Green-light emission of ZnO nanoparticles spontaneously precipitated in fluorinated polyimide films

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ABSTRACT

The light emitting property of zinc oxide (ZnO) nanoparticles, which were spontaneously precipitated and dispersed in fluorinated polyimide films has been studied because this hybrid material exhibits interesting properties and could be widely applied in optoelectronics and photonics. Polyimides (PI) provide high thermal and chemical stability and outstanding electrical properties. In addition, ZnO presents excellent optical properties due to its wide band gap (3.37 eV) at room temperature and large exciton bonding energy (60 meV), which can be used in light-emitting diodes, transparent electrodes, and piezoelectric devices.

By adding small amount of Zinc compounds (5 mol %), either Zinc hexafluoroacetylacetonate dihydrate or Zinc nitrate hexahydrate, to precursor solutions of polyimides followed by thermal curing at 350~390ºC, the green light emission at ca. 520 nm of polyimides has been significantly enhanced by 10 to 15 times respectively.

When zinc concentration excesses the saturation level, light emission decreases and emission peak was shifted to higher wavelengths due to the aggregation of ZnO. This can be explained by the quantum confinement mechanism and the interaction between the oxygen of ZnO and PI functional groups. Zinc compound precursors and curing temperature and atmosphere affect the light emitting behavior which will be discussed in detail.

Keywords: nanoparticle, ZnO, zinc oxide, fluorinated polyimide, photoluminescence, light emission

1. INTRODUCTION

Because polyimides (PIs) provide very strong, astoundingly thermal and chemical resistant and outstanding electrical properties, they often replace inorganic glass and metals in many demanding industrial applications such as electronics and aerospace application. Besides, they have potential as optical waveguide materials in telecommunication and optical interconnect technologies due to their exceptional thermal and optical properties.

On the other hand, potential materials for making short-wavelength light-emitting diodes (LEDs) and diode lasers have been attracting increasing interest as the demands for display, illumination and information storage. Zinc oxide (ZnO) has substantial advantages including large exciton binding energy (60 meV), as demonstrated by efficient excitonic lasing on optical excitation. Very recently, violet electroluminescence was demonstrated for specially prepared ZnO at room-temperature, and blue light-emitting LED was successfully demonstrated by Kawasaki et al[1]. If nano-particles of the light-emitting ZnO crystallites are uniformly dispersed in flexible matrices, the new material should exhibit highly functional and very unique optical properties, which may open up a new visual technology and display industry.

The matrix materials, which can be used in optical light-emitting applications, should exhibit high radiation durability in the UV (λ=200~380 nm) region, high transparency in the visible (λ=380~780 nm) and the near infrared (NIR) region (λ=780~1600 nm), low hygroscopicity, and high thermal stability. The most well known PI (PMDA/ODA) does not meet the criteria; therefore, new kinds of PI have been developed[2]. One approach is to add fluorine atoms in the materials which can improve several properties such as radiation durability against UV light, transparency in the visible and NIR regions, lower the glass transition temperature and increase in thermal expansion coefficient. Besides, the

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uniform dispersion of metal or metal oxide nano-particles into PIs can improve their radiation durability, transparency, refractive indices and birefringence properties[3].

ZnO nano-particles can be deposited directly onto PI film by pulse laser deposition[4] or by using stabilizer to prevent aggregation of ZnO nano-particles.[5] Another approach to synthesize metal oxide nano-particles in PI films has been proposed by Chung et al.[6] Metal oxide nano-particles imbedded in PI films were prepared by embedding thin film metal on quartz substrates, then coating them with poly(amic acid) solution and thermal curing the materials. Particle sizes of metal oxide varied due to metal types and the average size is 10 nanometers. In addition, the PI film containing ZnO nano-particles showed the absorption peak at 374 nm corresponding to exciton absorption; therefore, the optical band edge would be above 370 nm which is closely to that of bulk value.[7] Furthermore, to obtain large size of ZnO nano-particles (around 10 nm), the film had to be cured at high temperature (400 °C).[8]

