

Silica Gel Fabrication of [60]Fullerene Aggregates Utilizing Poly(*N*-vinylpyrrolidone) as a “Glue”

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Sol-gel polycondensation of tetraethoxysilane in the presence of [60]fullerene/poly(*N*-vinylpyrrolidone) (PVP) complex yielded novel silica particles composed of [60]fullerene, PVP and thin silica layer.

Since discovery of [60]fullerene,¹ it has been expected to become a new potential source of functional materials.² However, its strong cohesive nature and poor solubility have caused the researchers trouble for a long time, because these phenomena seriously hamper for the researchers to obtain the reproducible data. One potential solution to overcome these problems is to derive it into the amphiphilic compounds by introducing aliphatic chains or cholesteryl groups.^{3,4} In this derivative method, however, the electron conjugate system in [60]fullerene is inevitably damaged and the functionality may be partially reduced. Is there any convenient method to maintain [60]fullerene or its aggregates stably in the reaction system? This was the starting point of this study. Recently, we and others have been developing a new silica gel fabrication method, “sol-gel transcription”, by which one can finely transcribe the superstructures of organic assemblies into silica gel.^{5,6} The essential point of this method is to cover the surface of the organic assemblies with such functional groups that can interact with silica gel microparticles.^{5,6} It thus occurred to us that some amphiphilic compound that can interact both with [60]fullerene and with silica gel microparticles should act as a “glue” to fabricate [60]fullerene or its aggregates with silica gel. The primary candidate that can satisfy these requirements is poly(*N*-vinylpyrrolidone) (PVP), because it not only solubilizes [60]fullerene into aqueous solution⁷ but also acts as an adsorbent of silica gel particles.⁸ With this motif in our mind, we have found that sol-gel polycondensation of tetraethoxysilane (TEOS) results in stable particles composed of [60]fullerene, PVP and thin silica layer.

A toluene solution (2.0 ml) containing [60]fullerene (1.6 mg; 2.2×10^{-6} mol) was mixed with a CHCl_3 solution (2.0 ml) containing PVP (200 mg; average MW 4.0×10^4). The resultant solution was stirred at room temperature for 1 day and evaporated to dryness. The residual solid was dispersed by sonication into water (4.0 ml). The UV-vis absorption spectrum ($\lambda_{\text{max}} = 262$ and 340 nm) was basically same as that reported by Miyata et al.⁷ The sol-gel polycondensation was carried out by two different methods: [60]fullerene/PVP solution (1.0 ml), 1.0 mol dm^{-3} HCl solution (0.01 ml) and TEOS (0.04 ml) were mixed and the mixture was left at room temperature for 2 days (Method A); [60]fullerene/PVP solution (1.0 ml), benzylamine (0.01 ml) and TEOS (0.03 ml) were mixed and the mixture was left at room temperature for 3 weeks (Method B).⁹

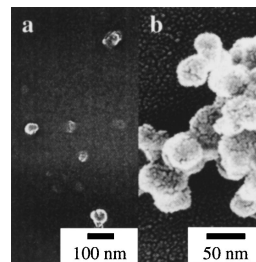


Figure 1. SEM image of the silica particles using [60]fullerene/PVP complex as a template (before calcination).

Figure 1 shows a SEM image of the resultant silica obtained from Method A. We can recognize both the discrete particles (Figure 1a) and their aggregates (Figure 1b). The size of the globular silica particles (50–150 nm) is basically comparable with that of [60]fullerene/PVP complex determined by dynamic light scattering in aqueous solution,¹⁰ which indicates that these silica particles grow up using [60]fullerene/PVP complex as a template. A SEM image obtained from Method B is basically the same as that in Figure 1. Figure 2a shows a TEM image of such silica particles. It is clearly seen from this picture that [60]fullerenes, which tend to absorb the electron beam and result in the dark shadow, are included in the silica particles. When comparing Method B with Method A, the TEM pictures obtained from Method B were totally filled with [60]fullerene-containing silica particles (as in Figure 2a), whereas those obtained from Method A include both [60]fullerene-containing silica particles and semitransparent silica particles without the [60]fullerene shadow contrast. Since sol-gel polycondensation occurs more rapidly under Method A, one can consider that the non-templated reaction can also take place in the HCl solution, which affords the semitransparent silica particles in the TEM pictures. On the other hand, when sol-gel polycondensation of TEOS was carried out in the presence of only PVP, only the hollow silica particles were yielded (Figure 2b).¹¹ When the silica particles containing [60]fullerenes in Figure 2a were calcined at 500 °C, they were converted to hollow silica particles (Figure 3), which indicates that combustion of [60]fullerene and PVP occurs through the calcination process. These findings consistently support the view that the black contrast in Figure 2a is ascribable to [60]fullerenes included in the silica particles.

