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Improved capacitance of NiCo₂O₄/carbon composite resulted from carbon

matrix with multilayered graphene

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Abstract

The optimized electric and ionic conductivity of metal oxides with pseudocapacitive properties can greatly improve their electrochemical performances and can effectively amplify their applications in super-capacitors. Carbon spheres with multilayered graphene formed in their matrix are prepared by annealing them with sodium metal and they are combined with NiCo₂O₄ spheres by a simple hydro-thermal treatment. Structures and electrochemical performances of resulted samples are examined with X-ray diffraction, Raman scattering spectra, X-ray photoelectron spectroscopy, infrared spectroscopy, electron microscopy, gas physisorption, cyclic voltammetry and electrochemical impedance spectra, respectively. The largest specific capacitance of resulted composites is measured about 920 F g⁻¹ at 1 A g⁻¹, which is about 3.7 times larger than that of pure carbon spheres and 2.8 times larger than that of pure NiCo₂O₄ spheres. The formation of multilayered graphene in the matrix of carbon spheres not only increases the high specific capacitance based on electric double layers, but also makes metal oxides combined with them display

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greatly increased pseudo-capacitance. The electric and ionic conductivity of resulted composites with various weight ratios of $NiCo_2O_4$ and carbon spheres are respectively investigated and their effects on their electrochemical performances are also discussed.

Keywords: NiCo₂O₄; carbon sphere; multilayered graphene; super-capacitor

1. Preface

Super-capacitors including electric double layer capacitors (EDLCs), pseudocapacitors and hybrid capacitors are one type of energy storage devices. They usually possess high power density and long cycle life, which are promising for their applications in portable electronic devices, electric vehicles, backup energy systems and user electronics [1-3]. However, their rate capabilities and energy densities need to be improved in order to enhance the efficiency of devices [4,5]. This greatly depends on the structural optimization of electrode materials in the devices.

Among them, one kind of redox electrochemical capacitors based on metal oxides with pseudo-capacitive properties can generate a high load in a short period of time and increase their final specific capacitance. Some transition metal oxides including cupric oxide [6], nickel oxide [7], manganese oxide [8], titanium oxide [9] or some complex metal oxides [10,11] are widely explored as electrode materials of pseudo-capacitors. Because their electric energy storage depend on Faradaic process generated at interfaces between metal oxides and electrolyte ions, their electrochemical performances including specific capacitance, rate capability and cycle

stability are mainly affected by their surface areas, electronic and ionic conductivity, mechanical and chemical stability. However, most of pure metal oxides usually display their poor electric and ionic conductivity because of their structural characteristics. Although most of them possess lower production cost and can display their prospect in super-capacitors, their electrochemical performances are greatly affected by their structure defects. So, a lot of attentions have been paid to the structural optimization including specific surface areas and porous structures of metal oxides [12-17]. One of strategies is the coating of metal oxides on metal substrates in order to improve their electric conductivity. For example, Li₄Ti₅O₁₂ nanowire arrays are grown on Ti foil [18], MnO₂ nanoneedles [19], hollow NiCo₂O₄ nanoparticles [20], porous NiCo₂O₄ nanowires [21]. Considering the fact that super-capacitors usually need to work at large charge-discharge current densities, the iterative oxidation and reductions of metal oxides to be carried out under large current densities usually cause a strong concussion in their structures and make them display their poor stability on substrates.

Under such a circumstance, another effective strategy to be carried out is the turning some metal oxides and carbon materials into their composites. Carbon materials not only act as supporters of metal oxides in the composites for their improved surface characters, but also can contribute to the capacitance based on the formation of electric double layers (EDLs) during a charge-discharge process [22-27]. They are explored as electrode materials and their electrochemical performance have been investigated. For example, NiCo₂O₄/three dimensional graphene composite are

