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Synchronous exfoliation and assembly of graphene on 3D Ni(OH)₂ for supercapacitors[†]

Liguo Ma,^a Maojun Zheng,*^{ab} Shaohua Liu,*^c Qiang Li,^a Yuxiu You,^a Faze Wang,^a Li Ma^d and Wenzhong Shen^a

Nowadays, new approaches to fabricate high-performance electrode materials are of vital importance in the renewable energy field. Here, we present a facile synthesis procedure of 3D Ni(OH)₂/graphene hybrids for supercapacitors via synchronous electrochemical-assisted exfoliation and assembly of graphene on 3D Ni(OH)₂ networks. With the assistance of an electric field, the electrochemically exfoliated high-quality graphene can be readily, uniformly assembled on the surfaces of 3D Ni(OH)₂. When serving as electrode materials for supercapacitors, the resulting 3D Ni(OH)₂/graphene composites exhibited excellent specific capacitance (263 mF cm⁻² at 2 mA cm⁻²), remarkable rate capability and super-long cycle life (retention of 94.1% even after 10 000 continuous charge-discharge cycles), which may be attributed to their highly porous, stable 3D architecture as well as uniform, firm anchoring of ultrathin graphene on their surfaces. Therefore, our approach provides a facile strategy for the largescale synthesis of high-quality graphene based composites towards various applications.

Supercapacitors with high capacitance and long lifespan have attracted considerable interest as energy-storage devices in recent years. At present, two kinds of supercapacitors have been developed based on the charge storage mechanism: electric double-layer capacitors and pseudocapacitors. By comparison, pseudocapacitors governed by Faradaic reactions at the electrode materials, such as RuO₂,¹ MnO₂,² NiO,³ Co₃O₄,⁴ and CuO,⁵ have higher theoretical capacitance. Despite that, those electrode materials usually suffer from poor stability, low conductivity

and large volume change during charge/discharge processes.⁶ Among the various redox-active materials, $Ni(OH)_2$ is an attractive candidate for high-performance supercapacitors because of its low-cost, various morphologies, high theoretical capacitance, ready availability and good stability in alkaline electrolytes.⁷ In attempts to further improve the electrochemical performance of Ni(OH)2-based electrodes, Ni(OH)2/carbon composites involving high surface-area conductive materials (carbon nanotubes,⁸ activated carbon⁹ and graphene¹⁰) have been explored. However, the fabrication of Ni(OH)2/carbon electrodes usually needs multi-step procedures. Taking Ni(OH)2/graphene as an example, graphene needs to be firstly prepared by Hummer's method or modified Hummer's method, and subsequently grows on Ni(OH)2 surfaces by hydrothermal treatment.¹¹ Obviously, such fabrication processes are complicated and costly for supercapacitor applications. Recently, high-quality graphene can be produced by a simple,

fast and green electrochemical exfoliation method. Müllen et al.12 manufactured high-quality few-layer graphene through anodic exfoliation. Yan et al.13 used a Na2SO4-containing electrolyte and other metal sulfate salts to exfoliate graphite and further fabricate Fe₂O₃-, Co₃O₄- and V₂O₅-graphene hybrids. Ji *et al.*¹⁴ produced NiO quantum dots/graphene flakes for supercapacitor applications by a green, one-step alternating voltage method. Nevertheless, one-step fabrication of Ni(OH)2/graphene hybrid materials by synchronous electrochemical-assisted exfoliation and assembly for supercapacitor electrodes still remains unrealized so far.

Here, for the first time, we demonstrate a facile approach for the preparation of Ni(OH)₂/graphene composites via in situ assembly of exfoliated graphene on 3D Ni(OH)₂ surfaces. As illustrated in Fig. 1, ultrathin high-quality graphene was obtained by the solution-based electrochemical exfoliation with a two-electrode system, using graphite flakes, Ni foam and a mixed solution containing $NH_3 \cdot H_2O$ and $(NH_4)_2SO_4$ (Fig. 1a) as the anode, cathode and electrolyte, respectively. When a direct current voltage of 8 V was applied to a two-electrode setup, vigorous bubbles were produced at electrodes, anodic graphite began to dissociate to form graphene sheets, suspended in the

^a Key Laboratory of Artificial Structure and Quantum Control, Ministry of Education, Department of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai, 200240, P. R. China. E-mail: mjzheng@sjtu.edu.cn; Fax: +86-021-54741040

^b Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing, 210093, P. R. China

^c Center for Advancing Electronics Dresden (cfaed) & Department of Chemistry and Food Chemistry, Dresden, 01062, Germany. E-mail: shaohua.liu@tu-dresden.de

^d School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai, 200240, P. R. China

