Article

Preparation and Electrochemical Properties of Co_3O_4 Supercapacitor Electrode Materials

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Abstract: A special gas-phase diffusion precipitation method with ammonia as the gas-phase diffusion precipitant was adopted. After fully reacting with different cobalt sources in a sealed space, the liquid funnel was separated and dried, and calcined at different temperatures for 2 h. The prepared Co_3O_4 powder was used as a supercapacitor (SCs) electrode to measure the electrochemical properties of the prepared material. The influences of different cobalt sources and sodium phosphate monobasic dehydrate on the preparation of Co_3O_4 SCs electrodes were investigated. The optimal performance of Co_3O_4 was $640 \text{ F}\cdot\text{g}^{-1}$ before modification, and this reached $1140 \text{ F}\cdot\text{g}^{-1}$ after modification, which was an improvement of 78.1%.

Keywords: Co_3O_4 electrode material; supercapacitor; gas-phase diffusion; phosphate modification; electrochemical property

1. Introduction

Supercapacitors (SCs) have been extensively studied due to their high specific power density, long cycle life and fast charge and discharge rate in important electrical energy storage devices [1–3]. In recent years, transition metal oxides have been widely studied for their variable oxidation states and high charge storage capacity [4–6]. Among them, RuO_2 has been considered for its good electrochemical properties [7], but its environmentally poisonous nature and relatively high cost make it limited in commercial application. For other transition oxides [8], Co_3O_4 has been found to be a better alternative material due to its low price and environmental friendliness [9]. Furthermore, recent research has shown that Co_3O_4 with different dimensions and special morphology exhibits excellent specific capacitance and electrochemical performance [10–12]. For example, Liu et al. prepared zero dimensional (0D) Co_3O_4 nanoparticles [13]. These Co_3O_4 nanoparticles showed a specific capacitance of $523.0 \text{ F}\cdot\text{g}^{-1}$ at $0.5 \text{ A}\cdot\text{g}^{-1}$. Venkatachalam et al. successfully fabricated Co_3O_4 one-dimensional (1D) rod-like arrays [14], which exhibited a specific capacitance of $655 \text{ F}\cdot\text{g}^{-1}$ at $0.5 \text{ A}\cdot\text{g}^{-1}$. Besides this, a two-dimensional (2D) Co_3O_4 nanosheet was prepared [15]. The electrode showed a specific capacitance of $233.6 \text{ F}\cdot\text{g}^{-1}$ at $0.5 \text{ A}\cdot\text{g}^{-1}$. Therefore, the research on Co_3O_4 SCs attracts more and more attention from researchers.

The preparation methods of the Co_3O_4 SCs materials have been widely reported [16,17], and include the hydrothermal method [18], the solvothermal method [19], chemical precipitation [20], thermal decomposition [21], the sol-gel method [22], the template method [23], electrodeposition [24],

chemical vapor deposition (CVD) [25], chemical bath deposition [26], the in-situ self-organization method [27], spray pyrolysis [28], galvanic displacement [29], laser ablation [30], the electrospinning technique [31], and so on. Although the Co_3O_4 electrode materials synthesized by one of these synthetic methods have excellent properties, they require difficult synthesis conditions or are confined to the laboratory stage, which affects the rapid development of their commercialization and industrialization. Therefore, developing a low-cost and simple synthesis method for Co_3O_4 electrode materials with excellent performance is an important work. The gas-phase diffusion precipitation method is an improvement of chemical precipitation. It retains the advantages of chemical precipitation, but also has the characteristics of being able to synthesize homogeneous and smaller particles of supercapacitor materials.

In addition, different cobalt sources have great influence on the properties of the materials in the process of synthesis [32]. Material post-treatment modification is also an important means by which to enhance the performance of Co_3O_4 electrode materials [33]. Herein, Co_3O_4 electrode materials for SCs have been prepared by the gas-phase diffusion precipitation method. Ammonium hydroxide is a gas-phase diffusion precipitator. It is placed in a sealed space with the cobalt source. After the full reaction of gas diffusion, precipitation is obtained. This is followed by separate drying and calcination for 2 h. The prepared Co_3O_4 was used as an SCs electrode to measure the electrochemical properties. The effects of ammonium hydrogen phosphate and different cobalt sources on the preparation of Co_3O_4 SCs electrode materials were investigated in order to obtain the best reaction conditions. In addition, the materials were tested and characterized via X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical properties.