Although the aforementioned methods have been used to placed ZnO nano-particles in PI film, this study had proposed a thermal decomposition method to synthesize ZnO nano-particles in PI film. Metal-nanoparticle dispersed fluorinated PI films have been prepared by thermal curing of poly(amic acid)s containing metallic salts or organometallic complexes by Sawada and Ando[9]. Metallic salts or organometallic complexes were decomposed to form metal oxides or metal during thermal curing process. The chemical states, average sizes, and spatial distribution of the metallic particles were examined, and the thermal and optical properties of the films have been compared with those of the colorless host PI. Copper and palladium complexes were oxidized to form metal oxide while silver complex and gold salts were transformed into metal particles during thermal curing process.

In this study PI films in which ZnO nano-particle were uniformly dispersed had been prepared by followed Sawada and Ando's method.[9] Zinc complex and zinc salt were chosen to disperse in poly(amic acid) solution followed by thermal imidization process. Two sets of PI monomers had also been used in this study. The main focus of this study is to develop a better understanding and a promising way of making a new series of PI films in which ZnO nanoparticles are uniformly dispersed. This material has high potential in optical light-emitting applications together with UV-resistant, thermally stable, and highly transparent film applications.

2. METHODOLOGY

2.1 Materials

Two types of fluorinated polyimide, PMDA/TFDB and 6FDA/TFDB (Figure 1), synthesized from pyromellitic dianhydride (PMDA) or 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2'-bis-(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB), were used in this study. The preparation of poly(amic acid) (PAA), the precursor of the polyimide, and the thermal, mechanical, and chemical properties of this polyimide have been described elsewhere[2]. This polyimide exhibits a high polymer decomposition temperature (610 °C), high glass transition temperature (>400 °C), low water absorption (0.7 wt %), and high optical transparency.

5 – 59 mol% of Zinc hexafluoroacetylacetonate dehydrate (Znhf) or Zinc nitrate hexahydrate (ZnNi) (Figure 2) was added to precursor solutions of polyimide (PAA) and stirred overnight. The PAA solution was then spin-cast onto a clean dry silicon substrate to obtain a uniform thickness thin layer of solution. The PAA solution was then cured at 350 ~ 390ºC in nitrogen atmosphere or vacuum oven in the following steps: 70ºC, 30 min, ramp up to 350ºC in 1 hr and isothermal at 350 ~ 390 ºC for 1 h. The heat treatment promoted imidization and converted PAA to polyimide.

2.2 Measurements

2.2.1 Thermogravimetry Analysis (TGA)

Decomposition temperature of PAA and zinc compound was measured by means of thermogravimetry analysis (TGA) with Thermogravimetric analyzer TGA-50 (Shimadzu) PAA films were heated to 900°C at 10°C/min under N2 and air.

2.2.2 Wide-Angle X-ray Diffraction (WAXS)

Nanoparticle ZnO polyimide films (6 – 20 μm) were characterized by wide-angle X-ray diffraction (XRD) at ambient temperature on X'Pert-MPD (PANalytical) with Cu Kα radiation of wavelength 1.54 Å with a scan speed of 0.003°/s. The pure polyimide films were studied for comparison.

2.2.3 Vis-NIR Spectrum Measurement

The transmission and reflectance spectra in the visible and near-infrared region (Vis-NIR, λ = 200 – 2000 nm) of the polyimide films on substrate were measured using a Hitachi U-3500 spectrophotometer.

2.2.4 Photoluminescence Measurement

Photoluminescence (PL) scans were carried out with a fluorescence spectrophotometer F-4500 (Hitachi). Three dimensional contour plots provide maximum spectral information which was shown in Figure 6 – 11.

2.2.5 Transmission Electron Microscopy (TEM)

Cross-sectional transmission electron (TEM) micrographs of ZnO-doped PIs were taken with JEOL TEM 200CX. The PI films were embedded in epoxy resin and sectioned into a thickness of 60 nm with a Reichert-Jung Werke ultramicrotome.

