

## Confinement of $\text{PMo}_{12}$ in Hollow $\text{SiO}_2\text{-PMo}_{12}\text{@rGO}$ Nanospheres for High Performance Lithium Storage

Hanbin Hu, Xueying Jia, Jiabin Wang, Wei Chen,\* Lei He\* and Yu-Fei Song\*

State Key Laboratory of Chemical Resource Engineering, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China. Email: songyf@mail.buct.edu.cn, helei@mail.buct.edu.cn, chenw@mail.buct.edu.cn;

Tel/Fax: +86 10-64431832.

### List of contents:

**Fig. S1** SEM images (a) PMMA spheres and (b)  $\text{PMMA@SiO}_2$  spheres.

**Fig. S2** FT-IR spectra of PMMA,  $\text{PMMA@SiO}_2$ ,  $\text{SiO}_2\text{-NH}_2$ ,  $\text{PMo}_{12}$  and  $\text{SiO}_2\text{-PMo}_{12}$ .

**Fig. S3** (a) XRD patterns of  $\text{SiO}_2\text{-PMo}_{12}\text{@rGO}$  and  $\text{SiO}_2\text{@rGO}$ . (b) TG curves of  $\text{SiO}_2\text{-PMo}_{12}\text{@rGO}$ , rGO and  $\text{PMo}_{12}$ .

**Fig. S4** High-resolution XPS spectrum of P 2p peak of the  $\text{SiO}_2\text{-PMo}_{12}\text{@rGO}$

**Fig. S5** High-resolution XPS spectra of Mo 3d and P 2p peaks of  $\text{PMo}_{12}$ .

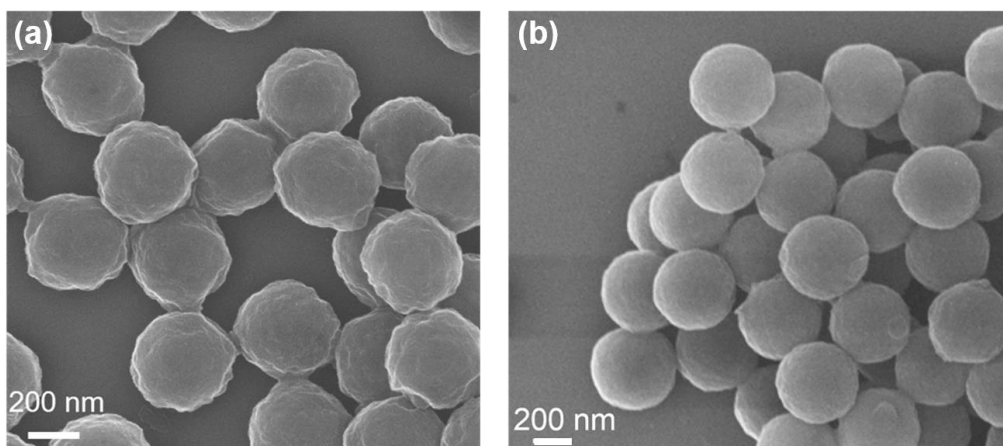
**Fig. S6** The charge-discharge profiles for different cycles of  $\text{SiO}_2\text{-PMo}_{12}\text{@rGO}$  under  $100 \text{ mA g}^{-1}$ .

**Fig. S7** (a) The CV of the  $\text{SiO}_2\text{@rGO}$ ; (b) The charge-discharge profiles for different cycles of  $\text{SiO}_2\text{@rGO}$  under  $100 \text{ mA g}^{-1}$ ; (c) Rate performance of  $\text{SiO}_2\text{@rGO}$  electrode; (d) Cycling performance and CE of  $\text{SiO}_2\text{@rGO}$  under  $100 \text{ mA g}^{-1}$  within a voltage of 0.01-3.0 V.

