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Preparation and characterization of expanded graphite/Ag nanoparticle composites for the improvement of thermal diffusion

Seok Hwan Hong and Won Gyu Lee†

Department of Chemical Engineering, Kangwon National University, 1, Gangwondaehak-gil, Chuncheon-si, Gangwon-do, 24341, Korea
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Abstract – Expanded graphite (EG)/Ag nanoparticle composites were synthesized by the chemical reduction of Ag ions, followed by the addition of expanded graphite into an Ag reducing solution. The prepared composites showed uniform dispersion of Ag nanoparticles on the surface of expanded graphite and exhibited relatively higher thermal conductivities than those of pure expanded graphite. In the case of 10% Ag content in the composite, the thermal conductivity in the thickness direction was 78% higher than the pure expanded graphite. We suggest that EG/Ag nanoparticle composites are a strong candidate for advanced heat spreading material.

Key words: Silver nanoparticles, Expanded graphite, Composite, Heat spreader, Thermal conductivity

1. Introduction

Due to their unique properties, metal nanoparticles are currently key players in various applications. Several methods have been reported for the preparation of nanoparticles with a balance among the control of size and shape, dispersing ability, and stability in aqueous buffered solutions [1-5]. The reduction of silver salts in reductants with different strengths is one of the conventional methods for the preparation of Ag nanoparticles [6]. Then, a mild and reproducible synthetic strategy is necessary.

Composites between metal nanoparticles and inorganic substrates have attracted wide attention for their potential to yield desirable properties coming from different nano scale building blocks that possess specific mechanical, optical, electronic, or physical properties [7-9]. The synthesis of valuable composites is a desirable approach to exploring their properties and applications. It is of critical interest if metal nanoparticles can be integrated with carbon-based materials to form a composite.

Among the metal nanoparticle composites, it is desirable to explore the creation of synergy between graphite and metal nanoparticles. The fabrication of graphite/metal nanoparticle composites is based on the attachment of metal nanoparticles on the graphite [10-14]. Therefore, to enhance the material properties of expanded graphite (EG)/metal nanoparticle composites, optimizing strategies for synthesizing the composites with high-quality are necessary. Expandable graphite is a synthesized intercalation compound of graphite that expands or exfoliates when heated, which is manufactured by treating flake graphite with various intercalation reagents. We proposed a simple approach for the synthesis of EG/Ag nanoparticle composites by the chemical reduction of Ag ions followed by the addition of EG to the solution. We demonstrated that the EG/Ag nanoparticle composites had uniform dispersion of Ag nanoparticles on the surface of EG.

Various methods of spreading heat are widely used in today's electronics, which is one of major applications of EG/Ag nanoparticle composites. Heat spreaders are used in die level packaging to spread heat from the microprocessor chip into the packaging. Several polymer-composites with a three-dimensional network have been prepared for highly enhanced anisotropic heat dissipation through-plane direction [15]. The potential of EG/Ag nanoparticle composites with minimized concentration of Ag nanoparticle for the heat spreader needs to be verified.

In this study, we performed and evaluated the synthesis of EG/Ag nanoparticle composites by chemical reduction of Ag ions in a reductive solution. The Ag nanoparticle size, the dispersion profile on the EG and other properties are reported according to the process conditions. We also measured and discuss the thermal conductivities of the composites.

2. Experimental

Ag nanoparticles were synthesized through the reduction of Ag ions from silver nitrate using sodium borohydride ($NaBH_4$) and trisodium citrate (TSC). Sodium borohydride and sodium citrate act as a primary reductant and as a secondary reductant as well as a stabilizing agent, respectively [6]. The reduction process was carried out at two different temperatures, 60 °C and 90 °C. A typical procedure was as follows: the required volumes of freshly prepared aqueous solutions containing $NaBH_4$ and TSC were mixed and heated to 60 °C for 30 minutes with stirring to produce a homogenous solution. After the pre-treatment, the required amount of $AgNO_3$ was added to the

† To whom correspondence should be addressed.
E-mail: wglee@kangwon.ac.kr

reduction solution and, subsequently, raised to 90 °C and kept for 30 min. To prepare 50 nm size Ag nanoparticles, the typical input amount of each ingredient was 5×10^{-4} mol of sodium borohydride, 2×10^{-3} mol of trisodium citrate, and 1.22×10^{-3} mol of silver nitrate on a base of 500 ml distilled water.

