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Abstract

We report the synthesis of two-dimensional (2D) NiCo₂O₄ nanosheet-coated three-dimensional graphene network (3DGN), which is then used as an electrode for high-rate, long-cycle-life supercapacitors. Using the 3DGN and nanoporous nanosheets, an ultrahigh specific capacitance (2173 F g⁻¹ at 6 A g⁻¹), excellent rate capability (954 F g⁻¹ at 200 A g⁻¹) and superior long-term cycling performance (94% capacitance retention after 14000 cycles at 100 A g⁻¹) are achieved.

Keywords

high, rate, long, cycle, life, supercapacitors, graphene, three, coated, networks, nanosheet, two, dimensional, nico₂o₄

Disciplines

Engineering | Physical Sciences and Mathematics

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Two-dimensional NiCo₂O₄ nanosheet-coated three-dimensional graphene networks for high-rate, long-cycle-life supercapacitors†

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We report the synthesis of two-dimensional (2D) NiCo₂O₄ nanosheet-coated three-dimensional graphene network (3DGN), which is then used as an electrode for high-rate, long-cycle-life supercapacitors. Using the 3DGN and nanoporous nanosheets, an ultrahigh specific capacitance (2173 F g⁻¹ at 6 A g⁻¹), excellent rate capability (954 F g⁻¹ at 200 A g⁻¹) and superior long-term cycling performance (94% capacitance retention after 14 000 cycles at 100 A g⁻¹) are achieved.

Supercapacitors are among the most promising energy storage devices due to their high power density, ultrafast charging–discharging rate, long-cycle-life, and low maintenance cost.^{1–6} There are mainly two types of supercapacitors, *i.e.* electric double-layer capacitors (EDLC) and pseudocapacitors. The pseudocapacitor undergoes reversible redox reaction that occurs in the electrode materials, such as metal oxides (RuO₂, MnO₂, Co₃O₄, NiCo₂O₄, CoMoO₄, *etc.*)^{7–16} and metal hydroxides (Co(OH)₂, Ni(OH)₂, *etc.*);^{17–19} it stores more charges and provides higher specific capacitance than does the EDLC.² Undoubtedly, supercapacitors with high-rate capability and long-term cycling stability are essential to the newly emerging applications such as hybrid electric vehicles (HEVs). Although high-capacitance pseudocapacitors have been achieved using pseudocapacitive materials as electrodes, they normally suffer from low power density and unstable cycling performance because of their intrinsically low electrical conductivity.^{20–22}

Due to their high porosity, large internal surface area, and outstanding electrical and mechanical properties,^{23,24} three-dimensional graphene networks (3DGNs) serve as a striking platform for construction of composite electrodes with enhanced properties for wide applications, such as

supercapacitors,^{20,24–28} Li-ion batteries,^{29–32} catalysis,^{33–35} and sensors.^{26,36} Particularly, supercapacitors constructed from 3DGN based-materials have been studied to achieve enhanced electrochemical performances including higher specific capacitance, better rate capability and longer cycle life. For example, in our previous work, the Ni₃S₂@Ni(OH)₂ coated 3DGN exhibited much higher specific capacitance and better cycling performance than did Ni₃S₂@Ni(OH)₂ on Ni foam.³⁷ However, the electrochemical performance of the aforementioned 3DGN-based materials still cannot meet the demands of practical applications. Particularly, their long-term cycling performance and high-rate capability should be improved.

Recently, ultrathin two-dimensional (2D) nanosheets (NS), especially graphene and transition metal dichalcogenides, have attracted increasing attention due to their unique physical, chemical, and electronic properties.^{38–44} The high specific surface area of these 2D NS makes them very promising for energy storage applications, especially after they are coated onto 3DGN. As a typical electrode material for pseudocapacitors, NiCo₂O₄ has been widely investigated in the past few years due to its ultrahigh specific capacitance (over 2000 F g⁻¹).^{45–48} Herein, we report the preparation of thin 2D NiCo₂O₄ nanosheet-coated 3DGN, referred to as NiCo₂O₄ NS/3DGN, for high-performance supercapacitor application. This novel NiCo₂O₄ NS/3DGN hybrid exhibits excellent electrochemical performance, such as ultra-high specific capacitance and excellent rate capability. Importantly, it shows superior long-term cycling stability with 94% capacitance retention even after 14 000 cycles at 100 A g⁻¹.

