This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Unique Synthesis of Hollow Co$_3$O$_4$ Nanoparticles embedded in Thin Al$_2$O$_3$ Nanosheets for the Enhanced Lithium Storage

Jiao Yang, Hua-Jun Qiu, Liang Peng, Wenxiang Li, Yu Wang*

The State Key Laboratory of Mechanical Transmissions and School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China

*Email: wangy@cqu.edu.cn; prospectwy@gmail.com

Abstract

The designed synthesis of advanced nanocomposite architecture is significant for their applications in energy storage, catalysis, sensing, etc. Herein, thin Al$_2$O$_3$ hexagon nanosheets with encapsulated hollow Co$_3$O$_4$ nanoparticles (Co$_3$O$_4$-HNP) are successfully synthesized by using Co$_6$Al$_2$CO$_3$(OH)$_{16}$·4H$_2$O nanosheets as templates and followed by two step annealing process. When used as an anode material in lithium ion batteries (LIBs), the homogeneous Co$_3$O$_4$-HNP/Al$_2$O$_3$ nanosheet composite exhibits an excellent performance with a high reversible capacity, rate capability, and enhanced cycling stability.

Keywords: hexagon nanosheet, encapsulated composite, hollow Co$_3$O$_4$, lithium ion batteries

Introduction

Developing advanced and green energy sources is very important for the sustainable development of modern society, especially with the decreasing amount of fossil energy sources and all these environmental problems caused by consuming them.$^{1,2}$ As a green power source, lithium ion batteries (LIBs) have been widely used nowadays and also attracted great research interest to enhance their performance due to the importance.$^{3-6}$ At present, various materials such as nanostructured carbon,
transition metal oxides, transition metal phosphides, etc., have been prepared and
studied as the anode materials for LIBs. Among them, the transition metal oxides
such as Co$_3$O$_4$ have attracted increasing research interest owing to its high theoretical
capacity (890 mAh g$^{-1}$). However, the remarkable volume changes and severe
particle aggregation during the Li insertion/extraction reaction would lead to electrode
pulverization, resulting in a significant capacity loss and poor cycling stability. To
conquer these problems, various strategies have been utilized, including the synthesis
of carbon-based nanocomposites, 1-D Co$_3$O$_4$ nanowires or 2-D Co$_3$O$_4$ nanosheets,
hollow structure, etc. Among these, the fabrication of composites with
graphene and/or other metal oxides has been demonstrated to be quite successful. However,
these Co$_3$O$_4$-based composites are usually prepared by simply growing one
component on the surface of the other. Due to the one-side simple attachment,
the prepared composite structure may be easily damaged during continuous
charge/discharge reactions. The encapsulation of one active component inside two
closely attached thin nanosheets could be an effective strategy to enhance the
structure integrity and stability. In our previous work, we have successfully
designed and synthesized metal oxides nanoparticles (NPs) encapsulated in carbon
nanosheets or nanotubes for enhanced Li storage. Besides, the coating of Al$_2$O$_3$
thin film on active materials has also been demonstrated to be a good strategy to
enhance the structure stability of the active component in LiBs. For example, Cho et
al., used a sol-gel method to coat Al$_2$O$_3$ on LiCoO$_2$ particle surface. Kang et al.,
used an atomic layer deposition method to coat Al$_2$O$_3$ on Fe$_3$O$_4$ nanocrystal surface.
However, the facile synthesis of closely encapsulated Co$_3$O$_4$-HNP inside of Al$_2$O$_3$
thin nanosheets remains a big challenge.

In this work, using Co$_6$Al$_2$CO$_3$(OH)$_{16}$·4H$_2$O hexagon nanosheets as templates, we
successfully designed and fabricated uniform thin Al$_2$O$_3$ nanosheets with Co$_3$O$_4$-
HNP encapsulated inside and remain the precursor hexagon architecture. Due to the
advanced structure design and enhanced material properties, the encapsulated hollow
Co$_3$O$_4$-HNP/Al$_2$O$_3$ nanosheets composite exhibits a large reversible capacity,
excellent cycling stability and high rate capability when used as an anode material for
LIBs.

**Experimental Section**
Synthesis of $\text{Co}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ hexagon nanosheets.

Ammonia (12.5 mL), ethylene glycol (12.5 mL), Co(NO$_3$)$_2$ aqueous solution (5 mL, 1 M), Al(NO$_3$)$_3$ (2 mL, 1 M), and Na$_2$CO$_3$ solution (5 mL, 1 M) were added step-by-step into a baker under continuous stirring condition. After stirring for 20 min, the mixed solution changed into burgundy. After that, the precursor solution was transferred into a 50 mL Teflon-lined autoclave, sealed and heated at 180 °C for 15 h. After it was cooled to room temperature, the samples were taken out and washed by centrifugation with deionized water and pure ethanol. Finally, the samples were dried in an oven at 60 °C overnight.

