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Research Article
Characterization of MEH-PPV/YAG:Ce Hybrid Nanocomposite Material for Fabrication of Optoelectronic Device by Solution Process

Dinh Van Chau and Dinh Van Thuong

Faculty of Engineering Physics and Nanotechnology, University of Technology and Engineering, Vietnam National University, Hanoi, 144 Xuan Thuy, Cau Giay, Hanoi, Vietnam

Abstract
The fabrication and the property investigation of the hybrid nanocomposite material made of poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1, 4-phenylene vinylene] (MEH-PPV) polymer and $Y_3Al_5O_{12}$:Ce (YAG:Ce) with relative weight ratio of 1:1 in order to apply for optoelectronic and light harvesting devices are reported. Thermal analysis showed that the hybrid materials deterioration/or decomposition when the temperature exceed 200°C under inert gas atmosphere. Rheological measurement concluded that the material solution is able to use for spinning or soft moulding lithography making large or flexible substrate surface. Optical properties of the hybrid material are investigated. The effect of thermal treatment on the optical properties showed that at 180°C under inert gas environment the optical properties were enhanced. A MEH-PPV/YAG:Ce hybrid nanocomposite converted LED lamp was fabricated showing that the hybrid material is suitable as conversion material for white LED fabrication.

Key words: Conversion white LED, hybrid nanocomposites, conducting polymer, YAG:Ce, MEH-PPV

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Corresponding Author: Dinh Van Chau, Faculty of Engineering Physics and Nanotechnology, University of Technology and Engineering, Vietnam National University, Hanoi, 144 Xuan Thuy, Cau Giay, Hanoi, Vietnam Tel: 0084 914 262 666

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Organic Polymer Light Emitting Diodes (OLEDs) play an important role in solid state lighting and flat panel display due to low power consumption, low cost and easy manufacturing (Hoven *et al*., 2008). For fabrication of white light sources in Solid State Lighting (SSL) area, the combination of Red (R), Green (G) and Blue (B) emitters is a major approach. Based on RGB combination, there are three considerations to generate white light (Muthu *et al*., 2002): (1) Using R, G and B Light Emitting Diodes (LED) to create a white light with the Color Rendering Index (CRI) higher than 80, (2) Used the ultraviolet (UV) radiation from UV LED chip for exciting phosphor to create a mixture of R, G and B light and (3) White light can be produced by combination of the blue light given by InGaN-LEDs chip and the yellow light given by blue-light excited $Y_3Al_5O_{12}$:Ce (YAG:Ce). The two last approaches based on the underlying principle of luminescence down-conversion (Stokes shift) dyes from shorter-wavelength light to longer-wavelength (Guha *et al*., 1997; Hide *et al*., 1997; Zhang and Heeger, 1998; Schlotter *et al*., 1999; Mueller-Mach *et al*., 2002; Tardy and Berthelot, 1999; Narukawa *et al*., 2002; Yamada *et al*., 2003; Sheu *et al*., 2003).

Many studies have shown that white light LEds can be obtained using GaN/conjugated polymers (Guha *et al*., 1997; Hide *et al*., 1997), GaN/low-molar mass organics (Guha *et al*., 1997; Schlotter *et al*., 1999; Mueller-Mach *et al*., 2002) or YAG hybrid materials (Zhang and Heeger, 1998; Mueller-Mach *et al*., 2002; Tardy and Berthelot, 1999; Narukawa *et al*., 2002; Yamada *et al*., 2003; Sheu *et al*., 2003). In these reports, the blue or near-ultraviolet (n-UV) light GaN-LEDs chip used as primary source and also confirmed that the conjugated polymers are thermal unstable and photo-induced oxidized deterioration while, the YAG is insufficient red emission and low CRI. Among the conducting polymers, the poly [1,4-phenylene vinylene] (PPV) and its derivatives specially Poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) are commonly selected in the fabrication of organic light emitting diodes (Morgado *et al*., 2003), since it is able to emit orange-red emission and easy to dissolve in organic solvent. The previous work showed that the peak absorption of MEH-PPV is at 500 nm while, the two emission peaks were reported at 590 and 640 nm (Dinh *et al*., 2009). For inorganic material, the YAG matrix doped with cerium atoms in substitution to yttrium ions (YAG:Ce^{+3}) is considered in white luminescence conversion light-emitting diodes, because of its high quantum yield (Schlotter *et al*., 1999). This materials was also reported that it has photo-stability, short transition time because of its fast parity allowed transition from d level to f level, both in bulk (around 70 nsec) and for nanoparticles (about 30 nsec) (Robbins *et al*., 1979; Zhou *et al*., 2006).

