

Supporting information

Improved electrochemical performance of SnO₂ - mesoporous carbon hybrid as a negative electrode for lithium ion battery applications

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A unified view of SnO₂ nanoparticle location in mesoporous carbon (CMK-5)

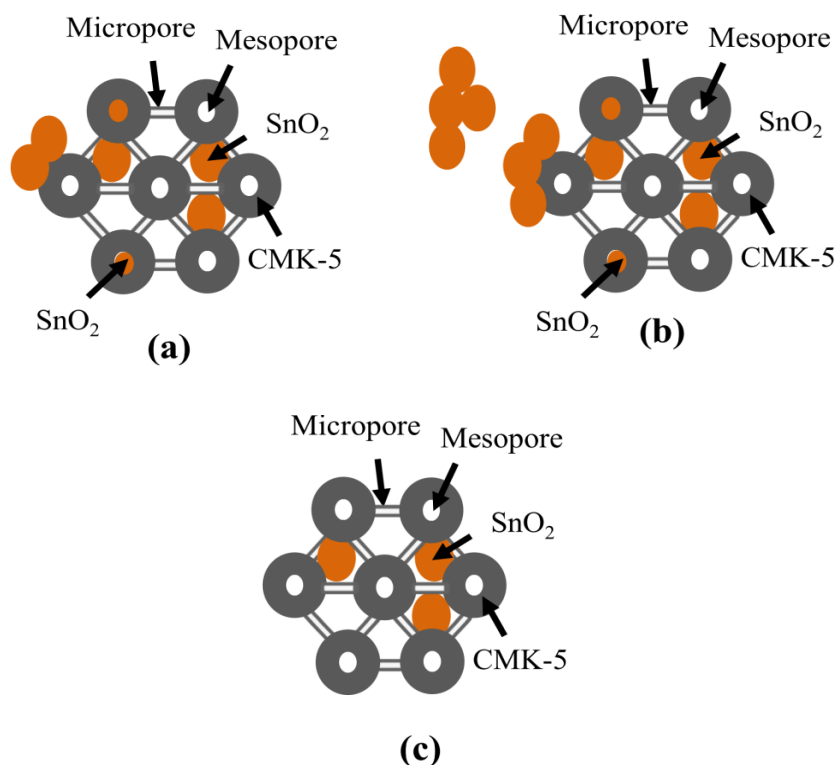


Fig. S1 A unified view of different possible SnO₂ nanoparticle location in mesoporous carbon (CMK-5) particles, based on reports in the literature.^{4,20-23} SnO₂ formation (a) both inside and on the outer surface of mesopores, present within a CMK-5 particle; (b) on both these surfaces, and in addition, also as isolated SnO₂ nanoparticles; (c) only on the outer surface of mesopores, present within a CMK-5 particle (as developed in the present work).

Among SnO₂-CMK family of electrodes reported so far,^{4,20-23} different synthesis approaches have led to the formation of SnO₂ nanoparticles in different regions of the CMK particles. In a recent report,²⁰ surface of CMK family is modified to allow the tin precursors inside the pores of mesoporous carbon, which leads to SnO₂ nanoparticles inside the pores during heating at high temperature under inert atmosphere. As a result, SnO₂ nanoparticle

formation occurs on the both inside and outer surface of mesopores, present within CMK-5 (Fig. S1a).

In other reports,²¹⁻²³ tin precursor is mixed with preformed CMK particles during the synthesis process of SnO₂-CMK hybrids. This synthesis protocol may lead to allow the tin precursor to diffuse inside and outer surface of the mesopores present in the CMK-5 or between the carbon rods in CMK-3. In addition, there is a possibility for aggregation of SnO₂ nanoparticles in the bulk state. (Fig. S1b).

