Fabrication of multi-layer CoSnO$_3$@carbon-caged NiCo$_2$O$_4$ nanobox for enhanced lithium storage performance

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\textbf{ABSTRACT}

Mixed transition metal oxides (MTMOs) are deemed as promising anode materials for lithium-ion batteries (LIBs) because of the high theoretical capacity and low cost. However, the low electrical conductivity, agglomeration effects, and huge volume variation during discharging/charging still seriously restrict the actual applications of MTMOs as anode materials. Herein, a novel core-shell structure of CoSnO$_3$@carbon-caged NiCo$_2$O$_4$ nanobox (CNC) is rationally designed. It starts from the preparation of CoSnO$_3$@ZIF-67 core-shell nanocubes, followed by chemical etching/anion exchange, dopamine coating and carbonization at high temperature in sequence. It is shown that the CNC achieves high activities from the applied MTMOs components, excellent relief of volume variation from the unique double hollow structure, improved conductivity and inhabited aggregations from the uniform-coated outmost carbon shell, and effective ion/electron transfer rates from the synergetic effects. As a result, the CNC exhibits a discharge capacity of 1548 mA h g\(^{-1}\) at the first cycle and a retention capacity of 992 mA h g\(^{-1}\) after 100 cycles at 0.1 A g\(^{-1}\). In addition, it exhibits a high reversible capacity of about 670 mA h g\(^{-1}\) after 500 cycles at a current density of 1 A g\(^{-1}\). The improved Li\textsuperscript{+} storage performances of CNC demonstrates that such rational design of double hollow structure could be a novel strategy to apply MTMOs as anode materials of LIBs.

\section{1. Introduction}

Today, over-exploitation of non-renewable fossil energy has serious impacts on our environment [1,2]. Great efforts and progresses on the technologies and products related to alternative energy have been made, especially on lithium-ion batteries (LIBs). LIBs have been deemed to be the ideal energy storage devices due to the high energy storage capacity, long cycle life and low pollution to the environment [3–5]. Nowadays, rechargeable LIBs have been vastly applied in portable electronic devices and electric vehicles, which greatly stimulate the market demands of high-performance LIBs [6–8]. However, layered graphite materials commonly used as anode materials for most commercial LIBs have been unable to contain the demands of high performance due to its limited theoretical capacity (372 mA h g\(^{-1}\)) [9,10]. Therefore, it has become an urgent task to explore more valid alternative anode materials to meet the rising requirements.

