

Research Article

The MEH-PPV/YAG:Ce Hybrid Nanocomposite Material for Solution Processing Fabrication of Optoelectronic Device

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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 the relative weight ratio of 1 : 1 in order to apply for optoelectronic devices are reported. Thermal analysis showed the hybrid material's deterioration or decomposition when the temperature exceeded $200^\circ C$ under inert gas atmosphere. Rheological measurement concluded that the material solution can be used 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 $180^\circ C$ under inert gas environment, the optical properties were enhanced. An 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.

1. 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 [1]. 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 [2]: (i) using R, G, and B light-emitting diodes (LEDs) to create a white light with the color rendering index (CRI) higher than 80; (ii) using the ultraviolet (UV) radiation from UV LED chip for exciting phosphor to create a mixture of R, G, and B light; and (iii) the possibility of producing white light by a 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 last two approaches are based on the underlying principle of luminescence downconversion (Stokes shift) dyes from shorter-wavelength light to longer-wavelength one [3–12].

Several reports have shown that white light LEDs can be fabricated by coating conjugated polymers- [3, 4], low-molar mass organics- [3, 6, 7], or YAG hybrid [5, 7–12]

materials on a blue or near-ultraviolet (n-UV) light GaN-LEDs chip, used as a primary excited source. However, the authors have also reported that there are some weak points of the coated materials such as the thermally unstable and photoinduced oxidized deterioration characteristics of the conjugated polymers or the insufficient red emission and low CRI of the YAG. 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 [13] since it is able to emit orange-red emission and easy to dissolve in organic solvent. The previous works showed that the peak absorption of MEH-PPV is at 500 nm while the two emission peaks were reported at 590 and 640 nm [14]. 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 [7]. These materials were also reported to have photostability and short transition time because of its fast parity allowed transition from d level to f level both in bulk (around 70 ns) and for nanoparticles (about 30 ns) [15, 16].

For performance of nanohybrid composite, nanoparticle (NP) network must be homogenous in the polymer matrix. This is a complex issue due to the 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 alter the mechanical properties of hybrid nanocomposite materials negatively affecting the advantageous properties of base polymers such as processability. Solution blending is frequently a process to fabricate the hybrid nanocomposites. By this way, the NPs are dispersed 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 microsize aggregates and cannot be separated from each other.

This work presents the fabrication of nanocomposite film by spin-coating from solution of MEH-PPV and YAG:Ce making a proposal technique to produce white LED based on an n-UV GaN chip LED as the primary source. Mechanical and optoelectronic properties of the hybrid nanocomposite film were also investigated and discussed.

2. Experimental

All the reagents used in this work originated from Sigma-Aldrich. The YAG:Ce particles having a size of about 200 nm used as NPs incorporated in the MEH-PPV matrix are prepared by following the method reported in literatures [17, 18]. The pristine polymer, MEH-PPV, having number of molecular weight (M_n) from 70,000 to 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 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 s, respectively, in order to obtain the smooth and uniform surface films. For all samples, the thermolysis process was performed at temperatures of 150°C and 180°C in 1 hr under argon gas to avoid possible oxidation of the surface film.

Decomposition temperatures of the samples were determined by thermogravimetric analysis under an argon atmosphere using Q500, TA Instrument, USA, performed at heating rate of 10°C/min. Rheological measurements were carried out by ARES-G2 (TA Instrument, USA) at 180°C. Samples of MEH-PPV and nanocomposites 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. UV-visible transmissions (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 was 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 an n-UV LED chip. The LED chip has size of 1.1 × 1.1 mm with wavelength peak from 420 to 425 nm and 1 W power.

3. Results and Discussion

3.1. 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 are 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°C to 305°C, similar to those of the MEH-PPV film, and is associated with decomposition of MEH group. The weight loss at higher temperatures for 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 [19]. Furthermore, the similar characteristics in the TG curves imply 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.

