# **RSC Advances**



# PAPER



Cite this: RSC Adv., 2016, 6, 90806

## Molybdenum carbide nanowires: facile synthesis, a new hybrid phase and their use as transparent electrodes

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Several synthetic routes exist for the production of bulk molybdenum carbides whereas production of larger quantities of different molybdenum carbide phases in the form of nanowires and nanowire networks is still challenging. Here we report a novel route for synthesis of molybdenum carbide nanowires by carburisation of  $Mo_6S_2I_8$  nanowire bundles. Gram quantities of molybdenum carbide nanowires composed of mainly MoC and  $Mo_2C$  phases were obtained and further reduced to single phase  $Mo_2C$  nanowires. By controlling the reaction conditions during the transformation, we can modify the ratio between MoC and  $Mo_2C$  phases in nanowires and produce a novel hybrid inorganic/organic nanomaterial that we identified as molybdenum carbide nanowires densely covered with carbon nanofibres. We used the same approach on nanowire networks and demonstrate a new use of molybdenum carbide in the form of nanowire networks as transparent electrodes. The sheet resistance of such robust and air-stable electrodes is around 1050  $\Omega$  sq<sup>-1</sup> at room temperature and their transmittance between 93% and 95% in the range of 200–900 nm. The electrodes are thus suitable for electro-optic applications, especially where high transparency in the UV region is required.

Received 22nd July 2016 Accepted 16th September 2016

DOI: 10.1039/c6ra18650e

www.rsc.org/advances

### 1. Introduction

Over the past decades, transition-metal carbides have been widely investigated mainly due to their interesting bulk and surface physico-chemical properties.<sup>1-5</sup> They are an attractive alternative to noble metal catalysts because they show high efficiency and suitability for reforming,<sup>6,7</sup> hydrogenation,<sup>8</sup> water-gas shift,<sup>9</sup> CO oxidation reactions,<sup>10</sup> and CO<sub>2</sub> conversion by H<sub>2</sub>.<sup>11</sup>

One of the most widely investigated transition-metal hybrid system is molybdenum carbide, mainly due to its low cost, high melting point, good conductivity, and high catalytic activity.12 Several different phases have been identified in the Mo-C system, but generally accepted phase diagram by Velikanova et al. indicates only two types of Mo<sub>2</sub>C and  $\gamma$ -MoC as thermodynamically stable phases at room temperature.<sup>13</sup> In contrast, η-MoC and  $\delta$ -MoC are placed as high-temperature phases, which become stable at temperatures above  $\sim 1700$  °C. However, recently four phases of molybdenum carbide ( $\gamma$ -MoC,  $\eta$ -MoC,  $\alpha$ - $MoC_{1-x}$ , and  $\beta$ -Mo<sub>2</sub>C) were synthesised from an amine-metal oxide composite material.14 The standard method for preparing transition-metal carbides with a large surface area is the temperature-programmed reduction method,<sup>15</sup> while some other procedures include gas-phase reactions of volatile metal compounds,<sup>2,16</sup> reaction of gaseous reagents with solid-state metal compounds,  $^{\scriptscriptstyle 2,17}$  pyrolysis of metal precursors,  $^{\scriptscriptstyle 18}$  and solution reactions.  $^{\scriptscriptstyle 19}$ 

In contrast to bulk materials, reports on the synthesis of molybdenum carbide in the form of nanowires are quite rare. Tsakalakos *et al.* synthesised Mo<sub>2</sub>C nanowires and ribbons on Si substrate using a two-step approach, in which metal oxide nanostructures were catalytically grown followed by *in situ* carburisation.<sup>20</sup> Mo<sub>2</sub>C nanowires with enriched nanoporosity have been successfully synthesised also through calcining the organic/inorganic hybrid nanowires with subnanometre periodic structures,<sup>21</sup> and very recently MoC-Mo<sub>2</sub>C heterowires, suitable for electrocatalysis, have been synthesised from MoO<sub>x</sub>-amine nanowires.<sup>22</sup> Large scale controllable fabrication of molybdenum carbide nanowires composed of different phases and fabrication of transparent molybdenum carbide nanowire networks, however, is still a challenge.

