



Decoration of MoSI Nanowires with Platinum Nanoparticles and Transformation into Molybdenum-nanowire Nased Networks

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In this communication, we present solution-based coating procedure of MoSI nanowires (NW) with platinum nanoparticles. The average particle diameter was found to be around 2.82 nm, showing a narrow size distribution. This single-step *in situ* reduction method at room temperature in water solution can easily be applied for large-scale applications. We also prepared two-dimensional networks of MoSI NW bundles by deposition via spraying from a purified stable dispersion in acetonitrile onto NaCl crystals and nonconductive silicon wafer with pre-assembled molybdenum electrodes. The formation of a conductive molybdenum network was achieved by annealing in hydrogen due to coalescence of the templates MoSI bundles during transformation. Stable water dispersion of molybdenum NW network was prepared by simply dissolving the NaCl substrate with molybdenum network on the surface.

Keywords: Nanowires, Platinum, Nanoparticles, Decoration, Molybdenum networks.

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1. INTRODUCTION

The main advantage of nanoparticle-decorated nanowires is their hybrid structure, combining the high aspect ratio and controllable structure of nanowires [1] with the large surface area of nanoparticles. Electrical, optical, and chemical properties of these hybrid materials can be adjusted by changing chemical compositions and morphologies of NPs and NWs independently, enabling additional functionalization of the NPs. One very promising possibility of using inorganic nanowires as catalysts is by decorating their surfaces with platinum nanoparticles [2].

Successful decoration of TiO₂ nanotubes with Pt nanoparticles has already been by done in a two-step photo-irradiation method and the resulting hybrid nanotube arrays show an excellent catalytic activity [3]. Also SnO₂ nanowires were investigated after their surface functionalization by atomic layer deposition of Pt particles, exhibiting very good gas-sensing properties [4]. Platinum nanoparticles were uniformly deposited also on ZnO nanowires by varying the number of atomic layer deposition reaction cycles. The Pt-decorated ZnO nanowires exhibited a much faster photon response and recovery speeds than the pristine ZnO nanowires [5]. Recently, high-density aligned n-type silicon nanowire arrays were decorated with 5-10 nm platinum nanoparticles, which have been fabricated by aqueous electroless Si etching followed by an electroless platinum deposition process. Coating on sidewalls yielded a substantial enhancement in photoconversion efficiency and in energy conversion efficiency [6]. However, only a few techniques have produced coatings with enhanced density, uniformity, and short and simple production.

It has been shown previously that Mo₆S_yI_z (8.2 < y + z < 10) nanowires (MoSI NW) have unique optical [7] and electronic properties [8] and can act as precursor material for bulk production of several types

of molybdenum-based nanowires and nanotubes. Here we report Pt decoration of MoSI nanowires using single step *in situ* reduction method in aqueous medium. Particle geometries produced by the described method are similar to those previously mentioned; however particle densities are substantially greater and can be varied as a function of the concentration of nanoparticles precursor salts. Our method of coating is simple to perform and requires a short processing time (typically < 15 min). This method may be a new way to produce superior coatings of platinum on various categories of MoSI NWs and may be applicable to other nanotubes and nanowires as well. Heating of MoSI nanowire bundles in Ar / H₂ mixture enables quantitative formation of pure molybdenum nanowires (Mo NW). We already produced Mo NW with a diameter of 4 nm that carried up to 30 μA current without suffering structural degradation [9].

In this work, we report on the fabrication of a stable conductive molybdenum nanowire network that was achieved due to coalescence of the 2D templates MoSI bundles during transformation into MoNW. Furthermore, we prepared stable water dispersion of Mo NW network, suitable for different applications.

2. EXPERIMENTS AND METHODS

The decoration of MoSI nanowires is carried out in a single step, at room temperature, and without reducing agents, which results in decoration of both side walls and ends of NW bundles. Bundles of MoSI nanowires were synthesized directly from the elements in a one-step procedure. The ampoule was left for 60 hours in a temperature gradient with lower temperature being 750 °C and higher temperature 850 °C. At the higher-temperature end, the remaining material was a dark-brown powder. We have shown previously that the obtained powder consists of bundles of nanowires, molybdenum grains and MoS₂ crystals [11]. After sonication in

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acetonitrile, the supernatant was extracted and separated by centrifugation (1250 g for one hour) to remove heavier MoS₂ crystals, molybdenum grains and bundles with larger diameters. The supernatant was filtered and dried at 40 °C, with resulting yield around 10 wt % and the average diameter of the bundles was around 20-80 nm and lengths up to several micrometers. By using a 2.5 mM water solution of Na₂[PtCl₄] as a source of Pt, the bundles were self-decorated in 20 mg/L MoSI water dispersion during constant ultrasound agitation for one hour. The density of Pt nanoparticles on MoSI NWs was controlled simply by changing the amount of the added Na₂[PtCl₄] solution. A high amount of platinum nanoparticles on the surface of nanowires were obtained after several tens of millilitre of Na₂[PtCl₄] solution were added. The materials were isolated by filtration and washed with water to remove salts.