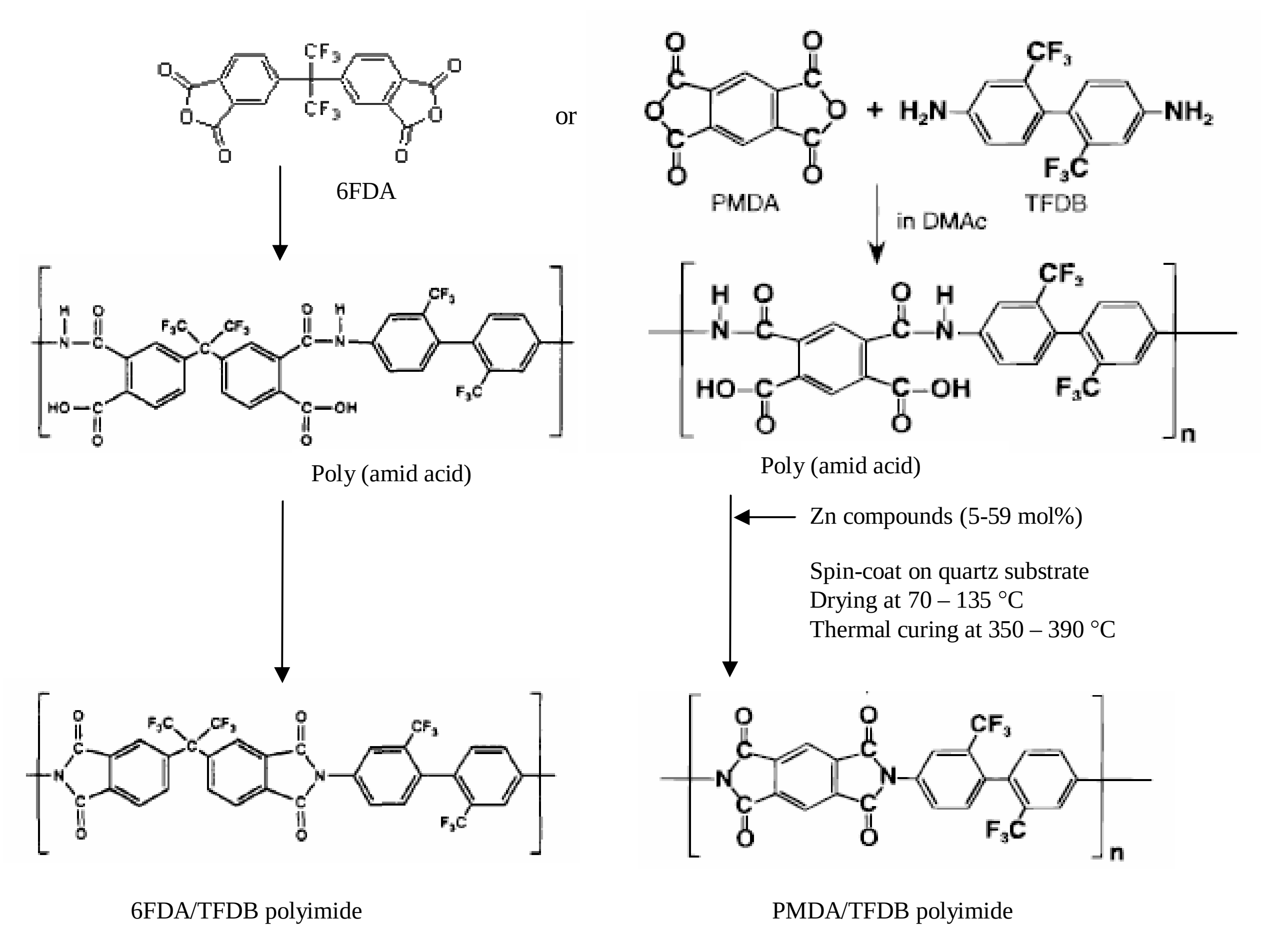
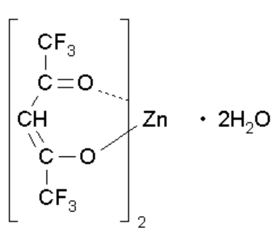


Figure 1 : Chemical structures of monomers and preparation of poly(amic acid) and polyimide.

