Electronic Supporting Information

Formation of hexagonal-molybdenum trioxide (h-MoO₃) nanostructures and their pseudocapacitive behavior

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Figure S1. (a) TEM and (b) HRTEM micrographs of the bulk of pyramidal nanorods.

h-MoO ₃ nanostructure	Route of synthesis	Synthesis time	Reference
Agglomerated h- MoO ₃ nanorods	Reflux and drying	24 hours	[1]
h-MoO ₃ microrods	hydrothermal	~24 hours	[2]
h-MoO ₃ microrods	hydrothermal	8 hours	[3]
h-MoO ₃ microrods	MoO ₃ Hydrothermal and vacuum crorods drying		[4]
Agglomerated h- MoO ₃ nanorods	erated h- anorods Probe sonication and drying		[5]

Table S1: Comparison of the reaction time to synthesize h-MoO₃ nano/micro-structures.

IR study of pyramidal nanords, prismatic nanorods and hexagonal nanoplates:

We further established the effect of ammonium ions on the bonding between Mo and O through

IR spectroscopy as shown in Figure S2. The octahedrons (MoO₆) of MoO₃ have three different

types of oxygen atoms that can be represented as $MoO_{1/1}O_{2/2}O_{3/3}$. The effect of ammonium ions was observed on the vibration of Mo – O₂, O₂, and Mo – O₃, O₃, bonds while band corresponding to terminal oxygen (Mo = O₁) remains unaffected. The shifting of bands towards higher wave number (cm⁻¹) values for pyramidal nanorods indicates stronger bonds are presented in MoO₆ octahedrons (as discussed in TGA analysis) while the opposite trend was observed in case of hexagonal nanoplates. The band positions of entire IR spectra are shown in Table S1.



Figure S2. IR spectrums of pyramidal nanords, prismatic nanorods and hexagonal nanoplates, inset of the figure shows magnified view of the IR bands of pyramidal (1), prismatic (2) and hexagonal nanoplates (3).

Table S2: IR	vibrational	bands in	Pyramidal	nanorods,	prismatic	nanorods	and h	exagonal
nanoplates.								

Pyramidal	Prismatic	Hexagonal nanoplates	Vibration mode
702 cm ⁻¹	671 cm ⁻¹	663.2 cm ⁻¹	vMoO ₂
869.9 cm ⁻¹	851.4 cm ⁻¹	848.8 cm ⁻¹	vMoO ₃
894.7 cm ⁻¹	894.7 cm ⁻¹	894.7 cm ⁻¹	$Mo = O_1$
1438 cm ⁻¹	1412 cm ⁻¹	1412 cm ⁻¹	In plane vNH_4^+



Figure S3: In the atomic representation of h-MoO₃, MoO₆ octahedra formed by three different kinds of O atoms (purple, red and black). The MoO₆, H and N atoms are indicated by arrows.







Figure S4. Cyclic voltammograms (CVs) of (a) pyramidal nanorods, (b) prismatic nanorods and (c) hexagonal nanoplates of $h-MoO_3$ in 1 M H_2SO_4 solution in a three electrode cell configuration.



Figure S5. BET isotherm of (a) pyramidal nanorods, (b) prismatic nanorods and (c) hexagonal nanoplates, and (d) pore size distribution of pyramidal nanorods, prismatic nanorod and hexagonal nanoplates.







Figure S6. Charge / discharge profiles of (a) pyramidal nanorods, (b) prismatic nanorods and (c) hexagonal nanoplates of h-MoO₃ at various applied current densities.

Evaluation of the cycling stability of h-MoO₃ in pyramidal shape:



Figure S7. (a) FESEM micrograph of the pyramidal nanorods before cycling, (b) nanorods after 300 charge/discharge cycles of cyclic voltammetry (CV), dotted red circles indicate broken parts of the pyramidal nanorods.

Bode plot of pyramidal nanords, prismatic nanorods and hexagonal nanoplates:

Figure S7 shows the Bode plot of pyramidal nanorods, prismatic nanorods and hexagonal nanoplates in the frequency range of 100 kHz to 100 mHz. In the high frequency region, impedance remains constant, while in the low frequency region below < 10 Hz, impedance of pyramidal nanorods improves 17 % compared to prismatic nanorods attributable to a slow diffusion of electrolyte ions originates from polarization resistance (adsorbed ions screen the potential of the electrode). However, hexagonal nanoplates show higher resistance value in both regions (high and low frequency regions) of Bode plot.



Figure S8. Bode plot of pyramidal nanorods, prismatic nanorods and hexagonal nanoplates.

Table S3: Evaluation of electrochemical performance of MoO_3 in thermodynamic stable phase α - MoO_3

Material System	C_{sp} (F/g)	Current density or	No. of	Reference
		scan rate (loading	cycles	
		mass)	(stability %)	
α - MoO ₃ nanorods	30	1 mV/s (1 mg)	100 (76%)	[6]
α - MoO ₃ nanobelts	369	0.1 A/g (0.5 mg)	500 (85%)	[7]
α - MoO ₃ nanowires	95	0.2 A/g (3 mg)	600 (80%)	[8]
α - MoO ₃ nanoplates	280	1mV/s (1.5 mg)	400 (83%)	[9]
α - MoO ₃ nanoribbons	140	1.3 A/g (0.01 mg)	1000 (84%)	[10]
h – MoO ₃ nanorods	230	0.25 A/g (1 mg)	3000 (76%)	This work

References:

- 1. P. Wongkrua, T. Thongtem and S. Thongtem, J. Nanomater., 2013, 702679,8.
- 2. S. Komaba, N. Kumagai, R. Kumagai, N. Kumagai and H. Yashiro, Solid State Ionics, 2002, 319, 152.
- 3. J. Song, X. Ni, L. Gao and H. Zheng, Mater. Chem. Phys., 2007, 102, 245.
- 4. A. Chithambararaj and A. Chandra Bose, J. Alloys Compd., 2011, 509, 8105.
- 5. S. R. Dhage, M. S. Hassan and O. Bong Yang, Mater. Chem. Phys., 2009, 114, 511.
- 6. I. Shakir, M. Shahid, H. W. Yang, D. J. Kang, *Electrochim. Acta*, 2010, 56, 376–380.
- J. Jiang, J. Liu, S. Peng, D. Qian, D. Luo, Q. Wang, Z. Tian, Y. Liu, J. Mater. Chem. A, 2013, 1, 2588
- 8. R. Liang, H. Cao, D. Qian, Chem. Commun., 2011, 47, 10305-7.
- 9. W. Tang, L. Liu, S. Tian, L. Li, Y. Yue, Y. Wu, K. Zhu, Chem. Commun., 2011, 47, 10058-60
- 10. Q. Mahmood, W. S. Kim, H. S. Park, Nanoscale, 2012, 4, 7855-60