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Phase and Dimensionality of Tin Oxide at graphene nanosheet array and its Electrochemical performance as anode for Lithium Ion Battery

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A B S T R A C T

We incorporated tin oxide nanostructures into the graphene nanosheet matrix and observed that the phase of tin oxide varies with the morphology. The highest discharge capacity and coulumbic efficiency were obtained for SnO phase of nanoplates morphology. Platelet morphology of tin oxide shows more reversible capacity than the nanoparticle (SnO_2 phase) tin oxide. The first discharge capacity obtained for SnO@GNS is 1393 and 950 mAh/g for SnO_2@GNS electrode at a current density of 23 μA/cm^2. A stable capacity of about 1022 and 715 mAh/g was achieved at a current rate of 23 μA/cm^2 after 40 cycles for SnO@GNS and SnO_2@GNS anodes, respectively.

1. Introduction

For compact, light-weight and powerful portable electronic devices needs the development of small and safe lithium ion batteries (LIBs) with high capacity [1–3]. As an n-type semiconductor with a wide band gap (Eg = 3.6 eV), tin oxide (SnO_2) has been known as a promising candidate for LIB anode applications due to its capability of reversibly forming alloys with lithium [4,5]. Apart from graphite, the most commercialized anode material in Li-ion battery (LIB), SnO_2 has a much higher theoretical specific lithium storage capacity of 790 mAhg^{-1} than graphite (274 mAh/g).

The main disadvantage for the use of tin based anodes in commercial application in LIBs is the large volume change during charge/discharge processes which leads to poor cyclability [6,7]. Large volume changes during lithiation and delithiation leads to the particle disintegration of SnO_2 and results in the poor cyclability. One of the many possible strategies to overcome the volume changes or the pulverization problem and maintain the structural stability is, to design porous nanostructures of SnO_2. Xiong Wen et al. synthesized template free SnO_2 hollow nanostructures and showed high Li storage capacity of 1140 mAhg^{-1} [8]. The use of hollow nanostructures of SnO_2 could provide more lithium storage capacity than that of pristine SnO_2 nanoparticles (645 mAhg^{-1}) [9]. This kind of hollow structure without a supporting matrix will be easily broken down during the reaction cycles [10]. In view of this, a continuous matrix layer has been suggested to be used to coat the SnO_2 hollow structures in an attempt to hold the SnO_2 hollow structure integrity [11]. Among many of the matrix materials, carbon has been definitely the most popular candidate due to its flexibility, good electronic conductivity and excellent compatibility with electrode applications [12,13]. Another approach is to cover electronically conductive layer, such as carbon.

In the present study, we developed an electrode with tin oxide nanostructures embedded in Graphene nanosheet (GNS) array through reactive e-beam evaporation of Sn granules in oxygen atmosphere. The morphology and phase of the Tin oxide particle varies with evaporation rate of tin granules. The Tinoxide@GNS anode was employed as anode for studies on Li-ion battery. By reducing the metal particle size to a nanometric level and supporting with porous graphene sheet matrix, the volume change may be controlled and the lithium diffusion length greatly reduced, thus improving the performance of the electrode in terms of both life and rate capability [3,14].

2. Experimental

The active material, Tin oxide@GNS has been made by two step process. At first, graphene nanosheet (GNS) was synthesized on copper substrate (cu foil of 12 mm diameter and 125 μm thick, Sigma Aldrich) through microwave plasma CVD technique, details of which given in our previous publication [15]. Further deposition of tin oxide nanoparticle was carried out via reactive e-beam evaporation of tin granules (Alfa Aesar, 99.99%) in oxygen ambience at a substrate temperature of 600^{0}C. The crucible containing Sn granules was placed 20 cm below the substrates and an

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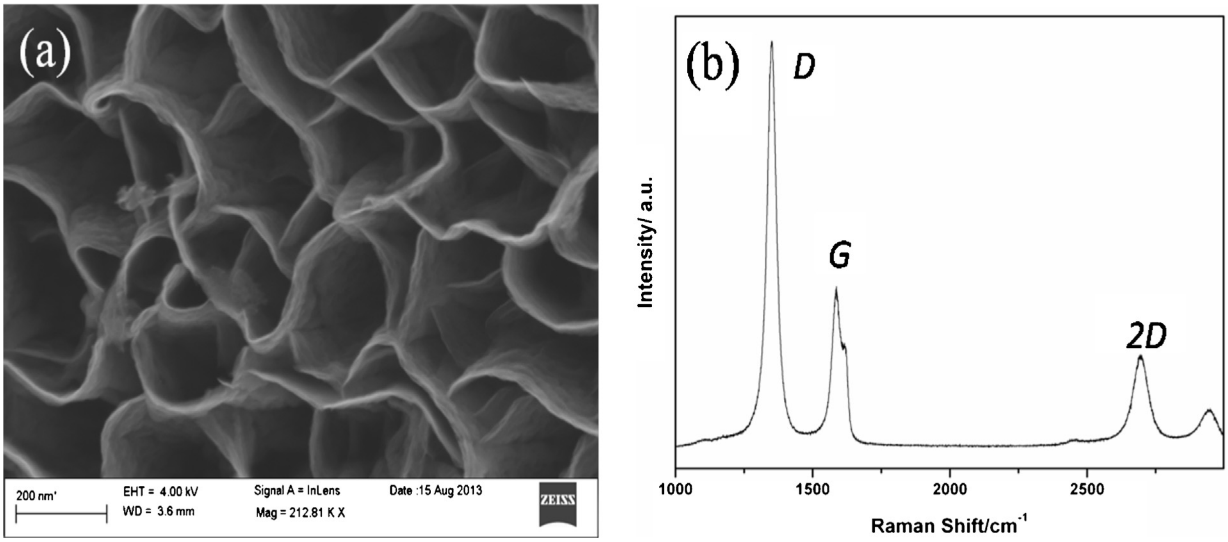