In the past decades, various active materials that can potentially work as anodes of LIBs have been widely studied. Due to the high capacity and the low price, transition metal oxides (TMOs) have attracted extra attention. More importantly, TMOs can significantly enhance safety by suppressing the formation of lithium dendrites compared to that of commercial graphite. Recently, the mixed transition metal oxides (MTMOs), a combination of two TMOs with a spinel-like structure, such as ZnCo$_2$O$_4$ [11], MnCo$_2$O$_4$ [12], ZnSnO$_3$ [13] and so on, have raised great attention. Compared with single transition metal oxide, MTMOs have more notable features: the regulable chemical composition can increase electrochemical activity; the desirable meso-porosity can promote ion diffusion; the synergistic effects can increase specific capacity that could reach 2–3 times higher than commercial graphite [14,15]. Among them, CoSnO$_3$ is a noteworthy member that owns an excellent
shows much better performance than the mixture of SnO
S. Huang et al. prepared succinctly by refluxing at 90
double hydroxides (ZIF-67/Ni-Co LDH) yolk-shelled structures were
Lou et al. reported the zeolitic imidazolate framework-67/Ni-Co layered
pathways due to the porous structure. Moreover, the experimental
induced mass relocation [27]. Compared with other methods, the hol
the candidate of high-performance anode materials for LIBs.
multi-shell hollow MTMOs-based active materials could possibly be
multi-shell hollow structure can offer the synergistic effects to give a
structure can only achieve limited enhancements on the lithium storage.
It was found that a multi-shell hollow structure can even further al-
viate volume expansion and shorten ion diffusion paths [23]. Further-
more, the structured multi-active materials (inner and outer layers) in
multi-shell hollow structure can offer the synergistic effects to give a
better electrochemical performance. Therefore, such properly-structured
multi-shell hollow MTMOS-based active materials could possibly be
the candidate of high-performance anode materials for LIBs.
At present, there are many synthetic methodologies being used for
fabricating multi-shell hollow structures, including hard- and soft-
templating methods [24,25], ion exchange [26], and thermally induced mass relocation [27]. Compared with other methods, the hol-
low structures formed by ion exchange of metal–organic frameworks
(MOFs) always own larger specific surface areas and more ion diffusion
pathways due to the porous structure. Moreover, the experimental
condition of ion exchange is often mild and easy-operated. For example, Lou et al. reported the zeolitic imidazolate framework-67/Ni-Co layered
double hydroxides (ZIF-67/Ni-Co LDH) yolk-shelled structures were prepared succinctly by refluxing at 90 °C for 1 h [28]. Attractively, after
annealing, the LDH layers were feasibly converted to ternary nickel cobaltilate (NiCo2O4), which is another active MTMOS being also applied
as effective anodic materials of LIBs owing to its advantages, such as
high electrical conductivity, abundant availability, low costs, and non-
toxic nature [29–31]. Among these TMOs candidates, NiCo2O4 pos-
sesses a higher electrical conductivity (0.1–0.3 S cm−1) and better
electrochemical performance. Particularly, MOF-derived NiCo2O4 with a
better porous structure provides a large amount of Li+ fast transfer channels and stores Li+ ions through an adsorption mechanism. More-
over, it inherits the structural stability of MOF precursor, and the formed
hollow structure reserves enough buffer space for the expansion of the
materials.
Herein, inspired by the above-mentioned ingenious strategies, we
fabricate a unique NiCo2O4@carbon-caged CoSnO3 nanoboxes (CNC)
with a double hollow nanostructure, where the double hollow nano-
structure is intended to provide enough buffer spaces for the volume
expansion, the components of dual active MTMOSs and carbon layers to
deliver synergistic effects, and the outermost carbon coating to improve the
conductivity and prevents the agglomeration. It is demonstrated that,
as an anode material of LIBs, the CNC delivers a high initial ca-
pacity of 1548 mA h g−1 at the current density of 0.1 A g−1 and stabilizes around 992 mA h g−1 after 50 cycles. Even after 500 cycles at a high rate
of 1 A g−1, the capacity still retains the reversible specific capacity of
670 mA h g−1. The excellent Li+ storage performances benefit from the
meticulously designed double hollow structure composed of CoSnO3
nanobox and NiCo2O4 nanocage.

2. Experimental section

2.1. Materials synthesis

2.1.1. Synthesis of CoSnO3@ZIF-67
CoSnO3 nanoboxes were synthesized as reported earlier [20]. 20 mg of
CoSnO3 nanoboxes were added into 50 mL methanol with ultrasonic
for 30 min. Then 1.2 g polyvinylpyrrolidone (PVP-K30) was added into the suspension with magnetic stirring for 15 min (solution A). Mean-
while, Co(NO3)2·6H2O (0.4 g) was dissolved in 50 mL methanol (solu-
tion B) and 2-methylimidazole (5.92 g) was dissolved in 100 mL methanol (solution C). Solutions B and C were added quickly to solution
A with magnetic stirring for 12 h. The resulting product was harvested
by several centrifugation cycles with methanol three times and dried at
60 °C for 12 h.

2.1.2. Synthesis of CoSnO3@Ni-Co/LDH
45 mg CoSnO3@ZIF-67 were dispersed into 30 mL ethanol. Then 90
mg Ni(NO3)2·6H2O was added into the above solution with magnetic stirring for 1 h. The green product was collected by centrifugation
and washed with deionized (DI) water and ethanol three times, then dried at 60 °C overnight.

2.1.3. Synthesis of CNC
80 mg CoSnO3@Ni-Co LDH of nanocages and 40 mg of dopamine were dispersed into a Tris buffer solution (100 mL, 10 mM) with mag-
netic stirring for 3 h. The black product was collected by centrifugation
and washed with deionized (DI) water and ethanol several times, then
dried at 60 °C overnight. Then, the product was annealed in tube furnace
at 350 °C under N2 for 2 h with a ramp rate of 1 °C min−1. The pro-
duction method of NiCo2O4@N-C and CoSnO3@N-C were the same as
above.

