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Study of ferric oxide nanoparticles-tris-(2,4-di-t-amylphenoxy)-(8-quinolinolyl) copper phthalocyanine composite LB film

Lihua Huo[a, b], Lixin Cao[a], Xinglin Li[a], Wei Li[a], Haining Cui[a], Dapeng Jiang[c], Guangfu Zeng[a], Shiquan Xi[a,*]

[a]*Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P.R. China*
[b]*College of Chemistry and Chemical Technology, Heilongjiang University, Harbin 150080, P.R. China*
[c]*Changchun Institute of Physics, Laboratory of Excited State Process, Chinese Academy of Sciences, Changchun 130021, P.R. China*

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Abstract

The ferric oxide nanoparticles-tris-(2,4-di-t-amylphenoxy)-(8-quinolinolyl) copper phthalocyanine ($CuPcA_2$) composite ultrathin film was obtained by LB (Langmuir–Blodgett) technique. Structure of the composite LB film was characterized by X-ray photoelectron spectra, transmission electron microscopy, infrared spectra and visible spectra. Gas sensitivity measurements indicate that the composite LB film is sensitive to 100–200 ppm C_2H_5OH at room temperature. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Composite LB film; Ferric oxide nanoparticles; Copper phthalocyanine derivative; Characterization

1. Introduction

It has been proved that nanoparticulate semiconductors are very important materials for their special physical and chemical properties [1,2]. Their thin or ultrathin films have widespread applications as multi-functional microelectronic and molecular devices, e.g. ferric oxide thin films. Some approaches, such as CVD, sputtering and electron-beam evaporation methods [3–5], have been used to prepare ferric oxide nanoparticulate thin film. However, the nanoparticles in these thin films were easy to aggregate and/or grow, and the thickness of these films could not be controlled precisely. These limitations have restricted application of these nanoparticulate thin films.

As we know, organized molecular film can be obtained by LB (Langmuir–Blodgett) technique. This kind of ultrathin film can be deposited monolayer-by-monolayer in order to control thickness of the film. However, it is difficult to obtain size-controlled inorganic particulate ultrathin film by LB technique. The nanoparticles need to be mixed with other amphiphilic molecules. Metallophthalocyanine having good chemical and thermal stability is a kind of p-type organic semiconductor material. There have been many studies on the preparation, characterization and gas sensitivity of LB films due to their potential application as gas sensor [6]. Therefore, LB films might be prepared by compositing ferric oxide nanoparticles with metal phthalocyanine. It is a very interesting issue to study on the preparation and properties of inorganic–organic composite LB film. New functional materials may be obtained by taking advantage of various properties exhibited by each component.

In this paper, composite LB film of ferric oxide nanoparticles and copper phthalocyanine derivative was prepared. The effects of the doped nanoparticles are studied on the spectral and gas-sensing properties of copper phthalocyanine derivative LB film.

2. Experimental details

2.1. Preparation of materials

Copper phthalocyanine derivative - Tris-(2,4-di-t-amylphenoxy)-(8-quinolinolyl) copper phthalocyanine ($CuPcA_2$) was synthesized [7]. After purification by column chromatography, elemental analysis was carried out [($C_{89}H_{93}N_9O_4Cu$): calculated (%) – C (74.65), H (6.25), N (8.80), Cu (4.4), found (%) – C (74.60), H (6.25), N (8.81), Cu (4.4)]. Its chemical structure is shown in Fig. 1.

Ferric oxide hydrosol - The hydrosol was prepared by a forced hydrolysis method: 5 ml solution of $FeCl_3$ (0.1 mol/dm^3) was poured into 175 ml boiling water under stirring,

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* Corresponding author. Fax: +86-431-5685653.
E-mail address: xisq@public.cc.jl.cn (S. Xi)

