

Self-assembled chains of graphitized carbon nanoparticles

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We report a technique which allows self-assembly of conducting nanoparticles into long continuous chains. Transport properties of such chains have been studied at low temperatures. At low bias voltages, the charges are pinned and the chain resistance is exponentially high. Above a certain threshold V_T , the system enters a conducting state. The threshold voltage is much bigger than the Coulomb gap voltage for a single particle and decreases linearly with increasing temperature. A sharp threshold was observed up to about 77 K. Such chains may be used as switchable links in Coulomb charge memories. © 1999 American Institute of Physics. [S0003-6951(99)03418-X]

One-dimensional (1D) arrays of small metallic islands weakly coupled by tunneling are expected to have remarkable transport properties.¹ Uniform arrays can be used in single electron memories² or in electron pumps which may allow a new metrological standard of capacitance.³ Collective charge pinning is predicted for disordered arrays.⁴ Such systems enter a conducting state only above a certain threshold voltage, which increases with the number of islands in the array. Therefore 1D arrays can serve as switchable electronic links for Coulomb charge traps. High operational temperatures and good reproducibility could be achieved if the arrays are composed of nanometer scale metallic particles synthesized chemically (see, for example, Ref. 5). New approaches should be developed in order to organize such nanoparticles into useful electronic devices.

This letter describes a self-assembly technique which is used to arrange conducting nanoparticles into long continuous chains. The process of electrostatic self-assembly takes place between a pair of voltage biased microelectrodes, immersed in a dielectric liquid with suspended nanoparticles. The electric field generated between the electrodes polarizes conducting particles and, due to the dipole-dipole attraction, leads to formation of a continuous chain which links the electrodes. Note that this chain formation effect⁶ is responsible for different electrorheological phenomena and was studied in macroscopic systems in this context.⁷ Here we demonstrate that this mechanism, if used on the micrometer scale, can produce continuous and electrically conducting chains of nanoparticles with very interesting and possibly useful transport properties. Our samples exhibit a Coulomb threshold behavior up to rather high temperatures ($T \sim 77$ K), even though we use relatively big particles of diameter $D \approx 30$ nm. Many of the properties of such self-assembled chains can be understood in the framework of the model of collective charge transport in disordered arrays, proposed by Middleton and Wingreen (MW).⁴

A pair of leads bridged by a $\approx 1.2 \mu\text{m}$ chain of nanoparticles is shown in Fig. 1(a). The Cr electrodes (10 nm thick) have been fabricated using standard optical lithography and lift-off techniques. Longer chains are also possible as is

shown in Fig. 1(b). In all cases we use “onion” type graphitized carbon nanoparticles,⁸ of diameter $D \approx 30$ nm, available commercially.⁹ We have verified in independent experiments that these particles are metallic down to at least 4.2 K. For the self-assembly, a small amount of particles is dispersed ultrasonically in a dielectric liquid (toluene) until a uniform and slightly gray colored suspension is formed. An oxidized Si substrate with Cr electrodes is immersed into the suspension and the leads are connected to a 40 V voltage source in series with a big resistor $R_s = 1$ G Ω . This resistor limits the current and serves to interrupt the process of self-assembly as soon as the first conducting chain is formed, similar to Ref. 10. Initially the current I between the electrodes is very low, $I < 10$ pA. After a few seconds it increases suddenly by a few orders of magnitude. This indicates that the first continuous chain has been formed. Immediately after this current jump, the substrate is rinsed gently, dried and cooled down. Low noise current measurements have been carried out with an Ithaco 1211 current preamplifier. At low tem-