a) 

b) $Zn(NO_3)_2 \cdot 6H_2O$

Figure 2 : Chemical structures of
a) Zinc hexafluoroacetylacetonate dihydrate (Znhf) and b) Zinc nitrate hexahydrate (ZnNi)

3. RESULTS AND DISCUSSION

3.1 Thermal Decomposition of zinc compounds and PAA

Figure 3 shows the thermal gravimetric profiles of PMDA-TFDB PAA with 5 mol% of Znhf compared with pure Znhf compound. It can be seen that decomposition temperature (measured at 95 wt%) of both PAA containing Znhf and Znhf compound is around 101 °C. The weight of Znhf compound began to decrease and was almost constant at 200°C and the residue was 5.3 wt%. While the weight of PAA containing Znhf decreased rapidly twice which indicated the decomposition of zinc compound and polymer matrix at different temperature range.

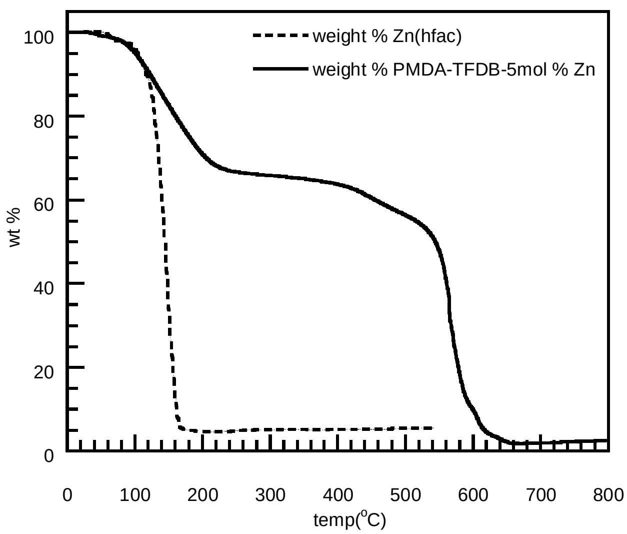


Figure 3 : TGA result of Znhf and PAA containing 5 mol% of Znhf

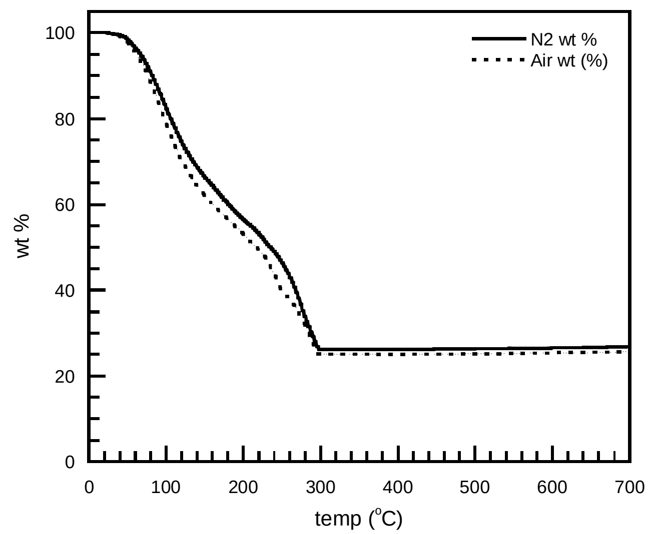


Figure 4 : TGA result of Zn Nitrate performing an experiment in air and in nitrogen atmosphere

