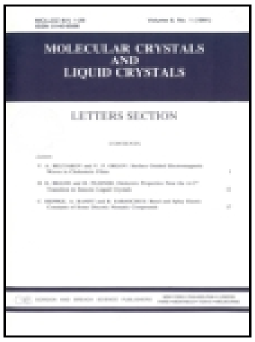

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ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Xuan Thang Cao, Ali Md Showkat, Kim Lien Nguyen Thi, Seong-Soo Hong & Kwon Taek Lim (2015) Synthesis and Properties of Poly(N-vinylcarbazole) Covalently Functionalized Zinc Oxide Nanocomposites, Molecular Crystals and Liquid Crystals, 618:1, 95-102, DOI: 10.1080/15421406.2015.1076298

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1076298

Mol. Cryst. Liq. Cryst., Vol. 618: pp. 95–102, 2015
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1076298

Synthesis and Properties of Poly(N-vinylcarbazole) Covalently Functionalized Zinc Oxide Nanocomposites

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*Poly(N-vinylcarbazole) covalently grafted zinc oxide nanoparticles (ZnO-*g*-PNVC) were synthesized with a simple route using surface initiated reversible addition-fragmentation chain transfer (RAFT) polymerization. Initially, the surface of ZnO nanoparticles was modified by the condensation reaction of 3-chloropropyltrimethoxysilane, and it was subsequently reacted with potassium xanthogenate to produce ZnO nanoparticles having RAFT functionality (ZnO-RAFT). The controlled radical polymerization of N-vinylcarbazole in the presence of ZnO-RAFT afforded ZnO-*g*-PNVC composites. FT-IR, EDX, XRD, and SEM analyses demonstrated the grafting of PNVC onto ZnO nanoparticles. Thermal stability of ZnO-*g*-PNVC composites was revealed by TGA analysis. UV-Vis absorption and photoluminescence results suggested ZnO-*g*-PNVC composites as a potential material in optical application.*

Keywords ZnO nanoparticles; poly(N-vinylcarbazole); RAFT polymerization; nanocomposites

1. Introduction

During recent years composites for engineering and biological applications through surface modification of inorganic materials have received a good deal of research attention. Among the potential metal oxides, zinc oxide (ZnO) has gained much interest because of its wide possible use in electronic and optical applications [1]. Especially modification of ZnO nanoparticles based on polymers was really important due to application in the opto-electronic devices, photocatalysis, chemical sensors, and biological labels [2–4]. Currently, controlled radical polymerization methods such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization have

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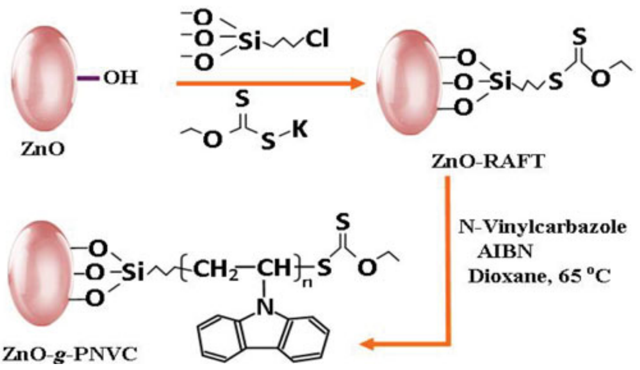
been widely used for surface modification approaches. The surface-initiated ATRP technique has been efficient for grafting from solid surfaces [5]. Rupert et al. reported that polystyrene or polymethacrylate could be grafted from the initiating groups modified ZnO nanowires via ATRP [6]. Surface bonded thiol groups were being also used as chain transfer agents in free radical polymerization because of their relative high chain transfer constant. Zhou *et al.* reported that ultra thin polymer films could be obtained via a surface chain-transfer reaction using 3-mercaptopropyl trimethoxysilane (MPTMS) as silane coupling agent [7]. Hu *et al.* demonstrated that the addition of n-dodecyl mercaptan with 2-pyrrolidinone in the bulk polymerization of methyl methacrylate led to the initiation of monomers [8]. Poly(N-vinylcarbazole) (PNVC) is one of the most famous conducting polymeric material with an interesting optoelectronic and other physicochemical properties [9]. Nanocomposites comprising PNVC and ZnO may be expected to have wide application in optoelectronic industry. Photoconductivity of the device fabricated from ZnO/PNCV nanocomposites was better than pure PNCV while photoelectric hybrid composites of N-vinylcarbazole-methyl acrylate copolymer and ZnO nanocrystals with good film-forming ability was illustrated [10,11]. The ultraviolet photodetectors based on ZnO and PNVC with high spectrum selectivity and enhancing photocurrent were demonstrated [12,13]. In this work, we represent the preparation of poly(N-vinylcarbazole) grafted ZnO nanoparticles by RAFT polymerization through *grafting from* strategy (Scheme 1).