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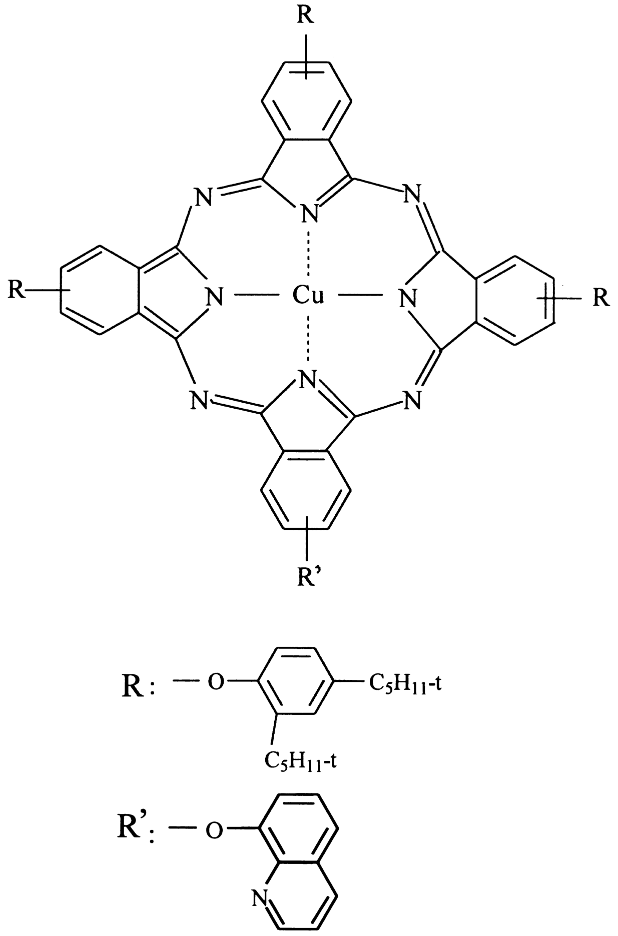

Fig. 1. The chemical structure of $CuPcA_2$ molecule.

and kept slightly boiling for 2 h. After quenching to room temperature, free Fe^{3+} ions were removed by placing the system into a semi-permeable membrane bag and dialyzing against deionized water. An orange-red hydrosol with pH value of 3.2 was obtained. The mean particle size of Fe_2O_3 nanoparticles was 5–7 nm.

Complex chloroform solution - $CuPcA_2$ embedding Fe_2O_3 nanoparticles solution was prepared by extraction of ferric oxide hydrosol with $CuPcA_2$ solution. Chloroform was used as the solvent. Concentrations of the solution were determined by TJA POEMS ICP-AES spectroscopy: Cu^{2+} 4.06×10^{-5} mol/dm^3, Fe^{3+} 3.04×10^{-5} mol/dm^3.

2.2. Preparation of composite Langmuir–Blodgett films

The determination of surface pressure–mean molecular area (π–A) isotherm and deposition of LB multilayers were carried out using a KSV-5000 system from Finland at 25.5 ± 0.1°C. Deionized and double distilled water (pH 6.5) were used as the subphase. The multilayers were deposited as Z-type mode at constant surface pressure of 40 mN/m. The dipping speed was 5 mm/min. Silicon, quartz and glass were used as substrates. Silicon and quartz were rendered hydrophilic by treating sequentially with $CHCl_3$, C_2H_5OH and pure H_2O, each for 20 min under the action of ultrasonic wave. Glass was pretreated in boiling isopropyl alcohol at least for 24 h. Glass was coated with 50 finger pairs of aluminum electrodes having a width of 50 μm, spaced 50 μm from the adjacent electrode.

2.3. The structural characterization and gas-sensing measurement of Langmuir–Blodgett films

IR spectra were obtained from Bio-Rad FTS-135 at a resolution of 4 cm^{-1}. Perkin–Elmer Lambda 9 spectrophotometer was used to obtain visible spectra.

X-ray photoelectron spectra (XPS) gave the component of the composite LB film. The spectra were carried out using VG ESCALAB MK-II X-ray photoelectron spectrometer with Al K_α radiation ($h\upsilon = 1486.6$ eV). The standard deviation for the binding energy values was 0.2 eV.

Transmission electron microscopy (TEM) studies of the monolayer were carried out with JEOL-2100 electron microscope. The electron energy was 200 kV. The sample was fabricated by depositing the monolayer onto 400 mesh-copper grid coated with formvar.

