

Aggregation of Polyynes on Metal Nanoparticles

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We investigated the interaction between polyynes (linear carbon chains) and various metal nanoparticles (Ag, Au, and Cu) to provide insight into the optical properties of metal-polyynes systems prepared by different experimental techniques. Polyynes were produced by laser ablation in deionized water, metal nanoparticles solutions, and copper chloride solution. Metal nanoparticles complexes with polyynes were analyzed by Raman, surface-enhanced Raman scattering, and UV-vis spectroscopy.

Key Words : Polyyne, Nanoparticle, Aggregation, Raman spectroscopy

Introduction

Polyynes are linear carbon chains of one dimensional structure with sp hybridization and terminated by atoms or groups. They are of significance in astrophysics and nanotechnology as well as in molecular science.¹ Along with recent developments in approaches to achieve their synthesis, polyynes stabilized by bulky end-capping groups have been investigated extensively.²⁻⁴ As polyynes are unstable at room temperature, attempts to stabilize them are of considerable importance. Recently, to stabilize polyynes in air, they have been incorporated into SiO₂ dried gels with sol-gel method or inserted into carbon nanotubes.^{5,6}

Polyynes are known to be relatively stable as long as they are dissolved in suitable solvents.^{7,8} However, their stability is lost at relatively high polyynes concentrations,⁷ at temperatures above room temperature,^{8,9} and after exposure to light¹⁰ because polyynes have a tendency to transform into the more stable sp² phases *via* chain-chain cross linking reactions.

One of methods to stabilize polyynes was to terminate the chain by heavy atoms or bulky groups: Yiledizhan *et al.*⁴ capped polyynes by the admantyl group. Cataldo *et al.*² suggested the synthesis of a stable metal nanoparticle-poly-yne complex. Another method for the stabilization of polyynes was to insert and to adsorb them on the linear carbon chain molecules in solid phase materials.¹¹ Recently, Nishide *et al.* have investigated the production of C₁₀H₂ inserted into single-wall carbon nanotubes (SWCN).¹¹ According to their Raman spectroscopy results, the C₁₀H₂ molecules were stable up to 300 °C in dry air.¹¹ Matsutani *et al.*⁶ used a sol-gel method to produce SiO₂ dried gel containing linear carbon chain molecules. Their results of the UV-vis absorption indicated that the typical absorption peaks of polyynes were stable up to seven days after they prepared polyynes by sol-gel method.⁶ In order to examine the stability of polyynes and the effects of SERS in the Ag-poly-yne/PVA film, Okada *et al.* performed absorption measurements at different holding times.¹² They reported that Ag-poly-yne aggregates are stable up to a month as well.

Here, we investigated and identified the interaction between polyynes and the metal nanoparticles prepared by laser ablation in liquid and analyzed the Raman, surface-enhanced Raman scattering (SERS), and UV-vis absorption spectra in metal nanoparticles and copper chloride solutions as well as in deionized water. While polyynes have been prepared mostly by organic synthetic strategies based on chemical reactions,^{3,4} the reaction yield is known to be quite low because these methods involve several chemical reaction steps.^{3,4} Alternatively, liquid laser ablation has been suggested to prepare polyynes.⁸⁻¹⁰ This method has a number of advantages: the cost is comparatively low, the recovery of product is higher than that of laser ablation in the gas phase, and the ablation surroundings can be easily changed by replacing solvents.

Experimental

The apparatus employed in this study is a slightly modified version of the laser ablation apparatus reported in earlier studies.^{9,13} Figure 1 shows the schematic view of the three experimental procedures, (I), (II), and (III). Polyyne solution was produced by laser ablation of a graphite target (99.99%) in a stainless steel vessel filled with 30 mL of deionized water. The surface of the graphite target was polished with 1200-grade emery paper prior to laser irradiation by a Q-switched Nd:YAG laser (Continuum, Surelite I, $\lambda = 1064$ nm, pulse duration 5 ns) operated at 10 Hz. The energy of the Nd:YAG laser was maintained at 40 mJ/pulse in order to avoid the generation of splashes. The laser beam was loosely focused using a lens with a focal length of 300 mm. The spot size of the focused laser beam was 2.0 mm in diameter and the typical irradiation time was 20 min. The solution was stirred using a magnetic stirrer during laser ablation. The target was also continuously rotated to minimize the effect of target aging and to provide some stirring effect.

