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# Synthesis of Three-dimensional Self-standing Graphene/Ni(OH)<sub>2</sub> Composites for high-performance supercapacitors

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# Abstract

With the existence of surface-active agents, three-dimensional (3D) self-standing graphene/Ni(OH)<sub>2</sub> composites with different morphologies, such as nanoflower, nanoslice and nanoparticle, are directly synthesized by a facile in-situ electrodeposition. SEM, Raman spectroscopy are used to investigate the morphology and structure. Detailed electrochemical characterizations reveal that 3D graphene/Ni(OH)<sub>2</sub> nanoflower exhibits high specific capacitance (718.2 F/g at 6.7A/g in 6.0 M KOH aqueous solution) and good cycling performance (84.2% capacitance retention after 500 cycles) compared to other Ni(OH)<sub>2</sub> morphologies. Nyquist plots investigation shows that 3D graphene/Ni(OH)<sub>2</sub> nanoflowers present a low equivalent series resistance. These researches indicate that the composite maybe a promising candidate for high-performance supercapacitors.

Key words: Three-dimensional graphene, Ni(OH)<sub>2</sub>, Supercapacitor

# Introduction

To date, a great deal of materials, including carbon-based materials, metal oxides/hydroxides, metal sulfide and conductive polymers, have been reported to fabricate supercapacitor electrodes.<sup>1-5</sup> The carbonaceous materials are normally utilized for electrochemical double layer capacitors (EDLC), which has capacitive performances inferior to pseudocapacitors. The pseudocapacitors can supply high current densities during charge/discharge processes by oxidation-reduction reactions of active materials.<sup>6</sup> However, certain electric insulativity of pseudo-active materials can hardly support fast electron transport at high rates. In response, many research groups adhere pseudo-active materials to conductive substrates with polyvinylidene fluoride (PVDF) as binder.<sup>7-8</sup> But this method not only drops the conductivity but also decreases the overall gravimetric specific capacitance of composite electrodes. It indicated that in-situ growth of active materials on conductive substrate is a expedient strategy to prepare supercapacitor electrodes. The synergistic effects between the substrate and active materials can largely promote its electrochemical performances.<sup>9-11</sup>

Graphene, an atomic-scale honeycomb crystal lattice, consists of single-layer sp<sup>2</sup>-hybridized carbon atoms. It possesses unusual mechanical strength, excellent transmittance, superb thermal conductivity, high electrical conductivity and huge specific surface area.<sup>12-13</sup> These properties make graphene have a lot of applications in many fields, for instance, field-effect transistors,<sup>14</sup> transparent conductors,<sup>15</sup> energy storage storages<sup>16-19</sup> and biosensors.<sup>20-21</sup> Graphene-based supercapacitors, a novel green energy storage device, have presented outstanding performance with high energy density and ultra long cycling life.<sup>22-25</sup> However, the practical applications are seriously restricted by the inclination of agglomeration between graphene sheets because of the

strong  $\pi$ - $\pi$  interaction. Recently, a novel 3D graphene foam was synthesized by chemical vapor deposition, which can overcome the  $\pi$ - $\pi$  interaction between graphene sheets and possess large specific area and high electrical conductivity.<sup>34</sup> It is an ideal material for the preparation of electrochemical electrodes for high performance supercapacitors.

Nickel hydroxide (Ni(OH)<sub>2</sub>), a material with low-cost and various morphologies, has been seemed as a promising candidate for high performance supercapacitors. In order to improve the electrochemical properties of Ni(OH)<sub>2</sub>, nickel foam, carbon paper, carbon nanotube, reduced graphene oxide and graphene are used to composite with it, respectively.<sup>26-31</sup> The results demonstrated that these conductive materials can greatly reduce the resistivity of the composites and the pathways of the electron and ion diffusion, which supply efficient charge exchange and mass transfer.

