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Stable Transport of Gas-born Ag Nanoparticles into Liquid Phase Mediated by Poly(vinylpyrrolidone) Molecules

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We demonstrate that gas-born nanoparticles can be transported into solution successfully. Our results show that Ag nanoparticles produced in gas phase are introduced into poly(vinylpyrrolidone) solution without structural changes such as nanoparticle aggregation. It is also shown that Ag nanoparticles in solution show surface plasmon resonance, suggesting that the optical properties of nanoparticles are not impaired by the transport from gas to liquid.

Metal nanoparticles are widely known to possess different chemical, physical, electronic, and optical properties compared to their corresponding bulk materials.[1,2] Various methods for nanoparticle production, such as chemical reduction,[3] laser ablation,[4] and gas vaporization,[5] have been reported. In particular, gas vaporization, which synthesizes nanoparticles in the gas phase, has attracted much interest in the production of novel nanomaterials. In our previous report, hybrid nanoparticles constructed of fullerene and Ag, which are difficult to produce in the liquid phase, were synthesized successfully by gas vaporization.[6,7] Although transport of the gas-born nanoparticles into solution is needed to apply their specific properties to the liquid phase, there are few reports on the transport of gas-born nanoparticles into solution. Additionally, it is expected that removal of various ions such as sodium, potassium, and chloride for chemical reduction is not required, because reducing agent is not needed for production of nanoparticles in gas phase. In this study, we attempted to develop transport methods for nanoparticles without impairing their specific properties. Ag nanoparticles were used as model nanoparticles. Ag nanoparticles are known to be easily produced by gas vaporization,[8] and it is possible to estimate particle structure from optical properties.

A schematic illustration of Ag nanoparticle production in the gas phase and their introduction into pure water containing poly(vinylpyrrolidone) (PVP) is illustrated in Figure S1.[16] The Ag nanoparticles produced in the furnace were carried into the solvent by N_2 gas. A UV spectrum of the solvent 24 h after Ag nanoparticle addition is shown in Figure 1 inset. This spectrum shows representative peaks of spherical Ag nanoparticles. The peak at 410 nm is ascribed to surface plasmon resonance (SPR),[9] indicating that the gas-born Ag nanoparticles maintain SPR even in the solvent. This SPR peak shows a linear increasing tendency depending on the gas flow time (Figure 1). This indicates that the size distribution of Ag nanoparticles in solvent remains unchanged, suggesting that the Ag nanoparticles are well dispersed in solution and not aggregated. An absorption at 300 nm also shows a similar tendency. This absorption is known to originate from an interband transition of Ag atoms,[10] which may be used as a measure of Ag concentration dispersed in the solution. This indicates that the amount of Ag introduced into the solvent increased constantly depending on the gas flow time.
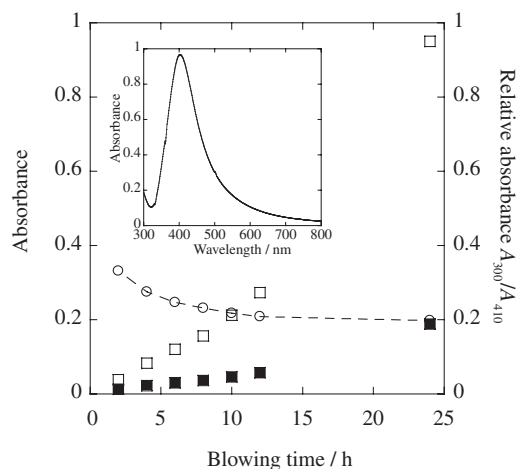

