Electronic Supplementary Information (ESI)

Generalized synthesis and evaluation of formation mechanism of metal oxide/sulphide@C hollow spheres

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Detailed synthetic procedure:

Experimental Section:

Chemicals. Ammonium heptamolybdate tetrahydrate $[(NH4)_6Mo_7O_{24} 4H_2O, 99.98\%,$ Sigma-Aldrich], Zinc(II) Nitrate hexahydrate $[Zn(NO_3)_2 6H_2O,AR]$, Iron(II) Sulphate heptahydrate $[FeSO_4 7H_2O, Merck]$, Ammonium metavanadate (NH_4VO_3, SRL) Cetyltrimethylammonium bromide (CTAB, Sigma-Aldrich), Succrose $(C_{12}H_{22}O_{11}, LR)$, Ammonium carbonate $(NH_4HCO_3\&NH_2CO_2NH_4, AR,SDF)$, Potassium ethyl xanthogenate(C₃H₅kOS₂, Sigma-Aldrich), Methanol extra pure (MeOH, AR,SRL)

Synthesis:

Hollow spheres synthesis was performed in hydrothermal conditions. In a simple experimental procedure, CTAB was dissolved in deionised water with constant stirring. After that sucrose was added to the solution. Sucrose binds with CTAB through electrostatic and H-bonding interaction. After that we added salt precursors and Potassium ethyl xanthogenate as sulphur sources. We have proved the binding interaction of CTAB, sucrose, and various salt molecules through isothermal titration calorimetry (ITC), particle size analyser. For hydrothermal synthesis we used a 50 ml Teflon line autoclave.

Synthesis of MoS₂ Hollow Spheres:

In a typical experiment 0.195 g of CTAB was dissolved in 35 ml deionised water. Then, aqueous solution (5ml) of 0.228 g/ 1.091g/ 2.06 g sucrose was added to the CTAB solution. After stirring for 5 minutes clear solution was obtained. Separately, 0.33 g of ammonium heptamolybdate tetrahydrate was dissolved in 5ml deionised water and this aqueous salt solution was added to the CTAB-Sucrose solution drop wise and a white precipitate appears. Addition of aqueous ammonium carbonate solution (1g in 5ml) made the solution clears again. 0.598 g Xanthate solution (2 ml) was added drop wise to the bulk solution and yellowish ppt appear due to metal Xanthate complexation. The pH of the solution was adjusted to 10 by adding 30% ammonium hydroxide solutions. After stirring for 10 min, 33 ml of the obtained turbid solution was transferred to a 50 ml Teflon- lined stainless steel autoclave and sealed tightly, heated at 130 °C for 12 h followed by 220 °C for 12 h. After cooling naturally, the obtained black precipitate was collected, washed with deionised water followed by methanol and dried at 70 °C for 24 h. The MoS₂@C composite were obtained after calcination of the dried material at 800 °C for 5h in a stream of 5% H₂ and 95% N₂ at a scan speed of 5 °C / min. In order to investigate the effect of sucrose and CTAB on the formation of hollow sphere, additionally the control experiments were performed without using CTAB or sucrose.

Synthesis of MoO₂ Hollow Spheres:

0.195 g of CTAB was dissolved in 35 ml water. Then, aqueous solution (5ml) of 0.228 g/ 1.091g/ 2.06 g. sucrose was added to the CTAB solution. After stirring for 5 minutes, separately prepared 0.33 g (0.267mole) of (NH4)₆Mo₇O₂₄ 4H₂O in 5 ml water was added to the solution mixture drop wise. Faint white precipitate appears which was disappeared on

addition of ammonium carbonate solution (1g in 5ml). After stirring for 10 min, 33ml of the obtained clear solution was transferred to a 50 ml Teflon- lined stainless steel autoclave and sealed tightly, heated at 130 °C for 12 h, followed by 220 °C for 12 h. After cooling naturally the black precipitate were collected, washed with deionised water followed by methanol and dried in oven at 70 °C for 24 h. The MoS₂@C composite were obtained after calcination of the dried material at 800 °C for 5h in a stream of 5% H₂ and 95% N₂ at a scan speed of 5 °C / min.

