jz-2024-00193j.R1

Name: Peer Review Information for "Processing and Functionalization of Vertical Graphene Nanowalls by Pulsed Laser Irradiation"

First Round of Reviewer Comments

Reviewer: 1

Comments to the Author

This manuscript reports novel and effective approach for modification and functionalization of vertical graphene carbon nanowalls by UV (248 nm) ns-pulsed laser irradiation. The major advance of this manuscript is related with demonstrated usefulness of approach in increasing quality of the carbon layers and possibility to construct hybrid structures by laser-induced synthesis of MoO2 nanoparticles. Such functionalization of vertical graphene nanowalls might be useful in nanoelectronics, energy storage devices, catalysis systems, and construction of sensors. Less attention was paid for providing physical insights into the mechanisms of studied processes. The major drawback of this work is in the absence of required statistical analysis of the data. I recommend publication in The Journal of Physical Chemistry Letters after major revision considering the several points provided below:

1) The structure of vertical graphene nanowalls is somewhat irregular and difference in intensity ratio of G and D bands as well as other spectral parameters may differ at various places of the same sample as well as for the different samples. Please provide Raman spectra (Figure 2a) and other correlations (Figure 2b-g) with standard deviation data.

2) In this work MoO2 nanoparticles instead of Mo were formed during the laser-induced treatment of Mo film on vertical graphene nanowalls. However, in many places authors state that Mo nanoparticles were produced. Please correct this matter.

3) Please provide discussion on the possible mechanism of laser-induced formation of MoO2.

Reviewer: 2

Comments to the Author

1. In the SEM and EDS micrographs it is not possible to observe the scale values in figures 1 and 3. I recommend using an image editor to write the scale value in a visible and easy to locate area.

2. In figures 3e and 3f,g, it is possible to increase the size by occupying the white area in figure 3e, to highlight the results after laser irradiation with high and low doses.

3. Figure 3i requires the label "50 nm Mo" to correctly identify the graph.

4. In line 59, the XRD results indicate the presence of MnO_2 after laser irradiation of the sample with 50 nm Mo /VGNW. It is not clear why Mo was oxidised if the sample was in an Argon gas controlled environment. Also, the word nanoparticles was used in this section, but the sizes are between 100 and 500 nm, and throughout the article they were only referred to as particles.

Why is formed the MoO_2?, and Do you have oxygen EDS signal that can be included and confirm the presence of oxygen?

Author's Response to Peer Review Comments:

Dear Editor,

Thank you for handling our submission and providing us with the technical comments and reviewer's comments. We deeply believe that the overall quality of the manuscript has improved upon the proposed revision and that it meets the standards for publication in its current form.

We provide detailed responses to all inquiries below.

Kind regards,

Dr. Stefanos Chaitoglou

1. **Please include annotated version(s) of your revised publication file(s) with colored text or highlights indicating the revisions that you have made, and upload them as "Supporting Information for Review Only." Please also upload "clean" copies for publication. (No highlighting, annotations, or colored text permitted.)**

We have uploaded both annotated and clean versions.

2. **Title: Please remove dot from title in both the main manuscript file and the Supporting Information.**

We have removed the dot from the title.

3. **Title: In both the main manuscript file and the Supporting Information, set the title in title case, with the first letter of each principal word capitalized.**

We have set the title in title case.

4. **Abstract: Shorten the abstract to 150 words or fewer.**

Abstract is shortened to 150 words.

5. **TOC Graphic: Please resize the TOC graphic per journal guidelines (2 in x 2 in).**

TOC graphic has been resized to 2 in x 2 in.

6. **References: In both the main file and the supporting information, fix the style of all references to use JPCL formatting (check all references carefully). ***JPC Letters reference formatting requires that journal references should contain: () around numbers; author names; article title (titles entirely in title case or entirely in lower case); abbreviated journal title (italicized); year (bolded); volume (italicized); and pages (first-last). Book references should contain author names; book title (in the same pattern); publisher; city; and year. Websites must include date of access.**

References have been fixed in style to follow the guidelines.