The expanded graphite (EG)/Ag nanoparticle composite was prepared as follows. The measured amount of EG was poured into the prepared Ag nanoparticle solution, and the solution was vigorously mixed for homogeneous dispersion between expanded graphite and Ag nanoparticles. The adsorption of Ag nanoparticles onto the surface and layer gap of EG was performed for over 1 hr with stirring at 4000 rpm with a homogenizer. The mixture was filtered by a sieve tray of 500 mesh for separation effectiveness and then divided into the filtered cake of EG/Ag nanoparticle composite and the waste solution. The filtered cake was put into a vacuum dry oven for 1 hr at 120 °C. Fine grains of the EG/Ag nanoparticle composite were obtained. The flowchart of the synthesis of the EG/Ag nanoparticle composites is shown in Fig. 1.

The particle size and shape of Ag nanoparticles and the morphology of EG/Ag nanoparticle composites were determined by a field emission transmission electron microscopy (FE-TEM, JEOL JEM 2100F),

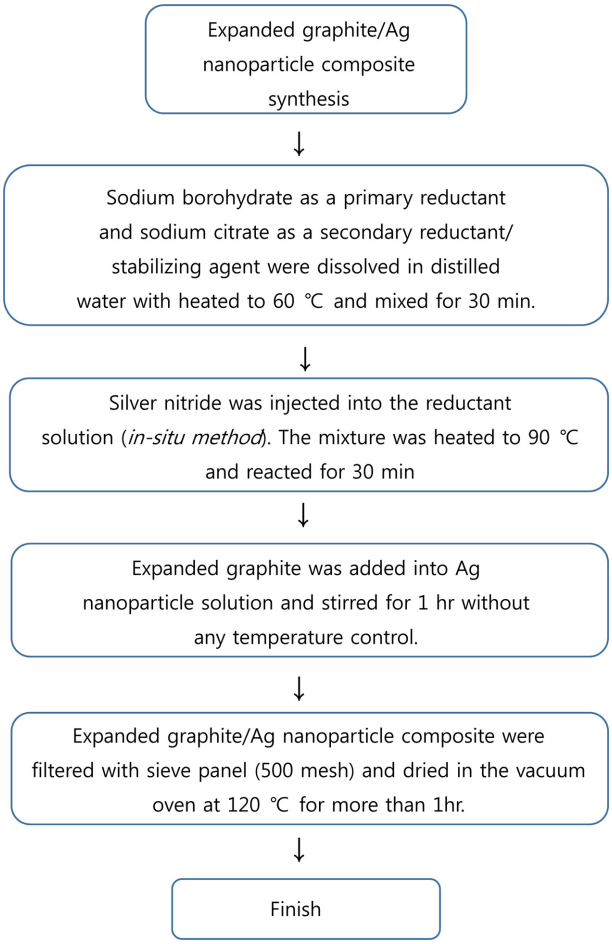

Fig. 1. The flowchart of the synthesis of expanded graphite/Ag nanoparticle composites.

an ultrahigh resolution scanning electron microscope (UHR-SEM, Hitachi S-4800), and a particle analyzer (Marlvern, Mastersizer 3000). The thermal conductivity of the EG/Ag nanoparticle composites was measured by a laser flash analyzer (LFA, LFA467).

