Supporting Information

Time Dependent Exfoliation Study of MoS₂ for its use as Cathode Material in High Performing Hybrid Supercapacitors

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Scheme S1. Schematic of the synthesis route for WO₃

c:\edax32\genesis\genspc.spc 30-Jun-2022 10:33:31 Chlorite (Nrm.%= 38.86, 20.96, 34.83, 1.14, 3.84, 0.28) LSecs : 35	Element	Wt %	At %
1.3 - MoL 1.0 - SK			
0.8 -	ОК	34.36	73.02
KCnt 0.5 -	MoL	59.99	21.26
0.3 - Мом	S K	05.26	05.58
0.0 2.00 4.00 6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00	MoK	00.39	00.14

Fig. S1 EDAX analysis of 5 h exfoliated MoS_2 sample



Fig. S2 (a) XRD Profile, (b) BET isotherm, BJH loop (inset), (c) SEM and (d) TEM micrographs of WO₃ nanoparticles

The structural property of the as-synthesized WO₃, was studied by XRD as shown in Fig. S2 (a). The XRD pattern exhibited crystalline nature with peaks, which were in good agreement with the JCPDS card no. 05-0363. The diffraction peaks at $2\theta \sim 23.1^{\circ}$ (002), 23.7° (020), 24.2° (200) and 34.1° (202) readily corresponds to the monoclinic phase of WO₃ with lattice parameters a = 7.31 Å, b = 7.53 Å, and c = 7.69 Å. The BET surface area of WO₃ nanoparticle was determined using N₂ adsorption/desorption isotherm, as shown in Fig. S2 (b). According to Brunauer classification, the synthesized nanostructures exhibited type-IV isotherm characteristic behaviour with surface area and pore radius recorded as 114.1 m² g⁻¹ and 1.60 nm respectively. SEM was used to examine the morphology of WO₃ nanostructures. Flakes like morphology, with uniform distribution, was confirmed from image shown in Fig. S2 (c). Also, transmission electron microscopy images (Fig S2. (d)) corroborated with the formation of flakes like structure.



Fig. S3 (a, b) Quantification graphs and (c, d) voltammetric charge variation of MoS₂ based electrode in three different electrolytes

The total specific capacitance is a combination of double layer capacitance and pseudocapacitance. In different electrolytes the respective contributions are different, which leads to the variation in the overall performance. For MoS_2 based working electrode, the electrochemical reaction at the surface and interfaces i.e. non Faradaic and Faradaic process are mentioned below (H₂SO₄, Na₂SO₄ and KOH electrolytes, respectively).

The electrochemical reaction of de-intercalation and intercalation mechanisms can be written as:

$$MoS_{2} + H^{+} + e^{-} \rightarrow (MoS - HS)_{Faradaic \ process}$$
$$(MoS_{2})_{surface} + H^{+} + e^{-} \rightarrow (MoS_{2} - H^{+})_{Surface \ (non \ Faradaic \ process)}$$
$$MoS_{2} + Na^{+} + e^{-} \rightarrow (MoS - NaS)_{Faradaic \ process}$$

$$(MoS_{2})_{surface} + Na^{+} + e^{-} \rightarrow (MoS_{2} - Na^{+})_{Surface (non Faradaic process)}$$
$$MoS_{2} + K^{+} + e^{-} \rightarrow (MoS - KS)_{Faradaic process}$$
$$(MoS_{2})_{surface} + K^{+} + e^{-} \rightarrow (MoS_{2} - K^{+})_{Surface (non Faradaic process)}$$

From the CV and charge-discharge profiles of MoS₂ in three different electrolytes, the charge storage mechanisms are quite clear. In both the neutral and alkaline electrolytes i.e. Na₂SO₄ and KOH, the nearly symmetric CV and triangular CD profile suggest dominant double layer charge storage on the surface of the electrode. While in the acidic H₂SO₄ electrolyte, the prominent redox peaks in CV and the asymmetric CD profile indicate the increase in the Faradaic combinations at the electrode electrolyte interface, resulting in enhanced overall specific capacitance value. To visualize it, a quantification study was performed for MoS₂ based electrode in all three electrolytes and the corresponding results are shown in Fig. S3(a, b). By the extrapolation of fitted linear line point towards zero scan rate. The double layer and pseudocapacitance in the acidic electrolyte can be clearly observed from this figure. MoS₂ showed ~75, 66 and 57% pseudocapacitance value in H₂SO₄, Na₂SO₄ and KOH electrolytes, respectively. The higher Faradaic reaction was also evident from the larger current value and higher overall specific capacitance value in acidic electrolyte, as discussed earlier in the manuscript.

