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Ultrastable Aqueous Graphite Nanofluids Prepared by Single-step Liquid-phase Pulsed Laser Ablation (LP-PLA)

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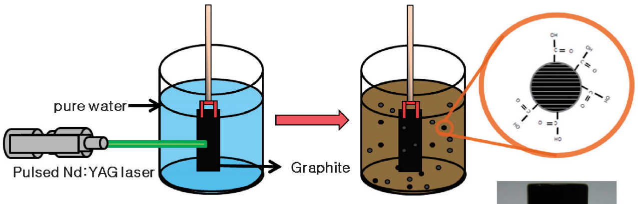
Ultrastable aqueous graphite nanofluids were prepared by single-step liquid-phase pulsed laser ablation (LP-PLA), and they showed an outstanding long-term stability without any agglomeration, even though no surfactant was used. It was revealed with FT-IR spectroscopy that the hydrophilic functional groups were introduced onto the surface of graphite nanoparticles and that such hydrophilic nature showing a high negative ζ potential was the origin of the outstanding long-term stability. Finally, aqueous graphite nanofluids demonstrated an enhanced thermal conductivity by 1.49% with low concentration (0.02 vol %), compared to pure water.



Energy	500mJ/pulse
Wavelength	1064nm
Pulsed duration	8–10ns
Repetition rate	10Hz
Base liquid	Pure water
Material	Artificial graphite plate
Beam size and divergence	8mm and 1.5m rad
Distance between water surface and target	≈30mm

Figure 1. Schematic illustration of single-step LP-PLA. Inset shows a picture of aqueous graphite nanofluids after 6 months from the initial preparation by LP-PLA.

Nanofluids, the suspension of nanosized particles in base fluids, have drawn great attention in the field of thermal science and technology, because of their superior thermal properties as working fluids in many potential applications.[1] The most important property in nanofluids is the suspension stability of nanoparticles in base fluids, because if the nanoparticles agglomerate and precipitate, it is impossible to employ them as working fluids bccause of clogging problem.[2] The current preparation methods of nanofluids can be classified into two kinds, single-step and two-step methods. Single step is simple and cheap; however, the drawback is either the difficulty in obtaining good suspension stability without any surfactant or the deterioration of thermal properties with surfactant, an intrinsic thermal insulator. In the case of two-step methods, even though good stability can be readily obtained, the process is relatively complex and expensive.[3]

In this study, we report the first challenge to prepare nanofluids by using pulsed laser ablation (PLA) in a single step. PLA is a well known and mature vapor-phase technology for the fabrication of metallic or semiconducting thin film and nanoparticles.[4,5] However, we employed liquid-phase PLA (LP-PLA) to prepare aqueous graphite nanofluids without any surfactant in a single step, expecting enhanced stability due to the introduction of surface hydrophilic functional groups in the formation of graphite nanoparticles by laser irradiation in water. As expected, the ultrastable aqueous graphite nanofluids were successively obtained, and their structural and thermal properties were examined by using TEM, XRD, FT-IR, zeta potentiometry, and transient hot-wire methods.

The general scheme of aqueous graphite nanofluids is shown in Figure 1. Q-switched first harmonic Nd:YAG laser (LO-IN0902, Laseroptek) irradiated the polycrystalline graphite plate target (Osaka gas, 99.99%) in DI water for 16, 24, and 32 h. The irradiating laser had a pulse length of 8–10 ns and energy of approximately 750 mJ per pulse. Morphology of graphite nanoparticles in the nanofluids was observed by transmission electron microscopy (TEM, JEM2011, Jeol), of which the accelerated electron energy was 200 keV. Fourier transform infrared (FT-IR, Nicolet 6700, Thermo) spectroscopy was employed to investigate the surface functional groups introduced in the formation of graphite nanoparticles by LP-PLA. The synchrotron radiation in the 8C2 beamline of Pohang Light Source (PLS) was employed to obtain the high-resolution X-ray powder diffraction pattern of graphite nanoparticles which were collected from the nanofluids by drying base water. The particle size distribution and ζ potential of graphite nanoparticle in aqueous graphite nanofluids were identified with dynamic light scattering and electrophoretic light scattering (ELS-8000, Otsuka Electronics). Finally, thermal conductivity of aqueous graphite nanofluids was measured with a transient hot-wire by using an electrical conductivity meter (LF11, SCHOTT).[6]

Figure 2 shows the FT-IR spectrum of graphite nanoparticles collected from the aqueous graphite nanofluids by drying base water. The remarkable peak at around 1600 cm^{-1} corresponding to C=O stretching in carboxy or carbonyl groups implies that graphite nanoparticles had become hydrophilic on the surface. Such hydrophilic functional groups can be introduced by the reaction of generated carbon radical with water molecules by laser ablation in water and are the key factor for outstanding colloidal stability.