We have shown previously that  $Mo_6S_2I_8$  (MoSI) nanowires are very suitable as precursors for bulk production of several types of molybdenum-based nanowires and nanotubes, including metallic Mo nanowires,<sup>23</sup> MoS<sub>2</sub> nanotubes and pea pods,<sup>24,25</sup>  $MoO_{3-x}$  nanowires<sup>26</sup> and superconducting MoN nanowires.<sup>27,28</sup>

Here we report on the synthesis of molybdenum carbide nanowires with MoSI bundles as starting material. The transformation of the precursors is done by heating in different hydrogen, argon, and ethane gas mixtures either directly from MoSI or *via* molybdenum wires. We implement the same approach on a nanowire mesh for the fabrication of stable conductive molybdenum carbide networks and demonstrate

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that the obtained networks can be used as transparent electrodes with exceptionally high transmittance in the UV region.

### 2. Experimental

#### 2.1 Synthesis

2.1.1 Mo<sub>6</sub>S<sub>2</sub>I<sub>8</sub> nanowires. Synthesis of molybdenum carbide nanomaterials was based on transformation of Mo<sub>6</sub>S<sub>2</sub>I<sub>8</sub> nanowires. The precursor nanowires were prepared in a horizontal sealed quartz ampoule (15 cm in length and 2.2 cm in diameter) directly from elements at 1040 °C, as reported previously.25 At a reaction time of 72 h around 90 wt% of Mo<sub>6</sub>S<sub>2</sub>I<sub>8</sub> nanowire bundles grew from the powder and showed a fur-like appearance. The remaining 10 wt% grew by vapour phase deposition on the inner surface of the ampoule, forming textilelike material. Both forms of nanowire material were collected after evaporation of non-reacted iodine. The textile-like material could be used as such, whereas the fur-like form required purification (dispersion in isopropyl alcohol followed by either sedimentation for 1 hour or centrifugation at 500 rpm for 10 min). During purification larger agglomerates of nanowires, MoS<sub>2</sub> flakes and Chevrel phase Mo<sub>6</sub>S<sub>6</sub>I<sub>2</sub>,<sup>29</sup> were removed. The bundles were collected by microfiltration and dried at 50 °C. Obtained Mo<sub>6</sub>S<sub>2</sub>I<sub>8</sub> material was put into a quartz boat, which was inserted into a quartz tube with gas inlet and outlet connections.

**2.1.2 Direct transformation.** The first method of molybdenum carbide nanowire fabrication was direct carburisation of  $Mo_6S_2I_8$  nanowires in a gas mixture comprising ethane (purity > 99.99%), argon (purity 5.0), and hydrogen (purity > 99.99%). Total flowing rate of the gas mixture passing through the quartz tube was around 70 cm<sup>3</sup> min<sup>-1</sup>, and controlled by mass flow controllers (MKS). Argon flow was fixed at 50 cm<sup>3</sup> min<sup>-1</sup>, whereas the flows of ethane and hydrogen varied from zero to 5 cm<sup>3</sup> min<sup>-1</sup> and zero to 15 cm<sup>3</sup> min<sup>-1</sup>, respectively. Carburisation was performed at 710 °C for four hours with a heating rate of 7.4 K min<sup>-1</sup>. Final reduction of molybdenum carbide nanowires was performed in a constant flow of argon/hydrogen mixture (50 cm<sup>3</sup> min<sup>-1</sup> and 5 cm<sup>3</sup> min<sup>-1</sup> flows, respectively) for three hours.

