

## Direct formation of $\alpha_1$ -MgPc films by the micelle disruption method

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Magnesium phthalocyanine (MgPc) films have attracted much attention as future materials for solar cell [1] and electrophotograph [2] applications. MgPc is known to exist in a number of polymorphic phases which arise from different molecular stacking arrangements. The  $\alpha$ -phase, which can be directly obtained by evaporation in vacuum, has an optical absorption maximum around 695 nm;  $\alpha_1$ -MgPc has a stronger absorption peak at 830 nm. This 830 nm strong absorption makes the  $\alpha_1$ -MgPc a better material than  $\alpha$ -MgPc for many of the above mentioned technological applications.

Up to now the only reliable method of preparing  $\alpha_1$ -MgPc has been an organic solvent treatment of evaporated  $\alpha$ -MgPc [1, 2], and the obtained  $\alpha_1$ -MgPc transforms to the  $\alpha$  phase by annealing at 250 °C in vacuum [3]. A serious problem of this technique is that it is difficult to make thick  $\alpha_1$ -MgPc films (>50 nm) [1]. Achievement of thicker MgPc films in  $\alpha_1$  modification is clearly necessary in order to make these films technologically applicable.

Recently, Saji *et al.* developed a new phthalocyanine thin film preparation technique known as the micelle disruption (MD) method [4–6]. This method was employed in the present work since it allows for simple and inexpensive formation of thick (> $2 \times 10^3$  nm) MgPc films. Saji *et al.*, however, used only one characterization technique, visible absorption spectroscopy, and concluded that the phase of MgPc (MD) was different from  $\alpha$ . In this work, we show unambiguously that the phase of MgPc (MD) is indeed  $\alpha_1$  and transforms thermally to  $\alpha$  phase, using visible optical absorption (VIS), X-ray diffraction (XRD) and infrared absorption (IR) measurements.

The deposition of MgPc (MD) was carried out in a three-electrode cell consisting of a saturated calomel electrode (SCE) as reference electrode, a carbon bar as counter electrode, and an indium tin oxide (ITO) plate as working electrode. The interior of the cell was filled with a sonicated and well-stirred aqueous solution containing 5.0 mM MgPc, 0.1 M LiBr, and 1.0 mM polyethylene(13)11-ferrocenylundecyl ether (FPEG). The ITO electrode was cleaned by sonication in acetone, ethanol, and distilled water for 15 min per step. MgPc films were prepared by controlled potential electrolysis. A constant potential of -0.5 V relative to SCE was applied to the ITO electrode. The molecules of the surfactant near the ITO electrode were ionized, causing MgPc particles to segregate from the aqueous solution. The deposition of MgPc particles

occurs on the surface of the ITO electrode as a result. Throughout the process, the solution was stirred slowly by magnetic stirrer and was bubbled continuously with nitrogen gas. MgPc films as deposited on ITO were air-dried at room temperature and rinsed with distilled water.

MgPc(MD) films on ITO electrodes were characterized at room temperature by VIS, XRD, and IR spectroscopy using ANA-Jenway JENA-6100 spectrometer, Rigaku Denki RAD-C and Bio-Rad FTS-65/UMA-300A Fourier Transform spectrometer, respectively. MgPc films in  $\alpha$  and  $\alpha_1$  modification were also prepared for comparison. The  $\alpha$ -phase samples were obtained by thermal evaporation of MgPc onto ITO substrates in a vacuum of  $1.33 \times 10^{-3}$  Pa, whereas,  $\alpha_1$  samples were obtained by dipping  $\alpha$ -MgPc samples in  $\text{CH}_2\text{Cl}_2$  solvent for 4 h at room temperature.

VIS spectra for MgPc(MD) films (a) as-prepared and (b) after annealing at 250 °C for 1 h in vacuum are shown in Fig. 1. A strong peak at 830 nm, the characteristic signature of  $\alpha_1$  phase [2], is clearly observed in the spectrum of (a). This peak shifts to the shorter wavelength of 695 nm in (b), indicating the complete change of phase from  $\alpha_1$  to  $\alpha$  due to the heat-treatment.