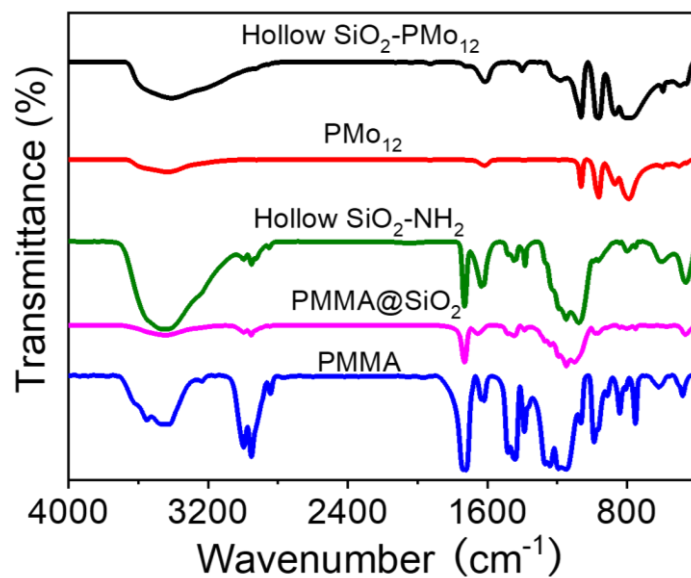
**Fig. S8** (a) The CV of the  $\text{SiO}_2\text{-PMo}_{12}$ . (b) The charge-discharge profiles for different cycles of  $\text{SiO}_2\text{-PMo}_{12}$  under  $100 \text{ mA g}^{-1}$ . (c) Rate performance of  $\text{SiO}_2\text{-PMo}_{12}$  electrode. (d) Cycling performance and CE of  $\text{SiO}_2\text{-PMo}_{12}$  under  $100 \text{ mA g}^{-1}$  within a voltage of 0.01-3.0 V.

**Fig. S9** TEM image of  $\text{SiO}_2\text{-PMo}_{12}\text{@rGO}$  after 100 cycles at  $100 \text{ mA g}^{-1}$ .

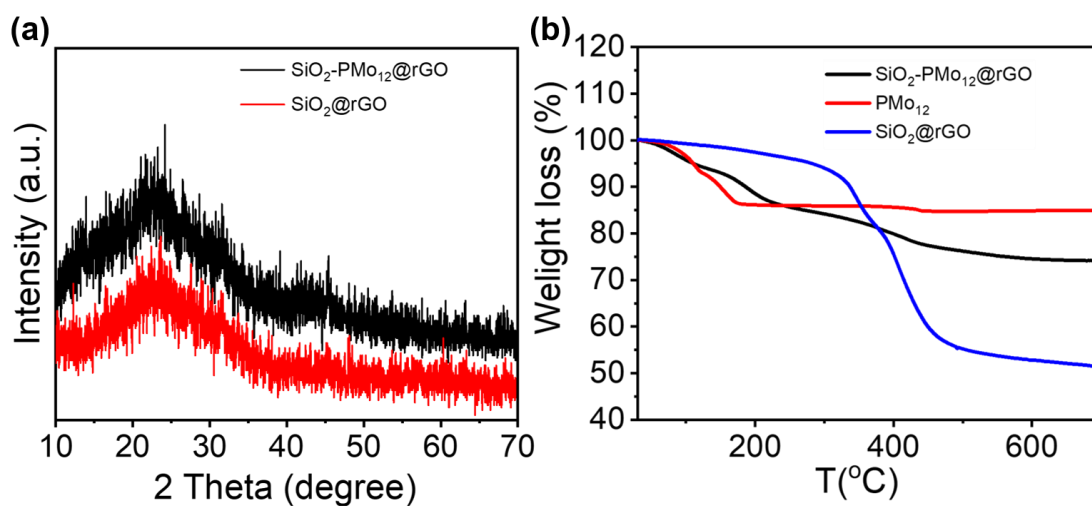
**Table S1.** Comparison of  $\text{SiO}_2\text{-PMo}_{12}\text{@rGO}$  with other reported  $\text{SiO}_2\text{-}$  and POM-based electrodes as LIBs anode materials.