**2.1.3 Transformation** *via* **molybdenum nanowires.** The second method of  $Mo_6S_2I_8$  transformation was done in two steps: first the nanowires were transformed into molybdenum nanowires in a constant flow of argon/hydrogen mixture for three hours as described previously,<sup>23</sup> followed by transformation into molybdenum carbide in a flow of ethane/argon/ hydrogen gas mixture, both at 710 °C. The material was then reduced as described previously. Before exposing the obtained material to the atmosphere, the quartz tube was purged with argon at room temperature for half an hour, followed by a mild surface oxidation (2 vol%  $O_2/N_2$  mixture at 20 cm<sup>3</sup> min<sup>-1</sup> for one hour) to achieve adequate passivation.

**2.1.4 Mo**<sub>2</sub>**C networks.** Mo<sub>2</sub>C networks were prepared on quartz and silicon substrates. First a dispersion of  $Mo_6S_2I_8$ -nanowire bundles in isopropyl alcohol (up to 50 mg l<sup>-1</sup>) was sprayed with an airbrush onto the substrate. By adjusting the spray parameters, such as air-flow rate, nozzle size, dispersion

concentration, and the nozzle-substrate separation, uniformly deposited meshes of nanowire bundles were fabricated with little agglomeration. Evaporation of the solvent during the spraying process was accelerated by heating the substrate with a back heating source to approximately 50 °C. The  $Mo_6S_2I_8$ nanowire meshes were then transformed into Mo<sub>2</sub>C nanowire networks exactly as before: carburisation at 710 °C in a constant flow of ethane/argon/hydrogen gas mixture for four hours and reduced in a constant flow of argon/hydrogen mixture for three hours. Networks on silicon wafers were used for SEM imaging, whereas transmittance and conductivity measurements were performed on networks deposited on quartz substrates. For sheet resistance measurements, molybdenum electrodes with a separation of 1 mm were prepared on the substrate before network deposition by laser lithography using a LPKF Proto-Laser LDI machine and a two-layer photoresist (Allresist ARP 5480/ARP3510).

#### 2.2 Characterisation

Materials were observed and analysed by scanning electron microscope (SEM, Jeol JSM-7600F) and high-resolution transmission electron microscope (HR-TEM, Jeol JEM-2100F, 200 keV). TEM samples were prepared from nanowire dispersions immediately after sonication by applying 30 ml of diluted dispersion (5% mixture in isopropyl alcohol) to a copper grid. Xray powder diffraction (XRD) was performed at room temperature using Bruker AXS D4 Endeavor diffractometer with Cu-Ka1 radiation and Sol-X energy-dispersive detector within angular range 2 $\Theta$  from 10° to 70° with a step size of 0.02° and a collection time of 2 s at a rotation of 6 rpm. Crystalline phases of the samples were identified by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) files. Crystallite sizes were calculated from the diffraction peak widths using Debye-Scherrer equation. Raman spectroscopic characterisation was performed on a NT-MDT INTEGRA SPECTRA confocal Raman microscope in a backscattering geometry with spectral resolution of 0.7 cm<sup>-1</sup>.

Optical transmittance measurements were done by a UV-Vis spectrophotometer (HP 8453) with the samples deposited on quartz substrates. For temperature resistance measurements, pre-assembled 50 nm thick Mo electrodes on silica substrate were designed to cover a surface of 1 mm<sup>2</sup>. Temperature dependent *I*–*V* characteristics were measured down to 30 K and the erasure by Joule heating was achieved by passing a current of 1 mA.