Scheme 1. Schematic representation for synthesis of ZnO-*g*-PNVC composites by RAFT polymerization technique.

2. Experimental Methods

2.1. Materials

All chemicals were purchased from Sigma-Aldrich. N-vinylcarbazole (NVC) was recrystallized from methanol at 40°C, freeze dried and stored in vacuum before use. 2,2'-Azobisisobutyronitrile (AIBN) were recrystallized with ethanol before use. 3-Chloropropyl-trimethoxysilane (CPTS), potassium xanthogenate, ZnO (≥99%), and all solvents of analytical grade were used as received.

2.2. Immobilization of the RAFT Agent on ZnO Nanoparticles (ZnO-RAFT)

The RAFT agent immobilized ZnO was synthesized by the following two-step approach. In a typical experiment, 2.0 g of ZnO nanoparticles were dispersed in toluene (10 mL) and distilled water (0.5 mL). Then CPTS (2.0 mL) was added to the solution and the mixture was stirred at 80°C for 12 h. The product ZnO-Cl was filtered, washed with toluene, and dried under vacuum at 40°C for 24 h. In the next step, a mixture of 1.5 g of ZnO-Cl, 1.0 g of potassium xanthogenate, and 20 mL of anhydrous ethanol was added into a 50 mL round bottom flask. The mixture was sonicated for 30 min. After that, the flask was immersed in an oil bath and stirred at 80°C for 12 h under nitrogen. The product was filtered, washed with anhydrous ethanol three times. The RAFT agent functionalized ZnO nanoparticles (ZnO-RAFT) was dried under vacuum at 40°C for 24 h.

2.3. Synthesis of ZnO-g-PNVC Composites Via RAFT Polymerization

ZnO nanoparticles were encapsulated by poly(N-vinylcarbazole) employing RAFT polymerization of N-vinylcarbazole. The ZnO-*g*-PNVC composites were prepared as follows. ZnO-RAFT (0.4 g), NVC (0.35 g), AIBN (10 mg), dioxane (3 mL), and a Teflon-coated spin bar were put into a 25 mL round flask equipped with a reflux condenser. The mixture was stirred for 24 h at 65°C under nitrogen. The product was purified by precipitating in excess amount of methanol, filtered, and washed with hot methanol. The final product was dried under vacuum at 40°C overnight. The grafted PNVC was cleaved from the ZnO surface as follows. 100 mg of the ZnO-*g*-PNVC were dissolved in 1 mL of HCl (2 M) and 4 mL of *N,N*-dimethylformamide (DMF). The solution was stirred at room temperature for 24 h. The cleaved PNVC in the organic layer was precipitated in methanol and dried under vacuum.

2.4. Instrumentation

The formation of ZnO-*g*-PNVC composites was studied by fourier transformed infrared spectrophotometry (FT-IR) using a BOMEM Hartman & Braun FT-IR spectrometer in the frequency range of 4000-400 cm^{-1}. Thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer Pyris 1 analyzer (USA). The samples were scanned within the temperature range of 50-800°C at a heating rate of 10°C min^{-1} under continuous nitrogen flow. The crystallographic state of the nanocomposites was studied by a Philips X'pert-MPD system diffractometer. The morphology and elemental analysis of the hybrids were carried out by using scanning electron microscopy (SEM) images equipped with an Energy Dispersive X-Ray (EDX) spectrometer (Hitachi JEOL-JSM-6700F system, Japan). UV-Vis diffuse reflectance spectroscopy (DRS) was performed on a Varian Cary 100 in the 200 to 800 nm range, using PTFE (polytetrafluoroethylene) as a standard. The photoluminescence (PL) spectra were recorded on a F-4500 spectro-fluorometer (Hitachi, Japan).