The electrical resistance of LB film under various gas concentrations at atmospheric temperature was measured with a set of home-made apparatus. Air was used as the diluent gas. Sensitivity (S) is defined as $S = R_a/R_g$, where R_a and R_g are the resistance of LB film measured respectively in air and air containing the tested gas. The response-recovery time is monitored as 90% of resistance change.

3. Results and discussion

3.1. π–A isotherm and Langmuir–Blodgett film deposition

The surface pressure-area (π–A) isotherm of $CuPcA_2$–Fe_2O_3 nanoparticles composite monolayer is shown in Fig. 2b. It is observed that the curve shape is similar to that of pure $CuPcA_2$ monolayer (Fig. 2a). Stable Langmuir film was formed at the air–water interface. The monolayer can be compressed to a fully condensed close-packed film. $CuPcA_2$–Fe_2O_3 complex has larger mean molecular area ($CuPcA_2$–1.27 nm^2, $CuPcA_2$–Fe_2O_3–1.89 nm^2) and lower collapse pressure ($CuPcA_2$–59 mN/m, $CuPcA_2$–Fe_2O_3–54 mN/m) than the pure $CuPcA_2$ monolayer. It means that ferric oxide nanoparticles are incorporated in the monolayer.

Transfer of the first monolayer onto the different substrates was always satisfying with the transfer ratio of 1.0 ± 0.1. But the transfer ratio gradually decreased with the multilayer deposition. The transfer ratio was in the range of 0.9–1.0 before deposition of 15 layers, and 0.8–0.9 between deposition of 15–25 layers. After deposition of 25 layers, the transfer ratio decreased to 0.7. Multilayer LB films could only be obtained by the Z-type deposition mode, while the pure $CuPcA_2$ monolayer was well transferred onto the

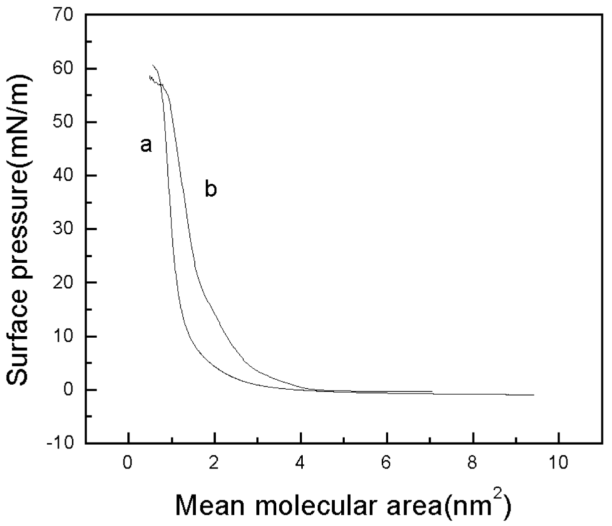

Fig. 2. π–A isotherms of complexes on the surface of pure water (a) $CuPcA_2$ and (b) $CuPcA_2$–Fe_2O_3.

substrates with Y-type. This is probably because the doped ferric oxide nanoparticles affect the film-forming ability and transfer of $CuPcA_2$ to some extent.

3.2. X-ray photoelectron spectra and Transmission electron microscopy

XPS was used to determine the component of the 15-layer composite LB film deposited on CaF_2 substrate. Fig. 3 shows that there is a distinct $Fe2p_{3/2}$ peak. The electron binding energy of $Fe2p_{3/2}$ is 711.1 eV. It reveals that ferric oxide nanoparticles exist in the composite LB film and in the α–Fe_2O_3 phase [8].

TEM image of the composite monolayer is given in Fig. 4. The nanoparticles are arranged evenly but not closely. The blank parts among the particles are the embedding molecules. It also indicates that the nanoparticles are embedded by copper phthalocyanine molecules. It is very interesting that there is no difference when the TEM image of this sample was observed two months later. It suggests that the embedding molecules can effectively restrain the nanoparticles from growing and aggregating further. It improves stability of the nanoparticulate LB film.