### 3. Results and discussion

#### 3.1 Precursors

Structure and morphology of precursor  $Mo_6S_2I_8$  nanowire bundles were determined using SEM, HR-TEM and XRD and are consistent with previously published data.<sup>30</sup> Fig. 1 shows SEM images of synthesised  $Mo_6S_2I_8$  nanowire bundles in fur-like (a) and textile-like form (b). In the latter form, which constituted up to 10 wt% of material, nanowire bundles are several tens to several hundreds of micrometres long and thus considerably



Fig. 1 SEM images of  $Mo_6S_2I_8$  nanowire bundles that were used as precursors in the synthesis of molybdenum carbide nanomaterials. The majority of the material was in fur-like form (a), with approximately 10% showing a textile-like morphology with significantly longer nanowire bundles (b).

longer and significantly less agglomerated than in the fur-like material, which is made of bundles typically a few microns long with a diameter of up to 200 nm. We have later confirmed that both forms can be used for transformation into molyb-denum carbides, producing up to around 1 g of material in a single experiment. However, the textile-like form of  $Mo_6S_2I_8$  nanowire bundles with a large interbundle distance is much more suitable for transformation into long molybdenum carbide nanowires and thus formation of conductive networks.

Mass of the final product is found to be 40–63% of the mass of the reactants. The large interval can be explained by production of different carbide phases and different amounts of deposited carbon, as will be discussed later. Although the mass is reduced, we observe that the quasi-one-dimensional morphology of starting bundles is preserved in all samples. There is, however, a slight decrease in the diameters of nanowires. When comparing molybdenum carbide with the initial  $Mo_6S_2I_8$  nanowires, we observe a decrease in diameter of roughly 30%.

#### 3.2 Direct transformation

Molybdenum carbide nanowires, obtained by direct transformation of Mo<sub>6</sub>S<sub>2</sub>I<sub>8</sub> (MoSI) are shown in Fig. 2. SEM image (a) shows carbide nanowires of lengths up to a hundred microns and diameters ranging from around 10 to 1000 nm. The shapes and sizes of nanowires correspond approximately to the typical dimensions of the starting material. A TEM image (b), however, reveals that carbide nanowires are highly inhomogeneous and composed of a large number of relatively small carbide nanoparticles of different sizes and shapes. We observe that the grainy structure appears almost independently of the gas mixture composition and the typical grain size is found to be between 10 and 20 nm (c and d). These TEM images also show that molybdenum carbide nanowires are covered with a thin layer of carbon. This can be explained by gas-solid interface reactions under largely excessive ethane with a high space velocity, which is somewhat inhomogeneous. Accordingly, higher contents of ethane in the gas mixture resulted in a larger amount of carbon deposited on the surface of molybdenum carbide nanowires (d) when compared to the samples prepared in lower concentrations of ethane (c).



Fig. 2 Molybdenum carbide nanowires obtained by direct transformation of MoSI. SEM (a) and TEM image (b). TEM clearly shows the highly inhomogeneous structure of nanowires, which are composed of individual grains. Larger magnification TEM images (c) and (d) show the grainy structure covered with a thin layer of carbon. Image (c) shows the deposition in the case of low amount of ethane (corresponds to the red line in (e)), while (d) shows a thicker layer of deposited carbon obtained at a larger amount of ethane (corresponds to the green line in (e)). (e) XRD spectra: precursor MoSI (black line), MoC nanowires (green line), brush-like hybrid phase (purple line), MoC + Mo<sub>2</sub>C nanowires (red line), and fully transformed Mo<sub>2</sub>C nanowires (blue line). Green squares: JCPDS no. 00-008-0384, purple diamonds: JCPDS no. 41-1487, red stars: JCPDS no. 00-006-0546, blue circles: JCPDS no. 00-035-0787.

Chemical composition and crystal structure of carbide nanowires were determined by XRD (Fig. 2e). Black line shows the starting  $Mo_6S_2I_8$  material with the peaks in accordance with the hexagonal lattice parameters a = 1.6405 nm and c = 1.1952nm. The second diffractogram (green line) was obtained after the transformation in argon and ethane only (50 cm<sup>3</sup> min<sup>-1</sup> and 5 cm<sup>3</sup> min<sup>-1</sup> flows, respectively) and the spectrum shows predominantly hexagonal  $\eta$ -MoC phase (JCPDS card no. 00-008-0384). Purple line was obtained from the sample at a molar ratio of hydrogen to ethane 2 : 1, which will be discussed in detail later on. By increasing the molar ratio of hydrogen to ethane to 7.5 : 1 (15 cm<sup>3</sup> min<sup>-1</sup> and 2 cm<sup>3</sup> min<sup>-1</sup> flows, respectively),