Metal nanoparticle solutions were prepared by the liquid laser ablation of metal targets such as Au, Ag, and Cu placed in a Pyrex cell filled with 10 mL of deionized water. The

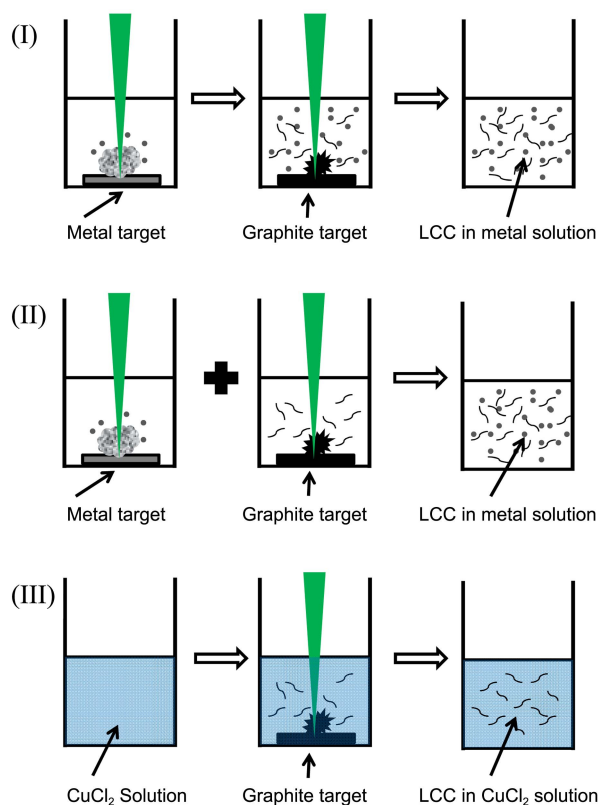


Figure 1. Schematic view of experimental procedure (LCC, linear carbon chain).

metal targets were irradiated vertically by a Q-switched Nd:YAG laser (Surelite III, $\lambda = 1064$ nm) operating at 10 Hz. The energy of the Nd:YAG laser was maintained at 50 mJ/pulse in order to avoid the generation of splashes. The laser beam was focused to a diameter of 0.5 mm. Three different methods for preparation of solutions containing complexes of metal nanoparticle (or metal) and polyynes are illustrated in Figure 1. The concentration of copper chloride solution was 4×10^{-4} M.

The optical properties of the nascent polyyne solutions were examined at several different experimental conditions by a UV-vis absorption spectrophotometer (Shimadzu UV1800). Normal Raman spectra were recorded by a commercial Raman spectrophotometer (HORIBA T64000) and SERS measurements were carried out with a home-built spectrometer.

Results and Discussion

Figure 2 shows the four spectra representing the UV-vis spectra of polyynes (a) in deionized water, (b) silver nanoparticle solution, (c) Ag-polyyne solution prepared by laser ablation of graphite in silver nanoparticles solution, and (d) Ag-polyyne solution prepared by mixing polyyne solution with silver nanoparticles solution. In the absence of interactions between metal nanoparticles and polyynes, peaks attributed to the Ag surface plasmon absorption located at 400 nm were observed as expected.¹⁴ As the metal nano-

