Hierarchical Porous MoS$_2$/C Nanospheres Self-Assembled by Nanosheets with High Electrochemical Energy Storage Performance

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**Abstract**
To overcome the deficiency of the volume expansion of MoS$_2$ as the anode material for lithium-ion batteries (LIBs), an effective strategy was developed to design hierarchical porous MoS$_2$/carbon nanospheres via a facile, easy-operated hydrothermal method followed by annealing. FESEM and TEM images clearly showed that nanospheres are composed of ultra-thin MoS$_2$/C nanosheets coated with carbon layer and possess an expanded interlayer spacing of 0.98 nm. As anodes for LIBs, MoS$_2$/carbon nanospheres deliver an initial discharge capacity of 1307.77 mAh g$^{-1}$ at a current density of 0.1 A g$^{-1}$. Moreover, a reversible capacity of 612 mAh g$^{-1}$ was obtained even at 2 A g$^{-1}$ and a capacity retention of 439 mAh g$^{-1}$ after 500 cycles at 1 A g$^{-1}$. The improved electrochemical performance is ascribed to the hierarchical porous structure as well as the intercalation of carbon into lattice spacing of MoS$_2$, which offers fast channels for ion/electron transport, relieves the influence of volume change and increases electrical conductivity of electrode. Meanwhile, the expanded interlayer spacing of MoS$_2$ in MoS$_2$/C can decrease the ion diffusion resistance and alleviate the volumetric expansion during discharge/charge cycles.

**Keywords:** Lithium-ion batteries, Anode materials, MoS$_2$/C, Porous structure, Electrochemical performance

**Background**
How to protect our sustainable planet while developing and using energy has become a major global issue. In the past decades, lithium-ion batteries (LIBs) highlight the advantages of high energy density, long service life and environmental compatibility, which has great applications in renewable energy storage, electronic devices and energy vehicles [1, 2]. Nevertheless, commercial graphite anodes present a low theoretical specific capacity of 372 mAh g$^{-1}$ [3–5], which is far from the ever-growing requirements for high-energy-density rechargeable batteries. Therefore, it is of great significance to develop desirable electrode materials for LIBs.

Recently, the transition metal sulfides (Co$_3$S$_4$ [6], SnS$_2$ [7], VS$_2$ [8], NbS$_2$ [9], WS$_2$ [10] and MoS$_2$ [11]) have been considered a series of potential anode materials owing to their low cost, high energy density and rich redox electrochemistry [12, 13]. Among these materials, molybdenum disulfide (MoS$_2$), a semiconductor with a typical two-dimensional (2D) layered structure, has been the most studied material in this family. More importantly, the larger interlayer distance ($d=0.62$ nm) of MoS$_2$ than graphite ($d=0.34$ nm) can accelerate the process of Li$^+$ intercalation/extraction, putting up a high storage capacity of 670 mAh g$^{-1}$ [14–16]. Unfortunately, the practical application of bare MoS$_2$ as LIBs is hindered from the poor cycling stability. This is because that the relatively low electronic/ionic conductivities and the electrochemical degradation of the active MoS$_2$ materials due to a polysulfide shuttling effect result in the capacity loss and poor rate capability [4, 17, 18]. To tackle these challenges, it has been proven to be particularly
effective by engineering various nanostructured MoS₂ and introducing the conductive carbonaceous materials [15, 19–21]. The essence of the former is to shorten the electronic transmission distance, while the latter aims to improve the overall electronic conductivity of the material, restrain the agglomeration of MoS₂ and maintain the electrode structure stability, for example, MoS₂/graphene [22, 23], MoS₂/CNTs [24], MoS₂/carbon nanofibers [25], MoS₂/RGO [26], etc.

