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Jingjing Ma

Shanghai Jiao Tong University

Jiulin Wang

Shanghai Jiao Tong University

Yu-Shi He

Shanghai Jiao Tong University

Xiao Zhen Liao

Shanghai Jiao Tong University

Jun Chen

University of Wollongong, junc@uow.edu.au

See next page for additional authors

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Abstract

A facile and controllable approach has been developed to synthesize three-dimensional (3D) graphene-based monoliths. Here, as a proof-of-concept experiment, self-assembled 3D CoO/graphene sheets (CoO/GS) composites with porous structures have been successfully fabricated in an ethanol medium by a one-step, in situ growth, solvothermal method. During the process, the in situ nucleation and growth of CoO particles on GS were tuned by the formation of a 3D GS network. In the as-prepared composites, the self-assembled 3D GS network around the CoO particles can not only provide a 3D conductive matrix, but also buffer the volume changes of CoO and restrain the aggregation of CoO particles during charge-discharge cycling. The CoO particles, which are uniformly anchored into the 3D GS framework, can also act as spacers to effectively avoid the close restacking of GS. Compared to the bare CoO, the 3D CoO/GS composites as Li-ion battery anodes show dramatically improved electrochemical performance, including cycling stability and rate capability, owing to the unique self-assembled 3D structure and the superior synergistic effect between the two components. Such a synthesis strategy can be a promising route to produce diverse 3D graphene-based monoliths in various solvents.

Keywords

one, step, situ, synthesis, solvothermal, self, strategy, assembled, 3d, graphene, composites, enhanced, lithium, storage, capacity

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Authors

Jingjing Ma, Jiulin Wang, Yu-Shi He, Xiao Zhen Liao, Jun Chen, Jiazhao Wang, Tao Yuan, and Zi-Feng Ma

A solvothermal strategy: one-step *in situ* synthesis of self-assembled 3D graphene-based composites with enhanced lithium storage capacity

Jinjin Ma,[†] Jiuling Wang,[†] Yu-Shi He,^{†,*} Jun Chen,[‡] Jia-Zhao Wang,[§] Tao Yuan,[†]

Xiao-Zhen Liao,[†] Zi-Feng Ma[†]

[†]*Institute of Electrochemical and Energy Technology, Department of Chemical Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China.*

[‡]*Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, University of Wollongong, Wollongong, NSW, 2522, Australia*

[§]*Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW, 2522, Australia.*

*Corresponding Author: Yu-Shi He

Tel: +86-21-54744533, Fax: +86-21-54747717

E-mail: ys-he@sjtu.edu.cn

ABSTRACT

A facile and controllable approach has been developed to synthesize three-dimension (3D) graphene-based monoliths. Here, as a proof-of-concept experiment, self-assembled 3D CoO/graphene sheets (CoO/GS) composites with porous structures have been successfully fabricated in ethanol medium by the one-step *in situ* growth solvothermal method. During the process, the *in situ* nucleation and growth of CoO particles on GS were tuned with the formation of 3D GS network. In the as-prepared composites, the self-assembled 3D GS network around CoO particles can not only provide a 3D conductive matrix, but also buffer the volume change of CoO and

restrain the aggregation of CoO particles. CoO particles which uniformly anchored on the 3D GS framework can also act as spacers to effectively avoid the close restacking of GS. Comparing to the bare CoO, the 3D CoO/GS composites as Li-ion battery anodes show dramatic improved electrochemical performance including cyclic stability and rate capability owing to the unique self-assembled 3D structure and the superior synergistic effect between the two components. Such a synthesis strategy can be a promising route to produce diverse 3D graphene-based monoliths in various solvents.