To meet the demand for energy and environment protection, we demonstrate a facial method to prepare 3D graphene/Ni(OH)<sub>2</sub> composites for high performance supercapacitors. Herein, 3D self-standing graphene foam is used as the conductive matrix for in-situ electrodeposited of Ni(OH)<sub>2</sub> nanoparticles. To overcome the difficulty that metal materials can hardly combine with the hydrophobic graphene, the sodium dodecyl benzene sulfonate (SDBS) and ethanol are used as surface active agent and the morphology of the 3D graphene/Ni(OH)<sub>2</sub> can be controlled by the surface active agent, respectively. Electrochemical measurements reveal that 3DG/Ni(OH)<sub>2</sub> exhibits a high capacitance performance and excellent cycling stability.

## **Experimental section**

#### Materials

NiSO<sub>4</sub>·6H<sub>2</sub>O, NaOH, KOH, hydrochloric acid, Na<sub>2</sub>SO<sub>4</sub> and ethanol were analytical reagents

purchased from Sinopharm Chemical Reagent Co. Ltd. The SDBS was chemically pure and purchased from Shanghai LingFeng Chemical Reagent Co. Ltd. Nickel foam was supplied by Alantum Advanced Technology Materials Co. Ltd. All materials were used without any further purification.

#### Synthesis of 3D graphene foam

Three-dimensional self-standing graphene foam was synthesized by chemical vapor deposition (CVD) method with nickel foam as substrate and ethanol as carbon source under atmospheric pressure.<sup>32</sup> In a typical experiment, the nickel foam was placed into a quartz tube and heated to 900 C at a heating rate of 20 °C/min. After annealing for 10 min to clean the nickel surface under hydrogen atmosphere, ethanol vapour was introduced into the quartz tube by bubbling hydrogen through an ethanol liquid. After 20 min of growth, the substrate was rapidly cooled down to ambient temperature. After the growth process, the nickel substrates were etched by HCl solution (10%) at 80 C overnight to get three dimensional self-standing graphene foams.

#### Preparation of 3D graphene/Ni(OH)<sub>2</sub> composites

In this work, 5.0 mM Ni<sub>2</sub>SO<sub>4</sub> dissolved in DI water or ethanol aqueous solution (30%) was used as electrolyte and Ni(OH)<sub>2</sub> precursors. The pH value of the electrolyte was regulated between 7.00 and 8.00 with NaOH solution (0.1 M). Prior to electrodeposition, 3D graphene was immersed into SDBS solution (1mg/ml) overnight to active the graphene surface. All the electrodeposition were executed in three-electrode system at room temperature. The saturated calomel electrode (SCE) and Pt foil electrode were used as the reference electrode and counter electrode, respectively. Ni(OH)<sub>2</sub> were electrodeposited for 300s on 3D graphene at a potential of -1.0 V. After electrodeposition, the composites were cleaned with DI water and dried in air at 50 °C.

#### Characterization

The structure of 3D graphene and graphene/Ni(OH)<sub>2</sub> composite were characterized by JY HR800 micro-Raman spectroscopy (laser wavelength 514 nm). The morphology and related EDS elemental mapping images were observed by field-emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan). Thermogravimetric analyses (TGA) were operated on Shimadzu DTG-60H thermogravimetric analyzer with a heating rate of 5 °C/min under air atmosphere.

#### **Electrochemical tests**

Electrochemical properties were performed using a conventional three-electrode cell (CHI 660E, Chenhua, China) in 6.0 M KOH aqueous solution at ambient temperature. The free-standing 3D graphene/Ni(OH)<sub>2</sub> composites with a mass of 1 mg acted as the work electrode, while a platinum foil and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. Electrochemical impedance spectroscopy (EIS) tests were conducted in the frequency range from 10 kHz to 1 Hz at an open-circuit potential as well as an ac perturbation of 5.0 mV.

