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Dissolution of copper phthalocyanine and fabrication of its nano-structure film

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The mono-protonated and di-protonated forms of copper phthalocyanine (CuPc) were obtained by increasing concentrations of trifluoroacetic acid (TFA) solution to a fixed concentration of CuPc solutions. UV-Vis spectrum shows that the Q bands of these two derivatives split and shift to the red, which means successive protonation happened and caused the two derivatives to lose their symmetry. After the protonation step, the solubility of protonated CuPc in organic solvent increased 60 times. The CuPc film was fabricated by the electrophoretic deposition (EPD) method from the protonated CuPc dissolved in nitromethane containing TFA. Scanning electron microscopy (SEM) showed that the deposited CuPc film on the indium tin oxide (ITO) substrate is composed of thread-like nanobelts with diameters between 100 nm and 200 nm. Furthermore, the CuPc film is in α phase with stacking direction (b-axis) parallel to the substrate, which was detected by X-ray diffraction.

CuPc, protonation, electrophoretic deposition, orientation

1 Introduction

Phthalocyanines and metal phthalocyanines are organic semiconductor materials. The width of their forbidden gap is nearly 1.8 eV. Copper phthalocyanine (CuPc) (Figure 1) is typical p-type semiconductor material which is of great value in many applications including gas sensing[1], organic light-emitting diodes (OLEDs)[2], organic field-effect transistors (OFET)[3], organic solar cell and other optical devices[4,5] because of its unique chemical stability, thermal stability and photo-stability. The traditional method of fabricating CuPc film is thermal evaporation in vacuum (dry process) which is costly and complicated for operation[6−8]. Fabrication of CuPc film from its solutions (wet process) has many advantages including cheapness, being facile to control the film structure, feasible for operation and manufacturing large area film. Unfortunately, the solubility of CuPc in organic solvent is too low to meet the desired concentration of wet process, therefore, it is significant to improve the dissolution of CuPc.

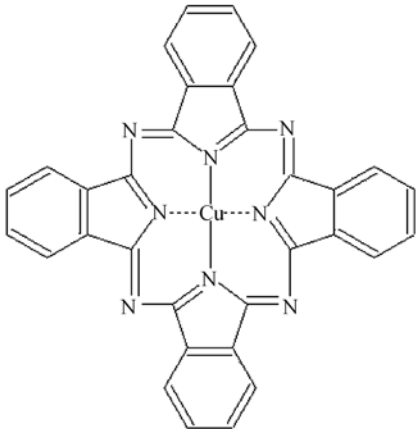

Figure 1 The molecular structure of CuPc.

Since Jenekhe reported dissolution of rigid-chain and ladder polymers by Lewis acid in 1990[9], there have been a lot of reports on the dissolution of phthalocya-

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nines. Luo[10] reported the mechanism of dissolution of CuPc in aprotic solvents by Lewis acid. It is shown that the complexes arise from a Lewis acid-base reaction at specific heteroatom electron pair donor sites N on CuPc are soluble in polar aprotic solvent because of the solvent effect. Additionally, metal phthalocyanines are soluble in organic solvents when protonated in the existence of protonic acid[11,12]. It was reported that four nitrogen atoms on CuPc not directly connected with the copper atom participate protonation, the other nitrogen atoms do not participate in the protonation[13].

There are several methods of fabricating organic semiconductor films from their solutions, such as spin-coating, Czochralsiki method and electrophoretic deposition (EPD)[14]. It is hard to control the structure of film by spin-coating method or Czochralsiki method. On the contrary, for the EPD method, the film structure is easy to be controlled by adjusting the applied voltage, current, deposition time, temperature etc. The difficulty of fabrication of CuPc films by EPD is preparing for the elertrolyte. The complexes arise from the reaction of Lewis acid and CuPc are soluble in polar aprotic solvent but carry no charge, which cannot be used as elertrolyte. Fortunately, in the existence of protonic acid, CuPc can be protonated and carries positive charges, which makes it feasible to fabricate CuPc films by EPD. Sulfuric acid and trifluoroacetic acid (TFA) are usually used as protonic acid. Sulfuric acid could change the molecular structure of CuPc because of strong oxidative, so we used TFA as protonic acid in this paper, studied the protonation of CuPc and fabricated CuPc orientated film by EPD.

2 Experiment

2.1 Materials

Copper phthalocyanine (CuPc, Aldrich), chloroform (AR), nitromethane (AR), trifluoroacetic acid (TFA≥99.0%), acetone (AR), isopropyl alcohol (AR), anhydrous alcohol (AR), deionized water.

