

An organic–inorganic hybrid ultrathin film: preparation and characterization of copper phthalocyanine derivative–ferric oxide nanoparticles

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A nanoparticulate ferric oxide–copper tris(2,4-di-*tert*-amylphenoxy)-8-quinolinolylphthalocyanine hybrid ultrathin film was constructed from alternate layers by the Langmuir–Blodgett technique. The composition, morphology and structure of the film were studied by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy, atomic force microscopy, small-angle X-ray diffraction, visible spectroscopy and polarized UV-Vis spectroscopy. All the above analyses suggest that the thin film is a kind of one-dimensional superlattice, composed of organic and inorganic components. The XPS data reveal that the nanoparticulate ferric oxide exists as an α -Fe₂O₃ phase in the films. Gas-sensing measurements show that the hybrid LB film has very fast response-recovery characteristics towards 2 ppm C₂H₅OH vapor.

1 Introduction

Inorganic semiconductor nanoparticles show special physical and chemical properties. Their thin films have been prepared by several methods in order to take advantage of these properties.^{1–3} However, the tendency of bare nanoparticles to aggregate or grow is a limitation which restricts their application in practice. In contrast, organic materials have good film-forming properties and stability when fabricated as ordered ultrathin films. However, the mechanical strengths of organic films are lower than those of inorganic films. Therefore, composites of organic and inorganic components might present better performance by making use of the different properties of each component.

Hybrid material has great potential for the creation of novel functional materials, especially organic–inorganic architecture at the nanosized level. This is presently an area of great interest in the field of materials science.^{4–6} Generally, there are two assembly methods for the preparation of nanocomposite thin films. One kind of film is obtained by transferring surfactant-stabilized nanoparticles from the air–water interface onto solid substrates using the Langmuir–Blodgett (LB) technique.^{7,8} The other type shows a kind of sandwich architecture and is formed by transferring an organic monolayer from the surface of an inorganic nanoparticulate subphase to substrates by the LB technique⁹ or by adsorbing ionic nanoparticles onto a negatively charged organic monolayer film by the self-assembly method.¹⁰

We have reported the preparation of a pure ferric oxide nanoparticulate LB film, with a three-dimensional ordered structure, which has good gas-sensing properties towards alcohols at room temperature.¹¹ Nevertheless, the sensitivity of the film was gradually reduced after being stored in ambient atmosphere for two months. It has been confirmed by atomic force microscopy that the nanoparticles aggregate and grow. A copper phthalocyanine derivative, a type of organic gas-sensing material, was chosen as the film-forming molecule to improve the stability of the nanoparticulate film. In this paper, the preparation and characterization of a ferric

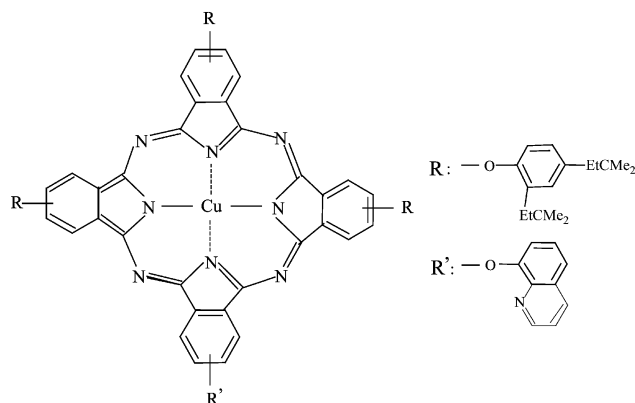
oxide nanoparticle–copper phthalocyanine derivative hybrid LB film, a kind of one-dimensional superlattice, are described. Compared with pure ferric oxide LB film,¹¹ the organic–inorganic hybrid film is much more stable and sensitive to alcohol at room temperature. The influence of copper phthalocyanine on the structure and gas sensitivity of the ferric oxide nanoparticulate LB film has been investigated.

2 Experimental details

2.1 Materials

Copper tris(2,4-di-*tert*-amylphenoxy)-8-quinolinolylphthalocyanine (CuPc) was synthesized as previously reported¹² and purified by column chromatography. The chemical structure is shown in Scheme 1. The spreading solvent was chloroform of A.R. grade. The concentration of copper phthalocyanine was 1.0×10^{-4} mol dm⁻³.