The molybdenum networks were prepared by two step process. First, the stable suspension of MoSI nanowires bundles in acetonitrile were sprayed with an airbrush onto NaCl crystals and nonconductive silicon wafer with preassembled molybdenum electrodes. By adjusting the spraying parameters, such as air flow rate, the nozzle size, dispersion concentration, and the distance between nozzle and substrate, quite uniformly deposited nanowire bundles networks were obtained with little agglomeration. The evaporation of them solvent during the spraying process was accelerated by heating the substrate with a back heating source to approximately 50 °C. In next step the reduction of MoSI NWs networks was performed by hydrogenation at 700 °C in a constant flow of H₂/Ar gas mixture for one hour.

Final materials were observed and analyzed by scanning electron microscope (SEM, Jeol JSM-7600F) equipped with energy dispersive spectrometer (EDS), high-resolution transmission electron microscope (HR-TEM, Jeol JEM-2100F, 200 keV) equipped with energy dispersive spectrometer (EDS). The diameters of nanowires and platinum nanoparticles were determined using Image Pro Analyzer. Distributions in particle size were obtained by evaluating over 100 nanoparticles per sample. TEM grids were prepared with immersion of Formvar / carbon coated copper grid directly in nanowire dispersions without sonication. Excess solution was allowed to dry and then grid was washed several times with Millipore water to dissolve and remove small crystals of NaCl.

3. RESULTS AND DISCUSSION

3.1 Decoration of MoSI Nanowires with Platinum Nanoparticles

We find that platinum nanoparticles appear on nanowires already after several minutes of deposition. A TEM image of a Pt-coated MoSI NW bundle is shown in Fig. 1. The NW bundle has a diameter of approximately 30 nm and a thorough decoration with platinum is observed. A proof that the obtained material are indeed MoSI nanowires covered with platinum is given by the energy-dispersive X-ray spectrum (EDS), shown in Fig. 2. The marked peaks can be attributed to mo-

lybdenum, sulphur, iodine and platinum. The unmarked peaks belong to copper, carbon and oxygen, which are present due to the holey carbon-coated copper mesh.

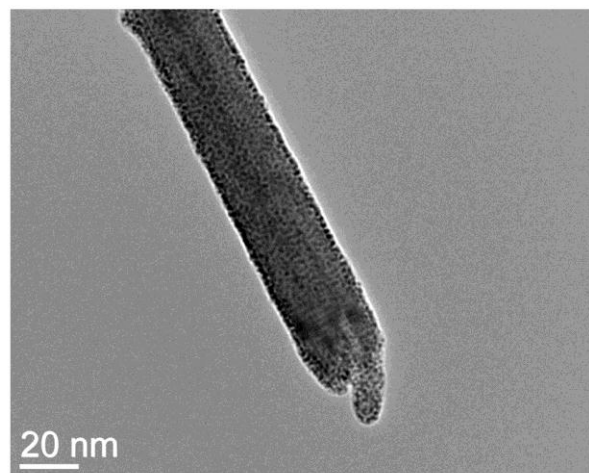


Fig. 1 – TEM image of bundles of MoSI nanowire decorated with platinum nanoparticles

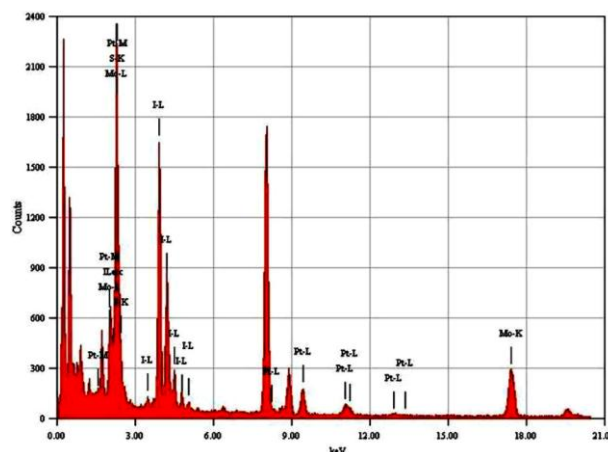


Fig. 1 – EDS spectrum confirming the composition of the obtained material. The marked peaks are belonging to molybdenum, sulfur, iodine and platinum

Particle analysis was performed on Pt-decorated NWs with initial bundle diameters of approximately 20-80 nm and with added 50 ml of 2.5 mM Na₂[PtCl₄] solution to starting dispersion of MoSI nanowires. Particle size distribution is shown in Fig. 3 and an example of a coated nanowire bundle is shown in Fig. 4. For determination of the average particle size, several wires were analysed and approximately 100 particle diameters per bundle were measured. We find the average overall particle size to be 2.82 nm with a standard deviation of 0.83 nm. The measurement also shows that the particle diameter is independent of the nanowire diameters.

