Materials Letters 159 (2015) 333–336

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Surface decoration of MoSI nanowires and MoS_2 multi-wall nanotubes and platinum nanoparticle encapsulation

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ARTICLE INFO

Article history:
Received 22 May 2015
Received in revised form
3 July 2015
Accepted 5 July 2015
Available online 9 July 2015

Keywords:
Nanoparticles
Nanocrystalline materials
Nanotubes
Molybdenum
Platinum
Encapsulation

ABSTRACT

Here we report on decoration of MoS_2 nanotubes with platinum nanoparticles and partial encapsulation of platinum during the transformation of decorated $Mo_6S_yI_z$ ($8.2 < y+z < 10$) nanowires into MoS_2 nanotubes. The proposed method enables direct decoration of both nanotubes and nanowires directly from aqueous solution of Na_2PtCl_4 at room temperature without reducing agents. A stable and uniform decoration is observed with average particle diameters of around 2 nm and a controllable surface density, covering up to 80% of the nanowire surface. Sulphurisation of decorated nanowires was performed, during which platinum nanoparticles aggregated into larger formations, and partial encapsulation of elongated platinum nanorods in the obtained multi-wall MoS_2 nanotubes is observed.

1. Introduction

Hybrid materials combining nanowires (NWs) or nanotubes (NTs) with noble metal nanoparticles (NPs) have recently attracted considerable attention due to their very high surface-to-volume ratio and consequently a wide range of possible applications in nanoelectronics and energy storage, or as nanosensors and catalysts [1]. Decoration and functionalisation of nanostructures can be customised and adjusted for selected applications by changing chemical compositions and morphologies of initial nanostructures and attached nanoparticles. Gold nanoparticles, for example, attached to quasi-one-dimensional nanostructures, were used as photocatalysts [2,3], or gas sensors [4,5] and palladium significantly enhanced catalytic properties [6] and hydrogen storage capacity [7]. Decoration with platinum nanoparticles results in materials with high catalytic activity [8] and gas sensing properties [9]. Obtained hybrid materials are also used for efficient energy conversion [10]. However, not all nanowires are suitable for functionalisation and sometimes complicated synthetic routes had to be developed for a uniform and stable decoration with varying degrees of success. Recent realisations include photo irradiation process [8], atomic layer deposition [9], or aqueous electroless etching and deposition [10].

We have previously suggested a method for direct decoration of $Mo_6S_yI_z$ ($8.2 < y+z < 10$) (MoSI) nanowires with gold nanoparticles and their transformation into decorated MoS_2 nanotubes [11]. Here we implement a similar and highly efficient route for both nanowire and nanotube decoration with platinum nanoparticles and describe the transformation of decorated nanowires into nanotubes. The main feature of this approach is its simplicity as the direct decoration occurs at room temperature and avoids chemical treatment or surface modification of the structures. In addition, sulphurisation of previously decorated nanowires enables fabrication of novel nanohybrids, composed of MoS_2 nanotubes partially filled with platinum nanorods.

2. Materials and methods

Bundles of MoSI nanowires were synthesized directly from elements in a chemical transport reaction [12] and additionally purified as in [11]. This one-step synthesis yielded thin nanowire bundles with an average diameter of around 40 nm. MoS_2 nanotubes were produced by sulphurisation of nanowires in gas (1% H_2S, 1% H_2, and 98% Ar at 750 °C for one hour) [13,14]. The obtained multi-wall MoS_2 nanotubes retained the outside shape of precursor nanowire bundles. Nanowire bundles and nanotubes were dispersed in ultra-pure water (Millipore, 18.2 MΩcm) at a concentration of 20 mg/1000 ml in an ultrasonic bath for one hour. Decoration of nanowires and nanotubes was done at room temperature in a water dispersion of nanowires by adding 10, 30, or

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http://dx.doi.org/10.1016/j.matlet.2015.07.021
0167-577X/

50 ml of 2.5 mM Na_2PtCl_4 in water to 1000 ml of prepared dispersion. The mixtures were sonicated for one hour, micro-filtrated, rinsed with water and isopropanol, and dried at 60 °C. Obtained hybrid material was finally re-dispersed in isopropanol.

Synthesized materials were observed and analysed by a high-resolution transmission electron microscope (HR-TEM, Jeol JEM-2010F, Jeol Inc., 200 keV) equipped with scanning (STEM) unit and energy dispersive x-ray spectrometer (EDXS). Samples were observed in conventional TEM mode of operation (bright-field TEM images) and in STEM mode using high-angle annular dark-field detector (HAADF-STEM) to reveal regions in specimens with different compositions, i.e. projected mass thickness. The particle size was determined by using Image-Pro Analyzer and the particle-size distributions were obtained by evaluating around 100 nanoparticles per sample.