investigated, but, their carbon substrates still display the character of typical amorphous carbons [28-31]; Zn₂SnO₄/MnO₂ core/shell nanocable-carbon microfiber hybrid composites are investigated, however, it is found that some composite display their performances mainly based on EDLs and the others do them based on the typical pseudocapacitance [32]; lithium ions in cotton textile are prepared and their electrochemical performances are investigated, but it can be seen the substrate in the composite is still composed of amorphous carbons [33, 34]. Moreover, 3D NiCo₂O₄ on carbon cloth [35], NiCo₂O₄ nanoneedles on carbon nanofibers [36], and NiCo₂O₄/N-doped graphene [37] are also investigated. On the other hand, some porous carbon materials with high specific surface areas are used to improve the distribution of metal oxides on them. For example, NiCo₂O₄ nanosheets on hollow carbon microspheres [38, 39]. In general, it can be seen that several main kinds of carbons have been used as substrates in metal oxide/carbon composites. According to above investigations, some of them can indeed exhibit their high electrochemical performances, however, little attentions have been paid to the structural optimizations of carbons, especially of amorphous carbons and their structural effects on the performances of resulted composites. It can be seen that they are usually prepared from metal oxides with different as-prepared carbons. The possess different structural characters and do their different effects on the performances of resulted composites. For example, 1D carbon materials usually possess higher electric conductivity and they are favor to the improvement of electric conductivity of metal oxides, but their poor porous characters make them be added little amount of metal oxides; 2D carbon

materials usually possess marvelous electric conductivity and larger specific surface, but, their low bulk density are not favor to their practical applications; 3D carbon materials possess high specific surfaces and marvelous porous structures and they are also used as supporters of metal oxides. Based on the working mechanism of supercapacitors, no carbon materials can completely meet their requirement, so, the structural optimization of carbons in matrix of the composites should be paid more attentions in the field of super-capacitors.

Based on the formation of EDLs on carbons, the accumulation state of microcrystalline graphite in matrix of carbons usually plays an important role in their electric and ionic conductivity. It does have an important effect on electrochemical properties both of carbons and metal oxide/carbon composites. For example, the matrix of typical amorphous carbons are composed of disordered microcrystalline graphite and usually make them possess large specific surfaces. They are favor to the addition of more metal oxides on carbon substrates, but the typical amorphous carbons usually possess poor electric conductivity and they are not favor to the improved electric conductivity of metal oxides. On the contrary, the matrix of typical graphite materials are composed of highly ordered micro-crystalline graphite and they make them with high electric conductivity, but they also result in their poor porous characters. They are not favor to the addition of more metal oxides on them. A marvelous carbon material used as the supporter of metal oxides should possess a high specific surface area, a proper porous structure and a high electric conductivity at the same time. However, these as-prepared carbons used as the matrix of metal

oxide/carbon composites are difficult to meet the requirement and further effectively improve their electrochemical performance of the composites. In view of amorphous carbons with the characters of easy access and low production cost, they can be used as supporters of metal oxides and display their prospective application in supercapacitors if their electric conductivity and porous characters are effectively improved.

In this paper, carbon spheres with multilayered graphene to be formed in their matrix and they are combined with NiCo₂O₄ spheres by a simple hydro-thermal treatment. Various structural characterizations about carbon spheres, NiCo₂O₄ spheres and resulted composites are examined and their electrochemical performances are also investigated, respectively. The specific capacitance of the composite is obviously larger than that of pure carbon spheres or NiCo₂O₄ spheres. The weight ratios of carbon and NiCo₂O₄ spheres in resulted composites have an obvious effect on their electrochemical performances. It is also found that the formation of C-O bond between carbon and NiCo₂O₄ spheres is related to the improved electric performances of resulted composites. It can be concluded that the formation of multilayered graphene in the carbons not only makes them possess high specific capacitance based on EDLs, but also make NiCo₂O₄ in the composites display their improved pseudo-capacitive properties.

2. Experimental

2.1 Materials

Glucose (AR), Co(NO₃)₂.6H₂O (AR), Ni(NO₃)₂.6H₂O (AR), NaCl (AR), isopropyl alcohol (AR), propanetriol (AR) and sodium metal (CP) were all purchased from Sinopharm Chemical Reagent Co., LtdS.

2.2 Preparation of carbon spheres with multilayered graphene structure

Glucose solution (aq. 0.5 mol L⁻¹) is added in an autoclave and heated at 190 °C for 12 h, then, resulted mixture is filtered, washed with water and dried at 80 °C in a oven, after that, it is carbonized at 400 °C for 4 h in nitrogen atmosphere and resulted carbon spheres are named as GC.

