One-step hydrothermal synthesis of nitrogen doping graphene based cobalt oxide and its supercapacitive properties

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ABSTRACT:

Nitrogen doping is considered to be a promising way to improve the performance of graphene-based supercapacitors. It is crucial to discuss that the role of nitrogen doping in regulating the electronic properties. Herein, we chose urea, $\text{NH}_3\cdot\text{H}_2\text{O}$ and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ as the nitrogen sources to modify the graphene based cobalt oxide composites to compare which nitrogen source made a great improvement on the supercapacitive performance of the composites. When the urea is used as the nitrogen source, the electrochemical performance was the best among the nitrogen-doped (N-doped) graphene based cobalt oxide composites (334.8 F g^{-1} at a current density of 5 A g^{-1} in 2 M KOH aqueous solution). Nitrogen doping worked as a modification to control the structure of graphene sheet and effectively improved the electrochemical performances.

Keywords: Nitrogen doping; Graphene based cobalt oxide; Supercapacitor

1. Introduction

Because of the urgent need for efficient energy storage devices, the electrochemical capacitor (also known as supercapacitor) becomes a widespread and concerted research hotspot, which has high power density, fast charge-discharge rate and excellent cycling lifetime.[1-3] And these advantages make supercapacitor as a promising candidate in the field of flexible electronics.[4]

Supercapacitor is generally classified into two different types by these charge-discharge mechanisms which are electrical double layer capacitor (EDLC) and

pseudocapacitor.[2, 5] The electric energy of formal stores by the electric charge gathers the face of electrode material, and is direct ratio with high specific surface area, so that the EDLCs usually choose carbon materials as electrode, such as active carbon[6] and carbon nanotubes.[7-12] Meanwhile, the pseudocapacitor store the charge in a faradic process, so that it constantly base on transition metal oxides.[13] In this paper, cobalt oxide which combined with N-doped graphene acted as provider of pseudocapacitor.

Among the carbon materials, graphene appears to be the most promising material for supercapacitor with the advantage of its outstanding properties, such as extremely high specific surface area, superior electronic conductivity, and excellent chemical stability[14-16] While N-doped graphene has been widely applied in supercapacitor to improve the electrical performance, due to that nitrogen doping can significantly improve the conductivity of graphene. For example, Lee et al.[17] reported that pyridinic-rich nitrogen-doped graphene nanoplatelets (PRGOs) which showed high performance of supercapacitors, including enhanced specific capacitance and long-term stability were synthesized by an acid-catalyzed dehydration reaction between GO and 3,4-diaminopyridine, the highest specific capacitance can reach 214 F g^{-1} at current density of 0.1 A g^{-1} . Xie et al.[18] demonstrated that flower-like molybdenum sulfide nanosheets/N-doped graphene (MoS_2/NG) prepared through one-pot hydrothermal method showed excellent special capacitance 245 F g^{-1} at 0.25 A g^{-1} (and 146 F g^{-1} at 20 A g^{-1}). The resultant N-doped graphene display excellent supercapacitor performance.

In our work, we chose urea, $\text{NH}_3 \cdot \text{H}_2\text{O}$ and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ as nitrogen sources to modify graphene based cobalt oxide via a one-step hydrothermal method. Compared with different nitrogen source composites, when acted as supercapacitor electrodes, they revealed the high specific capacitance at high current density. Especially, urea can be the excellent nitrogen source to increase the properties.

2. Experiment

2.1 Sythesis of Graphene oxide(GO) and N-doped graphene based cobalt oxide composites

In this typical synthesis process, GO was prepared by a modified Hummers method.[19] The N-doped graphene based cobalt oxide composites were synthesized by a simple one-step hydrothermal method. In a typical preparation process, 25 mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 1 g of urea were dissolved in 10 mL of deionized water. Then the required GO dispersion (4 mg/mL) was sonicated for 30 min and dropped into the above solution. Then, the mixed suspension was sonicated for 15 min and stirred for 10 min. The final solution was transferred to a Teflon-lined autoclave and hydrothermally heated at 150 °C for 12 h, and then naturally cooled down to room temperature. The resulted product obtained by filtering and watering with deionized water and absolute ethanol for several times and freezing drying. In our experiment, we also chose $\text{NH}_3 \cdot \text{H}_2\text{O}$ and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ as other different nitrogen sources, and no nitrogen source, we prepared these by the same procedure as the urea as nitrogen source. In order to convenience, we denoted the composites as urea, $\text{NH}_3 \cdot \text{H}_2\text{O}$, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and none, respectively.

