

Synthesis of lithium–graphite nanotubes – An *in-situ* CVD approach using organo-lithium as a precursor in the presence of copper



Vivek Dhand^a, Mandapati Venkateswar Rao^b, Garima Mittal^a, Kyong Yop Rhee^{a,*},
Soo Jin Park^{c,*}

^a Department of Mechanical Engineering, College of Engineering, Kyung Hee University, 446-701 Yongin, Republic of Korea

^b CEN, IST, JNTUH, Kukatpally, Hyderabad 500 085, India

^c Department of Chemistry, Inha University, Incheon, Republic of Korea

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ABSTRACT

An *in-situ* approach to synthesize lithium–graphite nanotubes (LGN) is demonstrated using chemical vapour deposition (CVD). Lithium acetate was used as precursor and as a self-intercalating agent in the presence of copper. Methane was selected as the secondary carbon source. To synthesize lithium–graphite nanotubes (LGN), CVD reactor was set to 500 °C in the presence of argon (200 sccm), hydrogen (40 sccm) and methane (75 sccm) gas under atmospheric conditions. X-ray diffraction shows that the samples are highly crystalline with the *c*-axis oriented toward the (002) and (111) planes of the graphitic carbon. High resolution transmission and scanning electron microscopic analyses of the samples shows that lithium has been doped into the layers of graphitic carbon matrix. They also show the formation of an alloy phase with distinctive lattice boundaries and stacked graphitic carbon with a small number of nanorods (lithium carbide). HR-Raman analysis shows the characteristic D and G bands of SP² carbon with a narrow G band and broad D band indicating defects produced through doping. X-ray photoelectron spectroscopy results show the presence of predominant lithium and carbon peaks. Thermal analysis shows that the sample is stable up to 300 °C in air.

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1. Introduction

Graphitic carbon, an allotrope of carbon with a sp² arrangement of atoms in hexagonal symmetry, forms a two-dimensional (2D) layered sheet arranged parallel to its plane [1]. This layered structure shows unique chemical and physical properties, including high specific surface area [2,3]. Due to these unique properties, graphitic carbon-based nanostructures have sparked global interest in the mass production (synthesis routes), characterization, analysis, properties, and a broad spectrum of applications. Since its discovery [4], several synthesis routes have been employed from the classic Hummer's method [5] to the exfoliation method. These routes include chemical vapour deposition (CVD) [6], pyrolysis and solvothermal route [7], electrolytic synthesis [8], and exfoliation [9].

Presently, much of the research on graphitic carbon is focused on alternative energy sources and forms. Along these lines,

graphitic carbon is a potential electrode material for lithium ion batteries due to its superior electrochemical properties, affordability, stability and benign nature [1,10,11]. Intercalation of nano-carbon using alkali metals has long been in use. Many of these alkali metals easily intercalate into graphite to create doped graphitic carbon layers [12,13]. Research has shown that graphitic carbon layers have a theoretic Li-storage capacity of 744 mAh/g if the lithium ions are attached on both sides of the graphitic carbon sheets [14]. Several attempts have been made to dope graphitic carbon with various nano-metals [15–17] or metaloxides [17–20]. The embedded nanomaterials within the graphitic carbon sheets have the ability to prevent further aggregation or stacking of the doped nano-sheets. This also helps in maintaining high surface area with improved electrochemical performance. Based on the intercalation and the type of doping material, these composite structures could therefore have possible applications in hydrogen storage, super-capacitors, and lithium ion batteries (LiB) [21–24] to name a few.

In this paper, authors present an *in-situ* approach to directly produce lithium–graphite nanotubes (LGN) from the reduction of

* Corresponding authors.

E-mail addresses: rheeky@khu.ac.kr (K.Y. Rhee), sjpark@inha.ac.kr (S.J. Park).

lithium acetate and methane gas in a thermal CVD reactor. This paper elucidates the properties and activity of organo-lithium catalyst for the synthesis of LGN by thermal reduction in CVD. The prepared sample will be utilized as energy storage devices for performance assessment in cyclic studies.

2. Experimental section

2.1. Reagents and instruments

Lithium acetate dihydrate (99.99%) was purchased from Sigma Aldrich, South Korea. The reaction gases: hydrogen (99.999%), argon (99.999%) and methane with 99.95% purity were purchased from Union Gas Korea. A 0.025 mm thick annealed uncoated 99.8% pure copper foil was purchased from Alfa Aesar, South Korea. A mixed-type mechanical grade Si wafer (100) from Wafernet Inc. (USA) with 0–100 Ω -cm resistivity and a thickness of 750–800 mm was utilized for XPS analysis. Automated thermal CVD equipment, from Scientific Engineers (S. Korea) was utilized to synthesize lithium doped graphitic carbon composites.