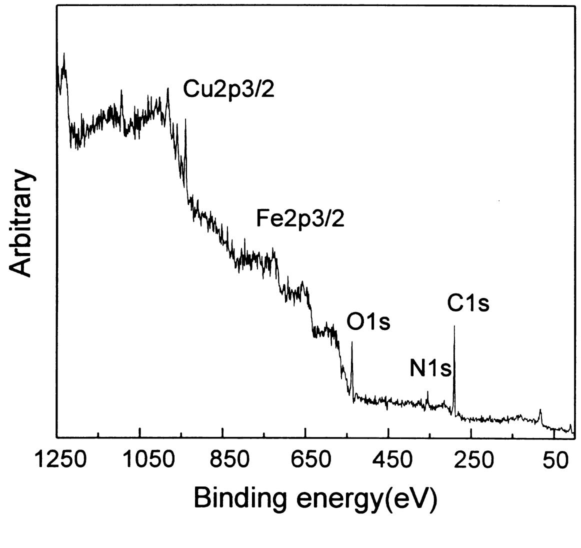

Fig. 3. XPS spectrum of $CuPcA_2$–Fe_2O_3 composite LB film.

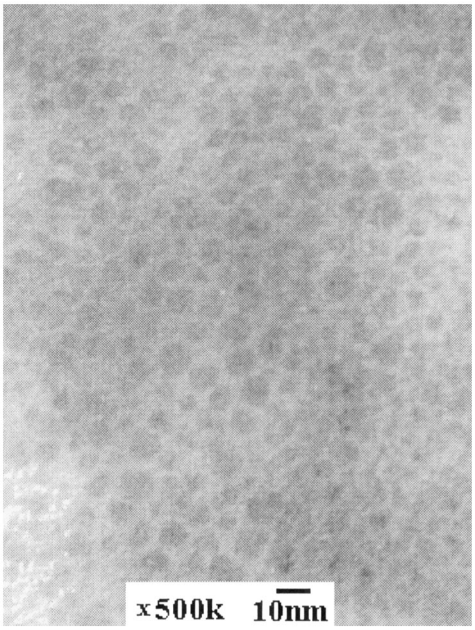

Fig. 4. TEM image of $CuPcA_2$–Fe_2O_3 monolayer deposited onto 400 mesh-copper grid coated with formvar.

3.3. Visible spectra

Visible spectra of $CuPcA_2$–Fe_2O_3 complex are shown in Fig. 5. There are a strong and narrow absorption band at 684 nm and a weak one at 618 nm in the diluted solution (10^{-6} mol/dm^3, see Fig. 5a). They are π–π^* electron transition of the monomer and dimer in phthalocyanine [9], respectively. This phenomenon is similar to those in pure $CuPcA_2$ solution (10^{-6} and 10^{-5} mol/dm^3). In concentrated complex solution (10^{-5} mol/dm^3, see Fig. 5b), splitting peaks at 687 and 682 nm were observed. It is well known that ferric oxide particles in the sol have positive charge. There are delocalized π electrons in the conjugated macrocycle of the phthalocyanine derivative. The symmetry of $CuPcA_2$ molecules could be decreased by interaction between the nanoparticles and $CuPcA_2$ in concentrated solution. It resulted in the Q-band splitting into two peaks.

In LB film, the baseline at low wavelength goes a little higher. It results from the band-edge absorption of the doped inorganic oxide nanoparticles. There is only one wide absorption band at 612 nm. It suggests that the complex mainly exists as dimeric aggregate in LB multilayers. Compared to the pure $CuPcA_2$ LB film, the absorption band is broadened and shifted to the blue by 6 nm, possibly because the electron density of $CuPcA_2$ molecule decreases