The fabrication process for NiCo₂O₄ NS/3DGN is schematically illustrated in Fig. 1. The 3DGN was fabricated by the ethanol-CVD process reported in our previous work.^{24,29} After deposition of graphene, the surface of Ni foam became wrinkled (Fig. S1 in ESI†). The Raman spectrum showed that there is no obvious D band (~1350 cm⁻¹) of graphene (Fig. S2 in ESI†), indicating that the high-quality 3DGN with few defects on graphene was obtained.^{23,26} The relatively low integral ratio of 2D to G band suggested that the 3DGN is composed of few-layered graphene sheets.^{24,28,31}

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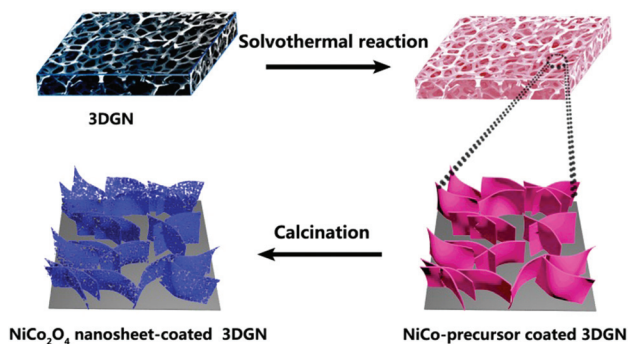


Fig. 1 Schematic illustration of the synthetic process of thin NiCo_2O_4 nanosheet-coated 3DGN.

The NiCo-precursor was coated on the surface of 3DGN, referred to as NiCo-precursor/3DGN, after solvothermal reaction using a mixture of Milli-Q water (5 mL) and methanol (30 mL) as the solvent. As shown in Fig. 2a and b, quite uniform NS were grown on the skeleton of 3DGN, which connected with each other to form a free-standing network, exhibiting a highly open and porous structure. AFM data showed that the thickness of a typical NiCo-precursor NS is ~ 3.9 nm (Fig. 2c). The Raman spectrum confirmed that the 3DGN is of high quality even after coating with NiCo-precursors (Fig. S2 in ESI†). Moreover, the NS forming a thin film on 3DGN is certainly beneficial for the transportation of electrons and ions. This structure is different from those hybrid materials reported previously which showed a relatively thick film coated on 3DGN, restricting the electrochemical performance.^{20,22,26}

The NiCo_2O_4 NS/3DGN hybrid can be obtained after the calcination of NiCo-precursor/3DGN at 300 °C. The as-prepared NiCo_2O_4 NS/3DGN hybrid is quite flexible. It can be bent to $\sim 45^\circ$ and $\sim 90^\circ$, and then recovered without any damage (Fig. S3 in ESI†). As shown in Fig. 2d, the NiCo_2O_4 NS/3DGN shows a similar morphology to that of NiCo-precursor/3DGN. The high-magnification SEM image indicates that many nanopores are present in the NiCo_2O_4 NS (Fig. 2e), which are different from the NiCo-precursor. The formation of nanopores

may be ascribed to the gas release during the decomposition of the NiCo-precursor. There is no doubt that the ultra-thin NS with many nanopores may highly enlarge the surface area and facilitate the electrolyte penetration. Moreover, the formation of nanopores on NiCo_2O_4 NS also increased their roughness and curvature. The thickness of NiCo_2O_4 NS increased to ~ 6.4 nm (Fig. 2f). The Raman spectrum and XRD patterns also confirmed the formation of NiCo_2O_4 on the high-quality 3DGN (Fig. S2 and S4 in ESI†). XPS results (Fig. S5 in ESI†) further confirmed the composition of NiCo_2O_4 NS/3DGN, *i.e.* Ni^{2+} , Ni^{3+} , Co^{2+} , and Co^{3+} . The formula of the as-prepared NiCo_2O_4 NS can be generally expressed as $\text{Co}^{2+}_{1-x}\text{Co}^{3+}_x[\text{Co}^{3+}\text{Ni}^{2+}_x\text{Ni}^{3+}_{1-x}]_2\text{O}_4$ ($0 < x < 1$), where the cations in the bracket are in octahedral sites and those outside occupy the tetrahedral sites.^{46,49–52}