Synthesis of $\text{Co}_3\text{O}_4$-HNPs /$\text{Al}_2\text{O}_3$ nanosheets.

The pink precursor was annealed at 750 °C for 200 min in a mixed H$_2$ and Ar atmosphere. After cooled to room temperature, the samples were further annealed at 450 °C for 200 min in air with a temperature programming of 1 °C/min. Because the composites is synthesis through annealing the precursor of $\text{Co}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ hexagon nanosheets. The molar ratio of Co and Al is 3:1 and the mass ratio of $\text{Co}_3\text{O}_4$ and $\text{Al}_2\text{O}_3$ is approximate 4.72:1. This indicates that the weight fraction of $\text{Co}_3\text{O}_4$ is 82.52% and can’t be adjusted.

For comparison, pure $\text{Co}_3\text{O}_4$ NPs were prepared by mixing water (12.5 mL), ammonia (12.5 mL), Co(NO$_3$)$_2$ aqueous solution (5 mL, 1 M) under stirring. After stirring for 30 min, the mixture was transferred into a 50 mL Teflon-lined autoclave, sealed and heated at 170 °C for 24 h. After it was cooled to room temperature, the samples were taken out and washed with water and ethanol. Finally, the black samples were dried in an oven at 60 °C overnight.

Material Characterizations.

All the samples were characterized by a powder X-ray diffraction (Bruker D8 Advance X-ray diffractometer) with Cu Kα radiation, scanning electron microscope (SEM, JEOL, JSM-7800F) with an energy dispersive spectrometer (EDS), transmission electron microscopy (TEM, JEOL, JEM-2100F), and Brunauer-Emmett-Teller surface-area and pore-size analyzer (BET, Quantachrome Autosorb-6B).

Electrochemical Measurements
A lithium metal was used as the counter electrode and a Cellgard2400 membrane was used as the cell separator. The electrolyte was 1 M LiPF₆ in ethylene carbonate and diethyl carbonate (EC-DEC, v/v=1:1). The working electrode was prepared by a slurry coating method. The slurry was prepared by mixing 80 wt% Co₅O₄-HNPs/Al₂O₃ composite, 10 wt% carbon black and 10 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl-pyrrolidinone (NMP). A homogeneous mixture was formed by magnetic stirring for 24 h. This slurry was spread on copper foil with diameter of 12mm and dried at 80 °C for 24 h. The mass loading of the active material in the examined electrodes is about 2.2 mg cm⁻². The cells were constructed in an Ar-filled glove box under 20 MPa pressure. The galvanostatic cycling was performed on NEWARE battery program-control testing system at rate of 0.145 A g⁻¹ with the voltage range of 0.01-3.0 V, and cyclic voltammetry (CV) was collected using Electrochemical workstation (CH660E) between 0 and 3 V with a scan rate of 0.2 mV/s. The specific capacity and current density were calculated based on the mass of the active material in the working electrode.

**Results and discussion**

**Preparation and characterization of encapsulated Co₅O₄-HNPs/Al₂O₃ nanosheets**

The fabrication procedure of the Co₅O₄-HNPs encapsulated in thin Al₂O₃ nanosheets is shown in Scheme 1a. First, pure Co₆Al₂CO₃(OH)₁₆·4H₂O hexagon nanosheets were synthesized by a hydrothermal method. The hexagon nanosheets were then annealed in H₂ and Ar atmosphere at 750 °C. This annealing process would decompose (reduce) the cobalt element into metal Co NPs encapsulated inside of thin Al₂O₃ nanosheets which inherit the morphology of the precursor hexagon nanosheets. After that, a second annealing in air was carried out to transform the encapsulated Co NPs/Al₂O₃ nanosheets into hollow Co₅O₄-HNPs/Al₂O₃ nanosheets. As explained in previous work, the mechanism for the formation of Co₅O₄-HNPs from Co NPs is due to the nanoscale Kirkendall effect which has also been observed by annealing Ni or Cu NPs in different atmospheres. For more electrode design strategies, one can refer to an excellent review published recently.

