Electrical conductivity of Au-nanoparticle-coated K$_2$SO$_4$ microcrystals deposited by DC trapping

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Abstract. Au-nanoparticle-coated K$_2$SO$_4$ microcrystals (nanoparticle-coated-crystals: NCCs) fabricated using the crystal-lattice-mediated-self-assembly method (CLAMS) were selectively deposited between gold electrodes by field-assisted trapping. Two different distances between electrodes were used, 2µm and 118nm. The electrical conductivity of NCCs was investigated using current-voltage (I-V) measurements at room and low temperatures and compared with that of bare tiopronin-coated Au nanoparticles. A hopping transport mechanism was found in both cases at low voltages and the corresponding activation energies were extracted. At higher voltages a power law was obtained in the case of NCCs and an exponential increase with voltage in the case of Au NPs.

1. Introduction
Nanoparticle-coated-crystals (NCCs), fabricated by self-assembly from powders in a solution, are of particular interest for use as building blocks for the fabrication of novel nanoelectronic devices. In this work, Au-coated K$_2$SO$_4$ microcrystals synthesized using the CLAMS method [1], in which a mixture of nanoparticles (NPs) and the crystalline material from aqueous solution co-precipitate in a water miscible solvent, were used. Their immobilization on a flat surface is a critical step towards their use in active devices. Self-assembly or self-organization on a solid surface are preferred patterning techniques, because they offer simplicity, flexibility and cost lowering. Different such techniques are used in the literature, including surface modification in order to bind the nanoparticles on a solid surface [2-5], and the use of magnetic [6] and mechanical [7] forces. In this work, electrostatic or ac-field assisted trapping [8] is used to deposit the NCCs between gold electrodes, with the aim to investigate their electrical transport properties.

2. Experimental
Details of the synthesis and characterization of gold-nanoparticle coated microcrystals are described elsewhere [1,3]. Firstly, water-soluble gold nanoparticles of an average of 3-5nm diameter were prepared and characterized according to a literature method [9]. The gold nanoparticles were coated with a protective monolayer of the peptide tiopronin (IUPAC name: N-(2-mercaptopropionyl)-glycine). This provides an outer charged carboxylate layer that imparts good water solubility even in salt solutions but low solubility in water miscible solvents such as acetonitrile. Secondly an aqueous
dispersion of these nanoparticles was used to prepare nanoparticle-coated K\textsubscript{2}SO\textsubscript{4} microcrystals via a single step self-assembly process, called Crystal Lattice Mediated Self-assembly (CLAMS) [1], in which a mixture of nanoparticles (NPs) and the crystalline material from an aqueous solution co-precipitate using a water miscible solvent. Nanoparticle-coated microcrystals are thus formed towards maximizing the loss of lattice energy [1]. For this study, an aqueous saturated K\textsubscript{2}SO\textsubscript{4} solution containing 30% gold nanoparticles was added to 60 ml of dry acetonitrile, drop wise, with rapid magnetic stirring, over one minute. The dark gold nanoparticle coated K\textsubscript{2}SO\textsubscript{4} microcrystals precipitated immediately and rinsed several times with dry isopropanol. The size distribution of the microcrystals was controlled by filtering the suspension using a 0.2µm syringe filter and several times centrifuging at 500rpm speed with removing the supernatant.

An SEM image of a collection of Au NP-coated K\textsubscript{2}SO\textsubscript{4} microcrystals on SiO\textsubscript{2} surface is presented in Fig. 1 by dropping the microcrystal suspension on the solid surface. The NCCs are quite regular and they exhibit a rectangular tablet-like shape with dimensions of the order of 1 micron by 1 micron and thickness of a few hundred of nm.

![Figure 1](image)

**Figure 1.** SEM image of Au-coated NCCs deposited on SiO\textsubscript{2} surface.

We applied DC or AC-field assisted trapping, in order to bind the NCCs between electrodes. Two different types of gold electrodes were fabricated on a thermally grown 100nm thick SiO\textsubscript{2} layer. The thickness of the electrodes was 30nm. A 5nm thick Cr layer was first deposited, in order to improve the adhesion of Au on SiO\textsubscript{2}. Optical or electron beam lithography was used to pattern the 2µm and 118nm distant electrodes respectively. In the first case the distance between the electrodes was 2µm and the area between the electrodes was 336·10\textsuperscript{4} nm\textsuperscript{2} (type 1 electrodes), while in the second case were 118nm and 16.8·10\textsuperscript{4} nm\textsuperscript{2} respectively (type 2 electrodes).

The Au-coated NCCs are negatively charged due to the carboxyl group of the tiopronin layer. By applying a DC bias voltage between the electrodes the NCCs are selectively deposited on the positive biased electrode, forming “bridges” between the electrodes. The density of deposited NCCs between the electrodes increases as the bias voltage is increasing. A great amount of Au-coated NCCs is deposited by applying 5V in type 1 electrodes (figure 2a). AC voltage was also used in order to selectively deposit the particles between the electrodes (figures 2b and 2c).

![Figure 2](image)

**Figure 2.** Examples of electrostatic trapping of Au NCCs between Au electrodes: (a) type 1 electrodes, DC bias: V=5V, (b) type 1 electrodes, AC bias: V\textsubscript{pp}=10V, f=1kHz, (c) type 2 electrodes, AC bias: V\textsubscript{pp}=10V, f=100Hz. The positive charged electrode, during deposition, is marked.
For comparison, water-soluble gold nanoparticles protected by monolayers of peptide tiopronin (IUPAC name: N-(2-mercaptopropionyl)-glycine) were also deposited between electrodes. A Brust-like procedure [9] was used for their synthesis. Their size was measured by high-resolution transmission electron microscopy [3] and was approximately 5nm. For this study, Au NPs were deposited between the type 2 gold electrodes with 4V applied voltage during deposition, while Au-coated NCCs were deposited between the type 1 electrodes with 5V applied voltage.