The present work focuses on the formation of SnO₂ nanoparticles on the outer surface of mesopores, present within CMK-5. (Fig. S1c). SnO₂ nanoparticles present on outer surface of mesopores will utilize the empty space created (after removal of SBA-15 by HF solution) in the CMK-5 particle for volume expansion during charging-discharging cycles. This strategy used in this material design would be a good platform to explore better electrochemical performance for the SnO₂-CMK-5 family, as well as other metal/metal oxide nanoparticle-ordered porous material hybrid.

Percentage removal of SBA-15 and SnO₂ by HF solution

Aqueous HF solution (20% by vol.) is capable of removing SBA-15 as well as SnO₂. Three samples (only SnO₂ nanoparticles, carbon coated SBA-15 particles and carbon coated SnO₂-SBA-15 particles) were chosen for finding the percentage of SnO₂ and SBA-15 removal during leaching process. First, carbon coated SBA-15 particles were stirred with HF for 30 min. After 30 min, there was no silicon (Si) present in the treated sample (confirmed by SEM-EDX). From this analysis, it is clear that 100 wt. % SBA-15 is removed within 30 min from carbon coated SBA-15 sample. Similarly, the percentage of weight loss (by

gravimetry after 30 min) of only SnO₂ nanoparticle and of SnO₂ particle from carbon coated SnO₂-SBA-15 is 4.7 wt% and 1.2 wt. %, respectively. Therefore, even though the SnO₂-CMK-5 hybrid sample contains nanostructured SnO₂, the percentage removal of SnO₂ is very less in comparison to silica in the carbon coated SBA-15.

Thermogravimetric analysis of SnO₂-CMK-5

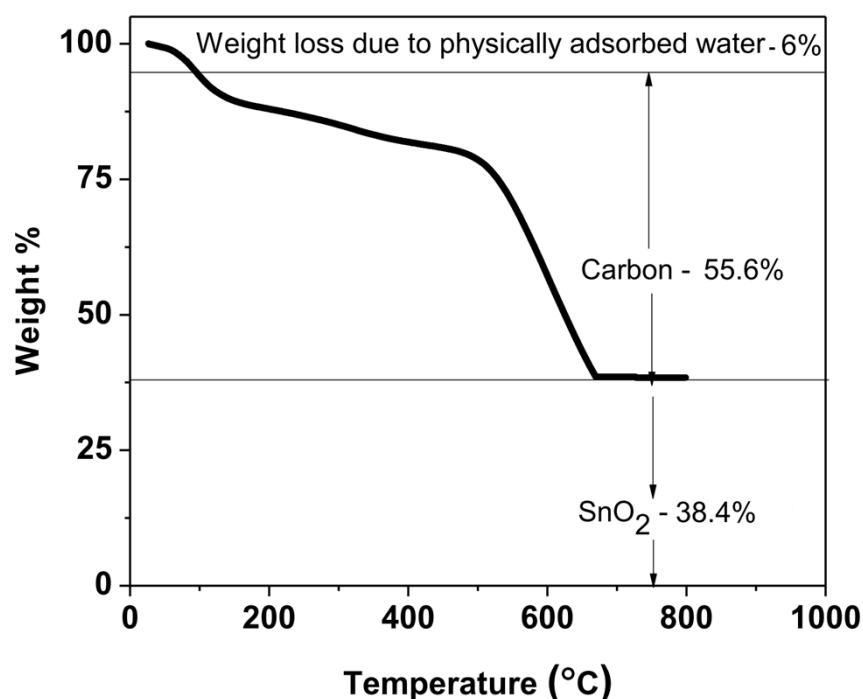


Fig. S2 Thermogravimetric analysis (TGA) profile for SnO₂-CMK-5.

Thermogravimetric analysis (TGA), carried out at a heating rate of 10 K min⁻¹, in the presence of air, was used to calculate the percentage of SnO₂ in SnO₂-CMK-5 sample. Before TGA analysis, there will be some amount of physically adsorbed moisture in the sample. The amount of water (6 wt.%, as shown in the Fig. S2 as the initial hump around 100 °C) is not considered for calculating SnO₂ amount in the final, dried SnO₂-CMK-5 hybrid sample. From the TGA graph, measured SnO₂ amount is 38.4 wt.% (including water content).