3. Results and discussion

When directly decorating the nanowires with platinum, we find that the self-decoration with platinum occurs quite rapidly as already after a few minutes the nanowires are covered with a large number of nanoparticles (Fig. 1a). Chemical composition of the nanoparticles was examined by EDXS confirming the presence of platinum by the characteristic peak at 2.05 keV and several peaks around 9.4 and 11 keV (Fig. 1b).

We performed a series of experiments with different amounts of added Na_2PtCl_4 to investigate the possibility of tuning the decoration parameters, such as particle size and surface density.

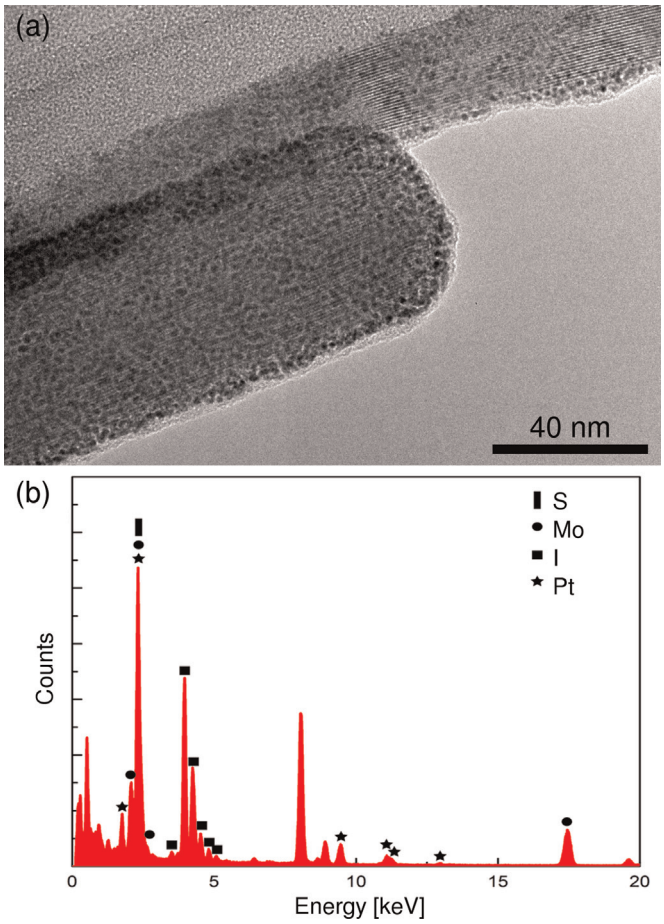

Fig. 1. Decoration of $Mo_6S_yI_z$ ($8.2 < y+z < 10$) nanowire bundles with platinum nanoparticles. (a) TEM image of a decorated nanowire bundle. (b) EDS spectrum confirms successful platinum decoration.

TEM images of the obtained NW/NP materials are shown in Fig. 2a, c and e, for added 10, 30, and 50 ml of 2.5 mM Na_2PtCl_4 solution, respectively. In all cases, the decoration procedure yielded a thorough and uniform decoration with platinum nanoparticles. Corresponding particle-size distributions are shown in Figs. 2b, d and f and the results summarised in Table 1.

By increasing the amount of added platinum complex by a factor of 5, the average particle diameter increases and the size distribution broadens by about 50%. We also observed some particles with diameters significantly larger than twice the average diameter. They represented less than 5% of all particles and their number can be further lowered by slowly adding Na_2PtCl_4 solution to the nanowire dispersion, rather that pouring, and constant mixing. These significantly larger particles were not included in further analysis. Also decoration of nanotubes was successful (Fig. 2g) with the same particle size as when coating nanowires (Fig. 2h).

We also measured surface particle density and observe that this decoration route enables tuning of nanowire surface coverage (Table 1). Obtained values were remarkably high, in some cases up to 80% of covered surface. This is due to homogeneous reactive nanowire surface, composed of iodine and sulphur atoms [11]. Surface coverage of nanotubes, however, is almost independent of Na_2PtCl_4 concentration. This can be explained by the known low reactivity of MoS_2 and nanoparticles forming mainly at surface defects with dangling bonds. The number of defects limits the surface density, keeping it almost independent of Na_2PtCl_4 concentration. We believe that the decoration surface density could be altered by changing the sulphurisation parameters (such as temperature or rate) that influence the number of formed surface defects.

Our previous research shows that MoSI nanowires can be transformed into MoS_2 nanotubes, even when decorated with gold [11]. We performed sulphurisation of platinum-decorated nanowires and observed that almost all platinum was removed from the nanotube walls, except at the open ends where platinum caps formed (Fig. 3a). Also larger platinum cubic-like arrangements, completely detached from the nanotubes, were found. These structures, formed most likely by Ostwald ripening, were several tens of nanometres in size.