As shown in XRD patterns in Figure 3, the lattice structure of graphite nanoparticles prepared by LP-PLA is perfectly identical to the original graphite powder, indexed with (111), (010), (110), (222), (112), (110), and (120), corresponding to rhomb-centered hexagonal graphite with lattice constant $a = 3.635$ Å. This obviously shows that the lattice structure of graphite was maintained after single-step LP-PLA. As can be seen in the inset in Figure 3, the graphite nanoparticles are in

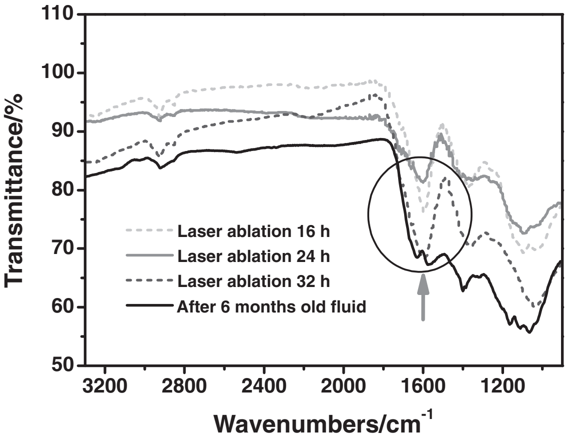


Figure 2. FT-IR spectrum of graphite nanoparticles prepared by LP-PLA. Black arrow indicates the introduction of surface hydrophilic functional groups.

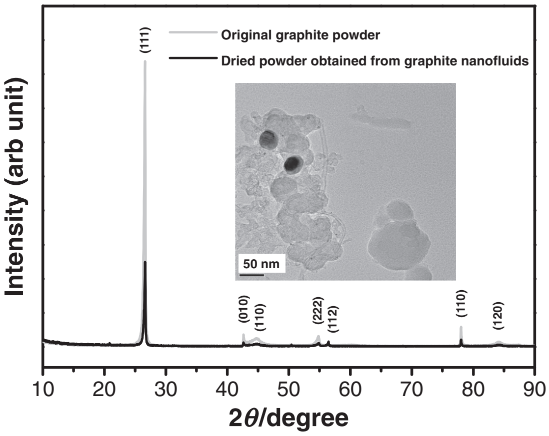


Figure 3. HRPD patterns of graphite nanoparticles (indexed by JCPDS card No. 75-2078). Inset shows TEM image of aqueous graphite nanofluids prepared by LP-PLA for 32 h.

finely dispersed state with round shape and have an average size of 2.648 µm as measured by dynamic light scattering.

The suspension stability of aqueous graphite nanofluids was identified to ζ potential measurements. They exhibited ζ potential values from -16.07–-28.93 mV in average 0.02 vol % of graphite nanoparticles. The negative value of ζ potential indicates that aqueous graphite nanofluids keep away from each other due to electrostatic repulsion, which plays the key role in stabilizing aqueous graphite nanofluids. Aqueous graphite nanofluids prepared by LP-PLA actually showed an outstanding colloidal stability even after 6 months without any dispersants (see the picture in Figure 1) and have maintained the hydrophilic characteristics on the surface of graphite nanoparticles as shown in Figure 2. They can, therefore, meet the most important requirements in nanofluid technologies as described above.[5] Finally, aqueous graphite nanofluids showed average thermal conductivity of 0.614 W mK^{-1}, which is 1.49% higher thermal conductivity than pure water (0.606 W mK^{-1}). Therefore, aqueous graphite nanofluids prepared by single-step LP-PLA showed not only outstanding suspension stability but also enhanced the thermal conductivity of water.

We have demonstrated the successful preparation of ultra-stable aqueous graphite nanofluids by using LP-PLA. The graphite nanoparticles in nanofluids had hydrophilic functional groups on their surfaces which were generated by the reaction of carbon radical in water and thereby electrostatic repulsion characteristics. Also, their lattice structure remained the same as the original graphite plate target.

Finally, the thermal conductivity of aqueous graphite nanofluids was increased by 1.49% compared to pure water, implying that this unique approach can be a powerful tool for the preparation of nanofluids as working fluids in many thermal technology fields.

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