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similar to the optimal values determined by Xiao *et al.*,<sup>31</sup> spectrum of molybdenum carbide nanowires (red line) clearly shows that the material is a mixture of two phases: predominantly  $Mo_2C$  (JCPDS card no. 00-035-0787) but also MoC (JCPDS card no. 00-006-0546). Further increase of hydrogen to ethane molar ratio results in an increase of  $Mo_2C$  phase relative to the MoC phase, suggesting that the described approach enables production of nanowires with different ratios of carbide phases simply by changing the gas flow composition. If the MoC and  $Mo_2C$  phase mixture is further heated at 710 °C for several hours in a 10% mixture of hydrogen and argon, the whole material transforms into stable and pure  $Mo_2C$  phase (blue line). The resulting material is textile-like comprising nanowires a few hundred microns up to several millimetres long.

#### 3.3 Hybrid phase

When molar ratio of hydrogen and ethane in the gas flow was 2:1, XRD spectrum of the transformed material (Fig. 2e, purple line) looks notably different from the ones we obtain at other molar concentrations. Beside the characteristic peaks of MoC (JCPDS card no. 00-006-0546) and  $\eta$ -MoC (JCPDS card no. 00-008-0384) phases, an additional broad peak appears in the range between 20° and 30° indicating the presence of carbon in the form of graphite (JCPDS card no. 00-041-1487).

The produced dark brown material was further observed with SEM and TEM, as shown in Fig. 3. In contrast to the nanowires obtained at different gas compositions (Fig. 2a), low magnification SEM image of the material reveals a fairly uniform surface coating. Larger magnification, however, shows nanowires covered with much thinner and shorter nanofibres growing radially from the nanowire surface, exhibiting a brushlike topology (Fig. 3a). We identify this material as a novel inorganic/organic hybrid material composed of molybdenum carbide nanowires covered with carbon nanofibres.

TEM image (Fig. 3b) shows a detailed view of the nanofibres. After three hours of growth, the typical nanofibre length is up to around 100 nm with a diameter of around 10–20 nanometres. At the tips of nanofibres, we observe molybdenum carbide nanoparticles, typically up to 15 nanometres in size without a specific shape (Fig. 3b inset). TEM images show that the nanofibres are composed of randomly distributed graphite layers, consistent with XRD observations of carbon. We find that these carbon nanofibres are tightly bound to the nanowire surface as, except for the fibre tips, they remained firmly attached to the nanowires even after prolonged ultrasonic agitation in isopropyl alcohol.

Based on the experimental observations, we propose the following mechanism for the formation of carbon nanofibres. First the fast decomposition and reduction of the topmost layers of  $Mo_6S_2I_8$  nanowires leads to formation of weakly bound active molybdenum nanoparticles. On their surfaces decomposition of ethane occurs, followed by formation of carbon atoms with concomitant desorption of molecular hydrogen (or reaction with sulphur and iodine atoms). Carbon atoms then dissolve into molybdenum nanoparticles and diffuse through them to the other side, where they deposit in the form of graphite.<sup>32,33</sup> The nanofibre grows. However, the catalytic



**Fig. 3** SEM (a) and TEM (b) images of molybdenum carbide/carbon hybrid phase show its brush-like structure. Inset: a molybdenum carbide nanoparticle is found at the tip of each carbon nanofibre.

molybdenum particles gradually convert to a stable molybdenum carbide, which stops the nanofibre growth, similar as was observed with cobalt.<sup>34</sup> Finally, the inner Mo<sub>6</sub>S<sub>2</sub>I<sub>8</sub> phase decomposes into molybdenum carbide nanoparticles fused in the shape of nanowires.

