ABSTRACT

New synthetic approaches to MS₂ (M = Sn, Nb, Mo, W) chalcogenide nanostructures are highlighted. Most chalcogenide particles can be functionalized directly with inorganic nanoparticles such as Au, ZnO or MnO. Depending on the Pearson hardness of the metal involved, the functionalization may be reversible or irreversible. A covalent functionalization strategy is based on a steric shielding of the coordination sphere of transition metal atoms in such a way that only coordination sites are available for bonding to the chalcogenide surface. This allows the immobilization of fluorophors, redox active groups or proteins onto chalcogenide nanoparticles.

KEY WORDS: Chalcogenide; nanotube; nanoparticle; graphene; metal oxide; functionalization.

INTRODUCTION

In addition to carbon nanotubes, non-carbon nanostructures have attracted much attention over the past few years. In particular, and due to their unusual geometry and promising physical properties, inorganic fullerene nanotubes have become one of the key topics in nanoscale research since the first report on WS₂ nanotubes. (Tenne et al., 1992) Various synthesis techniques for chalcogenide nanotubes have been established so far, the most successful one being oxide to sulfide conversion. (Tenne et al., 1992; Rothschild et al., 2000) Chalcogenide nanostructures are of interest for a variety of applications ranging from nanotribology, nanoelectronics or battery materials to the active use in heterogeneous catalysis. Similar as their carbon congeners (Smalley, 1992) chalcogenide nanoparticles are not equilibrium but high-temperature and low-pressure phases that are obtained by quenching “hot” gas phase species. Various approaches to chalcogenide nanoparticles have been established so far, among them oxide to sulfide conversion (Tenne et al., 1992), chemical vapor transport reactions (Remskar et al., 2003), or from the elements using metal droplets (Ouyang et al., 2007). Except for the oxide to sulfide conversion, which has been scrutinized, the growth mechanism of such nanostructures is still subject to discussion.

GRAPHENE-TYPE CHALCOGENIDE NANOPARTICLES

In the absence of external forces individual 2D sheets of layered materials roll up immediately forming closed structures such as quasi-0D onions (Kroto and McCay, 1988) or 1D tubes (Úgarte, 1995) in order to decrease the number of dangling bonds and the total energy; in fact, for a long time graphene was presumed not to exist in the free state and believed to be unstable with respect to other carbon compounds such as soot, fullerenes and nanotubes. Similarly, individual layers of chalcogenide layer-type phases are unstable towards bending and have a high propensity to roll into curved structures. Folding in the layered transition metal chalcogenides was recognized as early as 1979, well before the discovery of the carbon nanotubes.(Chianelli et al., 1979) Ten years later, single graphene-type sheets of molybdenum sulfide were obtained by a process of exfoliation, and then restacked with organic molecules to obtain interesting hybrid materials (Divigalpitiya et al., 1989).

An entirely new concept to the formation of stable, planar graphene-type metal chalcogenide sheets is based on the stabilization of laterally confined (approx. 50 nm) nanosheet crystals in stacked coin roll-type nanowires (CRNWs) by an internal force, i.e. structural strain, that prevents the formation of scroll-structures (Schmidt and Eberl, 2001) or nanotubes. As MS₂ (M = Nb, Mo, W, Re, Sn) form nanotubes that can be obtained by reductive sulfidization of the corresponding nanostructured oxides, (Rothschild et al., 2000; Therese et al., 2005, 2006) a potential strategy for the fabrication of “doped” MS₂ has to rely on the synthesis of “doped” metal oxide nanoparticles, either in a statistical or in an ordered (e.g. core-shell type) fashion. Thus, the first synthetic step in obtaining CRNWs is to control the 1D nanoparticle crystal structure by means of proper doping. The approach pursued here relies on core-shell nanowires with a Nb₂O₅ backbone and a W₁₈O₄₉ coating. Niobium oxide nanowires (NWs) were obtained in a sol-gel process. The product consists of mostly well separated niobium oxide NWs (lengths between 150 nm and 250 nm, diameters between 5 nm to 50 nm). Nb₂O₅ is the only crystalline phase as shown by powder X-ray diffraction investigations. The TEM images in Fig. 1a show that the NWs were not uniform along the rod direction, but aggregates of smaller particles. The structure directing agent might be responsible for the aggregation of the particles to form wires. After calcination the particles condensed to larger aggregates. Fig. 1b shows a TEM image of the NWs after calcination. HRTEM images of the Nb₂O₅ NWs obtained from the sol-gel process reveal that all rods grow along the c direction (Fig. 1c). The same orientation is preserved after the calcination. The lattice spacings indicate that the hexadecylamine surfactant is not intercalated into the product. These Nb₂O₅ NWs were coated with a tungsten oxide layer. Fig. 1c and d shows a TEM/HRTEM images of NWs, from which tungsten oxide appears to be coated onto the niobium oxide NWs. EDX data revealed the presence of both, tungsten and niobium.