Fig. 1. (a) Scanning electron image of vertically grown graphene nanosheet (GNS) array and (b) raman spectra of GNS.

accelerating voltage of 5 kV was applied to e-beam with emission current of 25 mA and evaporation was carried out at ~2.2 A°/s. The oxygen partial pressure has been maintained constantly at 4×10^{-4} mbar during the growth. The deposition was carried out for 20 minutes of time. After the deposition, the mass of the tin oxide deposited was about 7.3×10^{-5}g as against the mass of GNS which is about 2.7×10^{-5} gms.

For the deposition of nanoplatelets of tin oxide, the evaporation rate of tin granules was increased to ~ 8 A°/s and maintained the same oxygen partial pressure. The substrate temperature was kept at 600^{0}C and the deposition was carried out to 10 minutes of time. In this case, after the deposition, the mass of the tin oxide deposited was about 8.2×10^{-5}g as against the mass of GNS which is about 1.7×10^{-5} gms.

Electrochemical studies were carried out with half cells (swagelok type) using CH instruments work station (Model CHI660 C) with in potential range 0.01- 2 volts Vs (Li^+/Li). Both SnO_2@GNS and SnO@GNS are used as working electrodes and lithium metal foil as reference and counter electrode. 1 M $LiPF_6$ salt dissolved in 1:1(v/v) mixture of ethylene carbonate and dimethyl carbonate (EC: DMC) used as the electrolyte. The active area of the electrode was ~1.13 cm^2.

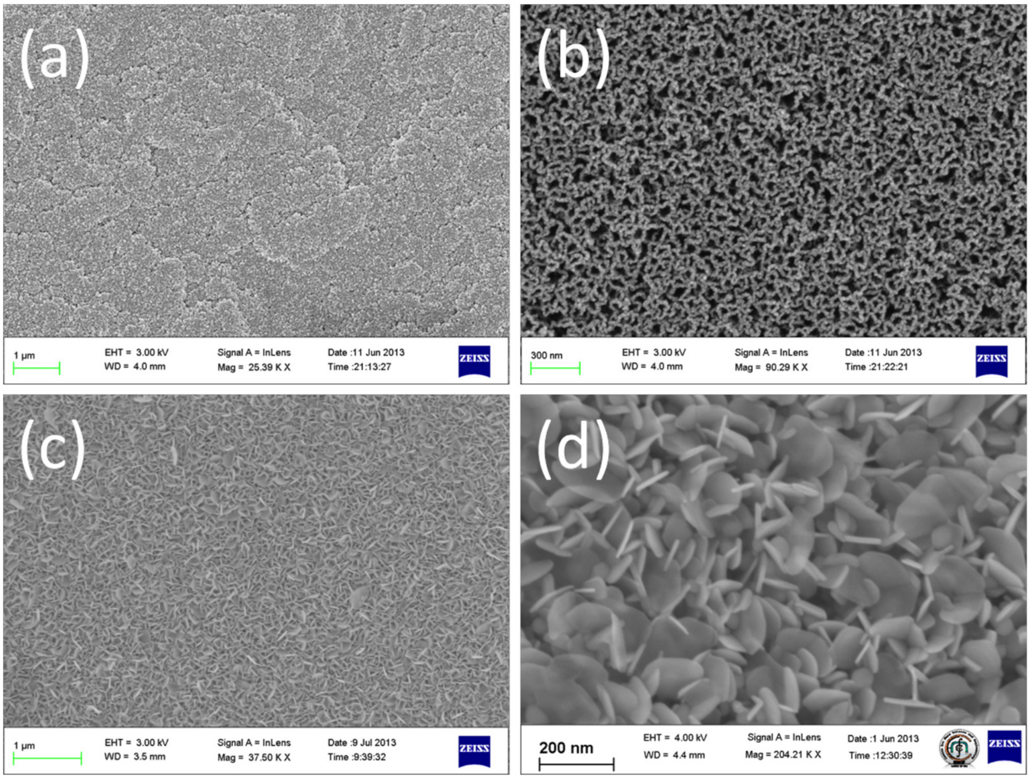

Fig. 2. SEM image of Tin Oxide nanostructures on GNS. (a and b) SnO_2 @GNS nanoparticles and (c and d) SnO@GNS nanoplatelets.