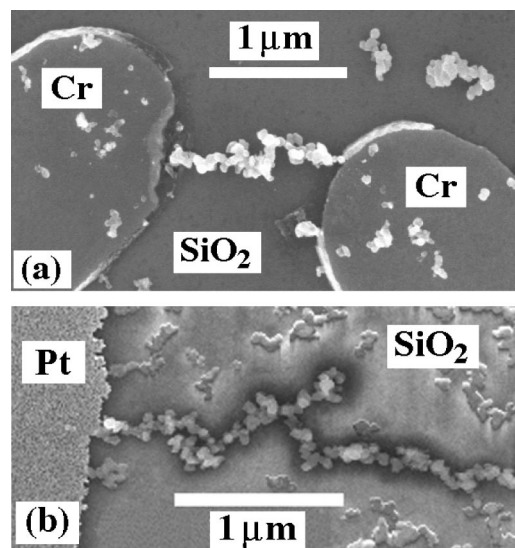


FIG. 1. (a) A scanning electron microscope (SEM) micrograph of a chain of graphitized carbon nanoparticles self-assembled between two Cr microelectrodes. The chain length is $L \approx 1.2 \mu\text{m}$. (b) An example of a longer chain. The image shows a part of a $\approx 6 \mu\text{m}$ chain and one Pt electrode.

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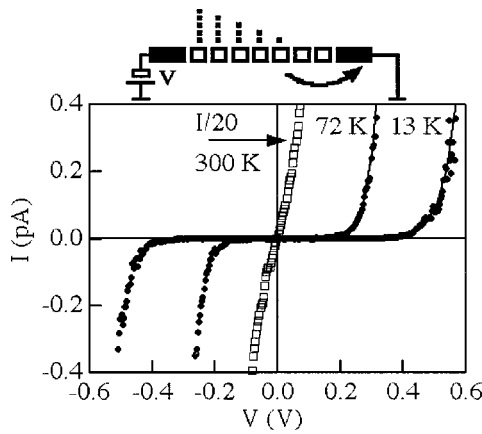


FIG. 2. Low current parts of three I - V curves measured on a $L \approx 1.2 \mu\text{m}$ chain at $T = 300, 72$ and 13 K . The 300 K curve is divided by a factor of 20. The continuous curves at $V > 0$ are the same exponential fits as in Fig. 3(b). The schematic on top shows a 1D array of islands (open squares) biased with a voltage which is slightly below the threshold. The number of induced extra electrons on each island is shown schematically by black dots above each island. The charge distribution is linear (see Ref. 4). This is similar to the flux distribution in type-II superconductors with strong pinning which are described by the Bean model.

peratures the noise was lower than 5 fA after averaging for $\approx 100 \text{ s}$.

Current-voltage (I - V) characteristics (averaged over ≈ 10 scans) measured on one representative sample are plotted in Fig. 2 for three different temperatures. The I - V curves are not hysteretic. At room temperature and low bias the I - V curve is linear with a zero-bias resistance of $\approx 12 \text{ G}\Omega$. Already at relatively high temperatures ($\approx 77 \text{ K}$) we observe a fully developed gap. Within the accuracy of our measurements ($\approx 5 \text{ fA}$) the current is zero below a certain threshold voltage V_T which increases with decreasing temperature. In the examples of Fig. 2 the threshold is $V_T \approx 0.18 \text{ V}$ at $T = 72 \text{ K}$ and it increases up to $V_T \approx 0.38 \text{ V}$ when the sample is cooled down to $T = 13 \text{ K}$. I - V curves measured on six $L \approx 1.2 \mu\text{m}$ samples were similar to those shown in Fig. 2. The absolute value of the threshold is subject to strong sample-to-sample fluctuations, probably due to irregularities in the chains. The averaged value of the threshold was found to be $\langle V_T \rangle = 0.3 \pm 0.2 \text{ V}$ at $T = 4.2 \text{ K}$. Measurements on a longer chain suggest that V_T scales linearly with the chain length, as expected from the MW model. For a chain of $L \approx 5.6 \mu\text{m}$ we have found $V_T \approx 1.1 \text{ V}$ (at $T = 4.2 \text{ K}$) while the expected value (for a 4.7 times longer chain) is $\approx 1.4 \pm 0.4 \text{ V}$. (The rms fluctuations ΔV_T are assumed to satisfy the usual relation $\Delta V_T \sim L^{1/2}$.)