GC (0.5 g) and sodium chloride (2.0 g) are mixed each other, then, the mixture and sodium metal (1.5 g) are settled in a alumina autoclave with a cover and it is annealed in nitrogen atmosphere at 850 °C for 2 h, after it being cooled at room temperature and opened in air for several hours, resulted product is washed in water to remove residual sodium chloride and sodium oxide, after that, it is dried at 120 °C and the resulted sample is named as G-GC.

2.3 Preparation of NiCo₂O₄ spheres

 $Co(NO_3)_2.6H_2O$ (0.5 mmol), Ni(NO₃)₂.6H₂O (0.25 mmol) and isopropyl alcohol (50 mL) are mixed by a strong stirring, then, propanetriol (15 mL) is dropped into the mixture and it is continuously stirred for 10 min, after that, the mixture is added in an autoclave with a Teflon inner liner and heated at 180 °C for 8 h, after it being cooled at room temperature, resulted product is filtered and washed by water and alcohol,

accordingly, after it being dried at 80 °C, the product is annealed in air atmosphere at 350 °C for 2 h and NiCo₂O₄ spheres are obtained.

2.4 Preparation of G-GC/NiCo₂O₄ composites

G-GC and NiCo₂O₄ spheres are mixed at various weight ratios of 1:2, 5 and 8, respectively, then, water (100 mL) is added to each mixture with a sonic oscillation for 1 h, after that, each mixture is added in an autoclave and heated at 180 °C for 12 h, after it being cooled to room temperature, it is filtrated and dried at 300 °C in nitrogen atmosphere. Resulted samples are correspondingly named as G-GC/NiCo₂O₄-2, -5 and -8.

2.5 Structural characterizations

XRD patterns are collected on a D8 FOCUS X-ray powder diffractometer. Acquisition conditions were CuK α radiation with 40kV/40mA, a step size of 0.01°/20 and a count time of 0.5s. A NIST SRM 640c silicon standard is used to correct the line position and broadening of patterns.

Raman spectra (Raman) are obtained on a Renishaw inVia laser Raman spectrometer, using 512 nm laser source.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a AXIS Ultra DLD equipment with Mg K X-ray excitation source and hemispherical electron analyzer.

Infrared spectrocopy (IR) measurements were carried out with an infrared

spectrometer 2015 (IS10).

Scanning electron microscopy (SEM) photographs are taken on a S-4800 microscope and Energy Dispersive X-ray Spectrometric Microanalysis (EDX) with SEM are also carried out.

Transmission electron microscopy (TEM) photographs are taken on a FEI TECNAI G² S-TWIN F20 microscope. Samples for TEM identification are prepared by grinding and dispersing them in ethanol, and placing a drop on a lacey carbon grid. These samples are observed in numerous regions.

Nitrogen adsorption and desorption isotherms of samples are measured with a volumetric adsorption system (Micromeritics Tristar 3000). The specific surface area and pore-width distribution are analyzed by the Brunauer-Emmett-Teller (BET) and BJH method.

2.5 Electrochemical measurements

In order to prepare working electrodes, resulted samples of GC, G-GC, NiCo₂O₄ spheres and G-GC/NiCo₂O₄ composites are used as active materials, respectively. Polyfluortetraethylene (PTFE) is used as a binder. The working electrode containing 2-3 mg active materials, they are mixed at a mass ratio of sample : PTFE = 8 : 1. Each mixture is wet by a little of ethanol to form a slurry. Each working electrode is fabricated by coating the slurry on a nickel mesh and it is dried under vacuum at 120 °C for 5 hours and weighed. They were all dipped in KOH (6 M) for 24 hours before electrochemical characterizations.

Cyclic voltammetry (CV) investigations are performed by using three-electrode system with a voltammetric analyzer (CHI600E) at various scan rates and the voltage is swept from -1.0 to 0 V and back to -1.0 V. Resulted samples are respectively used as working electrodes, the nickel mesh is used as the counter electrode and the Hg/HgO electrode is used as the reference electrode. KOH (6 mole dm⁻³) is used as the electrolyte.

The electrochemical impedance spectra (EIS) are also recorded on the same electrochemical workstation. The frequency scope is from 0.01 to 1000000 Hz, the amplitude is 0.005 V and the quite time is 2 s.