For performance of nano-hybrid composite, Nano-Particle (NP) network must be homogenous in polymer matrix. This is complex issue due to high surface to volume ratio of NPs that tend to form agglomerate to lower their surface energy. Furthermore, the addition of a NPs dense network to polymers can significantly alters the mechanical properties of hybrid nanocomposite materials negatively affecting the advantageous properties of base polymers such as proccesability. Solution blending is frequently process to fabricate the hybrid-nanocomposites. By this way, the NPs are disperses into polymer solution then the mixture can be dried in vacuum or can be used to obtain thin films by spin-casting. During these procedures, the NPs form micro-size aggregates and cannot be separated from each others.

This study presents the fabrication of nanocomposite film by spin-coating from solution of MEH-PPV and YAG:Ce making a proposal technique not expensive and ideal to produce white LED based on a n-UV GaN chip LED as primary source. Mechanical and optoelectronic properties of the hybrid nanocomposite film were also investigated and discussed.

MATERIALS AND METHODS

All the reagents used in this work originating from Sigma-Aldrich purchased under financially supported by the VNU Project No. QG.12.46 in the period of 2012-2015. The YAG:Ce particles having size of about 200 nm used as NPs incorporated in the MEH-PPV matrix is prepared by following the method reported in literatures (Jang *et al*., 2005, 2007). The pristine polymer, MEH-PPV, having number of molecular weight (Mn) from 70,000-100,000 was used without further purification. The precursor/polymer nanocomposite films were produced by spin-coating on glass slides from the solution of YAG:Ce and MEH-PPV in chloroform solvent with a respect weight/weight ratio of 1:1. The weight to volume ratio of soluble and solvent was set at 1 mg over 2 mL. The spin speed and time were set at 2,000 rpm in 10 sec, respectively in order to obtain the smooth and uniform surface films. For all samples, the thermolysis process was performed at temperatures of 150 and 180°C in 1 h under argon gas to avoid possible oxidization of the surface film.

Thermogravimetric analysis (Q500, TA Instrument, USA) was conducted with 1.5 L h^{-1} of argon as inert gas in heating rate of 10°C min^{-1} to investigate thermal degradation of the samples. Rheological measurements were carried out by a ARES-G2 (TA Instrument, USA) at 180°C. Samples of MEH-PPV and nanocomposites with a relative weight ratio of 4:1 were prepared by casting of solution in chloroform to obtain 1 mm thick films in order to evaluate the influence of YAG:Ce inclusion on MEH-PPV film mechanical properties.

Optical properties of annealed samples by means of Xe lamp (LC8 Hamamatsu) and HR460 monochromator were investigated on chloroform solutions obtained by samples deposited on glass. The UV-visible transmission (UV/VIS/NIR Spectrophotometer V570-JASCO) were performed in order to evaluate the absorbance of the specimens as ln(1/T). Photoluminescence (PL) spectra were carried out on the same chloroform solutions using a Varian Cary Eclipse Fluorometer, (excitation wavelength, 330 nm). The electroluminescence were measured using an integrating sphere equipped with a calibrated spectrophotometer "LCS 100" (LED measurement system).

White LED lamps were fabricated by the MEH-PPV/YAG:Ce-solution coated on a n-UV LED chip. The LED chip has size of 1.1×1.1 mm with wavelength peak from 420-425 nm and 1 W power.

RESULTS AND DISCUSSION

Thermogravimetric analysis: In order to determine the critical annealing temperature of the hybrid nanocomposite film, the TG analysis tests were performed. Figure 1 shows the TG curves of the MEH-PPV film and MEH-PPV/YAG:Ce hybrid nanocomposite film (a relative weight ratio of 1:1). It is found that the sample weight decreases with increasing temperature continuously from room temperature to 600°C. This observation implies that the polymer and hybrid nanocomposite film is degraded by heat treatment in the investigated temperature range. Total weight loss of about 72.8 and 42.0% is observed for the MEH-PPV and the hybrid nanocomposite sample, respectively. The first weight loss of the hybrid nanocomposite film takes place in the temperature range of 203-305°C, similar to those of the MEH-PPV film is associated to decomposition of MEH group. The weight loss at higher temperature for the both films corresponds to the decomposition of PPV structure. These results are consistent with the decomposition of MEH side group and PPV backbone at low and high temperatures reported in the literatures (Chuangchote *et al*., 2007). Furthermore, the similar characteristics in the TG curves implies that YAG:Ce composition is not affected by the heat treatment from room temperature to 600°C. Consequently, the results show that the MEH-PPV and YAG:Ce/MEH-PPV film can anneal under an inert gas atmosphere at temperature lower than 200°C without decomposition by heat treatment.

