The MoS₂ Nanohybrids Grown in a Confined Geometry of Nanotube Reactors

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ABSTRACT

We report on diversity of MoS₂ and WS₂ morphologies in a form of coaxial nanotubes, “mama”-tubes with encapsulated nano-onions, nanobuds, nanoboxes or weak assemblies of nano-onions released from nanotubes. Structural properties are explained by temperature dependent transformation process. The first results of hetero-assemblies inside liquid crystal phase of cellulose are presented.

KEY WORDS: Inorganic nanotubes; Nanotechnology, Low-friction materials; MoS₂; Cellulose; Self-assembly.

INTRODUCTION

Recent discovery of MoS₂ nanopods called “mama”- tubes (Remskar, 2007) with MoS₂ fullerene-like particles in-situ grown in a confined geometry of MoS₂ nanotubes and coaxial MoS₂ nanotube hybrids (Remskar, 2009) have opened a new way of synthesis of MoS₂ nanotubes from Mo₆S₂I₈ ternary compounds, which allows for production of mass quantities of pure nanomaterials. Relatively weak van der Waals interactions among MoS₂ molecular layers enable easy low-strength shearing and several possible stackings (Remskar, 1999). Molybdenum disulfide nanostructures are receiving considerable attention because of their potential applications as heterogeneous catalysts for desulfurization processes (Lauritsen, 2007), hydrogen evolution (Hinneman, 2005; Jaramillo, 2007) and as materials for thermolectric applications (Chiritescu, 2007). MoS₂ micro-platelets are used as solid lubricant or as additive in oil or grease already for more than 60 years. Disadvantage of commercial MoS₂ platelets is in their thickness. The crystallites are at their edges exposed to oxidation or to chemical reaction with the substrate, what cause their perpendicular reorientation with regards to the substrate and subsequently the friction enhancement. Therefore the thinnest flakes as possible are desired. Cage-like nanostructures or cylindrical geometry of MoS₂ nanotubes represent a new generation of lubricants with extremely low friction explaining by their size, small enough to fill micro and nano depletions of the objects in mechanical contact forming reservoirs of the lubricants, and by curved geometry of nanoparticles, which put them into constantly parallel orientation with the counterpart surfaces. We report here on structural diversity of MoS₂ nanomaterials and on self-assembly phenomena in different media.

EXPERIMENTAL

We used Mo₆S₂I₈ nanowires (Nanotul Ltd.) as precursor crystals for synthesis of MoS₂ nanotube-hybrids. The millimeter-long needles of metallic luster having a diameter from several tens to a few hundred nanometers were grown. These nanowires have been sulphurized at different temperatures in a range of 873K to 1215 K in flowing Ar gas containing 1% of H₂S and 1% of H₂. X-ray powder diffraction and x-ray energy dispersive analysis of the end product reveal the iodine-free MoS₂ compound with some traces of MoO₃.

The MoS₂ coaxial nanotubes were mixed into ordered nematic chiral liquid crystalline phase of cellulose. Acetyloxypropylcellulose (APC) (0.600 g) was dissolved in anhydrous dimethylacetamide (DMAc) (1 ml) in which 0.4% by weight of MoS₂ nano tubes were dispersed. The solution was allowed to homogenize during 2 weeks with brief stirring every two days. The prepared solution was then confined to a 5 ml syringe fitted with a round 18-gauge needle made of stainless steel; the feeding rate was controlled by means of a syringe pump for controlled feeding rates. The APC solution was transferred into the syringe and delivered to its tip by the syringe pump at a constant feeding rate. Photographs and movies were taken with a Casio Exilim EX-F1.

The MoS₂ nanotube derivates have been studied by 200 keV field emission transmission electron microscopy (Jeol 2010 F), and field emission scanning electron microscopy (FE-SEM, Supra 35 VP, Carl Zeiss).

RESULTS AND DISCUSION

Temperature Controlled Growth of MoS₂ Hybrids

Selective morphology of MoS₂ nanohybrids depends strongly on temperature during sulfurization process. A relatively low temperature (873 K - 1073 K), which enables a slow release of iodine leads in general to a formation of MoS₂ nanotubes composed of several coaxial cylinders showing a high concentration of structural defects (Fig. 1). Nanotubes keep an outside shape of the precursor Mo₆S₂I₈ nanowires. Difference in mass density between Mo₆S₂I₈ and MoS₂ compounds leads to a creation of an empty space inside the MoS₂ nanotubes. In a case of MoS₂ nanotubes this empty space separates the adjacent