3. Result and discussion

3.1 Improved performance from structural optimization of carbon spheres

Structure characterizations about GC and G-GC are presented in Fig.1. It can be seen the spherical morphology of GC with an average diameter about 300 nm in the photograph as shown in Fig.1a, indicating the successful preparation of carbon spheres from the hydrothermal treatment of glucose solution. The sphere morphology can be also observed in the SEM photograph of G-GC as shown in Fig.1b, indicating that the treatment of GC in sodium metal cannot destroy their sphere morphology. TEM photograph of GC is presented in Fig.1c. These disordered graphite crystallite in the matrix exhibit the amorphous character of GC. TEM photograph of G-GC is presented in Fig.1d. It can be seen multilayered graphene with 4-8 layers in the matrix

of G-GC, moreover, it can be also seen turbulent carbons around these multilayered graphene and typical amorphous carbons near these turbulent carbons. By comparing TEM photographs both of GC and G-GC, it can be seen that the initial disordered graphite crystallite in the matrix of GC are rearranged and turned into multilayered graphene, turbulent and amorphous carbons.

Fig.1 Structure characterization of GC and G-GC, SEM photograph of GC (a) and G-GC, TEM photograph of GC (c), TEM photograph of G-GC (c), XRD (e), Raman patterns of GC and G-GC (f), adsorption and desorption isotherm (g) and pore volume distribution curve of G-GC (h).

The diffraction pattern for GC as shown in Fig.1e exhibits two widened diffraction peaks at 20 about 26 and 43°, indicating the matrix to be composed of amorphous carbons. It can be certified by Raman spectrum as shown in Fig.1f. For example, D- and G-band peaks with almost equal intensities indicate the laser scatting mode on typical amorphous carbons. The amorphous carbon character of GC is resulted from the carbonization of glucose at 400 °C. XRD pattern for G-GC as shown in Fig.1f exhibits two sharpened diffraction peaks at 20 about 26° and 44°, respectively. By comparing them with those of GC, the diffract peaks for G-GC are more sharpened than those for GC. It is surely attributed to the formation of layered carbons in G-GC. Raman spectrum for G-GC as shown in Fig.1f displays obviously intensified G-band peak and greatly weakened D-band peak, which is identified as the laser scatting mode on layered carbons. Obviously, it is different from that for GC, indicating a different accumulation state of graphite micro-crystallite to be formed in matrix of G-GC.

The adsorption-desorption isotherm for G-GC is presented in Fig.1g. The isotherm with a hysteresis loop started at the relative pressure about 0.4 exhibits the character of type IV, indicating both micro- and meso-pores to be formed in the matrix. Moreover, a steep plateau can be clearly observed in the isotherm, indicating uneven micro-pores to be formed in the matrix. The pore volume distribution curve as shown in Fig.1h exhibits two pore volume distributions concentrated at the pore width about 1.5 nm and 4.0 nm, respectively. The specific surface area of G-GC is measured about 980 m² g⁻¹. It can be surely attributed to the fact that the formation of multilayered graphene that cause a series of movements of disordered crystalline graphite including their orientation, connection and stacking with the existence of sodium metal at 850 °C.



Fig.2 CV curves (a) and galvanostatic charge-discharge curves (b) of G-GC

Electrochemical performances of G-GC are presented in Fig.2. The rectangle feature can be clearly observed in CV curves at various scanning rates as shown in Fig.2a, indicating their electrochemical performances based on the formation of EDLs during charge-discharge process, moreover, the rectangle feature can be still observed in the curve at 200 mV s⁻¹. Galvanostatic charge-discharge curves for pure G-GC at

various charge-discharge current densities are shown in Fig.2b. These symmetrical charge-discharge branches with no obvious voltage drops can be observed in them, indicating a marvelous charge-discharge reversibility and the sample of G-GC with excellent electric and ionic conductivity at large charge-discharge current densities. The specific capacitance of G-GC is measured about 250 F g⁻¹ at 1 A g⁻¹. It is attributed to the improved electric conductivity from the formation of multilayer graphens and the optimized ionic conductivity from mesopores to be formed in G-GC.