Keywords: Solvothermal, *in situ*, self-assembled, 3D graphene, CoO, anode material

Introduction

Possessing a combination of remarkable electrical, optical, thermal, and mechanical properties,^{1, 2} graphene and graphene-based materials have shown outstanding potentials for a variety of applications, including energy storage,³⁻⁵ bioapplications,⁶ flexible electronics,⁷ sensors,⁸ etc. The main challenge in the synthesis of the graphene-based composites concentrates on how to effectively inhibit the restacking and agglomeration of GS to fully harness the unique properties of individual graphene sheet and adequately utilize the synergistic effect between GS and other component. The conventional direct high-temperature calcination can easily cause severe agglomeration of the GS.⁹ More recently, many efforts have been made for retaining the structure of graphene network, such as keeping the graphene solvated by vacuum filtration method¹⁰ and developing a range of 3D graphene-based composites by

spray drying or hydrothermal technique.¹¹⁻¹⁴ Shi et al.¹³ firstly demonstrated that graphene hydrogels composed of a randomly cross-linked 3D GS network can be readily formed when a high concentration of graphene oxide dispersion is hydrothermally reduced without the addition of any reducing agent. Nevertheless, some particular material has to be prepared in specific solvent. By the aid of solvothermal reduction method, some researchers found that GO dispersion can be directly reduced to GS dispersion in some solvents, such as NMP,¹⁵ ethanol,¹⁶⁻¹⁸ ethylene glycol,¹⁶ *N,N*-dimethylformamide (DMF)¹⁹ and 1-butanol¹⁶. However, there are still few reports on the direct preparation of self-assembled 3D graphene-based composites by the simple solvothermal reduction method. Recently, self-assembled 3D graphene-based organogels were prepared by solvothermal reduction of GO dispersion in propylene carbonate (PC).²⁰ Furthermore, by the solvothermal method and following freeze-drying process, we have also successfully synthesized various 3D GS aerogels in different solvents, including NMP, ethanol, ethylene glycol and DMF (Fig. 1). The obtained 3D GS aerogels can maintain the porous structure of 3D GS organogels *via* freeze-drying treatment, while naturally drying process will result in the drastic shrinkage of 3D GS and impair the porous structure.

Transition metal oxides (MOs) have been regarded as promising anode materials for next-generation rechargeable Li-ion batteries (LIBs) with high theoretical capacity ($>600 \text{ mAh g}^{-1}$) compared to that of conventional graphite (372 mAh g^{-1}).²¹

Unfortunately, the poor electrochemical performance of MOs, especially cycle stability and rate capability, has hindered their practical application. It can be attributed to their low conductivity and drastic volume variation during the Li ions insertion/extraction process which could cause electrode pulverization and loss of electrical continuity.¹⁸ Flexible GS-wrapped MOs have been attractive options to alleviate the problems.^{22, 23} However, the obvious capacity degradation associated with the aggregation and pulverization of MOs particles still exists due to the loose contact between GS and the MOs particles.

Here, as a proof-of-concept experiment, we demonstrate a one-step *in situ* growth solvothermal method in ethanol medium to prepare 3D self-assembled CoO/GS composites. The *in situ* controlled growth of CoO particles on the surface of GS can effectively avoid the occurrence of concentration gradient during initial reaction stage and form a more homogeneous composite and stronger interaction between GS and CoO particles with a tighter interface, which can contribute to the interfacial charge transfer and reduce the agglomeration and restacking of GS.²⁴ The solvothermal method offers significant advantages in preparation because no reducing agent, no filtration process, no calcination and no protective atmospheres are required. When employed as anode for LIBs, CoO/GS delivers superior cycling performance with stably reversible capacity of about 405 mAh g⁻¹ at a high current of 6400 mA g⁻¹. Above all, such a facile solvothermal strategy can be applicable for the synthesis of 3D graphene-based monoliths in different solvents.

