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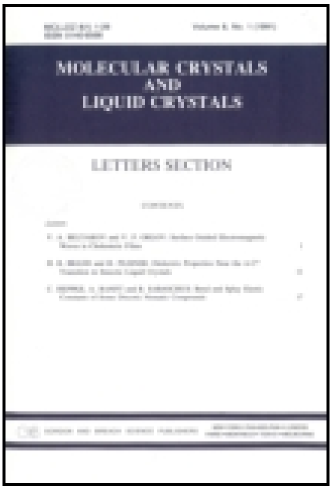

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Preparation and Characterization of Poly(4-vinylpyridine) Encapsulated Zinc Oxide by Surface-Initiated RAFT Polymerization

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Preparation and Characterization of Poly(4-vinylpyridine) Encapsulated Zinc Oxide by Surface-Initiated RAFT Polymerization

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Poly(4-vinylpyridine) was covalently wrapped onto ZnO nanoparticles through surface initiated Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization upon grafting from protocol. The surface of ZnO nanoparticles was initially modified by the coupling reaction with silane leading to trithiocarbonate functionalized ZnO nanoparticles (ZnO-RAFT). The controlled radical polymerization of 4-vinylpyridine in the presence of the ZnO-RAFT afforded PVP-g-ZnO nanocomposites. FT-IR, EDX, XRD and XPS analyses demonstrated the grafting of PVP on the surface of ZnO nanoparticles, while thermal stability of PVP-g-ZnO nanocomposites was confirmed by TGA analysis. The TEM and SEM images suggested that ZnO nanoparticles were embedded in the polymer, and the dispersibility of the nanocomposites was improved in an organic solvent dramatically.

Keywords ZnO nanoparticles; poly(4-vinyl pyridine); RAFT polymerization; grafting from

1. Introduction

In recent years, a large number of new materials for engineering and biological applications through surface modification of inorganic materials by polymer have been synthesized. Modification of zinc oxide (ZnO) nanoparticles based on polymers has attracted great attention due to application in the optical, optoelectronic devices, photocatalysis, chemical sensors, biological labels and so on [1–5]. Generally, there are two basic routes to deposit polymer on solid surface; one is physical adsorption and other is chemisorptions method. Covalently bonded polymers can usually overcome drawbacks of that prepared by physical adsorption, such as low grafting densities and adhesive force. At present, widely used surface modification approaches are controlled radical polymerization methods such as atom transfer radical polymerization, RAFT, nitroxide- mediated polymerization.

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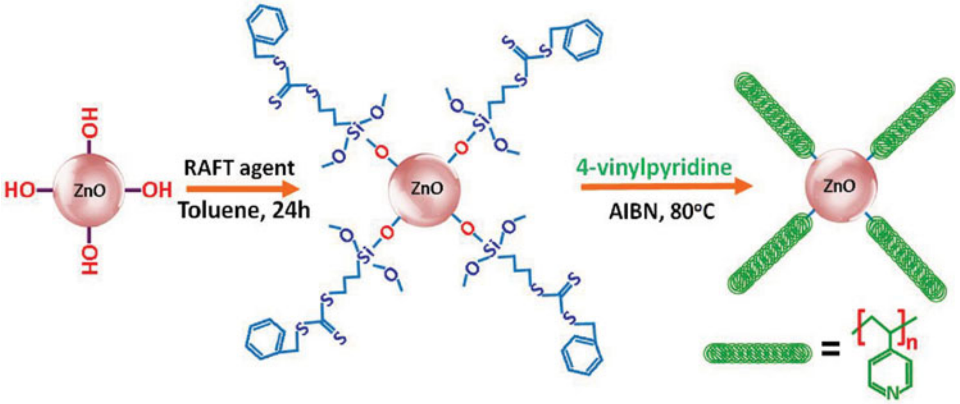

Scheme 1. A schematic representation for the synthesis of PVP-*g*-ZnO nanocomposites by RAFT polymerization technique.

Currently, the surface-initiated atom transfer radical polymerization (SI-ATRP) technique is very efficient for *grafting from* solid surfaces [6]. Liu et al. reported that Poly(hydroethyl acrylate) could be grafted from the initiating groups modified ZnO nanoparticles via SI-ATRP [7]. Rupert et al. used ATRP to modify the surface of ZnO nanowire with a variety of methacrylate and styrene polymers by controlling catalyst and reaction condition [8]. Surface bonded thiol groups are 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 [9]. Thiol alone can initiate polymerization *via* a charge transfer complex of comonomers such as methyl methacrylate/N-cyclohexylmaleimide [10]. Hu et al. demonstrated that the addition of *n*-dodecylmercaptan with ε-caprolactam or 2-pyrrolidinone in the bulk polymerization of styrene, methyl methacrylate led to the initiation of monomers [11, 12].

