Cryogel Synthesis of Hierarchical Interconnected Macro-/Mesoporous Co$_3$O$_4$ with Superb Electrochemical Energy Storage

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**Supporting Information**

**ABSTRACT:** In this contribution, we report a facile synthesis of ultrafine Co$_3$O$_4$ nanocrystals with an in situ construction of mesoporous and macroporous network for supercapacitor electrode material. The resultant ultrafine Co$_3$O$_4$ nanocrystals form an interconnected macroporous network with mesoporous hierarchical structure. The unique architecture is realized through a modified sol–gel process to formulate highly porous cryogel using freeze-drying in the presence of a soft template. Small-angle X-ray scattering and transmission electron microscopy are used to investigate the organization of the Co$_3$O$_4$ porous structure. The unique channels in this hierarchical pores network provide intimate electrolyte contact with cobalt oxide and facilitate electrolyte diffusion. This hierarchical structure presents superior electrochemical performance with a specific capacitance of 742.3 F g$^{-1}$ measured at a potential window of 0.5 V, unveiling one of the highest performance for sol–gel synthesized oxides to date, to the best of our knowledge. The capacity retention was 86.2% after 2000 cycles. The synthesis strategy highlights a versatile and facile dual template approach to independently tailor the porosity and particle sizes using a spontaneous nucleation approach. This serves as a major milestone toward high-performance porous metal oxide material for supercapacitor electrodes.

**INTRODUCTION**

Supercapacitors, widely used in hybrid electric vehicles, energy backups, and portable devices, are attracting increasing attention. Early transition metal oxides such as MnO$_2$, V$_2$O$_5$, NiO, and Co$_3$O$_4$ are a group of very promising supercapacitor electrode materials to replace expensive and toxic RuO$_2$. In particular, Co$_3$O$_4$ is of special interest due to its high theoretical capacitance (up to 3560 F g$^{-1}$) and well-defined redox behavior. There have been a lot of efforts paid on the preparation of different Co$_3$O$_4$ nanomaterials. However, these existing methods either resulted in poorly porous material that has relatively low capacitance or required complicated and high-pressure supercritical carbon dioxide drying treatment to achieve high porosity. It is generally accepted that the redox reaction during electrochemical characterization is confined within several nanometers of the metal oxide surface. Highly mesoporous nanomaterials not only possess large surface active sites for electrochemical reactions but also provide small crystal sizes as well. As one of the most efficient ways to produce highly porous metal oxide nanomaterials, the sol–gel method has been practiced for tens of years in various mesoporous materials synthesis, such as SiO$_2$ and TiO$_2$. The solvent removal of gel is crucial to obtain highly porous material because the pores tend to collapse during post treatment like normal oven drying. The freeze-drying method is a much more facile and safer drying method compared with supercritical drying. Meanwhile, it prevents pore structure from collapsing due to the reduction of capillary force by direct sublimation of solvent. In addition, it can deliver macro and supermacroporous networks because of the ice crystal template effect. These networks could offer an ease of electrolyte diffusion and give a better contact of electrode material with electrolyte as well. Cryogel has several advantages over traditional aerogel. First of all, cryogel delivers much more porous character because of the low surface tension during the drying process. Second, cryogel enables a macroporous structure benefitting from the ice formation during freezing. Third, cryogel has much lower agglomeration tendencies. To date, there are limited works dealing with cryogel mesoporous metal oxide for energy storage applications, like MnO$_2$, V$_2$O$_5$, and SnO$_2$. In the present work, we report for the first time a triblock polymer/ice crystal double templated sol–gel synthesis of Co$_3$O$_4$ cryogel to increase the structural control and to produce ultrafine Co$_3$O$_4$ nanocrystals after sintering. This ultrafine nanocrystal forms an interconnected macroporous network with a mesoporous hierarchical structure. This makes it attractive as a supercapacitor electrode. The Co$_3$O$_4$ cryogel showed a high specific capacitance of 742.3 F g$^{-1}$. The energy density and power density of a single electrode are 25.8 Wh kg$^{-1}$ and 125.12 W kg$^{-1}$ at a discharge rate of 0.5 A g$^{-1}$. This method offers a...
scalable protocol for high performance electrode material synthesis such as CoO, NiO, MnO₂, and related materials.