Experimental details

Synthesis of 3D CoO/GS. Graphite oxide was synthesized from natural graphite powder (Grade 230, Asbury Carbons) by a modified Hummer's method.²⁵ The graphite oxide (5 mg) was exfoliated into 10 mL 99.9% ethanol by sonication to form graphene oxide (GO) suspension. Then, a certain amount of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were added into the above solution in a weight ratio of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$: GO of 15 : 1,. The mixture was sealed into a glass sample vial. Thereafter, the vial was put in Teflon-lined autoclave and maintained at 180 °C for 12 h. After it was naturally cooled down to room temperature, a black columniform product was obtained and immersed in water overnight to remove the residual ions, designated as CoO/GS (15). 3D CoO/GS (10) and CoO/GS (20) were synthesized by the same method, except that the weight ratio of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$: GO were 10 : 1 and 20 : 1 respectively. Pure CoO and GS samples were also prepared by the same procedure for comparison. The all as-prepared samples were freeze-dried for the following tests.

Structural and morphological characterization. X-ray diffraction (XRD) measurements were carried out using a Rigaku D/MAX-2200/PC X-ray diffractometer at 40kV and 20mA, with a Cu $K\alpha$ radiation source. Raman spectroscopy was used to identify the surface characteristics of the samples using a BRUKER optic SENTERRA (R-200L) Raman spectrometer using a laser with a

wavelength of 523 nm at room temperature. FT-IR measurement was carried out on a Perkin- Elmer 936 infrared spectrophotometer from KBr pellets in the range of 500—4000 cm^{-1} . X-ray photoelectron spectrometer (XPS, Kratos Axis Ultra DLD) was utilized to analyze the surface chemistries of the samples. Thermogravimetric analysis (TGA) was performed using a STA 449F3 analyzer (NETZSCH Co., Germany) to evaluate the residual level of CoO/GS composite after calcination. The morphology and microstructure of the samples were monitored using a FEI Nova SEM 230 ultra-high resolution Field Emission Scanning Electron Microscopy (FESEM) equipped with energy dispersive X-ray spectroscopy (EDS, INCA X-Max 80, Oxford Instruments), Transmission Election Microscopy (TEM)/Scanning Transmission Electron Microscopy (STEM) (JEM-2100F, JEOL Ltd., Japan) was operated at 200 kV equipped with EDS (INCA-IET200, Oxford Instruments). Porosity and BET surface areas for the samples were measured using a nitrogen sorption instrument (Micromeritics, ASAP2020).

Electrochemical measurements. The CoO/GS hybrids were dried at 80 °C for 3h under Ar atmosphere. Then, 75 wt% active material (CoO/GS hybrids), 15 wt% acetylene black (Super-P), and 10 wt% polyvinylidene fluoride (PVDF) binder were mixed into N-methyl-2-pyrrolidinone (NMP). The obtained slurry was coated onto Cu foil disks to form working electrode, the electrode was dried, cut to $\Phi 14$ mm sheets, pressed at 3 MPa, and finally dried at 80 °C in vacuum for 4 h to remove the solvent. The active materials loaded on the electrode were about $1.5 \text{ mg}\cdot\text{cm}^{-2}$.

CR2016 coin cells were assembled in an argon-filled glove box with lithium metal as counter electrode and UP3025 separator (provided by UBE Industries, Ltd., Japan). The electrolyte contained 1 M LiPF_6 in dimethyl carbonate (DMC) and ethylene carbonate (EC) mixed solvent of 1:1 (LP30 from EM Industries, Inc.). Charge–discharge cycles of the half-cells were evaluated between 0.005 and 3 V vs Li^+/Li at room temperature using LAND CT2001A model battery test system (Wuhan Jinnuo Electronics, Ltd.) under constant current condition. The charge-discharge capacities were calculated according to the weight of CoO/GS material in the electrode. The AC electrochemical impedance spectra (EIS) tests of the cells were measured by a Solartron FRA 1260 frequency responses analyzer combined with a Solartron SI 1287 Electrochemical Interface with an amplitude of 10 mV over a frequency range from 100 kHz to 0.1 Hz. Cyclic voltammetry (CV) measurements were carried out by using a CHI instrument (CHI 660) at a scanning rate of 0.5 mV s^{-1} .

