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Self-organized amorphous titania nanotubes with deposited graphene film like a new heterostructured electrode for lithium ion batteries

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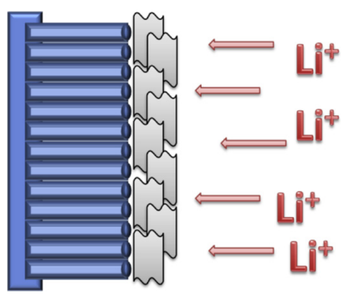
HIGHLIGHTS

- A novel nanotube-TiO_2/graphene heterostructure has been synthesized.
- Graphene-self organized titania nanotube electrodes display superior lithium storage capacity than bare titania nanotubes.
- Charge–discharge possible up to 300 C rate.

GRAPHICAL ABSTRACT



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ABSTRACT

Heterostructures composed of reduced graphene oxide and self-organized titania nanotubes (nt-TiO_2) are examined as novel electrode material for lithium-ion batteries. The novelty here resides in the deposition of a graphene-like film on self-organized nanotubes and that, as compared with previous materials, the differences in behavior are significant as the heterostructure combines previously reported advantages of self-organized nt-TiO_2 with those emerging from the graphene composites. The preparation of this nt-TiO_2/graphene hybrid electrode material is described here. The deposition of a graphene film on self-arranged amorphous nt-TiO_2 was confirmed by using SEM, Raman spectroscopy and mapping of composition. Lithium test cells display capacities that can exceed 300 mAh g^{-1} over 100 cycles and that are therefore superior to those of bare nt-TiO_2 and anatase or rutile TiO_2–graphene hybrid nanostructures. The excellent rate performance of these electrodes makes charge–discharge possible up to at least 300 C-rate. The impedance spectra show that the graphene-like film improves the interface properties in the hybrid electrode. In addition to the environmentally friendly nature of the active electrode material, the moderate working voltage offers an important safety advantage in that it protects the battery from the electroplating phenomena.

1. Introduction

Energy storage is currently a key parameter in the global economy due to the need for an efficient use of renewable energy in a variety of fields such as sustainable transportation and mobile electronics to name just two. Lithium-ion batteries are prominent electrochemical electricity storage devices that are under constant development. The future of lithium-ion batteries will probably be governed by environmental and sustainability issues and the continuous improvements in the energy and power density.

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Table 1
Characteristics of GO determined by Raman spectroscopy, XRD and fitted results of the C1s core level XPS spectra, C/O ratio and the carbon content of the GO.

		Raman			XRD	
		W_D	W_G	I_D/I_G	d_{001}	Lc
GO		1344 cm^{-1}	1603 cm^{-1}	0.91	0.853 nm	7.48 nm
XPS						
C/O	C	Csp^2 (284.5 eV)	Csp^3 (285.5 eV)	C–O (286.1 eV)	C–O–C C=O (287.0 eV)	C(O)OH (288.5 eV)
2.3	68.6%	35.7%	9.2%	26.1%	17.3%	11.7%

In recent years, graphene and graphene derivatives have been thoroughly tested in a wide variety of applications and sometimes with surprising success. Graphene has also made headway in the field of lithium batteries about which several interesting reports can be found in the literature [1–7]. Unable to intercalate, monolayer graphene is able to store lithium ions on the surface by a non-faradic mechanism which provides similar energy densities to Li-ion batteries but with even higher power densities [2]. In conjunction with other electroactive materials, hybrid nanostructures provide extremely high capacities. Insertion, alloying and conversion active oxide materials have been tested. Chen et al. recently reported graphene wrapped SnCo nanoparticles [8]. Conversion electrodes such as cobalt [9], manganese [10], iron [11], and nickel [12] oxides display a highly improved electrochemical behavior when wrapped with graphene layers, which yields capacities close to those of Li–Sn intermetallics [13]. An insertion electrode material such as anatase TiO_2 doubles its capacity at high rates when a graphene network is embedded in the oxide electrode [14]. The encapsulation of TiO_2 nanoparticles with carbon has been proposed [15]. A composite of single-wall carbon nanohorns and nanoporous anatase TiO_2 was proposed by Xu et al. [16].

