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Electrical transport properties of peptide nanotubes coated with gold nanoparticles via peptide-induced biomineralization

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Abstract

We present temperature dependent electrical transport measurements of peptide nanotube devices coated with monodisperse arrays of gold nanoparticles (AuNP). As the temperature is lowered, the current–voltage (I – V) characteristics become increasingly nonlinear and below 20 K conduction only occurs above a threshold voltage V_T . The current follows the scaling behavior $I \propto [(V - V_T)/V_T]^\alpha$ for $V > V_T$ with $\alpha \sim 2.5$ signifying two-dimensional (2D) charge transport. The temperature dependence of the resistance shows thermally activated behavior with an activation energy of 18.2 meV corresponding to the sequential tunneling of charges through 6 nm monodispersed AuNP arrays grown on a peptide surface.

1. Introduction

Nanocrystals of sub-10 nm dimensions are of intense research interest because of their size-dependent electronic and optical properties and their potential applications as a building block for future generations of nanoelectronic and photonic devices [1–3]. The conventional synthesis methods include ball milling, pyrolysis, and solvothermal methods; however, in general, extreme physical and chemical growth conditions are necessary to control their syntheses, morphologies, and assemblies [4, 5]. To assemble these materials into specific geometries for their potential applications, techniques such as Langmuir–Blodgett, self-assembly, crosslinking precipitation, DNA-based scaffolds, and fluidic flow-directed assembly have been applied [5–8]. Recently, one approach that has attracted considerable attention is the biological route of material synthesis due to its ability to synthesize nanomaterials in precise sizes and shapes in environmentally benign conditions as well as its ability to self-organize and assemble these materials in various geometries using biomolecules such as virus, protein, DNA, and peptide [9–12]. Progress has been made for

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the biological route of material synthesis and assembly for nanodevice development, however, detailed electronic transport investigation of these materials has not been explored in depth for applications in nanoelectronics.

In this paper, we report temperature dependent (300–4.2 K) electrical transport behavior of peptide nanotube devices coated with monodisperse gold nanoparticles (AuNPs) of 6 nm diameter. The current–voltage (I – V) characteristic of this inorganic–biomolecular hybrid nanotube device is linear at room temperature in the voltage region 1–1 V and the resistance (R) is ~ 3 M Ω corresponding to a lattice conductivity of ~ 0.44 S cm $^{-1}$. As the temperature is lowered, the I – V curves become increasingly nonlinear and below 20 K a finite threshold voltage V_T is needed for charge conduction with the current following the scaling behavior $I \propto [(V - V_T)/V_T]^a$ with $a \sim 2.5$ for $V > V_T$. The temperature dependence of the resistance shows thermally activated hopping behavior with an activation energy of 18.2 meV, in good agreement with sequential tunneling of charges through 6 nm sized 2D quantum dot arrays. Our results presented here regarding the conduction mechanism of large-scale AuNP arrays on the peptide templates are of great importance to the future development of bio-nanoelectronic devices.

2. Experimental details

The peptide nanotube (PNT) was self-assembled from bis(*N*- α -amido-glycylglycine)-1,7-heptane dicarboxylate monomers whose surface was programmed to bind synthetic peptides via hydrogen bonding [10]. The surface of the resulting nanotube was functionalized with Au-mineralizing peptides, DYFSSPYEQLF (NHBP-1 peptide) [13]. The NHBP-1 peptides were coated homogeneously on the tubular structure which acts like a bio-lithographic template. The AuNPs were then grown at those sites from a precursor, ClAuPMe $_3$ [10]. After five days of incubation, the AuNPs of diameter 6 nm were grown on the peptide nanotubes. Figure 1(a) shows a transmission electron micrograph (TEM) of AuNPs coated on one of the peptide nanotubes. From this image, we determined an average diameter of the AuNP to be 6 nm in a size distribution of less than 5% (monodispersed) with an average interparticle separation of 1 nm. In addition, AuNPs are homogeneously distributed over the cylindrical nanotube surface.

For electrical measurements, electrodes were fabricated on standard heavily doped silicon substrates capped with a thermally grown 250 nm thick SiO $_2$ layer, by a combination of optical and electron beam lithography. The electrodes consisted of an interdigitated array of 1 μ m spacing. After defining the patterns, 3 nm Cr and 30 nm thick Au were deposited followed by lift off in acetone. The electrodes were then treated in oxygen plasma for 10 min to remove any residual organics. The AuNP coated peptide nanotubes were placed between the electrodes by the drop casting method. Figure 1(b) shows a scanning electron microscopy image of a fabricated device with a PNT of diameter ~ 0.4 μ m and length ~ 1.5 μ m placed between source and drain electrodes. The samples were then bonded and loaded into a variable temperature cryostat. The electrical measurements were performed using a current preamplifier (DL instruments 1211) combined with a high resolution DAC card interfaced with LabView, capable of measuring pico-ampere current.