### METHODS

#### Synthesis of Co₃O₄ Cryogel

All the chemicals used in the experiments were analytical grade and were used without further purification. Co(NO₃)₂·6H₂O and citric acid monohydrate (C₆H₅O₇·H₂O) were purchased from Sigma-Aldrich, and triblock polymer P123 was from BASF.

There were three types of samples, which were labeled as Co—P123—PH₃, Co—P123, and Co—CA complexes. In a typical run for sample Co—P123—PH₃, 210 mg of citric acid monohydrate (1 mmol) and 232 mg of P123 (0.04 mmol) were dissolved in 30 mL of deionized water. After stirring for around 30 min, 1 mmol of Co(NO₃)₂·6H₂O was added into the solution, and the pH of the solution was adjusted to 3.33 with 30% ammonia solution. The final solution was kept at 70 °C until a dark red gel was formed. The gel was then frozen in liquid nitrogen and freeze-dried at 0.2 mbar for 1 day. The as-prepared cryogel was then sintered to 300 °C and kept for 5 h. The samples are labeled as Co—P123—PH₃. Sample Co—P123 was synthesized in a way similar to sample Co—P123—PH₃. The difference was that sample Co—P123 did not undergo pH adjustment after the addition of Co(NO₃)₂·6H₂O. The pH of Co—P123 sol is 2.43.

The sample Co—CA complex was synthesized by mixing 1 mmol of citric acid and 1 mmol of Co(NO₃)₂·6H₂O in 30 mL of DI water. The solution was heated to 70 °C until a red gel formed without the use of P123 and pH adjustment. The gel was dried and sintered in the same way as the rest of the samples.

#### Structure Characterizations

The as-prepared products were characterized using X-ray powder diffractionmetry (XRD; Shimadzu XRD-6000, Cu Kα radiation) at a scan rate of 2° min⁻¹, small-angle X-ray scattering (SAXS; PANALYTICAL, PW3830), scanning electron microscopy (FESEM; JEOL, JSM-7600F), and transmission electron microscopy (TEM; JEOL, JEM-2100 and JEM-2100F). N₂ adsorption/desorption was determined by Brunauer–Emmett–Teller (BET) measurements using a TriStar II surface area and porosity analyzer. The pore size distributions and pore volumes were calculated by the Barrett–Joyner–Halenda (BJH) method.

#### Electrochemical Characterization

The electrochemical tests were conducted using a three-electrode system in 2 M KOH using an Autolab PGSTAT 30 potentiostat. The Ag/AgCl electrode was used as the reference electrode and Pt plate as the counter electrode. The working electrode was prepared by mixing 85 wt. % Co₃O₄, 10 wt. % carbon black, and 5 wt. % polyvinylidene fluoride (PVDF) in ethanol. The mixture was then stirred overnight, and the slurry was loaded on the nickel foam (1 cm × 1 cm in area) as the current collector and dried in air at 80 °C for 4 h. The electrode was pressed under 40 MPa and dried overnight. The weight of the electrode was measured by a Mettler Toledo XS205DU microbalance with an accuracy of 0.01 mg. Typically, the loading mass of active material was around 2 mg cm⁻².

The Cₛp obtained by the cyclic voltammogram curve was calculated by eq 1, where Q is the corresponding voltammetric charge; m is the loading mass of active material; and ΔV is the electrochemical window of the CV test.

\[
C_{sp} = \frac{Q}{m \Delta V}
\]

The Cₛₚ from the charge/discharge test was calculated by eq 2, where I is the charge/discharge current; Δ is the discharge time; m is the loading mass of active material, and ΔV is the electrochemical window.

\[
C_{sp} = \frac{I \Delta t}{m \Delta V}
\]

### RESULTS AND DISCUSSION

#### Mechanism of Cryogel Formation

The synthesis method employed here involves the combined one-pot process of metal complex formation and in situ polymerization of organics, which is a modified Pechini-type sol–gel process as shown in Scheme 1. Briefly, citric acid coordinates with the cobalt ion (Co²⁺) to form a complex. Under heating at 70 °C, the evaporation of solvent and the slow polyesterification reaction (citric acid with P123), the solution becomes a sol. Then, further decrease of water content and polymerization reaction leads to the formation of gel. After freezing in liquid nitrogen, interconnected crystals of ice form within the matrix of the gel. When applying low vacuum condition, the ice begins to thaw and leads to slow cross-linking of the gel. Finally, the complete removal of ice results in a highly porous cryogel.