Based on the above considerations, recent researches mostly focus on constructing novel MoS₂/C-based nanocomposites, giving full play to their respective advantages to improve the cycling stability. Li et al. reported a novel 2D MoS₂/C hybrid nanosheet superstructure consisting of the alternative layer-by-layer interoverlapped single-layer MoS₂ and mesoporous carbon [4]. The unique hybrid nanosheets with perfect MoS₂/m-C interface contact result in the maximization of synergistic interaction. Their group also projected 3D ordered macroporous MoS₂/carbon flexible electrodes by assembling MoS₂/C nanostructure on carbon cloth with few-layered MoS₂ nanosheets homogeneously embedded into the interconnected carbon wall through the use of polystyrene (PS) nanospheres as the macropore template [17]. The flexible electrodes exhibited superior cycling stability when directly applied for LIBs. Zhang et al. achieved the growth of MoS₂ nanosheets onto the polypyrrole-derived carbon nanotubes (PCN) substrate and the coating of outer carbon layer onto the nanosheets to fabricate PCN@MoS₂@carbon sandwiched architecture [27]. In the architecture, ultrathin MoS₂ nanosheets are sandwiched between hollow PCN and thin carbon layer. Sun et al. successfully prepared 1T-MoS₂/C hybrids that consist of smaller and fewer-layer MoS₂ nanosheets via a facile hydrothermal method with a proper glucose additive [28]. The 1T-MoS₂/C anodes deliver superior cycling stability (maintain 870 mAh g⁻¹ after 300 cycles at 1 A g⁻¹) and high rate performance (a reversible capacity of 600 mAh g⁻¹ at 10 A g⁻¹). The superior electrochemical performance can be attributed to the higher intrinsic conductivity of 1T-MoS₂ and thin carbon layers covered on the surface with an enlarged interlayer spacing of 0.94 nm. Given the above, the modified MoS₂/C-based nanocomposites can indeed optimizing the electrochemical properties.

Herein, we demonstrate a facile, easy-operated and high effective hydrothermal method toward hierarchical MoS₂/carbon nanospheres. The nanospheres are self-assembled from ultra-thin MoS₂/C nanosheets coated with carbon layer, resulting in forming internal interconnected channels and exposing more active sites for electronic/ionic transmission and lithium storage. As a consequence, when employed as anode material in half cell LIBs, the as-prepared open porous structure of MoS₂/C nanospheres exhibits remarkable lithium storage properties, including high specific capacity, long cycling performance, as well as fast rate capability.

**Methods**

**Material Preparation**

**Synthesis of MoS₂/C**

The synthesis of MoS₂/C nanospheres was based on a previous procedure with modifications [19]. Typically, 0.6 g of sodium molybdate (Na₂MoO₄), 3 g of thiourea (CH₄N₂S) and 1 g of polyvinyl pyrrolidone (PVP) were dissolved in 30 mL deionized water with magnetic stirring to form a uniform solution. Then, we added 0.2 g of dopamine hydrochloride (DPH) into the above mixture with forming a red suspension. After continuously stirring for 30 min, the resulting suspension was put into a 50-mL Teflon-lined stainless steel autoclave kept at 200 °C for 18 h, followed by cooling down to room temperature naturally. The black precipitates were collected and washed with deionized water and absolute ethanol by centrifugation method, and dried under vacuum at 60 °C for overnight. Lastly, MoS₂/C nanospheres were obtained by the calcination of black precipitates in argon atmosphere at 700 °C for 3 h. For comparison, we bought commercial pure MoS₂ powder from Aladdin.

**Material Characterization**

The X-ray diffraction (XRD) patterns were measured using a TD-3500 X-ray diffractometer with Cu/Ka radiation (λ = 0.15406 nm) at the 2θ range of 5°–80° with a scanning rate of 4° min⁻¹. N₂ adsorption/desorption isotherms and Brunauer–Emmett–Teller (BET) surface area were performed by a Micromeritics ASAP 2020 analyzer. The Raman spectrums were tested on a LabRAM HR800 Raman spectrometer equipped with a laser light at 532 nm. The content of carbon in the MoS₂/C nanospheres was determined by a simultaneous DSC/TGA analyzer (TGA, SDT-Q600) at a heating rate of 10 °C min⁻¹ from 25 to 700 °C with a flow of air. The element composition and chemical state of the materials were evaluated through X-ray photoelectron spectroscopy (XPS, Thermo VG ESCALAB 250XI). The detailed morphologies and microstructure of the samples were examined using field emission scanning electron microscopy (FESEM, Sigma 500), and transmission electron microscopy (TEM, Tecnai G2 F20), respectively.