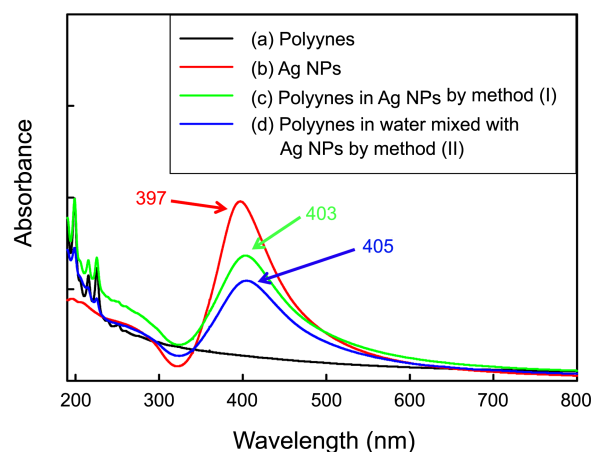


Figure 2. UV absorption spectrum of polyynes solution formed by liquid laser ablation of graphite target in deionized water and in silver nanoparticles solutions.

particles interacted with the carbonaceous shell, some differences emerged in the position and the shape of the plasmon absorption peak. The UV electronic transitions of carbon species were masked by the strong interband transitions of metals in the range of 200 to 350 nm.

In the spectrum (d) in Figure 2, the intensities of the polyynes peaks decreased significantly compared to those shown in the spectrum (c) while the change of the surface plasmon peak intensity was not quite distinct. These two spectra showed an apparent red shift in the surface plasmon absorption compared to the original silver nanoparticle solution, which indicates the aggregation of silver nanoparticles. D'Urso *et al.* reported the effects of the interaction of metal nanoparticles with polyynes¹⁴: in the absence of polyynes, silver nanoparticles preparation by laser ablation appeared separated well and homogenous in size. On the other hand, the position of the plasmon peak shifted to the red when graphite target was ablated in the presence of silver nanoparticles, which confirmed the aggregation silver nanoparticles. Also, the surface plasmon peak of silver nanoparticles decreased in intensity and broadened, indicating that aggregation took place in the liquid environment. We can clearly see that as the plasmon band position of silver nanoparticles shifted from 397.0 to 405.0 nm and the full width at half maximum (FWHM) of the plasmon peak increased from 80.0 to 86.0 nm in the spectra (b), (c), and (d).

We next examined gold metal nanoparticles and their interaction with polyynes. As in the case of Figure 2, we obtained the UV-vis spectra of polyynes solutions prepared under several different conditions, as presented in Figure 3. Here, the different lines indicate the UV-vis spectra of (a) polyynes and (b) gold nanoparticles prepared by laser ablation in deionized water, as well as those of polyynes solutions prepared by methods (I) and (II) in Figures 3(c) and 3(d), respectively. The interaction between gold metal nanoparticles and polyynes was achieved by mixing the prepared solutions as depicted in Figure 1. When gold metal

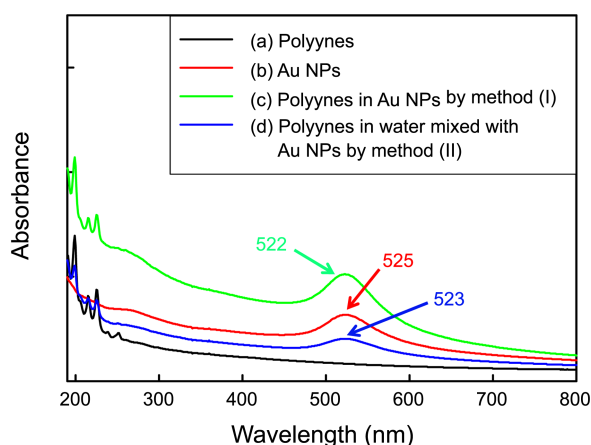


Figure 3. UV absorption spectrum of polyynes solution formed by liquid laser ablation of graphite target in deionized water and in gold nanoparticles solutions.