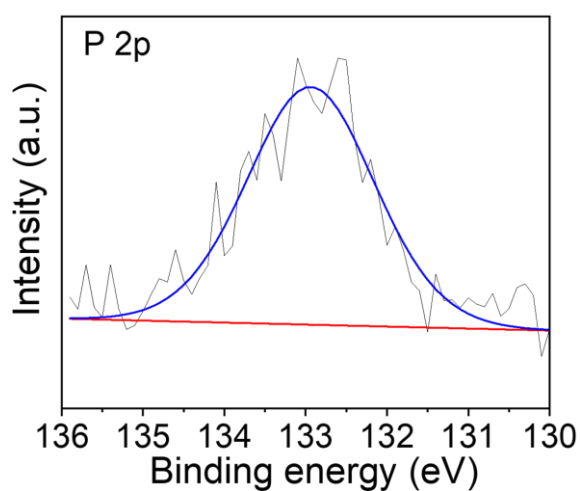
**Fig. S1** SEM images of (a) PMMA spheres and (b) PMMA@SiO<sub>2</sub> spheres.



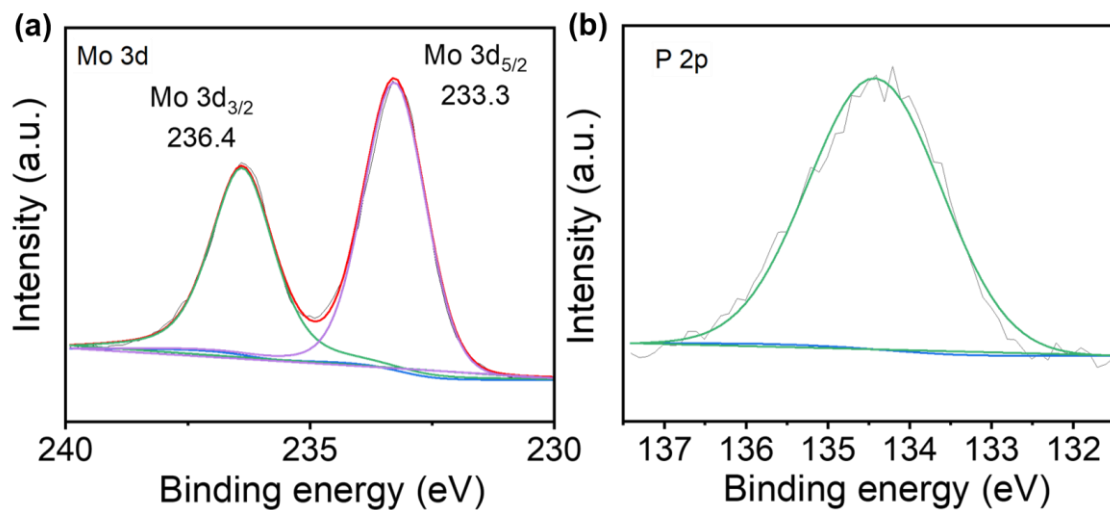
**Fig. S2** FT-IR spectra of PMMA, PMMA@SiO<sub>2</sub>, SiO<sub>2</sub>-NH<sub>2</sub>, PMo<sub>12</sub> and SiO<sub>2</sub>-PMo<sub>12</sub>, respectively.