In several cases we observed platinum formations within MoS_2 nanotubes. The presence of encapsulated platinum was confirmed by high-angle annular dark field (HAADF-STEM) imaging (Fig. 3b), showing a bright spot within a nanotube. EDXS was performed at the top of the bright structure and on nanotube walls (Fig. 3b, insets), clearly identifying platinum inside MoS_2. The encapsulated platinum nanostructures had a diameter of 10–20 nm and length of several tens of nanometres. Two possible mechanisms for this phenomenon were considered: either the platinum nanostructures grow within the tube, or already formed structures enter the tube. Since encapsulation was rather rare, we believe the second mechanism is more plausible. Platinum particles are first formed on the outer surface by Ostwald ripening (as observed in Fig. 3a) and then enter the nanotube through its open end if the inner nanotube diameter is large enough. This is in contrast to other standard procedures for production of encapsulated composite nanostructures, for example capillary filling of tubes with molten material [15] or with electro-deposition [16], where encapsulated structures are grown within the tubes.

4. Conclusions

We performed a simple and efficient method for uniform decoration of molybdenum-based nanowires and nanotubes with platinum nanoparticles, suitable for larger-scale production. High

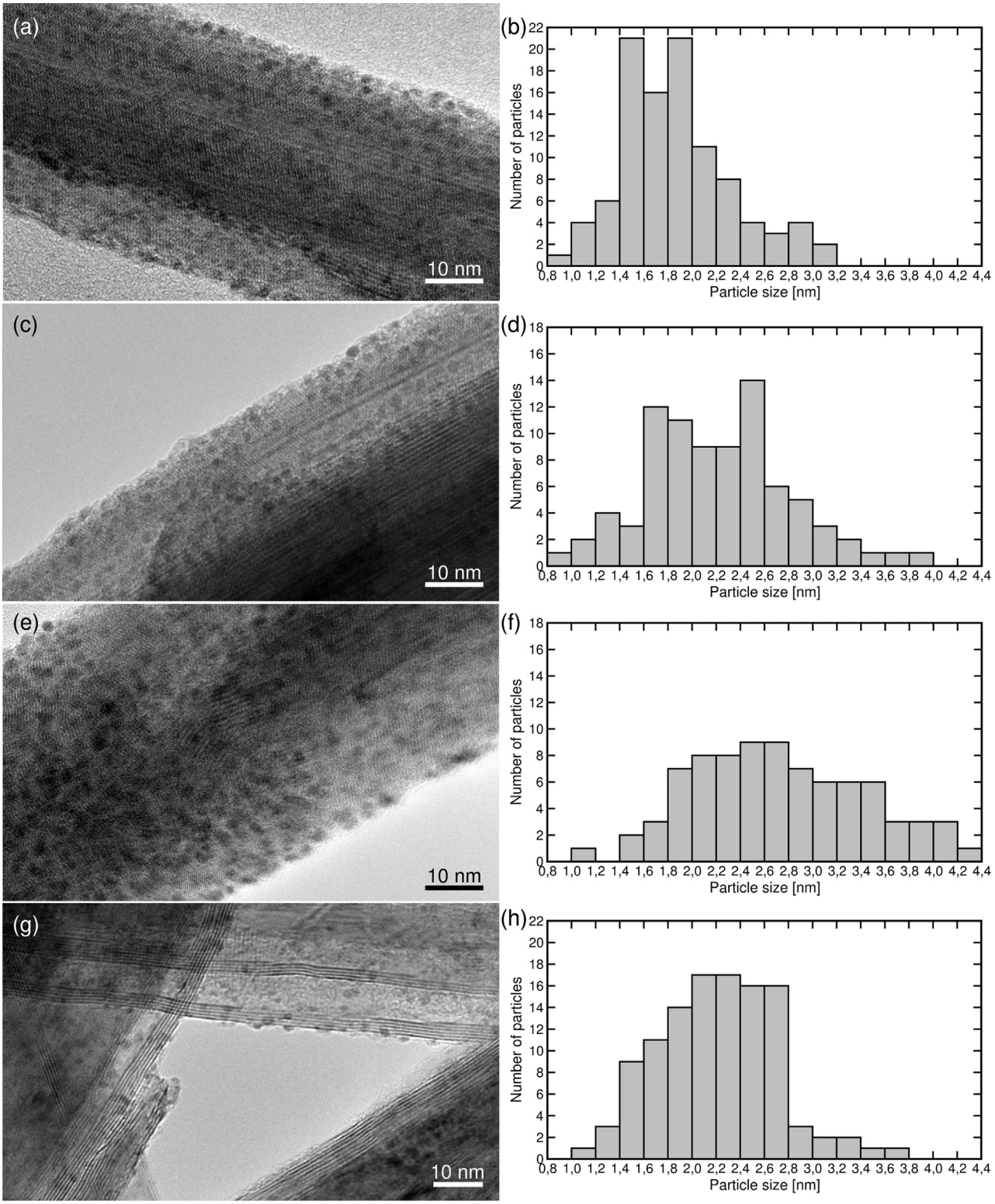