3.2. Rheological Properties of the Hybrid Nanocomposite Film. Figure 2 shows the viscosity of MEH-PPV and hybrid nanocomposite YAG:Ce³⁺/MEH-PPV with a relative weight ratio of 1:1 depending on the value of shear rate. It can be seen in Figure 2 that a Newtonian behavior occurs at the shear rate lower than 0.0317 s⁻¹ and 0.0103 s⁻¹ for the polymer film and the hybrid nanocomposite film, respectively, while a non-Newtonian fluid takes place at higher shear rate. Applying the Carreau model [20] for fitting the experiment data, a viscosity of $\eta_{01} = 5.804 \times 10^4$ Pa·s and $\eta_{02} = 5.687 \times 10^4$ Pa·s 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·s, shear rate of 0.0317 s⁻¹ for the MEH-PPV material and at viscosity of 4.19×10^4 Pa·s, shear rate of 0.0103 for the hybrid nanocomposite.

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

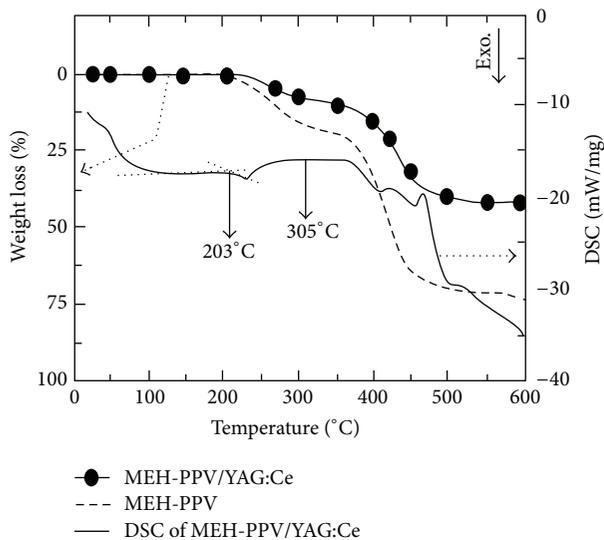


FIGURE 1: TG and DSC curves of the samples recorded in the temperature range from 25 to 600°C.

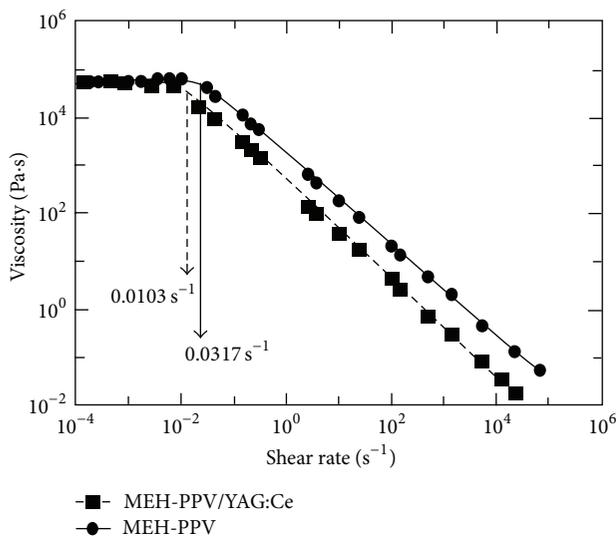


FIGURE 2: Rheological measurement of the pristine MEH-PPV and MEH-PPV/YAG:Ce hybrid nanocomposite.

3.3. 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 Figure 3. The absorption spectrum of MEH-PPV film before annealing has an absorption band at 503 nm. This band is associated with $\pi-\pi^*$ transition of the conjugated chain in MEH-PPV [21]. Another absorption edge at 367 nm is contributed by precursor [22]. For the annealed samples, an absorption band at 467 nm occurs and this band can be considered as an effect of YAG:Ce nanoparticle inclusion in the polymer matrix by transition between the electron state in conduction band and hole state in the valence band. The results also show the remaining

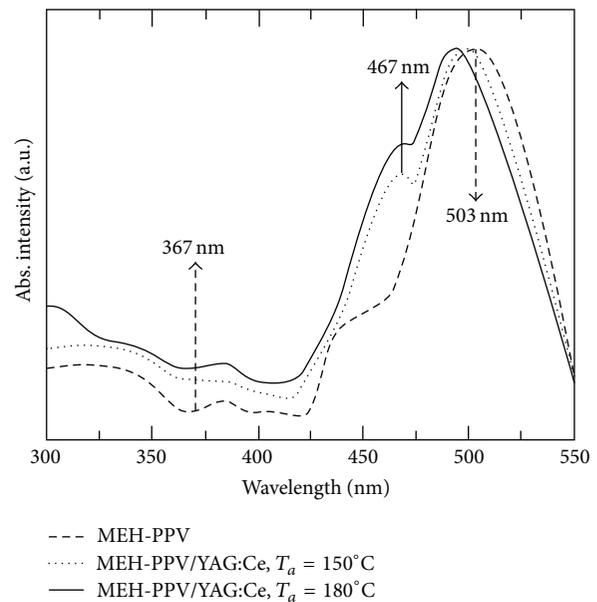


FIGURE 3: Absorption characteristic of the MEH-PPV and MEH-PPV/YAG:Ce hybrid nanocomposite.