The morphology of NiCo_2O_4 NS/3DGN was further investigated by TEM. Compared to the NiCo-precursor NS with a relatively smooth surface (Fig. S6 in ESI†), many nanopores can be clearly seen in the NiCo_2O_4 NS (Fig. 3a), which is consistent with the observations from SEM images in Fig. 2e. High-magnification TEM and HRTEM images (Fig. 3b and 3c) revealed that the NiCo_2O_4 NS is composed of many infinitesimal interconnected nanoparticles with a diameter of 3–10 nm and numerous nanopores with a size of 2–5 nm. The different crystal orientations of nanoparticles display clear lattice fringes as marked in Fig. 3c with interplanar spacings of ~ 4.7 Å and ~ 2.45 Å, corresponding well to the distances of (111) and (311) planes of the NiCo_2O_4 phase, respectively. The polycrystalline structure of NiCo_2O_4 NS can also be indicated by the SAED pattern that can be indexed as (111), (220), (311), (400), (511) and (440) diffractions of the NiCo_2O_4 phase (inset of Fig. 3c). Moreover, the energy dispersive spectroscopy (EDS) mapping shown in Fig. 3d provides clear information about the elemental distribution, further indicating the formation of NiCo_2O_4 NS.

To investigate the electrochemical performance of NiCo_2O_4 NS/3DGN, a series of electrochemical tests were carried out. Fig. 4a depicts the CV curves of NiCo_2O_4 NS/3DGN electrodes at various scanning rates from 5 to 500 mV s^{-1} in the electrolyte of 6 M KOH in the potential window of -0.1 to 0.5 V. All the CV curves consisted of a pair of clear redox peaks related

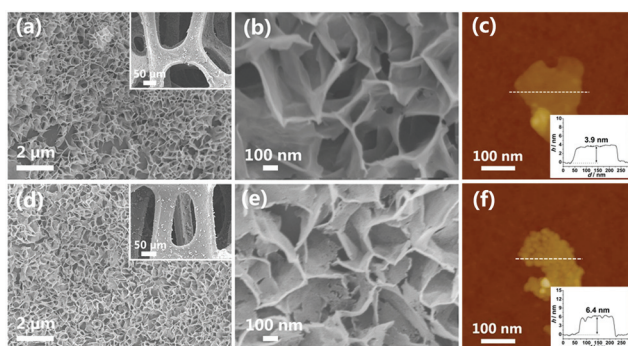


Fig. 2 SEM images of (a, b) NiCo-precursor/3DGN, and (d, e) NiCo_2O_4 NS/3DGN. Insets in (a) and (d): the corresponding low-magnification SEM images. AFM images and height profiles (inset) of (c) NiCo-precursor/3DGN and (f) NiCo_2O_4 NS/3DGN.

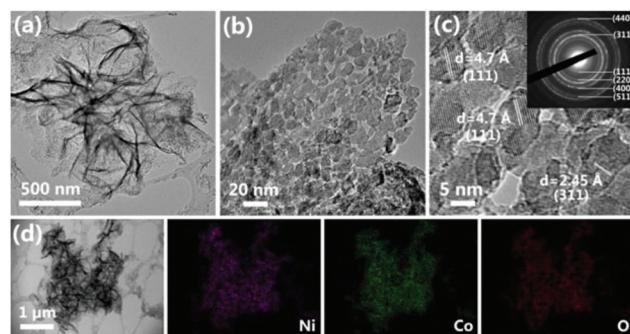


Fig. 3 (a, b) TEM and (c) HRTEM images of NiCo_2O_4 NS/3DGN. Inset: the corresponding SAED pattern in (c). (d) TEM image and the corresponding elemental mapping of NiCo_2O_4 NS/3DGN.

