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Akito Masuhara^a; Hitoshi Kasai^a; Takeshi Kato^a; Shuji Okada^a; Hidetoshi Oikawa^a; Yasuo Nozue^b; S. K. Tripathy^c; Hachiro Nakanishi^a

^a Institute for Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan ^b Department of Physics, Graduate School of Science, Tohoku University, Sendai, Japan ^c Departments of Chemistry and Physics, Center for Advanced Materials, University of Massachusetts—Lowell, Lowell, MA, U.S.A.

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HETERO-MULTILAYERED THIN FILMS MADE UP OF POLYDIACETYLENE MICROCRYSTALS AND METAL FINE PARTICLES

Akito Masuhara,^{1,*} Hitoshi Kasai,¹ Takeshi Kato,¹ Shuji Okada,¹
Hidetoshi Oikawa,¹ Yasuo Nozue,² S. K. Tripathy,^{3,†} and
Hachiro Nakanishi¹

¹Institute for Multidisciplinary Research for Advanced Materials,
Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

²Department of Physics, Graduate School of Science, Tohoku
University, Aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan

³Departments of Chemistry and Physics, Center for Advanced
Materials, University of Massachusetts—Lowell, Lowell, MA 01854

Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

We have successfully prepared the hetero-multilayered thin films composed of polydiacetylene microcrystals and gold and/or silver fine particles by means of electrostatic deposition technique, *i.e.*, layer-by-layer deposition method, characterized the morphological structure of the thin films, and evaluated their optical properties.

Key Words: Hetero-multilayered thin films; Polydiacetylene; Microcrystals; Metal fine particles; Layer-by-layer technique; Electrostatic deposition

*Corresponding author.

†Deceased.

INTRODUCTION

Nano fine particles such as metals and semi-conductors have been investigated extensively from the viewpoints of both fundamental science and some applications [1-3]. These nano fine particles may occupy the mesoscopic phase between an isolated single atom and/or molecule and the corresponding bulk crystals. It was worth noting that nano semi-conductor fine particles exhibited the enhancement of nonlinear optical (NLO) properties induced by quantum confinement effect [4]. However, little attention had been paid so far until we demonstrated that the reprecipitation method was available for fabricating many kinds of π -conjugated organic microcrystals. One could not apply the fabrication techniques for inorganic nano fine particles to prepare organic microcrystals, because organic compounds are commonly unstable thermally. The crystal size of organic microcrystals prepared was in the range of several tens nanometers to a few hundred nanometers, and their crystal structure, reactivity, optical properties, and microcrystallization processes were investigated in detail [5-8]. Interestingly, the excitonic absorption peak positions were shifted to short-wavelength region with decreasing crystal size, which could be explained simply by quantum size effect. This is now speculated to be due to a certain interaction between exciton and phonon in thermally softened organic microcrystal lattice.

Now, characteristic interactions between exciton, plasmon and their resonance effect in the hybridized systems between organic microcrystals and inorganic nano fine particles would make it possible to exhibit novel optical properties. As predicted theoretically, [9,10] the NLO property would be enhanced in organic microcrystals coated with metal thin layer. For example, the NLO property of polydiacetylene (PDA) thin film, in which gold fine particles were dispersed, was enhanced approximately two hundred times [11]. This fact suggests the possibility of some applications for new optical devices.

In the present article, we attempted to fabricate hetero-multilayered thin films made up of PDA microcrystals and metal fine particles, and evaluated the morphological structure of their thin films. In addition, their linear optical properties will be discussed in detail. As a fabrication technique, the so-called layer-by-layer deposition method was adopted by utilizing highly negative ζ -potential of PDA microcrystals. We have already prepared successfully the homo-multilayered thin films of PDA microcrystals by using this technique [12, 13].

