Development of novel mesoporous C–TiO$_2$–SnO$_2$ nanocomposites and their application to anode materials in lithium ion secondary batteries

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**Abstract**

Herein, we employed the tetra-constituent co-assembly method based on the acid–base pair of Sn and Ti precursors. Using this method, novel mesoporous carbon–TiO$_2$–SnO$_2$ nanocomposite materials were prepared, and their structural change with an increase of SnO$_2$ amount was investigated. In low amount of SnO$_2$, an ordered mesoporous structure was observed but it became collapsed at 64 wt.% SnO$_2$, while crystal size of anatase TiO$_2$ embedded within amorphous SnO$_2$ and carbon matrix became larger. When applied to anode materials in lithium ion batteries, an increase of the reaction peaks of Li$^+$ in SnO$_2$ was observed and peak associated with discharging in TiO$_2$ nano-crystal increased in spite of lower amount of TiO$_2$. This indicated that TiO$_2$ was highly utilized for lithium storage (275 mAh g$^{-1}$ in 19.9 wt.% TiO$_2$ case). In the nanocomposite electrode with 28.8% TiO$_2$, however, a high rate performance and a very stable cycle performance (95.3% retention at 40th cycles) were observed, which was attributed to the stable nanostructure.

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**1. Introduction**

Recently, the investigation about ordered mesoporous carbon (OMC) composite materials containing electrochemically active metal oxides has been vastly tried in order to apply into the anodes in lithium ion batteries (LIBs) [1–5]. It has been clarified that they have the beneficial features as anode materials. First, the high rate capability was attainable due to the fast diffusion of lithium ions within the nanosized pore walls and the easy transport of electrolyte through the ordered mesopores. Also, the charge accumulation at charge storage sites was facile due to the high surface area [1–6]. Among various metal oxides which can store lithium ions as anodes, several candidates such as CoO, SnO$_2$ and TiO$_2$ have been investigated as the nanocomposites with OMC [1–5]. Although it has been reported that OMC–TiO$_2$ nanocomposite anode electrodes have exhibited an improved anode performance, their intrinsically low capacity ($\sim200$ mAh g$^{-1}$) can be one of the shortcomings of their anode application [2,6]. In order to overcome this, the nanocomposite with other metal oxides such as SnO$_2$, Sb$_2$O$_3$, and SiO$_2$ was investigated, where a larger charge storage was observed due to its alloying reaction with lithium ion. Most research on OMC/TiO$_2$ or SnO$_2$ has employed a post-addition of Sn or Ti sources into the pores of OMC materials, which can give rise to the formation of inhomogeneous and bulky metal oxide crystals after thermal treatment of those composites [1,5].

In the typical preparation of carbon–TiO$_2$–SnO$_2$ nanocomposite (C–TiO$_2$–SnO$_2$), it has been reported that the crystal growth of TiO$_2$ and SnO$_2$ was severe due to the high carbonization temperature [1,5]. As for the crystal structure of TiO$_2$, various crystalline phases exist as rutile [7,8], anatase [9,10], TiO$_2$–B [11,12], brookite [13] and ramsdelite [14], which were applied as anode materials in lithium ion batteries. When they were prepared as nanostructures, high capacity from 200 to 300 mAh g$^{-1}$ was observed. Due to their structural instability, however, the high capacity above 200 mAh g$^{-1}$ was hard to maintain after long cycles. Although SnO$_2$ has a high theoretical capacity of 780 mAh g$^{-1}$, furthermore, the cycle performance was not satisfactory even after the nanostructure formation by the post-addition of Sn precursor into the OMC matrix, which was attributed to the large volume change of SnO$_2$ during charging–discharging [5]. In order to overcome these obstacles, it is highly required to prepare a complete C–TiO$_2$–SnO$_2$ nanocomposite by one-step process using carbon, Ti and Sn precursors. With this in mind, the tetra-constituent co-assembly (Tetra-CCA) method using Ti-citrate precursor was reported in our previous paper [3]. In this method, a block copolymer surfactant, oligomeric resol and silicate source were reacted with Ti-citrate solution. After aging and calcination, the C–TiO$_2$–SnO$_2$ nanocomposite containing ordered mesopores was obtained.