2. Materials and Methods

2.1. Materials and Instrumentation

The reagents were commercially purchased and not further purified. These mainly contained cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 99%, Shenyang Huadong Reagent Co., Ltd., Shenyang, China), cobaltous acetate tetrahydrate ($\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, 99%, Liaoning Quanrui Reagent Co., Ltd., Shenyang, China), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28 wt.%, Liaoning Quanrui Reagent Co., Ltd., Shenyang, China), sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, 99%, Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China), potassium hydroxide (KOH, 90%, Liaoning Quanrui Reagent Co., Ltd., Shenyang, China), nickel foam (Ni, 99.8%, 1 mm, Shanghai Tanqi New Materials, Ltd., Shanghai, China), acetylene carbon black (C, 40 nm, Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China), polytetrafluoroethylene (PTFE) ($-(\text{CF}_2-\text{CF}_2)_n-$, 5 μm , Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China), ethanol absolute ($\text{C}_2\text{H}_6\text{O}$, 99.7%, 0.82 g/mL, Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China) and deionized water.

A Bruker D8 X-ray diffractometer (Bruker, Karlsruhe, Germany) was used to measure the powder X-ray diffraction (XRD) data. A JEOL JSM-7500F scanning electron microscopy (SEM) device (JEOL Inc., Tokyo, Japan) was utilized to characterize the surface morphology of the Co_3O_4 samples. An Ivium Stat electrochemical workstation (IVIUM Inc., Amsterdam, The Netherlands) was employed to test the galvanostatic charge–discharge (GCD), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of the Co_3O_4 electrode materials. In addition, an SX2-4–10GJ muffle furnace, a DHG-9036A constant temperature drying oven, a JKKZ-4–10GJ centrifuge and a KQ-700 ultrasonic cleaner were incorporated into the preparation process of Co_3O_4 electrode materials.

The electrode active substance Co_3O_4 , an acetylene black conductive agent and a PTFE emulsion (diluted to 15%) were mixed uniformly in accordance with the mass ratio of 80:15:5. This mixture was poured into agate mortar and we added an appropriate amount of deionized water. The mixed paste substance was achieved by grinding for more than 1 h. A piece of nickel foam (1 cm $\times$ 3 cm) was taken to weigh the quality of nickel foam and recorded as m_1 . The mixed slurry material was uniformly coated on one side of the nickel foam with an area of 1 cm $\times$ 1 cm. The coated active material

was pressed at a constant pressure of 15 MPa for 1 min. The loading mass of the active material was acquired via measuring electrode with a microbalance with accuracy of 0.1 mg. Typically, the loading mass of the active material was ≈ 4.0 mg. The pressed electrode was placed in a drying oven for 10 h at 60 °C. After that, the electrode was taken out, and the quality of the dried nickel foam was weighed and recorded as m_2 . The accomplished electrodes were put in 6 M KOH solution for 24 h, after using a three-electrodes system and electrochemical workstation to measure the electrochemical properties of the electrodes. The Co_3O_4 electrode, the platinum plate and the Hg/HgO electrode were used as the working electrode, the counter electrode and the reference electrode, respectively.

2.2. Synthesis and Preparation

The schematic diagram of the gas-phase diffusion precipitation method for Co_3O_4 synthesis is shown in Figure 1. The materials for the synthesized Co_3O_4 electrode materials are provided in Table 1. The specific conditions for synthesis are as follows, taking synthesis B as an example. A quantity of 20 mL of $\text{NH}_3\cdot\text{H}_2\text{O}$ was loaded into beaker B₁. A measured amount of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (0.692 g, 3 mmol) was dissolved into beaker B₂ with 50 mL deionized water, and then the two beakers were put into an airtight container at the same time. After being heated at 20 °C for 10 h, the upper layer of beaker B₂ was a red solution, the lower layer was a blue-green precipitation, and there was small amount of ammonium hydroxide in beaker B₁. Beaker B₂ was taken out, and the precipitate in the beaker was separated by centrifuge. The product was washed several times with deionized water and ethanol respectively, and dried at 60 °C to obtain the dark green substance $\text{Co}(\text{OH})_2$. Finally, the prepared precursor was calcined in a muffle furnace at 300 °C for 2 h with a heating rate of 10 °C/min^{−1}. Co_3O_4 target product (B) was obtained. A was obtained by replacing $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ with $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ under the same reaction conditions.

Figure 1. Schematic illustration of preparing Co_3O_4 electrode materials by gas-phase diffusion precipitation method.

Table 1. Co_3O_4 electrode materials were prepared by gas-phase diffusion precipitation method.