2.2. Structural characterization

X-ray diffraction (XRD) patterns were conducted on a Rigaku D/max-
2500 X-ray diffractometer with a Cu Kα radiation (λ = 0.1542 nm) from
10° to 80° at a scanning rate of 8° min−1. The morphologies of samples
were characterized by transmission electron microscopy (TEM, 200CX,
200 kV), and field emission scanning electron microscopy (FE-SEM,
JSM-6700F, 5 kW). High-resolution transmission electron microscopy
(HRTEM) was discovered on a JEOL JEM-2100F electron microscope
operating at 200 kV. X-ray photoelectron spectroscopy (XPS) was car-
ried out on an X-ray photoelectron spectrometer with a monochromatic
Al Kα radiation. Raman spectra were collected on a Raman spectrom-
eter. The specific surface area of the samples was tested on a Micro-
metric Tristar 3020 analyzer at liquid-nitrogen temperature. Thermogravimetric analyses (TGA) were performed on TG-209C with
a heating rate of 10°C min−1 in the air.

2.3. Electrochemical measurements and characterization

The anode was prepared by mixing the active material (CNC, NiCo-
O2@N-C, CoSnO3@N-C), carbon black (Super P), and polymer binder
(polyvinylidene difluoride, PVDF) at a weight ratio of 7:2:1 in N-methyl
pyrrolidone. The mixture was stirred homogeneously and dripped onto
A clean piece of copper then dried in a vacuum at 60 °C for 12 h. The
electrolyte was 1.0 M LiPF6, which was dissolved in a mixture of
dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethylene car-
bonate (EC) (1:1:1 wt% ratio). The lithium foil with a diameter of 15 mm
and a thickness of 1 mm was selected as a counter/reference electrode.
The coin cell (2032) was assembled in an argon-filled glove box, then
tested on a LAND CT2001A cell test system which provided a current density range from 0.1 to 5C and a voltage window of 0.05 ~ 3.0 V. Cyclic voltammograms (CV) were conducted by a CHI660e electrochemical workstation.

3. Results and discussion

The preparation of CNC is schematically illustrated in Fig. 1. Firstly, the regular CoSnO$_3$ nanobox was synthesized according to reported literatures [20]. Secondly, the CoSnO$_3$@ZIF-67 was formed by the crystallization of ZIF-67 on the surface of PVP-modified CoSnO$_3$ nanobox. CoSnO$_3$@Ni-Co LDH double-shelled nanocages were then generated by Ni$^{2+}$ ion exchange on CoSnO$_3$@ZIF-67 [32]. Notably, during this process, ZIF-67 was gradually etched by protons generated from the hydrolysis of Ni$^{2+}$ ions, and the Ni-Co LDH was simultaneously formed through Ni$^{2+}$ ions coprecipitating with the released Co$^{3+}$ ions (Fig. 2g-i) [28,33]. Afterward, polydopamine (PDA)-coated CoSnO$_3$@Ni-Co LDH were produced and finally calcined to achieve CNC, where Ni-Co LDH and PDA are converted to NiCo$_2$O$_4$ and N-doped carbon, respectively.

The crystallographic structures and phase purities of as-prepared materials are examined by powder X-ray diffraction (XRD) (Fig. 2a). XRD analysis results of the CoSnO$_3$ nanoboxes show that a broad peak appears between 30 and 40$^\circ$, indicating the formation of amorphous CoSnO$_3$, which is consistent with the results in the literature [16]. There are no other obvious miscellaneous peaks, confirming the high purity of the synthesized CoSnO$_3$ nanoboxes. Compared with that of pure CoSnO$_3$ nanoboxes, there are the additional peaks indexed to ZIF-67 in the XRD pattern of CoSnO$_3$@ZIF-67 (Fig. S1, in Supporting Information), indicating the successful growth of ZIF-67 on the top of CoSnO$_3$ nanobox. Moreover, the diffraction peak of ZIF-67 completely disappeared after Ni$^+$ etching of CoSnO$_3$@ZIF-67, indicating that ZIF-67 was converted to Ni-Co LDH (as shown by the black curve in Fig. 2a). As proposed, after calcining at 350$^\circ$C, the Ni-Co LDH and PDA layers are intended to be converted to NiCo$_2$O$_4$ and nitrogen-doped carbon layers, respectively. The formation of NiCo$_2$O$_4$ was determined by the XRD pattern of CNC. As shown in Fig. 1a, the diffractions located at 18.9', 31.1', 36.7', 44.6', 59.1', and 64.9' of CNC are corresponding to the (111), (220), (311), (400), (511) and (440) planes of NiCo$_2$O$_4$ (JCPD card no. 20-0781), respectively.