3. Experiment

Lithium acetate dihydrate (0.3 g or 1.0 g) was weighed and immediately stored in a box made of 4 cm \times 4 cm copper foil which is 1-mm in its thickness. The material was then transferred into an ethanol and acetone cleaned CVD quartz tube and was sealed. The chamber was then evacuated very slowly in order to maintain the correct position of the foil with lithium acetate at the center of the furnace. The flow rates of argon (200 sccm), hydrogen (40 sccm) and methane (75 sccm) gas were set, and the experiment was initiated under atmospheric conditions. The temperature of the experimental chamber was then set to 500 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C per minute. Throughout the experiment, argon gas was continuously released at a constant rate in order to maintain an inert atmosphere. When the temperature reached \sim 150 $^{\circ}$ C, hydrogen (40 sccm) was released into the chamber; this enabled reduction of acetate and helped in dehydrating the precursor. Lithium acetate was chosen as a precursor for this experiment

because of its charge transfer properties, fast reactivity and non-corrosive behaviour [25]. When the final temperature (500 $^{\circ}$ C) was reached, methane (75 sccm) was released into the chamber, and the reaction continued for 30 min. After the reaction time was completed, only hydrogen and methane were stopped. The chamber was then allowed to cool to room temperature in the presence of argon, and the sample was then scratched from the foil, weighed and subjected to further analysis using the following instrumentation: X-ray diffraction (XRD, D8 Discover with GADDS-Bruker), field emission scanning electron microscopy (FE-SEM, LEO SUPRA 55, GENESIS 2000 (Carl Zeiss, equipped with EDAX), field emission transmission electron microscopy (FE-HRTEM, JEM-2100F-JEOL equipped with Oxford INCA EDS), thermogravimetric analysis (TGA Q5000 IR/SDT Q600-TA), high resolution Raman spectroscopy (RENISHAW In-via Raman), X-ray photoelectron microscopy (XPS, K-Alpha-Thermo Electron) and Veeco (D3100), USA AFM Instrument.

4. Results and discussions

4.1. X-ray diffraction (XRD)

Fig. 1 represents X-ray diffractograms of LGN obtained using 0.3 g and 1.0 g of lithium acetate as a precursor. Sample 1 (0.3 g) and Sample 2 (1.0 g) shows the characteristic (021) lithium carbide (LiC) phase (JCPDF # 14–0649) at a 2-theta angle of 21.3 $^{\circ}$ along with (111) and (002) planes of graphitic carbon (JCPDF # 89-8488 and 89–8491) at 31.7 $^{\circ}$ and 31.8 $^{\circ}$ respectively, and a (101) plane of lithium carbide (JCPDF # 65–2529) at a 2-theta angle of 30.6 $^{\circ}$. The presence of a LiC phase at several 2 theta angles in both the samples implies that lithium intercalated well within the graphitic carbon layers. The XRD results are also in good agreement with the FE-SEM and HRTEM analysis. Based on these observations, Udod et al. (1992) conditionally divided the chemical reaction during intercalation into two processes: (i) real intercalation of atoms occurring within the inter-planar regions of graphite, and (ii) filling up of the inter-crystalline regions by the alloy composite (LiC in our case). In this model, the later process is slower than the former. The first step results in a non-equilibrium reaction characterized as a “quasi-gas

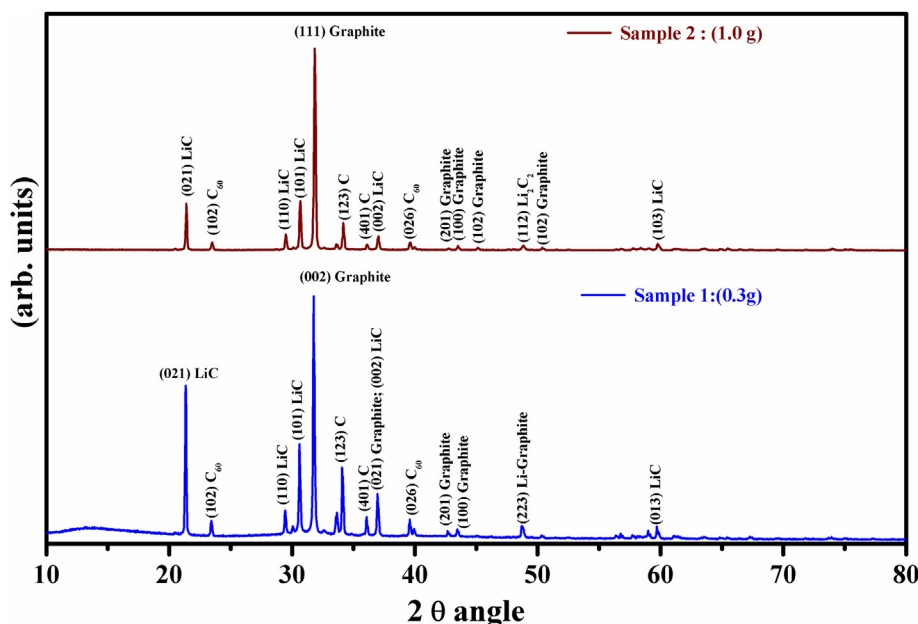


Fig. 1. X-ray diffraction patterns of lithium graphite nanotubes (LGN) synthesized using 0.3 g and 1.0 g lithium acetate as precursor.

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