**Electrochemical Tests**

The capacities and cycling properties of the as-prepared samples were performed by CR2032 coin-type cells assembled in an argon-filled glove box with lithium
The working electrodes were obtained by mixing in N-methyl-2-pyrrolidinone (NMP) solution, the active materials (MoS$_2$/C or MoS$_2$) with conductive additive (acetylene black) and polymer binder (PVDF) in a 8:1:1 mass ratio to form a homogeneous slurry. We coated the slurry on a copper foil and dried in a vacuum oven at 80 °C for 4 h. Subsequently, the electrodes were punched into circular disks and dried in a vacuum oven at 120 °C for 12 h. 1M LiPF$_6$ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volume ratio of 1:1 was selected as the electrolyte. The electrochemical performance was implemented using a battery testing system (Neware BTS-610) in a cut-off voltage window of 0.01–3 V at different current densities. Cyclic voltammetry (CV) curves were carried on an electrochemical workstation (CHI 760E) between 0.01 and 3 V at a scanning rate of 0.2 mV s$^{-1}$.

**Results and Discussion**

The preparation process diagram of hierarchical porous MoS$_2$/C nanospheres is shown in Fig. 1. Na$_2$MoO$_4$ supplies molybdenum ion, CH$_4$N$_2$S provides sulfur source, and DPH is carbon source. Polydopamine carbon materials have better electrochemical performance and better conductivity. PVP acts as the dispersant and stabilizer. In hydrothermal process, surfactant PVP preferentially adsorbs along MoS$_2$ nanograin boundary, causing MoS$_2$ crystal nucleus anisotropic growth and forming MoS$_2$ nanosheets. Due to the large specific surface area and high surface energy of MoS$_2$ nanosheet/carbon precursor, MoS$_2$ nanosheets are self-assembled into nanospheres. Finally, MoS$_2$/C nanospheres are prepared by calcination in inert atmosphere.

Figure 2a displays the XRD patterns of commercial MoS$_2$ and MoS$_2$/C nanospheres. The patterns of commercial MoS$_2$ are consistent with the standard card of hexagonal 2H-MoS$_2$ (JCPDS 87-2416). The diffraction peaks at about 2θ = 32.8° and 58.5° can be indexed to (100) and (110) planes of MoS$_2$ in both commercial MoS$_2$ and as-prepared MoS$_2$/C [19, 29]. Additionally, the generation of new structure may be proved by the two new peaks in MoS$_2$/C at around 2θ = 7.9° and 18.3°, which are pointed to expanded (001) and (002) crystal planes [27]. The expanded d-spacing is also stood by HRTEM observation results (Fig. 2g). The above analysis indicates that we have successfully synthesized MoS$_2$/C and the participation of DPH contributed to the expanded interlayer spacing. As shown in Fig. 1b, based on the N$_2$ adsorption/desorption isotherms analysis, the BET surface area of MoS$_2$/C was concluded to be 16.59 m$^2$ g$^{-1}$. The pore size distribution (inset of Fig. 2b) calculated using the BJH equation [2] presents a multi-scale porous structure with an average pore size of 20.66 nm. Such hierarchical porous structure will facilitate the intimate contact between electrode and the electrolyte and fast electron and ion transport, thereby further improving the lithium storage performance. As indicated in Fig. 2c, Raman spectrum of MoS$_2$/C confirms the existence and graphitization extent of carbon. Two typical peaks centered at 384 and 407 cm$^{-1}$ are associated with $E_{12g}$ and $A_{1g}$ vibration modes of MoS$_2$ [17, 29, 30], respectively. Another two characteristic peaks located at 1373 cm$^{-1}$ (D band) and 1605 cm$^{-1}$ (G band) can be direct to carbon phase [15, 21, 31]. Detailedly, the D band can be connected with the defective carbon or disordered amorphous carbon due to the $sp^3$-hybridization on the graphitic plane, while G band is ascribed to crystalline graphitized carbon [19, 32]. The ratio of intensity of D band to G band is calculated to be 0.85, suggesting relatively high graphitization degree of carbon. TGA measurements in Fig. 2d ulteriorly ascertain the carbon content in MoS$_2$/C composites. The 4.2% weight loss before 100 °C corresponds to the evaporation of adsorbed free water in the samples, and 37.54% weight loss reveals the oxidation of MoS$_2$ to MoO$_3$ in air [14, 15]. Hence, the weight percentages of adsorbed water, MoS$_2$ and carbon are determined to be 4.2, 64.78 and 31.02 wt%, respectively.