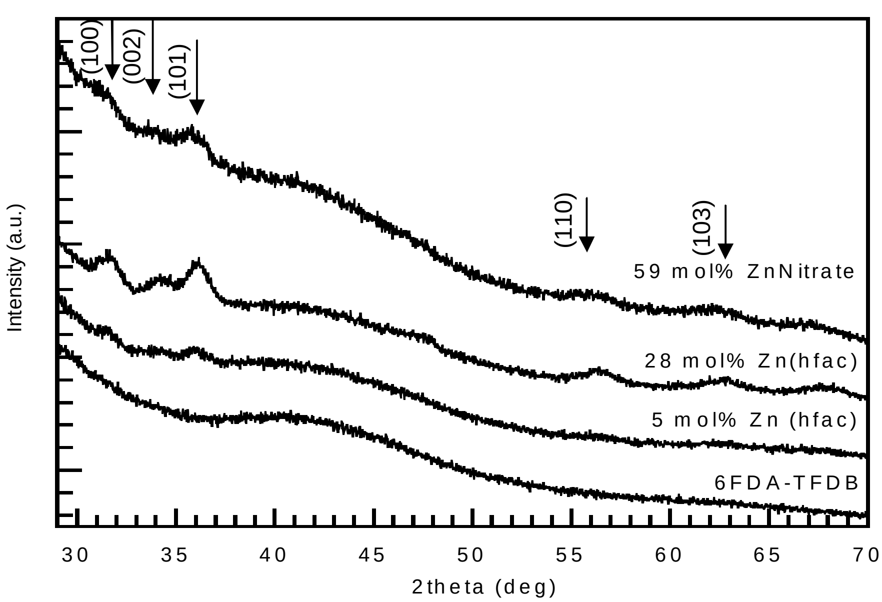


Figure 5 : XRD result of 6FDA-TFDB polyimide containing ZnO

From Figure 4, the decomposition profiles of zinc nitrate in both nitrogen and air atmosphere are similar. Therefore, imidization process of PAA containing zinc nitrate in nitrogen and air atmosphere would not affect the decomposition process of zinc nitrate. The similar zinc oxide formation would then be obtained.

3.2 X-ray Diffraction of Zinc Oxide in 6FDA-TFDB Polyimide Matrix

The XRD characterization results are reported in Figure 5. As shown in Figure 5, the XRD peaks, which correspond to the {100}, {002}, {101}, {110} and {103} basal reflection of the Zinc oxide, are indicative of crystal structure of nanoparticle Zinc oxide.[10, 11] 28 mol% Zn(hfac) in 6FDA-TFDB film shows the clearest peak indicating an existence of crystal zinc oxide in polymer film. Only XRD patterns showed here exhibit the crystal structure of zinc oxide while other samples contain only amorphous structures of zinc oxide or too small size of zinc oxide to be observed by XRD.

3.3 Photoluminescence and Vis-NIR Absorbance Spectra

Zinc oxide fillers were used because zinc oxide is a wide band gap semiconducting material, which has potential uses in optical applications. By having zinc oxide in the polyimide matrix, polyimide/ZnO hybrid with controlled properties would be expected. It can be seen from Figure 6 that by adding only 5 mol% of Zn(hfac) into PMDA-TFDB polyimide film, light emission at visible wavelength was enhanced by 2.8 times compared to that of its matrix. The peak was also shown blue-shift, i.e., light emission was shifted from 528.4 nm to 515.2 nm with ZnO containing in PI film. Note that there was no peak observed from XRD measurement. ZnO nanoparticles in some of these films which visible emission dominated the Photoluminescence (PL) spectra would be an amorphous form which the results was not consistent with results of Wang et al.[12]

In this study, two kinds of polyimide have been used as a polymer matrix, i.e., PMDA-TFDB and 6FDA-TFDB. Even though process conditions have been varied, the fluorescent intensity of zinc oxide in PMDA-TFDB polyimide film was not so high. Therefore, 6FDA-TFDB polyimide has been chosen to study the effect of zinc oxide on the optical properties instead.

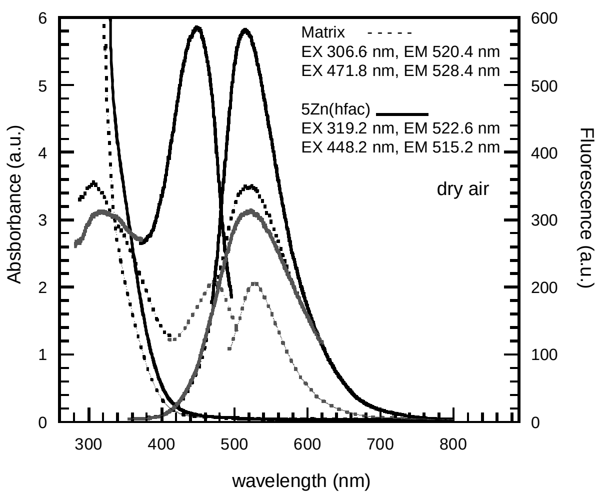


Figure 6 : Photoluminescence of 5 mol% Zn(hfac) in PMDA-TFDB film compared with that of PMDA-TFDB film