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Fig. 1 Schematic illustration of one-step fabrication of $Ni(OH)_2$ /graphene composites. (a) Setup of the electrochemical exfoliation of graphite (G). (b) The electrochemical exfoliation process of the graphite electrode and synchronous assembly of graphene on 3D $Ni(OH)_2$.

electrolyte (Fig. 1b). Meanwhile, the cathodic Ni foam firstly transformed into $Ni(OH)_2$ through $NH_3 \cdot H_2O$ treatment following reactions (1) and (2):

$$Ni + 6NH_3 + 2H_2O \rightarrow [Ni(NH_3)_6]^{2+} + 2OH^- + H_2\uparrow$$
 (1)

$$Ni^{2+} + 2OH^{-} \rightarrow Ni(OH)_{2}$$
⁽²⁾

The morphology and structure of the exfoliated graphene sheets were investigated by SEM, TEM and Raman spectroscopy shown in Fig. S1–S3 (ESI[†]), which clearly demonstrate the formation of high-quality few-layer graphene.¹² Further, graphene obtained by electrochemical-assisted exfoliation would spontaneously absorb and assemble on the cathodic 3D Ni(OH)₂ due to electrostatic interaction. Despite high quality, the resulting graphene derived from electrochemical-assisted exfoliation still possesses a few negative charges around its edges,¹² which would prompt their assembly on the Ni(OH)₂ surfaces with the assistance of an electric field. Notably, the Ni foam is not only the nickel source for the growth of Ni(OH)₂ thin layers, but also a skeleton to support the active materials of Ni(OH)₂/graphene composites, which affords a good electrical contact and strong mechanical adherence to their interfaces.¹⁵

The structure of the Ni(OH)₂/graphene composites was further characterized by Raman spectroscopy (Fig. 2a). The Raman spectrum of the Ni(OH)₂/graphene composites presents three obvious characteristic vibration bands at 1350 cm⁻¹, 1583 cm⁻¹ and 2700 cm⁻¹ corresponding to the D, G and 2D band of graphene, respectively. In addition, the Ni(OH)₂/graphene composites also present four peaks from Ni(OH)₂, at around 315 and 450 cm⁻¹ (longitudinal optical, A_{1g}(T) and E_g(T)), 983.5 cm⁻¹ (phonon mode, E_g(R)) and 3580 cm⁻¹ (internal hydroxyl symmetric stretching mode, A_{1g}(I)).¹⁶

X-ray photoelectron spectroscopy (XPS) was used to estimate various chemical states of bonded elements. Typical spectra of the as-prepared 3D Ni(OH)₂/graphene samples are presented in Fig. 2b–d. A single peak at around 840.8 eV presents the Ni LMM Auger spectrum.¹⁷ The Ni 2p XPS spectrum shows two major peaks centered at around 874.9 eV and 857.3 eV, corresponding to Ni $2p_{1/2}$ and Ni $2p_{3/2}$, respectively. The characteristic of the Ni(OH)₂ phase with a spin-energy separation of 17.6 eV coincides with a previous report.¹⁸ Moreover, a strong peak of the



Fig. 2 (a) Raman pattern (excitation laser wavelength: 532 nm) and (b-d) XPS spectra of the Ni(OH)₂/graphene samples.

O 1s spectrum at 532.3 eV is also associated with hydroxide groups (OH^{-}) , suggestive of the presence of Ni $(OH)_2$.¹⁸ Additionally, the XPS spectrum of C 1s shows three signals of C–C (284.6 eV), C–O (286.7 eV) and O–C=O (288.6 eV), which are possibly from the covalent oxygen groups on graphene (Fig. 2d).

The morphologies of the Ni(OH)₂/graphene composites were investigated by scanning electron microscopy (SEM). Fig. 3a and b show representative SEM images of Ni(OH)₂/graphene, revealing a highly porous architecture, which is composed of nanoflakes with a thickness of 20–30 nm. No collapse of the Ni foam struts or obstruction of the pores is observed, indicating the strong mechanical strength of the Ni(OH)₂/graphene and the uniform dispersion of the Ni(OH)₂ nanosheets. Furthermore, the elemental mappings of C, O and Ni were investigated from a small region on the foam (Fig. 3c–f), indicating a continuous, uniform distribution of Ni(OH)₂ and graphene on the 3D Ni



Fig. 3 Morphology and composition of the $Ni(OH)_2$ /graphene composites. (a and b) SEM images of the $Ni(OH)_2$ /graphene composite materials; (c) SEM image and the corresponding EDS elemental mapping images of (d) carbon, (e) oxygen, and (f) nickel.

foam surfaces. The corresponding EDS mapping also revealed that the C element content of the Ni(OH)₂/graphene composites is about 8% (atomic ratio, Table S1 in the ESI†), whereas there was no C element in the pristine Ni(OH)₂ without graphene on their surfaces (Fig. S4, ESI†). Fig. S5 (ESI†) shows that the sheet morphology of graphene and Ni(OH)₂ (black arrow markings), and a corresponding selected-area electron-diffraction pattern only indicate the typical sixfold symmetry expected for graphene. This result indicates an amorphous morphology of Ni(OH)₂. In addition, except for the peaks associated with the Ni foam substrate, no peaks are present in the X-ray diffraction pattern of Ni(OH)₂/graphene in Fig. S6 (ESI†), which further confirms the amorphous nature of the sample.