EXPERIMENTAL

Poly(DCHD) Microcrystals

Diacetylene monomer used in the present study was 1,6-di(N-carbazolyl)-2,4-hexadiyne (DCHD). [14] DCHD monomer microcrystals were fabricated by the conventional reprecipitation method, followed by solid-stated polymerization

with UV irradiation ($\lambda = 254$ nm) for 20 minutes [5, 8]. As a result, one could obtain poly(DCHD) microcrystals dispersed in an aqueous dispersion liquid.

Gold and Silver Fine Particles [15-18]

Au fine particles were prepared by the reduction of hydrogen tetrachloroaurate (III) tetrahydrate with trisodium citrate, whereas Ag fine particles were obtained by reducing silver nitrate with sodium borohydride. The diameters of the resulting Au and Ag fine particles were *ca.* 13 nm and *ca.* 15 nm, respectively.

Characterization

The crystal size and shape for poly(DCHD) microcrystals and metal fine particles were evaluated not only by dynamic light scattering (DLS: DLS-7000, Otsuka Electronics Co.) but also by scanning electron microscope (SEM: S-900, Hitachi Ltd.). The morphological structure of hetero-multilayered thin films were observed from the measurement with SEM. UV-VIS spectrometer (V-570DS, JASCO Ltd.) was employed to measure UV-VIS absorption spectra.

Layer-by-Layer Deposition Procedures for Fabricating Hetero-Multilayered Thin Film [12, 13, 18]

The ζ -potential of poly(DCHD) microcrystals dispersed in an aqueous liquid was *ca.* -40 mV by the measurement with ζ -potentiometer (ELS-8000, Otsuka Electronics Co.). On the other hand, the same physical quantities of Au and Ag fine particles were also -27 mV and -36 mV, respectively. By utilizing electrostatic deposition between poly(DCHD) microcrystals, metal fine particles, and some kinds of polyelectrolyte, the layer-by-layer deposition procedures were performed as follows [18]. Polyelectrolytes used were poly(dimethyldiallylammonium chloride) (PDAC: $M_w = 2.0 \times 10^5$ to 3.5×10^5 , ALDRICH), polyethyleneimine (PEI: $M_w = 2.5 \times 10^4$, ALDRICH), poly(allylamine hydrochloride) (PAH: $M_w = 7.0 \times 10^4$, ALDRICH), and poly(sodium 4-styrenesulfonate) (PSS: $M_w = 7.0 \times 10^4$, ALDRICH). Here, PDAC, PAH, and PEI are cationic polyelectrolytes, while PSS is an anionic one.

Figure 1 shows the schematic structure of hetero-multilayered thin film. The clean slide glass was first coated with PEI, followed by PSS and PAH. Metal fine particles were deposited on PAH-modified surface, and then covered with PDAC-PSS-PDAC layer. Poly(DCHD) microcrystals were further deposited on the surface of PDAC, and covered again with PAH-PSS-PAH layer. The sequence of these steps is as a whole called "1st layer". The immersing times required for electrostatic deposition were, respectively, 20 minutes for PEI and PSS, 5 hours for PAH, 2.5 hours for metal fine particles, and 1 hour for poly(DCHD) microcrystals.

