PRODUCTION AND CHARACTERIZATION OF $MoSe_2$ NANOTUBES BY ELECTRON IRRADIATION

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ABSRACT

In this work, we report the production of $MoSe_2$ (molybdenum diselenide) nanotubes formed by irradiating the samples with high doses of electron irradiation. The irradiation was performed on a 2 MeV Van de Graff accelerator at the following conditions: voltage 1.3 MeV, current 5 μA current, dose rate 25 Kgy/min, and total dosage 1 Mgy. We observed well-defined nanotubes of several nm long and few nm wide, which suppose to be hollow and capped at one end. As the level of irradiation was increased to 1 Mgy, elongated onion-like structures were observed.

Key Words: Electron irradiation; Nanotubes; Onion-like structures

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INTRODUCTION

Carbon nanotubes were discovered by Iijima[1] in 1991, which prompted numerous studies because of their superior mechanical properties[2] and unique electronic behavior.[3]

For example, nanotubes are expected to have a high strength-to-weight ratio[4] which is advantageous in advanced composites to be used in high performance materials such as aircraft frames. The small dimensions of the tubes shows promise for use as gas adsorption medium,[5,6] a field emitter for use in flat-panel display,[7] nanoscale electronic devices,[8] and lately they have been used as microscope probes.[9]

A significant brake through was made by Tenne and co-workers[10,15] who succeeded in constructing related MX_2 cages (M = Mo and W; X = S, Se, Te). This work has opened an exciting new area of research into sheet materials, which, unlike single-layer graphite and double-layer B-C-N, are multi-layer structures.

In 1992, Ugarte[16] reported that electron irradiation of carbon soot produced onion-like structures. Ugarte obtained such structures under a high flux of electrons in a transmission electron microscope (TEM).

The graphite structure is also showed by metal dichalcogenides, represented by MX_2 (M = Mo, W, Nb, etc., whilst X = S, Se, Te, etc.). In our case $MoSe_2$, which its layered structure is depicted in Fig. 1. Still all the members of these family might present similar behavior and possible formation of nanotubes and onion-like structures, only MoS_2 and WS_2 compounds and few variation of them,

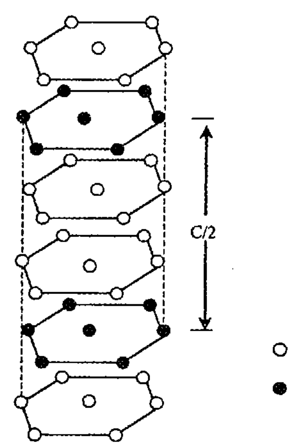

Figure 1. Layered structure of $MoSe_2$. Open circles represent Se atoms while closed circles represent Mo atoms respectively.

have been extensively synthesized up to now. Lately, Galván et el. reported nanotube formation on $MoTe_2$,[11] WSe_2[12] and $NbSe_2$.[13]

EXPERIMENTAL METHOD

In this work we report the formation of nanotube structures in $MoSe_2$ (molybdenum selenide) also known as Drysdallite. The initial samples were obtained from commercial powders (Alfa-Aesar 99.9% pure) of $MoSe_2$. Afterwards, the material was irradiated with electrons on a 2 MeV Van de Graff accelerator (High Voltage Engineering Corporation). The irradiation conditions were the following: 1.3 MeV voltage, 5 μA current, dose rate 25 Kgy/min, total dosage 1 Mgy. The dosimeter used was radiochromic films (FWT-60) from Far West Technology. X-ray analyses were performed in a Philips XRD/X'PERT system using Cu Kα radiation at 40 KV voltage and 45 mA current. For Transmission Electron Microscopy (TEM) observations, samples were ground in an agate mortar and placed on carbon coated copper grids. The microscope used was a JEOL JEM-2010 with a point to point resolution better than 0.19 nm.

RESULTS AND DISCUSSION

The layered structure for $MoSe_2$ is depicted in Fig. 1. The repeated motif in $MoSe_2$ is made of a sandwich composed by three layers of Se-Mo-Se with covalent bonds between the atoms of each plane and weak Van der Waals bonds holding adjacent selenium sheets together.

