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Ultra-high pseudocapacitance of mesoporous $ZnCo_2O_4$ nanosheets on reduced graphene oxide utilizing neutral aqueous electrolyte

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A novel strategy to prepare hierarchical mesoporous $ZnCo_2O_4$ nanosheet decorated on reduced graphene oxide/nickel foam template was constructed. This unique nanostructure electrode consisting of mesopores/micropores for pseudocapacitors showed high capacitance, excellent cycling performance and good rate capability.

For the last decade, nanostructuring metal oxides, among the next generation energy-related materials, have been extensively investigated for the wide application fields.[1-3] In recent years, supercapacitors and lithium-ion batteries have been triggered due to the release of new breakthroughs in terms of high specific energy, high specific power and long cycle life at relatively low cost. From the fundamental observation, it is well known that the enhancement of specific capacity and rate capability can be achieved by a large specific surface area and a short pathway for the fast transport of mass and charge.

A key requirement for realizing high-performance supercapacitors is extra active sites of porous nanostructures having with a large surface area and a high conductivity that should be used for specific energy storage. The most promising way to obtain both a high energy density and a high power density on a limited surface area is to integrate not only the supercapacitor components-current collector, but also the electrode and the electrolyte-in a three-dimensional (3D) arrangement. The careful design of the supercapacitor to obtain short transport distances between the electrode and current collector is very important factor. Recently, nickel foam (NF) has been commonly used as the scaffold of a current collector or an electrode for energy-storage matrices due to its high electrical conductivity, desirable 3D cross-linked open-pore structure, and corresponding merits.[4-8]

Most recently, growing nanostructured metal-oxides over graphene oxide (GO) and reduced graphene oxides (rGOs) with two-dimensional (2D) nanosheet have attracted tremendous attention owing to its remarkable electrical conductivity, mechanical flexibility, strong thermal/chemical stability, feasible ultra-thinness, and good protection effect for oxidation.[9-12] Generally speaking, oxygen-containing defects sites on GO and rGO can adsorb positive ion or nanoparticle and offer nucleation site as a seed layer for an effective growing of desirable nanomaterials. On the base of the above considerations, we intend to combine NF with rGO as a seed layer for nanostructure metal oxide by a unique rational design. Among numerous active electrode materials, zinc cobaltite spinel ($ZnCo_2O_4$) nanostructures has been recognized as a prominent electrode material in electrochemical capacitors due to its high reversible capacity, long cycling life, and environmental affinity (such as nanoparticles, nanotubes and nanowires).[13-17] Consequently, the $ZnCo_2O_4$ nano-sized materials might be considered a less attractive energy-storage material than other Co_3O_4 and related $NiCo_2O_4$ for supercapacitor. However, by contacting with a conductive ultra-thin substrate, 2D $ZnCo_2O_4$ ultrathin-nanosheets can have its own decreased electrical internal resistance due to the high in-plane charge mobility of 2D nanostructure.

Herein, we report the first synthesis of self-organized hierarchical 2D mesoporous nanostructured $ZnCo_2O_4$ electrodes *via* NF template coated with rGO as a seed layer. rGO coated NF can provide several advantages: controlling the nano-morphology of various transition metal oxides as a seed layer and a building blocks of nanostructured transition metal oxides; acting as a protective layer for the oxidation of NF metal substrates; playing a role as a buffer layer between the current collector and the metal oxide; providing a high rate due to the internal resistance between substrate and transition metal oxide and short pathway for ion transport; supplying additional ion storage. This unique nanostructure electrode of $ZnCo_2O_4$/rGO/NF for pseudocapacitors exhibits surprisingly high capacity, excellent cycling performance, and good rate capability in 0.1M Na_2SO_4 neutral electrolyte. Notably, the $ZnCo_2O_4$/rGO

hybrid supercapacitor shows superior values and stability compared to previous reports such as $NiCo_2O_4$/carbon nanofiber (1,450 $F \cdot g^{-1}$), $NiCo_2O_4$@$NiCo_2O_4$ (1,925 $F \cdot g^{-1}$) and $ZnCo_2O_4$/NF (1,625 $F \cdot g^{-1}$).[18,19]