3. Results and discussions

The inset in figure 2(a) shows the I - V characteristics of a representative device at room temperature (300 K) containing one PNT. The I - V curve is linear in the range of -1 – 1 V and shows a resistance value of ~ 3 M Ω . This corresponds to a lattice conductivity of ~ 0.44 cm $^{-1}$ assuming the charge conducts through the outer layer of the PNT where AuNPs are conjugated with a cross-sectional area of $\sim 4\pi R_p r$, with R_p and r are the radius of the PNT and the AuNP respectively. The PNT does not contribute to conduction as the controlled experiment showed no noticeable current. As the temperature is lowered, the I - V curves become increasingly nonlinear near zero-bias but remain symmetric at all temperatures. This is shown in figure 2(a) where we present the data for $T = 30$ – 4.2 K. It can be seen from here that, below 20 K the charge conduction is completely blocked below a certain threshold voltage V_T . This is due to the Coulomb blockade of charges as there is not enough thermal energy for charges to overcome the Coulomb charging energy of the AuNP quantum dot (QD) arrays on the nanotube. The lower the temperature is, the larger the V_T . The measured values of V_T were 10 mV at 20 K, 120 mV at 15 K, 410 mV at 10 K, and 730 mV at 4.2 K.

The voltage dependence of current above V_T depends on the number of accessible current paths through the AuNP assembly (superlattice). It is predicted that for a uniform array of identical nanoscale metallic islands separated by tunnel barriers, the current should follow $I \propto [(V - V_T)/V_T]^\alpha$ for $V > V_T$, where α is the scaling exponent that depends on the dimensionality of the array [14]. Figure 2(b) shows current plotted versus $(V - V_T)/V_T$ in a log–log scale for $T = 15$, 10, and 4.2 K. The symbols are the experimental data points while the solid lines are a fit to the above equation. The data are fitted for voltages away from V_T , as close to V_T the current is within the experimental error limit. From these fits, we obtain α to vary between 2.4 and 2.6. In the one-dimensional case there is one current carrying path and α should be unity [14]. For a two-dimensional (2D) array of nanoparticles, the theoretical value of α was predicted as 1.6 while numerical simulations yielded 2.0 [14] but an experimentally higher value of α (~ 2.5) was observed [15, 16]. Our α value implies that the AuNP arrays on the cylindrical surface of the PNT provide 2D charge conduction pathways.

The inset in Figure 2(b) shows the V_T versus T plot. V_T increases linearly as temperature decreases and extrapolation of this plot to 0 K provides the global threshold voltage ~ 1 mV. At 0 K, charge conduction through AuNPs takes place only when a potential higher than the total barrier of the AuNP QD array is applied between the electrodes and ~ 1 mV can be expressed as $\sim E_c/N$ [14] where, E_c is the charging energy of AuNPs, N is the number of AuNPs in the conduction path, and β is a proportionality constant whose value depends on the dimensionality of the system and for a 2D array $\beta = 0.3$ [14, 17]. In our devices where electrodes are separated by ~ 1 μ m (see figure 1(b)), nearly 140 AuNPs are required to bridge the gap since each AuNP of diameter 6 nm and interparticle separation of 1 nm occupies 7 nm of space. Using these values, we obtain E_c 21.2 meV. E_c can also be calculated from the geometry and capacitance of the assembly and is given by $E_c = e^2/2C_\Sigma$, where C_Σ is the total capacitance and can be expressed as $C_\Sigma = 6C + C_g$. Here C and C_g are interparticle capacitance and self-capacitance of the quantum dot, respectively [16]. The factor of six appears due to the number of nearest neighbors for the 2D system [16]. The values of C and

C_g are given by $C \sim 2\pi\epsilon_0\epsilon r \ln(1 + r/d)$ and $4\pi\epsilon_0\epsilon r$, respectively, where r is the nanoparticle radius (3 nm), $2d$ is the interparticle distance (1 nm), and $\epsilon(1)$ is the dielectric constant of the tunnel barriers (vacuum). By using these relations and values, the C_Σ is calculated to be 4.26 aF and E_c to be 18.8 meV, which is in excellent agreement with the value measured from the global threshold voltage. The estimated value of E_c via the charge tunneling through peptide ($e = 5$) [18] is 6.7 meV. Since this value is much lower compared to the measured one, we conclude that the peptide acts as a template of AuNP growth but it does not contribute to the charge conduction.