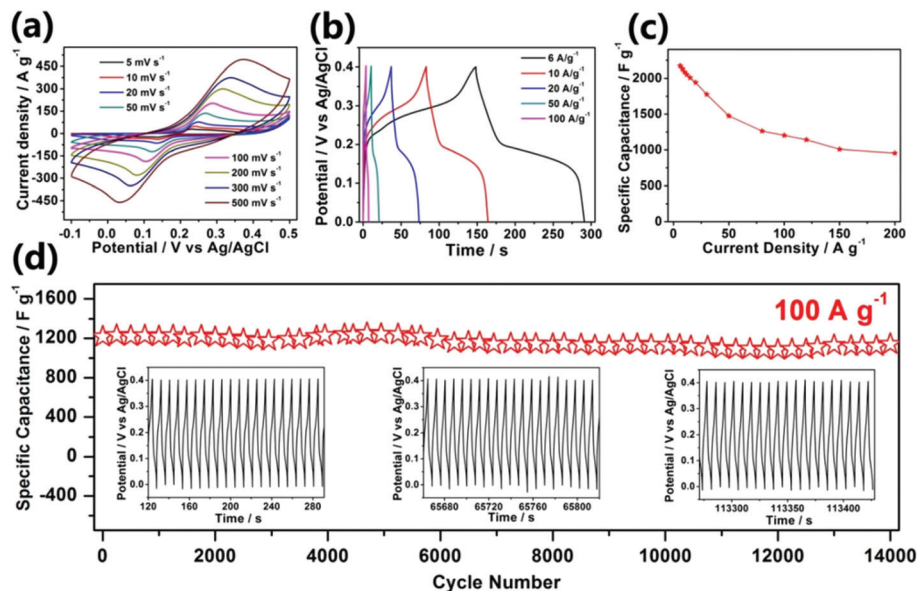


Fig. 4 (a) Cyclic voltammograms (CVs) of the NiCo₂O₄ NS/3DGN electrode at different scan rates (from 5 to 500 mV s⁻¹). The potential range of the CV test is from -0.1 to 0.5 V (vs. standard Ag/AgCl electrode). (b) The typical galvanostatic charge/discharge curves of the NiCo₂O₄ NS/3DGN electrode at various current densities. (c) The calculated specific capacitance as a function of current densities. (d) Cycling performance of the NiCo₂O₄ NS/3DGN electrode at the current density of 100 A g⁻¹. Inset: the corresponding charge/discharge curves of the initial 20 cycles (left), 8000–8020 cycles (middle) and the last 20 cycles (right). The potential range of the galvanostatic charge/discharge test is from 0 to 0.4 V (vs. the standard Ag/AgCl electrode).

to the Faradic redox reactions between M–O/M–O–OH (M represents Ni or Co) and OH anions,^{22,46,53,54} which are distinguishable from the ideal rectangular shape of electrical double-layer capacitors, indicating the pseudocapacitive characteristics. With a 100-fold increment in the sweep rate from 5 to 500 mV s⁻¹, there is no obvious distortion of the CV curve shape with only a slight shift of reduction peaks from 0.14 to 0.04 V, indicating the excellent electrochemical response of the NiCo₂O₄ NS/3DGN electrode. The peak current increasing linearly with the increment of the scan rate also suggests that the rates of electronic and ionic transportation were rapid enough with respect to the scan rates.²²

The selected galvanostatic charge/discharge curves of the NiCo₂O₄ NS/3DGN electrode (Fig. 4b) at different current densities in the potential window of 0–0.4 V exhibit the discharge voltage plateaus at around 0.2–0.1 V, which is in good agreement with the CV curves (Fig. 4a) and well consistent with previous reports.^{14,46,55} The specific capacitances of NiCo₂O₄ NS/3DGN are 2173, 2131, 2088, 2053, 2008, 1941, 1776, 1475, 1264, 1203, 1142, 1008 and 954 F g⁻¹ at current densities of 6, 8, 10, 12, 15, 20, 30, 50, 80, 100, 120, 150 and 200 A g⁻¹, respectively, indicating the excellent rate capability. Importantly, the NiCo₂O₄ NS/3DGN electrode demonstrates high areal capacitances of 1.77, 1.60, and 1.42 F cm⁻² at the current densities of 4, 12, and 24 mA cm⁻² (Fig. S7 in ESI†), respectively. Even at a high current density of 159.4 mA cm⁻², its high areal capacitance of 0.76 F cm⁻² can also be obtained. In addition, the stable specific capacitance of 1943 F g⁻¹ can be retained for the NiCo₂O₄ NS/3DGN electrode after 2800 cycles