The morphologies of CNC, CoSnO$_3$@Ni-Co LDH and CoSnO$_3$ nanoboxes, are then investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in SEM images of Fig. 2b, CoSnO$_3$ nanoboxes exhibit cubic morphology with an average diameter of 250 nm. The TEM analysis indicates that the conversion from CoSn(OH)$_6$ to CoSnO$_3$ boxes undergoes a topotactical transformation process without apparent collapse of the shells (Fig. 2c). Moreover, the CoSnO$_3$ nanoboxes are highly uniform with a shell thickness of around 30~40 nm as previously reported [21]. As shown in Fig. 2d-f, CoSnO$_3$ nanoboxes has been encapsulated in ZIF-67, and the obtained CoSnO$_3$@ZIF-67 show a polyhedral shape with a smooth surface and an average size of approximately 800 nm. After Ni$^{2+}$ etching for 1 h, a polyhedral shape was retained but a hollow structure and rougher surface were constructed (Fig. 2g-i) [28,33]. In addition, when prolonging the etching time to 2 h, the regular dodecahedron structure suffered a huge landslip (Fig. S2). Hence, to achieve proper Ni-Co LDH, the etching time was well controlled. Importantly, after calcining of CoSnO$_3$@Ni-Co LDH, the resultant CNC still maintains the shape of a regular dodecahedron (Fig. 2j-k). The formation of a multi-shell hollow structure is obviously confirmed by the clear edge of the inner CoSnO$_3$ nanobox and outer NiCo$_2$O$_4$ cage. The HRTEM images of CNC reveals two sets of lattice fringes with inter-planar spacings of 0.23 and 0.25 nm attributed to CoSnO$_3$ nanobox and CoSnO$_3$@Ni-Co LDH, respectively (Fig. 2m-n). In addition, the HRTEM image shows that NiCo$_2$O$_4$ derived from small pieces of NiCo-LDH is assembled disorderly on the surface (Fig. S3), resulting in obvious defects. The defects not only have strong adsorption capacity for foreign metal ions but also provide a wide space for foreign metal ions.
for ion storage, which is also one of the reasons for the increase in capacity [34]. Moreover, the thickness of the carbon layer on the surface of the nanocage is about 20 nm (Fig. S4).

Meanwhile, the thermogravimetric analysis (TGA) is used to determine the carbon content in CNC (Fig. 3a). When the temperature reached approximately 150 °C, the weight loss is nearly 6% attributed to the removal of physically adsorbed water [35]. The significant weight loss between 150 and 350 °C is ascribed to the combustion of amorphous carbon into carbon oxides [36]. It reveals that the ratio of carbon in CNC is about 36%. Fig. 3b displays the Raman spectrum of CNC. Two clear peaks around 1370 and 1560 cm⁻¹, respectively correspond to the D and G bands of carbon, further confirming the presence of the carbon layer. The intensity ratio of the D and G bands is 1.28, indicating the low graphitic crystallinity of the carbon layer [37]. To assess the specific surface area and pore size distribution of the CoSnO₃ nanoboxes and CNC, nitrogen adsorption/desorption isotherm measurements are carried out. Type IV isotherms with type H3 hysteresis loops can be observed in Fig. 3c, d, which implies the mesoporous structure of the sample. The specific surface area and average pore diameter of CoSnO₃ nanoboxes are 32 m² g⁻¹ and 28 nm, respectively. After covering NiCo₂O₄ and carbon, the specific surface area of CNC increases to 137 m² g⁻¹, but the average pore diameter reduces to 15 nm. During the discharge/charge process of LIBs, the large specific surface area provided by CNC will improve the conduction rate of electrons and ions [38].

The X-ray photoelectron spectroscopy (XPS) measurements are employed to verify the element valences of CNC. The survey spectrum of CNC indicates the presence of C, N, O, Co, Ni and Sn elements (Fig. S5). The high-resolution XPS spectra of individual elements are presented in Fig. 4a-f. As shown in C1s spectrum, there are three peaks located at 284.6, 285.8, 288.3 eV, corresponding to C–C, C–N, C = O, respectively (Fig. 4a) [39]. The spectrum for the O1s shows three sub-peaks as O₁, O₂, O₃ (Fig. 4b). The peak of O₁ at 529.5 eV is the characteristic peaks of metal–oxygen bonds [40]. The highest peak of O₃ at 531.3 eV