The subphase used was ferric oxide hydrosol, which was prepared by the forced hydrolysis method, described elsewhere.¹¹ The concentration of Fe₂O₃ was 1.6×10^{-3} mol dm⁻³, determined by ICP-AES spectroscopy (POEMS-I, TJA Co.).



Scheme 1 Chemical structure of the copper phthalocyanine derivative.

The mean particle size is about 6.2 nm, as observed by transmission electron microscopy (TEM).

2.2 Fabrication of copper phthalocyanine–ferric oxide hybrid film

Copper phthalocyanine solution (300 μL) was spread onto a fresh ferric oxide hydrosol surface with a microsyringe. After the solvent had evaporated, the monolayer was compressed to the target pressure of 30 mN m^{-1} , and the multilayer transfer started. The multilayers were deposited onto hydrophilic substrates as Z-type by using a NIMA-622 system (NIMA Technology, Coventry, UK). The dipping speed was 5 mm min^{-1} .

2.3 Characterization of the thin film

TEM studies of the monolayer were carried out using a JEOL-2100 electron microscope with 230-mesh copper grids as the substrate, covered by one layer of poly(vinyl formal) (PVF). Tapping-mode atomic force microscopy (AFM) was carried out using a Digital Instruments Multi-Mode AFM microscope, with mica as the substrate. Visible spectra of the film were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. The composition of the LB film was measured using a VG ESCALAB MK-II X-ray photoelectron spectrometer with Al-K α radiation ($h\nu = 1486.6 \text{ eV}$). The standard deviation for the binding energy values was 0.2 eV. The small-angle X-ray diffraction pattern was measured with a Rigaku D/Max-rA diffractometer using Cu-K α radiation. The incident X-ray beam was kept normal to the surface of the film.

The electrical resistance of LB films under various gas concentrations at ambient temperature was measured with a ZCG 17 B-type $10^{17} \Omega$ high resistance meter. Air was used as the diluent gas. Various amounts of the gas to be tested were injected into a container (1000 mL) with a microsyringe to obtain the desired gas concentration, and then mixed. After the resistance of the film reached a constant value in air, the film was immediately put into the vessel containing the gas mixture. The sensitivity (S) is defined as: $S = R_a/R_g$, where R_a and R_g are the resistance of the LB film measured in air and air containing the tested gas, respectively. The response-recovery time was monitored as 90% of the resistance change.

3 Results and discussion

3.1 π - A isotherms and deposition of multilayers

The surface pressure–area (π - A) isotherms of copper phthalocyanine monolayers on the surface of different subphases are shown in Fig. 1. Whatever the subphase is, a stable Langmuir film of the copper phthalocyanine can be formed. The limiting

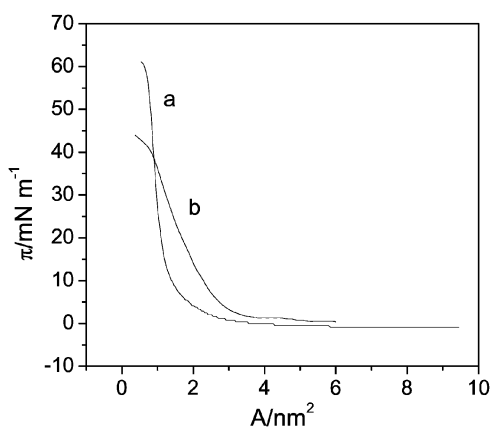


Fig. 1 π - A isotherms of copper phthalocyanine monolayers on different subphases: (a) water, (b) Fe_2O_3 hydrosol.

molecular area of the copper phthalocyanine on the surface of ferric oxide hydrosol is much larger than that at the air–water interface. The collapse pressure is accordingly decreased. The nanoparticles in the subphase have a considerable influence on the status of the copper phthalocyanine molecules.

Transfer of one alternative layer in an upward stroke was always successful, with the transfer ratio in the range $0.9 \sim 1.1$. In the case of a downward stroke, no Langmuir film could be deposited onto the substrates. The transferred multilayers are Z-type film.