Rheological properties of the hybrid nanocomposite film: Figure 2 shows the viscosity of MEH-PPV and hybrid nanocomposite YAG:Ce^{+3}/MEH-PPV with a relative weight ratio of 1:1 depending on the value of shear rate. It can see that a Newtonian behavior occurs at the shear rate lower than 0.0317

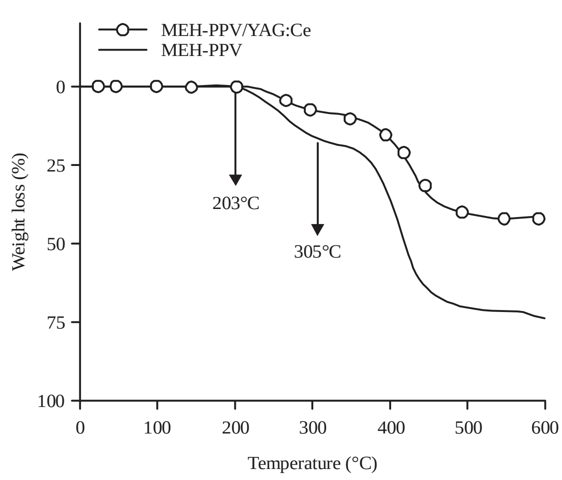

Fig. 1: TG curves of the samples recorded in the temperature range from 25-600°C

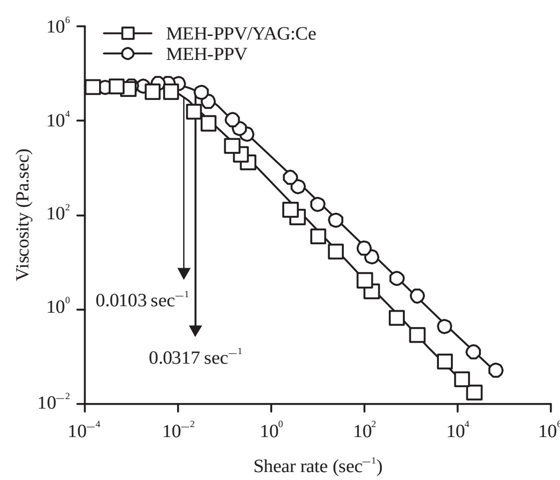

Fig. 2: Rheological measurement of the pristine MEH-PPV and MEH-PPV/YAG:Ce hybrid nanocomposite

and 0.0103 sec^{-1} for the polymer film and the hybrid nanocomposite film, respectively, while a non-Newtonian fluid takes place at higher shear rate. Applying the Carraeu model (Barnes *et al*., 1989) for fitting the experiment data, a viscosity of $h_{o1} = 5.804\times10^4$ and $h_{o2} = 5.687\times10^4$ Pa.sec was obtained for the pristine and hybrid nanocomposite, respectively.

Furthermore, the transition from a Newtonian to a non-Newtonian behavior is observed at viscosity of 4.27×10^4 Pa.sec, shear rate of 0,0317 sec^{-1} for the MEH-PPV material and at viscosity of 4.19×10^4 Pa.sec, shear rate of 0.0103 for the hybrid nanocomposite.

These observations mean that the incorporation of YAG:Ce nano material in the MEH-PPV matrix does not significantly change the deformation resistance of the polymer. Therefore, it can be said that the hybrid nanocomposite is able to coat on a large area, flexible surface using spinning or soft moulding lithography.

Optical spectroscopy analysis: The absorption spectra of the MEH-PPV and the MEH-PPV/YAG:Ce films before and after annealing in argon environment at temperatures of 150°C, 180°C are shown in Fig. 3. The absorption spectrum of MEH-PPV film before annealing has an absorption band at 503 nm. This band is associated to π-π* transition of conjugated chain in MEH-PPV (Resta *et al*., 2010). Another absorption edge at 367 nm is contributed by precursor (Laera *et al*., 2011). For the annealed samples, an absorption band at 467 nm occurs and this band can be considered as an effect of YAG:Ce nano particle inclusion in the polymer matrix by transition between the electron state in conduction band and hole state in valence band. The results are also shown that the remaining absorption peak at around 500 nm of MEH-PPV before and after annealing at set temperatures proving the absence of ground state charge transfer.

Figure 4 shows the PL spectra of the base polymer and the hybrid nanocomposite samples annealed at 150 and 180°C. It can see that the hybrid samples emit a broader band than those of the base polymer. This band is peaked at 550 nm associated to emission band of conjugated polymer. Furthermore, when the annealing temperature increases, the hybrid nanocomposite perform broader fluoresce as resulted from growth of nano-particle concentration by heat treatment (Petrella *et al*., 2008). The well-known emission peaks of MEH-PPV is at approximately 580 and 625 nm (Fig. 4) and is attributed to single-chain (intrachain) exciton emission and aggregation/or excimer (interchain) emission, respectively. The luminescence quenching of base polymer in hybrid samples proves that the polymer chain was aggregated during the heat treatment and it became more intensive with increasing temperature (Chen *et al*., 2007). Another point also observes in the Fig. 4 is that no red-shift in the emission spectra of the hybrid samples. Thus, it may say that there is no induced-aggregation of the polymer chain by incorporation of the inorganic nano-particles in the polymer matrix (Sharma *et al*., 2010).