#### **Results and discussion**

Fig. 1a shows the low-magnification SEM image of self-standing 3D graphene foam. It can be seen that the 3D graphene foam exhibits a macroporous structure with smooth and thin graphene skeleton. The pore diameter is about 100-200  $\mu$ m and the specific surface area of 3D graphene is nearly 670 m<sup>2</sup>/g.<sup>33</sup> The inset image presents a seamlessly continuous skeleton with micrometer scale smooth topographic domains, assuming the identical surface topology as nickel substrate coming from conformal CVD growth. The Raman spectra of 3D graphene and 3D graphene/Ni(OH)<sub>2</sub> composite is demonstrated in Fig. 1b. As shown, the Raman spectrum of 3D

graphene presents two obvious characteristic vibration bands at 1583 cm<sup>-1</sup> and 2717 cm<sup>-1</sup>,

corresponding to the G and 2D band of graphene, respectively. The Raman spectrum demonstrated that the 3D graphene foam consists of few layers without any defects, which ensured high electrical and mechanical performances.<sup>34</sup> Besides the characteristic peaks of graphene at 1583 and 2723 cm<sup>-1</sup>, the as prepared 3D graphene/Ni(OH)<sub>2</sub> composites also present two peaks emerged at around 514.2 cm<sup>-1</sup> (longitudinal optical, LO) and 983.5 cm<sup>-1</sup> (phonon modes, 2LO), indicating Ni(OH)<sub>2</sub> has been deposited on the surface of 3D graphene foam successfully.<sup>31,35-36</sup>

Fig. 2 shows the SEM images of 3D graphene/Ni(OH)<sub>2</sub> composites synthesized in different processes. It can be found that the resulting Ni(OH)<sub>2</sub> nanostructures have different morphology (nanoflower, nanoslice, and nanoparticle) merely by changing the surfactant. This phenomenon maybe come from the fact that the hydrophobicity of graphene surface was overwhelmingly decreased and the resulting Ni(OH)<sub>2</sub> particles could grow uniformly on the surface of graphene.<sup>37</sup> When the sodium dodecyl benzene sulfonate (SDBS) was used to reduce the water repellency of 3D graphene, the Ni(OH)<sub>2</sub> presents uniformly nanoflowers morphology and form highly ordered film attached on the graphene surface (Fig. 1a, b). The diameter of the nanoflowers is about 500-600 nm, as shown in the inset image of Fig. 2b. It can be concluded that the SDBS content can be controlled at certain concentration, in which circumstance Ni(OH)<sub>2</sub> formed flower shaped layer nanostructure in a self-assembly way.<sup>38</sup> On the contrary, the resulting Ni(OH)<sub>2</sub> synthesized in ethanol solution (30%) solution presents uniform nanoslices morphology owing to ethanol eliminate the hydrophobicity of graphene surface<sup>39</sup>, as shown in Fig. 2c, d. The inset of Fig. 1d shows that the length and thickness of Ni(OH)<sub>2</sub> nanoslices are about 300 nm and  $\sim$ 50 nm, respectively. In the case of without any pretreatment and the electrolyte was also applied in the

absence of any additives, the resulting Ni(OH)<sub>2</sub> film attached onto the surface loosely and is easy to fall off, as shown in Fig. 2d. The magnification image of Fig. 2f demonstrates that Ni(OH)<sub>2</sub> particles have an inhomogeneous distribution, indicating the hydrophobicity of graphene seriously prevents the crystal growth on the surface of graphene. The SEM images indicate that the surface-active agents and solution have a very important effect on the morphology and the size of Ni(OH)<sub>2</sub> nanoparticles in the 3D graphene/Ni(OH)<sub>2</sub> composites.

During the electrodeposition process, the Ni(OH)<sub>2</sub> crystals developed onto the surface of 3D graphene foam and formed different morphologies under the effect of surfactants. The structure and morphology of the 3D graphene/Ni(OH)<sub>2</sub> nanoflower composite were also observed by EDS mapping measurement (Fig. 3). The elemental mapping images further unravel the uniform distribution of oxygen and nickel throughout the 3D graphene framework, which further demonstrates Ni(OH)<sub>2</sub> nanoparticles distributed homogeneously on the surface of 3D graphene foam. The EDS spectrum was provided in Fig. 3e, which indicated the content of carbon, oxygen, nickel is approximately 18.33wt%, 27.04wt%, 54.63wt%, respectively. In the spectrum, sulfur comes from the nickel sulfate.