3.2 Structure and electrochemical performance of NiCo₂O₄ spheres



Fig.3 Structure characterization of pure NiCo₂O₄, SEM photograph (a) and (b), XRD

patterns (c) adsorption-desorption isotherm inserted with pore volume distribution curve (d)

Structural characterizations for NiCo₂O₄ spheres are presented in Fig.3. In SEM photograph as shown in Fig.3a, it can be seen the spheres with an average diameter about 500 nm and the porous surface morphology. A profile of one sphere is also observed in SEM photograph as shown in Fig.3b, exhibiting the morphology with internal compacted core and external porous surface. The structure feature can be ascribed to the hydro-thermal treatment of nickel and cobalt salts. At its early stage, the crystallization of NiCo2O4 is dominated by the large concentrations both of Ni²⁺ and Co³⁺ ions and the fast crystal growth of NiCo₂O₄ erystals results in the compacted core, while, at the latter stage of crystallization, the decreased concentrations both of Ni²⁺ and Co³⁺ ions cause the crystallization of NiCo₂O₄ and aqueous solution, resulting in the crystals with a porous surface. This is why some metal oxides with a porous morphology still possess a small specific surface area and a low specific capacitance.

XRD pattern for the sample is shown in Fig.3c. These diffraction peaks are identified as the component of crystalline NiCo₂O₄, indicating that the spheres are composed of NiCo₂O₄. Their adsorption-desorption isotherm is shown in Fig.3d. The isotherm with a hysteresis loop start at the relative pressure about 0.4 is belonged to type IV, indicating micro- and meso-pores to be formed in NiCo₂O₄ spheres. The steep plateau in the isotherm indicates uneven micro-pores formed in NiCo₂O₄ spheres. The pore volume distribution curve is shown in the insert of Fig.3d, exhibiting an obvious a pore volume distribution concentrated at the pore width about

5 nm. However, their small pore volume of meso-pores is attributed to their hard cores and porous appearances.



Fig.4 Galvanostatic charge-discharge curve (a) and capacitance retention curve (b) of NiCo₂O₄ spheres

Galvanostatic charge-discharge curve of NiCo₂O₄ spheres is shown in Fig.4a. The electrochemical performance displays typical pseudocapacitance character, indicating a redox reaction of NiCo₂O₄ to be carried out during the charge-discharge process. However, the charge-discharge branches display an asymmetrical style, indicating the reaction of NiCo₂O₄ with an inferior reversibility during the charge-discharge discharge process. The specific capacitance of NiCo₂O₄ spheres is measured about 330 F g⁻¹ at 1 A g⁻¹, while, the capacitance retention curve as shown in Fig.4b exhibits a steady specific capacitance about 290 F g⁻¹ after 10000 charge-discharge cycles.

3.3 Improved electrochemical performances from G-GC/NiCo₂O₄ composite

Electrochemical performances of various $G-GC/NiCo_2O_4$ composites are presented in Fig.5. According to widened CV curves with bulges as shown in Fig.5a, it can be seen that their electrochemical performances are based on oxidation-

reduction reactions from NiCo₂O₄ and EDLs from carbons, indicating that NiCo₂O₄ and carbon spheres do both contributions to electrochemical activities during the charge-discharge process. In galvanostatic charge-discharge curves as shown in Fig.5b, it can be seen that of G-GC/NiCo₂O₄-5 displays the largest charge-discharge interval, while, that of G-GC/NiCo₂O₄-2 displays the smallest charge-discharge interval. The capacitance of G-GC/NiCo₂O₄-2, 5 and 8 are measured about 800, 920 and 890 F g⁻¹, respectively. In their EIS diagrams as shown in Fig.5c, semicircles in them are obvious different each other, for example, the semicircle in that for G-GC/NiCo₂O₄-5 is the smallest, indicating the small transmission resistance of ions in the matrix, while, that for G-GC/NiCo₂O₄-8 displays a larger semicircle and that for G-GC/NiCo₂O₄-2 exhibits the largest one. The differences in these semicircles indicate different ionic conductivity in each composite. According to the insert as shown in Fig.5c, Resistance values of G-GC/NiCo₂O₄-2, 5 and 8 are valued as 0.8, 1.0 and 1.5 Ω , respectively, indicating them with different electric conductivity. The capacitance retention of the sample of G-GC/NiCo₂O₄-5 is presented in Fig.5d. The increased specific capacitance measured before 1000 circles is attributed to its instability during the measurement and the steady capacitance retention is found to remain at 94% after 5000 circles.