3. Results and Discussion

FT-IR spectroscopy was employed to reveal the anchoring of xanthate to the ZnO surface. The spectrum of ZnO nanoparticles (Figure 1a) shows strong absorption bands between 400 and 550 cm^{-1} due to the vibrations of Zn-O framework bonds. The broad absorption band at 3400 and 1616 cm^{-1} are ascribed to adsorbed H_2O on ZnO. Upon incorporation of the silane coupling agent having chloride functionality, ZnO-Cl is evidenced from the characteristic absorption bands at 2956 and 810 cm^{-1} which are assigned to CH_2- and Si-O stretching of the coupling agent, respectively (Figure 1b). After immobilization of xanthate onto ZnO, the resulting ZnO-RAFT was suggested to be formed via covalent bonding as indicated by two characteristic absorption bands at 1104 and 1001 cm^{-1} which are mainly due to

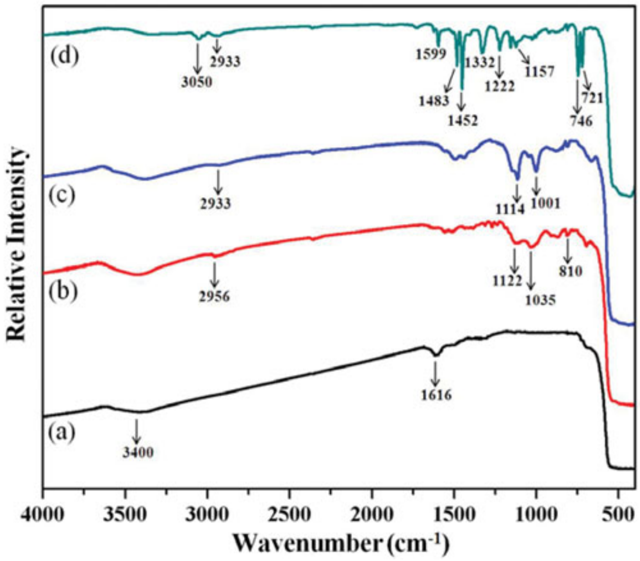


Figure 1. FT-IR spectra of (a) ZnO, (b) ZnO-Cl, (c) ZnO-RAFT, and (d) ZnO-*g*-PNVC.

the stretching vibration of C—O and C=S moieties, respectively (Figure 1c). As expected, the spectrum of ZnO-*g*-PNVC composites clearly exhibits new peaks at 3050 cm^{-1} due to aromatic C-H stretching vibrations. The C-N stretching is observed at 1599 cm^{-1}. The peaks at 1483, 1452 cm^{-1} are corresponding to the ring vibration of the carbazolyl moiety. The C-H vibration of the vinylidine group is observed at 1332 cm^{-1}, and the absorption bands at 1222 and 1157 cm^{-1} are due to the C-H in plane of aromatic ring. The C-H out of plane bending vibration of the aromatic ring appears at 746 and 721 cm^{-1} (Figure 1d).

The elemental mapping analysis of composites was carried out by EDX as shown in Figure 2. The characteristic peaks ascribed for C, O, and Zn elements appear in the EDX spectrum of ZnO (Figure 2a). The spectrum of ZnO-RAFT shows C, O, Zn, S, and Si indicating the anchored RAFT agent on the surface of ZnO (Figure 2b). The elemental mapping of pure PNVC is observed for C and N (Figure 2c), whereas the ZnO-*g*-PNVC spectrum demonstrates the presence of C, O, Zn, S, Si and N elements (Figure 2d). The results clearly reveal the successful grafting of PNVC from the surface of ZnO via RAFT polymerization.

X-ray diffraction (XRD) patterns of composites are shown in Figure 3. All the peaks of the ZnO-RAFT (Figure 3b) and ZnO-*g*-PNVC composites (Figure 3c) are perfectly indexed to hexagonal phase of ZnO with 2θ values of 31.8°, 34.5°, 36.4°, 47.6°, 56.7°, 62.9°, 66.4°, 68.0°, and 69.2° correspond to the crystal planes of (100), (002), (101), (102), (110), (103), (200), (112), and (201), respectively (Figure 3a). The above XRD results reveal that the polymer grafting does not alter the crystallinity of ZnO nanoparticles.