In order to investigate the accurate content of  $Ni(OH)_2$  in the 3DG/NF composite, thermogravimetric analyses (TGA) were carried out under air atmosphere. As shown in Fig. 4, the figure reveals that the 3D graphene still remains 8.0% of mass after TGA test, which is caused by the residual carbon.<sup>44</sup> The TGA curve of 3DG/NF at 800 °C means NiO and 3D graphene. However, the thermogravimetric analyses indicates that the content of Ni(OH)<sub>2</sub> is about 64.8 % in the 3DG/NF composites.

The electrochemical performances of 3D graphene/Ni(OH)<sub>2</sub> composites synthesized under

different conditions were characterized by electrochemical working station, as shown in Fig. 5. In Fig. 5a, the cyclic voltammetry (CV) curves were conducted at a scanning rate of 50 mv/s. It is obvious to find that all the composites present a pair of typical oxidation and reduction peaks

caused by reversible electrochemical reaction as follow: Ni(OH)  $_2 + OH^- \longleftrightarrow$  NiOOH  $+ H_2O + e^-$ .<sup>40</sup>

From the CV curves, it can be seen that the 3D graphene/Ni(OH)<sub>2</sub> nanoflowers (3DG/NF) exhibits the most strongest redox peaks current. In addition, the difference between the oxidation potential and the reduction potential is also larger than 3D graphene/Ni(OH)<sub>2</sub> nanoslices (3DG/NS), 3D graphene/Ni(OH)<sub>2</sub> nanoparticles (3DG/NP) and 3D graphene (3DG). Evidently, the area surrounded by the CV curve of 3DG/NF is dramatically larger than those of other composites indicating a large specific capacitance associated with the Ni(OH)<sub>2</sub> nanoflowers. In Fig. 5b, The galvanostatic discharge test further illustrated that 3DG/NF have an optimal gravimetric capacitance of 718.2 F/g at the current density of 6.7 Ag<sup>-1</sup>, which is critically bigger than 3DG/NS (446.7 F/g), 3DG/NP (177.2 F/g), and 3DG (17.4 F/g). Here, the specific capacitance is calculated by the following equation:  $C = I \times \Delta t / (m \times \Delta V)$ . Where, C (F/g) is the specific capacitance of the electrode, I (A) is the discharge current,  $\Delta t$  (s) is the discharge time, m (g) refers to the mass of the active materials and  $\Delta V$  (V) is the potential window for the cycling test. This phenomenon maybe come from the fact that the Ni(OH)<sub>2</sub> nanoflowers possessed higher specific surface area than others.<sup>41</sup>

The Nyquist plots in Fig. 6 show the electrochemical impedance spectroscopy of 3DG, 3DG/NF, 3DG/NS and 3DG/NP electrodes, respectively. The plots indicate that the 3DG/Ni(OH)<sub>2</sub> composites exhibit a lower equivalent series resistance (ESR) than that of 3DG, which may greatly

enhance the supercapacitor performance of the composites electrodes. In the high frequency range, the axis intercept of four electrodes indicates that the 3DG/Ni(OH)<sub>2</sub> composites possess the same internal resistances and the internal resistances of composites are lower than that of 3DG. The smallest semicircle diameter of 3DG/NF, related to the interfacial charge-transfer impendence (Rct), indicates that 3DG/NF possesses the lowest interfacial charge-transfer resistance. Moreover, the 3DG/NF exhibits a more vertical line, suggesting the Warburg resistance is not a determining factor and this kind of electrode can store charge more efficiently. All of these comparisons made us believe that the 3DG/NF composite is the best candidate for the supercapacitor electrode.