nanoparticles were not mixed with polyynes, a peak attributed to the gold surface plasmon absorption was observed at 525 nm as shown in Figure 3(b). In the UV-vis spectra of polyynes obtained by both methods, (I) and (II), the plasmon peaks of gold nanoparticles showed a slight blue shift. On the other hand, the UV-vis spectrum of the mixed Au-polyynes solution (method (II)) indicates different characteristics compared to those of the Au-polyynes (method (I)) or polyynes solution; in particular, the decrease in the plasmon band intensity of the mixed Au-polyynes is apparent. Also, the peak intensities related to polyynes decreased significantly as shown in Figure 3. It is of note that, unlike the case in the presence of silver nanoparticles, the plasmon band of gold nanoparticles in polyynes prepared by method (I) increased considerably compared to that of gold nanoparticles in deionized water. But the plasmon band broadened for gold nanoparticles solution (I), which manifests the occurrence of aggregation. The plasmon band position of gold nanoparticles shifted from 525.0 to 522.0 nm and the FWHM of the band decreased from 55.0 to 49.0 nm in (b), (c), and (d) of Figure 3. Interestingly, the plasmon band of gold nanoparticles shifted to the blue as they are prepared by method (I), while it shifted to the red for silver nanoparticles. Compared to the silver nanoparticles, the gold nanoparticles may be photo-fragmented further by 1064 nm irradiation in case of method (I).¹⁴ Unfortunately, however, the reason is not clear as yet.

Also, in order to examine the interaction of copper nanoparticles with polyynes, we compared the UV-vis spectra of polyynes in a copper nanoparticle solution by method (I) and (II). The UV-vis absorption spectra of polyynes solution formed by liquid laser ablation of a graphite target (a) in deionized water, (c) in copper nanoparticles solution, and (d) that of the mixture of both solutions are shown in Figure 4. Unlike the case for silver and gold nanoparticles solutions, the copper nanoparticles hardly aggregated to form linear carbon chains. In the UV-vis spectra of polyynes in copper nanoparticle solution, the peaks of polyynes were smaller than those in other metals (Ag and Au). Figure 4(b) is the UV-vis spectrum of copper nanoparticle solution, where the

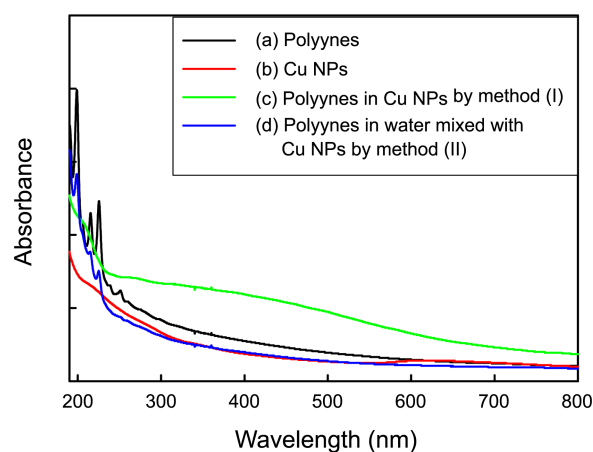


Figure 4. UV absorption spectrum of a polyynes solution formed by liquid laser ablation of graphite target in deionized water and in copper nanoparticles solutions.

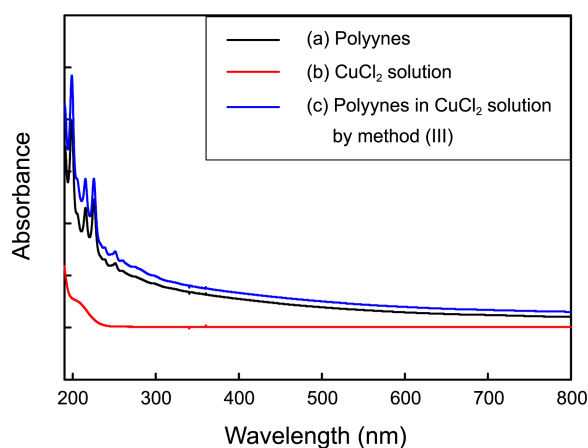


Figure 5. UV absorption spectrum of polyynes solution formed by liquid laser ablation of graphite target in deionized water and in copper chloride solution.