The high-resolution TEM image (Fig. 4) also shows that the coatings are typically very dense. However, we observed that some areas on several nanowires remained uncoated.

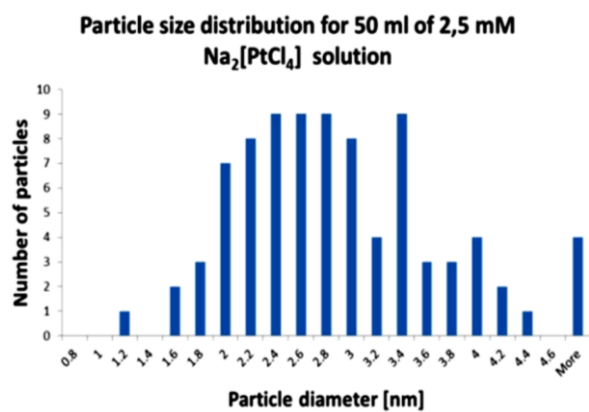


Fig. 3 – Particle size distribution for 50 ml of 2.5 mM Na₂[PtCl₄] solution

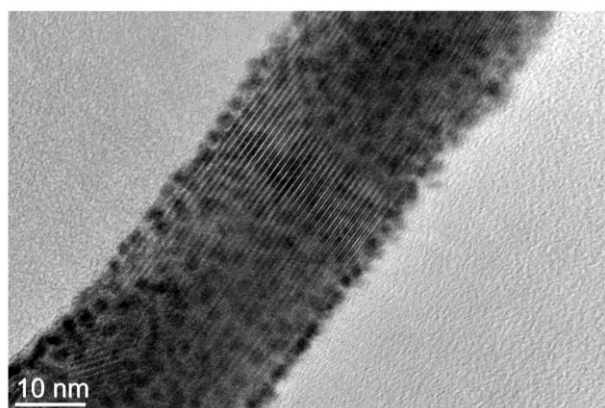


Fig. 4 – HRTEM image of a MoSI nanowire densely covered with platinum nanoparticles

The high-resolution image and the histogram clearly show that the Pt particle size distribution is small, with all the particles appearing very similar in shape and size and the decoration appears to be homogeneous. The coatings reported in this study offer the possibility for these nano-coated materials to act as an excellent catalyst thanks to the immense surface area that appears because of a large particle density and a small particle size.

3.2 Transformation of MoSI Bundles into Molybdenum-nanowire Based Networks

First we tried to fabricate molybdenum nanowire network using MoSI bundles as starting precursor. A typical SEM image of deposited MoSI NWs with air-brush onto surfaces of conductive silicon wafer is shown in Fig. 5. The obtained bundles have a typical diameter of up to a few tens of nanometres and lengths of several μm . Also visible are the molybdenum electrodes that were pre-assembled at a separation of 1000 μm .

The formation of a conductive molybdenum network can be obtained by annealing the sample in hydrogen, due to coalescence of the templates MoSI bundles during transformation as described in experimental part. Preliminary experiments show presence of stable molybdenum nanowire networks that have a transmission of over 85 % and sheet resistances as low as 400 Ohm/sq.

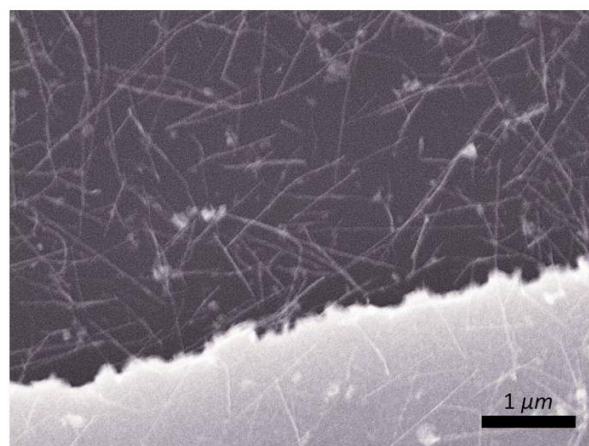


Fig. 5 – SEM images bundles of MoSINW random network after spray-coating on the surface of silicon wafer with molybdenum electrode

