Answers to the Reviewer’s comments

Thank you for your helpful comments and revision.

Reviewers’ comments:

Reviewer #1: This manuscript describes to fabricate the low crystalline MoO$_3$/carbon composite microspheres by wet synthesis for anodes in lithium-ion batteries. The composite attempt for MoO$_3$/carbon nanoparticle by one-step spray pyrolysis technique is a unique and an available result, and the authors express that MoO$_3$/carbon nanoparticle can obtain optimal electrochemical properties for lithium-ion secondary battery. Moreover, the authors’ original scope for the optimization of the anode active material in this study is explained well about the analytic locations of the effort among the authors’ results. However, the scientific locations for the effort should be clarified more specifically. For above reasons, this paper needs some revisions for the publication standard of this journal at the moment.

Authors would like to thank a reviewer1 for her/his time and comments on our manuscript.

[Q1] Please rewrite scale bars more clearly in the SEM, TEM images of all figures.

[A1] We highly appreciate the reviewer’s positive evaluation of our work and the reviewer’s helpful comments. As the reviewer commented, the scale bars in the SEM, TEM images were showed clearly in the revised manuscript, as shown below.
Figure 1. (a) SEM, (b) TEM, (c) high-resolution TEM images, (d) XRD pattern, and (e) elemental mapping images of MoO$_3$/C composite microspheres.

Figure 4. (a) SEM, (b) TEM, (c) high-resolution TEM images, (d) XRD pattern, and (e) elemental-mapping images of the bare MoO$_3$ powders.
Detailed effect of processing parameters on the property of composites for LIB shall be added, and its mechanism shall be revealed in detail, especially coupled with the author’s own results, to highlight the effect of processing parameters.

Thanks for the reviewer’s helper comment. As the reviewer commented, the processing parameters such as reaction temperature, the flow rate of carrier gas, the ratio between Mo salt and C precursor, and the concentration of spray solution, during spray pyrolysis could effect on the final morphologies, size, and crystallinity of the obtained MoO$_3$/carbon microspheres. Therefore, the optimum process conditions during spray pyrolysis is very important for producing powders for use in anode materials with high Li ion storage property in Li ion batteries. On these viewpoints, the authors considered the relationship between the parameters and a product and controlled the above parameters for synthesizing low crystalline MoO$_3$/carbon composite microspheres, in which MoO$_3$ nanocrystals are distributed homogeneously in the amorphous C matrix, directly by one-step spray pyrolysis. Although the data of the cells assembled with powders obtained with diverse processing parameters during spray pyrolysis were not provided, the electrochemical properties of the MoO$_3$/carbon composite microspheres were compared with the bare MoO$_3$, in this study. However, the authors totally accept the reviewer’s helper suggestion. Additionally, the authors are going to perform experiments to confirm the effect of processing parameters on properties of the MoO$_3$/carbon composite for LIBs, in the near future.

The authors should express the details of MoO$_3$/carbon nanocrystal structure. How about is the interface between MoO$_3$ and amorphous carbon matrix in a composite particle?

Thanks for the reviewer’s helper comment. In this study, low crystalline MoO$_3$/C composite microspheres were prepared by spray pyrolysis for a very short reaction time of 6 seconds. During the process, PVP in a solution was decomposed to amorphous C. Concurrently, the MoO$_3$ nanocrystals with low crystallite size were formed in C matrix by decomposition of Mo salt. In this study, MoO$_3$ nanocrystals have very low crystallite size due to the low reaction temperature and very short reaction time of 6 seconds during the process. Unfortunately, therefore, it was difficult to observe the interface between MoO$_3$ and amorphous carbon matrix in a composite despite performing high-resolution TEM work in Fig. 1c. However, the authors totally agree with the reviewer’s comment that it is important to confirm the interface between
MoO₃ and amorphous carbon matrix.

**[Q4]** The carbon matrix in a composite particle is a homogeneous amorphous matrix? The analysis of the synthesized carbon in a particle should be more clarified, for example, the 2D spectrum of Raman in Fig.3a and TEM/SEM image of Fig.1.