3. Results and Discussion

Reports on the synthesis of Ag nanoparticles have investigated their shape, size and stability controllability in the dispersion system [6,17]. Our study revealed that an excess of a strong reducing agent such as sodium borohydride is used for small sized nanoparticles, which facilitates instant Ag nuclei generation, resulting in the formation of monodispersed and uniform sized Ag colloids. However, when sodium borohydride is employed as a reductant, it is not easy to obtain larger-sized nanoparticles [18,19]. It was reported that the weaker reducing agent trisodium citrate would contribute to the formation of relatively large silver nanoparticles with a wider size distribution. Our study revealed a variation in the shape of nanoparticles: spherical nanoparticles were achieved with minimizing undesired generation of rods, cubes, and triangles [20,21]. Thus, using either of the reducing agents, it may be di?cult to synthesize silver nanoparticles both above 50 nm and below 10 nm with a well-defined shape and the desired monodispersity. Our target size of Ag nanoparticle was 50 nm in diameter. Fig. 2(a)-(b) show that the growth size of the Ag nanoparticles reached about 50 nm under the composition of ingredients listed in the experimental part. Ag nanoparticles were uniformly located on the surface of the EG substrate as shown in Fig. 2(c), which was confirmed by the Ag EDX profile as shown in Fig. 2(d).

The measured amount of EG with different weight was poured into the prepared Ag nanoparticle solution, and the mixture was vigorously stirred for homogeneous dispersion between EG and Ag nanoparticles. The synthesized EG/Ag composites contained Ag nanoparticles with a ratio of 2%:5%:10%:40% in each case. As expected, the apparent loading amount of Ag nanoparticles on the surface of EG was consistent with the ratio as shown in Fig. 3.

With an Ag content of 50 wt% in the EG/Ag nanoparticle composite, the morphology was monitored as shown in Fig. 4(a). According to the EDX analysis data, the detected elements were carbon, oxygen, sodium, aluminum, silicon, and silver. Among the elements, sodium might have originated from sodium borohydrate and trisodium citrate. The distribution of silver and sodium elements was fairly uniform, but the oxygen element was located at a specific place as shown in Fig. 4(d).

Graphite exhibits a high thermal conductivity in the plane of the sheet combined with a much lower thermal conductivity through the thickness of the sheet. As a result, a graphite sheet was very effective in eliminating localized hot spots in electronic components. Therefore, a graphite heat spreader was used instead of a conventional thermal management system consisting of a heat sink and cooling fan [22]. In this study, the heat spreading properties of the prepared EG/Ag nanoparticle composites were evaluated according to the