Fig.5 Electrochemical performances of composites , CV curves (a), galvanostatic chargedischarge curves (b) and EIS curves (c) and capacitance retention curve for G-GC/NiCo₂O₄-5 (d)

According to above investigations, it can be known that the specific capacitance of G-GC, NiCo₂O₄ spheres and G-GC/NiCo₂O₄-5 composite are measured as 250, 330 and 927 F g⁻¹ at 1 A g⁻¹, respectively. So, the specific capacitance of the composite is about 3.7 times larger than that of pure G-GC spheres and about 2.8 times larger than that of pure NiCo₂O₄ spheres. If they independently do their contributions to the electrochemical performance, carbon spheres with 33 wt % in G-GC/NiCo₂O₄-5 should possess the capacitance about 83 F g⁻¹ because of pure G-GC with the specific capacitance of 250 F g⁻¹ at 1 A g⁻¹, while, NiCo₂O₄ spheres with 67 wt% in the composite should possess the capacitance of 330 F g⁻¹ at 1 A g⁻¹, thus, the sum should be about 304 F g⁻¹ at 1 A g⁻¹. In fact, the measured specific capacitance of the composite is about 3 times larger than the sum. Obviously, it is one plus one is more than two. The obviously improved capacitance value is resulted from the common contributions of carbons with $NiCo_2O_4$ spheres because of the composite with its structure optimization.



Fig.6 Structural characterizations about G-GC/NiCo₂O₄ composites, SEM photograph of G-GC/NiCo₂O₄-5 (a), EDS spectrum (b), XRD patterns (c), Raman spectra (d), adsorption-desorption isotherms (e) and pore volume distribution curves (f)

Structural characterizations about G-GC/NiCo₂O₄ composites are presented in Fig.6. In SEM photograph of G-GC/NiCo₂O₄-5 as shown in Fig.6a, it can be seen spheres to be connected each other after the hydro-thermal treatment of G-GC and NiCo₂O₄ spheres. C, Ni, Co and O elements are detected in its EDS as shown in Fig. B, indicating the sample to be composed of G-GC and NiCo₂O₄. XRD patterns for various composites are presented in Fig.6c. According to these diffraction peaks,

crystalline NiCo₂O₄ in them are all detected in them. It can be also seen that their diffraction patterns become gradually weakened with the decreased weight ratio of NiCo₂O₄ in resulted composites. For example, the pattern for G-GC/NiCo₂O₄-8 displays clear diffraction peaks for crystalline NiCo₂O₄, while, that for G-GC/NiCo₂O₄-2 becomes ambiguous. It is attributed to the poor sensitivity to the lower crystalline content. Because of the annihilation from strong diffraction effect of crystalline NiCo₂O₄, the diffraction patterns for layered carbons cannot be clearly observed in them. However, they can be identified in their Raman spectra as shown in Fig.6d, for example, intensified G-band peaks and greatly weakened D-band peaks can be all observed in them, indicating G-GC to be added in these composites. It can be concluded that the composites are composed of G-GC and crystalline NiCo₂O₄.

Their adsorption-desorption isotherms are all presented in Fig.6e. The isotherms with hysteresis loops start at the relative pressure about 0.4 are belonged to type IV, indicating micro- and meso-pores to be formed in them. It can be also seen that with increasing ratios of NiCo₂O₄ in the composites, the plateaus in the isotherms become more and more lower and they are all lower than that in the curve for pure GC as shown in Fig.1f, indicating that the porous structures of the composites are obviously affected by the weight ratio of NiCo₂O₄. Their pore volume distribution curves are shown in Fig.6f. They display different pore volume distributions concentrated at the pore width about 3.5 nm, moreover, the curve for G-GC/NiCo₂O₄-5 displays an obvious pore volume distribution concentrated at the pore width about 6.5 nm. Specific surface areas of G-GC/NiCo₂O₄-2, 5 and 8 are measured about 384, 205 and

173 m² g⁻¹, respectively. Although their specific surface areas are all smaller than that of pure G-GC, it can be seen that the composite of G-GC/NiCo₂O₄-5 with the moderate specific surface area and crystallinity can display its marvelous performance. It can be attributed to its obvious pore volume distribution at the pore width range from 5 to 8 nm, which is favor to decreasing the ionic conductivity during the charge-discharge process and does have a positive effect on their electrochemical performances.