Formation of nanofibres seems to be very sensitive to the reaction conditions and it is not surprising that in the majority of our experiments only molybdenum carbide nanowires with surface deposited carbon were obtained. First, only specific gas composition and reaction temperature result in formation of molybdenum particles on the nanowire surface that act as catalysts for nanofibre growth. Secondly, a crucial parameter for the fibre growth is the molybdenum nanoparticle size. If the particles are too small, they react and transform into molybdenum carbide, which inhibits graphite nucleation. On the other hand, large particles can not be lifted from the surface due to enhanced metal–nanowire interaction.

#### 3.4 Transformation via molybdenum nanowires

The second approach to molybdenum carbide synthesis was a two-step method in which  $Mo_6S_2I_8$  nanowires were first transformed into molybdenum nanowires by reduction in argon/hydrogen mixture and later into molybdenum carbide as described above. Typical XRD spectra of the initial,

intermediate and final products are shown in Fig. 4. MoSI nanowires (black line) were transformed into molybdenum nanowires (green line), which show two distinctive peaks at  $40.5^{\circ}$  and  $58.6^{\circ}$  (JCPDS card no. 00-042-1120). The absence of other peaks demonstrates that the nanowires are almost pure molybdenum. In the next step, molybdenum nanowires were transformed into molybdenum carbide nanowires by heating in flow of gas mixtures containing hydrogen and ethane. At a molar ratio of 7.5 : 1 between hydrogen and ethane (flows 15 cm<sup>3</sup> min<sup>-1</sup> and 2 cm<sup>3</sup> min<sup>-1</sup>, respectively), molybdenum nanowires were transformed into molybdenum carbide nanowires (orange line). Again the nanowires are composed of two phases: the main phase is hexagonal MoC phase (JCPDS card no. 00-006-0546) with Mo<sub>2</sub>C phase (JCPDS card no. 00-035-0787) as a by-product. The absolute intensity of the (101) peak at  $39.4^{\circ}$ in comparison to the pure Mo<sub>2</sub>C phase suggests that the amount of Mo<sub>2</sub>C in MoC is around 5-10 wt%.

Increasing the reaction time or increasing the ethane flow to  $5 \text{ cm}^3 \text{ min}^{-1}$  at the hydrogen flow of  $10 \text{ cm}^3 \text{ min}^{-1}$  resulted in partial surface carbon deposition. However, no nanofibres were observed as in the case of direct transformation. This confirms the proposed fibre formation mechanism by catalytic vapour deposition growth and is consistent with the literature.<sup>32,35</sup>

The nanowires comprising MoC and Mo<sub>2</sub>C phases can be further transformed into pure Mo<sub>2</sub>C phase by reduction in flow of hydrogen/argon mixture for three hours at 710 °C. Similar as in the case of direct transformation, the resulting material is textile-like on the large scale but shows grainy structure on the nanoscale. The nanograins have a very similar size distribution as in the case of direct transformation, however, the interparticle separation seems to be smaller. This can be explained by depletion of amorphous carbon layer, especially within the nanowires.

The average size of molybdenum carbide crystallites forming the nanowires was also quantitatively evaluated. We calculated the size from XRD peak-width using the Scherrer equation  $d = 0.9\lambda/(B \cos \Theta)$  with shape factor 0.9. Parameter d is the mean diameter of crystal particles, B is the diffraction line broadening (peak width) measured at half its maximum intensity (in radians),  $\Theta$  is the angle of diffraction, and  $\lambda$  is the incident radiation wavelength (1.54 Å). The peak width was taken for the most intense peak at 39.4° (101). The average crystallite size was estimated to be 20.2 nm for directly transformed samples and 15.4 nm for Mo<sub>2</sub>C obtained *via* Mo nanowires. The values are in a very good agreement with TEM observations.

