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Facile synthesis of a mesoporous Co$_3$O$_4$ network for Li-storage via thermal decomposition of an amorphous metal-complex

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A facile strategy is developed to mass fabrications of porous Co$_3$O$_4$ network via the thermal decomposition of an amorphous cobalt-based complex. At a low mass loading, the achieved porous Co$_3$O$_4$ networks exhibit excellent performance for lithium storage, which has a high capacity of 587 mAh g$^{-1}$ after 500 cycles at a current density of 1000 mA g$^{-1}$.

Lithium-ion battery (LIB) is a promising power source for portable electronics and electric vehicles because of its high energy density when compared with other energy-storage devices.$^{1,4}$ The next generation of LIBs aims at combined characteristics of high energy density, high power density, long lifetime, and low cost, especially those for electric vehicles. Since the first report by Tarascon et al.$^5$ transition metal oxides have been considered as potential anode materials for LIBs because of their much higher capacity when compared with commercial graphite (with a theoretical value of 370 mAh g$^{-1}$). Among them, Co$_3$O$_4$ has stimulated tremendous research interests because of its high capacity of 990 mAh g$^{-1}$,$^6$ however, it suffers from common drawbacks of conversion-reaction-based metal oxide anodes, that is, poor cycling stability and rate performance, due to the poor conductivity and large specific volume change during battery cycling, which leads to pulverization and detachment of active materials from the conductive substrate. To overcome these problems, Co$_3$O$_4$ in various nanostructures, such as nanoparticles,$^7$ nanocubes,$^8$ nanotubes,$^9$ nanowires,$^{10,11}$ nanobelts,$^{12}$ nanosheets,$^{13,14}$ star-like structures,$^{15}$ and hollow structures,$^{16,17}$ has been fabricated and studied extensively. As an effective strategy, cobalt oxides were also composed with carbon materials to construct hybrid electrodes,$^{18-22}$ but the presence of the low-capacity carbon suppresses the battery capacity/weight ratio and makes the synthesis process more complex. Excellent electrochemical properties have been recorded for anode materials in the form of thin films because of the much improved conductivity;$^{23-26}$ however, their loading of active materials is too low.$^{27}$ Increasing the thickness of thin film anodes always sharply deteriorates the electrochemical performance.$^{26}$

A porous structure achieves more efficient ingress and infiltration of the electrolyte and partially accommodates the large volume change.$^{28}$ However, most approaches for porous transition metal oxides are template-assisted by using soft templates or hard templates, which need troublesome multi-step procedures. Recently, a bacterial template, which is inexpensive and easy to handle, was developed to synthesize porous Co$_3$O$_4$. As for template-free techniques, decomposition of pre-synthesized precursors is effective to achieve porous Co$_3$O$_4$. For example, mesoporous Co$_3$O$_4$ nanosheets were fabricated by thermal transformation of Co(OH)$_2$ prepared by electrodeposition.$^{30}$ Mesoporous Co$_3$O$_4$ nanowires were also obtained via thermal decomposition of Co(CO$_3$)$_2$(OH)$_2$·0.11H$_2$O, which is synthesized by a hydrothermal route.$^{31}$ Recently, metal-organic frameworks (MOFs) have been recognized as promising precursors to prepare mesoporous metal oxides.$^{32-36}$ Meng et al. prepared a cobalt-based MOF, which decomposed to porous Co$_3$O$_4$ particles via a two-step calcination treatment (in Ar gas and air).$^{34}$ Unfortunately, the synthesis of MOFs is relatively complex and costly.

With continuous efforts, the capacity of Co$_3$O$_4$ has been improved steadily in recent years; yet the lifetime is not satisfying.$^{3,21}$ It thus remains an urgent task yet a challenge to further improve the rate capability and cycling stability of Co$_3$O$_4$, especially for those fabricated by a simple and cost-effective synthesis technique.

Herein, we develop a facile strategy to mass fabrications of porous Co$_3$O$_4$ network via the thermal decomposition of an amorphous cobalt-based complex. The cobalt-based complex is prepared by a simple and rapid pyrolysis of cobalt nitrate and glycine. The achieved porous Co$_3$O$_4$ networks exhibit excellent performance for lithium storage because of the porous structure and fine nanoparticle blocks. At a low mass loading, the porous Co$_3$O$_4$ network exhibits a high capacity of 587 mAh g$^{-1}$ after 500 cycles at a high current density of 1000 mA g$^{-1}$.