Results and discussion

As shown in Fig. 2, the overall formation process of self-assembled 3D CoO/GS composite involves the following steps. Firstly, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ is sonicated with the wetted GO in ethanol to form uniform and opaque dispersion (Fig. 2a). At this place, the functional groups on the surface of GO sheets with negative charge could bind with Co^{2+} ions by electrostatic interactions and act as anchor sites. After that, the above mixture was solvothermal self-assembled at 180°C for 12 h, thus

forming a black ethanol gel of 3D CoO/GS (Fig. 2b). During the solvothermal reaction, Co^{2+} ions adsorbed on GO sheets reacted with OH^- ions to form CoO crystals under high temperature and pressure,²⁶ while GO was simultaneously reduced and self-assembled to form 3D GS network. The as-obtained 3D CoO/GS ethanol gel was freeze-dried for maintaining the 3D monolithic network to obtain 3D CoO/GS aerogel (Fig. 2c). It is noteworthy that the shape of the 3D product depends on the geometry of the autoclave.

The XRD patterns of CoO/GS (15) and bare CoO are shown in Fig. 3a. For the CoO/GS (15) composite and bare CoO, The major diffraction peaks at 2θ values of 36.5 (111), 42.4 (200), 61.5 (220), 73.7 (311), and 77.5 (222) match well with those of the standard cubic CoO (JCPDS 43-1004). No obvious characteristic of GO at about 11° (Fig. S1†) is observed in the 3D CoO/GS (15) composite, which suggests that GO was reduced to GS during the solvothermal process. Moreover, the characteristic (002) stacking peak of graphene at $22\text{--}28^\circ$ (Fig. S1†) is also absent here, indicating that the graphene sheets are evenly dispersed without obvious stacking and successfully covered with well-crystallized CoO. The similar phenomenon was also observed in the previous reports about the graphene-based hybrids.^{12, 27}

Fig. 3b exhibits the Raman spectra of CoO/GS (15), pristine GS and bare CoO. In the CoO/GS (15), the peaks below 1000 cm^{-1} are consistent with the characteristic peaks of bare CoO. Characteristic peaks for carbon materials include the disordered D band

at about 1350 cm^{-1} , the graphitic G band at about 1590 cm^{-1} , the 2D band at about 2700 cm^{-1} and D* at about 2900 cm^{-1} .²⁸ The distinct D band peak and the relative small 2D peak indicate a lot of dangling bonds, defects, and disordered structure present.²⁹ These defects could act as nucleation sites for CoO particles growing and allow uniform formation of CoO particles in 3D GS network.³⁰ Furthermore, in comparison with the pristine GS, the shift of the peaks can be clearly found for both D and G bands in the CoO/GS (15) composite, indicating a significant charge transfer between the 3D GS and CoO particles. The charge transfer between GS and CoO can effectively improve the electrochemical performance of the CoO/GS composite.³¹

The FT-IR spectrum of the CoO/GS (15) composite shows peaks at 550 and 665 cm^{-1} that can be assigned to the vibrations of Co-O (Fig. S2†).²³ The peak located at 1224 cm^{-1} is derived from epoxy (C-O-C) groups, while the peak presented at 1570 cm^{-1} corresponds to the stretching vibration of C=C.³²

XPS analysis was used to further characterize the surface chemical composition of CoO/GS (15) composite. Full XPS spectrum (Fig. 4a) firstly indicates the presence of only Co, O and C elements in the composite. In Fig. 4b, four different peaks which are corresponding to carbon sp^2 (C_g , $\sim 285\text{ eV}$), epoxy/hydroxyl groups (C-O, $\sim 286.5\text{ eV}$), carbonyl group (C=O, $\sim 287.8\text{ eV}$) and carboxyl group (O-C=O, $\sim 289.5\text{ eV}$), respectively, are detected.³³ The fraction of carbon-carbon bonding is about 71.9%, which is similar to the previously reported result.¹² It can be attributed to the efficient

removal of oxygen functional groups from the GO by the solvothermal reaction and demonstrate the formation of graphene. The high-resolution Co 2p spectrum of the 3D composite is shown in Fig. 3c. The peaks at 782.1 and 797.6 eV with a 15.5 eV peak-to-peak separation correspond to the binding energy of Co 2p $3/2$ and 2p $1/2$ of CoO, respectively, while two weak peaks at 787.4 and 803.8 eV should be the shake-up satellite peaks of above two main peaks, indicating the presence of Co (II).²⁷ The aforementioned XRD, Raman, FTIR and XPS characterizations confirm the successful preparation of CoO/GS composite.