#### Scheme 1. (a) Precursors of P123 and the Co²⁺–citric Acid Complex, (b) Micelle Formation of P123, (c) Polymerization of Precursors and Gel Formation at 70 °C, (d) Ice Crystal Formation When Frozen with Liquid Nitrogen, and (e) Hierarchical Pore System Formation after Water Content Removal

#### Structural Information

The organic components are completely removed under the heat treatment, as proven by TGA (Thermogravimetric Analysis) and FTIR (Fourier transform infrared spectroscopy) in Figure S1 and Figure S2 (Supporting Information). The XRD pattern of Co₃O₄ obtained at 300 °C is shown in Figure 1a. All the peaks are consistent with the standard pattern JCPD No. 78-1970 and match well with the reported literature. It shows that the as-sintered cryogel consists of Co₃O₄ without impurity phase. Field emission SEM in Figure 1b shows that the interconnected spheres form the macroporous structure of Co₃O₄. Each sphere is around 100 nm, which is also confirmed by low-magnification TEM in Figure 1c. Figure 1c shows that this sphere material is an assembly of many small crystals, introducing the mesoporous structure within the macroporous Co₃O₄ at the same time. In the high-magnification TEM image in Figure 1d,
nanocrystals of $\text{Co}_3\text{O}_4$ with a diameter around 10 nm can be seen. More importantly, further measurement of the nanocrystal diameter by X-ray small-angle scattering (SAXS) shows that the majority crystal size is 10 nm (shown in Figure 1f). The select area electron diffraction (SAED) identifies the polycrystalline nature of sintered cryogel, as there are obvious diffraction rings of random oriented $\text{Co}_3\text{O}_4$ nanocrystals.

**Effects of Dual Templates and pH.** As shown in Figure 2a and Figure 2b, addition of P123 into the sol–gel system leads to a significant change in the microstructure of the sintered cryogel. The micelles of P123 formed in the sol harness the template effect of P123, leading to smaller and more homogeneous particles in sample $\text{Co}^−\text{P123}$ (Figure 2a).

For the sample $\text{Co}^−\text{CA}$ without P123 as the template (sample $\text{Co}^−\text{CA}$ complex), an irregular macroporous structure was resulted after sintering as shown in Figure 2b. The absence of a sphere-like macroporous network is in a significant contrast to that of sample $\text{Co}^−\text{P123}−\text{PH3}$ in Figure 1b and sample $\text{Co}^−\text{P123}$ in Figure 2a. The morphology changes are also observed by SEM at varying pH (Figure S4, Supporting Information). Under low starting pH of 1.03, the cryogel shows a dense monolith like structure (Figure S4a, Supporting Information), while the increasing pH after 3.33 leads to the deformation of hierarchical sphere structure and results in disordered structures (Figure S4a and Figure S4b, Supporting Information). The morphology variations could be the result of pH-induced changes of coblock polymer micelle structures in solution.

Apart from the P123 template, the ice crystal template effect during the freeze-drying process also plays an important role. The ice crystals formed rapidly at $−196 \, ^\circ\text{C}$ (in liquid nitrogen) serve as the solid scaffolds for further gelation. Under low

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**Figure 1.** (a) XRD pattern of $\text{Co}_3\text{O}_4$ cryogel sintered at 300 °C, sample $\text{Co}^−\text{P123}−\text{PH3}$; (b) FESEM image of sintered $\text{Co}_3\text{O}_4$ cryogel, sample $\text{Co}^−\text{P123}−\text{PH3}$; (c,d) TEM image of $\text{Co}_3\text{O}_4$ cryogel of different magnifications, sample $\text{Co}^−\text{P123}−\text{PH3}$; (e) SAED of sample $\text{Co}^−\text{P123}−\text{PH3}$; (f) distribution of $\text{Co}_3\text{O}_4$ particle size calculated through SAXS, sample $\text{Co}^−\text{P123}−\text{PH3}$. 

