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Scanning transmission electron microscopy analysis of Ge(O)/(graphitic carbon nitride) nanocomposite powder

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ABSTRACT

Analytical electron microscopy has revealed the structure of particles that were synthesized by chemical reaction of GeO_2 with $NaBH_4$ in the basic solution including graphitic carbon nitride (g-C_3N_4) powders. The g-C_3N_4 was arranged by recrystallization of melamine at 600 °C under N_2 gas atmosphere. The samples were dried at 60 °C or 180 °C for 4 h. The g-C_3N_4 was observed as lamellae of several ten nm or less in size and had an amorphous-like structure with a distorted lattice in an area as small as a few hundred pm in size. The reaction product was Ge(O) particles as fine as several nm in size and composed of Ge and O atoms. Most of the particles must be of GeO_{2-x} with the amorphous-like structure that has also a distorted lattice in an area of a few hundred pm in size. In the sample dried at 60 °C, the particles were found to be dispersed in a wide area on the g-C_3N_4 lamella. It is hard to recognize those particles in TEM images. The particles in the sample dried at 180 °C became larger and were easily observed as isolated lumps. Hence, these powders can be regarded as GeO_2/g-C_3N_4 or Ge/GeO_2/g-C_3N_4 nanocomposites, and expected to be applicable to anode materials for high energy Li-ion batteries due to Ge catalysis effect, accordingly.

1. Introduction

Anode materials including Si and Sn have much higher theoretical capacities (4200 and 994 mAh g^{-1}, respectively) than commercial graphite (372 mAh g^{-1}). So, their high performance for Li-ion batteries has been expected. However, the major problem to use these metals is the huge volume change that causes cracking and climbing on the electrode surface [1–2]. To cope effectively with this problem, carbon could be used as supporting materials to buffer their volume change. Composite alloys of $Si_{0.66}Sn_{0.34}$ dispersed in crystalline and amorphous carbon (graphite) matrices were synthesized using wet and dry high-energy mechanical millings, respectively [1]. The composites resulted in reversible discharge capacities as high as 800 mAh g^{-1} with a capacity retention of 1.36% loss/cycle. Chou et al. prepared a Si/graphene composite by simply mixing of commercially available nanosize Si and graphene [3]. The Si/graphene composite maintained a capacity of 1168 mAh g^{-1} and accommodated to large volume charge of Si, keeping good electronic contact. Sn/graphene nanocomposites were also prepared for enhanced reversible lithium storage in Li-ion batteries and their properties were investigated [4,5].

Graetz et al. reported that amorphous Ge thin films 60–250 nm thick prepared on Ni substrates showed a stable capacity of 1700 mAh g^{-1}, and that Ge nanocrystals with a mean diameter of 12 nm showed reversible gravimetric capacities of up to 1400 mAh g^{-1} [6]. Ge is a promising negative electrode candidate for Li-ion thin-film batteries because of its higher room-temperature Li diffusivity (400 times) than that of Si [6]. The theoretical storage capacity for the lithium saturated germanium phase, $Li_{22}Ge_5$ is very high (1625 mAh g^{-1}). In fact, a fully lithiated crystalline composite, $Li_{15}Ge_4$, from evaporated and sputtered Ge showed a maximum storage capacity of 1385 mAh g^{-1} [7]. The large volume changes that occur during Li ion insertion–deinsertion limit the application of pure Ge as anode materials due to the cell pulverization after a few cycles. However, Ge nanoparticles evenly dispersed on carbon surface can enhance battery capacity and prolong battery life because the volume changes of Ge structure by Li ion insertion can be absorbed by carbon matrix [8].

Seng et al. have noted the catalytic role of Ge in a GeO_2/Ge/C nanocomposite anode material for Li batteries. The GeO_2/Ge/(thin C layer) composite showed high capacities of up to 1860 mAh g^{-1}. This was ascribed to the presence of elemental Ge nanoparticles that increase the reversibility of the conversion reaction of GeO_2 to Ge ($GeO_2 + 4Li^+ \rightarrow Ge + 2Li_2O$) [9]. The catalytic role of Ge was also investigated for synthesized $SnO_2(GeO_2)_{0.13}$/(graphene) nanocomposites, which delivered a capacity as high as 1200 mAh g^{-1} at a current density

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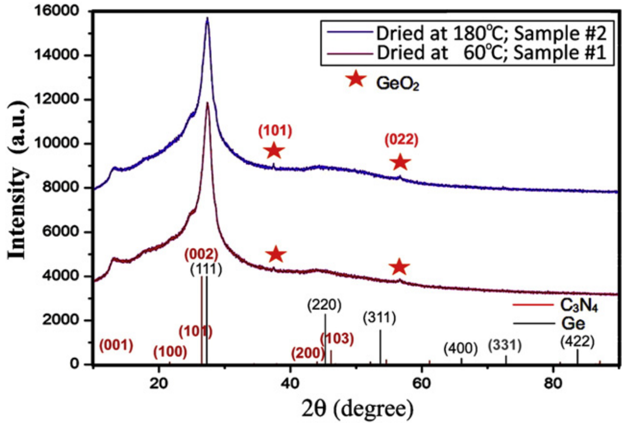

Fig. 1. X-ray diffraction patterns of the samples dried at 180 °C and 60 °C. The reflection peaks of the related powders (from PSD #83-0548 for GeO_2, # 87-1526 for C_3N_4, and #89-5011 for Ge) are indicated for references.

of 100 mA g^{-1} [10]. This enhanced electrochemical performance was attributed to the catalytic effect of Ge, which enabled the reversible reaction of metals (Sn and Ge) to metals oxides (SnO_2 and GeO_2) during the charge/discharge processes. A mesoporous Ge/GeO_2/C that was synthesized by a simple block copolymer directed self-assembly also showed greatly enhanced Coulombic efficiency, high reversible capacity (1631 mAh g^{-1}), and stable cycle life compared with the other mesoporous and bulk GeO_2 electrodes [11].