Fig. 1a shows the SEM image of the synthesized Co₆Al₂CO₃(OH)₁₆·4H₂O nanosheets. It is observed that the thin nanosheets are relatively uniform with an
average size of around 300 nm and a thickness of ~20 nm. From the zoom-in SEM image (Fig. 1b), it is observed that the thin nanosheet precursor is hexagon. XRD analysis (Fig. 1c) shows that the formed nanosheets are pure Co₆Al₂CO₃(OH)₁₆₄H₂O (JCPDS No. 51-0045). After the first annealing in H₂ and Ar atmosphere, the morphology of the nanosheets is well-inherited by the formed Al₂O₃ nanosheets (Fig. 1d and 1e). The formed Co NPs with a size of ~8 nm are uniformly distributed inside of the thin Al₂O₃ nanosheets from the bright-field STEM image (Fig. 1e). The XRD pattern (Fig. 1f) shows three main peaks which can be assigned to the (111), (200) and (220) diffraction of face-centered cubic cobalt (JCPDS No. 89-7093). After the second step annealing, the structure of the encapsulated Co NPs/Al₂O₃ composite is well retained by the encapsulated Co₃O₄-HNPs/Al₂O₃ nanosheets (Fig. 2a and 2b). The composite is further characterized by TEM. As shown in Fig. 2c, high density and uniform Co₃O₄-HNPs with a diameter of ~15 nm are homogeneously encapsulated inside the thin Al₂O₃ nanosheets, which is in good agreement with the SEM result. The clear color contrast between the hollow core and surface shell indicates that the Co₃O₄-HNPs have a hollow structure. The continuous lattice fringes in the HRTEM image (Fig. 2d) indicate the crystalline nature of the encapsulated Co₃O₄-HNPs. The lattice spacing of 0.28 nm and 0.23 nm corresponds to the (220) and (222) plane of Co₃O₄, respectively. The crystal structure of the Co₃O₄-HNPs/Al₂O₃ nanosheets is further examined by XRD (Fig. 2e). The diffraction peaks at the degree of 31.2° (220), 36.9° (311), 55.7° (422), 59.2° (511) and 65.2° (440) are consistent with the standard XRD data for Co₃O₄ (JCPDS No. 43-1003). The week peak at ~46° can be ascribed to (400) diffraction of α-Al₂O₃. To further demonstrate the existence of α-Al₂O₃, we dissolved the Co₃O₄-HNPs in a weak HCl aqueous solution. After the dissolution, the porous α-Al₂O₃ is well preserved with inner holes (Fig. S1a and S1b in supporting information). XRD analysis further confirms the α-Al₂O₃ crystal structure (Fig. S1c). The Brunauer–Emmett–Teller (BET) surface area of the composite is determined to be ~208 m² g⁻¹ and pore diameter is around 4 nm with the Barrett-Joyner-Hallender (BJH) method (Fig. 2f). These results suggest that the encapsulated Co₃O₄-HNPs/Al₂O₃ composites possess a high surface area and many small pores which would facilitate the free diffusion of electrolyte during electrochemical reactions.
The encapsulated Co$_3$O$_4$-HNPs in Al$_2$O$_3$ thin nanosheets are further characterized by EDS mapping. As shown in Fig. 3, the nano-composite is clearly comprised of Co, Al, and O. From the Fig. 3a and Fig. 3b, we can confirm that the encapsulated hollow NPs are Co oxides because the distribution of Co element is in good agreement with the hollow particles (two hollow particles are denoted by red circles).