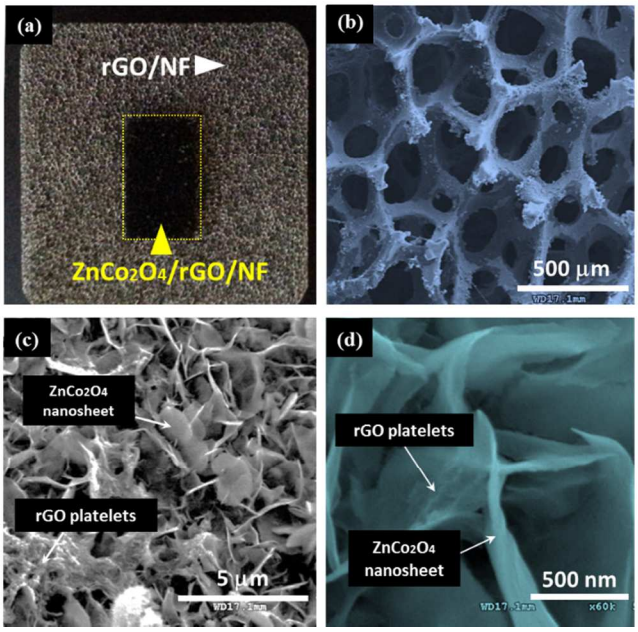

Fig. 1 (a) Digital picture of $ZnCo_2O_4$/rGO/NF on rGO/NF. (b) SEM image of rGO deposited on NF. (c and d) $ZnCo_2O_4$ nanosheet arrays supported on rGO/NF at different magnifications after annealed at 320 °C for 2 h.

Briefly, GO (20 mL: 3 $mg \cdot mL^{-1}$) was deposited on NF (size=1×1 cm^2) substrates by dip-coating with magnetic stirring for 24 h, followed by rinsing with DI water and vacuum drying for several times. The dried GO/NF sample was reduced by thermal annealing under 5% H_2/Ar at 800 °C for 30 min with a heating rate of 1 $°C \cdot min^{-1}$ in order to increase electrical conductivity. After the thermal annealing of GO/NF, its colour was changed from silver to dark-grey (see Fig. 1a). Actually, the presence of rGO can effectively accelerate to from $M(OH)_2$ (where M=Zn and Co) on the surface of the rGO by the mutual electrostatic interactions between the metal ions (Zn^{2+} and Co^{2+}) and OH- and/or COO- groups. Then it grows the desirable nanoforming active nucleation centres by hydrolysis *via* a heterogeneous nucleating growth with reducing the surface energy. After saturation adsorption on rGO surface, more $M(OH)_2$ self-assemble leads to the formation of the nanosheet-like structure on rGO in aqueous solution with surfactant and stabilizer.

Further oxidation of $ZnCo_2O_4$ is performed by surrounding O_2 in the hydrothermal reaction solution. As shown in Fig. 1a and Fig. S1-2, the entire NF framework was covered with rGO sheets. The large pore size (average aperture size of 580-800 μm) of NF allows GO nanosheet colonization in the inner structure of the 3D electrode. The morphology of the 3D rGO/NF was characterized by SEM as shown in Fig. 1b. rGO tended to agglomerate to form large particles of rGO platelets on NF framework after drying.[20] We etched the rGO/NF in HCl solution (3M) at 80 °C and obtained the 3D rGO foam structure, but it was crumbling too easily due to individual GO nanosheet coating on NF. Fig. S1e shows a representative SEM image of the rGO agglomeration obtained from the rGO/NF electrode (Figs. S2 and S3). The rGO sheets have a fairly smooth surface except for some folds. Therefore, the conductive rGO coating on NF is expected to serve as a seed layer for an effective growing of desirable nanomaterials, good seed layer, buffer layer of charge transfer from electrode, and the decrease internal resistance between substrate and transition metal oxide and short path lengths for ion transport. The next step was synthesized $ZnCo_2O_4$ nanosheets on NF coated with or without rGO by using a hydrothermal reaction with a mixture of $Zn(NO_3)_2 \cdot H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, hexamethylene-tetramine in H_2O:ethanol mixture at 90 °C for 12 h. Afterward, the thermal treatment was performed for the as-synthesized samples at 320 °C for 2 h with a heating rate of 2 $°C \cdot min^{-1}$ under air. Figs. 1c and d displays typical SEM images of $ZnCo_2O_4$/rGO/NF electrode obtained at 320 °C and their magnified images are exhibited as Figs. 1d and e. It can be found that $ZnCo_2O_4$ nanosheets are perfectly assembled on rGO/NF. Also, the $ZnCo_2O_4$ nanosheets did not detach from the rGO/NF substrate and basically maintains its own morphology after sonication. It is indicated that the as-synthesized $ZnCo_2O_4$ nanosheet has quite good mechanical adhesion. However, the self-organized 2D nanostructured $ZnCo_2O_4$ electrodes were not obtained using the same experimental condition without rGO on NF. As shown in Figs. 1c and d, few-layer rGO platelets covered on $ZnCo_2O_4$ nanosheets. This is may be due to the loosely attached rGO platelets on the rGO/NF surface in hexamethylene-tetramine solution, which is re-dispersed because of electrostatic stabilization resulting from ionization of carboxyl groups.[21]