The large value of the measured threshold voltage is a *collective* effect. Indeed, if it would be due to a single very small particle in the chain (which would have a very big Coulomb gap), then the threshold should be observed even at $T = 300 \text{ K}$ because the thermal energy at 300 K is only $k_B T \approx 26 \text{ meV}$, which is much lower than $eV_T \approx 300 \text{ meV}$. Experimental I - V curves do not show any gap at 300 K (Fig. 2).

It is instructive to compare the threshold voltage with the MW model which predicts that $I = 0$ for $V < V_T$, where V_T is proportional to the number of particles N . If the mutual capacitance between the particles C is much smaller than the self-capacitance (or capacitance to the gate) C_0 then V_T

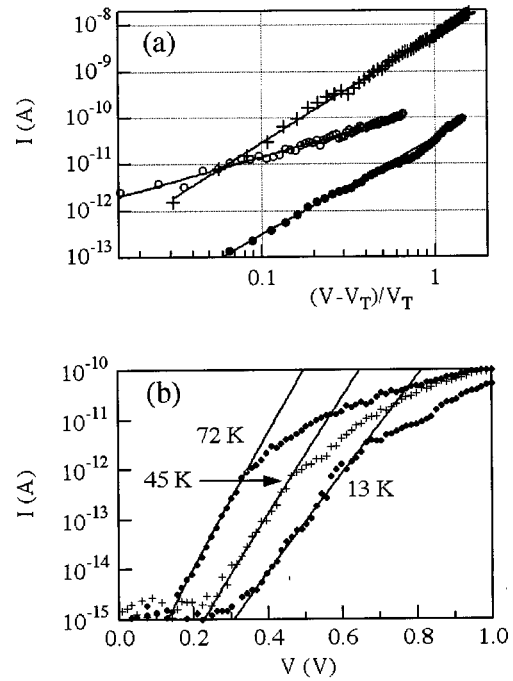


FIG. 3. (a) Log-log plots of the current vs normalized voltage for three different samples of $L \approx 1.2 \mu\text{m}$ at $T = 4.2 \text{ K}$. The bottom curve is shifted down by 1 decade for clarity. The linear fits are $I = I_0 [(V - V_T)/V_T]^\zeta$, where $\zeta = 1.03, 2.06,$ and 2.32 , respectively, and $I_0 = 0.15, 0.35,$ and 5.9 nA . Corresponding threshold voltages are $V_T \approx 0.3 \text{ V}, 0.615 \text{ V},$ and 0.385 V . (b) Semilog plots of I - V curves measured at $T = 72, 45$ and 13 K on the same sample. Straight lines represent the exponential fits $I = V/R_0 \exp(V/V_0)$. The parameters are $V_0 = 36, 40,$ and 48 mV , $R_0 = 5.1 \times 10^{15}, 7 \times 10^{16},$ and $1.9 \times 10^{17} \Omega$ at $T = 72, 45$ and 13 K , respectively.

$\approx Ne/2C_0$. In our case $C_0 \approx 2\pi\epsilon_0 D \approx 1.7 \times 10^{-18} \text{ F}$. To estimate C we assume that the idealized polyhedron shaped particles of graphitized carbon⁸ are assembled in the chain in such a way that the facets of neighbor particles are parallel to each other. Therefore $C \approx A\epsilon_0/d$, where $A = 3\sqrt{3}/2(D/4)^2 \approx 1.5 \times 10^{-16} \text{ m}^2$ is the area of each facet. The distance d between the facets can be approximated by the spacing between graphene layers in graphite, so $d \approx 3.35 \text{ \AA}$ and finally $C \approx 4 \times 10^{-18} \text{ F}$. [Therefore the charging energy of a single particle is $e^2/2(2C + C_0) \approx 8 \text{ meV}$.] Since C is of the same order of magnitude as C_0 , we have to use numerical results of MW: $V_T C_0 / eN \approx 0.09$ for $C/C_0 = 2.35$. With $N \approx L/D \approx 40$ as estimated geometrically, this gives $V_T \approx 0.34 \text{ V}$ which is in good agreement with the experimental value $V_T = 0.3 \pm 0.2 \text{ V}$ averaged over six samples.

