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Detailed TEM Studies of 1D Nanostructures based on Layered Cobalt Oxide

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Background incl. aims:

The oxide misfit layered compounds (MLC) are heterostructures with complex stacking usually formed by two ceramic oxide layers. These oxides exhibit remarkable structural and chemical complexity and show very interesting electronic, thermoelectric, and magnetic phenomena [1-5]. It is interesting to mention that due to the intrinsic asymmetry of MLCs, they tend to bend and shape into tubular structures in the form of 1D nanomaterials: nanotubes (NTs) and nano-scrolls (NS) [1-5]. There are two different synthesis routes of these nanomaterials, the starting material is either a mixture of the individual constitutive elements or directly is the corresponding bulk structure. Following the latter pathway, recently, we have developed novel synthesis method based on a crystal conversion process, which parts from a bulk structure with a different, related crystal structure [4,5]. Here, we will present the detailed electron microscopy analysis of nanotubes and scrolls based on layered CoO_2 that have been obtained using this method with two different starting compounds: $Sr_6Co_5O_{15}$ [4] and $Ca_3Co_2O_6$ [5].

Methods

The synthesis procedure starts from the mentioned bulk oxide materials with a quasi 1D crystal structure, which are treated in a hydrothermal process in basic environment. Under this environment, the structure becomes unstable, leading to the dissolution of Sr (Ca) ions and leaving behind cobalt oxide chains. These chains then bend to 1D tubular or scrolled nanostructures. To investigate these 1D systems, different TEM techniques (HR(S)TEM imaging, SAED, X-EDS and EELS) were performed using two aberration corrected Thermo Fisher Scientific Titan microscopes. Furthermore, the electronic/electrical properties of these nanostructures were investigated in-depth at the individual nano-object level by patterning with electron beam lithography.

Results

A large quantity of strontium deficient misfit $SrCoO_2$-CoO_2 (SCO) nanotubes is produced [4]. In these NTs, CoO_2 layers are stabilized by intercalation between $SrCoO_2$ layers (forming a misfit unit), possibly with the aid of Na ions. In comparison to a previous study on similar nanostructures [3], the NTs obtained by the crystal conversion process are Sr-deficient, yielding a structure predominantly made of CoO_2 layers, Figure (a)-(c). These NTs are semiconducting and possess an extremely high ampacity (10^9 A/cm²), which is the highest reported ampacity value to date in any inorganic oxide-based material, Figure (d) [4]. The nanotubes also show a breakdown power per unit channel length of 38.3 W/cm, the highest among the regularly used interconnect materials [4].
Regarding the calcium cobaltite (CCO) system, a large quantity of stable and pure CoO_2 nano-scrolls have been produced for the first time and investigated in depth, see Figure (g)-(j) [5]. These NSs possess a narrow range of diameter and wall width suggesting that the CoO_2 stabilization occurs under specific circumstances. These nanostructures are semiconducting with a high current-carrying capacity of 4 10^5 A/cm² and an extremely high breakdown voltage of up to 270 kV/cm.

Conclusion
These detailed structural and chemical investigations at the atomic level have demonstrated the existence of new 1D systems based on layered cobalt oxide, both as pure phase and in intercalated form in misfit layered compounds. Furthermore, we have shown that these 1D nanostructures are potential building blocks for high-power electronic applications, fulfilling the requirement suggested by ITRS.

Graphic
Figure: (a) Crystal structures of the Sr-deficient SCO-NTs with intercalated CoO_2 layers: (left) along the cross-sectional direction, and (right) along the a-axis. (b) HRTEM image of a CCO NT. Line profiles show two d-spacings at the NT border, which are attributed to intercalated CoO_2 (0.54 nm) and the SCO misfit structure (0.89 nm). (c) SAED pattern of the NT (inset (b)). Assignment of the different patterns corresponding to the $SrCoO_2$ and CoO_2 subsystems, respectively. (d) Comparison of the ampacity of SCO-NTs (with/without contact resistance) with other inorganic-based semiconductor nanowires/nanotubes (NWs/NTs). (e) Schematic representation of these 1D Nanostructures based on Oxide Misfit Layered Compounds illustrating their outstanding electrical and electronic characteristics. (f) Crystal structure of (left) $Ca_3Co_2O_6$ revealing the separation of Ca and Co columns and (right) schematic representation of a CoO_2 NT and a CoO_2 NS. (g) TEM image showing CoO_2 NS. (h) HRSTEM image of CoO_2 nano-scroll with lattice distances marked. (i) SAED pattern of the CoO_2 NS. (j) Id–Vd curve up to breakdown for the two-probe device (of a CCO NS/NT) shown in the inset.

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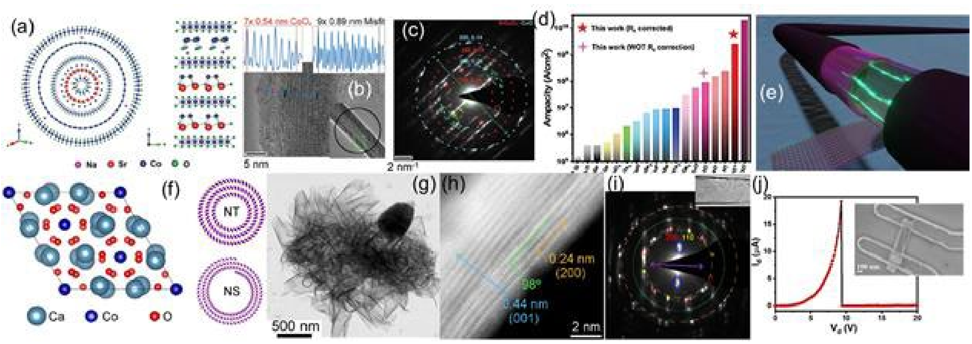
Graphic:



Keywords:

Ceramics, Oxide-misfit-layered-compounds, Nanotubes/Nano-scrolls, Electrical properties

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