

## Optical Properties of Inorganic-Organic Hybrid Silica Gel Glasses Doped with Copper Phthalocyanine

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Inorganic-organic hybrid silica gel glasses were successfully prepared by the sol-gel method. Copper phthalocyanine and vinyltriethoxysilane were used as optical active material and inorganic glass component, respectively. The absorption spectrum of copper phthalocyanine-doped hybrid glasses was recorded in the spectral range of 200-1000 nm. Optical band gap is determined from the UV-vis optical absorption spectra.

**Key Words:** Optical materials, Sol-gel processes, Optical properties.

### INTRODUCTION

Metallophthalocyanines (MPcs) with two-dimensional conjugated  $\pi$ -electrons delocalization have received a great deal of attention owing to their potential applications in optical data storage, photovoltaic cell, photodynamic sensitizers and semiconducting devices<sup>1-4</sup>. By the replacement of metal substitutions at the centre of phthalocyanine ring such as copper, nickel, iron and rare earths, many electrical and optical advantages can be modified.

One of the basic prerequisites for the employment of metallophthalocyanines-doped functional materials is the advantage not only to have excellent physical and chemical stabilities, but also to have good processability. Recently, remarkable advances have been achieved in metallophthalocyanines thin films and metallophthalocyanines-doped melting glasses<sup>5,6</sup>. However, the methods of fabricating metallophthalocyanines thin films and metallophthalocyanines-doped melting glasses are complicated and expensive. More importantly, metallophthalocyanines molecules may be decomposed seriously under the high melting temperature (usually above 800 °C). Hence, the choices of fabricating methods and the supporting matrixes for metallophthalocyanines molecules remain to be determined.

Inorganic-organic hybrid nanocomposites have been fabricated by the sol-gel method, which are investigated and confirmed that the photostability and thermal stabilities of the active chromophores can be largely enhanced, compared to organic polymer materials<sup>7</sup>. The main advantage of this method is high versatility for preparing materials, whose physical and

chemical properties can be modified. The improvements in the metallophthalocyanines-doped nanocomposites have still stimulated fresh interest in fabricating optoelectronic devices.

In this paper, a sol-gel derived copper phthalocyanines (CuPc)-doped inorganic-organic hybrid gel glasses is prepared successfully. Optical band gaps of indirect and direct transitions were determined for the hybrid materials from the UV-vis optical absorption spectrum.

### EXPERIMENTAL

The copper phthalocyanine (CuPc) dye (from Sigma-Aldrich Corporation, USA) was used as received. The bulk material was prepared by hydrolysis condensation of the organically modified precursors vinyltriethoxysilane  $\text{H}_2\text{C}=\text{CHSi}(\text{OC}_2\text{H}_5)_3$  (VTES) in ethanol under acid (HCl)-catalyzed hydrolysis and basic-catalyzed condensation. Details of preparation processing were described elsewhere<sup>8</sup>. The CuPc dye was dissolved in DMF/ethanol mixed solvent and sonicated for about 1 h and then introduced into sol-gel precursor solution. The derived CuPc-doped gel glasses (0.082 wt. %) were homogeneously doped. XRD analysis of the CuPc-doped hybrid gel glasses was performed using an X-ray diffractometer (D/Max-2550PC, Rigaku, Japan). The UV-vis absorption spectrum of the CuPc-doped hybrid gel glasses is recorded under room temperature using the JASCO V-570 spectrometer.

### RESULTS AND DISCUSSION

XRD analysis of the CuPc-doped hybrid gel glasses was performed to determine the chemical state of CuPc molecules