7. **Supporting Information: Please number SI pages in the following format: "S1, S2…"**

SI pages have been numbered accordingly.

Reviewer 1

This manuscript reports novel and effective approach for modification and functionalization of vertical graphene carbon nanowalls by UV (248 nm) ns-pulsed laser irradiation. The major advance of this manuscript is related with demonstrated usefulness of approach in increasing quality of the carbon layers and possibility to construct hybrid structures by laser-induced synthesis of MoO2 nanoparticles. Such functionalization of vertical graphene nanowalls might be useful in nanoelectronics, energy storage devices, catalysis systems, and construction of sensors. Less attention was paid for providing physical insights into the mechanisms of studied processes. The major drawback of this work is in the

absence of required statistical analysis of the data. I recommend publication in The Journal of Physical Chemistry Letters after major revision considering the several points provided below:

We thank the reviewer for evaluating our work and for providing very useful insights. We include the detailed responses in his/her inquiries below.

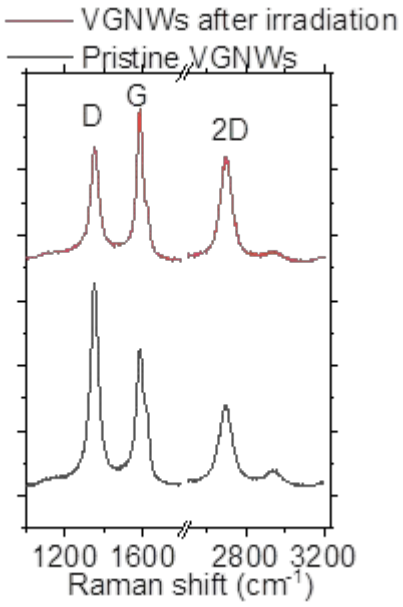
1) The structure of vertical graphene nanowalls is somewhat irregular and difference in intensity ratio of G and D bands as well as other spectral parameters may differ at various places of the same sample as well as for the different samples. Please provide Raman spectra (Figure 2a) and other correlations (Figure 2b-g) with standard deviation data.

We acknowledge the validity in reviewer's comment regarding the relative irregularity of the graphene nanowalls. We consider two kinds of irregularities, one in macroscopic level and one in microscopic.

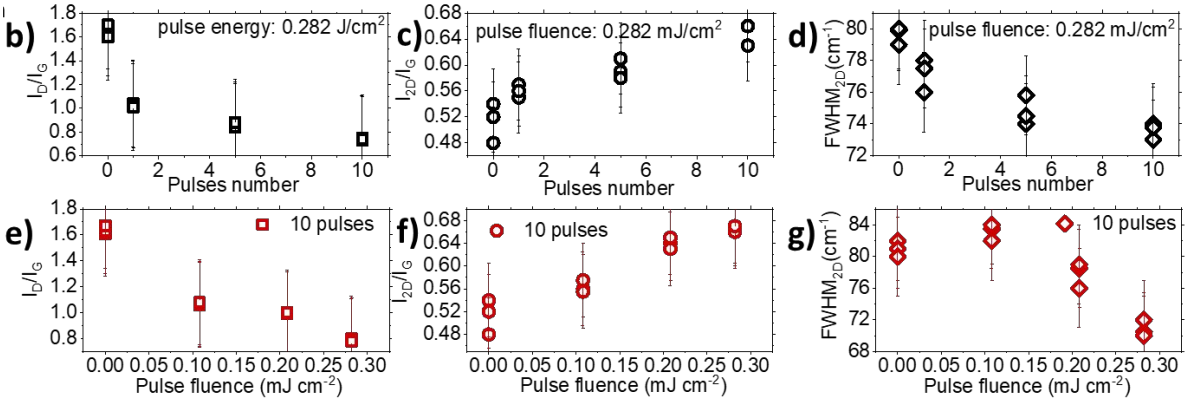
Regarding the first, when we investigate chemical vapor deposition processes, nucleation and growth are highly governed by gas precursor kinetics. Thus, it is common to observe irregularities in 2D materials grown in the centre and near to the substrate edges, where gas flow velocity and adsorption varies. In order to collect as much possible representative data of the material deposited in the centre of the substrate, we ensured that all Raman spectra, SEM images and EDS data were collected from the central area and always at least 100 μm away from the substrate edges. The following phrase has been added in the experimental section, provided in supplementary material, to underline the information regarding data collection.