In preparation, 1.250 g Co(NO$_3$)$_2$·6H$_2$O and 1.750 g glycine (C$_2$H$_4$NO$_2$) were dissolved in 10 mL deionized water in a crucible to form a pink solution, which was then transferred to a preheated furnace maintained at 400 ºC for ca. 16 minutes to finish the decomposition reaction, resulting in a black precursor. The as-synthesized precursor was then heated in air at 355 ºC for 1 h at a heating rate of 5 ºC min$^{-1}$ to achieve finally the porous Co$_3$O$_4$ network.

Fig. 1 illustrates schematically the synthesis procedure for mass fabrications of porous metal oxides. Inexpensive metal nitrate and glycine (the simplest amino acid) are used as raw
materials. The synthesis of cobalt-based amorphous precursor is similar to our previous report for synthesis of a zinc-based amorphous precursor, which, upon a subsequent calcination, decomposed to form macroporous ZnO networks.\textsuperscript{37} For a convenient observation of the synthesis process of the cobalt-based complex, the solution was also heated on a hot plate maintained at 400 °C, and the photographs taken at different reaction stages are exhibited in Fig. S1 in the Electronic Supplementary Information (ESI\textsuperscript{†}). Once being placed on the hot plate, the solution rapidly boiled (Fig. S1a). After several minutes, the initial pink color turned to blue (Fig. S1b), which is attributed to the change in the coordination environment of Co, namely, the gradual loss of its crystal water. The xerogel bubbled, decomposed and released lots of gases, resulting in the further change of color to black (Fig. S1c). Finally, a black product formed (Fig. S1d). The whole synthesis duration on the hot plate is shorter than that in furnace because of the difference in heat transfer conditions. The as-synthesized precursor was then calcined in air to obtain a porous metal oxide network.

![Fig. 1](image1.png)

**Fig. 1** A schematic illustration of the synthesis procedure for porous metal oxides.

![Fig. 2](image2.png)

**Fig. 2** (a) XRD patterns of the as-synthesized and calcinated powders, (b) TG-DTA curves of the as-synthesized powder.

No obvious diffraction peaks can be detected in the X-ray diffraction (XRD) pattern of the as-synthesized precursor (Fig. 2a), indicating its amorphous feature. The energy dispersive spectrum (EDS, Fig. S2) shows that the precursor contains Co, O, N, and C elements. The content of C, N, and H measured by an element analysis (Flash EA 1112, ThermoFinnigan) is 34.55 wt. %, 19.27 wt. % and 2.23 wt. %, respectively. X-ray photoelectron spectra (XPS) were carried out to further investigate the composition of the cobalt-based complex and the results are shown in Fig. S3. The Co 2p spectrum in Fig. S3a shows four peaks of the 2p\textsubscript{1/2} and 2p\textsubscript{3/2} doublet. The Co 2p\textsubscript{1/2} and 2p\textsubscript{3/2} binding energies at ca. 780.5 and 796.7 eV are in good agreement with the energies of the photoelectrons of Co\textsuperscript{2+}.\textsuperscript{38} The O 1s at 531.1 eV is attributed to O-Co bonds,\textsuperscript{38} and the peak at 532.6 eV corresponds to covalent bonds of O with H or/and C.\textsuperscript{39} The C 1s spectrum can be fitted into three peaks around 284.5, 285.5, and 287.4 eV, corresponding to the C–C, C–OH/C–N, and O=C–O bonds, respectively.\textsuperscript{40,41} The N 1s spectrum can be fitted to three peaks at 398.5, 399.7, and 401.0 eV, which may be assigned to Co-N bonds, N-H bonds,\textsuperscript{42} and ammonium ions/chemically absorbed nitrogen species,\textsuperscript{43,44} respectively.

Thermogravimetric and differential thermal analysis (TG-DTA) were performed in air atmosphere at a heating rate of 5 °C min\textsuperscript{-1} from room temperature to 800 °C and the results are shown in Fig. 2b. A sharp weight loss accompanied by a strong exothermic peak at 355 °C can be found, which indicates the decomposition of the as-synthesized amorphous complex to Co\textsubscript{3}O\textsubscript{4}. The weight loss is assigned to the removal of organic components (C, N, H, and partial O), which resulted in the formation of porous structure in the calcined products. The decomposition temperature here is much lower than that of the amorphous zinc-based complex previously reported\textsuperscript{37} (355 °C vs. 550 °C), which is beneficial for the formation of the present mesoporous Co\textsubscript{3}O\textsubscript{4} network with fine particle sizes.