XPS was investigated to assess the element composition and valence states of MoS$_2$/C in Fig. 3a–d. As shown in Fig. 3a, the main elements of Mo, S, C and O can be identified from the survey pattern; O derived from the oxygen adsorption on the surface. Figure 3b shows the

![Fig. 1 The preparation process diagram of hierarchical porous MoS$_2$/C nanospheres](image-url)
high-resolution spectrum of Mo 3d. Two major peaks centered at 229.8 and 233.1 eV are ascribed to Mo 3d_{5/2} and Mo 3d_{3/2} of Mo^{4+} in MoS_{2}/C [19, 29]. Another broad peaks located at 227.0 eV are generally connected with S 2s. And the rest of peak at 236.3 eV can be indexed to Mo^{6+} indicating the formation of C–O–Mo bond between MoS_{2} and carbon, which is consistent with other MoS_{2}/C composites [27, 30, 33]. A pair characteristic peaks of S can be clearly observed at 162.5 and 163.7 eV in Fig. 3c, corresponding to S 2p_{3/2} and S 2p_{1/2} of S^{2−} in MoS_{2}[5, 21]. The deconvoluted XPS spectrum of C 1s is shown in Fig. 3d; the signals can be fitted to three peaks: The main peaks centered at 284.7 eV correspond to C–C, whereas the two peaks at the 285.6 and 288.9 eV can be assigned to C–O and O–C=O, respectively [14, 29, 34, 35].

As depicted in Fig. 4, FESEM and TEM images disclosed the morphology and structure of MoS_{2}/C. The representative FESEM and TEM images of MoS_{2}/C are displayed in Fig. 4a–f, revealing porous nanospheres structure assembled from ultra-thin MoS_{2}/C nanosheets with an average diameter of 130–200 nm. The FESEM district elemental mapping analysis (Fig. 4c) confirms the existence of Mo, S, C elements and uniform distribution throughout the composites. What is more, the nanosheets are covered with thin carbon layer and closely contact with each other to form a nanosphere in Fig. 4e, f. Such open porous structure is in favor for electronic contact and rapid electron transfer during discharge/charge processes. Figure 4g shows a HRTEM image of MoS_{2}/C. The selected area electron diffraction (SAED) pattern indexes a diffraction ring to the polycrystalline nature of the MoS_{2} (inset of Fig. 4g).

The as-obtained MoS_{2}/C composites contain 31.02 wt% of carbon; for comparison, we add the same content of conductive activated carbon powder to the commercial MoS_{2} as the active material, and then mix it with PVDF and acetylene black to gain the electrodes. The two samples were assembled as CR2032 coin-type cells anodes to evaluate their electrochemical mechanism and performance. The first three CV curves of the MoS_{2}/C electrode were carried out over the potential window from
0.01 to 3.0 V at a scan rate of 0.2 mV s$^{-1}$. As seen from Fig. 5a, three reduction peaks are observed from 1.22 to 0.1 V in the first cathodic sweep. A broad reduction peak located at 0.73–1.22 V corresponds to the insertion of Li$^+$ into the MoS$_2$/C and lithiation processes of MoS$_2$ to form Li$_x$MoS$_2$[16, 36]. Another two reduction peaks centered at 0.58 V and 0.1 V can be attributed to the generation of the solid electrolyte interphase (SEI) film and the reduction of Li$_x$MoS$_2$ to Mo [14, 15, 25], respectively. For the first anodic sweep, only two remarkable peaks are noticed at 1.53 and 2.22 V, which are assigned to the oxidation of Mo to MoS$_2$ phase and delithiation processes of Li$_x$S to S [5, 21, 37]. In the following sweeps, the reduction peak (0.58 V) disappears and other two peaks shifts to 1.17 V and 1.90 V, indicating a multi-lithiation processes of MoS$_2$. Notably, the overlapped curves in second/third sweeps mean the high reversibility and great cycling stability of the as-made MoS$_2$/C in LIBs. The galvanostatic charge–discharge curves of MoS$_2$/C are conducted between 0.01 and 3.0 V at the current density of 0.1 A g$^{-1}$ in Fig. 5b. The arisen charge/discharge voltage platforms are in accordance with the CV results. The MoS$_2$/C electrodes deliver discharge capacity as high as 1307.77 mAh g$^{-1}$ and charge capacity of 865.54 mAh g$^{-1}$ with an initial coulombic efficiency (CE) of 66.18%. Moreover, the undesirable CE and capacity loss approximately 33% probably originate from the irreversible decomposition of electrolyte and the generation of SEI film on the electrode surface [5, 14]. The second and third charge/discharge voltage profiles repeat with each other; specific capacities are 845.58/879.20 mAh g$^{-1}$ and 836.13/810.92 mAh g$^{-1}$, respectively. This enhanced CE reveals the electrochemical reversibility of MoS$_2$/C anode is good.