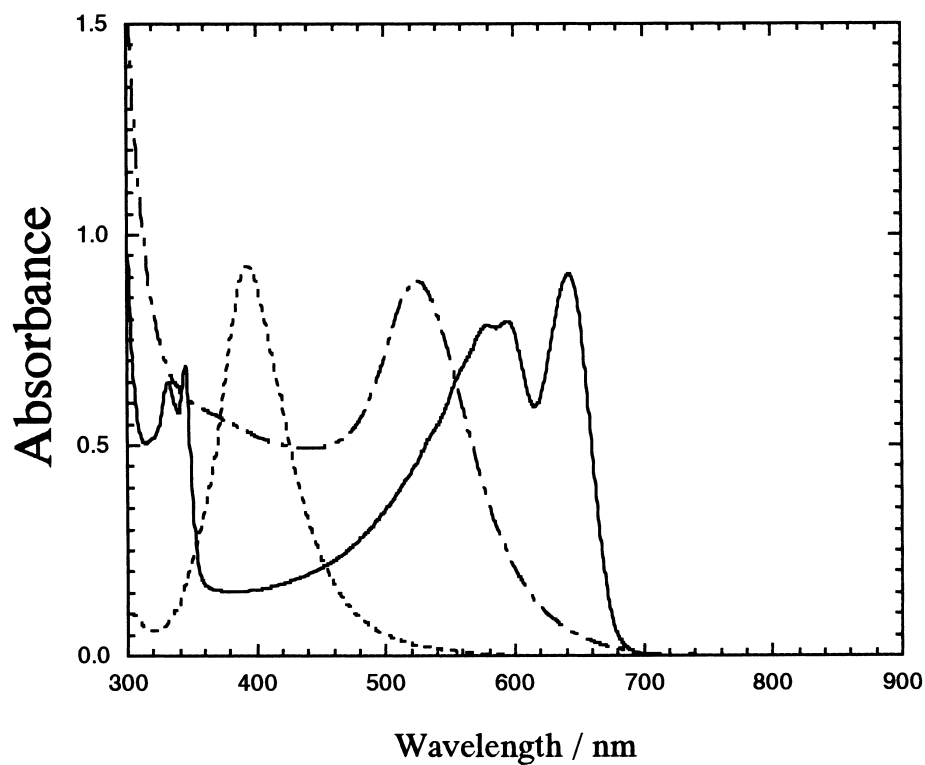


Figure 2. Absorption spectra of Au (one-dotted line) and Ag (dotted line) fine particles, and poly(DCHD) microcrystals (solid line) dispersed in an aqueous liquids.