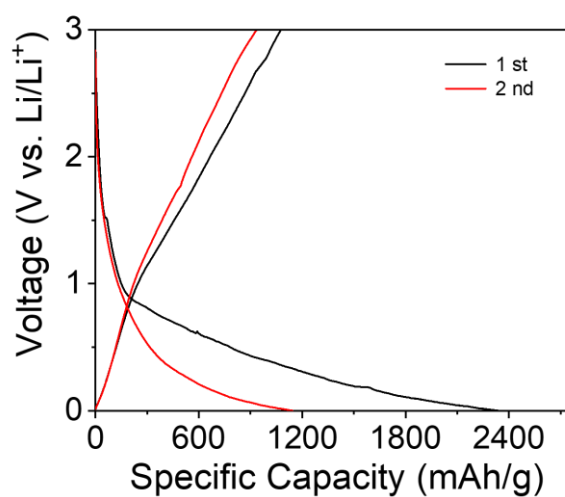
**Fig. S3** (a) XRD patterns of SiO<sub>2</sub>-PMO<sub>12</sub>@rGO and SiO<sub>2</sub>@rGO. (b) TG curves of SiO<sub>2</sub>-PMO<sub>12</sub>@rGO, rGO and PMO<sub>12</sub>.



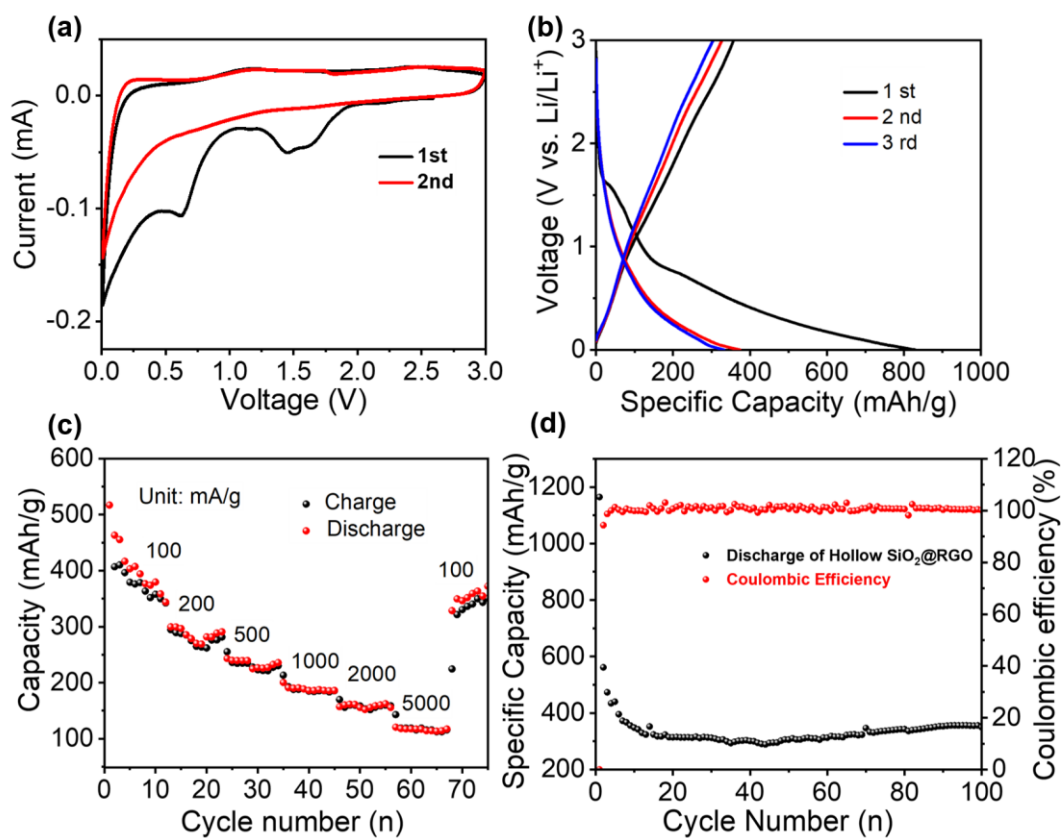
**Fig. S4** High-resolution XPS spectrum of P 2p peak of the SiO<sub>2</sub>-PMO<sub>12</sub>@rGO.