Figure 5c compares the cycling performances of the MoS$_2$/C and commercial MoS$_2$ anodes under the current density of 0.1 A g$^{-1}$ for 100 cycles. Commercial MoS$_2$ presents initial charge/discharge specific capacities of 671.70/952.52 mAh g$^{-1}$, which is far from the MoS$_2$/C composites (865.54/1307.77 mAh g$^{-1}$). This is because the existence of carbon in MoS$_2$/C improve the conductivity and the surface/interfacial storage of Li.
originated from the porous nanosphere structure and the reversible formation/decomposition of polymeric gel-like film (SEI) [38]. After 100 cycles, the MoS2/C and MoS2 anodes show discharge specific capacities of 587.18 and 350 mAh g\(^{-1}\) with high CE of approximate 99%. The rate capability of two samples was also evaluated at different current densities ranging from 0.1 to 2 A g\(^{-1}\) in Fig. 5d. The MoS2/C retains high discharge capacities at higher current densities: 878 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\), 806 mAh g\(^{-1}\) at 0.2 A g\(^{-1}\), 733 mAh g\(^{-1}\) at 0.5 A g\(^{-1}\), 673 mAh g\(^{-1}\) at 1 A g\(^{-1}\), 633 mAh g\(^{-1}\) at 1.5 A g\(^{-1}\) and 612 mAh g\(^{-1}\) at 2 A g\(^{-1}\) after 10 cycles. When reevaluated at current density of 0.1 A g\(^{-1}\), the discharge capacity rapidly reaches 754 mAh g\(^{-1}\) and remains 876 mAh g\(^{-1}\) after 40 cycles, which is almost close to that of first 10th cycle, suggesting the outstanding rate performance and structural stability of MoS2/C. As for MoS2, the discharge capacities from 0.1 A g\(^{-1}\) to 2 A g\(^{-1}\) after 10 cycles are 320 and 55 mAh g\(^{-1}\) with enormous capacity loss about 83%. The results reveal that the electrical conductivity of commercial MoS2 is no significant improvement due to the addition of activated carbon, thereby not achieving the effect of rapid charge and discharge. This is because simple physical mixing cannot effectively improve the electrical conductivity of commercial MoS2, but can accomplish the ideal goal by carbon coating like as-obtained MoS2/C.

The long-term cycling performance of two samples is shown in Fig. 5e at a large current density of 1.0 A g\(^{-1}\). In order to activate electrodes, the cells are tested at a low current density of 0.05 A g\(^{-1}\) for first two cycles. The MoS2/C exhibits high discharge capacities of 515, 443 and 439 mAh g\(^{-1}\) at 1.0 A g\(^{-1}\) for 100th, 300th, 500th cycles, respectively. Compared with the previously reported MoS2 anode materials from Table 1, it shows that hierarchical porous MoS2/C nanospheres have better electrochemical performance and they will show great potential to replace graphite anode materials. It is worth noting that the capacity curve of MoS2/C as a whole is relatively stable without particularly obvious decline except from the first few cycles, illustrating preeminent long-term cycling stability. However, the MoS2 anodes suffer from tremendous capacity loss with low discharge capacities of 114, 109 and 138 mAh g\(^{-1}\) at the same cycles. As a result, MoS2/C still exhibits more superior electrochemical properties than commercial MoS2, although activated carbon with the same relative weight ratio is introduced into MoS2 electrode. This can be attributed to the following advantages. I. MoS2/C composites possess open porous architecture that the nanosphere are self-assembled by ultra-thin MoS2/C nanosheets coated with thin carbon layer, which facilitate the intimate contact between electrode and the electrolyte and fast electron and ion transport. Meanwhile, open porous architecture is advantageous to form internal interconnected channels and expose increased number of active sites for electronic/ionic transmission and lithium storage. II. The thin carbon
layer derived from carbonization of DPH can not only act as a stable supporting matrix to impede the aggregation of MoS$_2$ nanosheets, but also improve the overall conductivity of the material. III. The expanded interlayer spacing of MoS$_2$ in MoS$_2$/C can decrease the ion diffusion resistance and alleviate the volumetric expansion during discharge/charge cycles.