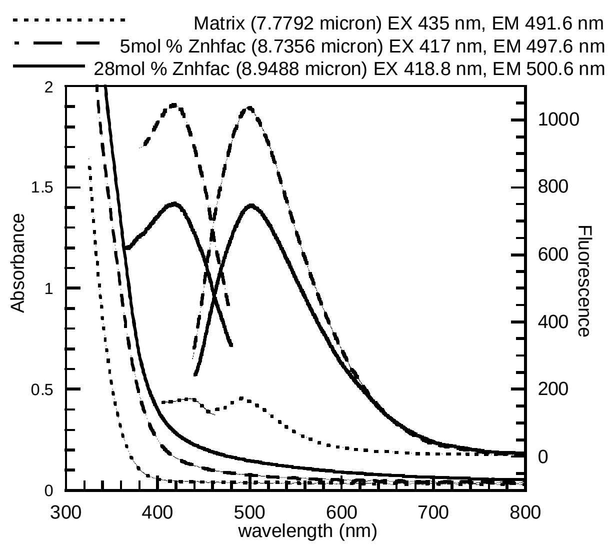


Figure 7 : Effect of Zn(hfac) concentration on photoluminescence of ZnO/6FDA-TFDB film

Figure 7 shows the effect of Zn(hfac) concentration on fluorescent intensity. 6FDA-TFDB polyimide matrix emitted very low light intensity compared with the matrix containing 5 mol% Zn(hfac). However, by having too much of zinc oxide (28 mol% Zn(hfac)) the fluorescent intensity decreased which could be due to the aggregation of zinc oxide.

Jeon et al[8] cured PI/Zinc stacks after drying at 135°C while we used 70°C as drying temperature. Therefore, the effect of drying temperature has been studied. It can be seen from Figure 8 that the drying temperature does not affect the fluorescent intensity so much.

The transformation of not only Zn(hfac) but also Zn nitrate to be ZnO nanoparticles in 6FDA-TFDB polyimide matrix has been studied and compared the properties. It can be seen from Figure 9 that the intensity of ZnO nanoparticles from Zn nitrate is much higher than that of Zn(hfac). Threfore, the effect of Zn nitrate concentration on the fluorescent intensity has been studied as shown in Figure 10.

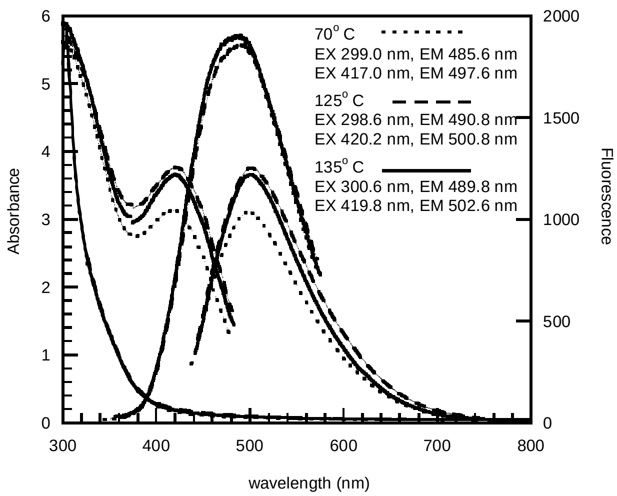


Figure 8 : Effect of drying temperature on photoluminescence of 5 mol% Zn(hfac) in 6FDA-TFDB film