Fig. 2. (a) XRD patterns of CNC, CoSnO₃@Ni-Co LDH, and CoSnO₃ nanoboxes; (b-c) SEM and TEM images of the CoSnO₃ nanoboxes; (d-f) SEM and TEM images of CoSnO₃@ZIF-67; (g-i) SEM and TEM images of CoSnO₃@Ni-Co LDH; (j-k) SEM and TEM images of CNC; and (l-n) the high-resolution TEM (HRTEM) image of CNC.
can be attributed to oxygen vacancies, which could improve the electrical conductivity [41]. The peak of O\textsubscript{3} at 533.1 eV is due to the water adsorbed on the sample surface. Fig. 4 c displays the high-resolution XPS of N 1 s, which can be divided into three peaks corresponding to pyridinic N (398.4 eV), pyrrolic N (399.8 eV), graphitic N (401.2 eV), respectively, suggesting successful N doping in the carbon framework. Meanwhile, the EDX spectrum (Fig. S6) shows that the N content in CNC is 7.19%, which further proves that N is successfully doped into C. In Fig. 4 d, the Co 2p emission spectrum is best fitted considering two spin–orbit doublets characteristic of Co\textsuperscript{3+} and Co\textsuperscript{2+} and two shakeup satellites. The fitting peaks at 780.5 and 795.9 eV are indexed to the Co 2p\textsubscript{3/2} and Co 2p\textsubscript{1/2} of Co\textsuperscript{3+} [9,31]. In Ni 2p spectra (Fig. 4 e), the fitting peaks at binding energies of 855.6 and 873.0 eV are attributed to Ni\textsuperscript{3+}, while the other two peaks at 853.9 and 870.8 eV belong to Ni\textsuperscript{2+}. Two satellite peaks of nickel at around 861.0 and 878.4 eV are also observed at the high binding energy side of Ni 2p\textsubscript{3/2} and Ni 2p\textsubscript{1/2} [42]. As for Sn 3d (Fig. 4 f), two weak peaks centered at 486.6 eV (Sn 3d\textsubscript{5/2}) and 495 eV (Sn 3d\textsubscript{3/2}) represent the presence of Sn\textsuperscript{4+} in CNC [43].

To evaluate the electrochemical lithium storage of CNC composites as anode materials for LIBs, various electrochemical measurements are carried out. Fig. 5 a and S7a-b respectively present the first five cyclic voltammetry (CV) curves of the CNC, NiCo\textsubscript{2}O\textsubscript{4}@N-C and CoSnO\textsubscript{3}@N-C at the scanning rate of 0.5 mV s\textsuperscript{-1} in the voltage range of 0.01–3.0 V versus Li/Li\textsuperscript{+}. Obviously, the curve of the first cycle is substantially different from the subsequent ones. In the first cathodic scan, two reduction peaks shown at around 0.6 and 0.9 V corresponds to the decomposition of NiCo\textsubscript{2}O\textsubscript{4} and CoSnO\textsubscript{3} into Ni, Co and Sn, as well as the formation of amorphous Li\textsubscript{2}O and the solid electrolyte interphase (SEI) film, while disappearing in the following cycling processes. In the subsequent cycles, the main reduction peaks respectively shift to higher potentials at 0.75 and 1.25 V, which is related to the changes in the crystal structure [57]. And the weak peak at 0.05 V is due to the alloying reaction between Sn and Li\textsuperscript{+} to generate Li\textsubscript{x}Sn alloys. Meanwhile, in the first anodic scan, three broad peaks at around 0.6, 1.3 and 2.19 V, which can be ascribed to the oxidation of Sn to Sn\textsuperscript{4+}, Ni to Ni\textsuperscript{2+}, Co to Co\textsuperscript{2+} and Co to Co\textsuperscript{3+}. Evidently, the reduction and oxidation peaks substantially overlap very well after the first cycle, indicating good electrochemical reversibility and stability for the Li\textsuperscript{+} insertion/extraction process. Cyclic voltammogram and the Li\textsuperscript{+} storage mechanism of SnO\textsubscript{2}, NiO, CoO and Co\textsubscript{3}O\textsubscript{4} have been previously reported [58–60], all the electrochemical processes can be expressed as follows:

\[
\text{CoSnO}_3 + 6\text{Li}^+ + 4e^- \rightarrow \text{Co} + \text{Sn} + 3\text{Li}_2\text{O}
\]
\[
\text{NiCo}_2\text{O}_4 + 8\text{Li}^+ + 8e^- \rightarrow \text{Ni} + 2\text{Co} + 4\text{Li}_2\text{O}
\]
\[
\text{Sn} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{Sn} (0 \leq x \leq 4.4)
\]
\[
\text{Sn} + 2\text{Li}_2\text{O} \leftrightarrow \text{SnO}_2 + 4\text{Li}^+ + 4e^- 
\]
\[
\text{Co} + \text{Li}_2\text{O} \leftrightarrow \text{CoO} + 2\text{Li}^+ + 2e^-
\]