![Fig. 3](image3.png)

**Fig. 3** SEM image (a), TEM image (b), HRTEM image (c), and selected area electron diffraction pattern (d) of the as-synthesized amorphous complex.

In calcination, cobalt components were oxidized to Co\textsubscript{3}O\textsubscript{4} and the organic components was removed. As shown in Fig. 2a, all the diffraction peaks of the product can be indexed to the face-centered cubic spinal phase Co\textsubscript{3}O\textsubscript{4} (JCPDS card No.
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Nitrogen adsorption-desorption measurement was further performed to get more information about the porous structure. The porous Co$_3$O$_4$ exhibited a type IV nitrogen isotherm (Fig. 5a), indicating the existence of mesopores. The specific surface area and total pore volume is determined to be 59 m$^2$ g$^{-1}$ and 0.261 cm$^3$ g$^{-1}$, respectively. Fig. 5b shows the pore size distribution calculated by BJH method from the desorption branch. The pores range from several nanometers to tens of nanometers with a peak at ca. 15 nm, which is in accordance with TEM observations (Fig. 4b, c).

The lithium storage tests of the porous Co$_3$O$_4$ network as an anode material were performed in a potential window of 0.005–3.000 V versus Li. The electrochemical performance was evaluated in coin type lithium half-cells using Li foil as counter and reference electrodes at room temperature. The electrodes consisted of 80 wt. % Co$_3$O$_4$ powders, 10 wt. % acetylene black, and 10 wt. % polyvinylidene fluoride (PVDF). The active material (Co$_3$O$_4$) was 0.4–0.6 mg/cm$^2$ on each electrode and the coating thickness was ca. 35 µm. Fig. 6a illustrates the voltage profile. For the first discharge at a current density of 100 mA g$^{-1}$, the potential abruptly falls to about 1.14 V with a long plateau, which can be attributed to the reduction of Co$_3$O$_4$ to Co, followed by a sloping down to the cut-off voltage of 0.005 V, exhibiting a capacity of 1483 mAh g$^{-1}$. Fig. 8 shows the first two cyclic voltammetry (CV) curves at a scan rate of 0.1 mV s$^{-1}$ in a potential range of 0.005–3.0 V vs. Li/Li$^+$. The peak at ca. 0.85 V in the first cathodic scan is attributed to the reduction of Co$_3$O$_4$ to Co accompanying the formation of Li$_2$O and the solid electrolyte interphase film.$^{37-49}$ A peak at ca. 2.03 V in the first anodic process corresponds to the oxidation reaction from Co to Co$_3$O$_4$ accompanying the decomposition of Li$_2$O. In the second cycle, the cathodic peak shifts to a higher potential of ca. 1.04 V. $^{47-49}$ The irreversible capacity in the first cycle is attributed to the formation of the SEI layer and some undecomposed Li$_2$O phase, which is common for metal oxide anodes. The initial columbic efficiency of the porous Co$_3$O$_4$ is 71.1%. The reaction mechanism of Co$_3$O$_4$ with Li in lithium-ion batteries is proposed as follows:

$$\text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \xrightarrow{\text{charge}} 4\text{Li}_2\text{O} + 3\text{Co}$$

The discharge capacity of the present porous Co$_3$O$_4$ initially decreases and then gradually increases during the discharge-charge cycling (Fig. 6b). After 100 cycles, the discharge capacity is 890 mAh g$^{-1}$, corresponding to 80% of the second cycle capacity, indicating the existence of mesopores. The specific surface area and total pore volume is determined to be 59 m$^2$ g$^{-1}$ and 0.261 cm$^3$ g$^{-1}$, respectively. Fig. 5b shows the pore size distribution calculated by BJH method from the desorption branch. The pores range from several nanometers to tens of nanometers with a peak at ca. 15 nm, which is in accordance with TEM observations (Fig. 4b, c).