To study of the $ZnCo_2O_4$ nanostructures, high-resolution TEM (HRTEM) and selected area electron diffraction (SAED) experiments were performed on intact $ZnCo_2O_4$/rGO/NF cross-sections (see Fig. 2).

The TEM and HRTEM images in Figs. 2a-c show the detailed structural characterization of the $ZnCo_2O_4$ nanosheet. As shown in Fig. 2b, it can be clearly observed that a lot of mesopores exist in the product of $ZnCo_2O_4$ nanosheet and some of them are still connected. We can also identify that the pore sizes are in the range of a few nanometres. It is believed that this mesoporous feature is helpful to the enhancement of electrochemical properties because mesoporous structure would lead to fast ion/electron transfer between electrode materials and electrolyte. A typical HRTEM image of the $ZnCo_2O_4$ nanosheet is shown in Fig. 2c. The two set of lattice fringe spacings (*d*) are ~0.451 and ~0.51 nm, corresponding to $ZnCo_2O_4$ (111) and (311) planes, respectively (see Fig. 2c). The SEAD pattern in Fig. 2d indicates the polycrystalline nature of the mesoporous $ZnCo_2O_4$, and all the diffraction rings can be indexed as (111), (220), (311), and (400) from in inside out, respectively. The presence of $ZnCo_2O_4$/rGO/NF has been revealed by energy-dispersive X-ray spectroscopy (EDS). The EDS analysis for $ZnCo_2O_4$/rGO/NF is reported in Table S1 and Fig. S4.

To demonstrate the effectiveness of the hierarchical mesoporous-nanosheet $ZnCo_2O_4$/rGO/NF in improving the

supercapacitance performance, the electrochemical capacitance of mesoporous $ZnCo_2O_4$/rGO/NF was evaluated with 0.1 M Na_2SO_4 as alkali metal sulfate neutral aqueous electrolyte because of its advantages of high ionic conductivity, low cost, non-flammability, good safety, eco-friendly and convenient assembly in air.[18,19] Fig. 3a shows cyclic voltammetry (CV) graphs with different scan rates ranging from 10 to 200 mV·s^{-1}.