Page S3; '' All data related to Raman spectroscopy and SEM are acquired my measurements performed in the central area of the substrate and always at least 100 μm away from the substrate edges, to exclude inhomogeneities originating form variations in gas flow velocities. ''

Fig. 2a has been revised to be clearer. Both Raman spectra of pristine and irradiated VGNWs are provided. The revised figure is attached below.



With respect to microscopic irregularities, these have their origin in the intrinsic nucleation and growth mechanism of the VGNWs. Regarding Raman characterization, the laser beam has a diameter in the order of 1 micrometer, which is larger than the length of individual VGNWs. Thus, in each Raman measurement more than 1 VGNWs contributes to the Raman signal. For these irregularities it is essential to include the standard deviation error bars in figures where Raman analysis is exhibited, which we have done. Thus, Fig. 2b-g have been revised to include the standard deviation. The revised figures are attached below.



2) In this work MoO2 nanoparticles instead of Mo were formed during the laser-induced treatment of Mo film on vertical graphene nanowalls. However, in many places authors state that Mo nanoparticles were produced. Please correct this matter.

We have taken into consideration this accurate observation. We have rephrased in all necessary parts of the manuscript to ensure that the term ‘’formed’’ (or ‘’formation’’) is used when describing the process for obtaining the Mo nanoparticles, thus we ensure to avoid any confusion that may arise by using other terms, like ‘’production’’.

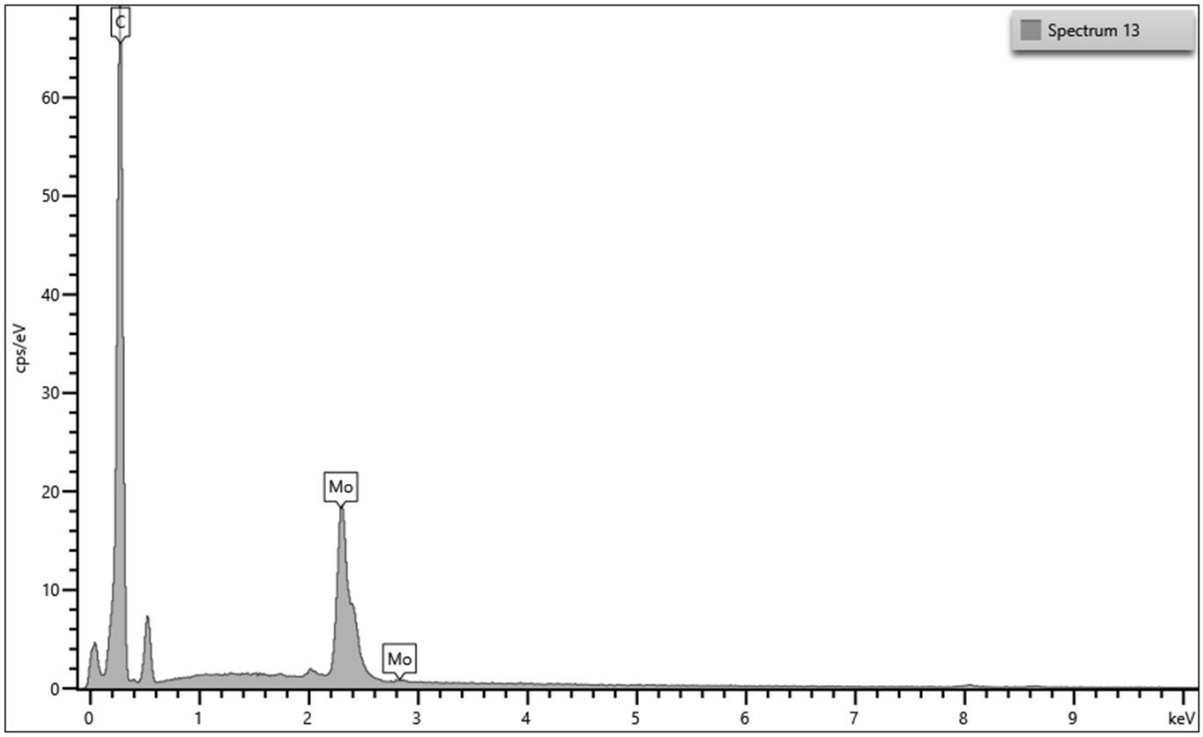
3) Please provide discussion on the possible mechanism of laser-induced formation of MoO2.