Fig. 3. (a) TG curve of the CNC; (b) Raman spectra of CNC; (c-d) Nitrogen adsorption/desorption isotherms and corresponding pore-size distribution curves of CoSnO\textsubscript{3} nanoboxes and CNC, respectively.
Ni + Li₂O → NiO + 2Li⁺ + 2e⁻
CoO + 1/3Li₂O ↔ 1/3CoO₁₋₂ + 2/3Li⁺ + 1/3e⁻

The discharge−charge profiles for the 1st, 10th and 50th cycles of CNC, NiCo₂O₄@N-C and CoSnO₃@N-C at the current density 0.1 A g⁻¹ in the voltage range 0.01−3.0 V are shown in Fig. 5 b and S8, respectively. There is a large difference between the charging/discharging curves of the three materials, which is caused by the polarization of the electrode during cycling. In the first charge and discharge process, CNC delivers a high discharge/charge capacity of 1548/1082 mA h g⁻¹. The initial Coulombic efficiency is approximately 70%, which is due to the formation of the amorphous Li₂O matrix and the surface reaction with Li-Ni/Li-Co compounds and the electrolyte [42]. In contrast, the initial discharge capacities of the NiCo₂O₄@N-C and CoSnO₃@N-C are 1372 and 1518 mA h g⁻¹, NiCo₂O₄@N-C and CoSnO₃@N-C deliver initial discharge/charge capacity of 1373/831 and 1518/1085 mA h g⁻¹, slightly lower than that of CNC. The coulombic efficiencies of the NiCo₂O₄@N-C and CoSnO₃@N-C are 61% and 71%, respectively. After 50 discharge–charge cycles, compared with the two control samples, CNC delivers a higher specific discharge capacity (912 mA h g⁻¹). The good capacity should be attributed to the multi-shell hollow CNC nanostructures. The multi-shell hollow structure could shorten the distance of Li⁺ transport and relieve huge volume expansion during charge/discharge, while the outer carbon shell increases the electrical conductivity and also relieves the huge volume expansion.

A comparison of cycling performance at a current density of 0.1 A g⁻¹ of CNC, NiCo₂O₄@N-C, and CoSnO₃@N-C is conducted as shown in Fig. 5c. CoSnO₃@N-C as an electrode has a high initial capacity but the worst cycle stability. After 100 cycles, the capacity can only be maintained at 180 mA h g⁻¹ which is only 12% compared with that of the 1st cycle. NiCo₂O₄@N-C delivers an initial discharge capacity of 1372 mA h g⁻¹, and only 411 mA h g⁻¹ is retained after the 100th cycle. As for CNC, after 100 cycles of charge and discharge, it can still maintain the capacity of 992 mA h g⁻¹, which reflects the excellent cycle stability. The discharge curve of CNC indicates a downward trend and then a slow increase. It could be explained by the following aspects: (i) CNC anodes undergo an activation process, and more active sites are exposed after activation [61]; (ii) some Co³⁺ ions (CoO) would further react with Li₂O to generate Co⁴⁺ ions (Co₂O₃) with cycle number and contribute to extra specific capacity [21]; (iii) CoSnO₂ and NiCo₂O₄ in multi-shell hollow structure present the synergistic effects. On the one hand, NiCo₂O₄ nanocages with good electrical conductivity directly grown on CoSnO₃ nanoboxes serve both as the backbone and electron “superhighway” for charge storage and delivery, improving the limited electrical conductivity of the entire CNC. Moreover, the MOF-derived mesoporous structure provides more channels for the contact between Li ions and the internal CoSnO₃. On the other hand, the unique double-hollow configuration of CNC can provide extra accommodating room. In addition, it is known that high capacity Sn-based materials undergo large volume changes during lithiation/delithiation, but the mutual buffering matrices due to different lithiation potentials of CoSnO₃ and NiCo₂O₄ are beneficial to suppress the diffusion and aggregation of Sn nanocrystals during lithium ions de-intercalation. This can be verified by the TEM and EDS energy spectra of CNC after 100th cycling at 0.1 A g⁻¹ (Fig. S9), it is found that there are no big changes in the structure configuration, which demonstrated the structural and chemical stability of the proposed composites.