Fig.7 XPS general spectrum of G-GC/NiCo₂O₄-5 (a), fitting curves for Ni 2p (b), Co 2p (c), O 1s (d) and C 1s (e)

XPS for pristine G-GC/NiCo₂O₄-5 are presented in Fig. 7. Core levels of Ni 2p, Co 2p, O 1s and C 1s can be identified from the survey of XPS. The general spectrum as shown in Fig.6a indicates carbon, oxygen, cobalt and nickle elements detected in the composite. It is attributed to the composite prepared from G-GC and NiCo₂O₄ spheres. The peaks with binding energy (BE) values of 855.7 and 873.7 eV are

assigned to Ni²⁺ and these of 854.1 and 872.0 eV are assigned to Ni³⁺ as shown in Fig.7b; these of 782.0 and 786.6 eV as shown in Fig.7c are assigned to Co 2p 3/2 and its shake-up satellite for Co2p ions, respectively; these of 529.5, 531.2 and 533.1 eV as shown in Fig.7d are assigned to the band between oxygen and metal, the oxygen ion and the absorbed H₂O, respectively; these of 284.8 and 288.2 eV as shown in Fig.7e are assigned to C1 and C2, respectively. It can be clearly seen that there are several active points between 284 and 874 eV, indicating that they can be used to restore energy. Moreover, according to the C-O bond detected in XPS spectrum, it can be seen that carbon and NiCo₂O₄ spheres are bonded each other after their hydro-thermal treatment.



Fig.8 IR spectra of G-GC (1), the composite of G-GC/NiCo₂O₄-5 composite (2) and the

simple mixture of G-GC and NiCo₂O₄ with a grinding treatment (3).

IR spectra of G-GC/NiCo₂O₄-5 composite and G-GC are presented in Fig.8. In the spectrum (1), the peak at 3487 cm⁻¹ is assigned to the vibration of hydroxyl group

in absorbed water, the peak at 1014 cm⁻¹ can be assigned to the stretching vibration between carbon and hydroxyl group and the peak at 801 cm⁻¹ can be assigned to the vibration between carbon and hydrogen atoms. In the spectrum (2), two peaks at 3413 and 3140 cm⁻¹, respectively, are also assigned to the vibration movements of hydroxyl groups. By comparing these peaks with that in the spectrum (2), the more vibration movements are attributed to the hydrothermal treatment. Moreover, it can be seen one peak at 1618 cm⁻¹ and another at 1399 cm⁻¹, which do not appear in the spectrum (2), the former is assigned to the vibration between metal oxide and carbons and the latter is assigned to the vibration between carbon and oxygen atoms [40, 41]. On the other hand, it can be seen the small peak at 1022 cm⁻¹, it can be attributed to the degeneration of the peak at 1014 cm^{-1} in the spectrum (1). In the spectrum (3), the peak at 3424 cm⁻¹ is also assigned to the vibration movements of hydroxyl groups, the weak peak at 1617 cm⁻¹ is also assigned to the vibration between metal oxide and carbons and the peak at 649 cm⁻¹ is assigned to oxide absorption band. Obviously, the spectrum for the composite is different from these of the others. It indicates the dehydration between hydroxyl groups and the formation of C-O band in it. This agrees with the conclusion from the XPS characterization that the formation of C-O band is carried out after the hydrothermal treatment of G-GC with NiCo₂O₄ spheres.

In view of the fact that the electric performances of pure G-GC or pure $NiCo_2O_4$ are obviously inferior to these of the composites as investigated in above sections, it can be deduced that their obviously improved performances are related to the following optimized structure characters.

Firstly, the formation of multilayered graphene in the matrix of G-GC can effectively improve its electric and ionic conductivity, which not only makes G-GC itself display the marvelous specific capacitance of 250 F g^{-1} , but also results in the composite with obviously improved electric and ionic conductivity. So, it does have an important effect on the improved electrochemical performance of resulted composite. Secondly, the hydro-thermal treatment of G-GC and NiCo₂O₄ spheres results in the formation of C-O band between them and causes more electrochemical active spots in the composite according to XPS characterization as shown in Fig.7 and the IR spectrum as shown in Fig.8. Thirdly, the ratio of carbon spheres in the composite does an important effect on them.