Synthesis of Fe₃O₄ Hollow Spheres:

0.195 g of CTAB was dissolved in 35 ml water. Then, aqueous solution (5ml) of 0.228 g/1.091 g/2.06 g sucrose was added to the CTAB solution. After stirring for 5 minutes, separately prepared 1.042 g of FeSO₄ 7H₂O was added to the solution mixture and resulted a brown turbid solution. Then, a 1g ammonium carbonate in 5 ml solution was added to it and stirred for 10 min. The 33ml of resultant solution was transferred in to the 50 ml Teflon- lined stainless steel autoclave and sealed tightly, heated at 180 °C for 24 h. After cooling naturally the black precipitates were collected washed with deionised water followed by methanol and dried in oven at 70 °C for 24 h. The Fe₃O₄@C composite were obtained after calcination of the dried material at 500 °C for 3h in a stream of 5% H₂ and 95% N₂ at a scan speed of 5 °C / min.

Synthesis of ZnS Hollow Spheres:

0.1948 g of CTAB was dissolved in 35 ml water. Then aqueous solution (5ml) of 0.228 g/1.091 g/2.06 g sucrose was added to the CTAB solution. After stirring for 5 minutes separately prepared 0.555 g of Zn (NO₃)₂ $6H_2O$ in 5 ml water was added to the solution mixture drop wise. White precipitate appears which on addition of ammonium carbonate solution (1g in 5ml) become clear. 0.5984 g Xanthate solution (2 ml) was added drop wise to the solution and yellowish precipitate appear due to metal Xanthate complexation. 30%

 NH_4OH solution was added to adjust the pH to 10 .After stirring for 5 min the obtained turbid solution was transferred to a 50 ml Teflon- lined stainless steel autoclave and sealed tightly, heated at 130 °C for 8 h . After cooling naturally, the precipitate were collected, washed with deionised water followed by methanol and dried in oven at 70 °C for 24 h. The ZnS@C composite were obtained after calcination of the dried material at 400 °C for 4h in a stream of 5% H₂ and 95% N₂ at a scan speed of 5 °C / min.

Synthesis of V₂O₃ hollow sphere:

0.1948 g of CTAB was dissolved in 30 ml water. Then, aqueous solution (5ml) of 0.228 g/1.091 g/2.06 g sucrose was added to the CTAB solution. After stirring for 5 minutes separately prepared 0.218 g of NH₄VO₃ salt in 5 ml water was added to the solution mixture drop wise. After stirring for 10 min the obtained clear solution was transferred in to the 50 ml Teflon- lined stainless steel autoclave and sealed tightly, heated at 220 $^{\circ}$ c for 24 h. After cooling naturally the black precipitate were collected washed with deionised water follow by methanol and dried in oven at 70 °C for 24 h. The V₂O₃/C composite were obtained after calcination of the dried material at 800 °C for 4h in a stream of 5% H₂ and 95% N₂ at a scan speed of 5 °C / min.

Characterizations:

Powder X-ray diffraction patterns were recorded in the 2 θ range of 2-80 on a Philips X'pert X-ray powder diffractometer using Cu K α (λ = 1.54178 Å) radiation. Thermo gravimetric analysis (TGA) was performed on Mettler-Toledo (TGA/SDTA 851e) in air at a heating rate of 10 °C/min. The nitrogen adsorption - desorption measurements at 77 K were performed on ASAP 2010 Micromeritics, USA, after degassing samples under vacuum (10-2 torr) at 250 °C for 4 h. The surface area was determined by Brunauer-Emmett-Teller (BET)

equation. Pore size distributions were determined using BJH model of cylindrical pore approximation. A scanning electron microscope (SEM) (Leo series 1430 VP) equipped with INCA was used to determine the morphology of samples. The sample powder was supported on aluminum stubs and then coated with gold by plasma prior to measurement. Transmission electronic microscope (TEM) images were collected using a JEOL JEM 2100 microscope and samples were prepared by mounting an ethanol dispersed samples on lacey carbon formvar coated Cu grid. The obtained average size of the CTAB-Sugar solution through DLS measurement were recorded in Malvern instrument (Zetasizer, Nano series, Nano-ZS90). Calcination of the powdered samples was carried out in High Temperature Vacuum Tube Furnace (MTI, OTF-1200X). Isothermal calorimetric titration was carried out in Microcal iTC200.