In addition, it is manifested that CNC provides higher cycling stability. The discharge capacities of CNC nanocages are 1105, 1003, 916, 822, 698 and 525 mA h g⁻¹ at the current densities of 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 A g⁻¹, respectively. When the current density returns to 0.1 A g⁻¹, the capacity can rise back to 1063 mA h g⁻¹ (Fig. 5d). This could be mainly ascribed to the combination of two MTMOs of CoSnO₃ and NiCo₂O₄ to improve the specific capacity of the composite, and the double hollow structure increasing the structural stability [62]. This could be mainly ascribed to the combination of two MTMOs of CoSnO₃ and NiCo₂O₄ to improve the specific capacity of the composite, and the double hollow structure increasing the structural stability. Fig. 5e exhibits the electrochemical impedance spectroscopy (EIS) measurements of the CNC, NiCo₂O₄@N-C and CoSnO₃@N-C. The radius enclosed by the CNC is smaller than the other two comparative samples, and the slope is greater than the comparative material, indicating that the combination of two MTMOs can effectively improve the conductivity of.
the electrode and accelerate the ion transmission rate [62]. Eventually, we evaluate the cycling stability of CNC at a large current density of 1 A g⁻¹. As shown in Fig. 5f, the discharging capacity stabilizes at 670 mA h g⁻¹ after 500 cycles, demonstrating excellent cycling performance of CNC even at the high current density. This should be explained by the unique multi-shell hollow structure and nitrogen-doped carbon skeleton that enhances the charge transferability. In addition, the carbon layer can effectively prevent the agglomeration between nanoparticles during the discharging/charging process [63]. Moreover, compared with the reported Ni/Co composted materials as anode materials of LIB, the prepared CNC exhibits more obvious competitive advantages (Fig. 5g).

4. Conclusion

In summary, we successfully prepare the multi-shell hollow structure CNC nanomaterial by using simple coprecipitation and a one-step calcination method. When it is served as the anode material of LIBs, the CNC exhibits a high initial capacity of 1548 mA h g⁻¹ and it stabilizes around 992 mA h g⁻¹ after 50 cycles. Even after 500 times cycling at a high current density of 1 A g⁻¹, CNC still maintains a specific capacity of 670 mA h g⁻¹. The excellent cycling stability and lithium storage capacity are attributed to the composite of two hollow MTMOs and the coating of carbon. The multi-

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**Fig. 5.** (a) Cyclic voltammograms of CNC; (b) the 1st, 2nd and 50th discharge-charge curves of CNC at the current density 0.1 A g⁻¹ in the voltage range 0.01 ~ 3.0 V; (c) Cycling performance of CNC, NiCo₂O₄@C and CoSnO₃@C and corresponding coulombic efficiency of CNC at a current density of 0.1 A g⁻¹; (d) Rate capability of CNC, NiCo₂O₄@N-C and CoSnO₃@C; (e) EIS Nyquist plots of CNC, NiCo₂O₄@N-C and CoSnO₃@N-C; (f) Cycling performance of CNC and the corresponding coulombic efficiency at a current density of 1 A g⁻¹. (g) The electrochemical performance comparison of CNC, NiCo₂O₄@SnO₂@C [44], NiO/Co₃O₄ [45], SnO₂@Co₃O₄ [46], NiCo₂O₄ nanodisks [47], and NiCo₂O₄ cages [48]. NiCo₂O₄@Graphene [31], CoSnO₃/Graphene [49], CoO@CoSnO₃@C [50], NiCo₂O₄@ZIF-67/GO [51], NiCo₂O₄ particles [52], NiCo₂O₄@NiCo₂O₄ arrays [53], NiCo₂O₄ nanorods [54], CoSnO₃@NC [37], NiCo₂O₄ microflowers [55], NiCo₂O₄ nanosheets [56].
shell hollow structure owns a buffer effect on volume variation, while the increased specific surface area could effectively enhance the storage of lithium ions. The carbon layer can effectively enhance the charge transfer ability and relieve the agglomeration of metal oxides during the charge and discharge process. This work reveals that such multi-shell structured MTMOs, like CNC, present the great potential to be high-performance anode candidates for LIBs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/jcej.2021.128458.

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