**Electrochemical measurement**

The Al$_2$O$_3$ nanosheets with encapsulated Co$_3$O$_4$-HNPs were then tried as an anode material for LIBs. For comparison, we also synthesized pure Co$_3$O$_4$ NPs, which were characterized by SEM, TEM and XRD (Fig. S2). The diameter of the Co$_3$O$_4$ NPs is around 10 nm (Fig. S2a, S2b). The XRD pattern (Fig. S2c) confirms that the samples are pure Co$_3$O$_4$ (JCPDS No. 01-1152). Fig. 4a shows the galvanostatic discharge-charge curves of the Co$_3$O$_4$-HNPs/Al$_2$O$_3$ nanosheets at 0.1 A g$^{-1}$ between 0.01 and 3.0 V (versus Li/Li$^+$). As shown that the Co$_3$O$_4$-HNPs/Al$_2$O$_3$ nanocomposite exhibits a high first discharge capacity of ~1787 mAh g$^{-1}$, which is much higher than the theoretical capacity of Co$_3$O$_4$ (890 mAh g$^{-1}$). The excess capacity discharged at first could be related to the initial formation of the solid-electrolyte-interface (SEI) layer caused by electrolyte degradation. It should be mentioned that the excess capacity during the first discharge is a common phenomenon and also detected in other anode materials.$^{36,37}$ Compared to pure Co$_3$O$_4$ nanoparticles electrode (Fig. S4a), the plateau with slight lean in first discharge for the Co$_3$O$_4$-HNPs/Al$_2$O$_3$ nanocomposite may be due to the presence of Al$_2$O$_3$ nanosheets. It is possible that the Al$_2$O$_3$ nanosheets can adsorb and release Li during the Lithiation/delithiation, which may slightly affect the electrochemical behavior of Co$_3$O$_4$.$^{33,38}$ The corresponding CV curves are shown in Fig. S3 which exhibits a typical electrochemical behavior of Co$_3$O$_4$ in LIB tests with oxidation peaks at ~2.2 V and reduction peaks at ~0.8 V. Started from the second cycle, the capacity decreases slightly to ~1278 mAh g$^{-1}$ and the charge/discharge reactions become quite stable (Fig. 4a). As shown in Fig. 4b, after even 150 cycles at 0.1 A g$^{-1}$, the capacity is still over 95% with a very high Coulombic efficiency (~99%). In comparison, the capacity of the bare Co$_3$O$_4$ NPs decreases quickly with the increasing cycle number at the same current density (Fig. S4a). These results indicate the excellent cycling stability achieved by encapsulating Co$_3$O$_4$-HNPs in thin Al$_2$O$_3$ nanosheets. The stabilized specific capacity (~1215 mAh g$^{-1}$ at 0.1 A g$^{-1}$) is
also very high when compared with many reported values from Co$_3$O$_4$-based anode materials such as Co$_3$O$_4$ octahedral nanocages (887 mAh g$^{-1}$ at 0.2 C), Co$_3$O$_4$/graphene composite (754 mAh g$^{-1}$ at 0.1 A g$^{-1}$) and Co$_3$O$_4$/carbon nanotubes (823 mAh g$^{-1}$ at 0.2 A g$^{-1}$). A detailed comparison is shown in Table S1. To test the rate capability of the Co$_3$O$_4$-HNPs/Al$_2$O$_3$ nanocomposite, we sequentially increased the current density from 0.1 A g$^{-1}$ to 5 A g$^{-1}$. As shown in Fig. 4c, the capacity decreases with the increasing current densities. When 5 A g$^{-1}$ is applied, the capacity is still ~643 mAh g$^{-1}$ (~53%), which also higher than those of previous reports, indicating the good rate capability of the encapsulated Co$_3$O$_4$-based composite electrode. Moreover, when cycled back to 0.1 A g$^{-1}$, the recovered capacity can reach ~1152 mAh g$^{-1}$, which further demonstrates the excellent performance of the designed composite electrode (Fig. 4d). To evaluate the contribution from the Al$_2$O$_3$, we also use the bare Al$_2$O$_3$ (Co$_3$O$_4$ has been dissolved in an acidic solution) as anode material in LIBs. The obtained result is similar to the result reported before. Based on the charge/discharge curve of bare Al$_2$O$_3$ (Fig. S4b), we can see that the specific capacity is ~80 mAh g$^{-1}$ at 0.1 A g$^{-1}$. It is concluded that the contribution from Al$_2$O$_3$ is very low and the overall capacity mainly comes from the active material Co$_3$O$_4$.

We also tested the ion and electronic resistance of the Co$_3$O$_4$-HNPs/Al$_2$O$_3$ nanocomposite and bare Co$_3$O$_4$ NPs, respectively (Fig. S5). The as-prepared Co$_3$O$_4$-HNPs/Al$_2$O$_3$ nanocomposite has a similar semicircle compared with bare Co$_3$O$_4$ NPs. This suggests that the Al$_2$O$_3$ thin film does not have any negative effect on the conductivity of the electrode. Thus, the high rate performance of Co$_3$O$_4$-HNPs/Al$_2$O$_3$ nanocomposite should be ascribed to the short Li$^+$ ion diffusion length and low internal charge-transfer resistance of the electrode. The SEM image of Co$_3$O$_4$-HNPs/Al$_2$O$_3$ after charge/discharge cycles can be seen in supporting information (Fig. S6). It is observed that most of the nanocomposites maintain the original architecture, which is consistent with the good electrochemical stability.

The high and stable charge/discharge performance should be owing to the designed advanced structure of the electrode. Firstly, the porous Al$_2$O$_3$ thin nanosheets can remarkably enhance the diffusion of electrolyte and ions. Moreover, due to the encapsulation in the thin Al$_2$O$_3$ nanosheets, the detachment, aggregation, and even
pulverization of the Co$_3$O$_4$-HNPs can be largely solved. Secondly, the efficient inner space from the Co$_3$O$_4$-HNPs would allow the volume change of the Co$_3$O$_4$ nano-shells while retaining the structure integrity.$^{45,46}$ Last but not least, the nanoscale Co$_3$O$_4$ hollow particles (~15 nm) with high surface areas will effectively improve the Li-ion exchange rate.