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°C and 180°C. As seen in this figure, the hybrid samples emit a broader band compared to those of the base polymer. The band has a peak of 550 nm associated with the emission band of conjugated polymer and is in consistency with the report of Chung et al. [23]. Furthermore, when the annealing temperature increases, the hybrid nanocomposite performs broader and higher intensity fluorescence as resulting from growth of nanoparticle concentration by heat treatment [24]. The well-known emission peak of MEH-PPV is at approximately 580 and 625 nm (see in Figure 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 [25]. Another point also observed in Figure 4 is no redshift 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 nanoparticles in the polymer matrix [26].

3.4. Luminescence Analysis of Fabricated White LED. The emission spectra of n-UV chip LED/180°C-treated-MEH-PPV/YAG:Ce-; 150°C-treated-MEH-PPV/YAG:Ce hybrid nanocomposite converted LED lamps under a forward bias as of 300 mA are the same behavior as seen in Figure 5. The band located at about 420 nm matches with n-UV emission of the LED chip by electroluminescence under the certain current. The broadened band ranging from 445 nm to 680 nm, peaked at approximately 547 nm, is contributed to

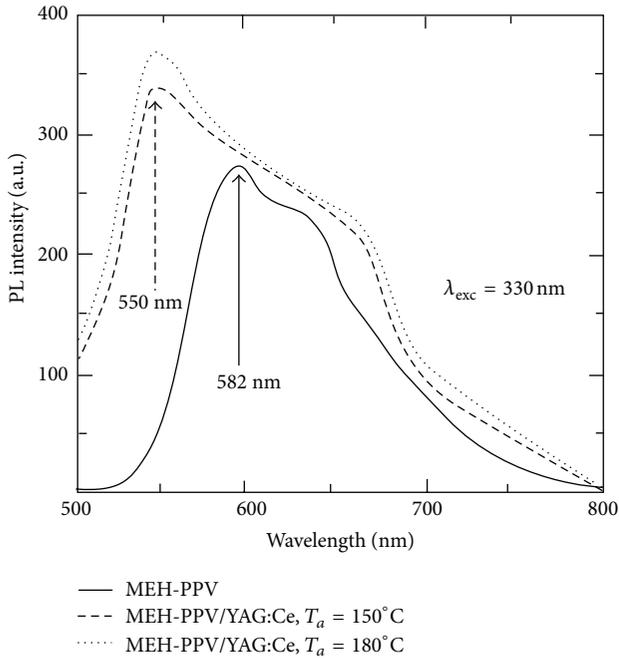


FIGURE 4: PL spectra of the MEH-PPV and MEH-PPV/YAG:Ce hybrid nanocomposite.

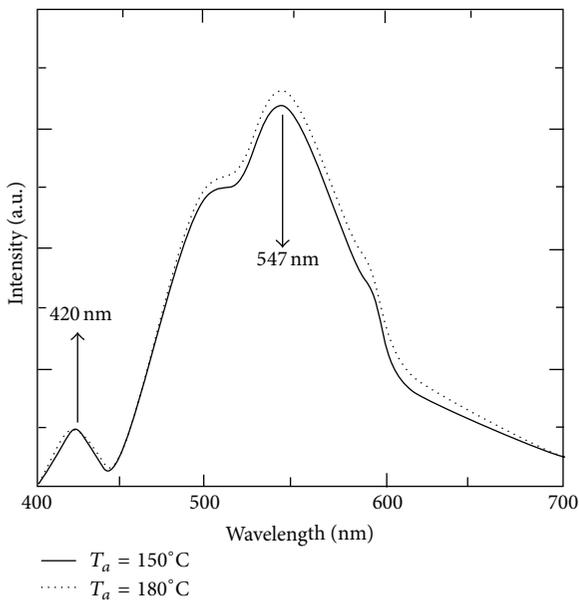


FIGURE 5: Emission spectrum of fabricated white LEDs.

photoluminescence of MEH-PPV/YAG:Ce excited by n-UV light from the chip LED. This result is consistent with the result discussed in Figure 4. The performance of the lamp fabricated using the MEH-PPV/YAG:Ce nanocomposite may give an ideal to another application area such as biomarker and pigment.