Electrochemical measurements:

Electrochemical properties of the synthesized hollow sphere shaped MoS₂@C nanoparticles were evaluated in 2032 type coin cells vs Li/Li+. A typical electrode was prepared from a slurry consisting of MoS₂@C nanoparticle powder (70 wt%), acetylene black (20 wt%) and PVDF binder (10 wt%) in n-methyl pyrrolidinone (NMP) solvent. The slurry was coated onto a 15 μ m thick copper foil (current collector) and dried at 110°C in an oven for 12 h. After pressing the coated foil at 4.0 ton inch⁻², circular disks of 15 mm in diameter were cut and used as electrode. Typical weight of the active material (excluding acetylene black and PVDF) was 3-5 mg. Coin cells were assembled with these electrodes using Li metal as counter as well as reference electrode, LiPF₆ in EC: DMC (1:2 vol%) as electrolyte and Celgard 2300 as separator within an argon filled glove box (M'BRAUN, Germany) where the moisture and oxygen levels were both kept below 1.0 ppm. Gavanostatic charge-discharge measurements were carried out using an automatic battery tester (Model: BT2000, Arbin, USA) in the potential window of 0.01- 3.0 V with a constant current density of 50

mAg⁻¹ for the initial formation cycle and at different current densities ranging from 150 mAg⁻¹ to 1.0 Ag⁻¹ for subsequent cycles. Same current density was for both discharge and charge in every case. Cyclic voltammetry was performed with a galvanostat-potentiostat (Model: PGSTAT 302N, Autolab, the Netherlands) in the potential window of 0.01-3.0 V at a scan rate of 0.1 mVs⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were carried out with the same galvanostat-potentiostat in the frequency range of 10 mHz-1.0 MHz at open circuit potential with an AC amplitude of 10 mV.





Due to carbon incorporation in the inside of the MoS_2 layers the interlayer spacing in between two neighbouring MoS_2 layers was increased and *in-turn* the XRD peak position of (002), for interlayer spacing, was shifted from 2θ =14.2 to 9.3. Due to the generation of carbon layer in between two MoS_2 layers, a new peak at 2θ =17.8 was generated, representing inter carbon- MoS_2 layers.



Fig. S1 XRD data of as-synthesized MoS_2 with varying amount of carbon content.



Fig. S2 SEM images of as synthesized spheres with varying amount of carbon. MoS₂@C-1 (a.b), MoS₂@C-2 (c.d), MoS₂@C-3 (e.f),



Fig. S3 The TEM images of synthesized pure MoS_2 , i.e., without carbon.





The TG carve reveals that the materials synthesized with Mo to sucrose molar ratio of 1:1 contain 10 %carbon (a), 1:2 contain 16% carbon (b) and (c) 1:3 contain 32% carbon.



Fig. S5 XPS spectra of the synthesized MoS₂@C-3.

In order to analyse the chemical and oxidation states, XPS was performed. In the full-scale XPS spectrum of the MoS₂@C-3 composite, presence of peaks for C, Mo and S in the respective binding energies confirm the presence of C, S and Mo (**Fig. S6a**). In the high resolution spectra, the corresponding peaks in the reason 294-280 eV, indicates considerable deoxygenation of carbon and formation of oxidised graphitic carbon in certain extent (**Fig. S6b**)¹. The Mo 3d XPS spectrum (**Fig. S6c**) shows two strong peaks 229.5 and 232.6 eV corresponding to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ respectively, which are characteristic of Mo⁴⁺ in MoS₂.^{2,3} However, a very little tailing spectra at about 236 eV for Mo $3d_{3/2}$ and Mo $3d_{5/2}$ in the composite are likely due the existence of a small amount of Mo⁶⁺ (ref: Nano Lett. 2011, 11, 4168). Existence of Mo⁶⁺ is may be due to the presence of very little amount of un-sufidated product in the form of MoO₃. The small peak in lower binding region of Mo at 226 eV can be assigned to S 2s. The peaks at 162.1 and 163.3 eV, corresponding to the S $2p_{3/2}$ and S $2p_{1/2}$ shift toward higher binding energies indicating that electron transfer occurs in the hybrid structure of the MoS₂/C sample.^{4,5} Thus it can be concluded that MoS₂ nanosheets are combined more tightly with the carbon matrix.

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Fig. S6 (a) SEM image of MoS_2 in presence of only sucrose, (b) TEM image of MoS_2 in presence of only CTAB.



Fig. S7 The obtained average size of soft templet *in-situ* formed through the CTAB-Sugar interaction obtained in the DLS measurement.



Fig. S8 FT-IR spectra of sucrose, CTAB, sucrose + CTAB and sucrose + CTAB + ammoniumheptamolybdate (salt)



Figure S9 Rate performance of MoS₂-C (32%) at different current densities

Table S1Impedance data for as-assembled cells fitted with the equivalent circuit shownin Fig.3c.

Sample	MoS ₂ @C(10%)	MoS ₂ @C(16%)	MoS ₂ @C(32%)
Rs (Ohm)	3.5	2.9	2.9
Rct (Ohm)	415.6	169.7	159.2
CPE (µF)	14.1	14.1	15.7
W (Ohm)	43.4	34.7	37.1