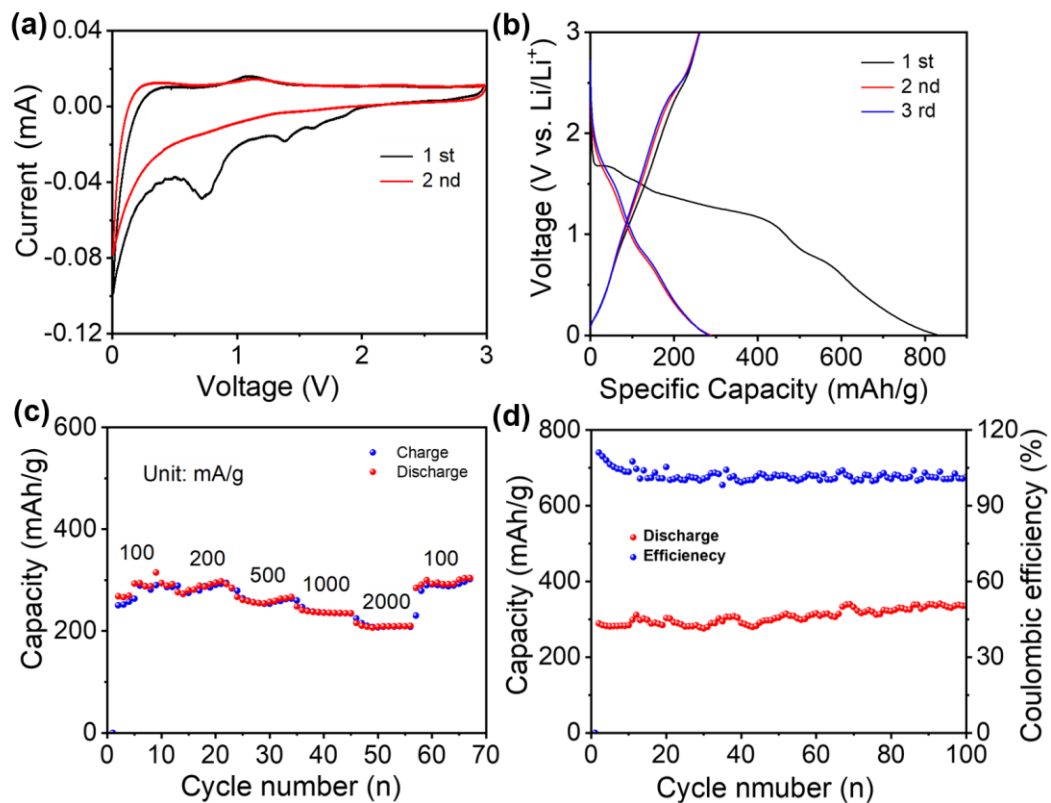
**Fig. S5** High-resolution XPS spectra of Mo 3d and P 2p peaks of PPMo<sub>12</sub>.



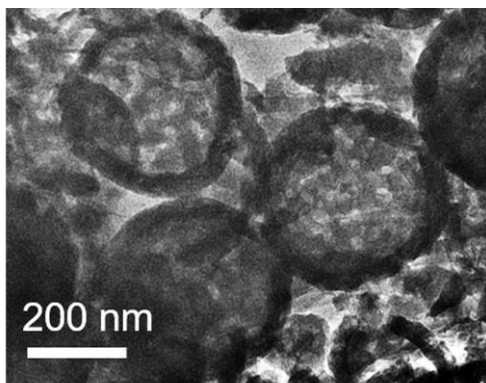
**Fig. S6** The charge-discharge profiles for different cycles of SiO<sub>2</sub>-PPMo<sub>12</sub>@rGO under 100 mA g<sup>-1</sup>.



**Fig. S7** (a) The CV of the SiO<sub>2</sub>@rGO; (b) The charge-discharge profiles for different cycles of SiO<sub>2</sub>@rGO under 100 mA g<sup>-1</sup>; (c) Rate performance of SiO<sub>2</sub>@rGO electrode; (d) Cycling performance and CE of SiO<sub>2</sub>@rGO under 100 mA/g within a voltage of 0.01-3.0 V.