2.2 The characterization of materials

The chemical composition of the products were determined by X-ray diffraction. Fourier-transform infrared (FT-IR) spectra of KBr power pressed pellets was recorded on a Spectrum One FT-IR in the range of 4000-400 cm^{-1} . Raman spectroscopy was recorded from 400 to 4000 cm^{-1} on a Renishaw Invia Raman microscope excited by an argon ion laser beam. X-ray photoelectron spectra (XPS) were determined by an X-ray photoelectron spectrometer good electrochemical performance.

2.3 electrochemical measurement

All electrochemical experiments were tested on a CS electrochemical workstation at room temperature. In a three-electrode system, we used aqueous 2 M KOH electrolyte solution. The cyclic voltammogram (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) were tested. In galvanostatic charge/discharge, the specific capacitance (Cs) can be calculated by the following equation:

$$Cs = \frac{I\Delta t}{m\Delta U} \quad (1)$$

where I is the current density (A g^{-1}), Δt is the discharge time (s) and ΔU is the voltage difference (V).

3. Result and discussion

3.1 Characterization

The structure of samples were analyzed by XRD. As showed in Fig. 1, the small peaks which are indexed to the (001) at about 13° were almost disappeared, while the broad peaks (002) at approximately 21.6° can be seen obviously. The (002) peak confirmed that a large proportion of the GO turned into reduced graphene oxide (rGO).[20, 21] The (001) peak of urea as nitrogen source is almost disappeared, which indicated that the reducing degree of conversion of GO to rGO of urea was greater than others.

Fig. 1 Typical XRD patterns of samples with different nitrogen source

The FT-IR spectra are showed in Fig. 2. The absorption bands of C=O and C-O nearly cannot be found in the spectra, suggesting that GO was reduced in the processing of hydrothermal reaction. Obviously, the stretching vibration band of O-H are at 3434.7 cm^{-1} . Meanwhile, the two obvious characteristic absorption peaks at 1556.3 and 1116.6 cm^{-1} can be assigned to C=N, C-N, respectively. For the spectrum,

it can be clearly observed that there are two strong absorption bands at 656.7 and 561.2 cm^{-1} , which suggests the production of cobalt oxide.[22, 23]

Fig. 3 demonstrates the micro-Raman spectra of samples with different nitrogen sources. The two peaks at around 1350 and 1590 cm^{-1} are D band and G band which are typical Raman characteristics of graphene. The D band indicates a high quantity of structural defects, while the G band ascribed to the E_{2g} phonons of the C sp^2 atom.[24] The I_D/I_G ratio refers to the disorder density of carbon material. When urea as nitrogen source, the I_D/I_G value is 1.09, which is lower than others, while the other values of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and none are 1.59, 1.11 and 1.13. The result is consistent with the result of above. The intensity of the 2D($\sim 2680 \text{ cm}^{-1}$) and S3 ($\sim 2910 \text{ cm}^{-1}$) peaks reveals better graphitization or no charge transfer due to the absence of nitrogen impurities.[25, 26]

Fig. 2 FT-IR spectra of samples with different nitrogen sources

Fig. 3 Raman spectra of samples with different nitrogen sources

To understand the chemical elements of the materials and the role of nitrogen functionalities in capacitor performance, the X-ray photoelectron spectroscopy (XPS) (Fig. 4) were introduced to make them clear. From the survey spectrum (Fig. 4a), it is clearly that the chemical elements (C 1s, N 1s, O 1s and Co 2p) in the composite can be seen. The C 1s and O 1s spectra are distinctly showed in Fig. 4b and 4c.[27] These are assigned to pyridinic (N-6), pyrrolic/pyridone (N-5), quaternary (N-Q) nitrogen, and pyridine-N-oxide (N-X), respectively. N 1s spectra as showed in Fig. 4d, 4e and 4f. Fig. 4d have two peaks with binding energy at 399.5 eV and 402.6 eV which correspond to the N-5 and N-X, respectively,[28, 29] while the Figure 4e also has the N-5 and N-X, but the former contains the ratio of N-5 is greater than the latter. Fig. 4f has a peak with binding energy at 400.6 eV which is the N-Q.