3. I-V characteristics and discussion
Temperature-dependent I-V characteristics of Au NCCs and Au NPs were performed under pure He atmosphere on well-dried films at controlled temperatures using an HP4140B Picoammeter and a liquid N₂ cryostat. A ramp rate of 0.05V/s was used. Between each measurement, the structure was discharged in room temperature under short-circuit for 30 minutes. In figure 3 the electrical measurements of Au-coated NCCs in the temperature range of 260-290K are presented, while in figure 4 the electrical measurements of tiopronin-coated Au NPs in the temperature range of 241-304K are shown for comparison.

![Figure 3. I-V curves of Au-coated NCCs deposited between type 1 electrodes with V=5V (suspension ATK-590-1).](image)

![Figure 4. I-V curves of Au NPs deposited between type 2 electrodes with V=4V (suspension: AT-4-2).](image)

At low applied voltages (V<1V) both systems exhibited an ohmic behavior, which is thermally activated. At higher voltages the two cases showed different behavior. In the case of Au NPs the current exhibited an exponential increase with voltage (figure 4), while the I-V characteristics of Au-coated NCCs showed power law dependence, with a power of 2.5 (figure 3). The last case is indicative of space charge limited conduction, in agreement with results in nanocrystal arrays from the literature [10]. Strong trapping effects were observed.

The thermally activated ohmic behavior, observed in both systems at voltages below 1V, suggests a hopping conductivity mechanism, in which the carrier tunnels from one Au nanoparticle to the other. In hopping mechanism the measured current I, depends on the temperature according to the equation [11]:

\[ I(T) = I_0 e^{-E/kT} \]  

where E is the activation energy for hopping. The activation energies for hopping in each system were extracted from the slope of the linear Arrhenius plot of the current at each temperature (figures 5 and 6).

It was found that the activation energy for hopping in the case of samples with Au-coated NCCs was 0.109eV and in the case of samples with Au NPs it was 0.062eV. The difference in activation energies between Au-coated NCCs and Au NPs is partly attributed to the different coverage with Au
NPs of the K$_2$SO$_4$ microcrystal surface compared with the direct deposition of NPs between electrodes.

\[ \log(\frac{\mathcal{I}}{A^{-1}}) = \frac{E}{kT} \]

**Figure 5.** Arrhenius plot of Au-coated NCCs.

**Figure 6.** Arrhenius plot of tiopronin-coated Au NPs.

Electrochemical measurements have been reported in the literature [12] for tiopronin-coated Au NPs and alkanethiolate monolayer protected Au clusters [13]. The activation energy for hopping transport that we found in this work is comparable to that reported for alkanethiolate monolayer protected Au clusters in reference 13.

4. Conclusions

The electrical transport mechanism of tiopronin-coated Au NPs and Au-nanoparticle-coated K$_2$SO$_4$ microcrystals was investigated and compared. Hopping conduction was found to dominate in both cases in the voltage range V<1V with activation energies equal to 0.109eV and 0.062eV for the Au NCCs and Au NPs respectively, while at higher voltages a power law increase with voltage with a power of 2.5 was obtained in the case of Au-coated NCCs and an exponential increase in the case of Au NPs.

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6. References

[1] PCT international Patent Application [GB 0116074.6 2001], Nanoparticle Structures, B. D. Moore.
[2] V.L. Colvin, A.N. Goldstein, A.P. Alivisatos 1992 *J. Am. Soc.* **114** 5221
[3] A.G. Nassiopoulou, A. Zoy, V. Ioannou-Sougleridis, A. Olzierski, A. Travlos, J-L Martinez-Albertos and B.D. Moore 2004 *Nanotechnology* **15** 1-5
[4] H. Miyata, K. Kuroda 1999 *J. Am. Chem. Soc.* **121** 7618
[5] H.Yang, N. Coombs, I. Sokolov, G.A. Ozin 1997 *J. Mat. Chem.* **7** 1285
[6] S.H. Tolbert, A. Firanzi, G.D. Stucky, B.F. Chmelka 1997 *Science* (Washington D.C.) **278** 264
[7] H. Miyata, K. Kuroda 1999 *Chem. Mat.* **11** 1609
[8] A. Bezryadin, C. Dekker and G. Schmid, Appl. Phys. Lett. 71 (9), 1273-5, 1997
[9] A.C. Templeton, S.Chen, S.M. Gross and R.W. Murray 1999 *Langmuir* **15** 66-76
[10] R. Parthasarathy, X-M. Lin, H. M. Jaeger 2001 *Phys. Rev. Lett.* **87** No 18 186807-1
[11] N.F. Mott and E.A. Davis, “Electronic processes in non-crystalline materials”, 1979 Clarendon Press
[12] A.C. Templeton, D.E. Cliffl and R.W. Murray 1999 *J. Am. Chem. Soc.* **121** 7081-7089
[13] W.P. Wuelfing, S.J. Green J.J. Pietron, D.E. Cliffl and R.W. Murray 2000 *J. Am. Chem. Soc.* **122** 11465-11472