Fig. 2. Decorated nanowires and nanotubes and corresponding platinum particle-size distributions. TEM images of decorated nanowires at three different Na_2PtCl_4 concentrations (a) 25 μM, (c) 75 μM, (e) 125 μM and decorated nanotubes at 75 μM (g), and corresponding particle-size histograms (b–h).

Table 1
Particle diameters and surface coverage depend on Na_2PtCl_4 concentration.

Material	c(Na_2PtCl_4) (μM)	Particle size (nm)	Surface coverage (%)
NW	25	1.9 ± 0.46	~20
NW	75	2.22 ± 0.59	~40
NW	125	2.73 ± 0.70	> 60
NT	75	2.2 ± 0.5	~15

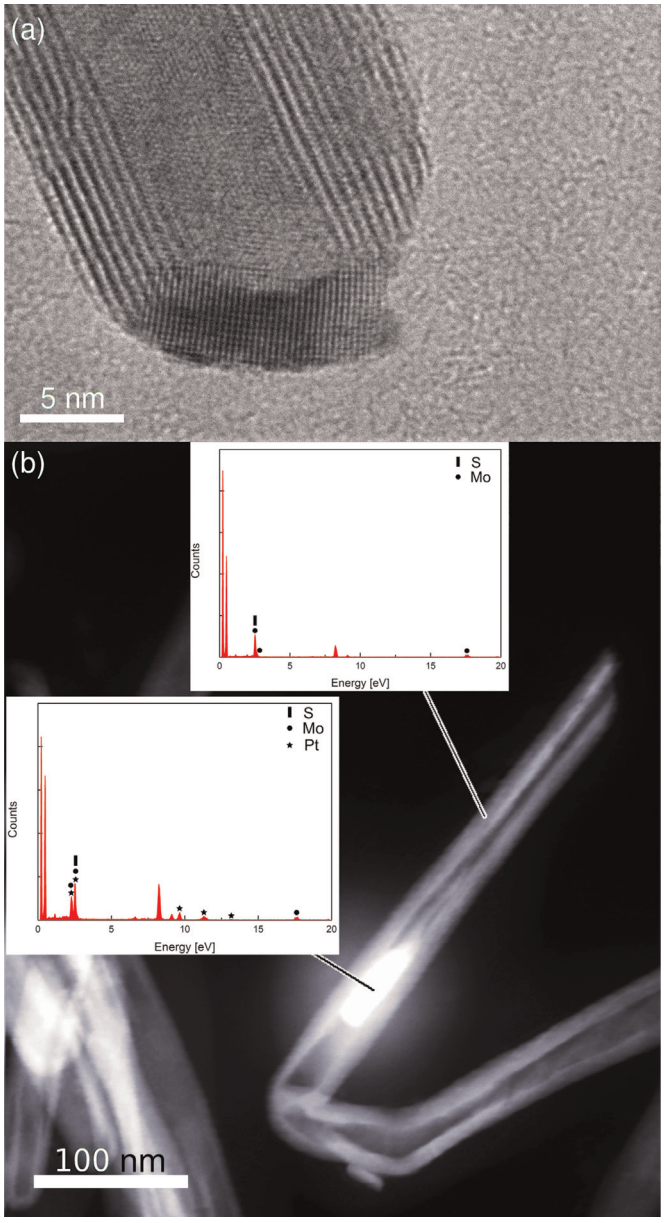

Fig. 3. Platinum encapsulation. (a) Platinum caps formed during sulphurisation of decorated nanowires. (b) HAADF-STEM image of a platinum formation within a MoS_2 nanotube. Nanobeam EDXS analysis (inset) confirms encapsulation.

surface density of the nanoparticles and their small diameter – both parameters can be fine-tuned by changing Na_2PtCl_4 concentration – result in a very large effective surface, making this composite nanomaterial suitable for catalytic applications. Sulphurisation of decorated nanowires produced larger platinum particles, some detached from the nanotubes, some closing their open ends, and some penetrating into the nanotubes, resulting in novel MoS_2/encapsulated platinum hybrid systems.

Acknowledgement

This work was supported by Slovenian Research Agency (P1-0040, P1-0192, and P2-0084).

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