Fig. 7a shows the cyclic voltammetry (CV) curves of 3DG/NF electrode at varied scan rates with potential range from 0 to 0.5 V. Two strong oxidation and reduction peaks coming from the redox reaction between Ni(OH)<sub>2</sub> and NiOOH can be seen clearly. With the increase of scanning rate, the peak current increases greatly. At the same time, the oxidation peaks drifted more positive while the reduction peaks drifted more negative. This phenomenon comes from the fact that external active sites only can support redox reactions completely during high scanning rates, which makes the internal diffusion resistance increase within the pseudoactive materials.<sup>32,33</sup> The Galvanostatic charge-discharge curves of the 3DG/NF electrode at different discharge current densities was shown in Fig. 7b. According to the equation C=I× $\Delta t/(m×\Delta V)$ , the specific capacitance of the 3DG/NF electrode is calculated about 718.2, 380.5, 327.2, 314.0 and 300.0 F/g at current densities of 6.7, 10.0, 13.3, 16.7 and 20.0 A/g, respectively. The result indicates fast and efficient electrolyte ions diffusion to the active sites surface and outstanding electron transfer within the 3D graphene framework. From Fig. 7c, it can be seen that the specific capacitance drop vast between the current density of 6.7 and 20.0 A/g, which maybe because there is not enough time for active

materials to response absolutely at high current densities. The cycling stability of the 3DG/NF electrode was tested with 500 cycles of charge and discharge at a current density of 10.0 A/g, as shown in Fig. 7d. As shown in the inset image, the charge-discharge curves display typical pseudocapacitance character and excellent symmetry after a long time charge and discharge. More important, the specific capacitance decreased from 380.5F/g to 320.4F/g after 500 cycles, still remaining 84.2%. It can be concluded that the 3DG/NF electrode possesses excellent rate stability even charge and discharge under high current densities, which makes it promising for the development of high-performance supercapacitors.

Compared with some similar reports in Table 1, the as-prepared 3DG/NF exhibits excellent specific capacitance even at high current density and wide potential window, which is most probably due to the nanoflower structure of Ni(OH)<sub>2</sub> particles and high electrical conductivity of 3D graphene. <sup>26-29,36,42-43</sup> It means the application of SDBS used as the surfactant can not only control the Ni(OH)<sub>2</sub> structure but also the electrochemical performance.

#### Conclusion

In summary, self-standing 3DG/Ni(OH)<sub>2</sub> composites with different Ni(OH)<sub>2</sub> morphologies (nanoflower, nanoslice and nanoparticle) were synthesized using a facile in-situ electrodeposition method with the existence of surface-active agents. The electrochemical measurements indicated that the 3DG/NF electrode exhibits better supercapacitor performance than that of 3DG/NS and 3DG/NP composites. The specific capacitance of 3DG/NF can reach to 718.2 F/g at 6.7 A/g, which is more outstanding than that of 3DG/NS (446.7 F/g) and 3DG/NP (177.2 F/g). The Nyquist plots further indicate the more efficient electrolyte ion diffusion of 3DG/NF. In addition, the 3DG/NF electrode presents excellent cycling stability after 500 cycles. The self-standing 3D

graphene/Ni(OH)<sub>2</sub> composite can supply novel possibilities for energy storage devices as well as various other applications.

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**Fig. 1** (a) SEM images of 3D graphene foam, the inset is the enlarged view of 3D graphene surface. (b) Raman spectra of 3D graphene and 3D graphene/Ni(OH)<sub>2</sub> composite.



Fig. 2 SEM images of 3D graphene/Ni(OH)<sub>2</sub> composites synthesized with different structures. (a, b) 3D graphene/Ni(OH)<sub>2</sub> nanoflowers. Inset shows an magnified image. (c, d) 3D graphene/Ni(OH)<sub>2</sub> nanoslices. Inset is the enlarged view. (e, f) 3D graphene/Ni(OH)<sub>2</sub> nanoparticles.



**Fig. 3** SEM images of (a) as-prepared 3D graphene/Ni(OH)<sub>2</sub> nanoflowers and the related EDS elemental mapping images of (b) carbon, (c) oxygen, and (d) nickel. (e) EDS spectra of 3DG/NF.



Fig. 4 TGA curves of 3D graphene and 3DG/NF.



Fig. 5 (a) CV curves of 3DG/Ni(OH)<sub>2</sub> synthesized in different conditions at a scan rate of 50 mV/s.
(b) Discharge curves of 3D graphene/Ni(OH)<sub>2</sub> composites and 3DG electrodes surveyed at a current density of 6.7 Ag<sup>-1</sup>.