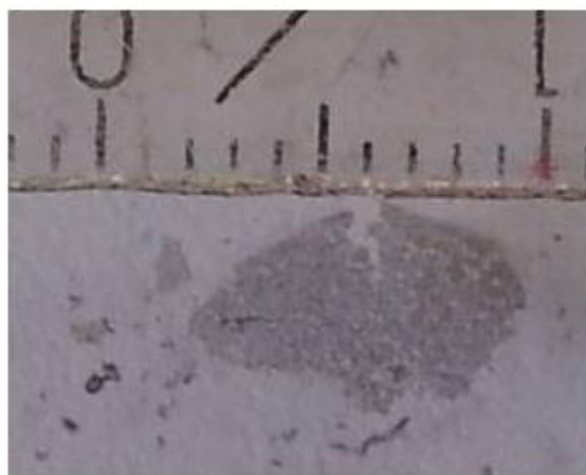


Fig. 6 – Photo of Mo NW networks on the water surface

Molybdenum nanowire networks were prepared also on surface of NaCl crystals with a surface area of around 1 cm². After the annealing in hydrogen, the crystals with the molybdenum nanowire network were immersed in water for one minute. Stable molybdenum nanowire networks visible to naked eye appeared on the water surface, as shown in Fig. 6. These molybdenum nanowire networks were stable on the water surface for weeks. We investigated the nature of these films using SEM microscopy. To facilitate SEM analysis, we transferred these films from water surface onto a conducting silica wafer and washed several times with Millipore water to dissolve residue of NaCl. Fig. 7 shows a SEM image of a network of molybdenum nanowires that, while clearly above percolation, can be considered sparse. There is no significant non-uniformity with holes in the network with diameters of several micrometers.

Networks were deposited also on TEM grids as described in experimental section without using ultrasound agitation. We have performed TEM microscopy on different parts of the network with higher and lower densities of molybdenum nanowires as seen in Fig. 8.

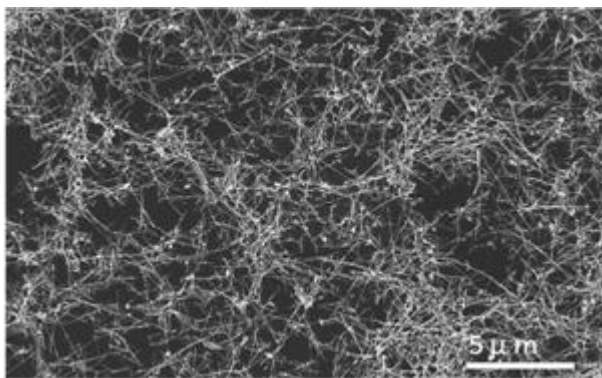


Fig. 7 – SEM image of molybdenum nanowire network

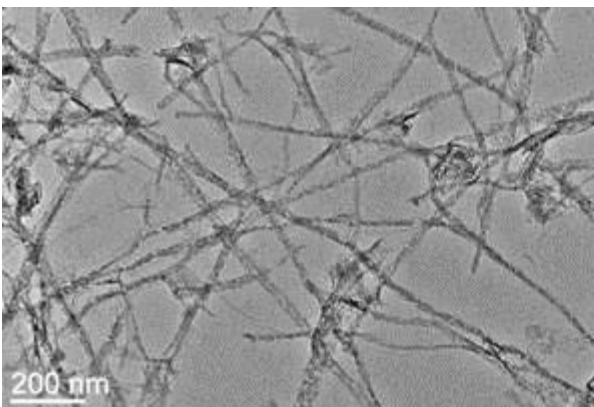


Fig. 8 – TEM image of molybdenum nanowire network

The diameters of the nanowires varied from 10 to 70 nm with a mean diameter of 40 nm. We find that the lengths of molybdenum nanowires are similar to those of starting MoSI nanowires, while the diameters are almost 30 % smaller. This observation is consistent with previous measurements of transformation of MoSI nanowire bundles into Mo nanowires.

4. CONCLUSION

We presented a simple, single-step efficient self-decoration of MoSI nanowires with platinum nanoparticles at room temperature without any additional reducing reagents. We were able to successfully decorate nanowires with platinum in the water dispersion. The described procedure is one of the few examples of redox templating at room temperature without use of reducing agent to produce platinum-decorated nanowires, which enables large scale production for different applications. In addition, an efficient, low-cost and scalable method has been developed to fabricate pure Mo nanowires networks. Stable water dispersion of molybdenum NW networks can be prepared by simply dissolving the NaCl substrate with molybdenum network on the surface. Decoration of MoSI nanowires, in combination with discovered transformation pathways of MoSI bundles, gives rise to novel noble metal/molybdenum hybrid networks, which are promising for electronic devices, sensors and conducting composites.

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