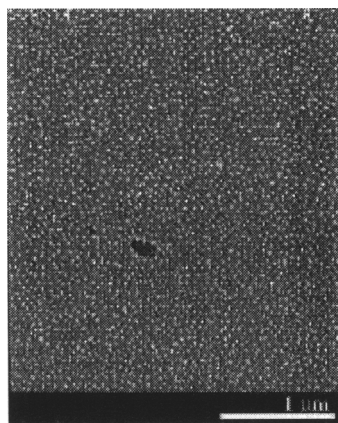
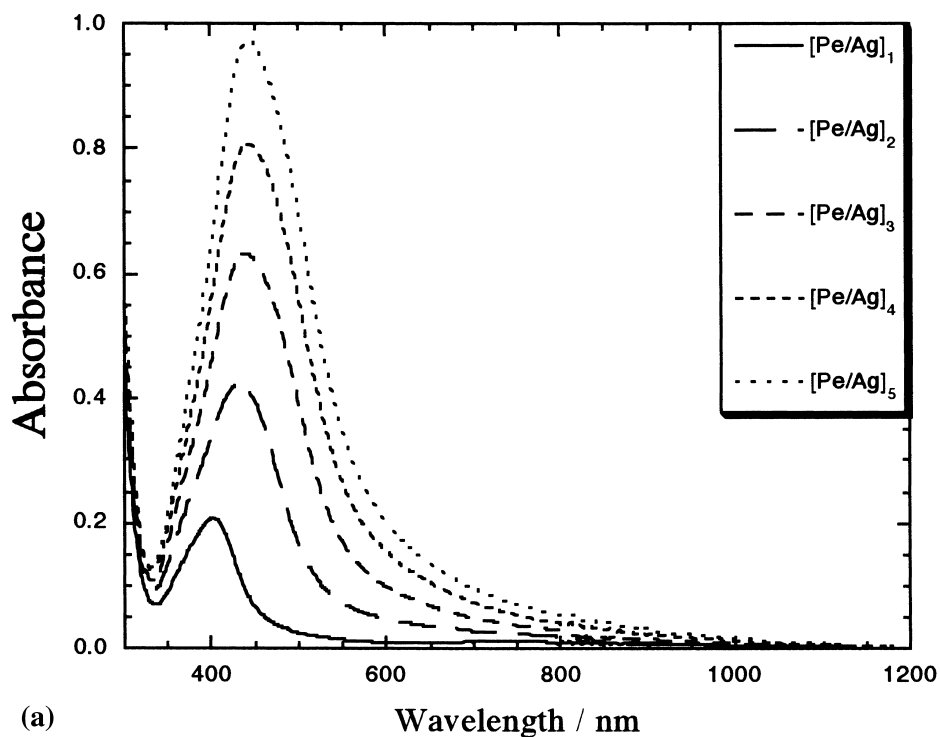
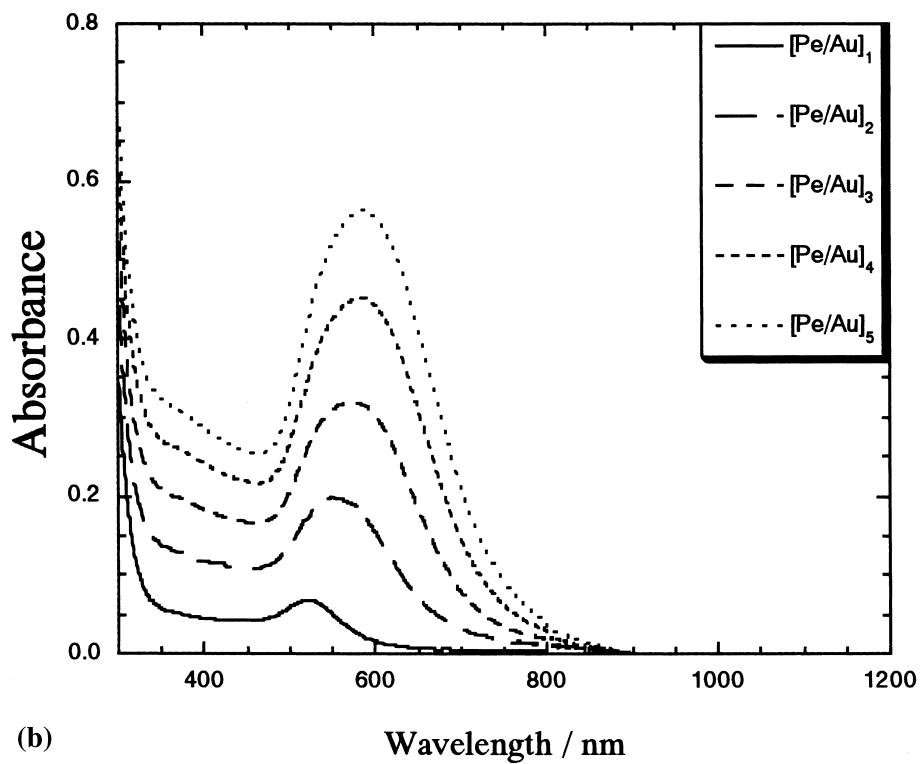


Figure 3. SEM photographs for the layered thin films of Au fine particles: [Au]₁.



(a)



(b)

Figure 4. Absorption spectra for layered thin films of metal fine particles: (a) [Ag]_n; (b) [Au]_n.

fine particles. The metal fine particles are considered to optically interact with each other, when the averaged distance between metal particles was comparable with their diameter [18]. In the present case, it is considered that the optical interaction between Au fine particles may be induced by the dipole–dipole interaction, *i.e.*, Frenkel excitonic effect, which actually decreases rapidly in proportion to distance between metal fine particles to the power of minus six. As shown in Figure 3, the average distance between metal fine particles at the n -th layer was *ca.* 20 nm, and was longer than their diameters as described in Experimental. On the other hand, the thickness of polyelectrolytes layer shown in Figure 1 is actually less than *ca.* 3 to 4 nm at the most [16]. It appears that the optical interaction is believed to predominantly bring about between metal fine particles in the nearest neighbor layers, rather than along the lateral direction in-of-layer.