Figure 2 shows XRD results for MgPc(MD) (a) as-prepared and (b) after 250 °C heat-treatment.

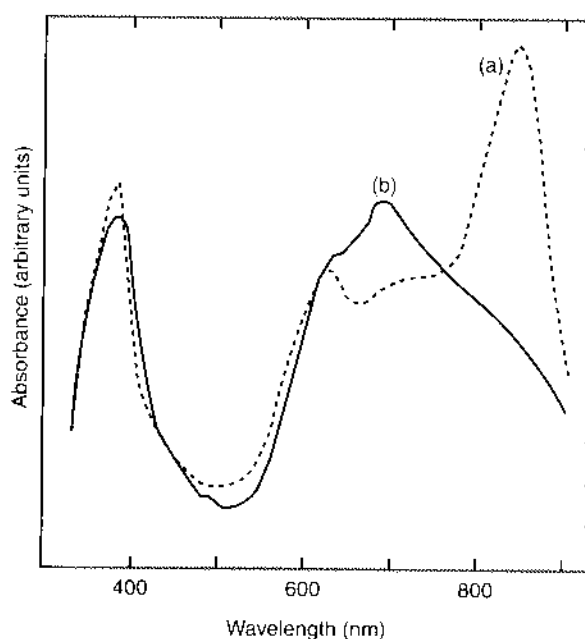


Figure 1 Visible absorption spectra of MgPc(MD): (a) as-prepared and (b) after heat-treatment at 250 °C for 1 h in vacuum.

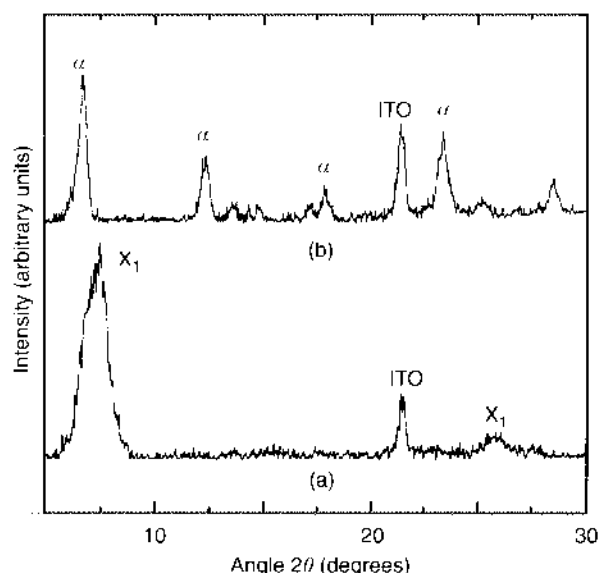


Figure 2 XRD patterns of MgPc(MD): (a) as-prepared and (b) after heat-treatment at 250°C for 1 h in vacuum. XRD is carried out using Ni filtered  $\text{CuK}\alpha$  radiation.

Previously reported XRD peaks of  $\text{X}_1$ -MgPc appear at  $2\theta = 7.6^\circ$  and  $25.3^\circ$ , corresponding to an interplanar distance of 1.16 nm and an intermetal spacing along the stacking axis of 0.35 nm [2]. Characteristic XRD peaks of  $\alpha$ -MgPc appear at  $2\theta = 6.2^\circ$ ,  $12.4^\circ$  and  $23.2^\circ$  [2]. XRD peaks of the annealed MgPc(MD) in Fig. 2 agree well with those of the  $\alpha$ -phase.

IR spectra of (a) as-grown MgPc(MD), (b)  $\text{X}_1$ -MgPc, (c) annealed MgPc(MD) and (d)  $\alpha$ -MgPc are shown in Fig. 3 and their typical absorption peaks are listed in Table I. Similar IR spectra for  $\alpha$ -MgPc have been found elsewhere [7, 8]. It is noted that the peak No. 8 is found in (a) and (b); i.e. as-deposited MgPc(MD) and  $\text{X}_1$ -MgPc, while peak No. 3 as observed in (c) and (d); i.e. annealed MgPc(MD) and  $\alpha$ -MgPc. The above results also confirm that the as-grown MgPc(MD) is in  $\text{X}_1$  phase and transforms to  $\alpha$  modification after heat-treatment.