#### 3.5 Raman spectroscopy

To further analyse the carburisation process and to obtain some information on the crystalline order of carbon, including the degree of long-range order and bonding topology, we performed Raman microprobe spectroscopy. In contrast to carbon deposits, pure Mo, MoC and Mo<sub>2</sub>C do not produce a Raman shift. Fig. 5 shows normalised Raman spectra of four different materials that were obtained under different reaction conditions: (a) the combined MoC and Mo<sub>2</sub>C phase, obtained by direct transformation of MoSI nanowires at a molar ratio of hydrogen to ethane of 7.5 : 1 (red line); (b) the hybrid phase with carbon nanofibres, obtained by direct transformation of MoSI nanowires at a molar ratio of hydrogen to ethane 2 : 1 (purple line), (c) MoC phase, heated in ethane and argon flow, without hydrogen (green line), and (d) the combined MoC and Mo<sub>2</sub>C phase, obtained via molybdenum nanowires (orange). All of these materials show two distinct peaks at around 1600 cm<sup>-1</sup> and 1355 cm<sup>-1</sup>, which confirm the presence of deposited carbon in all four samples.36,37 The so-called G band, corresponding to 1600 cm<sup>-1</sup>, is associated with an E<sub>2g</sub> mode of graphite and ascribed to the vibration of sp<sup>2</sup>-bonded carbon atoms in a two-dimensional hexagonal lattice.38 The D band, peaking at around 1355 cm<sup>-1</sup>, shows presence of disordered



**Fig. 4** Transformation of MoSI into Mo<sub>2</sub>C *via* molybdenum nanowires. XRD spectra of precursor MoSI nanowires (black line), molybdenum nanowires (green line), transformed nanowires comprising MoC and Mo<sub>2</sub>C phases (orange line), and fully transformed Mo<sub>2</sub>C nanowires (blue line). Green squares: JCPDS no. 00-042-1120, orange stars: JCPDS no. 00-006-0546, blue circles: JCPDS no. 00-035-0787.



Fig. 5 Raman spectra of different molybdenum carbon nanowires. Nanowires obtained directly at a ratio of hydrogen : ethane 7.5 : 1 (red line), hybrid material with carbon nanofibres (purple line), MoC nanowires obtained directly without hydrogen (green line), and combined MoC and Mo<sub>2</sub>C nanowires obtained *via* molybdenum nanowires (orange line).

graphite phase or glassy carbon. By measuring the relative intensity ratio  $I_D/I_G$ , we can determine the degree of graphitic order. We find that the  $I_D/I_G$  ratio of carbon structures deposited onto molybdenum carbide nanowires depends on the carburisation conditions: the ratio is the smallest – and the degree of graphitisation the highest – for the nanofibrous samples (b, purple) with  $I_D/I_G = 0.92$ , followed by samples (c, green) with a value of 0.98. Significantly higher ratio  $I_D/I_G$  of 1.3 and 1.31 have samples (a, red) and (d, orange) obtained by heating of MoSI or Mo nanowires, respectively, in mixtures with lower contents of ethane. The increase in  $I_D/I_G$  indicates the presence of significantly larger amounts of disordered carbon or other structural imperfections.

#### 3.6 Transparent electrodes

The synthesised molybdenum carbide nanowires were tested for their optical and electrical properties to determine their suitability for applications, such as transparent electrodes. Nanowire networks as large as several square centimetres were prepared as described in Section 2.1.4 and Fig. 6a shows a typical SEM image of such a  $Mo_2C$  network. We observe no significant difference between the networks prepared directly from  $Mo_6S_2I_8$  and the ones prepared *via* Mo nanowires.