The thermal properties of ZnO, ZnO-RAFT and ZnO-*g*-PNVC composites were studied by TGA as shown in Figure 4. The curve of ZnO shows a weight loss of ca. 1.7% in the whole temperature range due to the escape of absorbed water molecules on the surface and the release of the structural water resulted from the bonded hydroxyl groups (Figure 4a). The weight loss of the ZnO-Cl is found to be ca. 6.8% due to the degradation of the coupling agent (Figure 4b). In the case of ZnO-RAFT, the weight loss was estimated to be ca. 14.3%

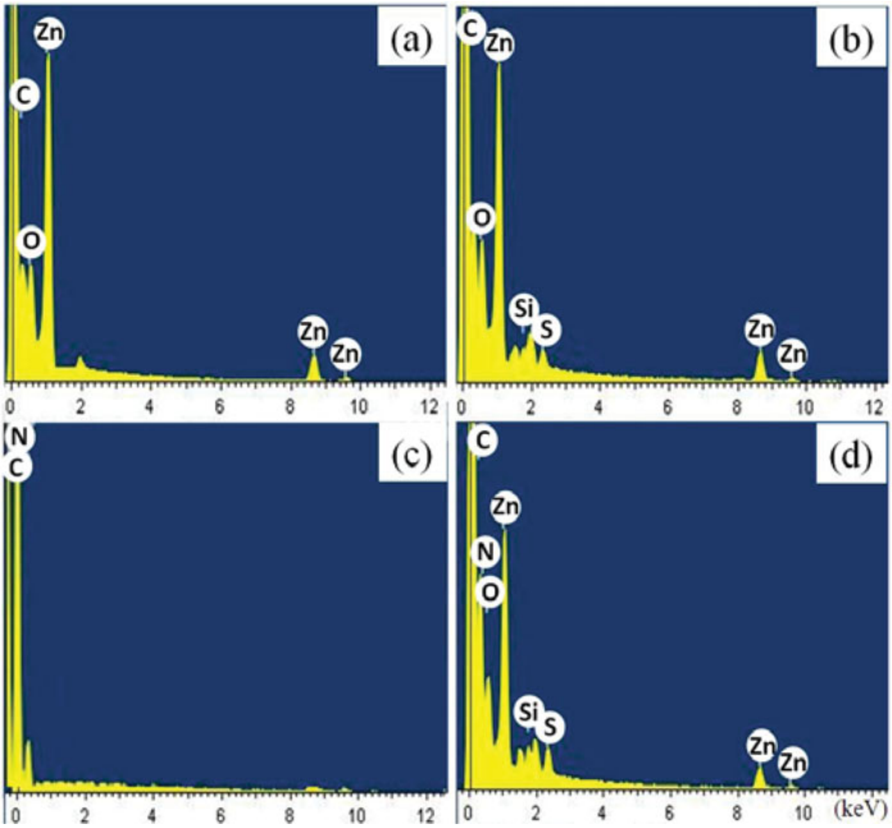


Figure 2. EDX analysis of (a) ZnO, (b) ZnO-RAFT, (c) pure PNVC, and (d) ZnO-*g*-PNVC.

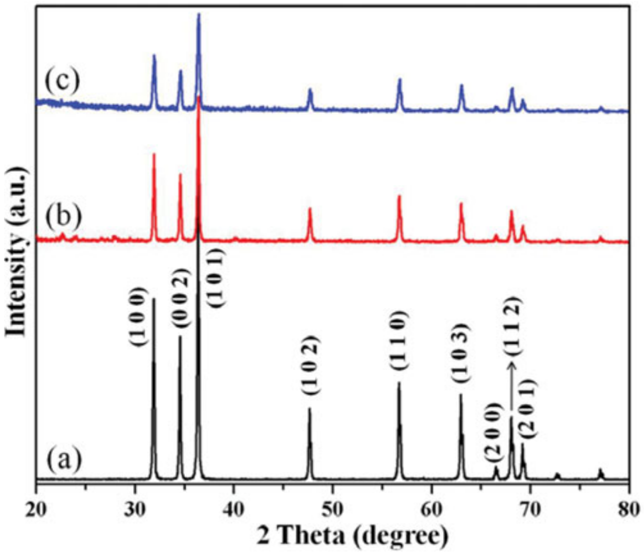


Figure 3. X-ray diffraction patterns of (a) ZnO, (b) ZnO-RAFT, and (c) ZnO-*g*-PNVC.