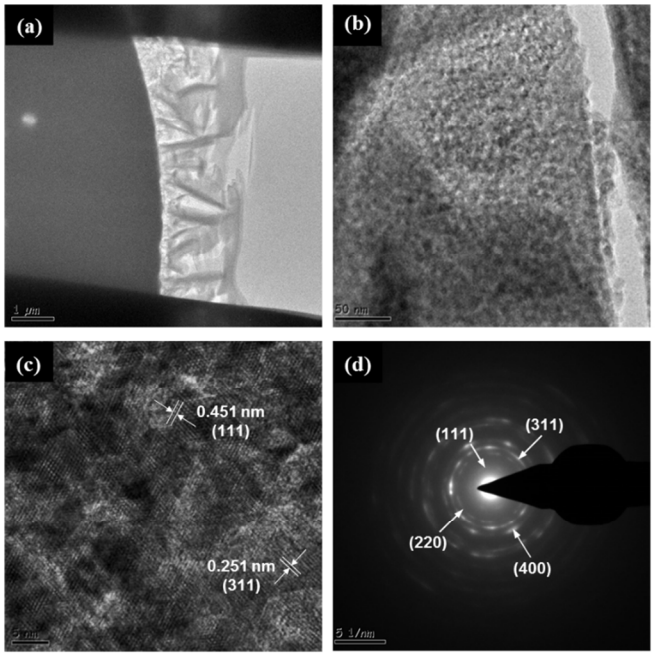

Fig. 2 (a) Cross-sectional FIB-TEM image of the $ZnCo_2O_4$/rGO/NF at low magnification. (b and c) high magnification of TEM images of nanosheet. (d) SEAD patterns of $ZnCo_2O_4$ nanosheet.

All CV curves show superior capacitive performance as straight rectangular shapes and symmetric current-potential characteristics of the CV shape representing the fast ionic diffusion and excellent electrochemical capacitance in the $ZnCo_2O_4$/rGO nanosheets. $ZnCo_2O_4$/rGO/NF electrode retained excellent "rectangular-shape" CV from 10 to 200 mV·s^{-1}, which even better than for $NiCo_2O_4$[19,22-24] and $ZnCo_2O_4$[19,25] electrodes.

The CV curve of $ZnCo_2O_4$/rGO/NF presents a slightly distorted rectangular shape at the faster of the scan rate, which indicates that the concentration polarization within the pores caused by ion transport limitations resulting in a more significant ohmic resistance to charge transport with increasing the scan rate.[26] It is well known that a rectangular-shape CV over a wide range of scan rate is very important due to the demand of high power in electrochemical capacitors, indicating rapid current response to the change of voltage sweep direction. The rectangular-shapes are indicated the ideal electrical double-layer capacitance behaviors and fast charging-discharging process characteristics, which were induced by intercalation-extraction of protons (H_3O^+) or alkali cations (Na^+) into-out of the channels of the $ZnCo_2O_4$/rGO nanosheets. Because the small CV area of rGO on NF (see Fig. S5), which indicates electrochemical capacitance from rGO is not noticeable. Even the scan rate up to 200 mV·s^{-1}, there is only slight distortion from the ideal symmetrical rectangle shape, which strongly shows a good rate capability of the electrodes.

It is worth noting that the rGO on NF is helped for making desired nanostructure as a seed layer, protecting layer for NF, and a buffer layer between active materials and current collector due to the high specific surface area with many nanoholes, good chemical stability and outstanding electrical properties.[27-29] CV current density increases with scan rate, suggesting that the electrodes have high power characteristics. Obviously, the increase in the applied of $ZnCo_2O_4$/rGO/NF results in a significant enlargement in the power characteristics which can be attributed to the intrinsically excellent electronic conductivity and dense-closed-contact between $ZnCo_2O_4$ and rGO/NF interface. Additionally, the nanosized porous structure of $ZnCo_2O_4$ nanosheet could ensure enough ions to contact the active materials in a short time and a high utilization of electrode materials, thus lead to the excellent capacitance behaviour and rate capability. The high gravimetric capacitance (C_{sp}) of 2,009 F·g^{-1} (normalized by pristine $ZnCo_2O_4$-rGO mass) was obtained at a scan rate of 10 mV·s^{-1} (see Fig. 3b). The calculation of capacitance was described in ESI. The C_{sp} of $ZnCo_2O_4$/rGO/NF retains, from 10 mV·s^{-1}, 49% at 100 mV·s^{-1} and 37% at 200 mV·s^{-1}. This may be induced by the bottleneck mesopores existing within the $ZnCo_2O_4$, which can slow down the ion transport at fast scan rates. Typical galvanostatic charge is displayed in Fig. 3c at different current densities. The *E-t* responses of the charge process show a triangular shape and mirror image with corresponding discharge counterparts confirming the formation of an efficient capacitor and excellent charge propagation across two electrodes in the Na_2SO_4 electrolyte indicating a rapid current-voltage response.