The lattice parameters for 2H-$MoSe_2$ are $a = 3.2870$ A, $c = 12.925$ A, space group $P6_3/mmc$ (194).[5] Figure 2 depicts an x-ray diffractogram for the irradiated (top figure), as well as for the non-irradiated samples (lower figure). The typical diffraction peaks for 2H-$MoSe_2$ had been identified for the non irradiated as well as for the 1 Mgy irradiation sample and compared with the XRD-Data file card No. 29-0914.

Notice that there are not major changes between both samples. Indicating that the irradiated sample, at least for 1 Mgy dosage, produce no change. The important fact here is to point out that irradiation, at this level, has produced neither broadening nor amplitude change on the cell dimensions. This could be corroborated with the existence of nanotubes, due that these tubules are extremely small, in the nm range.

A transmission electron micrograph of a big area where nanotubes and onion-like structures coexist is shown in Fig. 3. In the center of the micrograph, indicated with small arrowheads, onion-like structure had been identified.

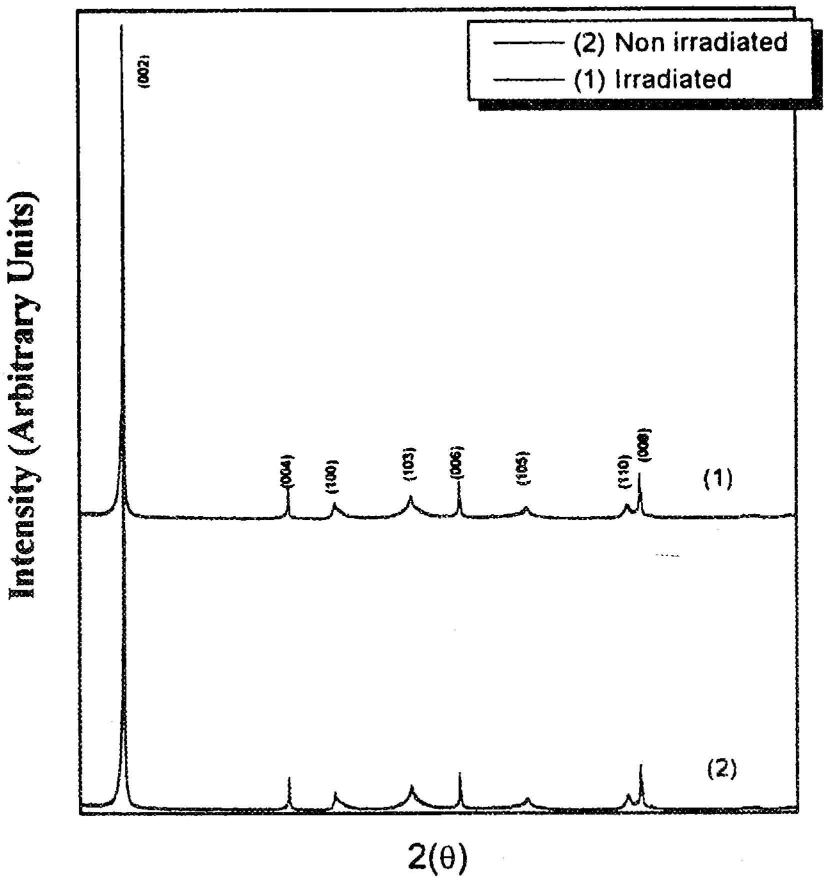

Figure 2. X-ray diffractograms of the non-irradiated and 1 Mgy irradiated $MoSe_2$ samples. The characteristic $MoSe_2$ reflections had been indicated.

Furthermore, on the left side of the micrograph, indicated with big arrowheads, open nanotubes had been located. We claim that these nanotubes are open using different color contrast. For the center of the nanotube, which suppose to be open, a gray color is recognized, while a dark gray color forms the walls of the tube.

A piece of a huge nanotube produced by irradiation has been identified in Fig. 4. The distance in between planes has been indicated by an arrow head, which corresponds to the characteristic spacing of the reflecting planes of $MoSe_2$ structure (according to JCPDS x-ray diffraction card No. 29-0914[14]) in the [0 0 2] orientation. The spacing between fringes is 0.6240 nm, which agrees with the distance between two neighboring layers $c/2$ (0.646 nm) provided by x-ray

Figure 3. Electron micrograph showing the formation of tubular and onion-like structures. Small arrowheads indicates onion-like structures, while big arrowheads indicate tubular hollow nanotubes.