To further understand the charge storage mechanism, the voltammetric charge accumulated on the electrode surface was estimated in various electrolytes using the following formula:

$$q^* = \frac{\int i dV}{Av}$$

where, i, V, A and v represent the voltammetric current, potential, area of the electrode, and scan rate, respectively. The voltammetric charge showed a decreasing trend with the scan rate in all the electrolytes, as shown in Fig. S3(c). Theoretically, at an infinite scan rate, only the outer region of the electrode becomes accessible to the ions. The charge accumulated, known as outer voltammetric charge can be estimated, as shown in Fig. S3(d). The outer voltammetric charge of MoS₂ in H₂SO₄, Na₂SO₄ and KOH electrolytes were estimated to be 0.161, 0.049, 0.022 C cm⁻², respectively. Hence, the quantification and voltammetric charge estimation corroborate well with the other electrochemical results. This study gives an idea about the charge storage mechanism of MoS₂ in different electrolytes. The higher capacitance and charge accumulation in H₂SO₄ electrolyte can be attributed to the enhanced redox reactions at the electrode-electrolyte interface.

The pseudocapacitance can vary in different electrolytes due to a number of factors such as radius of electrolyte ions, hydration radius of electrolyte ions, conductivity, mobility, etc. MoS_2 based electrode showed higher specific capacitance in H_2SO_4 electrolytes compared to KOH and Na_2SO_4 due to the smaller ionic size of H⁺ compared to that of the K⁺ and Na⁺. The smaller ionic radius of H⁺ increases the ionic mobility in the electrolyte solution, resulting in faster ion diffusion and overall improvement in the specific capacitance value. Further, Na⁺ has lower ionic radius compared to K⁺. Although K⁺ possesses higher ionic mobility and molar conductivity, presence of two cations in Na₂SO₄ electrolyte can increase the electrochemical activity of MoS_2 , superseding the performance of single cation based KOH electrolyte. Therefore, the overall performance trend of MoS_2 supercapacitor in different electrolytes was found to be H₂SO₄> Na₂SO₄>KOH.



Fig. S4 (a) CV, (b) CD, (c) specific capacitance variation with scan rate, (d) specific capacitance variation with current density, (e) quantification graph and (f) cycling Stability of WO_3 in 1 M H_2SO_4



Scheme S2 Schematic of (a) $MoS_2//WO_3$ supercapacitor device, (b) Coin cell fabrication process



Fig. S5 a) CV, (b) CD, (c) specific capacitance variation with scan rate and (d) specific capacitance variation with current density of MoS₂//WO₃ device in 1 M H₂SO₄



Fig. S6 Fitted Nyquist plot with equivalent circuit model for (a) 5 h exfoliated MoS₂, (b) 3 h exfoliated MoS₂, (c) pristine MoS₂ and (d) MoS₂//WO₃ device



Fig. S7 SEM images of (a) 5 h, (b) 6 h exf MoS_2 and (c) CV profiles of 5 h and 6 h exf MoS_2



Fig. S8(a) $MoS_2//WO_3$ device, (b) 9 device stacked together, (c) LED strips, (d) toy candle

Table S1. Series resistance and charge transfer resistance for pristine MoS_2 , 3 h exfoliated MoS_2 , 5 h exfoliated MoS_2 samples respectively

Electrode	Electrolyte	Charge transfer Resistance (Ω)	Series Resistance (Ω)	
Pristine MoS ₂	1 M H ₂ SO ₄	0.6	3.3	
$3 h exf. MoS_2$	1 M H ₂ SO ₄	0.4	2.7	
$5 h exf. MoS_2$	1 M H ₂ SO ₄	0.3	1.6	

Table S2. Series resistance, Warburg resistance and charge transfer resistance for 5 h exf. $MoS_2 /\!/WO_3$ device

Device	Electrolyte	Series Resistance ESR (Ω)	Warburg Impedance (Ω)	Charge transfer Resistance (Ω)
MoS ₂ //WO ₃	1 M H ₂ SO ₄	1.89	17.8	15.78