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vacuum, the sublimation of ice gives highly hollow networks of cryogel, which contribute to both mesoporous and macroporous properties.\(^{20}\)

To clarify the effect of solution pH in the reaction system, the pore diameters have been measured as shown in Figure 2c. Evidently, pH of the reaction system significantly affects the pore diameter of the samples, which is related to the alteration of the morphology of resulting micelles due to the change in packing parameter.\(^{21}\) The average pore diameter decreases from 20 nm (in Co\(^{-}\)P123) to 10 nm (in Co\(^{-}\)P123\(^{-}\)PH3) as depicted in Figure 2c. Moreover, it also provides a much narrower distribution of pore size around 10 nm. Apart from the pore diameter changes in the materials, the BET surface area of the three samples changes as well. The BET surface areas of Co\(^{-}\)CA, Co\(^{-}\)P123, and Co\(^{-}\)P123\(^{-}\)PH3 are 52.76, 62.86, and 82.8 m\(^2\) g\(^{-}\)1, respectively (Figure S3, Supporting Information).

**Electrochemical Tests.** The electrochemical performances of samples prepared at different pH are first investigated. In Figure 3a, the Co\(^{-}\)P123–PH3 sample exhibits the highest \(C_{sp}\) of 742.3 F g\(^{-}\)1 at a discharge current of 0.5 A g\(^{-}\)1. The electrochemical properties of samples Co\(^{-}\)P123–PH3, Co\(^{-}\)P123, and Co\(^{-}\)CA sintered at 300 °C are further investigated with cycling voltammetry and galvanostatic charge–discharge method. As can be seen from Figure 3b, all three samples have similar CV curves with two pairs of redox peaks. These peaks correspond to the redox reactions as follows:\(^{3,8b,22}\)

\[
\text{Co}_3\text{O}_4 + \text{OH}^{-} + \text{H}_2\text{O} \leftrightarrow 3\text{CoOOH} + e^{-} (3)
\]

\[
\text{CoOOH} + \text{OH}^{-} \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^{-} (4)
\]

The \(C_{sp}\) values of sample Co–P123–PH3, Co–P123, and Co–CA complexes are 742.3, 578.0, and 423.4 F g\(^{-}\)1, respectively, at a discharge current of 0.5 A g\(^{-}\)1 (Figure 3c). For sample Co–P123–PH3, a specific area capacitance (calculated from the \(C_{sp}/\text{BET surface area}\)) as high as 89.57 mF cm\(^{-}\)2 can be achieved, which is superior compared to the best reported values of 26.51 mF cm\(^{-}\)2 from sol–gel using a supercritical CO\(_2\) drying method and sintered at 200 °C.\(^{5}\) The high specific area capacitance arises from the unique preparation method, which will be elaborated later. Our result is comparable with the previous report by Gao et al. on the free-standing Co\(_3\)O\(_4\) nanowire on nickel foam.\(^{23}\) The specific area capacitance achievable in this work is also better than other preparation methods, like hydrothermal.\(^{17,24}\) Deng et al. reported an electrochemical deposition method\(^{46}\) with a specific capacitance of 2200 F g\(^{-}\)1. However, this is overshadowed by the disadvantages of a low loading mass of 0.1 mg cm\(^{-}\)2 and therefore a poor practical application value.

A previous attempt using a supercritical drying method\(^5\) showed a specific capacitance of 623 F g\(^{-}\)1, in which the BET surface area of the sample was 235 m\(^2\) g\(^{-}\)1. In this work, a remarkably higher capacitance of 742.3 F g\(^{-}\)1 can be achieved. However, the BET surface area of freeze-dried sample is only 82.8 m\(^2\) g\(^{-}\)1. It is clear that our sample has a better material utilization efficiency (experimental \(C_{sp}/\text{theoretical } C_{sp}\)) of 20.8% than 17.5% of the best record.\(^{5}\) We attribute this unique property to the formation of cryogel via the freeze-drying method. The freeze-drying method involves an ice crystalization and sublimation process, which facilitates ice crystal templating effects. Combining with the P123 template, this will provide three advantages over the conventional sol–gel process and supercritical drying method. First, it has been proven that the Faradic reaction of cobalt oxide originated from surface oxidation groups.\(^{25}\) The gelation of the Co\(^{2+}\) ion coordinated citric acid with P123 may provide an ideal precursor for surface active sites generation. However, for the organic epoxide sol–gel method, the gelation is triggered by the polymerization of