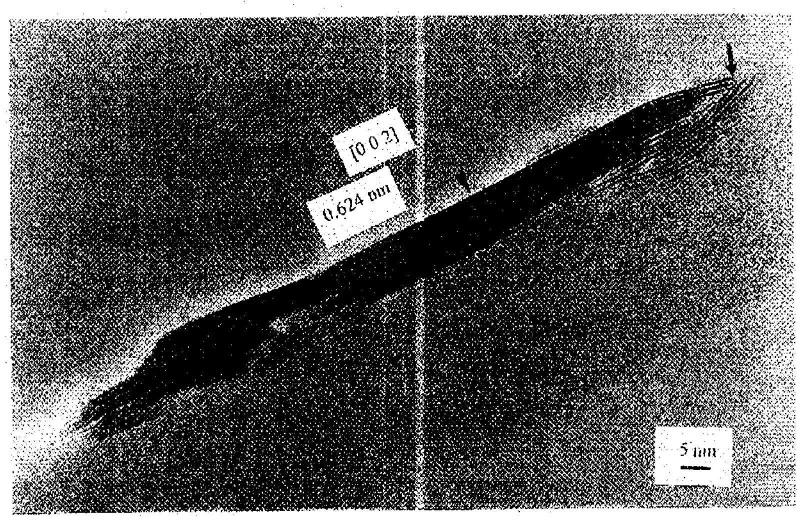

Figure 4. Electron micrograph of a $MoSe_2$ crystallite. Arrowhead indicates inter planar separation, while full arrow shows that this specific tube is capped at one end.

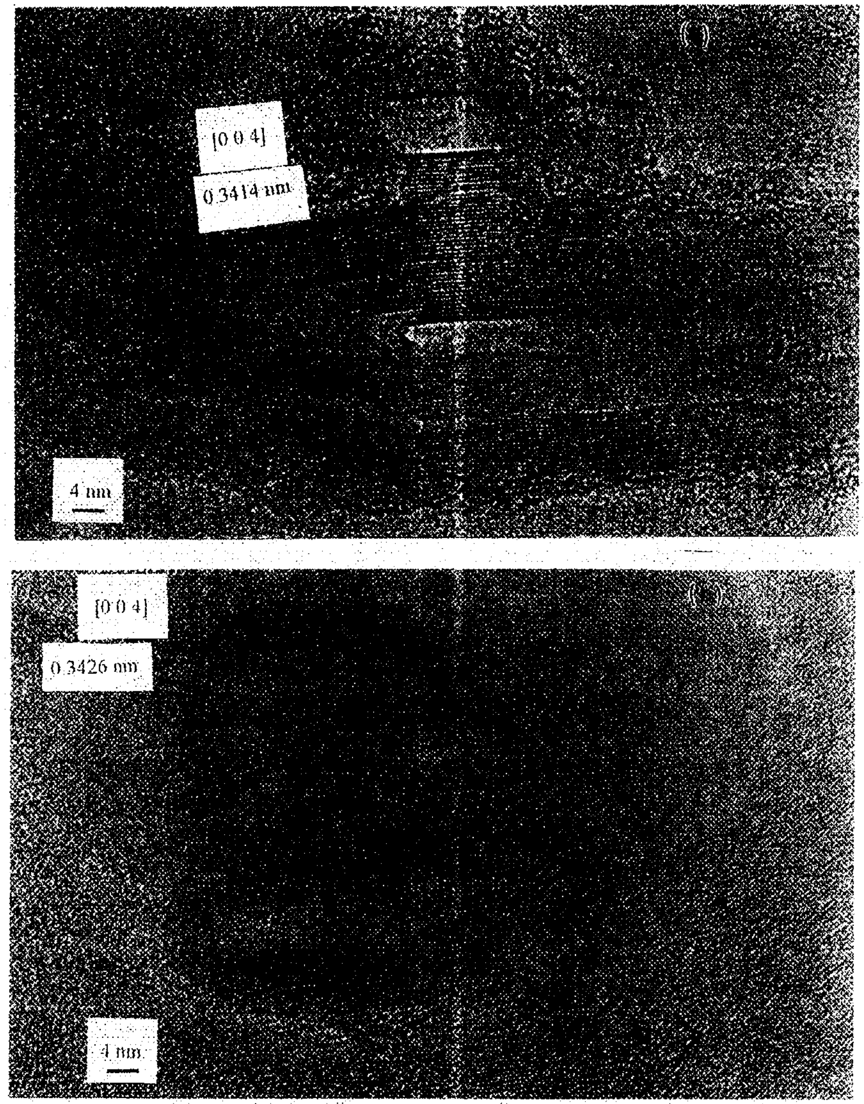

Figure 5. Parts (a) and (b) depict electron micrographs of elongated onion-like structures. Inter arrowheads indicate planar separations.