So, the calculated SnO₂ amount, based on excluding water content, is 40.9 wt. %. Therefore, this SnO₂ amount of 40.9 wt.%. (excluding water), is used for calculating theoretical specific capacity of hybrid.

EDX analysis of SnO₂-SBA-15 and SnO₂-CMK-5

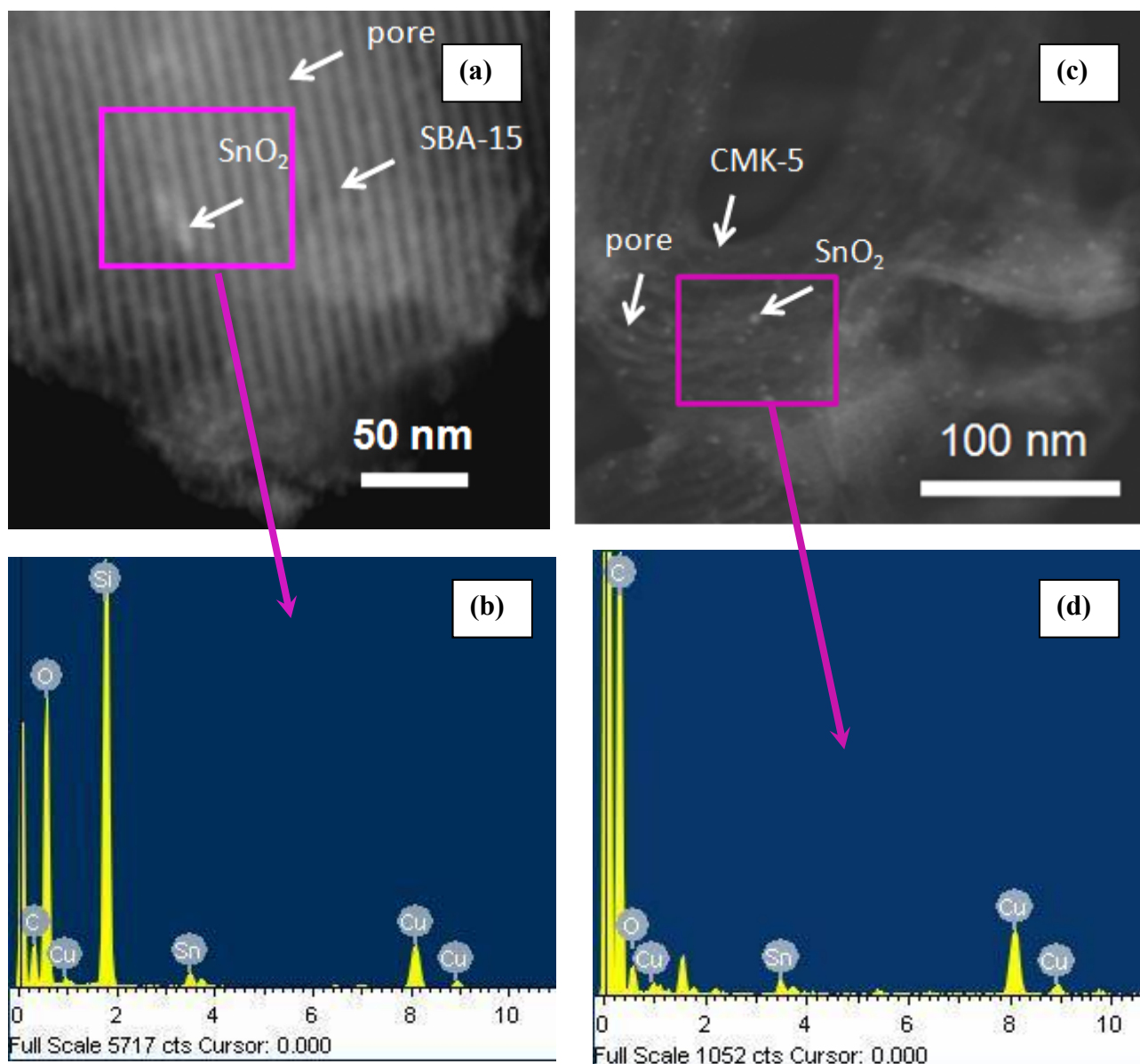


Fig. S3 (a) Dark field TEM image of SnO₂-SBA-15 hybrid (b) EDX spectrum of selected area of SnO₂-SBA-15 hybrid [from Figure S2 (a)]. (c) Dark field TEM image of SnO₂-CMK-5 hybrid (b) EDX spectrum of selected area of SnO₂-CMK-5 hybrid [from Figure S2 (c)].

Columbic efficiency of SnO₂, CMK-5 and SnO₂-CMK-5 electrodes

It is clearly seen from fig. S4 that the experimentally obtained columbic efficiency of first cycle is 55.8 % for SnO₂-CMK-5, 40.5 % for SnO₂ and 29% for