2.2 Instruments

Potentiostat/Galvanostat (ZF-9, Fangzheng, Shanghai) were employed to fabricate CuPc films, UV-Vis absorption was recorded by spectrophotometer (TU 1910, Purkinje General, Beijing), scanning electron microscope (JSM-7401F, JEOL Ltd., Japan) was employed to depict the morphology of CuPc film. The structure of CuPc film was recorded by X-ray diffraction analysis (XD-3A, Rigaku Corporation, Japan).

2.3 Protonation of CuPc

Protonation of CuPc was performed by increasing concentrations of TFA to a fixed concentration of CuPc solutions. The solvents were chloroform and nitromethane.

2.4 Fabrication of nano-structure CuPc film by EPD

The electrolyte was protonated CuPc dissolved in nitromethane containing TFA. The CuPc film was fabricated by EPD on indium tin oxide (ITO) glass substrates. An ITO glass and a platinum plate served as the cathode and anode electrodes respectively. The deposited film dried in vacuum at 70℃ for two hours.

3 Results and discussion

3.1 Protonation of CuPc

The UV absorption spectrum of CuPc exhibits five absorption peaks which are owing to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions. These absorption peaks are distributed in C band (220 nm), L band (240 nm), N band (270 nm), B band (around 270 nm) and Q band (650－700 nm). The B band of CuPc in acid solutions undergoes a blue shift, while the Q band undergoes a red shift[15]. Ogunsipe[16] reported the protonation of ZnPc, and obtained $[ZnPc{\cdot}H]^+$, $[ZnPc{\cdot}H_2]^{2+}$, $[ZnPc{\cdot}H_3]^3$ and $[ZnPc{\cdot}H_4]^{4+}$ derivatives when used sulfuric acid as protonic acid. The Q bands of $[ZnPc{\cdot}H]^+$, $[ZnPc{\cdot}H_2]^{2+}$ and $[ZnPc{\cdot}H_3]^3$ are spitted due to the loss of symmetry. The $[ZnPc{\cdot}H_4]^{4+}$ derivative regains symmetry, so its Q band is not spitted. They only got $[ZnPc{\cdot}H]^+$ and $[ZnPc{\cdot}H_2]^{2+}$ derivatives when used TFA as protonic acid since the strength of TFA is not as strong as sulfuric acid.

Figure 2 shows the UV-Vis spectrum of CuPc in $CHCl_3$ in the existence of increasing concentrations of TFA. (a1) is the spectra of CuPc solution without TFA, the absorption peak is in 672 nm and the absorbance is very weak due to the low solubility of CuPc in $CHCl_3$. (a2) is the spectra of CuPc with 0.4 mol/L TFA, this TFA concentration is the least concentration needed for mono-protonated derivative. The Q band of $[CuPc{\cdot}H]^+$ split into two peaks which exhibit in 688 nm and 713 nm due to the asymmetry of $[CuPc{\cdot}H]^+$. The Q band of $[CuPc{\cdot}H]^+$ undergoes a red shift compared with CuPc, which is coordinate with other authors' results[17]. (a3) is the spectra of CuPc with 2 mol/L TFA, which is the ab-

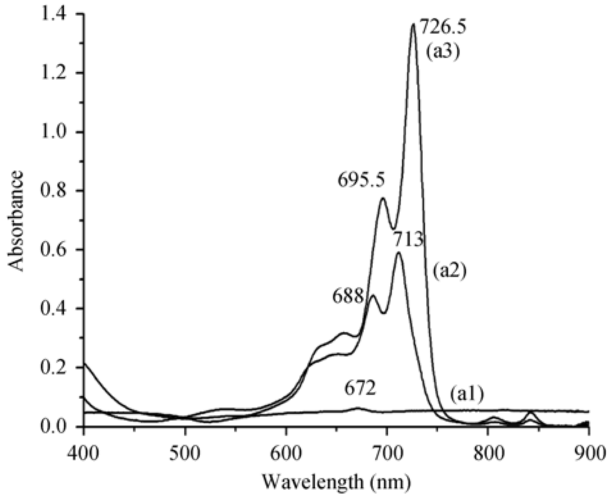

Figure 2 UV-Vis spectrum of CuPc in $CHCl_3$ containing different concentrations of TFA. Concentration of CuPc is 1×10^{-5} mol/L, concentrations of TFA in (a1), (a2) and (a3) are 0, 0.4 and 2 mol/L, respectively.