**Fig. S8** (a) The CV of the SiO<sub>2</sub>-PMo<sub>12</sub>. (b) The charge-discharge profiles for different cycles of SiO<sub>2</sub>-PMo<sub>12</sub> under 100 mA g<sup>-1</sup>. (c) Rate performance of SiO<sub>2</sub>-PMo<sub>12</sub> electrode. (d) Cycling performance and CE of SiO<sub>2</sub>-PMo<sub>12</sub> under 100 mA g<sup>-1</sup> within a voltage of 0.01-3.0 V.



**Fig. S9** TEM image of SiO<sub>2</sub>-PMo<sub>12</sub>@rGO after 100 cycles at 100 mA g<sup>-1</sup>.

**Table S1.** Comparison of SiO<sub>2</sub>-PMO<sub>12</sub>@rGO with other reported SiO<sub>2</sub>- and POM-based electrodes as LIBs anode materials.

Electrode materials	Current density (mA g <sup>-1</sup> )	Capacity (mA h g <sup>-1</sup> )	Cycles	Ref.
Hollow SiO <sub>2</sub> @CN	100	800	100	1
C/SiO <sub>2</sub> /C	300	300	70	2
SiO <sub>2</sub> /C hollow spheres	100	624	100	3
H-SiO <sub>2</sub> /C	200	564	400	4
CoW-POM-Cu foam	100	737	100	5
Py-Anderson-CNTs	0.5 mA cm <sup>-2</sup>	665	100	6
PMO <sub>12</sub> -PPy/RGO	100	1000	50	7
Hollow SiO <sub>2</sub> -PMO <sub>12</sub> @rGO	100	720	100	This work

## References

1. T.T. Xiao, W.F. Zhang, T. Xu, J.X. Wu and M.D. Wei, Hollow SiO<sub>2</sub> microspheres coated with nitrogen doped carbon layer as an anode for high performance lithium-ion batteries, *Electrochim. Acta*, 2019, **306**,106-112.
2. Z.Q. Gu, X.H. Xia, C. Liu, X. Hu, Y.X. Chen, Z.Y. Wang and H.B. Liu, Yolk structure of porous C/SiO<sub>2</sub>/C composites as anode for lithium-ion batteries with quickly activated SiO<sub>2</sub>, *J. Alloy. Compd.*, 2018, **757**, 265-272.
3. X.L. Liu, Y.X. Chen, H.B. Liu and Z.Q. Liu, SiO<sub>2</sub>@C hollow sphere anodes for lithium-ion batteries, *J. Mater. Sci. Technol.* 2017, **33**, 239-245.
4. Y. Jiang, D.B. Mu, S. Chen, B.R. Wu, Z.K. Zhao, Y.Z. Wu, Z.P. Ding and F. Wu, Hollow silica spheres with facile carbon modification as an anode material for lithium-ion batteries, *J. Alloy. Compd.* 2018, **744**, 7-14.
5. K. Sun, H.Q. Li, H.J. Ye, F.Q. Jiang, H. Zhu and J. Yin, 3D-Structured Polyoxometalate Microcrystals with Enhanced Rate Capability and Cycle Stability for Lithium-Ion Storage, *ACS Appl. Mater. Interfaces*, 2018, **10**, 18657-18664.
6. L. Huang, J. Hu, Y. Ji, C. Streb and Y.-F. Song, Pyrene-Anderson-modified CNTs as anode materials for lithium-ion batteries, *Chem. Eur. J.*, 2015, **21**, 18799-18804.
7. M. Zhang, T. Wei, A.M. Zhang, S.L. Li, F.C. Shen, L.Z. Dong, D.S. Li and Y.Q. Lan, Polyoxomolybdate-polypyrrole/reduced graphene oxide nanocomposite as high-capacity electrodes for lithium storage, *ACS Omega*, 2017, **2**, 5684-5690.