CMK-5. From first cycle onwards, there is always an increase in columbic efficiency from 85 to 98 % in all electrodes. The reason for lower columbic efficiency in the first cycle is irreversible capacity, which arises mainly due to SEI and Li₂O formation.

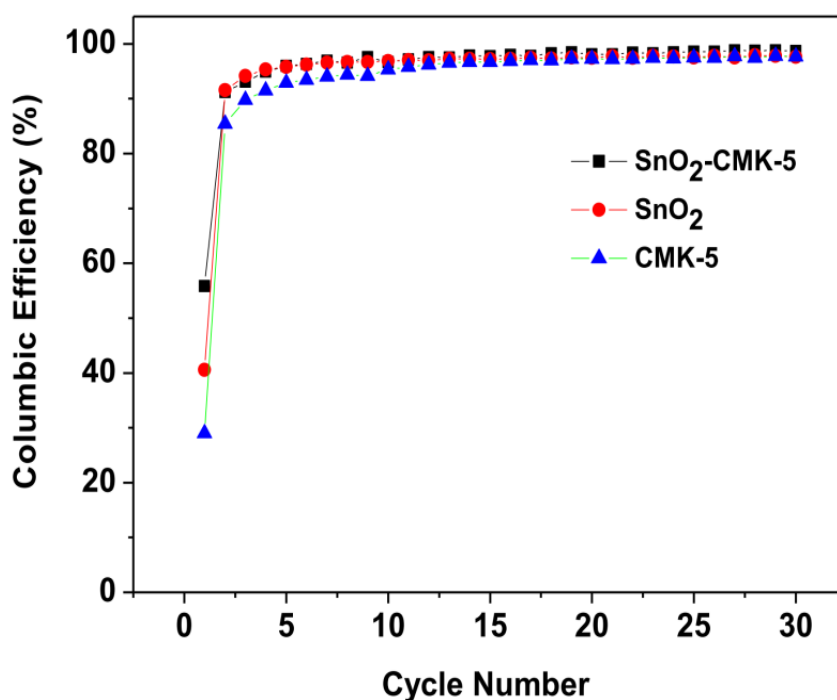


Fig. S4: Columbic efficiency of SnO₂, CMK-5 and SnO₂-CMK-5 electrodes

After the first cycle, columbic efficiency of all electrodes is drastically increased, due to negligible amount of further SEI formed in the subsequent cycles. However, it does not achieve up to 100% efficiency, as some SEI is still remaining. The above trend in the columbic efficiency plot is not only observed in the present case, but is also seen in other reports in the literature.²³