Fig. 6 Nyquist plots of 3DG/NF and 3DG/NS, 3DG/NP and 3DG.



**Fig. 7** Electrochemical measurements of the 3DG/NF electrode in 6.0 M KOH aqueous solution. (a) CV curves at different scan rates. (b) Galvanostatic discharge curves at different current densities. (c) Effects of current density on its specific capacitance. (d) The cycling performance of 3DG/NF at a current density of 10.0 A/g. The inset shows the charge-discharge curves of 3DG/NF electrode at 10 A/g.

found in the references.							
Electrode	Technique	Specific	Capacitance	potential	cell	electrolyte	Ref.
		capacitance	retention	window	type		
Ni(OH) <sub>2</sub> /	Electrodeposit	3152 F/g (4	52 % (4 A/g, 300	-0.05-0.45	2 ED	KOH (3%)	26
nickel foam	ion	A/g)	cycles)	V	3 ED		
$\alpha$ -Ni(OH) <sub>2</sub> /r	Chemical	521 F/g	87.9 % (50mv/s,	0.0-0.45V	3 ED	KOH (6M)	27
GO	precipitation	(50mV/s)	1000 cycles )				
Ni(OH) <sub>2</sub> /carb	Conformal	1416	66 % (20 A/g,	0.0-0.40V	3 ED	KOH (1M)	28
on fiber	coating	F/g(1A/g)	10000 cycles)				
Ni(OH) <sub>2</sub> /	Hydrothermal	166 F/g	65 % (10A/g,	0.0-0.50V	3 ED	KOH (6M)	29
graphene		(0.5A/g)	1000 cycles)				
Ni <sub>3</sub> S <sub>2</sub> @Ni(O	Hydrothermal	1037.5 F/g	99.1% (5.1A/g,	-0.15-0.55 V	3 ED	KOH (3M)	36
H) <sub>2</sub> /graphene		(5.1A/g)	2000 cycles)				
β-Ni(OH) <sub>2</sub>	Chemical	398 F/g	Unknown	0.0-0.50V	3 ED	KOH (2M)	42
	precipitation	(5mV/s)					
	Electrodeposit ion	745 F/g (1.4 A/g)	115%	0.0-0.50V	3 ED	KOH (3M)	43
N1O/graphen			(80mV/s,2000				
e			cycles )				
Our 3DG/NF	Electrodeposit	718.2 F/g (6.7A/g)	84.2%				
			(10A/g,500	0.0-0.50V	3 ED	KOH (6M)	Ours
			cycles)				
GO Ni(OH) <sub>2</sub> /carb on fiber Ni(OH) <sub>2</sub> / graphene Ni <sub>3</sub> S <sub>2</sub> @Ni(O H) <sub>2</sub> /graphene β-Ni(OH) <sub>2</sub> NiO/graphen e Our 3DG/NF	precipitation Conformal coating Hydrothermal Chemical precipitation Electrodeposit ion	(50mV/s) 1416 F/g(1A/g) 166 F/g (0.5A/g) 1037.5 F/g (5.1A/g) 398 F/g (5mV/s) 745 F/g (1.4 A/g) 718.2 F/g (6.7A/g)	1000 cycles ) 66 % (20 A/g, 10000 cycles) 65 % (10A/g, 1000 cycles) 99.1% (5.1A/g, 2000 cycles) Unknown 115% (80mV/s,2000 cycles ) 84.2% (10A/g,500 cycles)	0.0-0.45V 0.0-0.45V 0.0-0.50V -0.15-0.55 V 0.0-0.50V 0.0-0.50V 0.0-0.50V	3 ED 3 ED 3 ED 3 ED 3 ED 3 ED 3 ED	KOH (6M) KOH (1M) KOH (6M) KOH (3M) KOH (3M)	27 28 29 36 42 43 Ours

 Table 1
 Electrochemical performance comparison of similar electrodes. Complete data can be found in the references