Let us further consider the optical properties of $[\text{Au}]_n$ as shown in Figure 4(b). Figure 5 shows the plots of Δv_{max} vs. number of layers n , where Δv_{max} is the shifted difference in wave number defined as $[\Delta v_{\text{max}}(n) - \Delta v_{\text{max}}(n = 1)]$. When the number of N_0 of Au fine particles with the oscillator strength f may exist in a unit

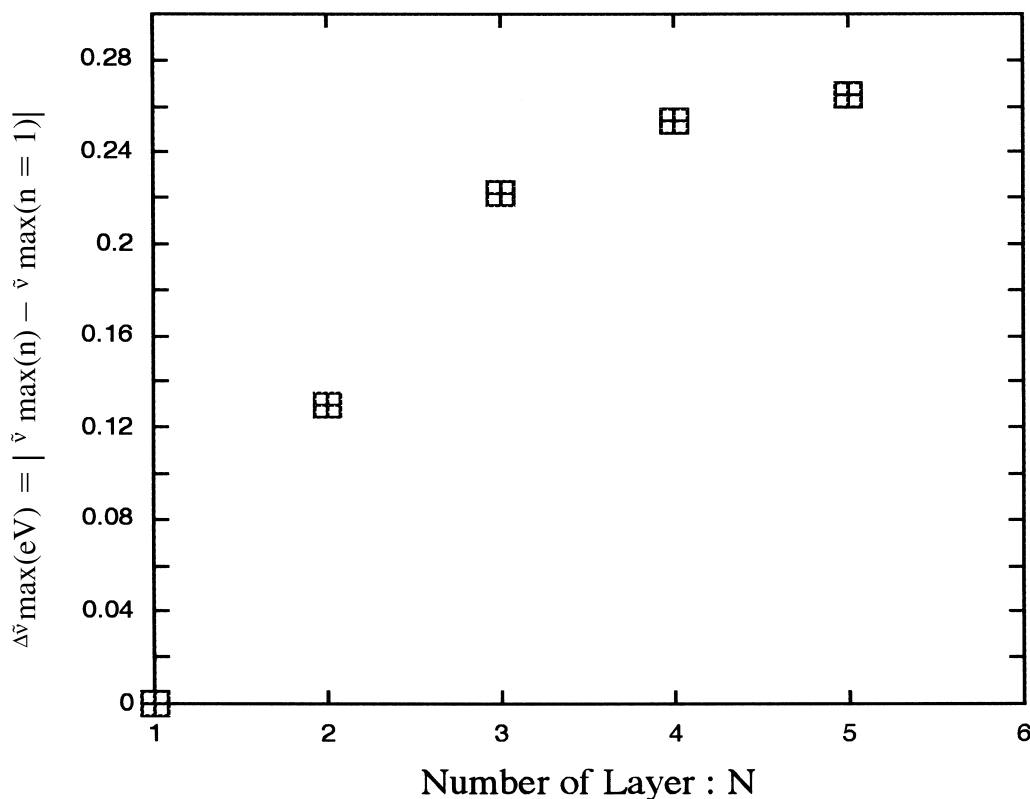


Figure 5. Plots of Δv_{max} vs. number of layers n . Δv_{max} is the difference in shifted wave number defined as $[\Delta v_{\text{max}}(n) - \Delta v_{\text{max}}(n=1)]$.