Figure 1. Time course of absorbance at 410 (open square) and 300 nm (filled square). Circle symbol indicates relative absorbance calculated from absorbance ratio at 300 to 410 nm. Inset shows absorption spectrum of the solution including PVP 24 h after blowing of gas-born Ag nanoparticles.
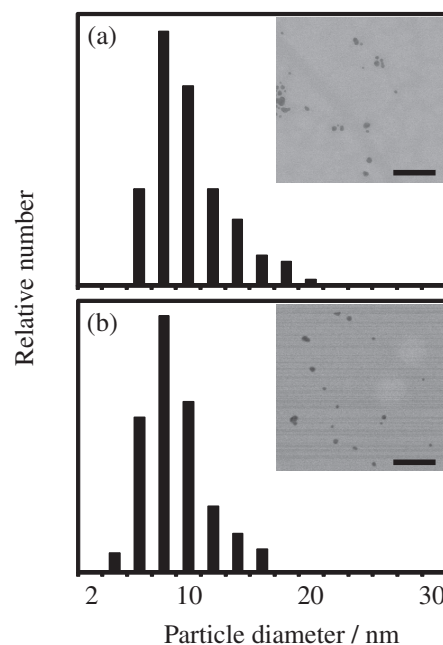

Figure 2. Diameter distribution of gas-born Ag nanoparticles (a) after and (b) before blowing into PVP-containing solution. Inset shows STEM image in each condition. Scale bar indicates 100 nm.
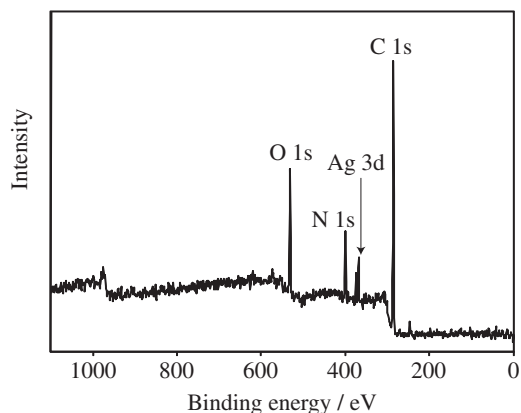
Figure 3. XPS survey spectrum of produced nanoparticles.

A relative absorbance between 300 and 410 nm is almost constant, indicating that the spectrum is stable throughout the gas flow time. When PVP was absent from the solvent, increases in both SPR and internal band signals were not observed 24 h after addition (data not shown). This shows that PVP plays an important role in both transport and dispersion of gas-born nanoparticles.

We observed the morphology of Ag nanoparticles by scanning transmission electron microscopy (STEM). The STEM image (Figure 2 inset) revealed the presence of spherical nanoparticles of various sizes. The particle-diameter histograms of the gas-born nanoparticles in gas phase or solvent were estimated from the STEM image. The peak diameter was found to be 8 nm in both the histograms (Figure 2). It was also found that the size distribution under each condition was almost the same, indicating that the aggregation of nanoparticles did not occur in during transport.

To confirm the effect of PVP on nanoparticle dispersion, the interaction between nanoparticles and PVP was examined by X-ray photoelectron spectroscopy (XPS). Figure 3 shows the XPS survey spectrum of the obtained solution. Peaks originating from Ag, C, N, and O atoms were clearly observed. Since the Ag 3d peaks were detected, the nanoparticles in the solution are confirmed to consist of Ag atoms. In addition, the relative abundance of C, N, and O atoms was estimated as 6.8:1:1.1 from the detection efficiency of the photoelectrons. This ratio agrees well with the stoichiometry of the PVP molecule $(C_6H_9NO)_nH_2$. This agreement indicates that the nanoparticles observed in the STEM image also consist of PVP molecules. Consequently, the nanoparticles in the solution are thought to be composed of Ag nanoparticles and PVP molecules.

In the Ag 3d spectrum (Figure 4a), the Ag $3d_{5/2}$ peak is observed at 367.9 eV. The binding energy of this peak is lower than that for metallic Ag (368.3 eV). This peak shift of −0.4 eV indicates that the electron density around Ag atoms is increased because of the existence of an electron-donating group such as a lone electron pair on the oxygen in the carboxyl group of the PVP chain.[11] In fact, similar peak shifts of −0.4 to −0.8 eV were also reported in previous studies on synthesis of PVP-coated Ag nanocolloids.[12–15] Consequently, the transported Ag nanoparticles are believed to be bound to PVP molecules.