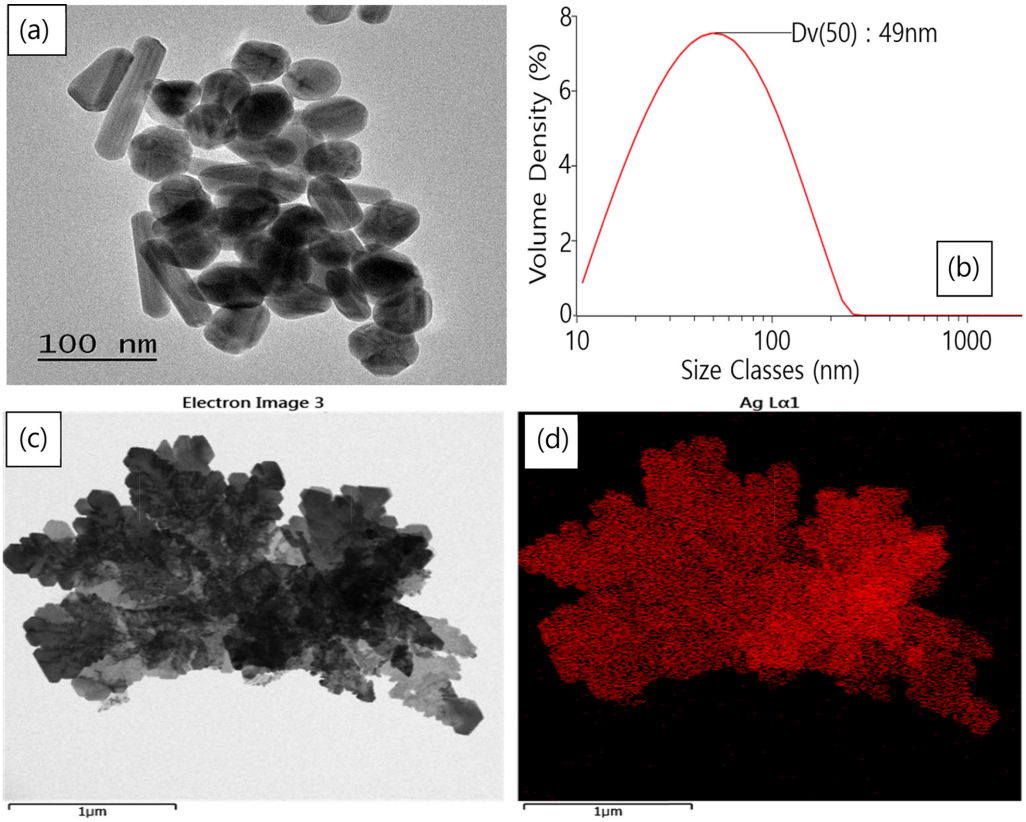

Fig. 2. The TEM images of Ag nanoparticles indicate a diameter of about 50 nm and almost spherical shape particles including some rod shapes in (a); (b) is the size distribution profile of Ag nanoparticles prepared in this study; (c) shows the dispersion status of Ag nanoparticles on the graphite substrate and (d) is the EDX profile of Ag element.

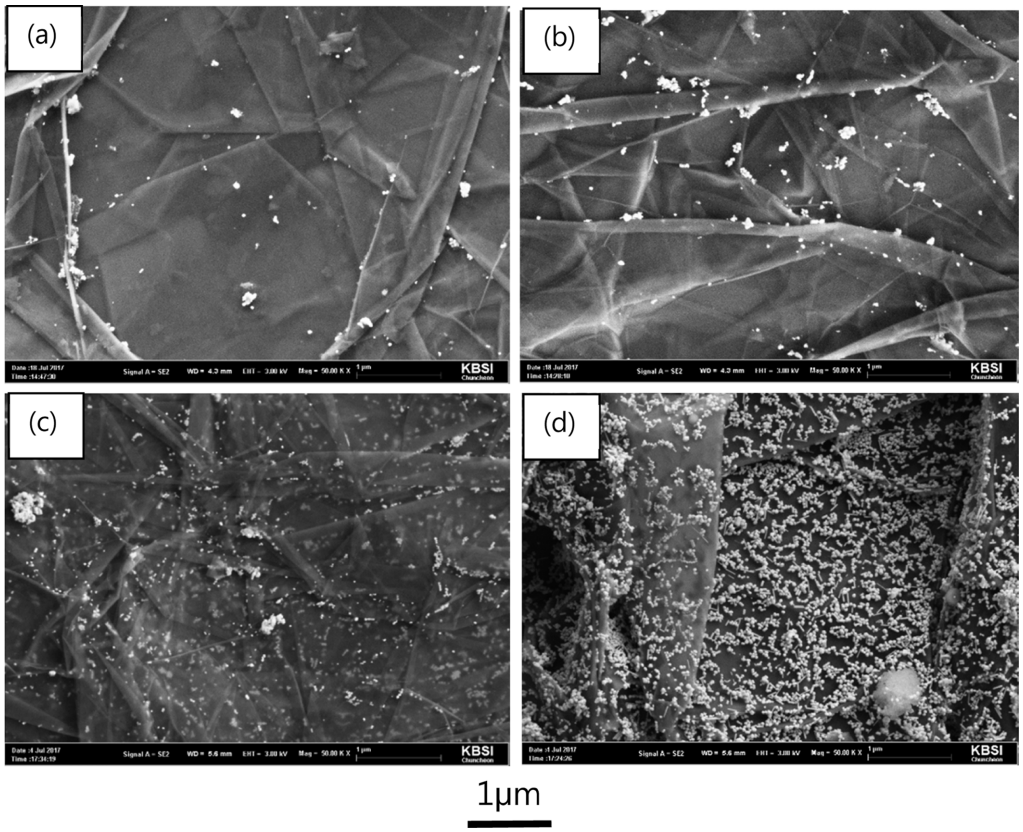

Fig. 3. SEM images (Mag.: 50.0KX) of Ag nanoparticles on the expanded graphite/Ag nanoparticle composites according to the content of Ag: (a) 2%, (b) 5%, (c) 10%, and (d) 40%.