**Fig. 5**  
(a) CV curves at scan rate 0.2 mV s$^{-1}$ between 0 and 3 V and (b) discharge/charge profiles at a current density of 0.1 A g$^{-1}$ of MoS$_2$/C nanospheres; (c) the cycling performance of MoS$_2$ and MoS$_2$/C nanospheres at a current density of 0.1 A g$^{-1}$ for 100 cycles; (d) rate performance of two samples at various current rates range from 0.1 to 2 A g$^{-1}$; (e) long-term cycling performance of two samples at a current density of 1 A g$^{-1}$ for 500 cycles.
Conclusions
In this work, we have fabricated hierarchical porous MoS$_2$/carbon nanospheres self-assembled by ultra-thin MoS$_2$/C nanosheets by a facile hydrothermal method followed by annealing. Benefiting from the rational structure design, the MoS$_2$/C provides fast channels for ion/electron transport and maintains high stability and conductivity of the whole electrode in lithium storage. Furthermore, the intercalation of C into interlayer spacing of MoS$_2$ can accommodate the volume expansion to make sure the integrality of electrode and enhance electronic conductivity. The as-fabricated MoS$_2$/C anode achieves high specific capacity (1307.77 mAh g$^{-1}$ at 0.1 A g$^{-1}$), excellent long cycling performance (439 mAh g$^{-1}$ at 1.0 A g$^{-1}$ for 500 cycles) and fast rate capability (612 mAh g$^{-1}$ at 2 A g$^{-1}$).

Abbreviations
LIBs: Lithium-ion batteries; 2D: Two-dimensional; PCN: Polypyrrole-derived carbon nanotubes; PS: Polystyrene; DPH: Dopamine hydrochloride; XRD: X-ray diffraction; XPS: X-ray photoelectron spectroscopy; FESEM: Field emission scanning electron microscopy; TEM: Transmission electron microscopy; TGA: Thermogravimetric analysis; BET: Brunauer–Emmett–Teller; BJH: Barrett–Joyner–Halenda; CV: Cyclic voltammetry; DMC: Diethyl carbonate; EC: Ethylene carbonate; PVDF: Polyvinylidene fluoride.

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Authors’ contributions
YL synthesized and characterized the samples. LZ analyzed the data. YL and HD L designed the experiments and wrote the paper. All authors read and approved the final manuscript.

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Availability of data and materials
All data are fully available without restriction.

Table 1 Comparison of the electrochemical properties of MoS$_2$

| Materials                      | Current density (mA g$^{-1}$) | Cycle number (n) | Reversible capacity (mAh g$^{-1}$) | References       |
|-------------------------------|-------------------------------|------------------|------------------------------------|------------------|
| Bulky MoS$_2$                 | 200                           | 100              | About 100                          | [39]             |
| MoS$_2$                       | 400                           | 30               | 391                                | [40]             |
| MoS$_2$/C nanostructure       | 100                           | 50               | 478                                | [41]             |
| MoS$_2$/C                     | 100                           | 100              | 479.1                              | [42]             |
| TiO$_2$–MoS$_2$ Hybrid        | 800                           | 300              | 361.5                              | [43]             |
| MoS$_2$/C nanocomposites      | 100                           | 60               | About 450                          | [44]             |
| MoS$_2$/C nanospheres         | 100                           | 100              | 587.18                             | This work        |
|                               | 1000                          | 500              | 439                                |                  |

Competing interests
The authors declare that they have no competing interests.

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