



# Evolution of the chemical bonding nature and electrode activity of indium selenide upon the composite formation with graphene nanosheets



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## ABSTRACT

Evolution of the chemical bonding nature and electrochemical activity of indium selenide upon the composite formation with carbon species is systematically investigated. Nanocomposites of  $\text{In}_4\text{Se}_{2.85}$ @graphene and  $\text{In}_4\text{Se}_{2.85}$ @carbon-black are synthesized via a solid state reaction between In and Se elements, and the following high energy mechanical milling of  $\text{In}_4\text{Se}_{2.85}$  with graphene and carbon-black, respectively. The high energy mechanical milling (HEMM) of  $\text{In}_4\text{Se}_{2.85}$  with carbon species gives rise to a decrease of particle size with a significant depression of the crystallinity of  $\text{In}_4\text{Se}_{2.85}$  phase. In contrast to the composite formation with carbon-black, that with graphene induces a notable decrease of (In–Se) bond covalency, underscoring significant chemical interaction between graphene and  $\text{In}_4\text{Se}_{2.85}$ . Both the nanocomposites of  $\text{In}_4\text{Se}_{2.85}$ @graphene and  $\text{In}_4\text{Se}_{2.85}$ @carbon-black show much better anode performance for lithium ion batteries with larger discharge capacity and better cyclability than does the pristine  $\text{In}_4\text{Se}_{2.85}$  material, indicating the beneficial effect of composite formation on the electrochemical activity of indium selenide. Between the present nanocomposites, the electrode performance of the  $\text{In}_4\text{Se}_{2.85}$ @graphene nanocomposite is superior to that of the  $\text{In}_4\text{Se}_{2.85}$ @carbon-black nanocomposite, which is attributable to the weakening of (In–Se) bonds upon the composite formation with graphene as well as to the better mixing between  $\text{In}_4\text{Se}_{2.85}$  and graphene. The present study clearly demonstrates that the composite formation with graphene has strong influence on the chemical bonds and electrode activity of indium selenide and the HEMM process with graphene nanosheet is fairly useful in exploring excellent electrode materials of metal chalcogenide–carbon nanocomposite for lithium ion batteries.

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## 1. Introduction

An exploration of new efficient anode materials is one of the most important issues for the researches of lithium secondary batteries [1–3]. While the cathode material working at high potential should be operated in terms of intercalation–deintercalation mechanism, the low working potential of anode material allows the contributions of diverse working mechanisms such as conversion, alloying–dealloying, intercalation–deintercalation, etc

[4–6]. As an alternative anode material for replacing currently-commercialized graphite, many kinds of inorganic materials such as metal elements and metal oxides are investigated because of their large theoretical capacity [7–16]. Similarly large numbers of layered metal chalcogenides are explored as intercalation anode materials for lithium secondary batteries [17–20]. However, there is still a plenty of room for the development of new efficient anode materials from non-layered metal chalcogenide operating in terms of non-intercalative mechanism, since only a few studies are carried out for this type of materials [21–23]. Despite their large theoretical discharge capacity, the electrode materials relying on non-intercalative mechanism suffer from severe capacity fading, which originates from remarkable volume change upon electrochemical cycling [4,24]. Such drawbacks of these materials can be relieved by the formation of nanocomposites with carbon species

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[25–27]. In addition, a coupling with highly conductive carbon species is fairly effective in improving the rate characteristics of metal chalcogenide [28–30]. The composite formation with conductive carbon would be easily achieved by a facile mechanical milling between electrode material and carbon species [31]. Additionally, high energy mechanical milling (HEMM) process can induce an effective exfoliation of graphite into graphene, since the shear stress from the ball milling process can overcome the  $\pi$ – $\pi$  stacking interaction between graphene layers [32]. To better understand the role of carbon species on the electrode performance of the resulting metal chalcogenide–carbon nanocomposite, it is quite important to elucidate the variation of chemical bonding nature of metal chalcogenide and carbon upon the composite formation. But at the time of the publication of the present study, we are aware of no systematic study about the synthesis of metal chalcogenide–carbon nanocomposites via mechanical milling method and the evolution of chemical bonding character upon the composite formation.

In the present study, the intimately-coupled nanocomposites of  $\text{In}_4\text{Se}_{2.85}$ @graphene and  $\text{In}_4\text{Se}_{2.85}$ @carbon-black are synthesized by the high energy mechanical milling (HEMM) of bulk  $\text{In}_4\text{Se}_{2.85}$  crystal with graphene and carbon-black (super P). To improve the electrical conductivity and electrode activity of indium selenide phase, the self-doped composition of  $\text{In}_4\text{Se}_{2.85}$  with Se deficiency is adopted for the synthesis of the present nanocomposites. In addition, the Se defect is supposed to act as active sites for interacting with hybridized carbon species. The effects of ball milling and composite formation on the crystal structure and morphology of  $\text{In}_4\text{Se}_{2.85}$  are systematically investigated along with the accompanying variation of chemical bonding nature. The obtained nanocomposites are applied as anode materials for lithium secondary batteries to study the influence of composite formation with carbon species on the electrode activity of indium selenide.