typical copper plasmon band did not show up. This implies that copper nanoparticles were oxidized in the solution phase. While the noble metals such as Pt, Ag, and Au are hardly oxidized, copper can be easily oxidized: Cataldo *et al.* reported that copper nanoparticles were oxidized in the air or in aqueous solvents and the peaks attributed to the copper surface plasmon located at 680 nm disappeared soon.²

In order to investigate the interaction between copper ions and polyynes, we compared the UV-vis spectra of (a) polyynes solutions in deionized water, (b) copper chloride solution, and (c) copper chloride solution with polyynes by method (III) as shown in Figure 5. The polyyne peaks prepared in copper chloride solution were little larger than those of polyynes prepared in deionized water. This suggests that the copper ions in the solution did not have significant interaction with polyynes to induce heavy aggregations.

Even though the formation of polyynes in deionized water and their aggregation with metal nanoparticles were confirmed by UV-vis absorption spectroscopy, we also employed Raman spectroscopy to elucidate the molecular structures of polyynes and their aggregates. The Raman spectra of

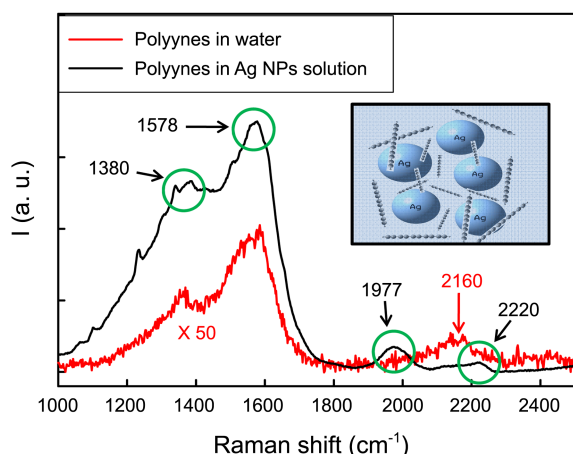


Figure 6. Raman spectra of polyynes prepared by laser ablation of graphite target in deionized water and in silver nanoparticle solution. The inset is a imaginary model for surface enhanced Raman spectroscopy.

polyynes prepared by laser ablation of a graphite target in deionized water and in silver nanoparticle solution are shown in Figure 6. In accordance with the previous results on SERS from polyynes aggregated on metal nanoparticles,¹⁰ the spectra in Figure 6 show peaks located at around 1200 and 2200 cm^{-1} .^{12,15-17} The broad peak in the 1300-1700 cm^{-1} region can be attributed to amorphous carbon or graphite (or graphite-like) particles, which can be decomposed into the D band at around 1380 cm^{-1} and the G band at around 1580 cm^{-1} . These features reveal a highly distorted bond length and angle.¹⁸ In Figure 6, the disordered component (G band) of the graphite-like band is slightly larger than the D band for both Raman spectra. In contrast, the presence of Raman bands located around 2200 and 1977 cm^{-1} regions can be attributed to the carbon triple bonds of free and aggregated polyynes, respectively.^{10,18} In the silver nanoparticle solution, the peak at 1977 cm^{-1} was highly pronounced, which indicates the interaction of polyynes with the silver nanoparticles.¹⁰ This aggregation phenomenon is considered to originate from strong interactions between polyynes and silver nanoparticles. In Figure 6, it is gratifying that the peak intensity of polyynes in a silver nanoparticles solution is about 100 times higher than that of polyynes in water, which reflects the adsorption of polyynes onto the surface of silver nanoparticles.

Conclusion

By employing UV-vis and Raman spectrometry, we investigated the interaction between polyynes and different metal nanoparticles to provide an insight into optical properties of

metal-polyynes systems produced by various preparation methods. It turned out that polyynes formed aggregates with metal nanoparticles (Ag, Au) but there was no significant change in polyynes when they were produced in copper chloride solution. The enhancement of Raman peaks *via* SERS effect was clear, which indicates adsorption of polyynes on metal surfaces. Immobilization of polyynes in the solid phase may yield further insight into the stabilization of polyynes at room temperature and trigger their applications in diverse fields.

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