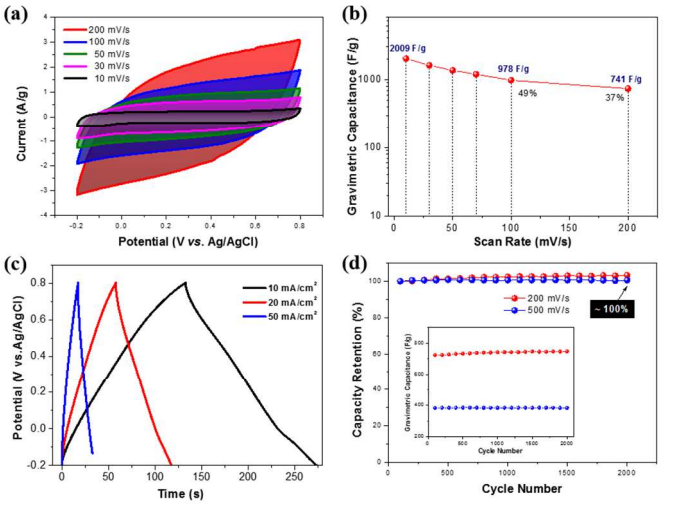

Fig. 3 (a) CV measurements for $ZnCo_2O_4$/rGO/NF supercapacitor performed under different scan rates of 10, 30, 50, 100 and 200 mV·s^{-1} in aqueous 0.1M Na_2SO_4 solution. (b) gravimetric capacitance as a function of scan rate. (c) galvanostatic CD curves at different current densities. (d) cycling performance at a scan rate of 200 and 500 m V·s^{-1}. Inset: gravimetric capacitance curves.

Additionally, both the increased current density and decreased *IR* drop, it show good symmetry and fairly linear

slopes at the current densities ranging from 10 to 50 mA·cm^{-2}. This result indicates that the $ZnCo_2O_4$/rGO/NF electrode can greatly reduce the internal resistance and fast Faraday redox reaction. The areal capacitance is calculated by the formula, $C = I\Delta t/S\Delta V$ (F·cm^{-2}), where I is the discharge current, Δt is the discharge time, ΔV is the potential change during discharge and S is the nominal electrode area. An estimated mass loading of 0.38 mg·cm^{-2} and the areal capacitances are as high as 1.4, 1.2, and 0.8 F·cm^{-2} when the values of Δt are 139.6, 59.5, and 15.3 s at discharge current densities of 10, 20, and 50 mA·cm^{-2}, respectively. The areal capacitance corresponding to the gravimetric capacitance of ~1960 F·g^{-1} is 1.4 F·cm^{-2} when the actual mass of active material is 1.85 mg, which is reasonably high value for highly porous structure based hybrid supercapacitor electrodes.[30] Therefore, the electrochemical performance by using the charge-discharge (CD) indicate that an electrode of $ZnCo_2O_4$ mesoporous nanosheets on rGO/NF delivers an ultrahigh capacitance normalized with respect to both the nominal area of the template and the mass of the electrochemically active material. Also, the CD curves show a linear and triangle profile and insignificant IR drops, implying good coulombic efficiency with a quick electrical response for the electrode due to success contact between $ZnCo_2O_4$-rGO and NF resulting in relatively low resistance of hybrid foam. The supercapacitor stability was also confirmed by the cyclic measurement. Fig. 3d shows the capacity retention versus cycle number for the $ZnCo_2O_4$ hybrid foam at high scan rates of 200 and 500 mV·s^{-1}. $ZnCo_2O_4$ hybrid foam electrode exhibits excellent stable cycling performance with remarkable ~100% retention of specific capacitance after 2,000 cycle. The specific capacitances is shown as 710 and 380 F·g^{-1} at each scan rate of 200 and 500 mV·s^{-1}, respectively. The superior electrochemical performance of $ZnCo_2O_4$/rGO/NF supercapacitor can be attributed to the following aspects: 1) With the high surface area of $ZnCo_2O_4$ nanosheet and an extremely narrow gap between the $ZnCo_2O_4$ nanosheets can effectively shorten the diffusion and migration paths of electrolyte ions during the rapid CD process; 2) The excellent interfacial contact and increased contact area between $ZnCo_2O_4$ and rGO/NF significantly improve the accessibility of the active electrode to the electrolyte ions; 3) rGO acts as a good at conducting of electricity was an effectively as a corrosion-inhibiting coating on NF in aqueous electrolyte and was decreased resistance between $ZnCo_2O_4$ nanosheets and NF; 4) The short pore length of $ZnCo_2O_4$ nanosheets are harmonious for forming a larger amount of double layers and facilitates the transport of the electrolyte ions, providing both enhanced energy storage and good rate capability.