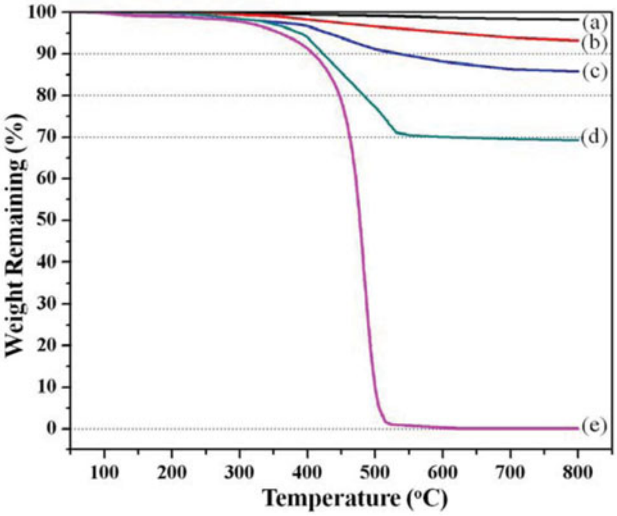


Figure 4. TGA spectra of (a) ZnO, (b) ZnO-Cl, (c) ZnO-RAFT, (d) ZnO-*g*-PNVC, and (e) pure PNVC.

in the same temperature zone (Figure 4c). Thus, the content of the RAFT agent on the surface of ZnO was determined to be ca. 8%. In Figure 4d, the curve of the ZnO-*g*-PNVC composites starts to degrade at 400°C, and loses 29% of weight at 535°C, which is due to the thermal degradation of the grafted PNVC. Thus, the content of PNVC moieties

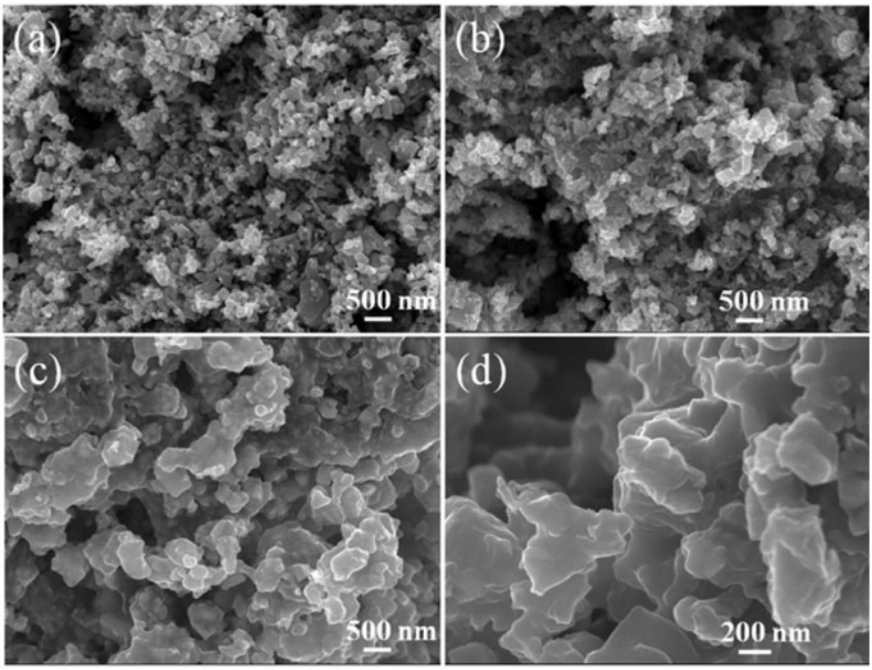


Figure 5. SEM pictures of (a) ZnO, (b) ZnO-RAFT, and (c,d) ZnO-*g*-PNVC.