**Conclusions**

Uniform Al$_2$O$_3$ hexagon nanosheets with encapsulated hollow Co$_3$O$_4$-HNPs was facilely prepared by using Co$_6$Al$_2$CO$_3$(OH)$_{16}$4H$_2$O nanosheets as templates, and followed by two-step annealing process. This designed and synthesized composite material possesses many advanced structure properties such as intimate contact between the encapsulated hollow Co$_3$O$_4$-HNPs and thin Al$_2$O$_3$ nanosheets, high nanoporosity, large specific surface area, etc. Owing to the unique nano-architecture, the Co$_3$O$_4$-HNPs/Al$_2$O$_3$ nanosheets exhibits a high and stable Li storage capability when used as an anode material in LIBs. The strategy presented in this work may be helpful for designing advanced encapsulated nanocomposites for various applications such as catalysis, sensing, etc.

**Acknowledgements**

This work was financially supported by the Thousand Young Talents Program of the Chinese Central Government (Grant No.0220002102003), National Natural Science Foundation of China (NSFC, Grant No. 21373280, 21403019), Beijing National Laboratory for Molecular Sciences (BNLMS), the Fundamental Research Funds for the Central Universities (0301005202017) and Hundred Talents Program at Chongqing University (Grant No. 0903005203205).
Reference


Figure captions:

Scheme 1. Schematic illustration of the designed synthesis process of the hollow Co$_3$O$_4$-HNPs/Al$_2$O$_3$ nanosheets composite.

Fig. 1. SEM/STEM images of Co$_6$Al$_2$CO$_3$(OH)$_{16}$.4H$_2$O nanosheets before (a, b) and after (d: STEM image, e) the first annealing. (a and d: low magnification; b and e: high magnification) and XRD patterns of the precursors before (c) and after (f) the first annealing process.

Fig. 2. SEM images (a, b), TEM (c), HRTEM (d), XRD pattern (e) and nitrogen absorption/desorption curve (f) of the Co$_3$O$_4$-HNPs/Al$_2$O$_3$ nanosheet composite. Inset in (f) is the corresponding pore size distribution.

Fig. 3. STEM image (a) and EDS mapping results (b, c and d) of the encapsulated Co$_3$O$_4$-HNPs/Al$_2$O$_3$ nanosheet composite.

Fig. 4. Galvanostatic charge-discharge curves at different cycles at 0.1 A g$^{-1}$ (a). Cycling performance and coulombic efficiency at a current density of 0.1 A g$^{-1}$ (b). Galvanostatic charge-discharge curves (c) at different current densities and the rate capability results (d) of the encapsulated hollow Co$_3$O$_4$-HNPs/Al$_2$O$_3$ nanosheet composite.
Scheme 1

- Hydrothermal reaction
- Calcinations at inert atmospheres
- Annealing in air

Co metal nanoparticles
Co$_3$O$_4$ hollow spheres

hexagons nanosheet (Co$_6$Al$_2$CO$_3$(OH)$_{16}$·4H$_2$O)
Co metal nanoparticles
Al$_2$O$_3$
Co$_3$O$_4$ hollow spheres
Fig. 1
Fig. 2
Fig. 3
Fig. 4

(a) Potential / V vs. Li\textsuperscript+ / Li vs. Capacity / mAh g\textsuperscript{-1}
- 1\textsuperscript{st} cycle
- 2\textsuperscript{nd} cycle
- 5\textsuperscript{th} cycle
- 10\textsuperscript{th} cycle
- 20\textsuperscript{th} cycle
- 30\textsuperscript{th} cycle

(b) Coulombic efficiency (%)
- Co\textsubscript{3}O\textsubscript{4} Discharge capacity
- Co\textsubscript{3}O\textsubscript{4} Charge capacity

(c) Potential / V vs. Li\textsuperscript+ / Li vs. Capacity (mAh/g)
- 0.1 A/g
- 0.5 A/g
- 1 A/g
- 2 A/g
- 5 A/g

(d) Capacity (mAh/g) vs. Number of cycles
- Co\textsubscript{3}O\textsubscript{4} Discharge capacity
- Co\textsubscript{3}O\textsubscript{4} Charge capacity
- 0.1 A/g
- 0.5 A/g
- 1 A/g
- 2 A/g
- 5 A/g
A table of contents:

Hollow Co$_3$O$_4$ nanoparticles encapsulated in thin Al$_2$O$_3$ hexagon nanosheets are fabricated and exhibit an excellent performance in LIBs.