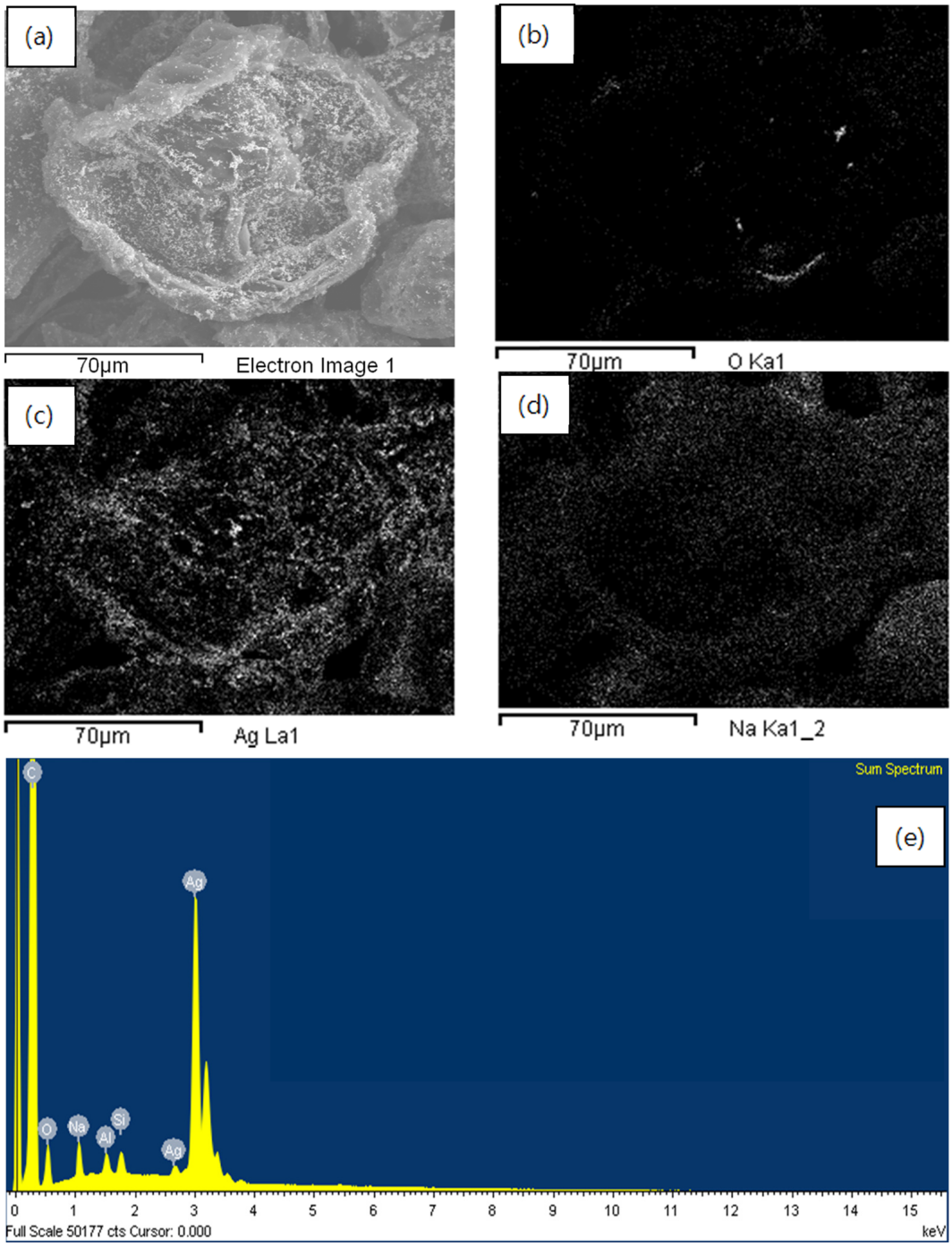

Fig. 4. (a) Ag distribution of an expanded graphite/Ag nanoparticle composite with 50% Ag content. EDX analysis results of the oxygen element (b), Ag element (c), and sodium element (d) are shown; (d) is EDX full spectrum.

content of Ag in the nanoparticle composites. The thermal properties are presented along with the thickness direction of the nanoparticle composite sheet with a laser flash analyzer, as shown in Fig. 5.

The prepared EG/Ag nanoparticle composites were molded into a spherical disk of a half-inch diameter. The thermal conductivity of pure expanded graphite in the thickness direction (through-plane) was ~4.6 W/m·K. The amount of Ag nanoparticles in the composites showed a strong influence on the thermal conductivity of the composite sheet. As the content of Ag increased, the thermal conductivity linearly increased as shown in Fig. 5. For Ag of 10% and 40%, the thermal conductivity reached 8.2 and 9.2 W/m·K, respectively, showing large improvement in thermal conductivity in comparison with the pure expanded graphite. These results are very valuable for improving the thermal conductivity of EG/Ag nanoparticle composites because the increasing effect in the thickness direction (through-plane) reveals the construction of a 3D network in the EG/Ag nanoparticle composite that is a typical hierarchical structure with embedded Ag nanoparticles in the interspaces of expanded