Volume changes during lithiation/delithiation

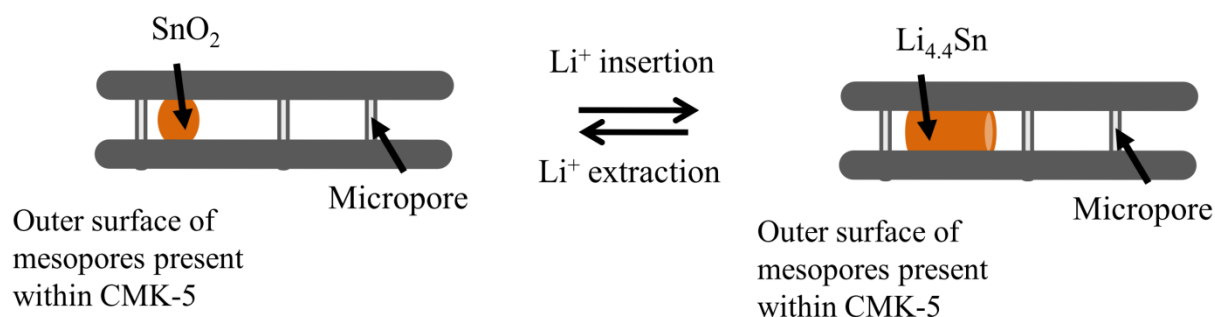


Fig. S5 Schematic representation of volume change during Li⁺ insertion /extraction

The empty space between the ordered mesopores helps SnO₂ nanoparticle to expand freely during the cycling process and also prevents electrode deterioration. The impact of CMK-5 during cycling is shown in fig where SnO₂ nanoparticles can expand along the mesochannels present in the CMK-5 during Li⁺ insertion and contract during Li⁺ extraction. Furthermore, CMK-5 channels can facilitate fast electron transport during the cycling process.

Comparison of electrochemical performance of SnO₂-CMK-5 of our present work with other reports in the literature

Table S1 above shows a comparison of cyclic performance of SnO₂-mesoporous carbon (CMK-5) with different forms of carbon based SnO₂ electrodes in recent studies. The entries in the above table have been arranged according to the following sequence of electrode materials: (i) nanostructured SnO₂ electrodes (ii) CMK electrodes and (iii) SnO₂-CMK-5 electrodes with different forms of carbon.

Table S1: Comparison of cyclic performance of SnO₂-CMK-5 electrode from present work with different forms of carbon based SnO₂ electrodes in recent literature.

Type of material	Current density (mA g ⁻¹)	Cycling Performance		Initial efficiency (%)	Voltage range (V)	Reference
		No of cycles	Reversible capacity (mAh g ⁻¹)			
SnO ₂ nanoparticles (~7nm)	178	30	42	40.5	0.02-3	Present work
SnO ₂ nanowire (~40 - 60 nm diameter; length more than 1 μm)	782	50	510	37.4	0 -1.2	[9]
SnO ₂ nanotube (180 nm diameter; 450 nm length)	100	30	468	40.4	0.005-1.5	[17]
Mesoporous carbon (CMK-3)	100	20	350	40.1	0.005-3	[18]
Mesoporous carbon (CMK-5)	178	30	218	29	0.02-3	Present work
SnO ₂ -mesoporous carbon	100	60	425	46	0.01-3	[22]
SnO ₂ -mesoporous carbon	100	100	593	65.3	0.01-3	[23]
SnO ₂ -mesoporous carbon	178	30	598	55.8	0.002-3	Present work
SnO ₂ -graphene	100	30	626	49	0.01-2	[13]
SnO ₂ -graphene	50	30	570	43	0.05-2	[12]
Carbon coated SnO ₂ nanotube	100	30	492.5	53.1	0.01- 2	[16]
Mesoporous SnO ₂ -MWNT	33.3	50	345	74	0.005-2	[14]
Carbon coated mesoporous SnO ₂	160	65	500	37.3	0.005-2.5	[8]
SnO ₂ /Ferrocene -SWNT	150	40	905	60	0.05-3	[10]

The objective is to highlight the most important parameters such as current density, reversible specific capacity, operated voltage range and initial efficiency. SnO₂ nanoparticles synthesized in the present work show poor reversible specific capacity (42 mAh g⁻¹) in comparison to SnO₂-CMK-5 (598 mAh g⁻¹) and CMK-5 (218 mAh g⁻¹) electrodes synthesized in this work, at the same current density (178 mA g⁻¹). The reason for better reversible specific capacity in case of SnO₂-CMK-5 is that CMK-5 plays an important role in accommodating volume expansion during cycling performance.