value, the excited state should be in general split into the longitude wave mode (ω_L , $\varepsilon = 0$) and traverse wave mode (ω_T , $\varepsilon = \infty$) as follows:

$$\omega_L^2 = \omega_T^2 + \frac{4\pi N_0 e^2 f}{m_0 \varepsilon_\infty}, \quad (1)$$

where m_0 and e are electron rest mass and elementary electric charge, respectively. Since the center ω_1 of the energy level split into longitude wave mode and traverse wave mode is not essentially shifted in an isotropic systems, we can obtain Equation 2:

$$\omega_1 = \frac{2\omega_T + \omega_L}{3}, \quad (2)$$

In addition, the oscillator strength of Au fine particles is approximately the same as the total number of 6s-electron in one Au fine particle. The value of f is approximated to be unity in this case and N_{Au} is the number of 6s-electron with Au fine particles, Equation 3 is derived from Equation 1:

$$\omega_L^2 = \omega_T^2 + \frac{4\pi N_0 N_{Au} e^2}{m_0 \varepsilon_\infty}, \quad (3)$$

Here, we now introduce the packing parameter or the dipole–dipole interaction strength parameter. When $\rho = 0$, Au fine particles are at an isolated stage and did not interact with each other ($0 \leq \rho \leq 1$). (If the whole space may be occupied by Au, which corresponds to $\rho = 1$, the square of second term at the right hand side in Equation 3 is estimated to be about 9 eV at $\rho = 1$, so Equation 3 is assumed to be written as Equation 4, introducing the parameter, ρ :

$$\omega_L^2 - \omega_T^2 \cong 8 \rho, \quad (4)$$

The value of ω_1 in Equation 2 is roughly 2 eV from the typical absorption spectra as shown in Figure 4(b). Therefore, one can obtain Equation 5 from Equations 2 and 4:

$$\omega_1 - \omega_T \cong 7\rho, \quad (5)$$

In other words, the term of $\omega_1 - \omega_T$ in Equation 5 represents the difference in excited energy on the basis of $\rho = 0$, and may correspond to Δv_{\max} in Figure 5. The parameter ρ is closely related to the number of layers. However Δv_{\max} in Figure 5 increased not proportionally as predicted by Equation 5, but gradually

with the number of layers. This tendency suggests the dipole–dipole interaction may occur predominantly between the nearest neighbor layers as described previously. The reason for the shift in absorption peaks as shown in Figure 4(b) seems to be more complex, reflectivity Ag fine particles varied remarkably λ around 600 nm.

Hetero-Multilayered Thin Film

The SEM photographs for the hetero-multilayered thin films are displayed in sequence in Figure 6. Poly(DCHD) microcrystals were cubic, and the crystal size was about 100 nm. The size and shape of poly(DCHD) microcrystals deposited were almost the same ones at each n-th layer (Figures 6(b), 6(d), and 6(f)), which means that poly(DCHD) microcrystals scarcely condense and aggregate during