Regarding the formation of Mo oxide, we argue that oxygen species bonded in the VGNWs migrate towards Mo and result in its oxidation, due to surface heating induced by the laser irradiation. XPS characterization of the pristine VGNWs has been used before to verify the presence of oxygen, which is possibly adsorbed on defective sites of the nanostructure. See our previous publication:

10.1016/j.apsusc.2022.153327

Moreover, eds characterization of the laser-irradiated samples reveal the presence of both Mo and O, see the attached spectra below.

Supplementary figure 2: EDS spectra of the Mo particles deposited on the VGNWs nanostructure.



We have added the above figure as a new supplementary figure 2. The following text has been added to explain in detail the mechanism of Mo oxidation during the laser irradiation step.

‘’ We argue that the formation of the Mo oxide phase occurs due to migration and reaction with oxygen species that are loosely bonded, or physisorbed, on defective sites of the VGNWs, as has been confirmed by x-ray photoemission spectroscopy in previous studies (23). Surface heating due to laser irradiation induces the migration and metal oxidation. EDS characterization reveals the presence of C, O and Mo on the resulting irradiated nanostructures (Suppl. Fig. 2).’’

Reviewer 2

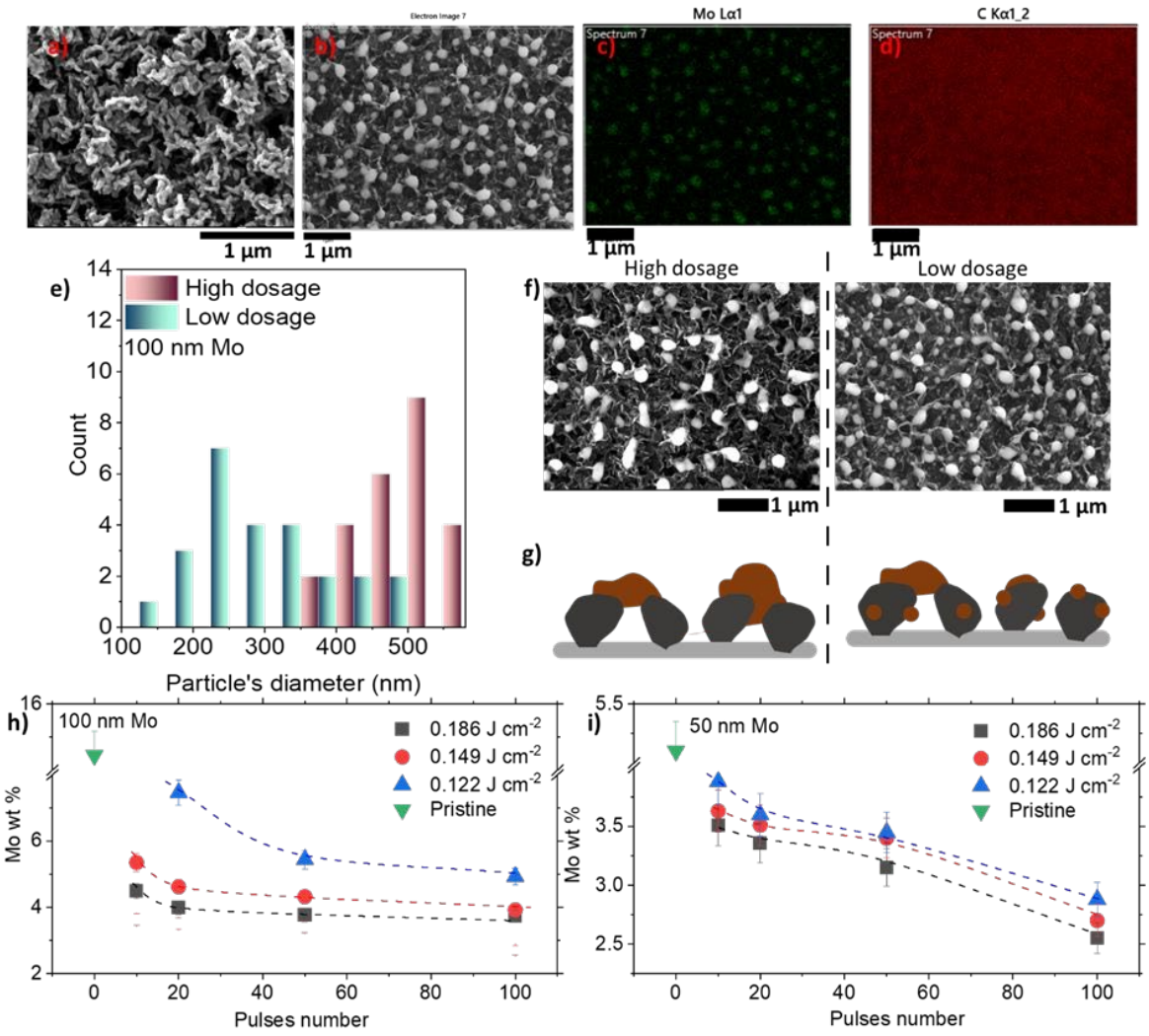
We thank the reviewer for evaluating our work and for providing very useful insights. We include the detailed responses in his/her inquiries below.

1. **In the SEM and EDS micrographs it is not possible to observe the scale values in figures 1 and 3. I recommend using an image editor to write the scale value in a visible and easy to locate area.**

We have edited the images to ensure that scale bars and values are visible.

2. **In figures 3e and 3f,g, it is possible to increase the size by occupying the white area in figure 3e, to highlight the results after laser irradiation with high and low doses.**

We have adjusted the size of Fig. 3 e and g to fill white area and highlight the presented results. The edited Fig. 3 is presented below.



3. Figure 3i requires the label "50 nm Mo" to correctly identify the graph.

We have added the missing legend in Fig. 3i

4. In line 59, the XRD results indicate the presence of MnO2 after laser irradiation of the sample with 50 nm Mo /VGNW. It is not clear why Mo was oxidised if the sample was in an Argon gas controlled environment. Also, the word nanoparticles was used in this section, but the sizes are between 100 and 500 nm, and throughout the article they were only referred to as particles.

Why is formed the MoO2?, and Do you have oxygen EDS signal that can be included and confirm the presence of oxygen?