EL analysis of fabricated white LED: The electroluminescence spectrum of a MEH-PPV/YAG:Ce hybrid nanocomposite-converted LED lamp under a forward bias as of 300 mA is shown in Fig. 5. It can see that the lamp emits an broaden

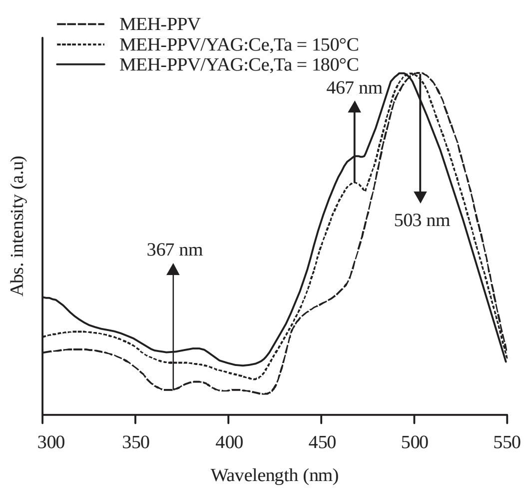

Fig. 3: Absorption characteristic of the MEH-PPV and MEH-PPV/YAG:Ce hybrid nanocomposite

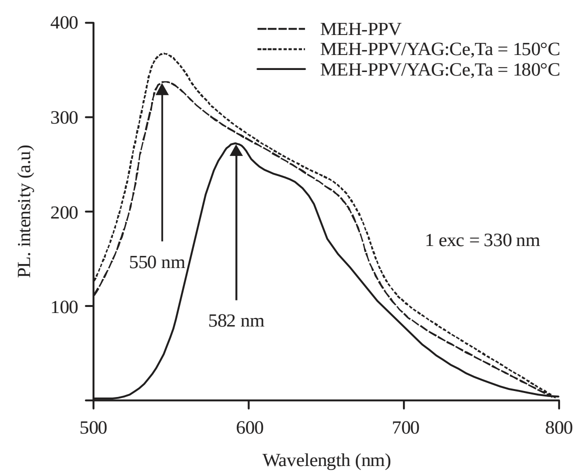

Fig. 4: PL spectra of the MEH-PPV and MEH-PPV/YAG:Ce hybrid nanocomposite

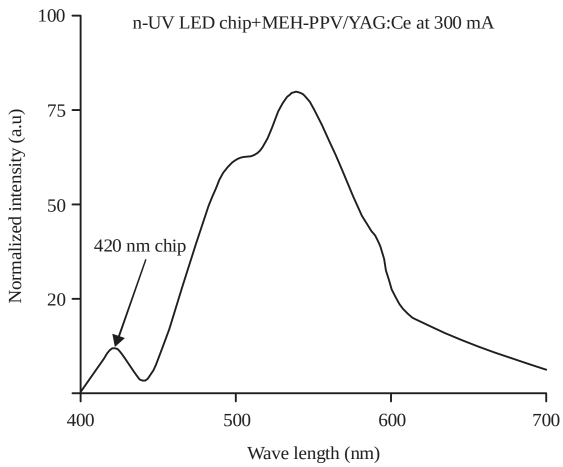

Fig. 5: EL spectrum of a fabricated white LED

band ranging from 445-680 nm, peaked at approximately 547 nm. This result is consistency with the result discussed in Fig. 4. Performance of the lamp fabricated using the MEH-PPV/YAG:Ce nanocomposite can extend to another application area such as biomarker, pigment, etc.

CONCLUSION

The fabrication and the property investigation of the MEH-PPV/YAG:Ce hybrid nanocomposite material were presented. We demonstrated that the hybrid nanocomposite can be suitable for coating technique applying on large or flexible area using spinning or soft moulding lithography. We found that the optical properties of the hybrid material suite for application in optoelectronic and light harvesting. Thermal treatment effect on the material's properties was also carried out showing that the treatment enhanced these properties. A temperature level to avoiding decomposition/or deterioration of the base polymer was also pointed out. A MEH-PPV/YAG:Ce hybrid nanocomposite converted LED lamp was fabricated showing that the hybrid material is suitable as conversion material for white LED fabrication.

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