In conclusion, we have reported the simple and cost-effective synthetic method of a novel hybrid 3D interconnected mesopores-$ZnCo_2O_4$/rGO/micropores-NF electrode. A relatively high capacitance of 2009 F·g^{-1} in neutral 0.1M Na_2SO_4 electrolyte was achieved. When the galvanostatic discharge loop, the specific areal capacitance was 1.4 F·cm^{-2} at 10 mA·cm^{-2} corresponding the gravimetric capacitance of ~1960 F·g^{-1}. This kind of hybrid supercapacitor exhibited good electrochemical performance, outperforming many other currently available carbon- and metal oxide-based supercapacitor systems. Particularly, the impressive capacitance retention of ~100% over 2000 CD cycles propels a new direction for novel growth of transition metal oxide on rGO/NF toward high-performance energy storage devices, which is a protecting oxidation of NF by graphene coating. Our work presents a new and competitive approach to design hybrid electrode architectures for high-performance energy storage devices as well as opening up the possibility to zinc cobaltite spinel into a promising pseudocapacitve material.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, fabrication process of rGO foam, SEM images, EDS analysis of the hybrid nanostructure, and CV curves. See DOI: 10.1039/c000000x/

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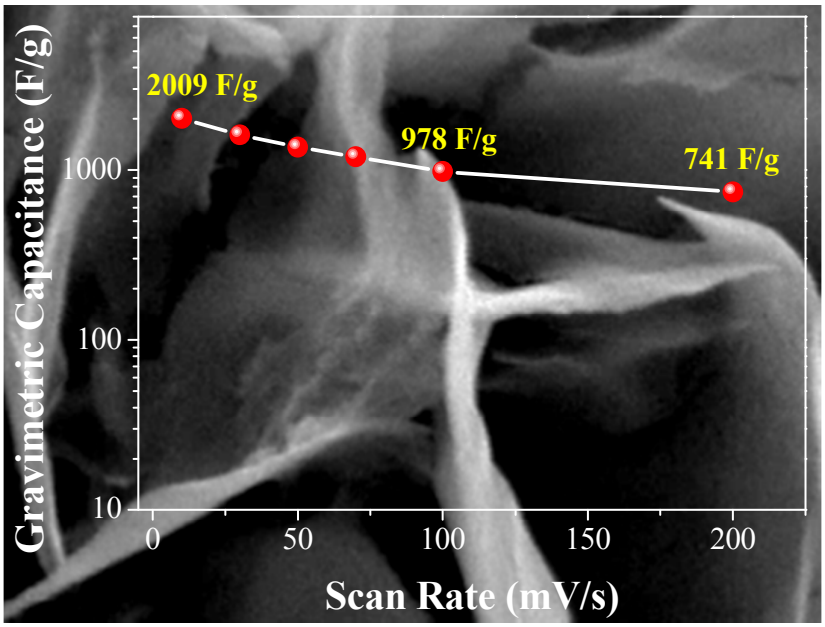
Graphical Abstract



A mesoporous $ZnCo_2O_4$ nanosheet on reduced graphene oxide/nickel foam network was employed as a supercapacitor electrode. It shows ultrahigh specific capacitances of 2009 $F \cdot g^{-1}$ at 10 m $V \cdot s^{-1}$ and excellent capacitance retention of ~100% in neutral 0.1M Na_2SO_4 electrolyte.