The lithium storage tests of the porous Co$_3$O$_4$ network as an anode material were performed in a potential window of 0.005–3.000 V versus Li. The electrochemical performance was evaluated in coin type lithium half-cells using Li foil as counter and reference electrodes at room temperature. The electrodes consisted of 80 wt. % Co$_3$O$_4$ powders, 10 wt. % acetylene black, and 10 wt. % polyvinylidene fluoride (PVDF). The active material (Co$_3$O$_4$) was 0.4–0.6 mg/cm$^2$ on each electrode and the coating thickness was ca. 35 µm. Fig. 6a illustrates the voltage profile. For the first discharge at a current density of 100 mA g$^{-1}$, the potential abruptly falls to about 1.14 V with a long plateau, which can be attributed to the reduction of Co$_3$O$_4$ to Co, followed by a sloping down to the cut-off voltage of 0.005 V, exhibiting a capacity of 1483 mAh g$^{-1}$. Fig. 8 shows the first two cyclic voltammetry (CV) curves at a scan rate of 0.1 mV s$^{-1}$ in a potential range of 0.005–3.0 V vs. Li/Li$^+$. The peak at ca. 0.85 V in the first cathodic scan is attributed to the reduction of Co$_3$O$_4$ to Co accompanying the formation of Li$_2$O and the solid electrolyte interphase film.$^{37-49}$ A peak at ca. 2.03 V in the first anodic process corresponds to the oxidation reaction from Co to Co$_3$O$_4$ accompanying the decomposition of Li$_2$O. In the second cycle, the cathodic peak shifts to a higher potential of ca. 1.04 V. $^{47-49}$ The irreversible capacity in the first cycle is attributed to the formation of the SEI layer and some undecomposed Li$_2$O phase, which is common for metal oxide anodes. The initial columbic efficiency of the porous Co$_3$O$_4$ is 71.1%. The reaction mechanism of Co$_3$O$_4$ with Li in lithium-ion batteries is proposed as follows:

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The porous Co$_3$O$_4$ exhibits a high discharge capacity of 1111 mAh g$^{-1}$ in the 2nd cycle at a high current of 100 mA g$^{-1}$. The discharge capacity of the present porous Co$_3$O$_4$ firstly decreases and then gradually increases during the discharge-charge cycling (Fig. 6b). After 100 cycles, the discharge capacity is 890 mAh g$^{-1}$, corresponding to 80% of the second
discharge capacity (Fig. 6b). At a much higher current density of 1000 mA g\(^{-1}\), the second discharge capacity is still as high as 560 mAh g\(^{-1}\) and the capacity retains at 587 mAh g\(^{-1}\) after 500 cycles, exhibiting an extraordinary cycling stability (Fig. 6c). The parallel experiment indicates that the commercial Co\(_3\)O\(_4\) nanoparticles show a rapidly decreased capacity, which is 403 mAh g\(^{-1}\) after 60 cycles at a current density of 100 mA g\(^{-1}\) (Fig. S9). The capacity increasing with cycling has been also seen in many cobalt oxides as well as other metal oxide anode materials.\(^{15,20,50-52}\) This phenomenon may be partly attributed to the reversible growth of a polymeric gel-like film resulting from the reaction of anode materials with electrolyte.\(^{50}\)

The small particle size greatly decreases the diffusion length of lithium ions. The present synthesis strategy can also be extended to mass productions of other porous metal oxides, such as porous ZnCo\(_2\)O\(_4\) and porous NiO (the corresponding SEM images and XRD patterns are shown in Fig. S12 and S13, respectively).

In summary, porous Co\(_3\)O\(_4\) networks were synthesized in a large scale by a simple top-down synthesis strategy. Firstly, an amorphous cobalt-based complex was prepared by a simple and rapid pyrolysis of a solution containing cobalt nitrate and glycine. Thermal decomposition of the cobalt-based complex in air results in the formation of the mesoporous Co\(_3\)O\(_4\) network. The synthesis route is simple and the raw materials of metal nitrates and glycine are cheap and widely available. The mesoporous Co\(_3\)O\(_4\) network exhibits a stable capacity of ca. 587 mAh g\(^{-1}\) for 500 cycles at a current density of 1000 mA g\(^{-1}\) at a low mass loading because of its porous structure as well as fine particle size. The porous architecture improves ion transportation and partially accommodates the large volume change during cycling process. Furthermore, the small particle size greatly decreases the diffusion length of lithium ions. The present synthesis strategy can also be extended to mass productions of other porous metal oxides, such as porous ZnCo\(_2\)O\(_4\) and porous NiO.

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Notes and references

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