In order to further understand the electronic transport mechanism through the AuNP coated PNT, we study the temperature dependence of resistance of our devices. The temperature dependence of resistance can provide evidence about monodispersity of Au NPs and the degree of disorder of the NP assembly [19, 20]. Figure 3(a) shows the R versus T plot in the temperature range of 260–20 K. R was calculated by measuring current at a constant $V = 20$ mV as the temperature was lowered. We have also measured $I-V$ curves at a few selected temperatures and obtained the R values from the ohmic part of the $I-V$ curves. The R values were in agreement from the two measurements. Below 20 K, the $I-V$ curves were non-ohmic below 20 mV and those data were discarded from this plot. It can be seen from figure 3(a) that R changes by over four orders of magnitude in the temperature range of 260–20 K. According to the QD array model, if QDs are monodisperse, the temperature dependence of resistance should follow thermally activated behavior $R \sim R_0 \exp(E_c/K_B T)$ [19, 21], while if the nanocrystals have significant size variation (polydispersed) it should follow $R \sim R_0 \exp(T_{ES}/T)^{1/2}$, [19, 22], where T_{ES} is a material constant related to the disorder of the material. In order to determine the exponent value we have considered a generalized formula $R(T) = R_0 \exp(T_0/T)^p$ and calculated the value of p from $\log W = A - p \log T$, where $W = -\ln R(T)/\ln T = p(T_0/T)^p$ is the reduced activation energy and A is a constant [23]. By plotting $\log W$ versus $\log T$, the value of p can be determined from the slope of this plot. Figure 3(b) shows W versus T plot in a log–log scale from which we calculate $p = 1$ signifying an activated hopping conduction mechanism. The agreement between the theory and the measurements also confirms that the size of AuNPs is monodisperse and their distribution is homogeneous. In order to derive the activation energy of the hopping conduction, R can be fitted to T^{-1} on a semi-logarithmic scale, as shown in figure 3(c). The fitting is linear over four orders of change in R over the entire temperature range. From the slope of this activation plot we calculate $E_c = 18.2$ meV, in excellent agreement with the E_c obtained from the capacitance calculation and global threshold voltage data. It should be noted that similar temperature dependences of the $I-V$ curve, activated hopping, and charging energy were reproducible with three other AuNP array samples that we have studied.

4. Conclusions

In conclusion, we presented detailed electrical transport properties of peptide–AuNP hybrid bionanotube devices coated with gold nanoparticles (AuNPs) of 6 nm diameter within the temperature range of 300–4.2 K. We show that with the reduction of temperature, the $I-V$ curves become increasingly nonlinear and below 20 K a finite threshold voltage V_T is needed for charge conduction. For $V > V_T$, the current follows $I \propto [(V - V_T)/V_T]^a$ with $a \sim$

2.5, suggesting that the charge conduction is through 2D arrays of AuNPs on the peptide assembly. The temperature dependence of the resistance shows thermally activated hopping behavior with an activation energy of 18.2 meV, in excellent agreement with the sequential tunneling model of charge transport through 6 nm size AuNP quantum dot arrays. Our results presented here regarding the conduction mechanism of large AuNP arrays on the peptide templates are of great importance to the future development of bio-nanoelectronic devices.

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Figure 1.

(a) Transmission electron micrograph of a typical AuNP coated peptide nanotube showing the particles are monodisperse with an average size of 6 nm. (b) Scanning electron micrograph of a typical device with 1 μm electrode separation.

Figure 2.

(a) I - V characteristics for a AuNP coated peptide nanotube for temperatures 30, 20, 15, 10, and 4.2 K. Below 20 K, a finite threshold voltage V_T is needed for charge conduction; inset is the I - V curve at 300 K. (b) I versus $(V - V_T)/V_T$ curves plotted in a log-log scale. The slope of the curves provides the exponent $\alpha = 2.4$ – 2.6 ; inset shows the dependence of V_T on T .

(This figure is in colour only in the electronic version)

Figure 3.

(a) Resistance R plotted versus temperature in a semi-log scale showing four orders of change in R in the temperature range 4.2–260 K. (b) Reduced activation energy W versus T on a log–log scale. The slope $p = -1$ indicates the activated hopping mechanism. (c) Arrhenius plot of R versus T^{-1} (semi-log scale) for the determination of activation energy E_c . We obtain $E_c = 18.2$ meV.