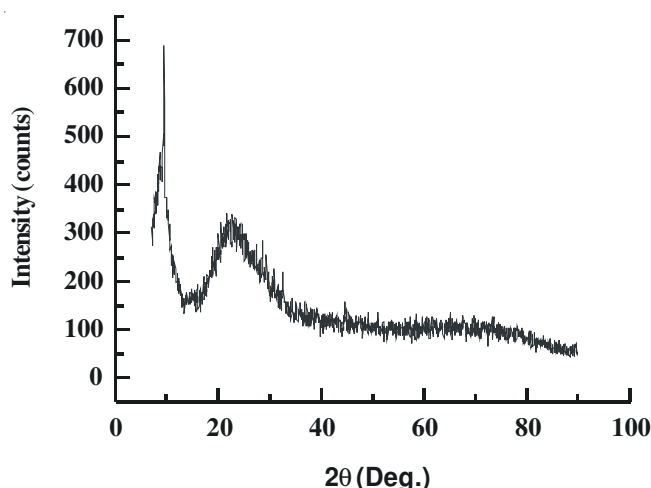


Fig. 1. X-Ray diffraction pattern of VTES-derived hybrid gel glasses doped with CuPc dye (0.082 wt. %)

after being incorporated into the hybrid gel glasses. Fig. 1 shows the characteristic diffraction peak between 20-30° for the CuPc-doped hybrid gel glasses. These results identify that the CuPc-doped hybrid gel glasses are amorphous.

In general, metallophthalocyanines show two characteristic absorption bands in the ranges of 300-400 and 600-800 nm, assigned to be B-band and Q-band, respectively<sup>9</sup>. Furthermore, metallophthalocyanine molecules usually exist as forms of monomers, dimers and aggregations. The UV-vis absorption spectrum in Fig. 2 shows that both the B-band in the ultraviolet region and the Q-band in the visible region appear. The absorption band within 550-1000 nm can be attributed to the Q-band absorption. This indicates successful encapsulation of CuPc molecules into the gel glasses.

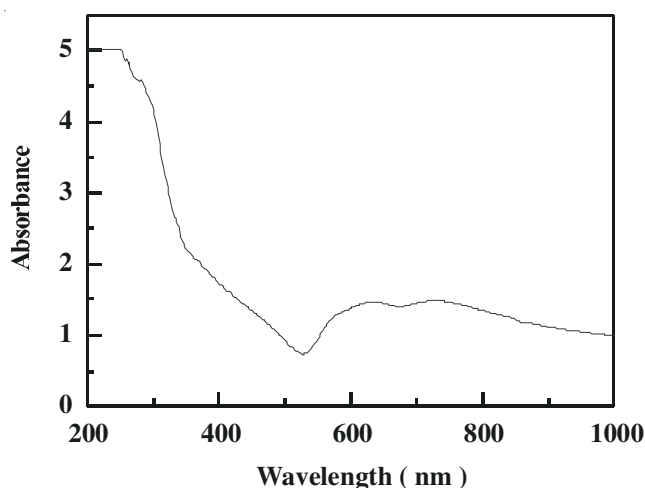


Fig. 2. Absorption spectrum of VTES-derived hybrid gel glasses doped with CuPc dye (0.082 wt. %)

The UV-vis absorption spectrum for the CuPc-doped hybrid gel glasses originates from the molecular orbitals within the aromatic 18 $\pi$  electron system and from the overlapping orbitals at the central metal of copper atoms. The direct electronic transitions from  $\pi$ - $\pi^*$  result in an intense band (the Soret band) within the 300-500 nm, which gives the absorption edge

in the CuPc-doped hybrid gel glasses. According to one electron theory of Bardeen, the absorption edge of the CuPc-doped hybrid gel glasses can be analyzed<sup>10</sup>. The proposed relation between absorption coefficient and photon energy should be expressed as:

$$\alpha = (h\nu - E_g)^n A/h\nu \quad n = 2, 1/2$$

where  $E_g$  = optical band gap,  $\alpha$  = absorption coefficient and  $A$  is a constant. Fig. 3 shows the plot of  $(\alpha h\nu)^2$  versus  $h\nu$  in order to find the optical band gap of direct transition ( $E_{gd}$ ). The  $E_{gd}$  is about 3.72 eV by extrapolation of the plot to  $(\alpha h\nu)^2 = 0$ . Fig. 4 shows the plot of  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  in order to find the optical band gap of indirect transition ( $E_{gi}$ ). The  $E_{gi}$  is about 3.47 eV by extrapolation of the plot to  $(\alpha h\nu)^{1/2} = 0$ .