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### Keywords

Ordered mesoporous materials

TiO$_2$

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Anode

Lithium ion batteries

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In order to prepare a mesoporous nanocomposite of carbon–TiO2 and SnO2 via one-step synthesis, herein, the tetra-constituent co-assembly (Tetra-CCA) method based on the acid–base pair concept is employed. It is expected that carbon skeleton which is helpful in maintaining an ordered structure makes a high electrical percolation network. An acid–base pair between Ti alkoxide and Sn chloride is added in order to avoid a formation of inhomogeneous metal oxide phase and make a stable nanostructure. Using the evaporation-induced self-assembly (EISA), a homogeneous film-type gel is obtained and heat-treated to produce an ordered mesoporous C–TiO2–SnO2 nanocomposites.

2. Experimental section

2.1. Preparation of composites

The resol as carbon precursor was prepared according to the literature [17]. The final resol precursors were dissolved in ethanol (20 wt.% ethanolic solution) for direct use. For Tetra-CCA preparation of C–TiO2–SnO2 nanocomposite, typically, 1 g of P123 (EO1000, PO20EO2000, Aldrich, Mw = 5800) was dissolved in 20 g of ethanol under stirring until a clear solution was acquired. Then 0.973 g (3.6 mmol) of SnCl4 (Aldrich) and 1.528 g (6.7 mmol) of Ti(OEt)4 (Aldrich) was added dropwise under vigorous stirring separately. Upon stirring for 10 min, 2 g of 20 wt.% resol ethanolic solution was dropped slowly when the solution turned orange immediately. Upon further stirring for 2 h, the clear solution was poured into several Petri dishes and kept in a humidity-controlled ambient environment for full evaporation of ethanol. Afterwards the result film was polymerized at 100 °C for 24 h in an oven with a brittle transparent film forming. The as-prepared film was ground into fine powders, calcined at 450 °C for 2 h and further at 600 °C for 2 h under an inert atmosphere (N2). After cooling down to the room temperature, the product was taken out, which produced Ti, Sn and carbon nanocomposite named as TSC-1. Similarly, a TSC-2 and a TSC-3 composite are prepared by adjusting the Sn/Ti molar ratio to 5:5 and 6.7:3.6 separately with the total molar amount of Ti and Sn maintained as 0.01 mol.

2.2. Characterization and anode performance investigation

The pore size distribution (PSD) was analyzed using an N2 adsorption measurement (Micromeritics ASAP 2010). The external morphology of the carbon was examined using a scanning electron microscope (SEM, JEOL JSM-840A), whereas the pore image was scanned by a transmission electron microscope (TEM, JEOL JEM-2010). The energy dispersive X-ray analysis was conducted using the EDX analyzer equipped with the TEM in point mode and area mode. The X-ray diffraction (XRD) patterns were obtained with a Rigaku D/Max-3C diffractometer equipped with a rotating anode mode. The X-ray diffraction (XRD) patterns were obtained with a Rigaku D/Max-3C diffractometer equipped with a rotating anode mode. The X-ray diffraction (XRD) patterns were obtained with a Rigaku D/Max-3C diffractometer equipped with a rotating anode mode. The X-ray diffraction (XRD) patterns were obtained with a Rigaku D/Max-3C diffractometer equipped with a rotating anode mode. The X-ray diffraction (XRD) patterns were obtained with a Rigaku D/Max-3C diffractometer equipped with a rotating anode mode.

3. Results and discussion

In Fig. 1, the schematic explanation of the overall preparation is summarized. In this approach, Tetra-CCA method was employed in order to obtain a mesoporous nanocomposite that was composed of TiO2, SnO2 and carbon. As carbon precursor, PF resin was added for the purpose of increasing the structural strength of mesoporous structure forming an amorphous glue-like background for the controlled in situ crystallization of metal oxides and making a high electrical percolation within mesostructure [1,3,15,16]. As Ti and Sn precursor, Ti(OEt)4 and SnCl4 were utilized because an acid–base pair can be formed between them, which can have an interaction with P123 surfactant and also prevent isolated phases formation of metal oxides after high temperature sintering [17]. After the evaporation induced self-assembly (EISA) procedure, the composite was carbonized at 600 °C. During this step, an ordered mesoporous nanocomposite composed of C–TiO2–SnO2 was prepared. To the best of our knowledge, this is the first preparation of ordered mesoporous nanocomposite materials composed of carbon, TiO2, and SnO2 using simple one-step synthesis. In general, multi-step procedures have been utilized for the preparation of similar nanocomposites. In addition, the prepared materials were applied as anode materials in lithium ion batteries. The weight fraction of TiO2, SnO2 and carbon was calculated by ICP methods, which was listed at Table 1.