FESEM images in Fig. 5 show the surface morphologies of (a,b) bare CoO (c,d) pristine GS and (e,f) CoO/GS (15). The SEM images of the bare CoO (Fig. 5a and 5b) display irregular particles about 200-500 nm in diameter with rough surfaces. From Fig. 5c and 5d, it can be clearly observed that the pure GS exhibits an easily recognizable and interconnected 3D porous framework with the pore sizes ranging from submicrometer to several micrometres. The formation of the self-assembled 3D GS framework is derived from the regional overlapping and coalescing of flexible GS through π - π stacking interactions during solvothermal treatment.^{13, 34} As shown in Fig. 5e and 5f, CoO/GS (15) still possesses a fully interconnected macroporous architecture, which is similar to pristine GS. But it is evident that the pore sizes of the 3D GS network in the composite became much larger due to the introduction of CoO particles. The sphere-like CoO particles with a mean diameter of about 350 nm in the CoO/GS (15) composite are uniformly and closely anchored on the 3D GS network,

suggesting effective assembly between the CoO particles and GS during solvothermal treatment. And the surface morphology of the CoO particles in the composite is totally different from the bare CoO, which is ascribed that the oxygen-containing functional groups (hydroxyl, carboxyl and epoxy etc.) on GO surface/edge could improve the crystallization of CoO and also act as anchor sites for in situ formation of CoO particles.³⁵ It is notable that most of CoO particles are clearly encapsulated in the GS matrix and the graphene shells present a typical crumpled and rippled morphology (Fig. 5f). It has been reported that the crumpled GS encapsulation not only enhances interface contact, but also suppresses the aggregation of particles and provides elastic void spaces to accommodate the strain and stress of the volume change of electrode materials during cycling.³⁶

From the result of the EDS mappings in a relatively large area (about 4 μm X 4 μm) for carbon, oxygen and cobalt elements (Fig. S3[†]), it can be found that the CoO particles are uniformly distributed in the 3D GS network. The graphene layer on some CoO surface may be too thin to be visible in the SEM image. So combined with EDS analysis (Fig. 6f), a STEM image (Fig. 6a) and corresponding elemental mapping images (Fig. 6c-e) of the small region indicated in Fig. 6b provide additional evidence to further confirm the homogeneous distribution of carbon, oxygen and cobalt on the surface of individual CoO particle.

Microstructures of various samples were further characterized by TEM and high-resolution TEM (HRTEM) (Fig. 7). A typical TEM image of the prepared bare

CoO sample can be observed in Fig. 6a. The morphology of the CoO particles with rough surfaces is irregular, which is identical with the SEM observation. The corresponding selected-area electron diffraction (SAED) pattern (inset in Fig. 7a) shows clear diffraction spots, demonstrating the single-crystal-like nature. In Fig. S4[†], the pure GS exhibits a transparent feature with a wrinkled structure. Fig. 7b and 7c show the TEM images of the CoO/GS (15) composite. As expected, the CoO particles are well wrapped by the GS and are distributed homogeneously in the network. The inset in Fig. 7b depicts the corresponding SAED pattern of the CoO/GS (15) hybrid. There are two sets of diffraction patterns that belong to the CoO and GS, respectively. Note that the weak diffraction rings from GS are obvious due to multilayer graphene and the diffraction spots for CoO demonstrate the single-crystal in nature of the CoO in CoO/GS (15) composite.^{23, 26} The HRTEM image of the CoO/GS (15) composite in Fig. 7d indicates that the CoO particle is encapsulated by the multiple overlapping GS. And the regular lattice fringes show a spacing of 0.24 nm, which can be assigned to the (111) plane of CoO.²³ In addition, the graphene content in the CoO/GS composite could significantly influence the morphology of the product. Based on the TEM images of CoO/GS (10) (Fig. S5a[†]), CoO/GS (15) (Fig. 7b) and CoO/GS (20) (Fig. S5b[†]), it can be found that, with the decrease of the graphene content, the sizes of the CoO particles gradually become larger. This result illustrates that the size of as-synthesized material particles in 3D GS network is controllable by the *in situ* growth solvothermal process.

