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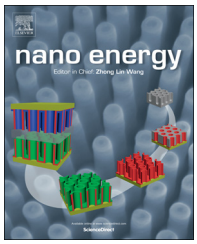


RAPID COMMUNICATION

# Highly oriented macroporous graphene hybrid monoliths for lithium ion battery electrodes with ultrahigh capacity and rate capability

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**Abstract**
The highly oriented macroporous graphene monoliths hybridized with carbon-coated metal oxide or phosphate (C/M/GM) with core/shell structure were fabricated by an ice-templating co-assembly of M/GO nanosheets (metal oxide/phosphates decorated graphene oxide) and polyvinyl alcohol (PVA), and following thermal treatment. With either tin oxide ($SnO_2$) or iron phosphate ($FePO_4$), the resulting C/M/GMs possess periodic macropores with diameters ranging from 5 to 20 μm and high loading contents of active components (~70 wt%). Served as the anode in LIBs, C/$SnO_2$/GM maintains an ultrahigh capacity of 1665 mA h $g^{-1}$ at a current density of 0.2 A $g^{-1}$ for 200 cycles. Even at an ultrafast charge rate of 10 A $g^{-1}$, a decent capacity of 300 mA h $g^{-1}$ can still be achieved, with excellent cycling stability. And C/$FePO_4$/GM also delivers a highly reversible capacity of 175 mA h $g^{-1}$ at a current density of 0.05 A $g^{-1}$ for 150 cycles and a good capacity of 57 mA h $g^{-1}$ at 2 A $g^{-1}$ when as the LIB cathode electrode.


## Introduction

Developed for more than two decades, lithium ion batteries (LIBs) have been utilized as the major power supply of mobile electronic devices and electric vehicles since they offer the highest energy density in comparison to other commercial battery systems. To improve the lithium storage ability of LIBs and reduce their cost, enormous efforts have been devoted to the exploration of various high capacity anode and cathode materials, such as tin oxide ($SnO_2$) [1,2], iron(II, III) oxide ($Fe_3O_4$) [3,4], cobalt oxide ($Co_3O_4$) [5-7], zinc oxide (ZnO) [8,9], iron phosphate ($FePO_4$) [10], and lithium iron

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phosphate ($LiFePO_4$) [11,12]. However, the practical application of these materials is greatly hampered by their unsatisfying cycling performance or low capacity arising from their poor electronic conductivity, severe aggregation, and huge volume expansion during Li insertion/extraction processes. To overcome these obstacles, the hybrids of inorganic materials with carbon nanotubes (CNTs) or graphene have been proposed, which can substantially improve the efficiency of charge transfer through shortening Li ion diffusion length and enhancing electrical conductivity [2,13–16]. However, a truly sustainable high-rate capability and a high capacity for electrode materials have rarely been achieved because of the discontinuous transfer of charge carriers in the powder-like electrode material. The construction of three-dimensional (3D) monoliths with well-accessible macroporous channels provides an ideal solution to effectively enhance the electrochemical performance of the electrode, especially, using graphene as the scaffolds [17]. In this respect, the graphene-based macroporous architectures can not only provide 3D interconnected pathway for electron transport but also promote the diffusion of electrolyte within the networks of the electrode [18–22]. However, most of the previously reported 3D macroporous LIB electrodes only owned the irregular porosities [17,19,23], which inevitably led to electrode polarization and substantial loss of the intrinsic capacity at high charging/discharging rate [24,25].

Herein, we developed an unprecedented fabrication strategy towards highly oriented macroporous graphene monoliths hybridized with carbon-coated metal oxide or phosphate nanoparticles (C/M/GM), employing an ice-templating co-assembly of M/GO nanosheets (metal oxide/phosphates nanoparticles decorated on graphene oxide) and polyvinyl alcohol (PVA), and followed by thermal treatment [26–32]. With either $SnO_2$ or $FePO_4$ as representative materials, the resulting C/M/GMs possess oriented macropores with diameters ranging from 5 to 20 μm and high loading contents of active components (~70 wt%). Serving as the anode in LIBs, $C/SnO_2/GM$ maintains an ultrahigh capacity of 1665 mA h $g^{-1}$ at a current density of 0.2 A $g^{-1}$ for 200 cycles. Even at an ultrafast charge rate of 10 A $g^{-1}$, a decent capacity of 300 mA h $g^{-1}$ can be achieved for $C/SnO_2/GM$. Such performance is superior to those of the state-of-art Sn or $SnO_2$-based LIB anodes [33–36]. Our fabrication protocol further renders the construction of high performance LIB cathodes with unique macroporous architectures. As exemplified in this work, $C/FePO_4/GM$ delivers a highly reversible capacity of 175 mA h $g^{-1}$ at a current density of 0.05 A $g^{-1}$ for 150 cycles and an excellent capacity of 57 mA h $g^{-1}$ at 2 A $g^{-1}$.