3.2 Composition and morphology of the hybrid film

XPS data gives structural information about the LB films. The composition of a 15-layer Fe_2O_3 -CuPc LB film measured by XPS is shown in Fig. 2. There are distinct Cu (2p3/2) and Fe (2p3/2) peaks in the spectrum, revealing that the LB film is composed of the copper phthalocyanine derivative and ferric oxide. The binding energies for Fe 2p (711.1), Fe 3s (93.6) and Fe 3p (55.6 eV) imply that the ferric oxide nanoparticles are in an α - Fe_2O_3 phase.¹¹

A TEM image of the Fe_2O_3 -CuPc derivative monolayer is shown in Fig. 3(a). The nanoparticles are packed regularly and fairly closely to each other. No obvious changes were observed in the TEM image of a sample kept in air for about six months. This result suggests that the nanoparticles can be restrained from growing further or aggregating by being sandwiched with organic molecules. In other words, the copper phthalocyanine molecule improves the stability of the nanoparticulate film. The AFM micrograph [Fig. 3(b)] also gives the same structural information, *i.e.* that the nanoparticles in the hybrid monolayer are arranged in a close-packing model, which is similar to the arrangement of ferric oxide nanoparticles in the pure nanoparticulate film with a three-dimensional ordered structure.¹¹

3.3 Visible spectra

The visible spectra between 400 and 800 nm of the pure Fe_2O_3 and CuPc films and the hybrid LB film are shown in Fig. 4. There is no absorption peak in the spectrum of the pure ferric oxide LB film [Fig. 4(b)]. The strong peak at 618 nm and weak boundary peak at 684 nm in the spectrum of the pure copper phthalocyanine LB film are due to the dimeric and monomeric absorbance of the Q-band [Fig. 4(a)]. In the case of the hybrid film [Fig. 4(c)], the spectrum reveals a unique absorption band at 615 nm that is blue-shifted by 3 nm in comparison to that of the pure CuPc film. This results from decreased electron density due to the interaction between the nanoparticles and the phthalocyanine macro-rings. The baseline in the ultraviolet region of the hybrid film is a little enhanced. These results are related to the presence of the nanoparticles.

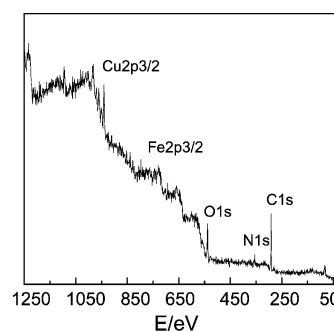


Fig. 2 XPS pattern of an Fe_2O_3 -CuPc LB film deposited on a CaF_2 substrate.

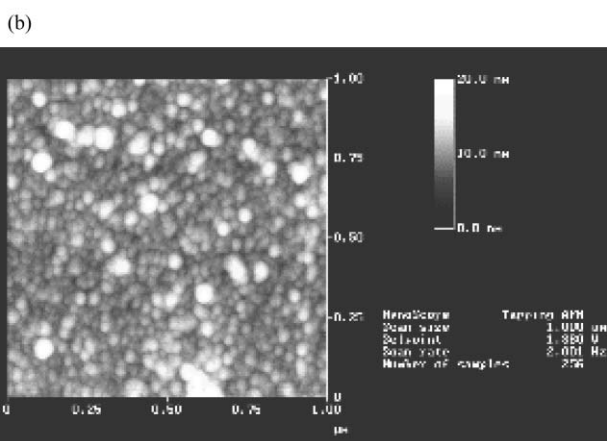
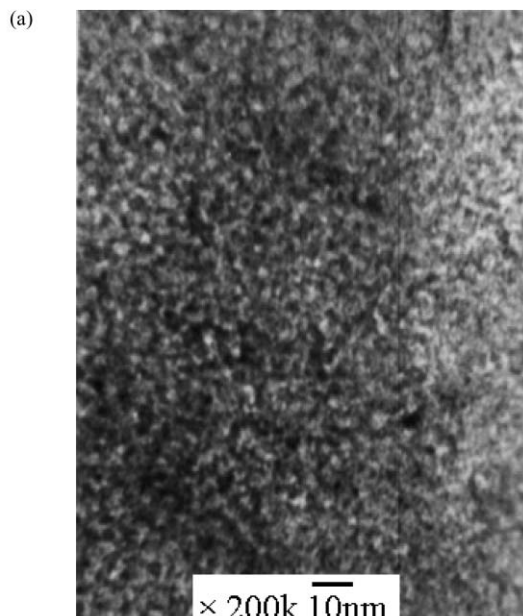


Fig. 3 TEM and AFM images of the hybrid monolayer: (a) TEM, film deposited on a copper grid; (b) AFM, film deposited on a mica substrate.

