Insulator-metal transition with high conductivity and high current carrying capacity on individual cobalt based misfit oxide nanotubes synthesized in large quantities by a combination of solid-state and solution based methods

Kankona S Roy and Leela S Panchakarla

Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India.

Email: panchakarla@chem.iitb.ac.in

Abstract

Misfit layered compounds (MLCs) are consist of two alternating sub-lattices with different lattice constants in at least one of the directions. One can selectively alter one of the sub-lattices without affecting the structure of the other one but can tune the properties of the overall compound. Among them calcium cobaltite ($Ca_3Co_4O_9$)[1] and strontium cobaltite ($Sr_3Co_4O_9$)[2] are gained tremendous interest as potential thermoelectric materials in their bulk state. Bringing them to low-dimensions could drastically enhance their properties. Synthesizing them in one-dimensional structure is extremely difficult. Recently, we have synthesized cobalt-based misfit oxide nanotube[3] and found out metal to semi-conductor transition from bulk to nanotube.[3] However, the yield of these nanotubes is low. Physical properties of these nanotubes have not been studied yet. Here, we present the synthesis of 1D nanaotubes (NT) from oxide misfit compounds with a very high yield (80%) by a combination of solid-state and solution-based synthesis. We have also studied their electrical properties on individual nanotube level by using electron beam lithography.

To synthesize Ca_xCoO_2 tubular (CCO) structures, we have applied conversion of high energy face-sharing cobalt octahedron ($Ca_3Co_2O_6$) to relatively low-energy edge-sharing octahedron by hydrothermal synthesis. The starting material, $Ca_3Co_2O_6$, is synthesized by the solid-state method using respective nitrates. By applying a similar strategy, we could synthesize nanotubes of Sr_xCoO_2 (SCO) from $Sr_6Co_5O_{15}$. It is found that the crystal structure widely varies in case of nanotubes from the bulk. Absorption studies show the band gap of 2.7 eV and 1.7 eV in case of CCO and SCO NTs, respectively. We have fabricated source-drain channels on individual nanotubes by electron beam lithography to find out the electronic properties of individual nanotube. In case of CCO nanotubes, it is found that the nanotubes are of p-type semiconductor with a high charge carrier concentration of $7.05*10^{19}$ per cm^3, which leads these NTs as a promising conductive material with a current-carrying capacity of $6.5*10^5$ A/cm^2 (for an individual nanotube). Surprisingly, in the case of SCO nanotube, it show a very high current carrying capacity of $0.8*10^8$ A/cm^2 for a single NT. These values are close to the reported WS_2 NTs having a highest current capacity value of $2.4*10^8$ A/cm^2 among the inorganic nanotubes.[4] Temperature dependent resistivity measurements show that both the nanotubes are semiconducting in nature. However, we have observed a voltage-induced semiconductor to metal transition in the case of SCO NT. We have observed the four-probe resistance for the SCO nanotube to be 10 kOhm which is lowest among the existing oxide-based inorganic nanotubes. We believe electronic properties can be further tuned by changing the chemical

composition between Ca/Co and Sr/Co. These results demonstrates that the high conductivity of these nanotubes could be a potential building block for future thermoelectric devices.

1. Yuzuru Miyazaki, Solid State Ionics. **2004** , *172* , 463–467.
2. Jakub D. Baran, Demie Kepaptsoglou, Marco Molinari, Nuth Kulwongwit, Feridoon Azough, Robert Freer, Quentin M. Ramasse and Stephen C. Parker, Chem. Mater. **2016**, *28*, 7470−7478.
3. Leela S. Panchakarla, Luc Lajaunie, Ashwin Ramasubramaniam, Raul Arenal, Reshef Tenne, ACS Nano. **2016** , *10* , 6248−6256.
4. Roi Levi, Ora Bitton, Gregory Leitus, Reshef Tenne, Ernesto Joselevich, Nano Lett. **2013** , *13* , 3736−3741.