## Experimental

### Suspension of $SnO_2$/GO nanosheets

Graphene oxide (GO) was synthesized from natural graphite flakes (Aladdin) by a modified Hummers method [37]. First, 100 mL GO suspension in DMF (1 mg $mL^{-1}$) was mixed with 10 mL aqueous solution of $SnCl_4$ (25 mg $mL^{-1}$) and a concentrated HCl solution was then added to the above mixture until the pH<7. The resulting suspension was ultrasonicated for 20 min and then kept at 80 °C under stirring for 12 h. After that, the as-prepared suspension of $SnO_2$/GO was washed and centrifuged with water to remove excessive acid.

### $C/SnO_2/GM$

PVA (1788, MW=22,000, Aladdin) was first added to the $SnO_2$/GO aqueous suspension. PVA-to-GO weight ratios of 0.5:1, 1:1, 20:1 were typically used. The resulting mixture was then placed in a 1 mL insulin syringe, which was later immersed in liquid nitrogen for 12 h. The unidirectional frozen cryogels were then freeze-dried for 48 h, and taken out from the syringe as intact monoliths (Figure S1a). Finally, the as-prepared samples were thermally treated at 300 °C in $N_2$ for 2 h.

### $C/FePO_4/GM$

The aqueous suspension of GO (200 mL, 0.25 g $L^{-1}$) was ultrasonicated with the presence of 600 mg iron(III) chloride ($FeCl_3$, AR, Aladdin) for 30 min. Subsequently, 430 mg ammonium phosphate monobasic ($NH_4H_2PO_4$, CR, Aladdin) dissolved in 50 mL distilled water was added to the mixture of GO and $FeCl_3$ and then stirred at 25 °C for 10 h. The resulting brown products were centrifuged and washed with water for three times to remove the excess salt. PVA (the weight ratio of PVA-to-GO was 1:1) was added to the dispersion of $FePO_4$/GO nanosheets and the resulting mixture was then placed in a 1 mL insulin syringe, which was later immersed in liquid nitrogen for 12 h. Afterwards, the unidirectional frozen cryogels were freeze-dried for 48 h and removed from the syringe as intact monoliths. Finally, the as-prepared samples were thermally treated at 300 °C in $N_2$ for 2 h.

### $SnO_2/GM$ and $FePO_4/GM$

The dispersion of $SnO_2$/GO and $FePO_4$/GO nanosheets were directly placed in a 1 mL insulin syringe, which were later immersed in liquid nitrogen for 12 h, respectively. The unidirectional frozen cryogels were then freeze-dried for 48 h, and taken out from the syringe as intact monoliths. Finally, the as-prepared samples $SnO_2/GM$ and $FePO_4/GM$ were thermally treated at 300 °C in $N_2$ for 2 h.

### Samples characterization

Scanning electron microscopy (SEM) measurements were performed on an FEI Sirion-200 field emission scanning electron microscope. Transition electron microscopy (TEM) studies were conducted on a JEOL-2100 electron microscope at an operating voltage of 200 kV. The samples were dissolved in water and the suspension was dropped onto a copper grid covered with carbon film. Atomic force microscopy (AFM) images of the materials on a freshly cleaved mica surface were taken with a Nanoscope III in tapping mode using a NSC14/no Al probe (MikroMash, Wislsonville, Oregen). The X-ray diffraction (XRD) analysis was performed on a RigakuD/Max 2500 X-ray diffractometer with Cu Kα radiation ($\lambda$=1.54 Å) at a generator voltage of 40 kV and a generator current of 50 mA with a scanning speed of 5°/min from 10° to 80°. Nitrogen adsorption/desorption isotherms at 77 K was determined by Micromeritics ASAP 2010. For TGA measurements, a TA Instrument Q-5000 IR model was used with a heating rate of 20 °C $min^{-1}$ in air or $N_2$. Raman measurements were recorded on an Invia/Reflrx Lasser Micro-Raman spectroscope (Renishaw, England) with excitation laser beam wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS)

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