Fig. 4 (a) XPS of survey spectra of urea doped composite. High-resolution XPS spectra of the deconvoluted C 1s, O 1s and N 1s peaks, (b) C 1s, (c) O 1s, (d) N 1s peaks of urea doped composite, (e) N 1s peak of $\text{NH}_3 \cdot \text{HO}_2$ doped composite and (f) N 1s peak of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ doped composite

3.2 electrochemical performance

In order to evaluate and compare the electrochemical performance of samples with different nitrogen sources, we employed a three-electrode system to measure cyclic voltammogram (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). [28, 30-33] We chose the 2 M KOH aqueous solution as electrolyte. The CV was showed in Fig 5a, at scan rate of 50 mV/s, it can be seen from the curves that there are anodic peaks and cathodic peaks were well-defined, which signified the faradaic redox. The peak current and the cyclic voltammogram curves area are obviously different. When the urea as nitrogen source, both the peak current and CV curve area are the largest than other samples, which are consistent with the Fig. 5b showed. The capacitor of composites can be calculated from equation 1 from the GCD curves of Fig. 5b. The shape of the discharge curves have an obvious characteristic pseudo-capacitance of a plateaus, which is consistent with the CV results. Additionally, negligible voltage drop (IR drop) can be seen from the curves, demonstrating a low internal resistance which is an important element for electrodes. The specific capacitances of nitrogen-doped composites are 334.8, 167.0,

261.2 and 192.5 F g⁻¹ at current density of 5 A g⁻¹, which respectively corresponded to urea, NH₃·H₂O, N₂H₄·H₂O and none N-doped. As a result, using urea as nitrogen source really can improve the specific capacitance, and it is 1.74 times than without nitrogen source. The electrochemical impedance spectroscopy (EIS) is a very effective measurement that the resistance of the electrode material and electrolyte. A Nyquist impedance spectrum is consist of two parts. Obviously, from the Fig 5c, there is a semicircle in the high frequency region and a straight line inclining about 45° to the real axis in the low frequency region. The semicircle at high frequency is controlled by electrode reaction dynamics which are charge transfer process, and corresponded to the charge transfer resistance. The straight line at low frequency is controlled by diffusion rate of the electrode reaction of reactant or production, which also reflects the rate of the substance diffusion and transport in the electrolyte. The intersection of curve and the real axis is the equivalent series resistance of the electrode materials, from the plot, the equivalent series resistances are 0.575, 0.562, 0.623 and 0.572 ohm to the material that doped with urea, NH₃·H₂O, N₂H₄·H₂O and none N-doped, respectively, which all are relatively small. In a word, the resistance of samples is small, which is beneficial to the capacitor performance.

Fig. 5 (a) Cyclic voltammograms of samples with different nitrogen source at scan rate of 50 mV/s; (b) galvanostatic charge-discharge of samples with different nitrogen source at current density of 5 A/g; (c) Nyquist plots of the EIS for the samples with different nitrogen source, Inset is the magnification of Warburg semicircles from the spectra

Hence, it can be seen from the above discussion that the urea sample expressed a good electrochemical performance. This phenomenon is likely to that the type and ratio of N and reducing degree of GO can significantly improve the conductivity of graphene, and acted on the performance.

4. Conclusion

In summary, it is clearly that N-doped graphene based cobalt oxide composites were successfully synthesised by a one-step hydrothermal method, and which made the materials performance optimization. The type of different nitrogen sources plays a different role. When using urea as the nitrogen source to modify graphene based cobalt oxide, the type of N is N-5 which has the bigger percentage, the reducing degree of GO and the electrochemical performance is greatly improved. After testing, the specific capacitance can reach to 334.8 F g^{-1} at the current density of 5.0 A g^{-1} . The results demonstrate that the synergistic effect of nitrogen-doped and graphene based cobalt oxide composites potentially a promising candidate for the enhancement of excellent electrochemical performances.

Acknowledgments

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