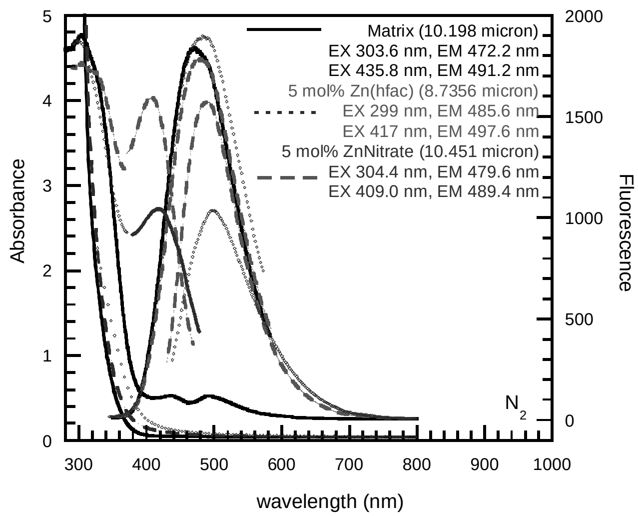


Figure 9 : Comparison of the photoluminescence of 5mol% Zn(hfac) and Zn nitrate in 6FDA-TFDB film

From Figure 10, Zn nitrate was increased from 5 to 10, 15 and 59.7 mol% in 6FDA-TFDB polyimide matrix. The fluorescent intensity of 10 and 15 mol% Zn nitrate is higher than that of 5 mol% Zn nitrate as the amount of ZnO nanoparticles increase. However, the fluorescent intensity of 59.7 mol% Zn nitrate is much lower due to the aggregation of ZnO nanoparticles.

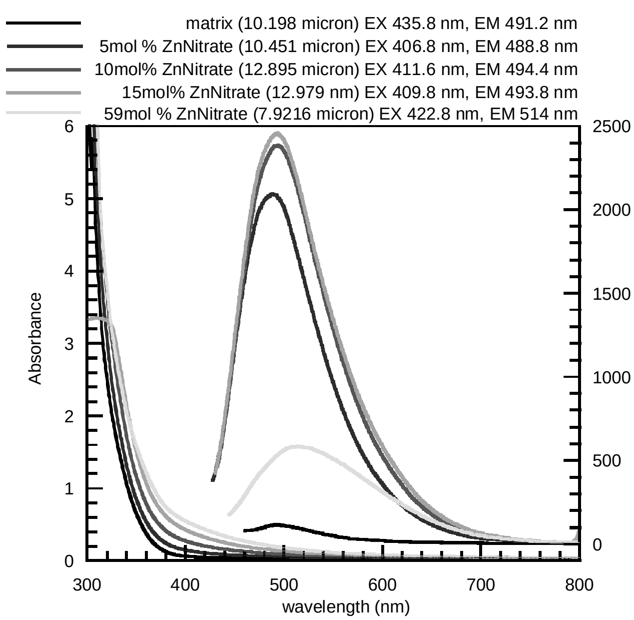


Figure 10 : Effect of Zn nitrate concentration on photoluminescence in 6FDA-TFDB film