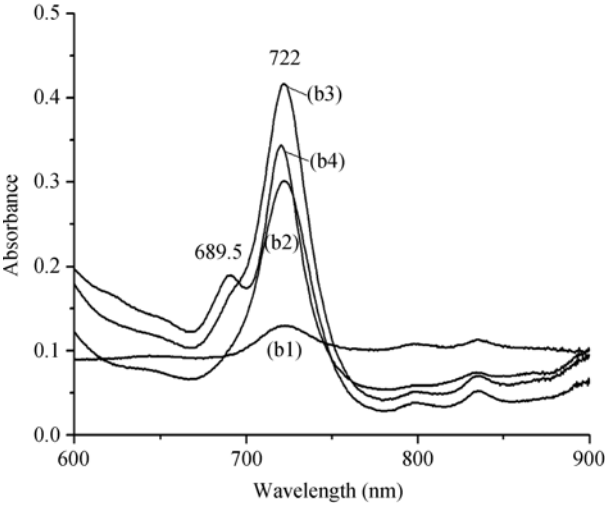

Figure 3 UV-Vis spectrum of CuPc in CH_3NO_2 containing different concentrations of TFA. Concentration of CuPc is 2×10^{-5} mol/L, concentrations of TFA in (b1), (b2), (b3) and (b4) are 0.02, 3, 4, and 7 mol/L, respectively.

sorption spectrum of di-protonated derivative $[CuPc{\cdot}H_2]^{2+}$. The fact that the Q band of $[CuPc{\cdot}H_2]^{2+}$ is spitted demonstrates that *trans* (of D2h symmetry) protonation occurs, since *cis* di-protonation is of C2v symmetry and expected to show a single Q band[6].

Figure 3 is the UV-Vis spectrum of CuPc in CH_3NO_2 containing different concentrations of TFA. The concentrations of TFA in (b1), (b2) and (b3) solutions are 0.02, 3 and 4 mol/L respectively. The Q band of (b1) undergoes a red shift and does not undergoes further red shift with the increasing concentrations of TFA, as shown in the absorption spectrums of (b2) and (b3). The Q bands of (b1), (b2) and (b3) are not split demonstrates that CuPc in these solutions are not protonated because there are only mono-protonated and di-protonated derivatives in solution when used TFA as protonic acid, the Q band are both split. When the concentration of TFA reaches 7 mol/L (b4), the CuPc begins to be protonated. The concentration of TFA which needed to effect protonation increased linearly with solvent basicity. The less basic solvents encourage protonation more than the more basic solvents[16]. The basicity of CH_3NO_2 is more than the basicity of $CHCl_3$, so the concentration of TFA needed to effect protonation in CH_3NO_2 is higher than in $CHCl_3$.

Afterwards, we studied the solubility of CuPc in CH_3NO_2. We found that the solubility of CuPc in CH_3NO_2 was 0.2 g/L, while the solubility of protonated derivate of CuPc in CH_3NO_2 was 12 g/L, increased by 60 times; moreover, the protonated CuPc did not undergo de-protonate in two weeks.

3.2 Morphology and crystal structure of CuPc film

The CuPc film was fabricated by EPD with the solution of protonated CuPc dissolved in CH_3NO_2 as electrolyte. The concentration of CuPc is 1.7×10^{-4} mol/L. The UV-Vis spectrum of fabricated CuPc film is shown in Figure 4. The Q band of the film blue shifts to 615 nm and 694 nm comparing with the protonated CuPc solution and the relative intensities of the two peaks are revised, which demonstrate that some protonated CuPc

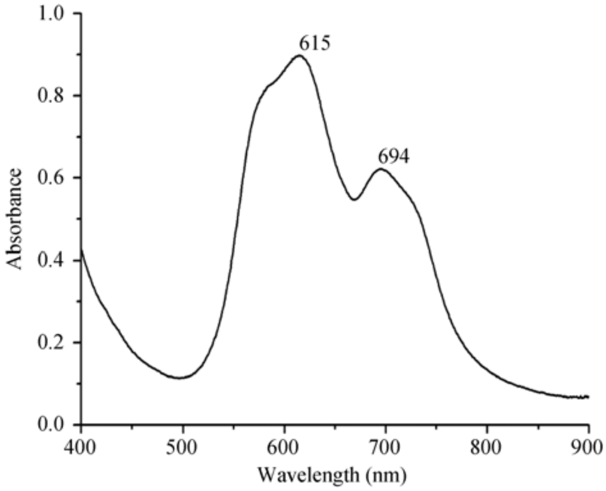

Figure 4 UV-Vis spectrum of CuPc film.

derivates are de-protonated to CuPc during the EPD process[15]. The Q band of CuPc film fabricated by EPD method at around 615 nm and 694 nm shows typical features of α phase CuPc film[18].