In a recent report,⁹ SnO₂ wire electrode showed reversible specific capacity of 510 mAh g⁻¹ after 50 cycles, at a current density of 782 mA g⁻¹, over an applied voltage of 0 - 1.2 V. The applied voltage range in the above report is less in comparison to other reports in literature,⁹⁻¹⁸ which helps in achieving a high reversible specific capacity, at a high current density. Generally, capacity fading is drastic for the SnO₂ system, when it is operated above 1.3 V.³⁴ This phenomenon occurs mainly due to deterioration of Li₂O at 1.3 V. In the present work, stable cyclic performance is achieved over a wide voltage range of 0.002V-3V, confirming the value in adding CMK-5.

In a few reports,^{12,13} carbon coating or addition of other forms of carbon (graphene, carbon nanotube) is done with SnO₂ nanostructures, in order to accommodate volume expansion during cycling process. Among all carbon based SnO₂ electrodes in table S1, the performance of SnO₂-CMK-5 electrode is reasonably good, in terms of applied potential range, reversible capacity and current density.

In another recent report,¹⁰ ferrocene was introduced inside a single wall carbon nanotube (SWNT) and subsequently SnO₂ nanoparticles were attached on ferrocene-SWNT hybrid. The role of ferrocene in the hybrid is that of an electron mediator. It shows slightly better performance (reversible specific capacity of 905 mAh g⁻¹, at a current density of

150 mA g⁻¹ and initial efficiency of 60%), compared to the SnO₂-CMK-5 electrode synthesized by us, the latter has a reversible specific capacity 598 mAh g⁻¹, at a current density of 178 mA g⁻¹, and initial efficiency of 58.8 %.

Theoretical specific capacity calculation

Present work

A simple calculation is done to estimate the theoretical specific capacity of our synthesized SnO₂-CMK-5 electrode.²²

TS - Theoretical capacity of SnO₂ (782 mAh g⁻¹)

TC - Theoretical capacity of CMK-5 (430 mAh g⁻¹)

MS – Wt. % of SnO₂ (41%)

MC – Wt. % of CMK-5 (59%)

So, theoretical capacity of SnO₂-CMK-5 = ((TS x MS) + (TC x MC)

$$= [(782 \times 0.41) + (430 \times 0.59)] \text{ mAh g}^{-1}$$

$$= 574.32 \text{ mAh g}^{-1}$$

Now, the experimentally measured specific capacity of SnO₂-CMK-5 in the present work is 598 mAh g⁻¹, which is slightly higher than the calculated theoretical capacity of 574 mAh g⁻¹. This excess capacity contribution may be due to electrolyte decomposition (LiPF₆). The above calculations are included in supplementary information of the revised manuscript.

Other reports in the literature

Similarly, if calculated, the theoretical capacity for the recent report on SnO₂ - mesoporous carbon containing SnO₂ (20 wt. %) and CMK-3 (80 wt. %).²³ would be = 500

mAh g⁻¹, whilst their experimentally measured specific capacity of SnO₂-CMK-3 = 593 mAh g⁻¹, is somewhat less, just like our present work.

It is seen in another report²¹ that SnO₂-mesoporous carbon has specific capacity of 978 mAh g⁻¹ at a current density of 200 mA/g. Apart from this particular work, the observed specific capacity of SnO₂-mesoporous carbon in most of the reports^{8, 22, 23} in literature is in the range of 400-600 mA h/g, at a current a density of 100-200 mA h/ g. Our present work also shows a specific capacity at 598 mAh g⁻¹at a current density of 178 mA g⁻¹, similar to literature. Therefore, the discharge capacity and current density values in the present work are not on the higher side.