Solution Plasma Process to Synthesize Silver Nanofluids and Their Thermal Conductivity Behaviors

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A solution plasma process (SPP) was recently introduced as an effective method to synthesize various metallic and nonmetallic nanoparticles. In this work, the synthesis and characterization of Ag nanoparticles (AgNPs) and Ag nanofluids (AgNFs) using the SPP were investigated. The results showed that various shapes and sizes of AgNPs could be synthesized successfully using the SPP, and their size and shape were strongly affected by discharge time. As the discharge time increased, the morphologies of the synthesized AgNPs changed from spherical to dendritic in shape. The dispersion stability of the AgNPs in the solution also showed a close dependence upon the discharge time, showing a maximum zeta potential after discharging for 300 s. The thermal conductivity of the AgNFs increased as the discharge time increased. An increase in the thermal conductivity of the AgNFs of approximately 12% was observed after discharging for 900 s at 900 V and fully developed dendritic AgNPs were observed in the solution.

Keywords: nanostructured materials, solution plasma processing, thermal conductivity, transmission electron microscopy (TEM), microstructure

1. INTRODUCTION

Nanofluids are defined as fluids with suspended nanometer-sized particles, both metallic and non-metallic. Nanofluids have been found to provide enhanced unique properties such as thermal conductivity, superior critical heat flux, minimal clogging in flow, enhanced mass transport and convective heat transfer coefficients compared to those of base fluids [1-7]. Preparation of nanofluids is the important step in the use of them and various approaches have been employed. Two kinds of methods are applied to produce nanofluids, namely, one-step and two-step methods [8,9]. In two-step method, solid nanoparticles are first produced by chemical or physical techniques and then they are dispersed in a liquid host with an intensive magnetic force agitation, ultra-sonication and high-shear mixing. However, agglomeration of nanoparticles easily takes place in the preparation of the nanofluids from nanoparticles in the process of drying, storage, and transportation of nanoparticles.

To overcome disadvantages of two-step method, a solution plasma process (SPP) has been recently introduced as a one-step method to synthesize and disperse nanoparticles in the fluid concurrently [10,11]. SPP is an effective method for the synthesis of nanoparticles and nanofluids since solution plasma provides strong reaction fields where the plasma discharged in the liquid environment generates numerous numbers of highly active species (H, O, and OH radicals), energetic electron and UV radiation [12]. The high reaction rate without the requirements of temperature, pressure and humidity are great benefits of developing solution plasma in various applications such as polymeric decomposition and sterilization [13,14].

Once high voltage is applied, the hydrogen radicals produced from the dissociation of water molecules play a role of reducing agent so that metallic ions can be reduced without chemical reductants [11,12,15-19]. In addition, solution plasma provides the electrons and electric energy resulting in many charged nanoparticles, which is suggesting the dispersion of nanoparticles could be stable due to the increasing surface energy of the particles [15].

In this work, the synthesis and characterization of AgNPs and AgNFs using the SPP were investigated. AgNPs are of great interest due to their superior thermal conductivity (429 W/mK at 300 K), oxidation resistance and a safe material for human being. Special attention was given to the effects of the unipolar DC pulse voltage and discharge time on the improvement of the thermal conductivity of the AgNFs.
2. EXPERIMENTAL PROCEDURES

AgNPs were synthesized using the SPP at unipolar 800-1,000 V pulse DC voltage with a 75-25% duty ratio at 25 kHz (EN Technologies, IAP-1010/20). A stock solution consisting of 0.5 mM of silver nitrate (AgNO₃, 99.9%, Kojima) in 200 ml of distilled water was used. Discharge duration was set from 120 sec to 900 sec. Tungsten(W) wires (diameter: 2 mm) were used as electrodes and gap distance was 1 mm. A UV-Vis spectra of AgNFs was collected with a visible ray ranging from 200 to 800 nm on a UV3600 UV-Vis-NIR spectrophotometer (Shimadzu, Japan). AgNPs were characterized by TEM (JEM 2500SE, JEOL, Japan) operating at 200 kV. The dispersion stability of the nanoparticles was measured using a zeta potential analysis (90Plus, Brookhaven, USA). The thermal conductivity of the nanofluids was measured using a KD2 Pro thermal property analyzer (Decagon Devices Inc.).

3. RESULTS AND DISCUSSION

The absorbance spectra of AgNPs with various unipolar DC voltages and discharge times are shown in Fig. 1. The maximum absorbance peak (λ_max) of the optical spectra was found to be around 365-375 nm, depending upon the DC voltage and the discharge time, indicating the formation of AgNPs. In all DC voltages, the intensity of the λ_max increased continuously as the discharge time increased. This indicates that the amount of AgNPs synthesized using the SPP increased as the discharge time increased.

It was also observed at all voltage conditions that as the discharge time increased, the λ_max became red shifted slightly. This could be attributed to the agglomeration and growth of the AgNPs. Pérez-Juste et al. reported that the λ_max of nanoparticles generally shifted toward higher wavelengths with an increase in particle diameter [20]. This could be attributed to the electron momenta of the nanoparticles, which change from multiple to dipole mode [21]. Nanoparticles have the vibration of an electromagnetic wave due to dipole momentum. However, as the diameter or size of nanoparticles increases, the vibration of the nanoparticles becomes irregular in different directions, and the multiple mode becomes dominant. Therefore, in the present study, as the particle diameter or size increased, the absorption coefficient showed a red shift in the visible region. The red shift of the absorption coefficient spectra suggests that the size of the AgNPs increased.

TEM images of AgNPs with various discharge times from 120 to 900 s at 1,000 V, and the measured average particle sizes are summarized in Fig. 2. It is noted that the discharge time has a strong effect on the morphology of AgNPs, in that they changed from spherical to dendritic in shape as the discharge time increased. Also the size of the AgNPs or Ag dendritic particles increased as the discharge time increased.

The zeta potential values of the Ag nanofluids were measured to evaluate the dispersion stability. The results are summarized in Table 1. At the discharge of 800 V, the zeta potential values of the Ag nanofluids increased as the discharge time increased. The highest zeta potential, -29.5 ± 1.0 mV, was