Fig. 2 displays the small angle and wide angle X-ray diffraction (XRD) patterns. In TSC-1 material, a broad peak was observed at 2θ = 0.7°, which was probably associated with a long-range ordering of mesopores. In TSC-2, the ordered peak became sharper and moved to a lower angle, indicative of increasing cell parameter. However, the ordered structure was collapsed and no peak was observed in TSC-3, which reflected that higher addition of SnCl4 resulted in a collapse of ordered structure. Fig. 2(b) displays the wide angle XRD patterns. Interestingly, only anatase phase TiO2 was observed and, no crystal structure of SnO2 and carbon appeared. Note that the peak intensity for [101] plane of TiO2 crystal became higher as SnO2 increased, in spite of a decrease of TiO2 weight fraction. This implies that SnO2 and carbon remained amorphous, but the crystallinity of TiO2 became higher according to an increase of SnO2. This observed tendency in crystal structure is possibly relevant to the molar ratio between Ti and Sn. It has been reported that crystallinity of anatase TiO2 was less developed than our TSC-1 in the case of mesoporous material having 80% carbon and 20% TiO2, indicating that carbon phase retarded a crystal growth of TiO2. In our experiment, on the contrary, a high interaction between carbon and SnO2 could accelerate crystal growth of TiO2 or the lower concentration of titania source could promote its crystal growth, which require a further investigation. In addition, there are small bumps at around 2θ = 31° for all the three samples, which corresponded to the rutile TiO2 phase. Small amount of rutile phase formed during high-temperature calcination because of its high thermodynamic stability. Because nanosized rutile TiO2 shows excellent capacity retention and a high
rate performance as lithium battery anode, it is expected that formation of small amount of rutile TiO₂ can possibly give additional benefit to our designed materials [3,7].

Fig. 3 shows the TEM images of the prepared materials. As can be seen, wormhole-like mesopores with a long range ordering appeared in TSC-1 and -2. Also, thick walls which consisted of TiO₂, SnO₂ and carbon are observed. This multi-components wall became thicker in accordance with an increase of SnO₂. From high resolution TEM images of Fig. 3(b), (d) and (f), nanosized anatase TiO₂ crystals embedded within the amorphous SnO₂ and carbon matrix were observed. Their size became larger as SnO₂ increased, which coincided with wide-angle XRD results in Fig. 2(b).

In order to confirm the uniform distribution of Ti and Sn metal within the mesoporous nanocomposites, elemental analysis using EDX for point and area modes were conducted for TSC-1 material, which was shown in Fig. 4. Carbon, Ti and Sn were located homogeneously within the ordered structures in TSC-1. In the literature, it was reported that small sized crystals of titania were observed after high temperature heat treatment (>400 °C) [15]. In our preparation, however, the crystal size of TiO₂ can be controlled by a change of SnCl₄ adding amount. Furthermore, the transition state of Ti and Sn was investigated by XPS analysis.

Fig. 5 displays XPS spectra for Ti 2p from 454 to 468 eV and Sn 3d spectra from 480 to 505 eV. As seen, the symmetric Ti 2p peaks at 458.9 and 464.6 eV indicate stoichiometric TiO₂ with a low concentration of defects. Ti 2p₃/₂ peak position at 458.9 eV in TSC-1 spectrum is similar to that of pure TiO₂ (458.6 eV), reflecting that Ti in TSC-1 has +4 transition state (Ti⁴⁺) [18,19]. Similarly, peak positions of Sn 3d5/₂ and 3d3/₂ were located at 487.2 and 495.5 eV, respectively. This exhibited the oxidation state of amorphous SnO₂ is nearly +4, which coincided with the peak positions of Sn 3d₃/₂ and 3d₅/₂ in nanoparticles (486.7 and 495.1 eV, respectively) [20].