A dominant peak with a slight shoulder at a higher binding energy is observed at 530.7 eV in the O 1s spectrum (Figure 4b).
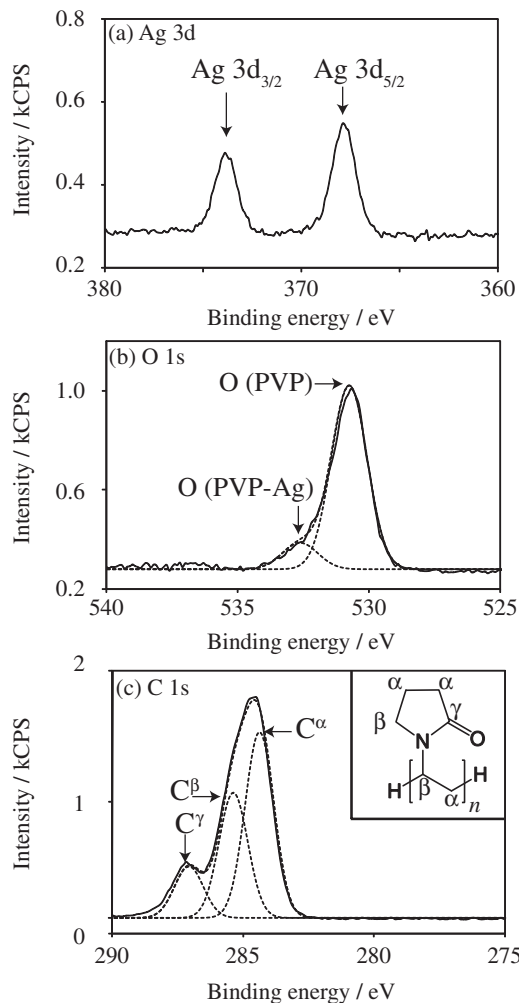

Figure 4. High-resolution XPS spectra of produced nanoparticles: (a) Ag 3d, (b) O 1s, and (c) C 1s.

This peak can be deconvoluted into two peaks with binding energies of 530.7 and 532.0 eV. The binding energy of 530.7 eV is equal to that for pristine PVP molecules. Meanwhile, the higher peak can be attributed to the oxygen in the carboxyl group of the PVP chain interacting with the surface of Ag nanoparticles, because electron-attractive Ag atoms decrease the electron density of the oxygen. This interaction is confirmed by the consistency of the combination of the increased electron density of Ag atoms and the decreased electron density of oxygen in PVP molecules. In addition, since the binding energy of the oxygen interacting with Ag nanoparticles was also reported as 531.6 to 532.1 eV,[12–15] the Ag nanoparticles in solution are complexed with PVP molecules through the interaction between the oxygen and the metal surface.

Figure 4c shows the C 1s spectrum. When the spectrum was fitted by a Gaussian function for which the full width at half-maximum value was constrained at 1.3 eV, fitting curves with binding energies and relative abundances listed in Table S1[16] were obtained. The envelope estimated from these fitting curves was found to reproduce the observed spectrum well. The binding energies for the nanoparticles correspond well to those for pristine PVP molecules, as shown in Table S1.[16] Namely, these

peaks can be ascribed to the C atoms in the pristine PVP molecules shown in the inset of Figure 4c. This correspondence also indicates that the C atoms of the PVP molecules in the produced nanoparticles do not interact with the Ag nanoparticles directly. The relative abundances of the nanoparticles roughly reproduce the stoichiometry of the PVP molecules, as shown in Table S1.[16] This reproduction indicates that the C atoms in the produced nanoparticles are composed only of PVP molecules and not contaminated by fragmented molecules and impurities.

In conclusion, we first demonstrated that gas-born nanoparticles can be transported into solution successfully without impairing the nanoparticle properties. Both STEM and UV–vis spectroscopy showed that Ag nanoparticles produced in gas phase are present in PVP solution without structural changes such as nanoparticle aggregation. Further, XPS analysis revealed that the Ag nanoparticles transported into solution interact with PVP molecules through their oxygen atoms. Our results imply that the interaction between gas-born Ag nanoparticles and PVP would occur at the gas–liquid interface of bubbles in solution and that the complexes would be transported into solution. Further studies are necessary to confirm this idea.

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