Based on the basic working mechanism of super-capacitors, it can be known that the comprehensive effects of the structure characters both of carbon and metal oxide matrix. For example, their larger surfaces can provide more quantities of electrochemical active substances, their rich porous structures can make the electrolyte ion transport in their matrix with less resistance and their improved material characteristics result in their marvelous electric conductivity. Obviously, the bonding between G-GC and NiCo₂O₄ in resulted G-GC/NiCo₂O₄ results in them with more active points to restore energy and results in a close connection between G-GC and NiCo₂O₄ that does a favor to their improved electrolyte ion transmission and electric conductivity.



Fig.9 Sketch for carbon and NiCo₂O₄ phase varied in the composites

The effects of optimized structural characters on the improved performances of the composites can be understood by the sketch as shown in Fig.9. The more content of G-GC in C-GC/NiCo₂O₄-2, for example, carbon spheres with that of 33 wt%, is favor to the formation of a continuous carbon phase in the matrix of the composite as being symbolically described in Fig.9a and the composite possess the smallest impedance value of 0.8 Ω , indicating the matrix with a high electric conductivity, however, the continuous carbon phase results in a large ionic transmission resistance as it being shown in Fig.5c; on the contrary, carbon spheres with the content of 11 wt% and NiCo₂O₄ spheres with that of 89 wt % in G-GC/NiCo₂O₄-8 is favor to the formation of a continuous phase of NiCo₂O₄ in the matrix of the composite as it being symbolically described in Fig.9b, so, it makes the composite possess a high impedance value of 1.5 Ω as it being shown in Fig.5c because of the large electric resistance of the oxide; however, the content of G-GC with 17 wt% and that of NiCo₂O₄ with 83% in G-GC/NiCo₂O₄-5 may result in an optimized structure as symbolically described in Fig.9c, which possess a smaller electric resistance and the

largest ionic conductivity as shown in Fig.5c, so, it results in the greatly increased specific capacitance.

4. Conclusion

Multilayered graphene formed in the matrix of amorphous carbons not only make carbons themselves possess high specific capacitance based on electric double layers, but also make metal oxide on them display the greatly increased pseudocapacitive properties. The formation of C-O bonds between the carbon spheres and NiCo₂O₄ spheres can be simply carried out by a hydro-thermal treatment of the two components. The weight ratios of NiCo₂O₄ and carbon spheres in the composites have an obvious effect on the electric and ionic conductivity of resulted composites and a moderate weight ratio in the composite can result in the greatly improved electrochemical performances. The structural optimization of carbon substrate is an effective route for improved electrochemical performance of metal oxides.

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Titles of figures

Fig.1 Structure characterization of GC and G-GC, SEM photograph of GC (a) and G-GC, TEM photograph of GC (c), TEM photograph of G-GC (c), XRD (e), Raman patterns of GC and G-GC (f), adsorption and desorption isotherm (g) and pore volume distribution curve of G-GC (h).

Fig.2 CV curves (a) and galvanostatic charge-discharge curves (b) of G-GC

Fig.3 Structure characterization of pure NiCo₂O₄, SEM photograph (a) and (b), XRD patterns (c) adsorption-desorption isotherm inserted with pore volume distribution curve (d).

Fig.4 Galvanostatic charge-discharge curve (a) and capacitance retention curve (b) of NiCo₂O₄ spheres.

Fig.5 Electrochemical performances of composites , CV curves (a), galvanostatic chargedischarge curves (b) and EIS curves (c) and capacitance retention curve for G-GC/NiCo₂O₄-5 (d).

Fig.6 Structural characterizations about G-GC/NiCo₂O₄ composites, SEM photograph of G-GC/NiCo₂O₄-5 (a), EDS spectrum (b), XRD patterns (c), Raman spectra (d), adsorption-desorption isotherms (e) and pore volume distribution curves (f)

Fig.7 XPS general spectrum of G-GC/NiCo₂O₄-5 (a), fitting curves for Ni 2p (b), Co 2p (c), O 1s (d) and C 1s (e).

Fig.8 IR spectra of G-GC (1), the composite of G-GC/NiCo2O4-5 composite (2) and the

simple mixture of G-GC and NiCo2O4 with a grinding treatment (3).

Fig.9 Sketch for carbon and NiCo2O4 phase varied in the composites.