In Fig. 6(a), the N₂ sorption isotherms for TSC series are shown. Here, characteristic H₂ type hysteresis defined from IUPAC was commonly observed [23,24]. This hysteresis loop at around 0.5 P/P₀ was relevant to the mesopores, which became larger as SnO₂ increased. Note that a large increase of adsorbed volume in TSC-3 was observed. The pore size distributions (PSDs) by BJH method from the adsorption branch are given in Fig. 6(b). For TSC-1 material, less-developed pore structure was observed, which was clearly improved in TSC-2 material. Three kinds of pores (2, 3.5 and 7 nm) were observed in TSC-3 materials, which was relevant to pore formation of interstitial sites between the large TiO₂ crystals and carbon/Sn amorphous phase. This abrupt formation of high mesoporosity can raise the collapse of ordered structure in TSC-3. This PSD change coincided with TEM image as shown in Fig. 3.

From the crystallographic and morphological analysis conducted

<table>
<thead>
<tr>
<th>TSC</th>
<th>TiO₂ (wt.%)</th>
<th>SnO₂ (wt.%)</th>
<th>C (wt.%)</th>
<th>TiO₂/SnO₂ (molar ratio)</th>
<th>Vₘeso (cm³ g⁻¹)</th>
<th>Vₘicro (cm³ g⁻¹)</th>
<th>Cch (mAh g⁻¹)</th>
<th>Cdis (mAh g⁻¹)</th>
<th>IE (%)</th>
<th>Rate (%)</th>
<th>Cycle (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSC-1</td>
<td>42.3</td>
<td>37.7</td>
<td>20.0</td>
<td>2.11</td>
<td>232</td>
<td>0.042</td>
<td>0.078</td>
<td>629</td>
<td>229</td>
<td>36</td>
<td>49</td>
</tr>
<tr>
<td>TSC-2</td>
<td>28.8</td>
<td>53.9</td>
<td>17.2</td>
<td>1.01</td>
<td>235</td>
<td>0.054</td>
<td>0.076</td>
<td>901</td>
<td>277</td>
<td>31</td>
<td>53</td>
</tr>
<tr>
<td>TSC-3</td>
<td>19.9</td>
<td>63.9</td>
<td>16.2</td>
<td>0.59</td>
<td>281</td>
<td>0.079</td>
<td>0.091</td>
<td>883</td>
<td>378</td>
<td>43</td>
<td>45</td>
</tr>
</tbody>
</table>

The fraction of TiO₂, SnO₂ and C were obtained by TGA and ICP methods.

The molar ration of TiO₂/SnO₂ is converted from the mass ratio of TiO₂/SnO₂.

BET surface area (Aₜₐₙ) and mesopore volume (Vₘeso), micropore one (Vₘicro) were obtained by N₂ sorption analysis.

Initial charging capacity (Cch), discharging capacity (Cdis) and initial efficiency (IE) were obtained by galvanostatic charge–discharge experiment.

Rate capability was obtained by a comparison between the discharge capacities at 30 mA g⁻¹ and 300 mA g⁻¹. Cycle performance was estimated by discharge capacity after 40th cycles by that of first cycle.
above, it was concluded that TiO$_2$ crystals became larger and the mesoporosity became more developed according to an increase of SnO$_2$, while the ordered structure was collapsed.

Fig. 7 shows anode performance results of the TSC electrodes in the voltage range from 0 to 2.5 V vs. Li/Li$^+$. The individual components of TiO$_2$, SnO$_2$ and carbon in the prepared composite materi-
als can make a different contribution in the capacity. Typically, the reversible capacities of SnO2 and TiO2 appear below and above 2 V, respectively, which are associated with their characteristic electrochemical reactions with Li+ [7–12]. As for amorphous carbon, Li+ can be stored uniformly at overall potential according to our previous research. As shown in Fig. 7(a), the galvanostatic charge–discharge profiles are shown. As can be seen, charging capacity ($C_{ch}$) became larger from 629 to 900 mAh g$^{-1}$ and discharging capacity ($C_{dis}$) increased from 229 to 378 mAh g$^{-1}$ as SnO2 increased. This capacity increase is mostly due to a larger amount of SnO2, which has a 780 mAh g$^{-1}$ theoretical capacity as the crystal phase [2,20]. As for the capacity of TiO2, it is known that be highly dependent on temperature of heat treatment, preparation method and morphology difference [7–14]. Capacity became smaller with an increasing temperature and the nanostructured TiO2 electrodes exhibited an improved capacity while their cycle performance became poor [7–14]. Note that the reversible capacity of the amorphous carbon material which was prepared without addition of Sn and Ti precursor, was about 200 mAh g$^{-1}$ (not shown here). In Fig. 7(a), interestingly, a plateau was observed in TSC-3 electrode in spite of its smaller weight fraction of TiO2 (19.9 wt.%). In contrast, this plateau disappeared in TSC-1 electrode although it contained 42.3 wt.% TiO2. This unpredicted result is discussed later. In Fig. 7(b), cyclic voltammetry of TSC-2 electrode is displayed. From this figure, the characteristic two peaks at 0.5 and 1 V were observed in anodic scan in upward direction to higher voltage, which were attributed to the Li$^+$ discharge at SnO2 and TiO2, respectively.