4. Conclusion

The fabrication and the property investigation of the MEH-PPV/YAG:Ce hybrid nanocomposite materials 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 suit 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 avoid decomposition or deterioration of the base polymer was also pointed out. An 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.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] C. V. Hoven, R. Yang, A. Garcia et al., "Mechanism of electron injection in multilayer polymer light-emitting diodes using conjugated polyelectrolyte as the electron transporting layer," *Proceedings of the National Academy of Sciences*, no. 105, pp. 12730–12735, 2008.
- [2] S. Muthu, F. J. P. Schuurmans, and M. D. Pashley, "Red, green, and blue LEDs for white light illumination," *IEEE Journal on Selected Topics in Quantum Electronics*, vol. 8, no. 2, pp. 333–338, 2002.
- [3] S. Guha, R. A. Haight, N. A. Bojarczuk, and D. W. Kisker, "Hybrid organic-inorganic semiconductor-based light-emitting diodes," *Journal of Applied Physics*, vol. 82, no. 8, pp. 4126–4128, 1997.
- [4] F. Hide, P. Kozodoy, S. P. DenBaars, and A. J. Heeger, "White light from InGaN/conjugated polymer hybrid light-emitting diodes," *Applied Physics Letters*, vol. 70, no. 20, pp. 2664–2666, 1997.
- [5] C. Zhang and A. J. Heeger, "Gallium nitride/conjugated polymer hybrid light emitting diodes: performance and lifetime," *Journal of Applied Physics*, vol. 84, no. 3, pp. 1579–1582, 1998.
- [6] P. Schlotter, R. Schmidt, and J. Schneider, "Luminescence conversion of blue light emitting diodes," *Applied Physics A*, vol. 64, no. 4, pp. 417–418, 1997.
- [7] P. Schlotter, J. Baur, C. Hielscher et al., "Fabrication and characterization of GaN/InGaN/AlGaN double heterostructure LEDs and their application in luminescence conversion LEDs," *Materials Science and Engineering B*, vol. 59, no. 1–3, pp. 390–394, 1999.
- [8] R. M. Mach, G. O. Mueller, M. R. Krames, and T. Trottier, "High-power phosphor-converted light-emitting diodes based

