FIT and thermal activation conduction model (Kaiser expression) consistent with the complex structures composed of ordered metallic region in series with disordered conduction barriers in such quasi-1D

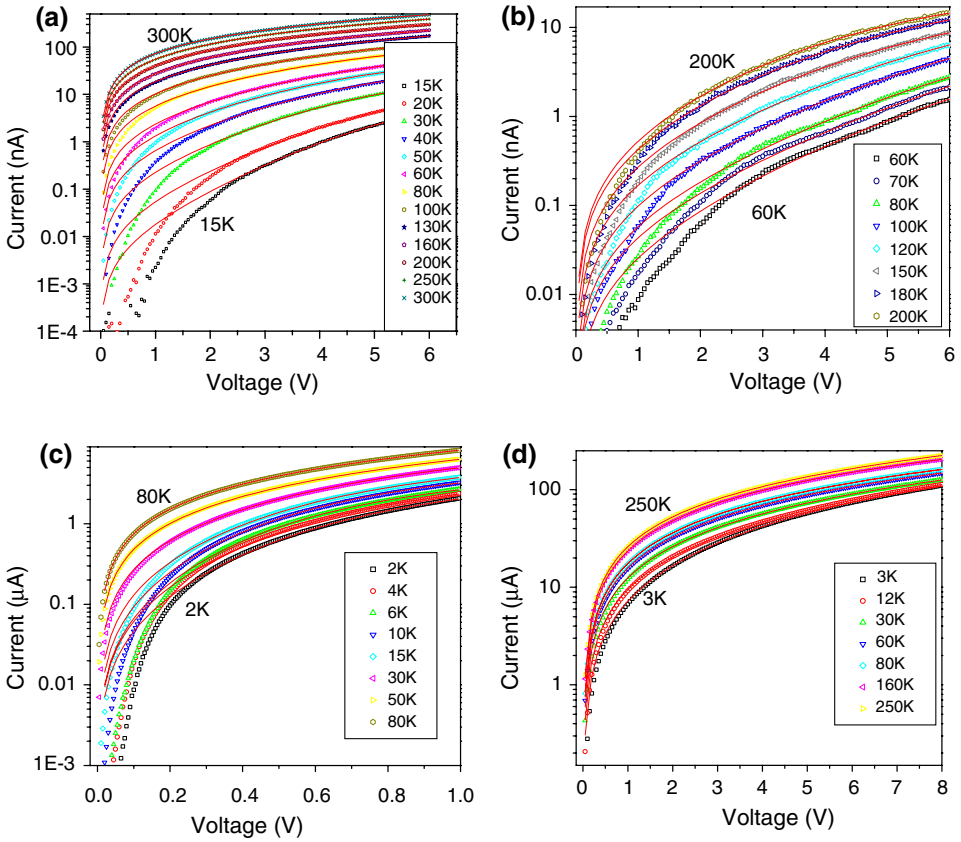

Fig. 5 The corresponding log-linear plot of the *I–V* characteristics for **a** polypyrrole nanotube, **b** CdS nanorope, **c** PEDOT nanowire, and **d** polyaniline nanotube

systems. We conclude that Kaiser expression is a possible way to explain the electrical behavior at relatively high temperatures and propose that the deviations emerged in low-field region at low temperatures are possibly due to the enhanced EEI in quasi-1D nanofibers with nanoscale inhomogeneous structures.

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