In Fig. 8, the differential capacity per voltage was plotted against potential, which was calculated from the discharge profiles in Fig. 7(a). This differential capacity per voltage is useful to separately analyze potential-dependent electrochemical reactions. As can be seen, two large peaks below 1.5 V and sharp peak near 2.2 V commonly appeared. As SnO2 increased, two peaks below 1.5 V became larger and a higher peak near 2.2 V was observed while the position of the latter peak moved to a lower value. Moreover, a small peak at 1.7 V was observed in TSC-3 electrode. The changes of the electrochemical reaction peaks are associated with characteristic electrochemical reactions in SnO2 and TiO2. Typically, electrochemical reaction for Li$^+$ storage in SnO2 anode can be described as following equations [20]:

\[
\text{SnO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Sn} + 4\text{Li}_2\text{O} \quad (1)
\]

\[
\text{Sn} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Sn} \quad (0 \leqslant x \leqslant 4.4) \quad (2)
\]

\[
\text{Li}_x\text{Sn} \rightarrow \text{Sn} + x\text{Li}^+ + xe^- \quad (0 \leqslant x \leqslant 4.4). \quad (3)
\]

During the first charging (reduction) process to downward direction of potential, the reaction of Eq. (1) happens with reduction of SnO2 to metallic Sn and Li2O, which is known to be observed at 0.9 V during the first charging. As shown in Fig. 5(a), the capacity from Eq. (1) reaction became higher when SnO2 increased. Then voltage declined continuously from 0.5 to 0.02 V, which can be attributed to the formation of different alloy phases, producing Li$_{4.4}$Sn finally as shown in Eq. (2). During discharge process, typical two peaks at 0.5 and 1 V were observed in Fig. 6, which is relevant to de-alloying of lithium from Li$_{4.4}$Sn (Eq. (3)). In the literatures, it has been reported that the peak at 0.5 V is main one while the latter peak is broad and weak [5,20]. On the contrary, the two peaks were similar in TSC-1 and -2 electrodes, but the peak at 1.0 V was very strong in TSC-3 sample, which was possibly due to nanocom-
posite effect with carbon and TiO$_2$. Similar to the materials which were prepared by SnO$_2$ incorporation into the pores of OMC, the reversible peak at 1.3 V was observed, which was associated with a reversible reaction of Eq. (1). When considering the theoretical capacity of SnO$_2$ (780 mAh g$^{-1}$), TSC-1 and -3 should show 294 and 498 mAh g$^{-1}$ discharge capacity above 1.7 V, respectively but a less capacity of 204 and 323 mAh g$^{-1}$ were observed, which was due to the amorphous nature of SnO$_2$ and an additional carbon content ($\sim$20 wt.%).

Another important feature in discharge peak in Fig. 8 is the increasing peak intensity near 2.2 V, which is related with the discharging process within TiO$_2$ phase [7–10]:

$$\text{TiO}_2 + x\text{Li}^+ + e^- \rightarrow \text{Li}_x\text{TiO}_2. \quad (4)$$