- on III-nitrides," *IEEE Journal on Selected Topics in Quantum Electronics*, vol. 8, no. 2, pp. 339–345, 2002.
- [9] J. Tardy and L. Berthelot, "White emission from organic and inorganic dyes dispersed polymers excited by GaN blue LEDs," in *Organic Light-Emitting Materials and Devices III*, vol. 3797 of *Proceedings of SPIE*, pp. 398–407, Denver, Colo, USA, December 1999.
- [10] Y. Narukawa, I. Niki, K. Izuno, M. Yamada, Y. Murazaki, and T. Mukai, "Phosphor-conversion white light emitting diode using InGaN near-ultraviolet chip," *Japanese Journal of Applied Physics*, vol. 41, no. 4, pp. L371–L372, 2002.
- [11] M. Yamada, T. Naitou, K. Izuno et al., "Red-enhanced white-light-emitting diode using a new red phosphor," *Japanese Journal of Applied Physics, Part 2: Letters*, vol. 42, no. 1, pp. L20–L23, 2003.
- [12] J. K. Sheu, S. J. Chang, C. H. Kuo et al., "White-light emission from near UV InGaN-GaN LED chip precoated with blue/green/red phosphors," *IEEE Photonics Technology Letters*, vol. 15, no. 1, pp. 18–20, 2003.
- [13] J. Morgado, N. Barbagallo, A. Charas, M. Matos, L. Alcácer, and F. Cacialli, "Self-assembly surface modified indium-tin oxide anodes for single-layer light-emitting diodes," *Journal of Physics D: Applied Physics*, vol. 36, no. 5, pp. 434–438, 2003.
- [14] N. N. Dinh, L. H. Chi, T. T. Chung Thuy, T. Q. Trung, and V.-V. Truong, "Enhancement of current-voltage characteristics of multilayer organic light emitting diodes by using nanostructured composite films," *Journal of Applied Physics*, vol. 105, no. 9, Article ID 093518, 2009.
- [15] D. J. Robbins, B. Cockayne, J. L. Glasper, and B. Lent, "Dependence of rare-earth activated garnet phosphors II. A comparative study of Ce^{3+} , Eu^{3+} , Tb^{3+} , and Gd^{3+} in $Y_3Al_5O_{12}$," *Journal of The Electrochemical Society*, no. 126, pp. 1221–1228, 1979.
- [16] S. Zhou, Z. Fu, J. Zhang, and S. Zhang, "Spectral properties of rare-earth ions in nanocrystalline YAG:Re (Re= Ce^{3+} , Pr^{3+} , Tb^{3+})," *Journal of Luminescence*, vol. 118, no. 2, pp. 179–185, 2006.
- [17] H. S. Jang, W. B. Im, D. C. Lee, D. Y. Jeon, and S. S. Kim, "Enhancement of red spectra emission intensity of $Y_3Al_5O_{12}$: Ce^{3+} phosphors via Pr co-doping and Tb substitution for the application to white LEDs," *Journal of Luminescence*, vol. 126, no. 2, pp. 371–377, 2007.
- [18] H. S. Jang, W. B. Im, and D. Y. Jeon, "Luminescent properties of $(Sr_{1-x}M_x)_3SiO_5:Eu^{2+}$ (M = Ca, Ba) phosphor for white emitting light source using blue/near UV LEDs," in *Proceedings of the 12th International Display Workshops in Conjunction with Asia Display (IDW/AD '05)*, pp. 539–542, December 2005.
- [19] S. Chuangchote, T. Srihirin, and P. Supaphol, "Color change of electrospun polystyrene/MEH-PPV fibers from orange to yellow through partial decomposition of MEH side groups," *Macromolecular Rapid Communications*, vol. 28, no. 5, pp. 651–659, 2007.
- [20] H. A. Barnes, J. F. Hutton, and K. Walters, *An Introduction to Rheology*, Elsevier, Amsterdam, The Netherlands, 1989.
- [21] V. Resta, A. M. Laera, E. Piscopiello, M. Schioppa, and L. Tapfer, "Highly efficient precursors for direct synthesis of tailored CdS nanocrystals in organic polymers," *The Journal of Physical Chemistry C*, vol. 114, no. 41, pp. 17311–17317, 2010.
- [22] A. M. Laera, V. Resta, M. C. Ferrara, M. Schioppa, E. Piscopiello, and L. Tapfer, "Synthesis of hybrid organic-inorganic nanocomposite materials based on CdS nanocrystals for energy conversion applications," *Journal of Nanoparticle Research*, vol. 13, no. 11, pp. 5705–5717, 2011.
- [23] D. N. Chung, D. N. Hieu, T. T. Thao, V.-V. Truong, and N. N. Dinh, "Synthesis and characterization of Ce-doped $Y_3Al_5O_{12}$ (YAG:Ce) nanopowders used for solid-state lighting," *Journal of Nanomaterials*, vol. 2014, Article ID 571920, 7 pages, 2014.
- [24] A. Petrella, M. Tamborra, P. Cosma et al., "Photocurrent generation in a CdS nanocrystals/poly[2-methoxy-5-(2'-ethyl-xyloxy)phenylene vinylene] electrochemical cell," *Thin Solid Films*, vol. 516, no. 15, pp. 5010–5015, 2008.
- [25] H.-J. Chen, L. Wang, and W.-Y. Chiu, "Effects of annealing treatment on the properties of MEH-PPV/titania hybrids prepared via in situ sol-gel reaction," *European Polymer Journal*, vol. 43, no. 11, pp. 4750–4761, 2007.
- [26] S. N. Sharma, U. Kumar, T. Vats et al., "Hybrid organic-inorganic (MEH-PPV/P3HT:CdSe) nanocomposites: linking film morphology to photostability," *The European Physical Journal—Applied Physics*, vol. 50, pp. 20602–20607, 2010.



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