**[A4]** In this study, the carbon matrix of the MoO₃/C composite microspheres was characterized by means of Raman spectroscopy. The degree of graphitization of the carbon material can typically be evaluated according to the intensity ratio of the D and G bands of carbon at approximately 1350 and 1590 cm⁻¹, respectively. The peak intensity ratio between the D and G bands (I_D/I_G) for the MoO₃/C composite microspheres was approximately 3.2, demonstrating that the carbon formed in the composite was fairly disordered. However, as the reviewer commented, it is necessary to confirm the 2D spectrum at ~2685 cm⁻¹ of Raman. Therefore, the authors showed a Raman spectrum in the range of up to 3000 cm⁻¹ to identify the 2D band at ~2685 cm⁻¹. As a result, the 2D band was not observed, meaning the C matrix formed in the composite was fairly disordered amorphous carbon.

Additionally, the authors corrected the following sentence in the revised manuscript and the revised Raman spectrum was reflected in the manuscript.

“The peak intensity ratio between the D and G bands (I_D/I_G) for the MoO₃/C composite microspheres was approximately 3.2, demonstrating that the carbon formed in the composite was fairly disordered.”

⇒ “The peak intensity ratio between the D and G bands (I_D/I_G) for the MoO₃/C composite microspheres was approximately 3.2 and the absence of the 2D band at ~2685 cm⁻¹ demonstrate that the carbon formed in the composite was fairly disordered.”
Figure 3. Raman spectrum of the MoO$_3$/C composite microspheres.

[Q5] The fabrication condition of the anode electrode in the study should be added clearly in your manuscript.

[A5] As the reviewer commented, the following sentences were added in the section of Electrochemical measurements of the revised manuscript.

“Lithium cell assembly was made in Ar-filled glove box at room temperature where water and oxygen concentration was kept less than 1 ppm.”

“The working electrodes were formed by coating the slurry onto copper foils and subsequently dried at 70 °C for 3h.”

[Q6] How weight is the specific gravity of a MoO$_3$/carbon composite? The comparison between the MoO$_3$/carbon composite and bare MoO$_3$ should be explained for an analysis of mAh/cc.

[A6] As the reviewer commented, electrode density and volumetric capacity of the electrode are important. Thus, calculations were made to check the exact volumetric energy density of the samples. In this work, the mass loading of MoO$_3$/C composite and bare MoO$_3$ powders on Cu current collector are 0.75 and 0.87 mg cm$^{-2}$, respectively. Also, the thickness of the electrode
was 15 μm. From these information, the densities of the synthesized MoO$_3$/C composite and bare MoO$_3$ powders were calculated as 0.50 and 0.57 g ml$^{-1}$, respectively.

Therefore, the following sentence was corrected

“The discharge capacity of the MoO$_3$/C composite microspheres decreased slightly from 1,066 mA h g$^{-1}$ to 808 mA h g$^{-1}$ from the 2$^{nd}$ cycle to the 100$^{th}$ cycle, whereas that of the bare MoO$_3$ powders decreased rapidly from 1,090 mA h g$^{-1}$ to 239 mA h g$^{-1}$ in the same cycle range.”

→ “The discharge capacity of the MoO$_3$/C composite microspheres decreased slightly from 1,066 mA h g$^{-1}$ (533 mA h cc$^{-1}$) to 808 mA h g$^{-1}$ (404 mA h cc$^{-1}$) from the 2$^{nd}$ cycle to the 100$^{th}$ cycle, whereas that of the bare MoO$_3$ powders decreased rapidly from 1,090 mA h g$^{-1}$ (621 mA h cc$^{-1}$) to 239 mA h g$^{-1}$ (136 mA h cc$^{-1}$) in the same cycle range.”

Additionally, the following Figure was added in the revised supporting information.