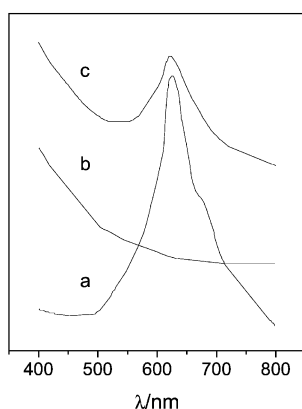


Fig. 4 Visible spectra of three LB films: (a) CuPc, (b) Fe₂O₃ and (c) the hybrid film.

3.4 Orientation of the phthalocyanine ring in the film

In order to investigate the orientation of the phthalocyanine ring in the film, polarized UV-Vis spectra were measured. According to the method proposed by Yoneyama *et al.*,¹³ the tilt angle of the phthalocyanine ring in the film can be

calculated from the following expressions:

$$D_{\beta} = \frac{A_{\parallel}}{A_{\perp}} = \frac{\langle \cos^2 \phi \rangle + \langle \cos^2 \theta \sin^2 \phi \rangle}{\{\langle \sin^2 \phi \rangle + \langle \cos^2 \theta \cos^2 \phi \rangle\} \{\cos^2 \beta + \langle \sin^2 \theta \rangle \sin^2 \beta\}}$$

$$\langle \cos^2 \theta \rangle = \frac{D_0 - (1 + D_0 \sin^2 \beta)}{(1 - 2 \sin^2 \beta) D_{\beta} - (1 + D_{\beta} \sin^2 \beta) D_0}$$

$$\langle \sin^2 \theta \cos^2 \phi \rangle = \frac{D_0 - \langle \cos^2 \theta \rangle}{1 + D_0}$$

$$n_1 \sin^2 \beta' = n_2 \sin^2 \beta$$

where A_{\parallel} and A_{\perp} is the absorbance of the film for polarized light with electric vectors parallel (\parallel) and perpendicular (\perp) to the dipping direction, respectively, $\langle \rangle$ denotes a statistical average, and n_1 and n_2 are the refractive indices of air and the LB film and are set at 1 and 1.39,¹⁴ respectively. The polarized UV-Vis spectra of the film at incident angles of 0 and 90° are shown in Fig. 5. The tilt angle of the phthalocyanine ring with the normal of the substrate is calculated to be 15.8°, which is much smaller than that in pure copper phthalocyanine LB film.¹⁵ The nanoparticles also influence the packing of the copper phthalocyanine molecules in the hybrid LB film.

3.5 Periodic structure of the hybrid LB film

The small-angle X-ray diffraction pattern of 31-layer Fe₂O₃-CuPc hybrid film deposited onto a glass substrate under a surface pressure of 25 mN m⁻¹ is given in Fig. 6. The obvious Bragg peak at 1.54° suggests that the hybrid LB film has a well-ordered periodic structure along the film normal. This is the (002) diffraction peak, corresponding to a long spacing of 11.4 nm, according to the Scherrer equation. The TEM and AFM images show that the nanoparticles are arranged

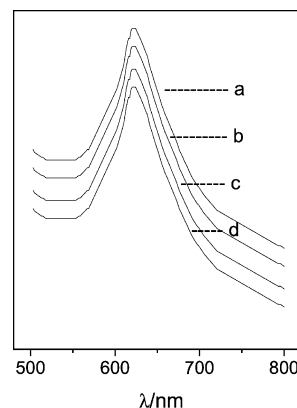


Fig. 5 Polarized UV-Vis spectra of the hybrid LB film: (a) 30°, \perp ; (b) 30°, \parallel ; (c) 0°, \parallel ; (d) 0°, \perp .

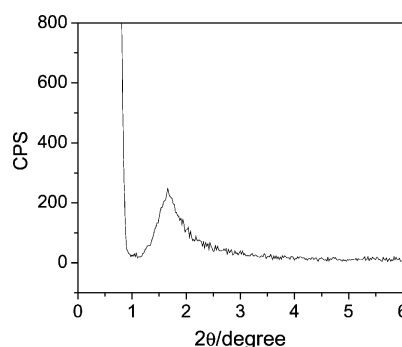


Fig. 6 Small-angle X-ray diffraction pattern of a 31-layer hybrid LB film deposited on glass.

