



# Three-dimensional graphene sheets with NiO nanobelt outgrowths for enhanced capacity and long term high rate cycling Li-ion battery anode material

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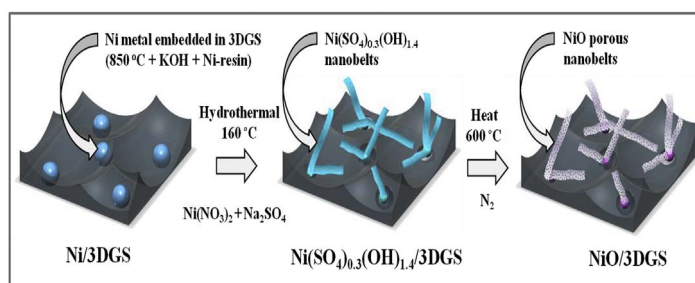
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## HIGHLIGHTS

- NiO nanobelt outgrowths are seeded from 3D graphene sheets (3DGS).
- NiO/3DGS has high rate longterm cycling stability as Li-ion battery anode material.
- 3DGS and strong NiO attachment buffer volume change in NiO nanobelts during cycling.
- NiO boosts volumetric and specific capacities of 3DGS by 75 and 41%, respectively.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

An efficient synthesis method to grow well attached NiO nanobelts from 3D graphene sheets (3DGS) is reported herein. Ni-ion exchanged resin provides the initial Ni reactant portion, which serves both as a catalyst to form 3DGS and then as a seeding agent to grow the NiO nanobelts. The macroporous structure of 3DGS provides NiO containment to achieve a high cycling stability of up to 445 mAh g<sup>-1</sup> after 360 cycles (and > 112% capacity retention after 515 cycles) at a high current density of 2 A g<sup>-1</sup>. With a 26.8 wt.% content of NiO on 3DGS, increases in specific and volumetric capacity were 41.6 and 75.7% respectively over that of 3DGS at matching current densities. Therefore, the seeded growth of NiO nanobelts from 3DGS significantly boosts volumetric capacity, while 3DGS enables high rate long term cycling of the NiO. The high rate cycling stability of NiO on 3DGS can be attributed to (i) good attachment and contact to the large surface of 3DGS, (ii) high electron conductivity and rapid Li-ion transfer (via the interconnected, highly conductive graphitized walls of 3DGS) and (iii) buffering void space in 3DGS to contain volume expansion of NiO during charge/discharge.

## 1. Introduction

Li-ion batteries (LIBs) are in high demand for use in both portable and transport applications due to their high efficiency and high energy density [1,2]. At present, LIBs primarily use graphite as an anode material due to its low cost, relatively high specific capacity, low anode

voltage, good cycling stability and high coulombic efficiency [3,4]. However, graphite is limited to the theoretical specific capacity of LiC<sub>6</sub> (372 mAh g<sup>-1</sup>) and has limited rate capability and poor cycling stability at high current densities [5,6]. Therefore, to help increase the charging speed of LIBs (e.g. as required for widespread acceptance of electric vehicles), developing anode material of longer term higher rate

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cycling stability than graphite is of practical interest.

Transition metal oxides such as CuO, Fe<sub>3</sub>O<sub>4</sub>, CoO and NiO are promising alternative LIB anode materials due to their high theoretical specific capacities [7–9]. NiO has attracted much attention due to its high theoretical specific capacity (718 mAh g<sup>-1</sup>), low cost, and high volumetric capacity (due to NiO having at least three times higher density than graphite) [7–12]. However, like many transition metal oxides, NiO suffers structural degradation due to large volume change during charge/discharge and due to its low electron conductivity and low Li-ion diffusion coefficient; thus, as an isolated electrode material it has poor cycling performance and rate capability [13–15]. To improve the electrochemical performance of NiO, carbonaceous materials such as CNTs [16], porous carbon [17], graphene [18], CMK-3 [19] etc., offer high electrical conductivity and mechanical flexibility as a supporting matrix [20–23]. Many previous studies have focussed on graphene as a support due to its excellent electronic conductivity, high electrochemical stability, strong mechanical properties, and large theoretical surface area [18,24,25]. Furthermore, Li-ions can be stored on both sides of the graphene sheet and at other defects in graphene. Thus, the theoretical specific capacity of graphene can be twice or more than that of graphite, e.g. LiC<sub>3</sub> thus forms a high capacity and highly conductive support [26]. However, at high current density, bare graphene has poor cycling stability and low reversible specific capacity. This is due to its 2D structure, which tends to restack or aggregate through van der Waals forces [27], resulting in decreased surface area (< 100 m<sup>2</sup> g<sup>-1</sup>) for Li-ion storage. Previous studies indicate that decorating NiO particles on graphene supports long term cycling at low current density, wherein NiO presumably helps hold the layers apart and prevents restacking [26,28]. However, there appears to be no reports where NiO/2DG hybrids were cycled long term (e.g. > 100 cycles) at or above 1 A g<sup>-1</sup> (Table S1), which may reflect poor cycling stability at high current density.

Only a few recent studies have reported long term high rate performance in NiO/carbon hybrids. Most recently, Xu et al. [16] achieved over > 95% capacity retention at 502 mAh g<sup>-1</sup> for 300 cycles at 2 A g<sup>-1</sup> in a CNT-MOF-derived NiO/carbon hybrid. Furthermore, Feng et al. [12] reported electrodeposited sandwich-like NiO/C arrays on Ti foil of outstanding rate performance and cycling stability of ~1250 mAh g<sup>-1</sup> at 1 A g<sup>-1</sup> with > 90% retention after 300 cycles. These results categorically show excellent high rate long term cycling stability. However, the synthesis procedures for these composite NiO/carbon structures are either quite costly or challenging (involving CNT/MOF synthesis and electrodeposition on Ti foil respectively) particularly for bulk synthesis of battery electrode material. Therefore, matching such high performance with a cost effective synthesis method is a logical next step in this field of research.