Taking the above findings into account, we were interested to find a facile method to synthesize poly(4-vinylpyridine) grafted ZnO nanoparticles *via* chemisorption technique which would be a promising candidate for electrophoretic display application [13, 14]. Our strategy was to modify the ZnO surface by a one-step direct anchoring of trithiocarbonate group. ZnO nanoparticles were encapsulated with poly(4-vinylpyridine) through *grafting from* strategy (Scheme 1).

2. Experimental Details

2.1. Materials

(3-mercaptopropyl)trimethoxysilane (MPTMS, 95%), sodium methoxide (95%), carbon disulfide (CS_2) (99.9%), benzyl bromide (98%), 4-vinylpyridine (4-VP, 95%), zinc oxide (ZnO, 99.7%), 2, 2′-Azobis(isobutyronitrile) (AIBN) (98%) was recrystallized in methanol prior to use. N, N′- dimethylformalmide (DMF), toluene, ethyl ether, dichloromethane were used as received. S-benzyl S′-trimethoxysilylpropyltrithiocarbonate (RAFT agent) was synthesized as reference [15]. All chemicals were purchased from Aldrich, Korea.

2.2. Anchoring of RAFT Agent Groups onto ZnO Nanoparticles (ZnO-RAFT)

To a 500 mL three-neck flask was added 10.0 g of ZnO nanoparticles in 200 mL of toluene and an excess amount of RAFT agent in 50 mL of dry toluene. The reaction mixtures was kept at 100°C for overnight and maintained at 120°C for another 3 h under nitrogen. The mixture was cooled down, filtered off and washed repeatedly with dichloromethane. The products were dried under vacuum at 40°C for 24 h.

2.3. Preparation of PVP-g-ZnO Nanocomposites via RAFT Polymerization

2.0 g of 4-vinylpyridine, 0.2 g of ZnO-RAFT, 0.02 g of AIBN and 4 mL of DMF were placed in a 25 mL round flask. The mixture was heated to 80°C and kept stirring for 4 h with a reflux condenser under nitrogen. The mixture was cooled, precipitated in ethyl ether, filtered off and washed repeatedly with DMF and dried under vacuum at 40°C for 24 h. To investigate characterization of the grafted PVP, PVP brushes were cleaved from the ZnO surface in the following way: 100.0 mg of the PVP-*g*-ZnO were dissolved in 1 mL of HCl (2 M) and 10 mL of DMF. The solution was allowed to stir at 80°C for 24 h. The cleaved PVP in the organic layer was precipitated in diethyl ether and dried.

2.4. Instrumentation

The bonding nature in the synthesized nanocomposites were recorded by Fourier Transformed Infrared Spectrophotometry (FT-IR) using a BOMEM Hartman & Braun FT-IR. The surface composition was investigated using X-ray Photoelectron Spectroscopy (XPS) (Thermo VG Multilab 2000) in ultra high vacuum with Al Kα radiation. Thermogravimetric analysis (TGA) was conducted with Perkin-Elmer Pyris 1 analyzer (USA). The crystallographic state of the nanocomposites was studied by a Philips X'pert-MPD system diffractometer. Transmission Electron Microscopy (TEM) images were recorded using a Hitachi H-7500 instrument operated at 80 kV. 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).