Finally, it is important to note that all the results shown above are practically thickness independent. Because it is simple to grow more than  $2 \times 10^3$  nm thick MgPc films using this technique, the MD film

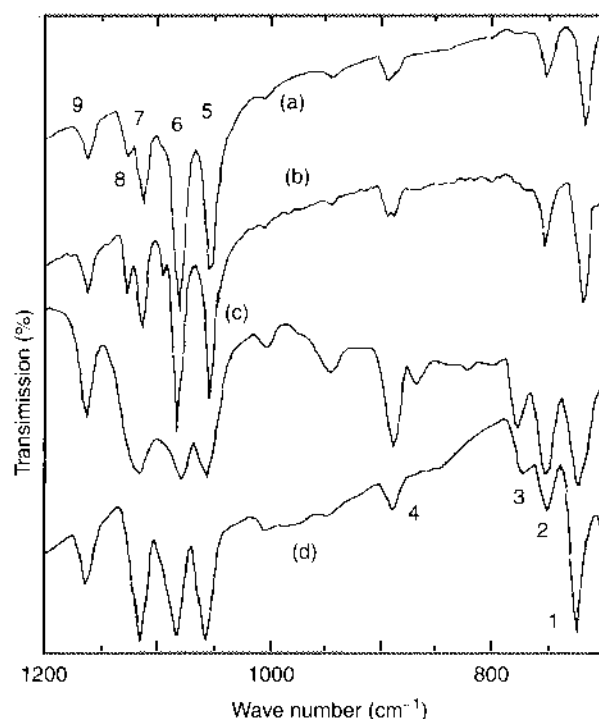


Figure 3 IR spectra of (a) as-grown MgPc(MD), (b)  $\text{X}_1$ -MgPc, (c) heat-treated MgPc(MD) and (d)  $\alpha$ -MgPc.

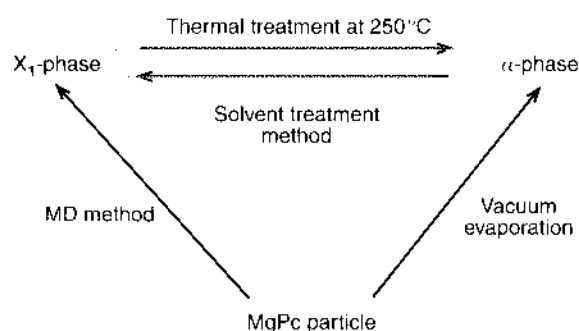


Figure 4 Phase transition scheme of MgPc.

deposition method may become technologically important for applications in which  $\text{X}_1$ -MgPc is needed.

In summary, the results obtained in this work, consistently proved that the MD method leads to growth of  $\text{X}_1$ -MgPc, which becomes  $\alpha$  phase by annealing. The phase transition scheme of MgPc is shown in Fig. 4. The MD technique allows for the growth of thick ( $>2 \times 10^3$  nm)  $\text{X}_1$ -MgPc.

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## References

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TABLE I Typical IR peaks of MgPc in Fig. 3

Line No.	Absorption frequencies ( $\text{cm}^{-1}$ )			
	(a) MD-MgPc	(b) $\text{X}_1$ form	(c) annealed MD-MgPc	(d) $\alpha$ form
1	720(s)	720(s)	725(s)	725(vs)
2	755(m)	755(m)	755(s)	752(m)
3	-	-	780(m)	775(w)
4	896(vw)	895(vw)	890(m)	889(vw)
5	1055(vs)	1055(vs)	1057(s)	1058(s)
6	1084(vs)	1085(vs)	1080(s)	1082(s)
7	1115(m)	1115(m)	1118(s)	1115(s)
8	1128(w)	1128(w)	-	-
9	1165(w)	1164(w)	1166(m)	1164(m)

s = strong, m = medium, w = weak and v = very.

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