For quantifying the amount of graphene in the CoO/GS composites, TGA was carried out at a heating rate of 10 °C min⁻¹ from 40 °C to 700 °C in air. In Fig. S6†, the weight loss at the temperature below 100 °C is attributed to the evaporation of residual water in the samples and the rapid mass loss between 220 and 350 °C could be due to the combustion of the graphene.^{23, 37} Therefore, the weight fractions of graphene in the CoO/GS (10), CoO/GS (15) and CoO/GS (20) were determined to be about 17.78%, 12.41% and 8.44%, respectively.

Fig. 8 shows the electrochemical performance of the CoO/GS (15) composite. To identify the mechanism of the electrochemical reactions, the CV profiles of the CoO/GS (15) for the first, second and tenth cycles were measured at a scan rate of 0.5 mV s⁻¹ as shown in Fig. 8a. In the cathodic polarization process of the first cycle for CoO/GS (15), two peaks, one obvious and one inconspicuous, were observed at about 0.28 and 0.98 V, which were ascribed to the Li insertion into CoO/GS composite and the formation of solid electrolyte interphase (SEI) film.³⁷ Apparently, the reaction indicates the occurrence of some irreversible processes in the first cycle. Meanwhile, one broadened peak was recorded at about 2.2 V in the anodic process, corresponding to the reversible oxidation of cobalt to cobalt oxide.³⁸ During the subsequent cycles, the cathodic peak potential transfers to higher voltage potentials and the CV curves show good reproducibility, suggesting the good reversible reaction. For CoO/GS electrode, the electrochemical reversible reaction mechanism of Li with CoO and carbon in lithium ion battery could be described as follows:³⁹

Fig. 8b show the charge (delithiation) and discharge (lithiation) voltage profiles for the CoO/GS (15) composite at a current density of 200 mA g⁻¹ at room temperature. In the first discharge cycle, an extended potential plateau at around 0.8 V demonstrates the conversion reaction and the formation of SEI film, which is consistent with the CV results. The first discharge capacities (1413 mAh g⁻¹) of the composite is much higher than the theoretical capacity of CoO (716 mAh g⁻¹), which may derive from the decomposition of electrolyte, the formation of the SEI layer and the reduction of oxygenated functional groups on the surface of graphene in the CoO/GS (15) composite.^{22, 23} Furthermore, it was reported that graphene can also contribute additional lithium storage capacity apart from the intrinsic theoretical capacity, which is due to significant disorder/defects of graphene.⁴⁰ The coulombic efficiency (CE) of the CoO/GS (15) composite is around 77% at the first cycle and CE rises to more than 98% after 1 cycle. For the composite, it is notable that no obvious capacity loss was observed after 2 cycles and the electrode could still maintain a reversible capacity of approximately 960 mAh g⁻¹ after 10 cycles.

To evaluate the electrode kinetics of bare CoO, CoO/GS (10), CoO/GS (15) and CoO/GS (20), the rate capability of the samples is shown in Fig. 8c. It is clearly seen that the CoO/GS composites, especially the CoO/GS (15) composite with 12.3% graphene, illustrate much better rate performance comparing to the reference bare CoO and other CoO@GS composites. When the charge/discharge current density

increases to 1600 mA g^{-1} , the reversible capacity of the CoO/GS (15) composite still keeps a stable value above 730 mAh g^{-1} . In the contrast, at this high rate, the bare CoO can only deliver an average reversible capacity of *ca.* 270 mAh g^{-1} . When the current density is returned to 200 mA g^{-1} , the CoO/GS (15) electrode can still release a high reversible capacity (1036 mAh g^{-1} , 95.5% of the initial reversible capacity) after the 50th cycle, indicating good reversibility.