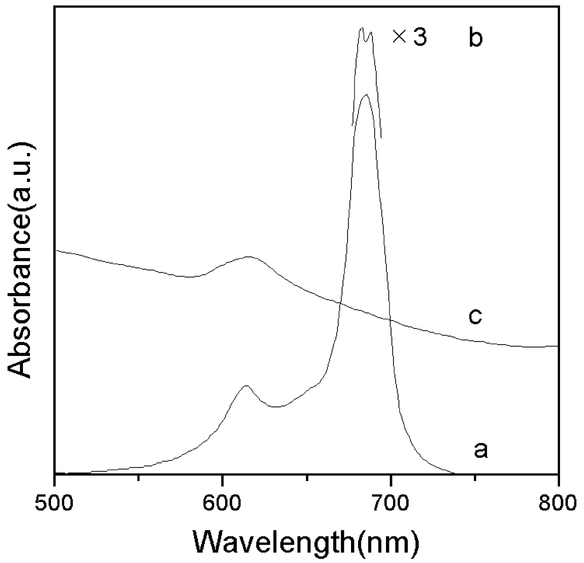

Fig. 5. Visible spectra of $CuPcA_2$–Fe_2O_3 complex (a) solution of 10^{-6} mol/l, (b) solution of 10^{-5} mol/l and (c) 12-layer LB film deposited onto SiO_2 substrate.

owing to interaction between the nanoparticles and $CuPcA_2$ molecules. Conjugation of the copper phthalocyanine decreases accordingly. The maximum absorbance at 612 nm as a function of the number of deposited layers is shown in Fig. 6. The good linear relationship indicates a constant transfer ratio during the multilayer deposition. It also suggests that the composite LB film has a highly ordered layered-structure normal to the substrate.

3.4. IR spectra

IR spectrum of $CuPcA_2$–Fe_2O_3 (1500–1000 cm^{-1}) is given in Fig. 7. The absorption bands of 1262, 1234, 1093, 1055 and 1017 cm^{-1} are assigned to vibrations of $\nu_{\text{C–C}}$, $\nu_{\text{C–O–C}}$, $\nu_{\text{C–N}}$, $\delta_{\text{C–H}}$ and $\delta_{\text{C–H}}$, respectively. Compared with pure $CuPcA_2$ LB film [10], there are two differences in the IR spectrum of the composite film. One is the baseline move higher at lower frequency, as in the visible spectrum. This is also due to the existence of ferric oxide nanoparticles. The other is that the peak at 1262 cm^{-1} is considerably enhanced and the one at 1234 cm^{-1} is reduced. Since the ferric oxide nanoparticles have oxygen interval defects, there should be some interaction between oxygen atoms in the side chains of $CuPcA_2$ and the ferric oxide nanoparticles. This interaction could weaken the bond parameter of C–O–C bonds, resulting in a decrease of the 1234 cm^{-1} peak intensity. The intensity of 1262 cm^{-1} peak increases accordingly.

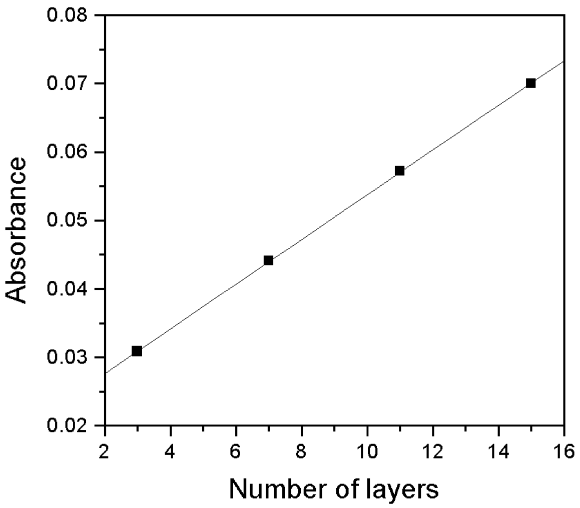

Fig. 6. Maximum absorbance at 612 nm of $CuPcA_2$–Fe_2O_3 LB films vs. the number of layers.