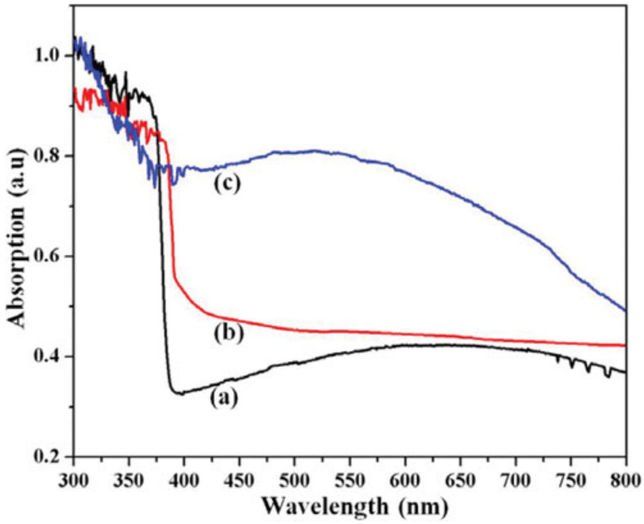


Figure 6. UV-Vis spectra of (a) ZnO, (b) ZnO-*g*-PNVC, and (c) pure PNVC.

was estimated to be ca. 19% in the composites. In comparison with the cleaved PNVC (Figure 4e), the ZnO-*g*-PNVC demonstrates an improvement in the thermal stability.

SEM analysis was used to investigate the morphology of composites as shown in Figure 5. Upon RAFT polymerization, the morphology of ZnO was changed by grafting of PNVC on the surface of ZnO as shown in Figure 5c and d. The needle-like particles were encapsulated by a thin layer of the polymer resulting in irregular shapes of nanoparticles. The nanoparticles were observed to be aggregated tightly and the presence of the polymer layer is relatively prominent in the images.

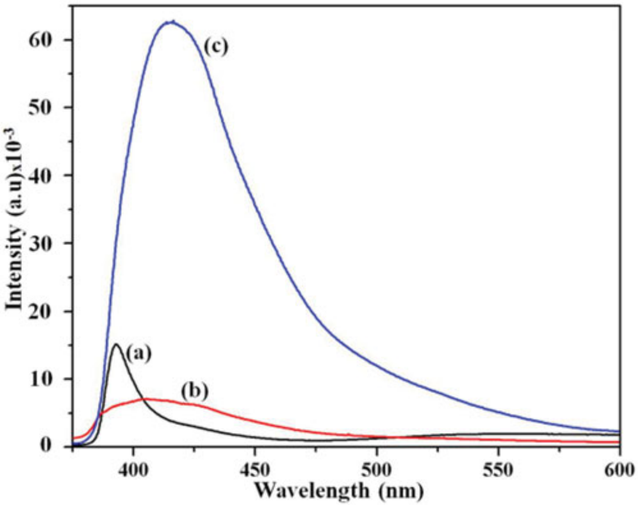


Figure 7. PL spectra of (a) ZnO, (b) ZnO-g-PNVC, and (c) pure PNVC.

Figure 6 shows the UV-Vis DRS of pure ZnO, ZnO-*g*-PNVC composites, and cleaved PNVC. In contrast to the pure ZnO (Figure 6a), the visible light absorption of ZnO-*g*-PNVC is remarkably enhanced (Figure 6b). The extension of optical absorption seems to be reasonable with appearance of PNVC whose electronic transitions are attributed to the exchange interactions between carbazole moieties and photogenerated charge carriers in the ZnO bands.

The PL spectra of the composites were investigated, as shown in Figure 7. The PL intensity of the ZnO-*g*-PNVC (Figure 7b) is greatly reduced compared to both the ZnO (Figure 7a) and the pure PNVC (Figure 7c). When the composites absorbs photons, the charge transfer at the interface reduces the transition probability of the excited electrons from lowest unoccupied molecular orbital (LUMO) to highest occupied molecular orbital (HOMO), which reduces the PL intensity[10]. Consequently, the observed PL of composites indicates an efficient charge transfer process between ZnO and PNVC.

4. Conclusion

The ZnO-g-PNVC composites were synthesized by RAFT polymerization. The FT-IR, EDX, and SEM analyses suggested the chemical immobilization of PNVC on ZnO, while XRD showed that the polymerization process did not alter the crystallinity of ZnO nanoparticles. The TGA results illustrated the improved thermal stability of the ZnO-g-PNVC composites compared with pure PNVC. It was proved that the visible light absorption of ZnO-g-PNVC was enhanced by the presence of the carbazole ring as indicated by UV-Vis spectra. In addition, PL spectra demonstrated that the ZnO nanoparticles in the composites were effective electron trappers.

Funding

This work was supported by the Technology Innovation Program (No. 10052923, The Development of Light Extraction Complex Substrate for Curved-OLED Lighting with High-CRI) funded by the Ministry of Trade, Industry & Energy.

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