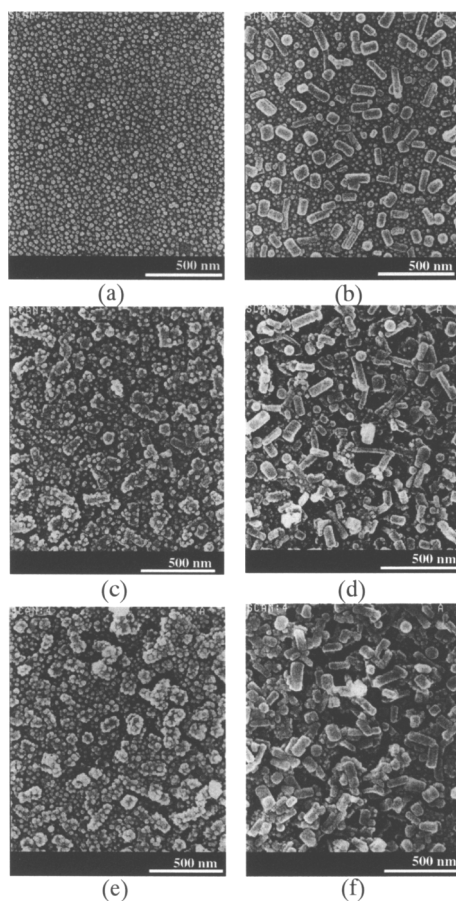


Figure 6. SEM photographs of the hetero-multilayered thin films: (a) $[\text{Ag}]_1$; (b) $[\text{Ag}/\text{DC}]_1$; (c) $[\text{Ag}/\text{DC}]_2/\text{Ag}$; (d) $[\text{Ag}/\text{DC}]_3$; (e) $[\text{Ag}/\text{DC}]_6/\text{Ag}$; (f) $[\text{Ag}/\text{DC}]_7$.

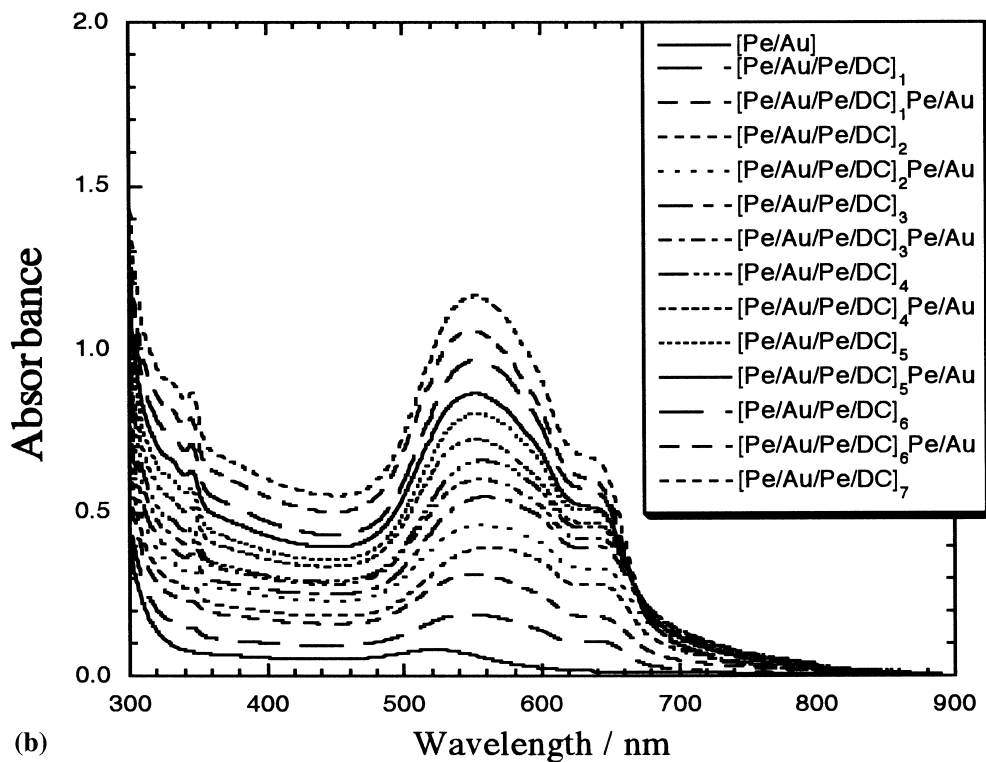
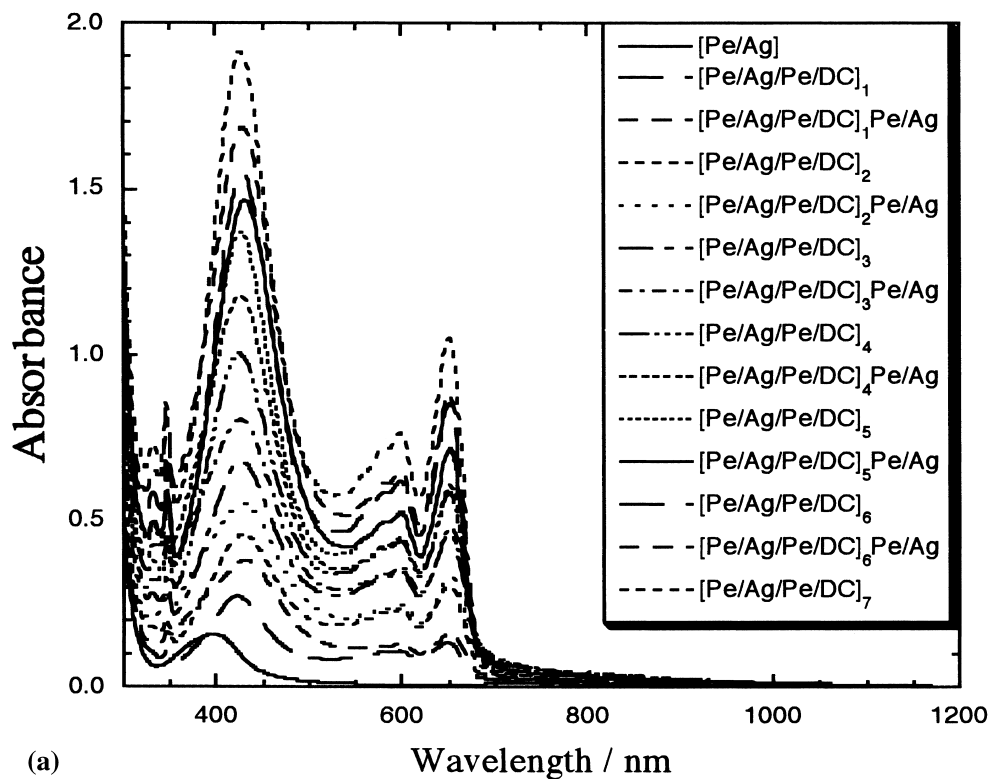