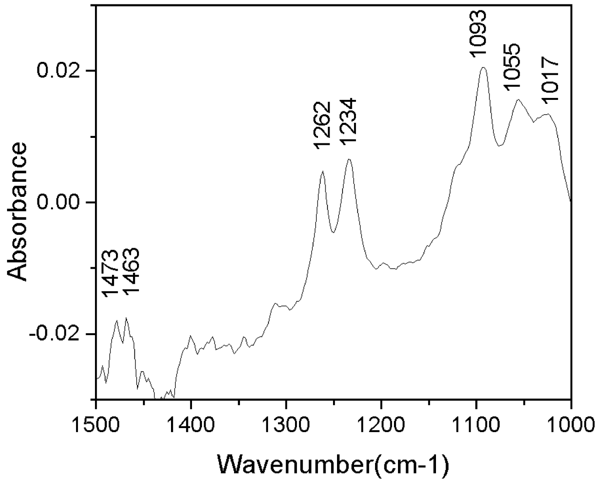

Fig. 7. IR spectrum (1500–1000 cm^{-1}) of 25-layer $CuPcA_2$–Fe_2O_3 LB film deposited onto silicon wafer.

The absorption band at 1467 cm^{-1} is the scissoring vibration of CH_2 in pure $CuPcA_2$ powder. It splits into two bands at 1473 and 1463 cm^{-1} in composite LB film, which is coincident with those in pure $CuPcA_2$ LB film. It suggests that the hydrocarbon chain of $CuPcA_2$ molecule is also in orthorhombic subcell packing in the composite LB film [11,12]. The doped nanoparticles have no effect on the substituent packing of copper phthalocyanine.

3.5. Gas sensitivity

It is well known that ferric oxide and metallophthalocyanine are all gas-sensing materials. Therefore, the gas-sensing properties of the composite LB film were measured at ambient temperature. It is found that the composite LB film has a fast response to 100–200 ppm C_2H_5OH as shown in Fig. 8. The response time to 100 ppm C_2H_5OH is only 15 s.

Compared to inorganic oxide films, organic LB film usually has poorer atmospheric stability. It has been found that the film resistance was unstable when the pure $CuPcA_2$ LB film remained in the air for a long time, but no obvious changes of the resistance of the composite LB film were observed in the same condition. The composite film shows good humidity-resistance. It is seen that the doped nanopar-

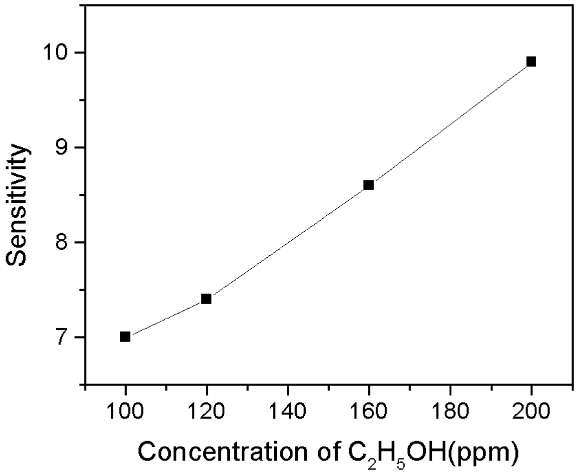

Fig. 8. Gas concentration dependence of sensitivity of 31-layer $CuPcA_2$–Fe_2O_3 composite LB film.

ticles improve the environmental stability of the composite film. This is important for application of LB films as gas sensors working in ambient condition.

4. Conclusions

The complex of tris-(2,4-di-t-amylphenoxy)-(8-quinolinolyl) copper phthalocyanine ($CuPcA_2$) embedding ferric oxide nanoparticles could form stable monolayer on the pure water surface. Ferric oxide nanoparticles-copper phthalocyanine composite ultrathin film could be fabricated by LB technique. XPS, TEM, visible spectra and IR spectra reveal that ferric oxide nanoparticles exist in the composite LB film. The doped nanoparticles result in the *Q*-band of phthalocyanine LB film shifting to the blue in electronic spectra, and vibrational absorption intensities of υ_{C-O-C} and $\nu_{C=C}$ changing. It has no effect on the substituent packing of copper phthalocyanine.

Gas sensitivity measurements indicate that the composite LB film has fast response to 100–200 ppm C_2H_5OH at room temperature and good environmental stability.

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