## 2. Experimental

### 2.1. Synthesis

The bulk crystal ingot of n-type  $\text{In}_4\text{Se}_{2.85}$  was synthesized by conventional melting and annealing process with high purity In (>99.999%, CERAC) and Se granules (>99.999%, 5N Plus Materials Inc., USA). The raw materials in an evacuated quartz tube (under  $10^{-4}$  Torr) were congruently melted by torch. Then, two-step annealing of the ingot was performed at 773 K for 48 h, and then at 733 K for 24 h in order to produce a homogenous  $\text{In}_4\text{Se}_{2.85}$  phase. The anion deficiency in the  $\text{In}_4\text{Se}_3$  phase was introduced to enhance its electrical conductivity by n-type self-doping effect. Graphene nanopowder (AO-1, THK~3 nm) was purchased from graphene supermarket inc. (USA). The  $\text{In}_4\text{Se}_{2.85}$ @carbon-black and  $\text{In}_4\text{Se}_{2.85}$ @graphene nanocomposites were prepared by HEMM (Spex-8000) for the mixture of  $\text{In}_4\text{Se}_{2.85}$  and carbon-black/graphene; The pristine  $\text{In}_4\text{Se}_{2.85}$  and carbon-black/graphene were put into a hardened steel vial having a capacity of 80 cm<sup>3</sup> with stainless steel balls (diameter: 3/8" and 3/16", a ball-to-powder ratio of 20:1). The HEMM process was conducted under an Ar atmosphere for 6 h. The mass ratio of  $\text{In}_4\text{Se}_{2.85}$  (ingot):C (graphene or Super P) was adjusted to an optimal value of 7:3. As a reference, the carbon-free ball-milled  $\text{In}_4\text{Se}_{2.85}$  material was prepared by applying the same HEMM process for the pristine  $\text{In}_4\text{Se}_{2.85}$  ingot without carbon species.

### 2.2. Characterization

The crystal structures of the pristine  $\text{In}_4\text{Se}_{2.85}$ , the ball-milled  $\text{In}_4\text{Se}_{2.85}$ , and the  $\text{In}_4\text{Se}_{2.85}$ @graphene and  $\text{In}_4\text{Se}_{2.85}$ @carbon-black

nanocomposites were studied with powder X-ray diffraction analysis (XRD, Rigaku,  $\lambda = 1.5418 \text{ \AA}$ , 25 °C). Elemental analysis (Perkin Elmer 2400 Series II) was carried out to determine the content of carbon species in the present nanocomposites. The evolution of crystal morphology upon the composite formation and HEMM process was examined with field emission-scanning electron microscopy (FE-SEM, Jeol JSM-6701F). High resolution-transmission electron microscopy (HR-TEM) analysis was carried out for the present  $\text{In}_4\text{Se}_{2.85}$ @graphene and  $\text{In}_4\text{Se}_{2.85}$ @carbon-black nanocomposites using a Jeol JEM-2100F electron microscope to probe their composite structures. The chemical bonding nature of the present nanocomposites was studied with X-ray absorption near-edge structure (XANES) experiments at In K- and Se K-edges. The XANES experiment was carried out using extended X-ray absorption fine structure (EXAFS) facility installed at the 10C beam line at Pohang Accelerator Laboratory (PAL) at Pohang in Korea, operated at 2.5 GeV and 180 mA. All the present XANES spectra were collected in a transmission mode using gas-ionization detectors at room temperature with a Si(111) single crystal monochromator. The obtained XANES spectra were energy-calibrated by simultaneously measuring the spectrum of In or Se element. The measured raw data was processed using ATHENA program in the Demeter 0.9.20 package [33]. X-ray photoelectron spectroscopy (XPS) was utilized to characterize the chemical bonding nature of carbon species in the present nanocomposites. The XPS data was recorded with K-alpha (Thermo VG) spectrometer, in which a monochromated Al K $\alpha$  line with the energy of 1486.6 eV was used as an excitation source. The possible spectral modification by charging effect was prevented by using flood gun. The chemical bonding nature of the present nanocomposites was investigated with micro-Raman spectroscopic analysis using Renishaw system 1000 Raman spectrometer with an Ar<sup>+</sup> laser at 514 nm and a 1800 line mm<sup>-1</sup> grating. The  $\text{In}_4\text{Se}_{2.85}$ @graphene and  $\text{In}_4\text{Se}_{2.85}$ @carbon-black nanocomposites as well as the ball-milled  $\text{In}_4\text{Se}_{2.85}$  were tested as anode materials for lithium secondary batteries. For complete removal of water in the electrode materials, the obtained nanocomposites were vacuum-dried at 200 °C for 3 h, since the presence of water has detrimental effect on the electrode performance of the materials through the formation of corrosive HF species. The composite electrode was fabricated with the homogeneous mixture of active nanocomposite material, carbon-black (Super P), and polyvinylidene fluoride (PVDF) binder (80:10:10 mass ratio). The mixture was prepared as slurry in N-methyl-2-pyrrolidone (NMP), pasted on Cu-foil via doctor-blade method, and vacuum-dried at 110 °C for 12 h. After roll-pressing, the composite electrode was assembled with lithium metal in 2016 coin-type cell with an electrolyte of 1 M LiPF<sub>6</sub> solution in ethylene carbonate (EC):diethyl carbonate (DEC) (50:50 v/v). All the galvanostatic charge–discharge cycling experiments were performed in a galvanostatic mode with the potential range of 0.01–3.0 V. Several current densities of 100–3200 mA g<sup>-1</sup> were applied to study the rate characteristics of the present nanocomposites. All the galvanostatic charge–discharge cycling data were measured with WBCS 3000 Battery cyler (WonATech). The electrochemical impedance spectroscopy (EIS) analysis was performed using IVIUM impedance analyzer with the frequency region of 0.1–10<sup>5</sup> Hz to probe the effect of composite formation on the electrical transport property of indium selenide.

## 3. Results and discussion

### 3.1. Powder XRD measurements and elemental analysis

Fig. 1 represents the powder XRD patterns of the pristine  $\text{In}_4\text{Se}_{2.85}$ , the carbon-free ball-milled derivative, and the nanocomposites of  $\text{In}_4\text{Se}_{2.85}$ @graphene and  $\text{In}_4\text{Se}_{2.85}$ @carbon-black.

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