Figure 7. Absorption spectra of the hetero-multilayered thin films: (a) [Ag/DC]_n and [Ag/DC]_nAg; (b) [Au/DC]_n and [Au/DC]_n/Au.

the deposition process. However, the deposited layer of Ag fine particles (Figures 6(c) and 6(e)) was somewhat different $[Ag]_1$ shown in Figure 6(a). One can see poly(DCHD) microcrystals deposited, just under the layer of Ag fine particles. In other words, the present hetero-multilayered structure is said to be rough to some extent, due to a large difference in crystal size between poly(DCHD) microcrystals and Ag fine particles.

Figure 7 shows the typical UV-VIS absorption spectra for the hetero-multilayered thin films. The absorbance was multiplied evidently with increasing number of layers. In spite of the hetero-multilayered thin films, the absorption peak positions from Ag and Au fine particles already started to be red-shifted after the deposition of the first poly(DCHD) layer in the same manner as those in Figures 4(a) and 4(b). Probably, this is weak interaction between Ag fine particles and poly(DCHD) microcrystals due to the roughness of the disordered layer structure along the vertical direction as described previously in Figures 6(c) and 6(e). On the contrary, λ_{max} from poly(DCHD) microcrystals was almost constant, not changed, in any n-th layer, which described unexpectedly that there not strong, but only weak optical interaction not only between layered poly(DCHD) microcrystals but also between organic microcrystals and metal fine particles.

CONCLUSION

We have succeeded in fabricating the hetero-multilayered thin films made up of poly(DCHD) microcrystals and Au and/or Ag fine particles by means of the layer-by-layer deposition technique, and have evaluated the morphology and the optical properties. The optical interaction for layered thin films of Au fine particles was explained quantitatively on the basis of resonance energy transfer induced by the dipole-dipole interaction, *i.e.*, Frenkel exciton effect. However, only a weak interaction has been found for hetero-layered thin films. Therefore, the hetero-nanocomposite formation which both organics and metals has direct contact with each other. Peculiar optical interactions would be expected in the near future.

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