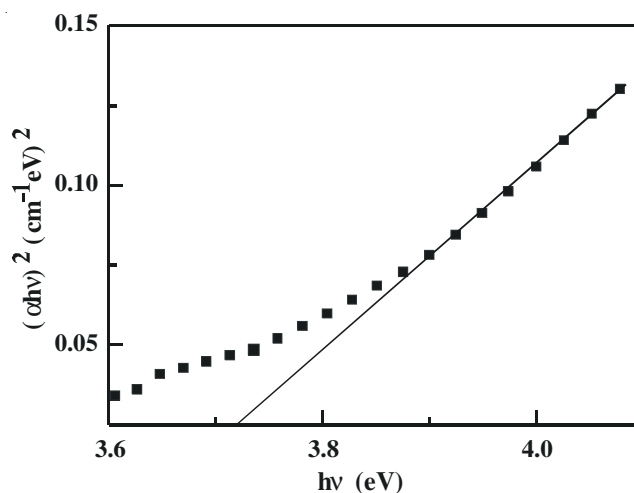


Fig. 3. Plot of  $(\alpha h\nu)^2$  versus  $h\nu$  for VTES-derived hybrid gel glasses

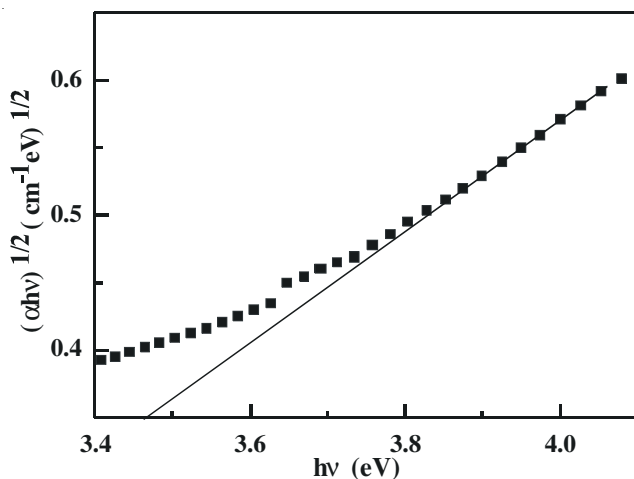


Fig. 4. Plot of  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  for VTES-derived hybrid gel glasses

Optical constants of the CuPc-doped gel glasses are influenced by various factors such as crystallinity, treating temperature and supporting matrixes. Table-1 shows the band gap values of CuPc-doped different supporting matrixes. The band gaps of direct and indirect transitions for the CuPc-doped gel glasses are 3.72 and 3.47 eV, respectively. These values are larger than that for the CuPc-doped potassium borate melting glass, but little lower than that for the CuPc-doped sodium borate melting glass. The differences among the direct and

TABLE-1  
BAND GAP VALUES OF CuPc-DOPED  
DIFFERENT SUPPORTING MATRIXES

Matrixes	$E_{gd}$ (eV)	$E_{gt}$ (eV)
CuPc-doped sodium borate melting glass <sup>11</sup>	3.76	3.57
CuPc-doped potassium borate melting glass <sup>12</sup>	3.55	2.45
CuPc-doped hybrid gel glasses	3.72	3.47

indirect band gaps may be due to many reasons. The main reason can be attributed to the different chemical structures of supporting matrixes. The CuPc-doped inorganic-organic hybrid gel glasses are three-dimensional network, leading to different micro-chemical environment, compared to borate melting glasses. The CuPc molecules tend to exist in the tiny pores of the gel glasses.

### Conclusion

We have studied optical band gaps of indirect and direct transitions for the sol-gel derived CuPc-doped inorganic-organic hybrid gel glasses. The band gaps of indirect and direct transitions for the hybrid gel glasses are 3.72 and 3.47 eV, respectively. Complementary dielectric experiments are in progress in our laboratory to investigate the behaviour of optical band gaps for metallophthalocyanines-doped hybrid gel glasses.

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