Sample	Cobalt Source	Solvent	Precipitator	$\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$
A	$\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$	H_2O	$\text{NH}_3\cdot\text{H}_2\text{O}$	Unmodified
B	$\text{CoCl}_2\cdot 6\text{H}_2\text{O}$	H_2O	$\text{NH}_3\cdot\text{H}_2\text{O}$	Unmodified
C	$\text{CoCl}_2\cdot 6\text{H}_2\text{O}$	H_2O	$\text{NH}_3\cdot\text{H}_2\text{O}$	Modified

The Co_3O_4 electrode was modified by $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ with heat treatment under the protection of an Ar atmosphere. To introduce phosphate ions, the as prepared B products were further thermally annealed in the presence of $\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$. With a ratio of B to $\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$ of 5, the B material and $\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$ were respectively placed in two separate positions in a porcelain boat, whereby $\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$ was at the upstream side of the furnace. After introducing Ar gas into the tube furnace for 30 min, the tubular furnace was heated to 250 °C with a heating rate of 5 °C/min^{−1} and held at this temperature for 30 min. Then, the tube furnace was naturally cooled to room temperature under Ar, and the black powder was obtained, which was abbreviated as C.

3. Results and Discussion

3.1. Structural and Morphological Characterization

As shown in Figure 2, A is the XRD pattern of Co_3O_4 prepared by $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, B is the XRD pattern of Co_3O_4 prepared by $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, and C is the XRD pattern of B modified by $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$. The XRD pattern of them all can be well indexed as face-centered cubic (fcc) Co_3O_4 (PDF no. 80–1542). The diffraction peaks at 18.98° , 31.32° , 36.90° , 44.84° , 59.64° and 65.35° can be denoted as (1 1 1), (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) reflections of Co_3O_4 , respectively [34]. The XRD data confirmed that Co_3O_4 was obtained by the calcining of the $\text{Co}(\text{OH})_2$ precursor at 300°C .

Figure 2. XRD pattern of A, B and C Co_3O_4 electrode materials.

To observe the morphology of the Co_3O_4 electrode materials, SEM images with different magnification are shown in Figure 3. We can find that sample A has a micro-spherical morphology (Figure 3a). It is about $1\ \mu\text{m}$ in diameter. From SEM images with high multiples, it can be confirmed that the morphology of A is a hollow micro-spherical morphology (Figure 3b), which is composed of nanoflocculent Co_3O_4 electrode materials. As for B, it has a flower-like microsphere (Figure 3c), which is composed of thin nanosheets (Figure 3d). The thickness of the nanosheet is about 10 nm. Here, it becomes apparent that the cobalt source plays the most significant role in directing the morphological habit of the aerogel structure. The SEM images of the materials resulting from the cobalt source syntheses reveal variability in the microstructures. This variability results from the selection of the precursor metal salt [32]. The phosphate modification of sample B resulted in sample C. It can be seen that the morphology of sample C has not changed significantly (Figure 3e). However, it can be observed that there are some small nanoparticles in the middle of the petals (Figure 3f). This is due to phosphate modification [33]. Generally, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ will decompose and form PH_3 gas at a temperature greater than 150°C , according to the reaction equation:

In the copresence of PH_3 gas and H_2O gas, the Co_3O_4 was modified. The small nanoparticles in the middle of the petals were Na_2HPO_4 and phosphate residue after modification.

Figure 3. (a) Low and (b) high magnification SEM images of A (Co_3O_4 electrode material prepared by $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), (c) low and (d) high magnification SEM images of B (Co_3O_4 electrode material prepared by $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$), and (e) low and (f) high magnification SEM images of C (B modified by $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$).

3.2. Electrochemical Performances

To evaluate the electrochemical performances of the Co_3O_4 electrode materials, galvanostatic charge–discharge (GCD), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to test. Figure 4a–c show that the GCD measurements of A–C Co_3O_4 electrodes in the potential window 0–0.45 V exhibited the current densities of 1, 2, 5 and $10 \text{ A} \cdot \text{g}^{-1}$. There is a big deviation between the discharge curve and the straight line, especially for C, indicating that the capacitance is mainly caused by faradic redox reactions. Therefore, the Co_3O_4 electrode has typical pseudo-capacitance characteristics. According to Figure 4d, it can be found that the C discharge time increases significantly after phosphate modification at $1 \text{ A} \cdot \text{g}^{-1}$. The specific capacitances from the discharge curves are calculated from the following equation:

$$C = I\Delta t / m\Delta V \quad (3)$$

where I is the discharging current, Δt is the discharging time, m is the mass load of the active materials and ΔV is the discharging potential range.