In the typical electrochemical reaction of anatase TiO$_2$ nanoparticle, $x$ is known to be about 0.5 (160.8 mAh g$^{-1}$) [8,9]. As shown in Fig. 8, peak near 2 V became larger and moved to lower value according to SnO$_2$ increase. While the small peak in TSC-1 electrode indicated a low capacity, a large capacity was observed in TSC-3 electrode in spite of less weight fraction of TiO$_2$ (19.9%), indicative of its higher utilization for Li$^+$ charging. From approximate calculation, $C_{\text{dis}}$ above 1.7 V of TSC-1 and -3 were 25 and 55 mAh g$^{-1}$, which reflected that discharge capacities by TiO$_2$ itself were 67 and 275 mAh g$^{-1}$, respectively. This is probably attributed to more available Li$^+$ storage sites in well-developed TiO$_2$ crystals in TSC-3.
In order to investigate a change of lithium storage features, electrochemical impedance spectroscopy (EIS) was carried out for the TSC-1 and -3 electrodes in the $5 \times 10^{-3}$ to $10^5$ Hz frequency region at 2 V vs. Li/Li$. Fig. 9 displays the EIS spectra as Nyquist plots. Here, the EIS spectra comprised of one or two semi-circles in the high frequency region followed by a straight line with decreasing frequency, which is characteristic in Faradaic reactions in the anode for an LIB [9,21]. At the highest frequency, the intercept resistance in $Z_{\text{real}}$ axis ($R_0$) corresponded to a bulk electrolyte resistance between working and counter electrode [21,22]. $R_0$ of TSC-1 and -3 were identical, indicative of same cell structure. In this figure, the resistance from the highly distributed semi-circle ($R_s$) can include overall electrical/electrolyte conduction within the electrode or ionic transport within the surface film [9,21]. $R_s$ of TSC-3 was larger than that of TSC-1, indicating a larger resistance and a low rate capability. Although a resistance corresponding to the charge transfer reaction at the interface was hard to locate, a sloped straight line with a decreasing frequency exhibited a different behavior in TSC-1 and -3 electrodes. The slope of TSC-1 electrode was steeper than that of TSC-3, indicative of more polarizable electrode feature caused by a smaller Faradaic peak in Fig. 8.

Fig. 10 displays the rate capability and cyclability of TSC electrodes. As for the rate capability, TSC-2 electrode showed a slightly higher rate performance as 53% at 150 mA g$^{-1}$ current rate. Because the alloying–dealloying process of SnO$_2$ is the most sluggish process, it is expected that a lower SnO$_2$ fraction should result in a better rate performance but the observed low rate capability in TSC-1 electrode is probably due to a retarded Li$^+$ transport in less-developed mesostructure and a low Li$^+$ solid-state diffusion within smaller TiO$_2$ crystals [21]. In Fig. 10(b), cycle performance was investigated for three electrodes until 40 cycles at 30 mA g$^{-1}$ current rate. For TSC-1 and -3 electrodes, a decrease of capacity was observed until five cycles and stable cycle performance appeared afterward. In TSC-2 electrode, an invariant capacity change was observed, indicative of a good cyclability. The capacity retentions after 40 cycles were compared at Table 1. As seen, TSC-2 electrode showed a very good cycle performance (95.3% retention), while the cycle performances in TSC-1 and -3 electrodes were not satisfactory. In order to investigate a change of capacity contribution after cycles, the differential capacities per voltage of TSC-2 and -3 electrodes after 40 cycles were compared in Fig. 11. In TSC-2 electrode, shape and position of peaks remained invariant. On the contrary, a large peak change was observed in TSC-3 electrode, which displayed that the peak at 1.0 V was collapsed severely, while the decrease of peak intensity of the other two peaks was small. This indicated that the charging–discharging behavior of TSC-3 electrode after long cycles became similar to the conventional SnO$_2$ electrode [5,20]. As for TSC-2 electrode, the stable nanostructure maintained after long cycles, which was probably attributed to a high interaction between its components with an optimized TiO$_2$ crystal size.

### 4. Conclusions

Using the tetra-constituent co-assembly (Tetra-CCA) method based on the acid–base pair between Sn and Ti precursors, novel mesoporous carbon–TiO$_2$–SnO$_2$ nanocomposite materials were prepared. Here, the influence of SnO$_2$ amount was investigated. According to SnO$_2$ increase, the ordered mesoporous structure was initially observed but its collapse happened afterward. Furthermore, nanosized anatase TiO$_2$ crystals were embedded within the amorphous SnO$_2$ and carbon matrix and their size became larger. When applied into anode materials in lithium ion batteries, the discharge capacity and the initial efficiency became larger. For the electrode material containing large crystal TiO$_2$, it exhibited a reversible capacity of 378 mAh g$^{-1}$ and a very high utilization of TiO$_2$ for lithium storage (275 mAh g$^{-1}$). However, a high rate performance and a very stable cycle performance were observed in the nanocomposite electrode with 28.8% TiO$_2$, which was attributed to the stable nanostructure after long cycles.

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