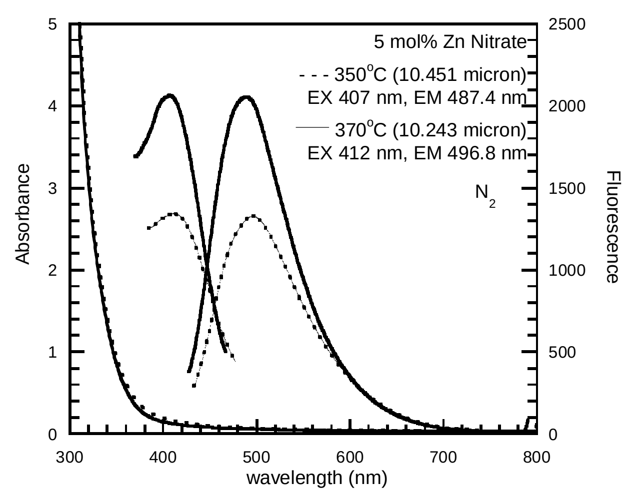
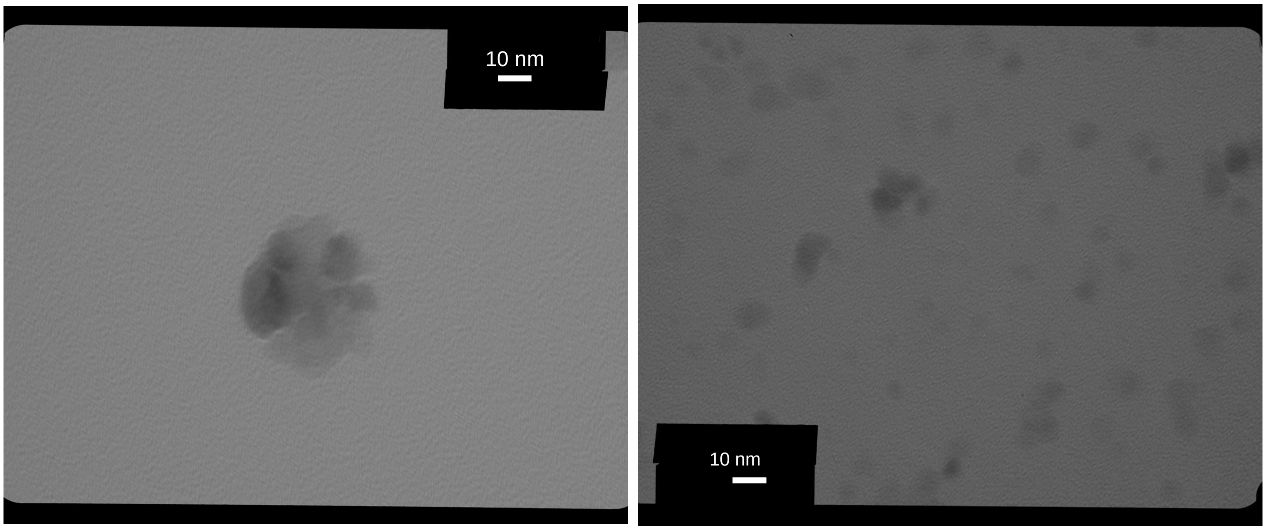


Figure 11 : Effect of imidization temperature on photoluminescence 5 mol% Zn(hfac) in 6FDA-TFDB film

Figure 11 shows the effect of imidization temperature on the fluorescent intensity of ZnO/6FDA-TFDB polyimide film from 5 mol% Zn nitrate. Film imidized at higher temperature (370°C) shows higher fluorescent intensity than the one imidized at 350°C.



28 mol% Zn(hfac) (2.94 wt% ZnO)   59.7 mol% ZnNitrate (6.26 wt% ZnO)

Figure 12 : TEM micrographs of zinc oxide in 6FDA-TFDB polyimide film

3.4 Transmission Electron Microscopy (TEM)

Figure 12 shows the TEM micrograph of 28 mol% Zn(hfac) and 59.7 mol% Zn nitrate in 6FDA-TFDB polyimide matrix. It can be seen that the size of ZnO nanoparticles from 28 mol% Zn(hfac) is much bigger than those from 59.7 mol% Zn nitrate. These smaller ZnO nanoparticles from Zn nitrate could emit higher fluorescent intensity than bigger ZnO nanoparticles from Zn(hfac) (from photoluminescence data). Note that there is no ZnO nanoparticles observed in TEM micrograph of other ZnO/polyimide films prepared in this study which could be due to the limitation of TEM resolution capacity.

4. CONCLUSIONS

In this study, Zn nitrate is more suitable to use as a precursor to obtain ZnO nano-particles in polyimide film than Zn(hfac) because it can transform to be small ZnO nanoparticles dispersed thoroughly in polyimide film and emit high fluorescent intensity. Around 15 mol% Zn nitrate would be the optimal concentration to emit high fluorescent intensity. In addition, even though 15 mol% Zn nitrate in 6FDA-TFDB polyimide film emitted highest fluorescent intensity compared with other ZnO/PI films in this study, the XRD pattern of ZnO in this film is not clear and ZnO nanoparticles cannot be observed by TEM method. This could be due to the limitation of TEM, the size and degree of crystallinity of ZnO nanoparticle.

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