Figure 4. The galvanostatic charge–discharge (GCD) curves of the different Co_3O_4 electrodes: (a) A, (b) B, (c) C and (d) GCD curves of the different Co_3O_4 electrodes at $1 \text{ A}\cdot\text{g}^{-1}$.

The plot of specific capacitance at different discharge current densities is shown in Figure 5. The capacitance of the A electrodes is $564 \text{ F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$ and $331 \text{ F}\cdot\text{g}^{-1}$ at $10 \text{ A}\cdot\text{g}^{-1}$, with a capacitance retention of 58.7%. It shows the best rate performance among the three samples. The capacitance of B retains 85.3%, 72.3% and 54.7% at $2 \text{ A}\cdot\text{g}^{-1}$, $5 \text{ A}\cdot\text{g}^{-1}$ and $10 \text{ A}\cdot\text{g}^{-1}$, versus $640 \text{ F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$. The sample of C shows the maximum capacitance of $1140 \text{ F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$. It can retain 96.5% at $2 \text{ A}\cdot\text{g}^{-1}$, and 41.8% at $10 \text{ A}\cdot\text{g}^{-1}$. The phosphate ion groups $(\text{H}_2\text{PO}_4)^-$ formed on the surface of Co_3O_4 were key to enhancing the electrochemical performance of the electrode materials [35]. With the increase in discharge current density, the specific capacitance decreases gradually. This is due to an increase in the potential drop, and only the external active substance participates in the electrochemical redox at a higher current density [36]. Especially for sample C, dissociating small particles can accelerate the reaction but hinder the movement of ions at higher current densities [37]. There are some small nanoparticles present in the middle of the petals on electrode C, which are phosphate particles left after modification. By comparing with the literature [35], it can be found that the remaining particles are larger. Although these particles can accelerate the redox reaction, they will affect the charge transfer, especially under the condition of a large current density, so the deterioration of capacitance is significant at a high current density. The performances of Co_3O_4 samples synthesized via different methods are shown in Table 2.

Figure 5. The specific capacitance of the different Co_3O_4 electrodes at different current densities: A, B and C.

Table 2. Electrochemical performance of Co_3O_4 electrode materials.

Method	Structure	Specific Capacitance	Rate	Ref.
Hydrothermal	Nanoflake	1500 $\text{F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$	55.2% at $10 \text{ A}\cdot\text{g}^{-1}$	[10]
Template	Nanosheet	1121 $\text{F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$	77.9% at $25 \text{ A}\cdot\text{g}^{-1}$	[12]
Solvothermal	Nanoparticle	523.0 $\text{F}\cdot\text{g}^{-1}$ at $0.5 \text{ A}\cdot\text{g}^{-1}$	66.9% at $5 \text{ A}\cdot\text{g}^{-1}$	[13]
CVD method	Nanosphere	128 $\text{F}\cdot\text{g}^{-1}$ at $10 \text{ A}\cdot\text{g}^{-1}$	90% at $20 \text{ A}\cdot\text{g}^{-1}$	[25]
Chemical bath deposition	Nanowire	850 $\text{F}\cdot\text{g}^{-1}$ at $5 \text{ mV}\cdot\text{s}^{-1}$	85% at $100 \text{ mV}\cdot\text{s}^{-1}$	[26]
In-situ self-organization	Nanorods	1486 $\text{F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$	72.9% at $15 \text{ A}\cdot\text{g}^{-1}$	[27]
Galvanic displacement	Nanosheet	1095 $\text{F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$	61.9% at $15 \text{ A}\cdot\text{g}^{-1}$	[29]
Laser ablation	Nanosheet	762 $\text{F}\cdot\text{g}^{-1}$ at $6 \text{ A}\cdot\text{g}^{-1}$	82.7% at $36 \text{ A}\cdot\text{g}^{-1}$	[30]
Electrospinning technique	Nanofiber	340 $\text{F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$	87.1% at $10 \text{ A}\cdot\text{g}^{-1}$	[31]
Sol-gel	Netlike	708 $\text{F}\cdot\text{g}^{-1}$ at $5 \text{ A}\cdot\text{g}^{-1}$	71.9% at $50 \text{ A}\cdot\text{g}^{-1}$	[32]
Chemical precipitation	Nanonet	739 $\text{F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$	72.1% at $15 \text{ A}\cdot\text{g}^{-1}$	[38]
Thermal decomposition	Nanoflake	576.8 $\text{F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$	49.2% at $50 \text{ A}\cdot\text{g}^{-1}$	[39]
Electrodeposition	Nanoplate	517 $\text{F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$	39.1% at $20 \text{ A}\cdot\text{g}^{-1}$	[40]
Spray pyrolysis	Thin film	412 $\text{F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$	93% at $4 \text{ A}\cdot\text{g}^{-1}$	[41]
Gas-phase diffusion precipitation	Nanofloc	564 $\text{F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$	58.7% at $10 \text{ A}\cdot\text{g}^{-1}$	A
Gas-phase diffusion precipitation	Nanosheet	640 $\text{F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$	54.7% at $10 \text{ A}\cdot\text{g}^{-1}$	B
Gas-phase diffusion precipitation	Nanosheet	1140 $\text{F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$	41.8% at $10 \text{ A}\cdot\text{g}^{-1}$	C