Recently, 3D graphene, (3DG), has drawn much attention both as an electrode material and as a support for metal oxides. 3DG not only offers the intrinsic merits of 2D graphene, but also solves the aggregation problem, improves electrolyte penetration, and particularly in the special case of interconnected 3D porous morphology, provides short Li-ion diffusion distances [29–31]. However, its synthesis is again challenging typically requiring e.g. CVD of high energy low yield [31], costly templates [32], hydrogel/freeze drying [33]. Furthermore, solid metal oxide particles can agglomerate on 3DG during lithiation/delithiation resulting in poor electrochemical performance [18], and insufficient immobilization/containment of the particles can cause their detachment [34]. Therefore, the development of a 3DG-metal oxide hybrid where these issues are solved is of significant interest.

Herein, a bulk 3D graphene sheet (3DGS) synthesis procedure is modified conveniently to seed NiO nanobelts from the 3DGS structure. The method uses the Ni component in a Ni-ion exchanged resin for both graphene sheet catalysis and seeding of well attached NiO nanobelts throughout the 3DGS. In evaluating the synthesis method, the role of Ni and KOH in 3DGS formation is examined along with the effect of NiO wt.% loading on cycling performance. An optimal NiO wt.% loading of

26.8 wt.% was found to produce best overall cycling performance showing a synergistic effect of 22.1% over the expected total theoretical specific capacity contribution of the NiO and 3DGS. The presence of NiO raised the specific and volumetric capacity of the 3DGS by 41.6 and 75.7% respectively at matching current densities for the bare 3DGS and NiO/3DGS material. In accordance with the well-contained nature of the seeded NiO nanobelts, NiO/3DGS achieved excellent cycling stability at high rate over 500 cycles.

## 2. Experimental section

### 2.1. Synthesis of Ni/3DGS and 3DGS

Nickel embedded in 3D graphene (Ni/3DGS) was prepared from a macroporous acrylic-type cation-exchange resin exchanged with Ni<sup>2+</sup> followed by heating with KOH-activation. All chemical reagents were of analytical grade and directly used as purchased without further purification. The cation-exchange resin (50 g) was soaked in nickel chloride hexahydrate solution (0.6 mol L<sup>-1</sup>, 70 mL) with magnetic stirring for 6 h, then filtered and dried at 80 °C for 12 h. The dried Ni-ion exchanged resin (50 g) was then added to 100 mL deionized water containing 50 g of KOH and magnetically stirred at 90 °C for 12 h to evaporated the water. Finally, the dried mixture was heated in a tube furnace in flowing N<sub>2</sub> atmosphere at a heating rate of 5 °C min<sup>-1</sup> to 850 °C (held for 2 h). After cooling to room temperature, the Ni/3DGS product was filtered and washed with deionized water to a rinse value of pH 7, and then dried at 90 °C for 12 h 3DGS without Ni was prepared by washing the Ni/3DGS sample in 2 mol L<sup>-1</sup> HCl followed rinsing in deionized water and drying as before.

### 2.2. Preparation of Ni(SO<sub>4</sub>)<sub>0.3</sub>(OH)<sub>1.4</sub>/3DGS

Ni(SO<sub>4</sub>)<sub>0.3</sub>(OH)<sub>1.4</sub>/3DGS was prepared from Ni/3DGS as follows. Nickel nitrate (1.0 mmol) and sodium sulfate (0.5 mmol) were dissolved in 20 mL of deionized water and stirred for 5 min. The solution was then transferred to a 25 mL Teflon-lined stainless steel autoclave with 300 mg of the Ni/3DGS powder and stirred for 10 min. Heating at 160 °C for 12 h enabled hydrolysis and etching in a self-sustained cycle reaction, after which the autoclave was naturally cooled to room temperature. The product was washed with deionized water several times to remove impurities and then dried at 80 °C for 12 h. The detailed reaction principle and formulae are provided in the [Supporting information](#).

### 2.3. Preparation of NiO/3DGS from the Ni(SO<sub>4</sub>)<sub>0.3</sub>(OH)<sub>1.4</sub>/3DGS precursor

The final NiO/3DGS product was prepared by heat treatment of the Ni(SO<sub>4</sub>)<sub>0.3</sub>(OH)<sub>1.4</sub>/3DGS precursor in flowing N<sub>2</sub> at a heating rate of 10 °C min<sup>-1</sup> to 600 °C (held for 2 h) followed by cooling to room temperature.

### 2.4. Electrode preparation and electrochemical measurements

The electrochemical performance of NiO/3DGS as a Li-ion battery anode in half-cell format was evaluated in 2016-size coin cells. All cells were assembled in a glove box with argon atmosphere. The cells comprised lithium metal as a counter/reference electrode, Celgard 2325 as separator, with 1 mol L<sup>-1</sup> LiPF<sub>6</sub> in dimethyl carbonate (DMC) and ethylene carbonate (EC) (1:1 in volume) as electrolyte. The working electrode slurry comprised 80:10:10 wt.% active material (e.g. NiO/3DGS), Super P, 10binder polyvinylidene difluoride (PVDF), and N-methyl-2-pyrrolidone (NMP) as the liquid component. The slurry was uniformly coated on copper foil current collectors at a spreading thickness of 150 μm, and finally dried at 85 °C for 10 h in a vacuum oven to yield a typical loading density of 0.903 mg cm<sup>-2</sup> total solids

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