Solution-Based Route to Transitional Metal Oxide One-dimensional Nanostructures: Synthesis, Characterization and Their Properties

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One-dimensional (1-D) nanostructures have drawn continuous research attention because of their unique electrical, optical and magnetic properties different from that of bulk and nanoparticles as well as their potential applications in mesoscopic research and nanodevices. One of the main challenges in this area is how to precisely control the sizes, dimensionalities, compositions and crystal structures in nanoscale, which has been regarded as critical factors for the tailoring of physical/chemical properties of materials in a controllable way. Chemistry as the most powerful tools to synthesize new materials has been playing important roles in the development of 1-D nanostructures research fields, including the exploration of new synthetic strategy and synthesis of novel 1-D nanostructures.

In this dissertation, valuable explorations have been carried out on the new chemical synthetic strategies (mainly solution-based routes) to transitional metal oxides (TMO) one-dimensional nanostructures, the synthesis of new-type 1-D TMO as well as their formation mechanism and the novel physical/chemical properties of the as-obtained new-type nanostructures. As the main theme, a rolling mechanism has been put forward to give a relative general understanding on the growth of various TMO 1-D nanostructures under solution conditions. The main points can be summarized as follows:

On the basis of the redox reactions of MnO_4^- and/or Mn^{2+}, a rational low-temperature hydrothermal chemical synthetic way has been developed to selectively prepare MnO_2 nanowires/nanotubes with different crystal structures, including alpha, beta, gammar and delta MnO_2. The structural stability of different structures has been fully discussed, and especially the layer-structured δ-MnO_2 is found to be the intermediates for the formation of MnO_2 1-D nanostructures, based on which a rolling mechanism of from layer-structured delta-MnO_2 to MnO_2 nanowires/nanotubes with different structures has been introduced to explain the growth of MnO_2 nanowires/nanotubes under hydrothermal conditions. By properly designing redox reactions in Mn-related chemical species, the chemistry in MnO_2-related system has been successfully applied in the precisely-controlled synthesis of MnO_2 low-dimensioanl nanostrucures.

By effectively tuning the chemical potentials in the aqueous system, a new chemical synthetic strategy has been established to synthesize series of rare earth nanowires, nanotubes and inorganic fullerene-like new-type nanostructures, which greatly enriched the categories of low-dimensional nanostructures. Different chemical

reactions, such as dehydrate, sulfuration etc., have been applied to generate various rare earth compound nanostructures, during which the great flexibility of rare earth chemistry has been utilized in generating various rare earth compound nanomaterials. Based on the experiment results, the nanotubes have been obtained at a lower temperature condition than that of the nanowires, and the structure transitions of from rare earth nanotubes to nanowires have been investigated in details in different rare earth systems. A similar rolling mechanism to that of the MnO_2 system has been established to guide the growth of these rare earth low-dimensional nanostructures, which shows the generality of this mechanism. Based on the successful synthesis of these nanostructures, some preliminary optical properties have been investigated. Owning to the interesting combination of novel nanostructures and functional compounds, these rare earth low-dimentional nanostructures can be expected to bring some new opportunities in vast research areas of and application in biology, catalysts and optoelectronic devices.

This proposed rolling mechanism has also been evidenced in the silicates series. A water-ethanol mixed-solution hydrothemal route has been developed to prepare series of Silicates nanowires and nanotubes, based on the chains and layer structures of silicates respectively. The as-obtained nanotubes have tunable nanometer-scale pore sizes, narrow size distributions and large BET surface areas, and have shown excellent catalytic oxidation performance at low temperature range and a hydrogen storage capacity of up to 1.8% at room temperature. Compared with the well-known mesoporous materials, the as-obtained nanotubes have shown better thermal/hydrothermal stabilities and compared with the zeolites, these nanotubes have larger pores, which can satisfy the requirement in catalytic synthesis of macromolecules. Since silicates are the most affluent minerals on the earth, the synthesis of these novel 1-D nanostructures of silicates can be expected to find wide applications in gas separation/adsorption and catalysis fields.

Besides above-mentioned systems, a facile hydrothermal chemical method has been illustrated to control the dimensionality of series of transtional metal oxides including ion, nickel, cobalt and molybdenum. A general understanding on the controlling of dimensionalities have been tried to make from designed experiments and numerous experiment results.

In this dissertation, three systems of MnO_2, rare earth compounds and silicates have been chosen to illustrate the methodology in controlled synthesis of 1-D TMO nanostructures under aqueous synthetic conditions. Various chemical reactions such as redox, precipitation, complexation reaction etc., have been widely employed in the investigation of the controlled growth of TMO 1-D nanostructures, and shown amazing abilities in yielding new nanostructures with designed compositions, dimensionalities and crystal structures. Undoubtedly, as the main task of chemistry, the creation of new molecular and new materials will bring us much more opportunities than ever, and will always be the central topic of science.

Publications

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