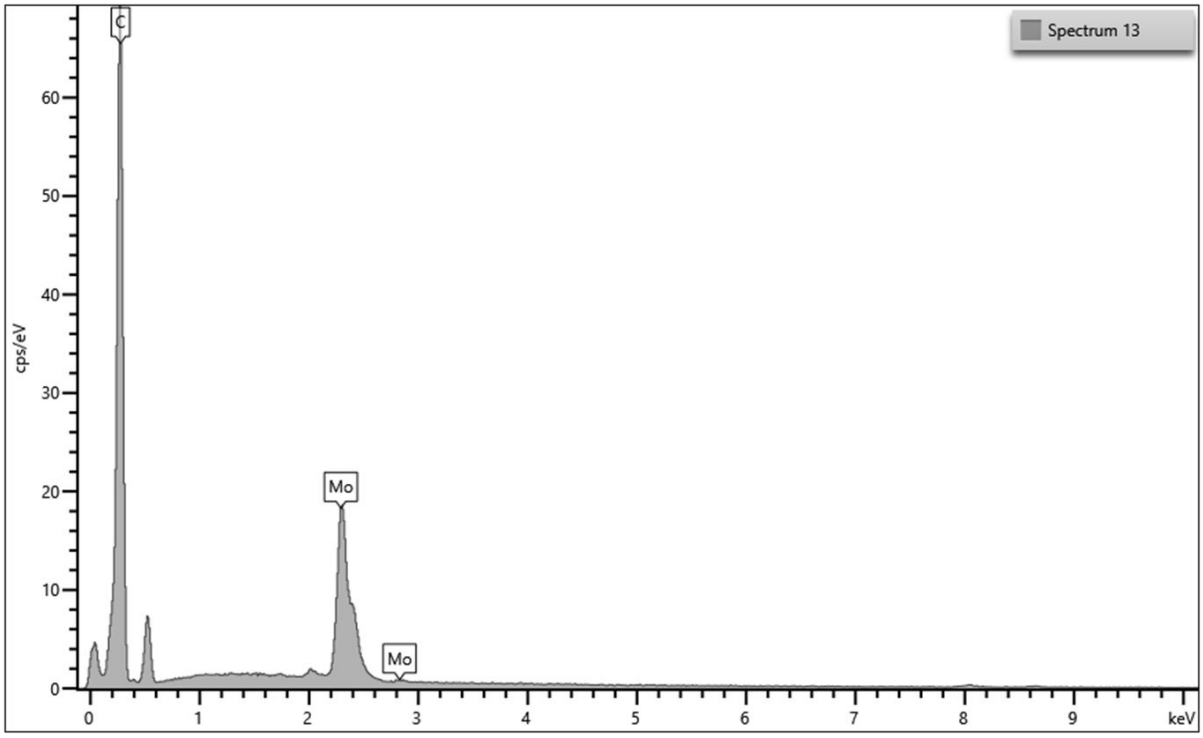
We have edited the term nanoparticles and use the term particles in the respected section.

Regarding the formation of Mo oxide, we argue that oxygen species bonded in the VGNWs migrate towards Mo and result in its oxidation, due to surface heating induced by the laser irradiation. XPS characterization of the pristine VGNWs has been used before to verify the presence of oxygen, which is possibly adsorbed on defective sites of the nanostructure. See our previous publication:

10.1016/j.apsusc.2022.153327

Moreover, eds characterization of the laser-irradiated samples reveal the presence of both Mo and O, see the attached spectra below.

Supplementary figure 2: EDS spectra of the Mo particles deposited on the VGNWs nanostructure.



We have added the above figure as a new supplementary figure 2. The following text has been added to explain in detail the mechanism of Mo oxidation during the laser irradiation step.

‘’ We argue that the formation of the Mo oxide phase occurs due to migration and reaction with oxygen species that are bonded on defective sites of the VGNWs, as has been confirmed by x-ray photoemission spectroscopy in previous studies (23). Surface heating due to laser irradiation induces the migration and reaction steps. EDS characterization reveals the presence of C, O and Mo on the resulting irradiated nanostructures (Suppl. Fig.

2).’’