Titanium dioxide in the form of nanoparticles can exhibit superior electrochemical performance because of the short diffusion path and more sites for lithium accommodation [17]. Self-organized TiO_2 nanotubes (nt-TiO_2) are known to be prepared by anodization procedures [18], and were recently found to perform very well in lithium microbatteries, particularly before being crystallized into an anatase structure [19–21]. Further studies have shown how to combine this material in nanocomposites with other alloying (Sn) [22] and conversion (Fe_2O_3) [23] electrode materials.

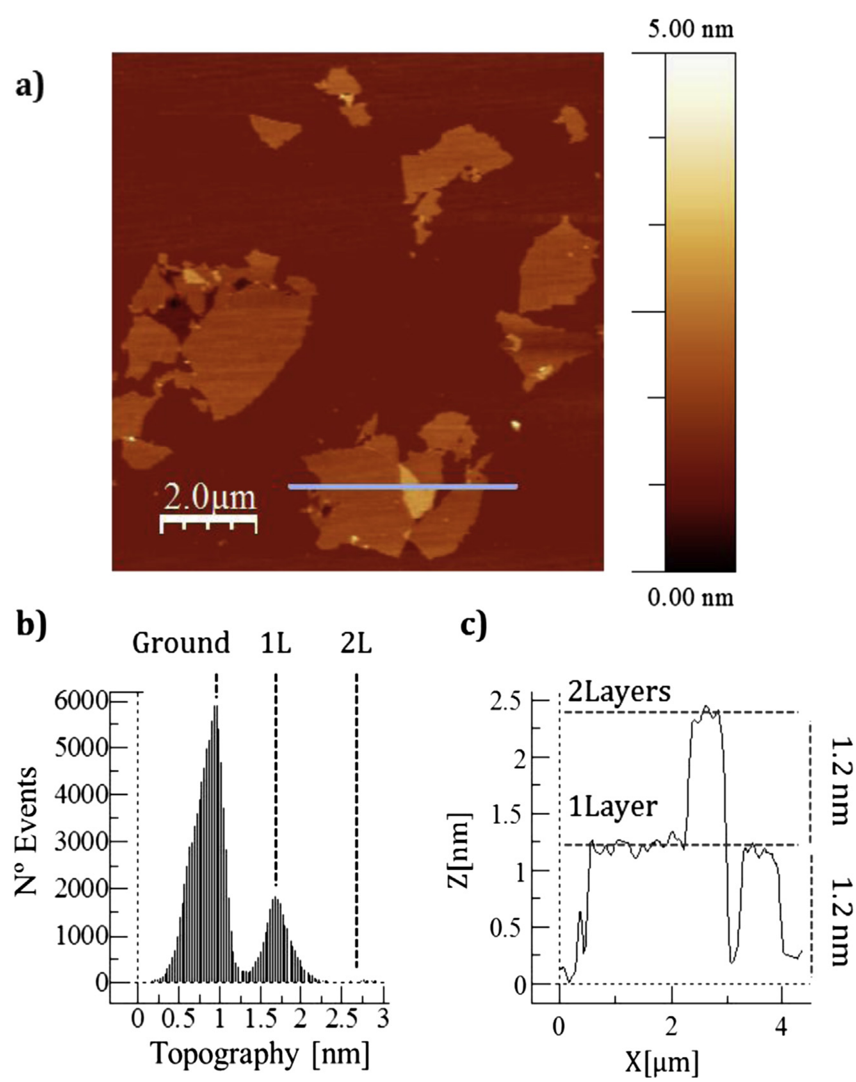

Fig. 1. (a) AFM image of GO, where the horizontal line indicates the sections corresponding to the trace shown on the right. (b) Histogram showing the height distributions of the sheets analyzed. (c) Graphene layer number as a function of the distance.