data file card No. 29-0914. Also, on the lower right corner of the figure, and indicated with a medium size arrow, the walls of the tube bends, indicating that the nanotube is capped in one end.

Transmission electron micrographs of typical polyhedral forms are indicated in Figs. 5(a) and (b), similar forms had been reported by Tenne et al.[15] in WS_2. Fig. 5(a) depicts two elongated onion-like structures; the one at the top of the micrograph is indicated by the head of an arrow, while the one shown at the center of the micrograph resembles more to a tube like structure. Note that the inter planar distance is indicated by an arrowheads, corresponding to the [0 0 4] orientation.

Another area of the irradiated sample, showing elongated onion-like structures, as mentioned before in Fig. 5(a), is depicted in Fig. 5(b). For so much, inter planar distance is indicated by arrowheads, which corresponds to the [0 0 4] orientation. It is good to note, that these structures appear to be closed in three dimensions as Tenne et al.[15] showed in WS_2, due to the fact that tilting the specimen in the electron microscope causes their lattice images to remain the same.

Searching very carefully through other areas of the sample, we located onion-like structures, as depicted in Fig. 6, indicated by capital letter A and shown with arrowheads. As in the case of carbon, structures tend to be more

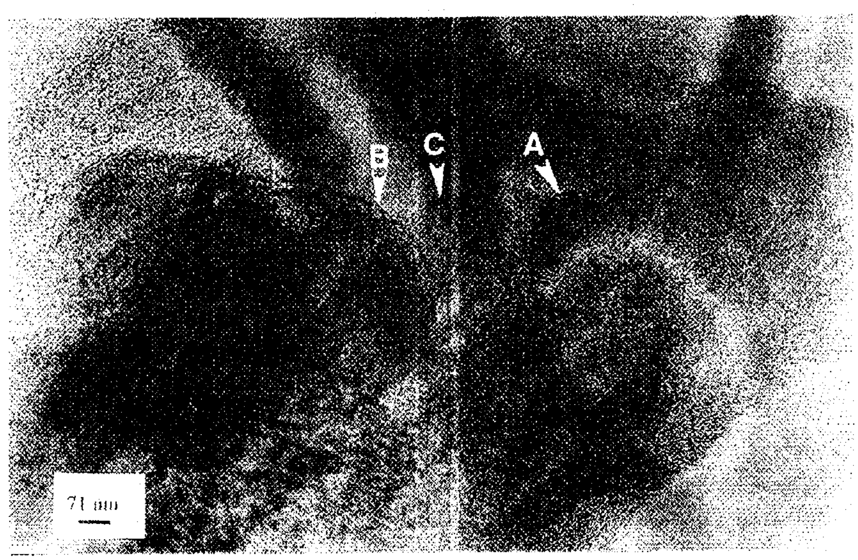

Figure 6. Depicts an electron micrograph of an area where onion-like structures A, and tubular $MoSe_2$, B and C are indicated.

rounded in shape. In the same Fig. 6, another tube-like structures are indicated by capital letters B and C. A tube-like structure capped at one end and presumably to be hollow at the center of the tube is indicated by C.

Notice that there is evidence of the layers that form the tubular structure bends at the specific end. On the other hand, in the same Fig. 6, indicated by B, a bigger tubular structure is indicated.

Recently, curling and closure of graphitic structures has been observed under electron beam irradiation.[16] The same type of curling was also observed in MoS_2,[17,18] WS_2[19,20] and WSe_2[20] samples.

CONCLUSIONS

To our knowledge, this is the first time that it has been shown the production of nanotubes of different sizes, onion-like structures of $MoSe_2$ by electron irradiation. Although, our production method lacks of uniform distribution of these structures through out the matrix, the production method is not as expensive as other reported methods of production.

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