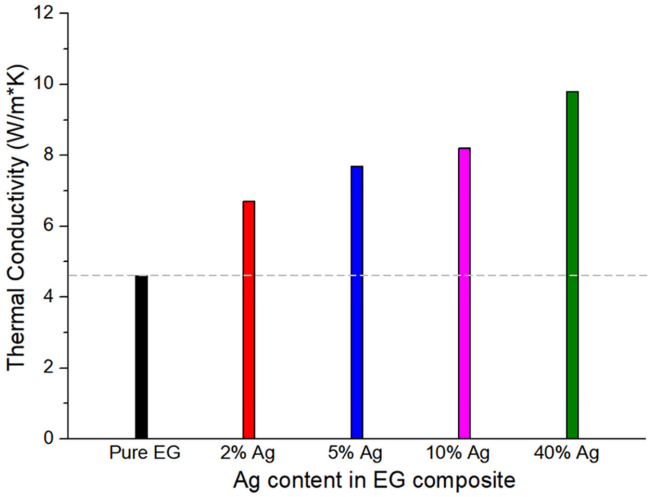

Fig. 5. Thermal conductivity of expanded graphite/Ag nanoparticle composites with various amount of Ag along with the thickness direction (through-plane) of their composite sheet.

graphite. Ag nanoparticles, which are placed on the surface of EG with a nano scale gap, may minimize heat resistance and enhance the heat conduction network. 3D network with Ag nanoparticles in the composite is a key factor to enhance heat spreading efficiency for through-plane direction.

4. Conclusions

We successfully developed a simple synthesis of expanded graphite/Ag nanoparticle composites by the adsorption of Ag nanoparticles onto the surface of expanded graphite. The Ag nanoparticles were prepared from the chemical reduction of Ag ions in a solution containing sodium borohydride, trisodium citrate and silver nitrate. The proposed synthesis procedure offeres a useful way to directly and uniformly attach Ag nanoparticles to the surface of expanded graphite. The prepared expanded graphite/Ag nanoparticle composites exhibited relatively high thermal conductivity. At an Ag content of 10 wt%, the thermal conductivity in the thickness direction was 8.2 W/m·K, which was about 78% higher value than that with pure expanded graphite.

Acknowledgement

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