Optical transmittance of the directly synthesised  $Mo_2C$  nanowire network was measured in the range from 200 nm to 900 nm. First the transmittance of sprayed  $Mo_6S_2I_8$  nanowires was recorded and is shown in Fig. 6b (black line). The



**Fig. 6** Mo<sub>2</sub>C networks as transparent electrodes. (a) SEM image of Mo<sub>2</sub>C network obtained by direct transformation of Mo<sub>6</sub>S<sub>2</sub>I<sub>8</sub>. (b) Transmittance of Mo<sub>2</sub>C network (blue line) compared to the transmittance of starting Mo<sub>6</sub>S<sub>2</sub>I<sub>8</sub> material (black line). (c) Sheet resistance of Mo<sub>2</sub>C *versus* temperature (blue dots) and the best fit of logarithmic function describing bad metal (red line).

transmittance was found to be between 88% and 90% for all wavelengths (88.8% at 550 nm) with two characteristic peaks around 420 and 650 nm. Carburisation of nanowires leads to formation of Mo<sub>2</sub>C network and, as shown in Fig. 6b with blue line, disappearance of the two characteristic peaks. Transmittance increases significantly in the whole range of wavelengths so that the obtained transmittance for visible light (550 nm) was found to be around 94%, which is comparable or even better than the materials that are already widely used in opto-electronic devices.<sup>39</sup> The difference is even more significant in the UV range, where transmittance increases with decreasing wavelength and reaches over 95% at 200 nm, making the Mo<sub>2</sub>C electrodes very suitable for applications where UV transparency is required, such as UV light emitting diodes.

We also measured sheet resistance of Mo<sub>2</sub>C networks on a quartz substrate as a function of temperature from room temperature down to 30 K (Fig. 6c). The measured resistance at room temperature was around 1050  $\Omega$  sq<sup>-1</sup> and increased to about 1250  $\Omega$  sq<sup>-1</sup> at 30 K. The observed increase in the resistance can be attributed to the interaction effects and localisation of electrons, which is a common effect in layered systems and could also be referred to as bad metal.<sup>40</sup> Taking into account logarithmic corrections to resistivity that have been observed and calculated for two-dimensional systems,<sup>41</sup> and fitting the proposed logarithmic function  $R = R_0(1 - s \ln(T/T_0))$ , we obtain  $R_0 = 889 \Omega$ , s = 0.11 and  $T_0 = 1900$  K. The value of *s* is similar to the ones obtained for other two-dimensional samples,<sup>39</sup> and the resistance and temperature constants yield reasonable values.

The transparent electrodes that we produced were firmly attached to the substrate, making them sufficiently robust for handling. We additionally tested the temporal stability of molybdenum carbide networks. After leaving the samples exposed to air for over two months, we observe no change in the transmittance and resistance values of the transparent electrodes.

### 4. Conclusions

We have developed an efficient and scalable method for fabrication of molybdenum carbide nanowires and nanowire networks. Depending on the synthesis route, different MoC and Mo<sub>2</sub>C phases were obtained, including a hybrid inorganic/ organic nanomaterial composed of molybdenum carbide nanowires covered with carbon nanofibres. We find that the overall morphology of the synthesised molybdenum carbide nanowires corresponds to the morphology of initial Mo<sub>6</sub>S<sub>2</sub>I<sub>8</sub> nanowire bundles. This method is also applicable for fabrication of Mo<sub>2</sub>C nanowire networks on quartz substrate with transparency of 94% in the visible - and even higher in the UVregion – and sheet resistance around 1050  $\Omega$  sq<sup>-1</sup>. In contrast to many other metal nanowires, including silver and copper, we find that these nanowires show significantly higher resistance to oxidation as their properties do not change even upon several-months long exposure to the air. Combining the high optical transparency with fairly low electrical sheet resistance and a very good temporal stability and robustness, we

demonstrated that the  $Mo_2C$  networks are suitable for use in optoelectronic devices.

### Acknowledgements

The authors acknowledge the financial support from the Slovenian Research Agency (research core funding No. P1-0040, P1-0192, and P2-0091) and the Center of Excellence in Nanoscience and Nanotechnology. We also thank Daniele Vella for Raman spectroscopy.

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