Chemical Synthesis

1	Supporting Materials
2	Revealing the dynamic formation mechanism of porous Mo ₂ C: an <i>in-situ</i> TEM
3	study
4	
5	Yongzhao Wang ^{1,2,#} , Yiming Niu ^{1,2,#} , Yinghui Pu ^{1,2} , Shiyan Li ³ , Yuefeng Liu ³ , Bingsen
6	Zhang ^{1,2,*}
7	
8	¹ Shenyang National Laboratory for Materials Science, Institute of Metal Research,
9	Chinese Academy of Sciences, Shenyang 110016, China
10	² School of Materials Science and Engineering, University of Science and Technology
11	of China, Shenyang 110016, China
12	³ Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics,
13	Chinese Academy of Sciences, Dalian 116023, China
14	[#] Authors contributed equally to this work.
15	
16	Correspondence to: Prof. Bingsen Zhang, Shenyang National Laboratory for
17	Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72
18	Wenhua Road, Shenyang 110016, China. E-mail: <u>bszhang@imr.ac.cn</u> .
19	

СС

© The Author(s) 2021. Open Access This article is licensed under a Creative Commons Attribution 4.0 International License (https://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, sharing, adaptation, distribution and reproduction in any medium or

format, for any purpose, even commercially, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.



www.chesynjournal.com



21 Supplementary Figure 1. Typical XRD pattern (A), low-magnification TEM (B),

22 HRTEM (C) images of MoO₃ nanobelts after calcination in air, and the local FFT (D)

23 of the enlarge part in (C).

24



26 Supplementary Figure 2. TPSR profiles of the carbonization process under 20 vol.%





29 Supplementary Figure 3. SEM images and XRD patterns of MoO₂ (A-C) and Mo₂C

- 30 (D-F) samples, respectively.
- 31
- 32



Supplementary Figure 4. STEM images and EDX elemental maps of MoO₂ (A-C)
and Mo₂C (D-F) samples, respectively.

- 36
- 37



38

39 Supplementary Figure 5. TEM images of MoO₂ (A) and Mo₂C (B). (C) EEL spectra

 $40 \qquad of \ MoO_2 \ and \ Mo_2C \ samples.$









Supplementary Figure 7. In-situ TEM image (A) of MoO₂ and the corresponding PSD

- histogram (B) under 20 vol.% CH₄/H₂ atmosphere at 600 °C.



54 Supplementary Figure 8. In-situ TEM images of the structural evolution of adjacent

55 MoO₂ NPs to Mo₂C nanocrystals under 20 vol.% CH₄/H₂ atmosphere at 700 $^{\circ}$ C.

56 57

53



59 Supplementary Figure 9. In-situ TEM images of the structural evolution of adjacent

- 60 MoO₂ NPs to Mo₂C nanocrystals under 20 vol.% CH₄/H₂ atmosphere at 700 $^{\circ}$ C.
- 61
- 62



Supplementary Figure 10. *In-situ* TEM images regarding the growth process on
Mo₂C within and between MoO₂ NPs under 20 vol.% CH₄/H₂ atmosphere at 700 °C.

66



69 Supplementary Figure 11. In-situ TEM images regarding the growth rate on Mo₂C

- vithin and between MoO₂ NPs under 20 vol.% CH_4/H_2 atmosphere at 700 °C.
- 71
- 72



73

74 Supplementary Figure 12. In-situ TEM images (A, B) and statistical analysis of pore

75 width (C) and length (D) of Mo₂C.



Supplementary Figure 13. $N_{\rm 2}$ adsorption/desorption isotherms of $MoO_{\rm 2}$ (A) and 79 Mo₂C (B) samples. (C) The pore size distributions of MoO₂ and Mo₂C samples. 80

- 81
- 82



85 Supplementary Figure 14. In-situ TEM images of Mo₂C sample under 20 vol.%

- 86 CH_4/H_2 atmosphere at 700 °C (A) and 750 °C (B). (C, D) Enlarged TEM images from
- 87 the dashed boxes in (A) and (B).