Recently, graphite-like C_3N_4, graphitic carbon nitride (g-C_3N_4), has attracted considerable attention as a novel organic, metal-free semiconductor applicable to emission devices, surface modification, medical science, photocatalyst, *etc.* [12–14]. The advantage of g-C_3N_4 over graphite materials is the presence of nitrogen lone pair electrons, which can enhance electron conductivity and basic surface functionalities; important properties for catalysts. Moreover, it is the most stable allotrope among carbon nitride compounds at ambient temperature [15]. Many g-C_3N_4 based composites such as g-C_3N_4/Fe_3O_4 [16], g-C_3N_4/TiO_2 [17], g-C_3N_4/ZnO [18], g-C_3N_4/CdS [19], and g-C_3N_4/Au [20], which enhance the photocatalytic activity, were investigated.

g-C_3N_4 based composites are therefore expected to be applied to Li-ion battery anode materials due to the presence of rich electrons on the surface, facilitating electron conductivity and reduction of heat emission from a battery. Thus, we have synthesized Ge·GeO_2/g-C_3N_4 powders by chemical reaction to study the structure. The present paper deals with characterization of the produced nanocomposite powders by means of analytical electron microscopy.

2. Materials and methods

The g-C_3N_4 was prepared by recrystallization of melamine at 600 °C under N_2 (99.99%, TIG) gas atmosphere. The final color was yellow. Ge particles were precipitated by chemical reaction of GeO_2 (99%, Merck) with $NaBH_4$ (98%, Himedia) in the basic solution including the g-C_3N_4 powders. The reaction started by dissolving GeO_2 in deionized water at 90 °C for 4 h. Then 38% NH_4OH was dropped into the solution until the clear solution was observed. After that, a cool $NaBH_4$ solution was added. The reaction was allowed to proceed at ambient temperature for 12 h. After the filtration process, the product was divided to two

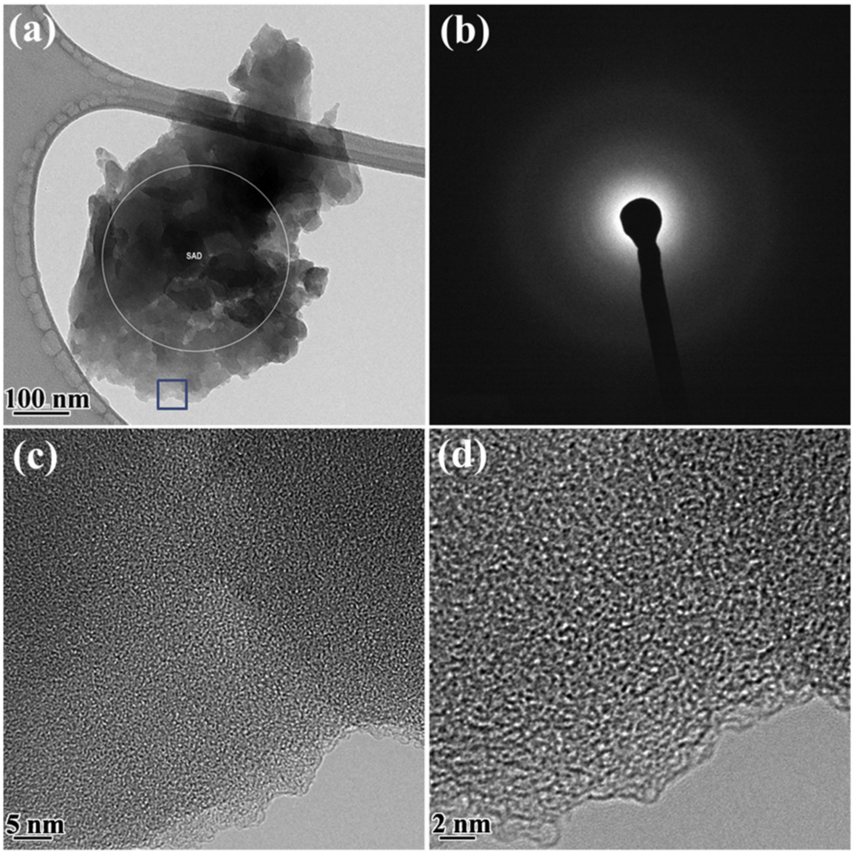

Fig. 2. (a) Low magnification zero-loss (0 ± 5 eV) TEM image of Sample #1, mounted on a holey carbon Cu mesh. (b) Selected area electron diffraction pattern from the circle indicated in (a). (c) and (d) High-resolution TEM images (0 ± 5 eV) in a square indicated in (a).