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**Figure 2.** (a) FESEM image of Co–P123 sintered at 300 °C; (b) FESEM image of Co–CA (without template) sintered at 300 °C; (c) pore distribution of sample Co–P123–PH3 and Co–P123 sintered at 300 °C.
epoxide. That may lead to a weaker interaction between the organic component and inorganic salts. In the end, the cobalt oxide is largely produced from the decomposition of cobalt nitrate, which preserves less surface active sites. Second, the template effect of both P123 and ice crystal leads to a mesoporous system combining with macroporous structure. Benefiting from the hierarchical porous structure, facile electrolyte diffusion is expected and will be proven in EIS (electrochemical impedance spectrum) measurements (as discussed later). It is similar to the case in heterogeneous catalysts such as zeolites, where hierarchical structure facilitates the catalytic behavior. In addition, the surface functional groups may assist the diffusion of the electrolyte by increasing the surface hydrophility. Third, the freeze-drying formation of cryogel produces a highly stable network of ultrafine metal oxide powders than conventional methods. As mentioned above, the average crystal size of the sintered Co₃O₄ cryogel is around 10 nm. TEM studies are performed for samples Co−CA, Co−P123, and Co−P123−PH3 before and after 2000 cycling tests. As shown in Figure S8 (Supporting Information), the sphere-like structure remains intact after 2000 cycles, and the nanocrystals are highly crystalline. Considering that high surface active sites density and better accessibility benefitted from the porous system, it achieves a high electrochemical performance. Overall, these three effects result in a high specific area capacitance.

**Figure 3.** (a) Relationship between specific capacitance and pH. The specific capacitance was obtained at a discharge current density of 0.5 A g⁻¹. (b) CV curves of samples Co−P123−PH3, Co−P123, and Co−CA at 5 mV s⁻¹. (c) Relationship between specific capacitance discharge current of samples Co−CA, Co−P123, and Co−P123−PH3. (d) Galvanostatic discharge curves of different current densities of sample Co−P123−PH3. (e) Average specific capacitance versus cycling number of sample Co−P123−PH3 at a scan rate of 20 mV s⁻¹. (f) Nyquist plots of sample Co−P123−PH3 obtained at a bias of 0 V vs SCE and an AC magnitude of 10 mV.
In practice, the ability of charge/discharge at high current density is crucial in capacitor application. As we can observe from Figure 3c, for a discharge current of 0.5 A g$^{-1}$ to as high as 20 A g$^{-1}$, the $C_{ip}$ maintains at 54.4% for sample Co–P123–PH3. This indicates the good stability towards high power applications. Meanwhile, the $C_{ip}$ decreases only 13.8% after 2000 cycles at a scan rate of 20 mV s$^{-1}$, as shown in Figure 3e. Our Co$_3$O$_4$ cryogel has enhanced stability compared with previous reports. The small capacitance loss during cycling may attribute to peeling of minute active materials after long time cycling.

CONCLUSION

In summary, we have successfully synthesized ultrafine nanosized Co$_3$O$_4$ materials with interconnected macroporous and mesoporous structure, through a simple sol–gel method followed by freeze-drying. The resulting cryogel has several advantages over the conventional sol–gel process, namely, high material utilization efficiency, ultrafine Co$_3$O$_4$ nanocrystals, and hierarchical structures. As a result, the Co$_3$O$_4$ cryogel gives superior electrochemical performances. The specific capacitance was up to 742.3 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$, delivering good rate and cycling stabilities. This facile method offers a promising way for low cost, large-scale production and high power application.

ASSOCIATED CONTENT

Supporting Information
TGA tests of samples Co-CA and Co–P123–PH3; FTIR of as-prepared and sintered cryogel of sample Co–P123–PH3; isotherm curves of samples Co–Co, Co–P123, and Co–P123–PH3; SEM images of samples prepared from different pH; specific capacitance of different samples prepared from different starting pH; TEM images of samples Co–Co, Co–P123, and Co–P123–PH3 before and after 2000 CV cycles. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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