The discharge-charge cycling performance of CoO/GS (15) at high current densities was further evaluated in Fig. 8d. All cells were cycled at a current density of 200 mA g^{-1} for the initial two cycles before each test. The composite exhibited a good cycling performance at high current densities. After 50 cycles, stable reversible capacities of about 706 , 503 and 405 mAh g^{-1} can still be retained at current densities of 1600 , 4800 and 6400 mA g^{-1} , respectively. Moreover, the high-rate cycling performance of CoO@GS (15) composite is much better than that of bare CoO, whose reversible capacity is only 211 mAh g^{-1} after the same 50 cycles at a current density of 1600 mA g^{-1} .

Evidently, the CoO/GS composites show significantly enhanced cycling and rate performance perhaps benefited from the unique self-assembled 3D structure of GS and simultaneous growth of CoO particles anchored on 3D GS framework during the solvothermal route, which can ensure the integrity of the electrodes over many discharge/charge cycles. This can be confirmed by examining the microstructure

variation of the bare CoO and the CoO/GS (15) composite after 50 cycles at a charge/discharge current density of 1600 mAh g^{-1} using TEM (Fig. 9). In Fig. 9a, it is obviously observed that the bare CoO particles became smaller and cracked after 50 cycles, indicating the pulverization of the particles during cycling that leads to the poor cycling stability of bare CoO particles. In contrast, in Fig. 9b, the CoO particle anchored on GS still retained its original morphology and did not further break after 50 cycles. This demonstrates the long-term stability of the as-obtained CoO/GS (15) cycling and the pulverization of the CoO particles is inhibited under the protection of flexible 3D GS network. Additionally, the corresponding SAED results indicate that the CoO/GS (15) electrode exhibits better crystallinity than the bare CoO electrode after 50 cycles,

In order to further clarify the improved electrochemical performance after introducing the graphene into the CoO/GS composite, the Nyquist plots of the AC impedance for the bare CoO and CoO/GS (15) composite were measured after 1 and 50 cycles at a charge/discharge current density of 1600 mAh g^{-1} (Fig. S7†). To maintain uniformity, EIS was performed on working electrodes in the fully charged (delithiated) state. The depressed semicircle in the high-medium frequency is related to the capacitance property of the electrode interface. And the inclined line in the low frequency range represents the Warburg impedance, which corresponds to solid-state diffusion of Li ions within the electrodes.²⁹ After 1 cycle, the semicircle of the CoO/GS (15) electrode in the high-medium frequency is similar to that of the bare CoO electrode in

Fig. S7a†. Nevertheless, after 50 cycles, it is evident that the semicircle for the CoO/GS (15) electrode is much smaller than that of the bare CoO electrode in Fig. S7b†, which suggests that the CoO/GS (15) electrode possesses lower ohmic and capacitive resistances, which means the improved electronic connection and charge/discharge property of the CoO electrode could be achieved by effective encapsulation and adherence of highly conductive and flexible GS.

Overall, the improved cycle and rate performance of CoO/GS composites as anode materials for lithium storage may be attributed to the following three aspects. First, almost every individual CoO particle can be encapsulated into GS and keep intimate contact with GS *via* the one-step *in situ* growth solvothermal process. Second, the self-assembled GS in the CoO/GS composites constitutes not only 3D continuous and highly conductive network, but also provides elastic void spaces to buffer the strain and stress of the volume change of CoO and inhibit the aggregation and pulverization of CoO particles during cycling, and thus ensures favorable transport kinetics for lithium ions and electrons. Third, CoO particles are uniformly anchored into the GS matrix as spacers, which can effectively prevent the closely restacking of GS and consequently maintain the large contact area between the electrode and electrolyte.