Figure 5 shows the CuPc film morphology probed by SEM. The thread-like nanobelts with diameters between 100 nm and 200 nm are packed in high density and form network structure.

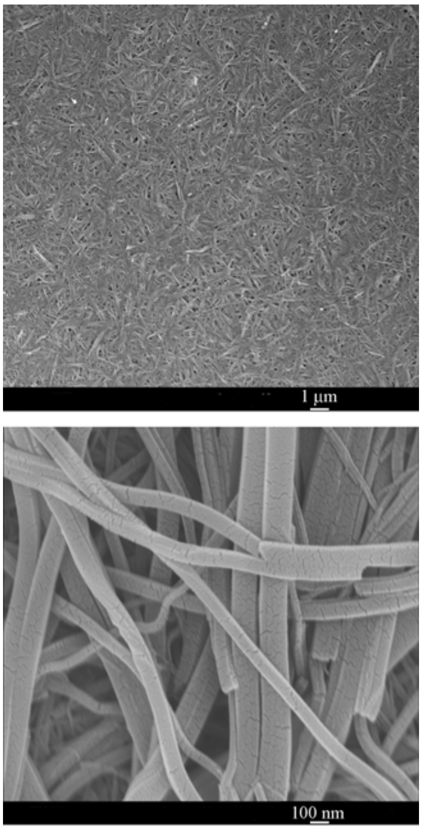

Figure 5 SEM images of CuPc film.

There are lots of reports about the crystal structures of CuPc films[18−20]. The most common structures are designated as α and β phases which both are stable at low temperatures. The α phase of CuPc film would transform into β phase after being annealed[19,20]. The X-ray diffraction pattern of CuPc film fabricated by EPD is shown in Figure 6. It is obvious that the film is oriented. The 2θ peak is at 6.819°, corresponding to the interplanar space (d) of 12.95 Å, which is a typical feature of α phase CuPc film[20], and it is coordinate with Figure 4. We speculate it might be that the temperature of the electrolyte is too low to provide enough energy for the formation of β phase of CuPc film. The proposed orientations of CuPc molecules are shown in Figure 7. The stacking direction (b-axis) is parallel to the substrate[6].

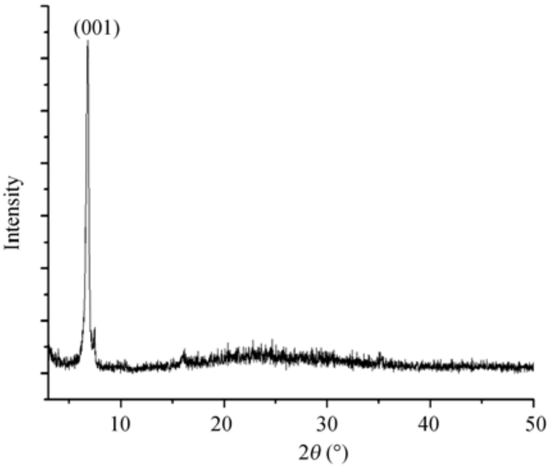

Figure 6 XRD spectrum of CuPc film.

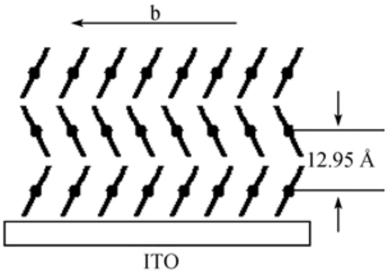

Figure 7 Proposed orientations of CuPc molecules.

4 Conclusions

In this work we studied the protonation of CuPc and fabricated oriented CuPc film by EPD. We got several results as follow:

(1) The solubility of CuPc in organic solvents is very low, while the solubility could be increased after protonated.

(2) The mono-protonated $[CuPc{\cdot}H]^+$ and di-protonated $[CuPc{\cdot}H_2]^{2+}$ were obtained by the addition of increasing concentrations of TFA solution into a fixed concentration of CuPc solution. The Q bands of these two derivatives are split due to the loss of symmetry of CuPc.

(3) The network structure of CuPc film fabricated by EPD is composed thread-like nanobelts with diameters between 100 nm and 200 nm. The CuPc film is in α phase with the stacking direction (b-axis) parallel to the substrate.

The CuPc film fabricated in this work is oriented, and the photoelectric properties still need further studies.

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