Further, we evaluated the electrochemical performance of the as-prepared Ni(OH)₂/graphene composites in a three-electrode test cell. The capacitive behavior of the electrode material is generally characterized using cyclic voltammetry (CV) curves. Fig. 4a presents typical CV curves of the Ni(OH)₂/graphene samples in a 1 M KOH electrolyte at various scan rates between 0.0 and 0.5 V. Two strong redox peaks can be observed in each curve. For electric double-layer capacitors, CV curves appear nearly rectangular. Our results thus indicate that the capacitance characteristics are mainly due to Faradaic redox reactions. For the Ni(OH)₂ electrode materials, the surface Faradaic reactions will proceed as:

$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$

To further evaluate the electrochemical properties and estimate the stable potential windows of the as-prepared $Ni(OH)_2$ /graphene composites, galvanostatic charging and discharging of the films in 1 M KOH solution were performed using a Pt counter electrode and a saturated calomel reference electrode. The charge–discharge curves (Fig. 4b) at different current densities (2–16 mA cm⁻²)



Fig. 4 Three-electrode electrochemical measurements of the Ni(OH)₂/ graphene composites in 1 M KOH aqueous solution. (a) CV curves at different scan rates; (b) gravimetric specific capacitance of Ni(OH)₂/graphene composite as a function of the current densities; (c) galvanostatic charge discharge curves at various current densities; and (d) cycling performance of Ni(OH)₂/graphene composites at 2 mA cm⁻².

between 0.0 and 0.6 V display slight nonlinearities that are very distinct from those of typical pure double-layer capacitors. This result indicates the occurrence of Faradaic reactions in the Ni(OH)₂/graphene composites.

The specific capacitance of the Ni(OH)₂/graphene electrode can be calculated from the discharge curve according to $C = I \times \Delta t/(A \times \Delta V)$,¹⁹ where *I* is the discharge current (A), Δt is the discharge time (s), *A* is the area of the active material in the electrode (cm²) and ΔV is the potential change during discharge (V). The specific capacitances obtained were 267, 233, 187, and 133 mF cm⁻² at current densities of 2, 4, 8 and 16 mA cm⁻², respectively. Clearly, the specific capacitance gradually decreases with increasing current density.

Good cycling stability is another important characteristic for high-performance supercapacitors. Fig. 4d reveals the cycle performance of the Ni(OH)₂/graphene samples measured at a current density of 2 mA cm^{-2} for 10000 cycles. Afterward, the capacitance retention was 94.1% of the initial capacitance, indicating excellent long-term stability of the Ni(OH)₂/graphene composite electrode, which exceed those of the previously reported Ni(OH)₂-based materials (usually with a capacitance retention of 51.0-63.2% within 10000 cycles).15,20 By comparison, the 3D Ni(OH)₂ film without graphene presented a capacitance retention of only 41.4% even after 1000 cycles. These results highly highlight the vital role of the incorporation of graphene into electrochemical active electrode materials (Fig. S7, ESI⁺). Obviously, Ni(OH)₂/graphene has the smaller equivalent series resistance (ESR) value than Ni(OH)₂ as shown in Fig. S8 (ESI[†]), reflecting the enhancement in the electronic and ionic conductivities of $Ni(OH)_2$ with the presence of graphene. This result indicates that Ni(OH)₂/graphene composites exhibit good current rate properties, which are consistent with the cycle performance results.

In summary, we present a facile strategy to synchronously exfoliate graphite and assemble the high-quality graphene on 3D Ni(OH)₂ surfaces. High-quality graphene and the unique architecture of 3D skeleton provided Ni(OH)₂/graphene hybrids with high conductivity, strong mechanical stability, ion diffusivity as well as the capability to accommodate volume changes during Faradaic reactions. As a result, the resulting 3D Ni(OH)₂/ graphene composites exhibited excellent specific capacitance, remarkable rate capability and super-long cycle life when used as electrode materials for supercapacitors. Such a simple and cost-effective synthetic approach would open new doors for the development of a serial of high-quality graphene based materials, and offer promising applications for high-performance energystorage devices.

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