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A novel facile synthesis and characterization of heterostructures composed of carbon nanotubes and few-layer molybdenum disulfide sheets containing organic interlayers

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ABSTRACT

A novel convenient room-temperature method for surface covering of carbon nanotubes (CNTs) with few-layer MoS_2 shell was developed. For this purpose, liquid-phase single-layer dispersions of molybdenum disulfide produced by chemical exfoliation of its compound with lithium, $LiMoS_2$, were applied. As evidenced by XRD and TEM studies, the dispersed MoS_2 layers readily attach to the outer CNT surface and tend to envelop it. Measuring the interlayer distances in the vicinity of the MoS_2–CNT interface showed, that deposited particles typically contain 1–3 (rarely, up to 10) MoS_2 layers, which are in close contact with graphitic CNT walls. Similar deposition performed in the presence of cationic polymers containing polydiallyldimethylammonium units was found to lead to incorporation of polymer molecules in the sulfide shell of CNT in the form of 0.5 nm thick organic interlayers between the layers of MoS_2. The same sequence of the layers of MoS_2 and the polymer is also realized in the absence of CNT due to self-organization of the components. The method presented in this work has a great potential for designing other nanohybrid structures with participation of layered metal sulfides.

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1. Introduction

In the last years, great attention was focused on graphene-like mono- and few-layer sheets of molybdenum disulfide [1–3], which was found to show attractive semiconducting [3] and catalytic [4,5] properties. A large number of effective applications of these MoS_2 nanosheets may be reached if they are incorporated into nano-heterostructures, where they are combined with the particles of another substances [e.g., 6–8]. Currently, particular interest is focused on the heterostructures constituted by semiconducting MoS_2 layers and highly-conductive carbonaceous materials such as graphene [9–10], CNTs [11–17] and nanofibers [18]. These nanohybrids show prospects for designing effective electrode materials for lithium batteries [11,16], components of solar cells [10,13] and highly active and stable electrocatalysts for production of hydrogen from water [15,17,18]. However, the problem of nanofabrication of MoS_2–CNT heterostructures currently presents a challenge. MoS_2 is a non-volatile and insoluble solid, the deposition of its few-layer particles onto the surface of CNTs and related materials is thus complicated by the necessity to use the precursors, such as sodium molybdate [5], ammonium molybdates [12,14] or molybdenum pentachloride [18], which should be initially deposited onto CNT surface and then converted to MoS_2 using sulfidation reactions. This process is rather complex, it requires autoclave technique and high-temperature treatments and often leads to MoS_2 species of low-crystallinity [11].

The present work aims to develop a radically new approach to the formation of MoS_2 nanosheets on the surface of CNTs and related materials. This approach consists of the use of the MoS_2 single-layers 'solution' produced by chemical exfoliation of bulk molybdenum disulfide crystals as a source of sulfide component and allows for performing the process at room temperature.

There are two main liquid-phase methods to cleave bulk MoS_2 crystals into mono- or few-layer sheets in mild conditions are described. One of them is based on solvation of these particles by appropriate organic solvents which allow for their extraction from sonicated powder of MoS_2 [19]. However, the yields of the thinnest particles in this case are scarce. Many multilayer particles are found among the deposited ones. Another method is an exfoliation of Li-intercalated derivate of MoS_2 [20]. This procedure leads to the formation of single-layer liquid-phase dispersions containing negatively charged $(MoS_2)^{x-}$ layers, lithium cations and hydroxide anions according to Eq. (1) [21].

$$MoS_2 \xrightarrow{Li^+,e^-} Li^+(MoS_2)^- \xrightarrow{H_2O} [Li^+ + (MoS_2)^{x-} + (1-x)OH^-]_{aq} \xrightarrow{-e^-} MoS_2 \tag{1}$$

$$[Li^+ + (MoS_2)^{x-} + (1-x)OH^-]_{aq} \xrightarrow{B^+} B_x^+(MoS_2)^{x-} \tag{2}$$

Previously, these dispersions were used for preparation of thin-layer films and powders of bare MoS_2 [1,2,22] and its heterolayered compounds with various cationic molecules (B^+) as outlined in Eqs. (1) and (2), respectively [21,23–25]. As compared to solvation method, the last exfoliation technique has the advantage of allowing full exfoliation of the starting MoS_2 and modification of its deposited few-layer particles by cationic additives. For these reasons, it was applied in our study.

It is obvious that for coating CNTs with 'ready-made' MoS_2 particles, the morphology of these particles should 'adjust' to the geometry of CNTs (Fig. 1). Principal possibility of MoS_2 layers to exhibit appropriate flexibility is undoubtedly proved by existence of closed-cage nanotubular, and even nanopod-like MoS_2 structures [26–28]. Importantly, the evident possibility of MoS_2 layers to bend was evidenced by TEM studies not only in these structures obtained in rigorous conditions of high-temperature sulfidation [26] or laser ablation [27], but also in the materials produced via above-mentioned room-temperature exfoliation of MoS_2 crystals: in the 'restacked' bare MoS_2 [6,29] and in its heterolayered compounds [30–32].

In the present work, we have studied the use of chemically exfoliated MoS_2 crystals for room-temperature coating of CNT surface with few-layer MoS_2 shell, the way to modify this shell with organic interlayers constituted by polycationic polymers polydiallyldimethylammonium (P1) or poly(acrylamide-*co*-diallyldimethylammonium) (P2) and revealed the microstructure and morphology characteristics of the obtained heterostructures.