Photopolymerization of diacetylene with gold cluster

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Thin films of gold-polydiacetylene nanocomposite were prepared and their morphology was characterized by scanning electron microscopy. After UV irradiation of thin films of gold-diacetylene nanocomposite, red-shifted absorption peaks, attributed to polydiacetylenes, were observed besides the surface plasma resonance of gold clusters, and their absorbance increased with increase of UV irradiation time. The mono-distributed and 5 nm-sized gold clusters were segregated by using an ethyl cellulose matrix. However, with the addition of diacetylene, about 10-fold larger clusters were formed.

Among nanoscale materials, nanocomposites have attracted much attention due to their advantageous characteristics for electronic and optical device applications.[1] Polydiacetylene ($\{C(R_1)–C \equiv C–C(R_2)\}_n$), on the other hand, is the most widely investigated polymer material, with third-order nonlinear optical properties and anisotropic electrical conductivity.[2] In comparison with inorganic materials, a metal-organic composite possesses various advantageous characteristics for preparation and processing, such as film-forming properties. We have previously reported the photopolymerization of diacetylene (10,12-pentacosadiynoic acid) in gold colloidal solution.[3] In this paper we describe the preparation of thin films of a gold-diacetylene nanocomposite and their photopolymerization in the solid state.

The gold-diacetylene nanocomposite was prepared from a mixture of dispersed gold clusters (Perfect Gold, Au101α, Vacuum Metallurgical Co., Ltd.) and diacetylene (10,12-pentacosadiynoic acid) solution. In addition, ethyl cellulose was added to segregate the gold clusters. Nanocomposite films were prepared on a quartz substrate by using a spin-coating method, and irradiated with a high-pressure mercury lamp (Ushio UI-501C, 100W). The photopolymerization of diacetylene was investigated by optical absorption measurements as a function of the UV irradiation time. Scanning electron microscopy (SEM, Hitachi S-900) was also performed to study the change in morphology of the gold clusters prepared on indium tin oxide (ITO) substrates.

An absorption band at 530 nm, due to the surface plasma resonance of gold clusters, was observed as shown in Fig. 1.

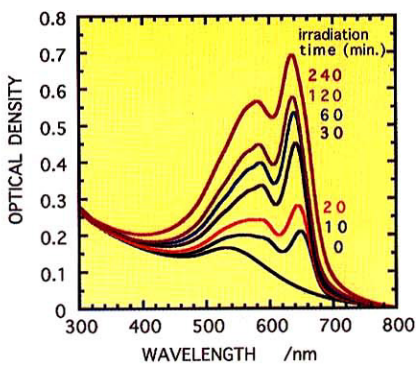
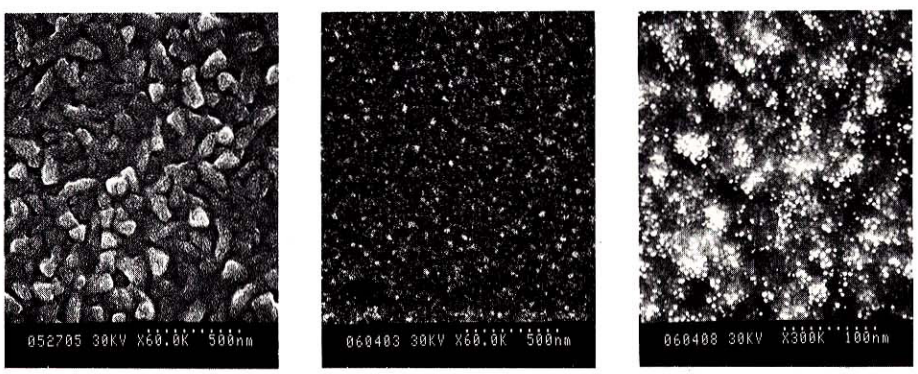


Fig. 1. Optical absorption spectra of gold-diacetylene (DA) nanocomposite film with ethyl cellulose (EC), as a function of the UV irradiation time (Au : EC : DA = 1 : 1 : 2).



(a) (b) (c)

Fig. 2. SEM photographs of Perfect Gold Au101α (Au, ×60 K) (a) and gold clusters segregated by the addition of ethyl cellulose (Au : EC = 1 : 1, ×60 K) (b), (Au : EC = 1 : 1, ×300 K) (c).

Red-shifted absorption peaks were observed after UV irradiation and their absorbance increased with increase of UV irradiation time. These absorption bands, at around 600 and 650 nm, were attributed to polydiacetylene[4] and the degree of polymerization increased with increase of UV irradiation time.

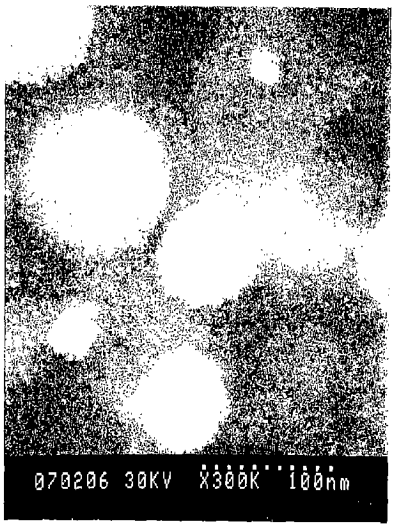


Fig. 3. SEM photograph of gold-polydiacetylene nanocomposite in an ethyl cellulose matrix after photopolymerization (Au : EC : DA = 1 : 1 : 2, ×300 K).

We investigated the morphology of the gold cluster films by SEM. Figure 2(a) shows the aggregation of gold clusters in the films prepared without the addition of ethyl cellulose. As a matrix, ethyl cellulose allows the segregation of gold clusters as shown in Fig. 2(b). Gold clusters used in this study had a mono-distributed 5 nm-size as observed in Fig. 2(c). However, the co-existence of diacetylene molecules led to the formation of about 10-fold larger clusters as shown in Fig. 3. After photopolymerization of diacetylene, reduction of secondary electron emission was also observed in SEM measurements. This gold-polydiacetylene nanocomposite film allows us to carry out further studies for the clarification of its nonlinear optical properties.

References

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