Conclusions

In conclusion, a simple but effective and controllable method has been developed to prepare 3D graphene-based monoliths. Here, 3D self-assembled CoO/GS aerogels

have been successfully fabricated in ethanol medium by the one-step *in situ* growth solvothermal method and subsequent freeze-drying process, which can be used as anode materials for LIBs. In this way, CoO particles can *in situ* nucleate and grow on the surface of GS with the simultaneous formation of 3D GS network. In such a unique macroporous structure, CoO particles are evenly anchored into the GS matrix. The 3D GS in the composites not only acts as an electronically conductive matrix, but also provides double protection against the aggregation and pulverization of CoO particles during cycling. And so the synergistic effect between 3D GS and active particles is fully utilized. As a consequence, the as-formed 3D CoO/GS composites show superior cyclic stability and rate capability. The different forms of graphene-based materials can be used in various applications because the outcome is likely to vary with size, morphology and chemical structure. So our study suggests that the size of as-synthesized material particles in 3D GS architecture can be further controlled for other applications by changing concentration of reactants, reaction temperature and reaction time. Most importantly, this study is also a base for developing various 3D graphene-based monoliths in different solvents by the one-step solvothermal strategy for wide applications in near future.

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**A solvothermal strategy: one-step in situ synthesis of
self-assembled 3D graphene-based composites with
enhanced lithium storage capacity**

Fig. 1 SEM images of freeze-dried 3D GS aerogels obtained in different solvents (a) NMP, (b) ethanol, (c) ethylene glycol and (d) DMF at 180 °C for 12h in a Teflon-lined autoclave. Insets are the corresponding digital images. GO concentration: 1 mg mL⁻¹.

Fig. 2 Formation process of self-assembled 3D CoO/GS composite. a) Uniform and opaque black dispersion of GO and $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in ethanol. b) 3D CoO/GS hybrid ethanol gel synthesized by solvothermal self-assembly in ethanol. c) 3D CoO/GS hybrid aerogel obtained after freeze-drying.

Fig. 3 (a) XRD patterns for the CoO/GS (15) and bare CoO. (b) Raman spectra for the CoO/GS (15), pristine GS and bare CoO obtained using the standard procedure.

Fig 4. XPS spectra for the CoO/GS (15) composite: (a) survey spectrum and high-resolution (b) C 1s and (c) Co 2p spectra.

Fig. 5 FESEM images of (a,b) bare CoO, (c,d) pristine GS, (e,f) CoO/GS (15).

Fig. 6 STEM, Elemental mapping and EDX spectrum of CoO/GS (15). (a) Typical STEM image; (b) STEM image taken from the square region marked in (a) and corresponding elemental mapping images of (c) Co, (d) O and (e) C, and (f) EDS spectrum suggest the homogeneous distribution of Co, O and C in CoO/GS (15).

Fig. 7 TEM images of (a) bare CoO and (b-c) CoO/GS (15); HRTEM image of (d) CoO/GS (15). The insets in (a) and (b) are the electronic diffraction patterns of bare CoO and CoO/GS (15), respectively

Fig. 8. (a) CV curves of the CoO/GS (15) composite in the potential range of 0.005–3 V at a scan rate of 0.5 mV s⁻¹. (b) Charge–discharge curves of the CoO/GS (15) composite at a current density of 200 mA g⁻¹. (c) Rate performance of the CoO/GS composites with different graphene contents and bare CoO at various current densities. (d) Cycling behavior of bare CoO and CoO/GS (15) at high current densities. Hollow and solid point symbols represent lithium insertion and extraction.

Fig. 9 TEM images of (a) bare CoO and (b) 3D CoO/GS (15) composite after 50 cycles at a current density of 1600 mA g^{-1} . The insets in (a) and (b) are the corresponding electronic diffraction patterns.