at 20 A g⁻¹ with capacitance retention of almost 100% (Fig. S8 in ESI†). Specifically, the charge/discharge curves of NiCo₂O₄ NS/3DGN remain undistorted after 2800 cycles (Fig. S6 in ESI†), suggesting the excellent reversibility of NiCo₂O₄ NS/3DGN. In addition, the capacitance of the pure 3DGN electrode was negligible to the NiCo₂O₄NS/3DGN electrode since the reversible capacitance is only about 75 F g⁻¹ at 2 A g⁻¹ (Fig. S9 in ESI†), which can be further confirmed by the CV result (Fig. S10 in ESI†). The long-term cycling performance at high current density is another critical requirement for supercapacitors to meet the demands of practical applications. As displayed in Fig. 4d, the NiCo₂O₄ NS/3DGN electrode exhibited a high initial specific capacitance of 1216 F g⁻¹, and 1141 F g⁻¹ can be retained after 14 000 cycles at an ultra-high current density of 100 A g⁻¹, corresponding to the capacitance retention of 94%. Importantly, the charge/discharge curves remain almost the same, with an IR drop of only 0.07 V after 14 000 cycles (inset of Fig. 4d and Fig. S11 in ESI†), further demonstrating the super stable electrochemical activity of NiCo₂O₄ NS/3DGN. Moreover, the morphology of the NiCo₂O₄ NS/3DGN electrode after 14 000 cycles was characterized. Although some NiCo₂O₄ NSs agglomerated, they were still coated on 3DGN after long-term charge/discharge processes (Fig. S12 in ESI†), suggesting good stability of the electrode.

Table S1† compares the electrochemical properties of NiCo₂O₄-based materials, metal oxides, metal hydroxides and their hybrid composites. Although ultrahigh specific capacitances have been reported for NiCo₂O₄-based materials, the cyclic stability or rate capability should be further

improved.^{45,46,56} In addition, although good cycling performance has been achieved for NiCo₂O₄, it suffers from low capacitance, especially the high-rate capacitance.^{14,54,57} In this work, the supercapacitor performances of NiCo₂O₄ NS/3DGN, especially the rate capability and long-term cycling stability, are much better than those of many other pseudocapacitor electrode materials (Table S1 in ESI†). The excellent electrochemical performances of NiCo₂O₄ NS/3DGN could be ascribed to the following factors. First, the CVD-grown 3DGN on Ni foam with outstanding electrical conductivity benefits the electron transportation and electrolyte ion diffusion.^{24,37} Second, the thin 2D NiCo₂O₄ NS with numerous nanopores not only enlarges the interface surface area and increases the material utilization, but also accommodates its volume change and allows effective strain relaxation upon cycling.^{13,39} Third, the thin NiCo₂O₄ NS connected with each other to form a nanosheet network with highly open space can serve as an “ion-buffering reservoir” for OH⁻ ions, ensuring a sufficient Faradaic reaction occurring even at very high current density.⁴⁶ Lastly, the strong coupling between NiCo₂O₄ NS and 3DGN renders good mechanical adhesion and electrical connection, avoiding the use of polymer binders and conductive additives and leading to enhanced electrochemical kinetics, which is good for high-rate capability and long-term cycling performance of supercapacitors.^{12,22,27}

In summary, we have successfully fabricated high-capacitance, high-rate, and long-cycle-life supercapacitors by synthesis of thin 2D NiCo₂O₄ NS with a thickness of ~6.4 nm on 3DGN. The novel NiCo₂O₄ NS/3DGN hybrid demonstrates excellent electrochemical performances including ultrahigh specific capacitances as well as excellent rate capability of 2173 and 954 F g⁻¹ at high current densities of 6 and 200 A g⁻¹, respectively, and superior long-term cycling stability with only 6% capacitance loss after 14 000 cycles at 100 A g⁻¹, which is obviously superior to most of the previously reported pseudocapacitor electrodes (Table S1 in ESI†). Our work not only opens up the possibility of constructing the binder- and additive-free pseudocapacitive materials with excellent rate capability and long-cycle-life, but also presents a novel and effective way to design three-dimensional graphene based materials for energy storage devices with excellent performance.

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