![Figure S3. Cycle properties of the MoO$_3$/C composite microspheres and the bare MoO$_3$ powders.](image)

**Figure S3.** Cycle properties of the MoO$_3$/C composite microspheres and the bare MoO$_3$ powders.

**[Q7]** From the cycle characteristics in Fig.5c, the capacity of the bare MoO$_3$ degraded on around 20 cycles comparing with the MoO$_3$/carbon composite. The authors should explain scientifically and systematically the reason of the electrochemical optimizations in Figs.5c and d with including the results of Fig.5b, Fig6 and Fig.7 in the chapters of Results and Discussions or Conclusions of your manuscript.

**[A7]** Thanks for the reviewer’s helper comment. The following sentences were added in the revised manuscript.
3. Results and discussion

“On the other hand, the structural destruction of the bare MoO$_3$ powders during repeated Li$^+$-ion insertion and desertion processes resulted capacity fading continuously.”

“The high structural stabilities the MoO$_3$/C composite microspheres with high lithium-ion storage capacities resulted in low Rct values during cycling. The MoO$_3$/C composite microspheres with high structural stability during repeated lithium insertion and desertion reactions showed excellent cycling and rate performance, as shown in Figure 5.”

4. Conclusions

“The superior Li$^+$-ion storage properties of the MoO$_3$/C composite microspheres compared to those of the bare MoO$_3$ were supported by EIS analysis and observing morphologies of the samples obtained after 100 cycles.”
Thank you for your helpful comments and revision.

Reviewers' comments:

Reviewer #2: The manuscript reports a detailed characterization of MoO$_3$/C material that can be used for anodes in Li-on batteries. The work is interesting, very well explained and written. The characterization of the material is complete, the electrochemical results are exhaustively discussed. There are no critical issues in this work, which deserves to be published in the present form.

Authors would like to thank a reviewer2 for her/his time and comments on our manuscript.
Thank you for your helpful comments and revision.

Reviewers' comments:

Reviewer #3: The manuscript entitled Large Scale Process for Low Crystalline MoO$_3$-Carbon Composite Microspheres Prepared by One-Step Spray Pyrolysis for Anodes in Lithium-Ion Batteries" reports an interesting work in the world of anode electrodes. This work is possible to be published in Nanomaterials after the following revision.

Authors would like to thank a reviewer3 for her/his time and comments on our manuscript.

Q1] The author should be meticulously revise the English language and include the recent investigations on MoO$_3$ for this kind of applications and more details about the samples preparation.

[A1] We highly appreciate the reviewer’s positive evaluation of our work and the reviewer’s helpful comments. As the reviewer commented, the manuscript was revised by a qualified proofreader. Additionally, some sentences for the recent investigations on MoO$_3$ were newly added into the Introduction part of the revised manuscript to clearly distinguish this work from the other works for the synthetic strategy of the low crystalline MoO$_3$-C composite microspheres in lithium ion batteries. Therefore, the following sentences were added into the Introduction part of the revised manuscript.

"Molybdenum oxides are candidate anode materials for LIBs because MoO$_3$ exhibit good electrochemical properties, low cost, and low environmental friendly [19-21]. Therefore, MoO$_3$ nanomaterials with diverse morphologies such as nanoparticles, hollow, nanobelts, nanowires, and porous structures have been prepared. Lee et al. [22] synthesized MoO$_3$ nano-particles using hot filament chemical vapor deposition method (HFCVD) under an argon atmosphere. Zhao et al. [23] also synthesized MoO$_3$ hollow microspheres by a template-free solvothermal route and subsequent heat treatment in air. The MoO$_3$ hollow microspheres have a relatively
high specific surface area. Chen et al. [24] prepared MoO$_3$ nanobelts by hydrothermal method, in which the morphology of MoO$_3$ nanobelts is affected with the addition of PEG. MoO$_{3-x}$ nanowires were prepared by Sunkara et al. [25] in a hot-filament chemical vapor deposition reactor. Ko et al. [26] prepared three-dimensional ordered macro-porous structured MoO$_3$ by using polystyrene bead template via ultrasonic spray pyrolysis.”