The silica particles including [60]fullerene and PVP were further characterized by spectroscopic methods. The particles (before calcination) were washed with water 3 times. In the first time and the second time PVP was detected in the supernatant by a UV-vis spectroscopic method, but it was no longer detected in the third supernatant. This sample was washed 3 times by acetone and then 3 times by methanol. After drying in vacuo, it was subjected

to the spectroscopic analyses. The IR spectrum (KBr) gave a strong band at 1646 cm^{-1} ascribable to a C=O stretching band in addition to 960 cm^{-1} ($\nu_{\text{Si-OH}}$) and 1055 cm^{-1} ($\nu_{\text{Si-O-Si}}$) bands.

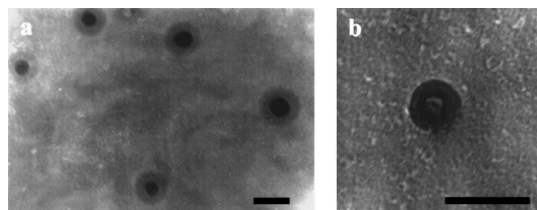


Figure 2. TEM images of the silica particles prepared from (a) [60]fullerene/PVP/TEOS/benzylamine (Method B) and (b) PVP/TEOS/benzylamine. The length of the scale bar is 50 nm.

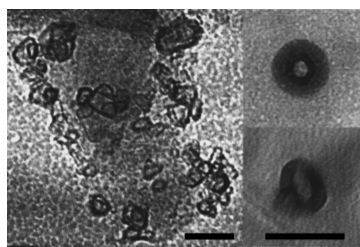


Figure 3. TEM image of the silica particles prepared by Method B after calcination. The length of the scale bar is 50 nm. Two typical particles are enlarged in the right side.

For a reference experiment we prepared silica particle samples coated with PVP by dipping them (40 mg) in an aqueous PVP solution (50 mg in 1.0 ml water) (Method C). When they were subjected to the above washing treatment, the 1646 cm^{-1} band entirely disappeared. The sample for the UV-vis spectroscopy was prepared by casting the silica particles (before calcination) of aqueous suspension onto a quartz plate. The thin film thus obtained was immersed in toluene and subjected to the spectral measurement once a day. After 1 day and 2 days the absorption bands ascribable to [60]fullerene somewhat decreased but after 2 days the decrease in the absorbance was stopped and reached the constant value (Figure 4). The same result was obtained when the film was immersed in water. The structure of the silica particles was further characterized by X-ray photoelectron spectroscopy (XPS). The peak intensity of N atoms (at 409 eV) was very weak, with the relative intensity of 0.8:3.0 to the peak intensity of Si atoms (at 112 eV). On the other hand, the intensity ratio of N atoms vs. Si atoms for the reference silica from Method C was 6.0:6.6. The difference indicates that PVP detected by IR spectroscopy for the silica particles from Methods A and B exists at the particle inside but not on the particle surface. As a summary of the foregoing spectral analyses one can conclude that the silica particles stably include [60]fullerene and PVP which cannot be extracted either by water or by toluene.

In conclusion, the present study demonstrated a novel silica gel fabrication method for [60]fullerene. It has been shown that amphiphilic polymer, PVP can act as an efficient "glue" for this fabrication process. We are currently extending this fabrication method to [70]fullerene, higher-order fullerenes, carbon nanotubes, etc. and exploring the functions inherent to this new silica-fabricated [60]fullerene, e.g., for redox reactions, electron pools, cast film devices, etc.

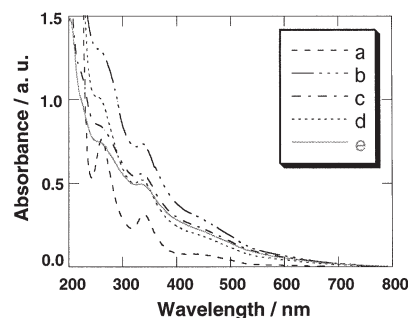


Figure 4. UV-vis absorption spectra of (a) [60]fullerene (0.06 mg)/PVP (5.0 mg) complex in aqueous solution (1.0 ml) and [60]fullerene-containing silica particles immersed in toluene for (b) 0 day, (c) 1 day, (d) 2 days and (e) 7 days at $25\text{ }^{\circ}\text{C}$; the ordinate for silica particles is given by arbitrary unit.

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