Figure 6a–c shows the CV measurement curves of three Co_3O_4 electrodes with a potential window of 0–0.45 V at scan rates of 20–100 $\text{mV}\cdot\text{s}^{-1}$, respectively. The integral area of the CV curves increased with the increase in scanning rate. The CV curves of three Co_3O_4 electrodes show peaks that indicate the pseudocapacitive nature of three Co_3O_4 electrode. For the three Co_3O_4 electrodes, a couple of redox peaks can be observed on the CV curves. Compared with other electrodes, the C electrode has the largest CV area, indicating the highest levels of stored charge (Figure 6d). However, it can be found that as the scanning rate increases, the area of sample C increases most slowly. This is related to the morphology of the modified sample, as evidenced by GCD.

Figure 6. CV curves of the different Co_3O_4 electrodes: (a) A, (b) B, (c) C and (d) CV curves of the different Co_3O_4 electrodes at $20 \text{ mV}\cdot\text{s}^{-1}$.

EIS technology was used to research the electrochemical behavior of the Co_3O_4 electrode material in an electrolyte. Figure 7 reveals the Nyquist plots of three Co_3O_4 electrodes in a frequency range

from 1 to 10^5 Hz. The Nyquist impedance curve is the plot of the imaginary component (Z'') of the impedance against the real component (Z'), which consists of a semicircle at a high frequency region (charge transfer process) and a straight line at a low frequency region (diffusion-limited process). The X-intercept of the Nyquist plot is defined as the equivalent series resistance (R_s). It is obvious that C has a lower solution resistance (corresponds to curve intercept with real axis), $R_s = 0.12 \Omega$, than A and B (0.25Ω). The Nyquist plot shows a small semicircle at high frequency regions. The diameter of the semicircle is related to the charge-transfer resistance (R_{ct}) of the redox reactions [38]. Comparing the semicircle diameter of three Co_3O_4 samples ($C < B < A$), it can be concluded that the charge transfer resistance (R_{ct}) of B synthesized by $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ is smaller than that of A synthesized by $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, and the R_{ct} of C modified by sodium phosphate monobasic dehydrate is smaller than that of the unmodified B. The steep slope of the straight line at the lower frequency can show the ion diffusion speed. At the low frequency range, the slope of the straight line represents the diffusion of ions in the electrolyte. The curve slopes decrease in the order of A, B and C, which demonstrates the fastest ion transfer speed of C between the inner channel of the electrode and the electrolyte in, accordance with the specific capacitance of the three samples. In all three areas, the Co_3O_4 electrodes of the C sample have good presentation. This is due to phosphate modification [42].

Figure 7. EIS of the different Co_3O_4 electrodes.

4. Conclusions

Three Co_3O_4 supercapacitor materials were prepared by a special gas-phase diffusion precipitation method. A has a hollow nano-spherical morphology, while B and C have flower-like microsphere. The Co_3O_4 of B prepared from $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ has a good electrochemical performance. The capacitance of the A electrode is $564 \text{ F} \cdot \text{g}^{-1}$ at $1 \text{ A} \cdot \text{g}^{-1}$, with a high capacitance retention. It shows the best rate performance among the three samples. The capacitance of B is $640 \text{ F} \cdot \text{g}^{-1}$ at $1 \text{ A} \cdot \text{g}^{-1}$. The C sample shows the maximum capacitance of $1140 \text{ F} \cdot \text{g}^{-1}$ at $1 \text{ A} \cdot \text{g}^{-1}$, which improved by 78.1% after $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ modification.

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