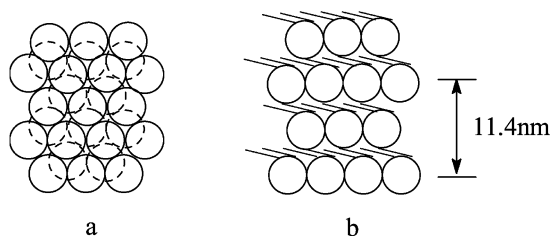


Fig. 7 Schematic of the superlattice structure of the hybrid LB film: (a) top view, (b) lateral view.

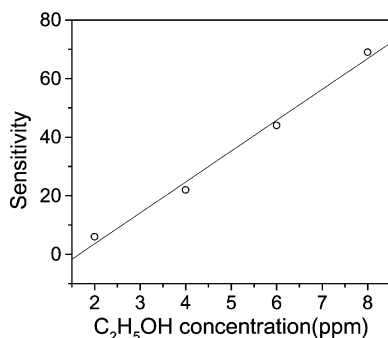


Fig. 8 C₂H₅OH concentration dependence of the sensitivity of the hybrid LB film.

fairly close to each other in the film (Fig. 3). The copper phthalocyanine molecules might act as a spacer located between the layers of nanoparticles owing to the Z-type film.

Polarized UV-Vis spectra show that the tilt angle of the phthalocyanine ring on the film is about 15.8°. The edge of the square plane of the phthalocyanine macro-ring is about 1.2 nm.¹⁶ Herein, the thickness of a copper phthalocyanine derivative bilayer is at least 0.6 nm. The thickness of the nanoparticulate Fe₂O₃ layer is not more than 10.8 nm. This value is much closer to the calculated thickness¹¹ of the bilayer of ferric oxide nanoparticles: 10.7 nm if the nanoparticles are arranged in hexagonal closed-packing. Thus, one repeating period of the hybrid film is composed of a bilayer of nanoparticles and a bilayer of copper phthalocyanine molecules, as shown in Fig. 7. This structure can also be considered a kind of one-dimensional superlattice.¹⁷

3.6 Gas-sensing properties

In order to investigate the effect of composites of organic and inorganic materials on the properties of the separate material, the gas-sensing properties of 31-layer pure ferric oxide and pure copper phthalocyanine LB films and their hybrid film were measured at room temperature. The ferric oxide and copper phthalocyanine LB films show good sensitivity to alcohols and ammonia, respectively.¹⁸ The hybrid film was very sensitive to these two kinds of gases, in particular the detection limit for C₂H₅OH vapor is lowered down to 2 ppm. The sensitivity of the hybrid film versus alcohol concentration is plotted in Fig. 8. A good linear relationship between the sensitivity and concentration of C₂H₅OH vapor was obtained. The hybrid film effectively improves the gas sensitivity of the nanoparticulate and copper phthalocyanine LB films.

Combining the two kinds of material also results in a great improvement in the stability of the composite LB film toward its environment. The film resistance of pure ferric oxide and copper phthalocyanine LB films decreased by 2–3 orders of magnitude immediately after exposure to 90% ambient humidity. But the change in resistance for the hybrid film under the same conditions was small, within 1 order of magnitude. The humidity-resistance of the hybrid film is much better than

those of the pure component films. Additionally, the sensitivity of the film to alcohol showed no obvious reduction during measurements over six months. The response and recovery times of the hybrid film to alcohol are 15 s and 3 min, respectively. Therefore it can be used as a C₂H₅OH sensor in the range 2~8 ppm where fast response-recovery characteristics are important. All the results suggest that the performance of an LB film can be improved by combination with the appropriate materials to produce a composite.

4 Conclusions

A ferric oxide–copper phthalocyanine derivative hybrid ultrathin film was constructed by the LB technique. XPS data reveal that the ferric oxide nanoparticles exist as the α-Fe₂O₃ phase in the film. The film is highly covered by the copper phthalocyanine derivative and the nanoparticles are arranged rather closely; the nanoparticles were deposited onto the substrate with the copper phthalocyanine derivative monolayer. The phthalocyanine rings in the LB film are stacked, with a tilt angle of 15.8°, obtained by polarized UV-Vis spectroscopy. Small-angle X-ray diffraction data indicate that the hybrid LB film is a kind of one-dimensional superlattice with a long spacing of 11.4 nm. The hybrid film can detect C₂H₅OH vapor at concentrations as low as 2 ppm at room temperature and shows better stability than the pure nanoparticulate LB film. Thus, the performance of LB films can be improved by the construction of the appropriate composites.

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