Another MW prediction is that above the threshold, when the voltage is high enough to populate the entire chain with electrons, the current follows a power law $I \sim [(V - V_T)/V_T]^\zeta$, where $\zeta = 1$ and $5/3$ in the 1D and 2D cases, respectively (the MW numerical simulation for the 2D case gives a different value of $\zeta \approx 2$). Experimentally we do observe a power-law behavior [see Fig. 3(a)]. The sample-dependent exponent is $\zeta \geq 1$. Note that exponents bigger than unity ($\zeta \approx 1.4$) were measured previously on artificial 1D arrays.¹¹

This type of power-law I - V dependence suggests that a true transport threshold exists in our chains. This conclusion can be strengthened further if one can confirm experimentally that *below* the threshold the current is indeed sup-

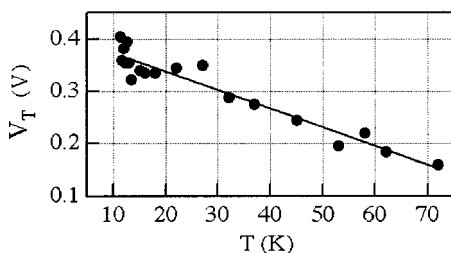


FIG. 4. Temperature dependence of the threshold voltage measured on the same sample as Fig. 2. The linear fit is $V_T(T) = V_T(0) - T \cdot dV_T/dT$, where $V_T(0) = 0.41$ V and $dV_T/dT = 3.6$ mV/K.

pressed. The idealized MW model predicts a strictly zero current for $V < V_T$. Such a prediction cannot be verified experimentally. On the other hand, in any real system the current will not be exactly zero. It should rather be suppressed exponentially below the threshold. This is true insofar as the dynamic state is separated from the static state by an energy barrier which can be overcome due to thermal or quantum fluctuations. (A process which leads to a nonzero subgap current is illustrated in the schematic of Fig. 2.) An exponential I - V dependence should occur below the threshold if such a barrier appears at $V = V_T$ and then increases with $(V_T - V)$ when the voltage is decreased. We indeed observe such exponential tails in our samples. Figure 3(b) illustrates that at very low currents (typically lower than 1 pA) the I - V dependence is exponential, while above the threshold it exhibits the power-law behavior as it was discussed above.

Another important property of our samples is a relatively slow, namely linear (see Fig. 4), dependence of the threshold on temperature.¹² The temperature dependence of $V_T(T)$ can be qualitatively understood in the following way. At $T = 0$, a nonzero current appears at $V = V_T$ when the voltage on a single junction is $V_1(0) = V_T(0)/N$ on average. This is just enough for electrons to overcome the Coulomb barriers between the particles. At $T > 0$, thermal fluctuations help overcome the barrier, so current appears at a lower voltage

$V_1(T) \approx V_1(0) - k_B T/e$. Therefore the threshold voltage for the chain is reduced to $V_T(T) \approx V_T(0) - N k_B T/e$, and $dV_T/dT = -N k_B/e$ should be compared with the experimental value -3.6 mV/K (Fig. 4). Inserting the estimate $N \approx 40$, one obtains -3.5 mV/K, in good agreement with experiment.

In conclusion, we have developed a new technique which is used to self-assemble nanoparticles into long continuous chains. The electrons in the chains are collectively pinned at low voltages by Coulomb energies. At the threshold voltage (which decreases linearly with temperature) the chains switch into a conducting state. The Coulomb blockade was observed up to $T \approx 77$ K.

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¹² Each data point in Fig. 4 is determined from an averaged I - V curve measured at a certain temperature. The absolute value of the threshold voltage fluctuates somewhat from one voltage scan to another, even if the temperature does not change. We attribute the deviations from the linear behavior, seen in Fig. 4, to these fluctuations.