3. Results and Discussion

FT-IR spectroscopy studies were employed to confirm PVP-*g*-ZnO nanocomposites formation. The spectrum of ZnO nanoparticles (Fig. 1A) possesses strong absorption bands between 400 and 550 cm^{-1} which are assigned to the vibrations of Zn—O framework bonds. The broad absorption bands at 3400 and 1616 cm^{-1} suggest the —OH stretching vibrations and H—O—H bending vibrations, respectively. The chemical bond of RAFT agent on the surface of ZnO exhibits broad absorption bands at 2844 and 2924 cm^{-1} which are assigned for CH_2-moiety of the RAFT agent and shows a weak but visible band at 3061 cm^{-1} assigning for sp^2 C—H stretching of aromatic ring (Fig. 1B). Ring stretch absorption of RAFT agent was also observed at 1650 and 1490 cm^{-1}. The band at 810 cm^{-1} is assigned to the Si—O stretching mode. As expected, the spectrum of PVP-*g*-ZnO nanocomposites (Fig. 1C) clearly exhibited new absorption bands at 1609, 1551, and 1418 cm^{-1} represent the pyridyl ring-stretching vibrations. In case of PVP-*g*-ZnO nanocomposites (Fig. 1C), the peak at 810 cm^{-1} disappeared and the peak around 1100 cm^{-1} was also decreased compare to Fig. 1B possibly due to encapsulation of ZnO in PVP. The result suggests that the polymerization of 4-VP is performed successfully.

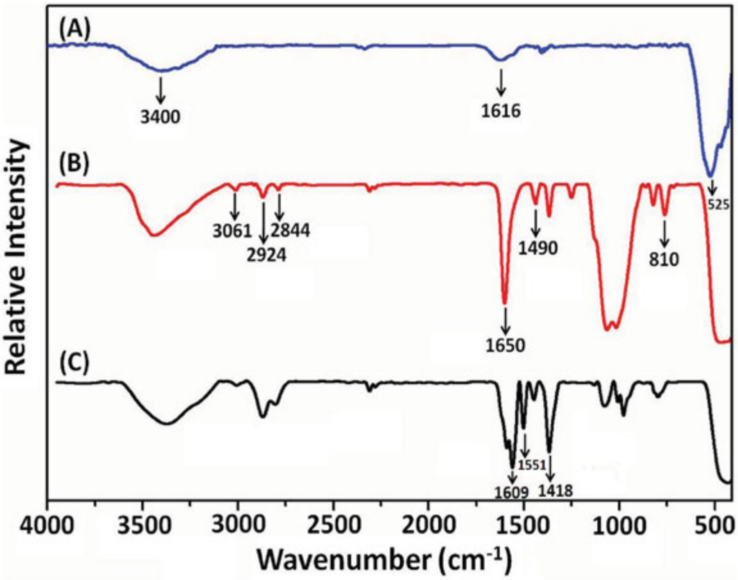

Figure 1. FT-IR spectra of (A) ZnO nanoparticles, (B) ZnO-RAFT and (C) PVP-*g*-ZnO.

The formation of ZnO-RAFT, PVP-*g*-ZnO nanocomposites from ZnO nanoparticles were confirmed by XPS analysis. The appearance of the Si and S in the wide-scan spectrum of ZnO-RAFT represents the successful immobilization of the RAFT agent on the surface of ZnO nanoparticles (Fig. 2B). On the other hand, the major peak at the binding energy of 400.8 eV is attributed to the amine-like (-NH ═) structure, which account for the presence of amine group of 4-VP units on the PVP-*g*-ZnO surface (Fig. 2C). In addition, the C1s peak in

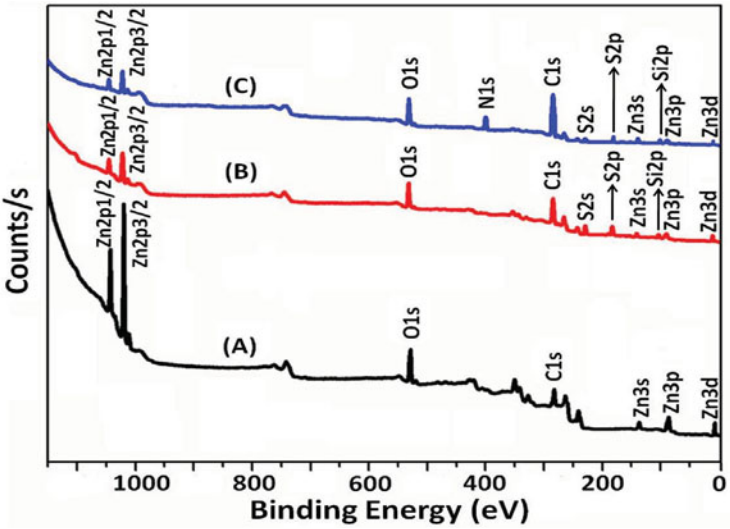

Figure 2. Wide-scan spectra of (A) ZnO nanoparticles, (B) ZnO-RAFT and (C) PVP-*g*-ZnO surface.

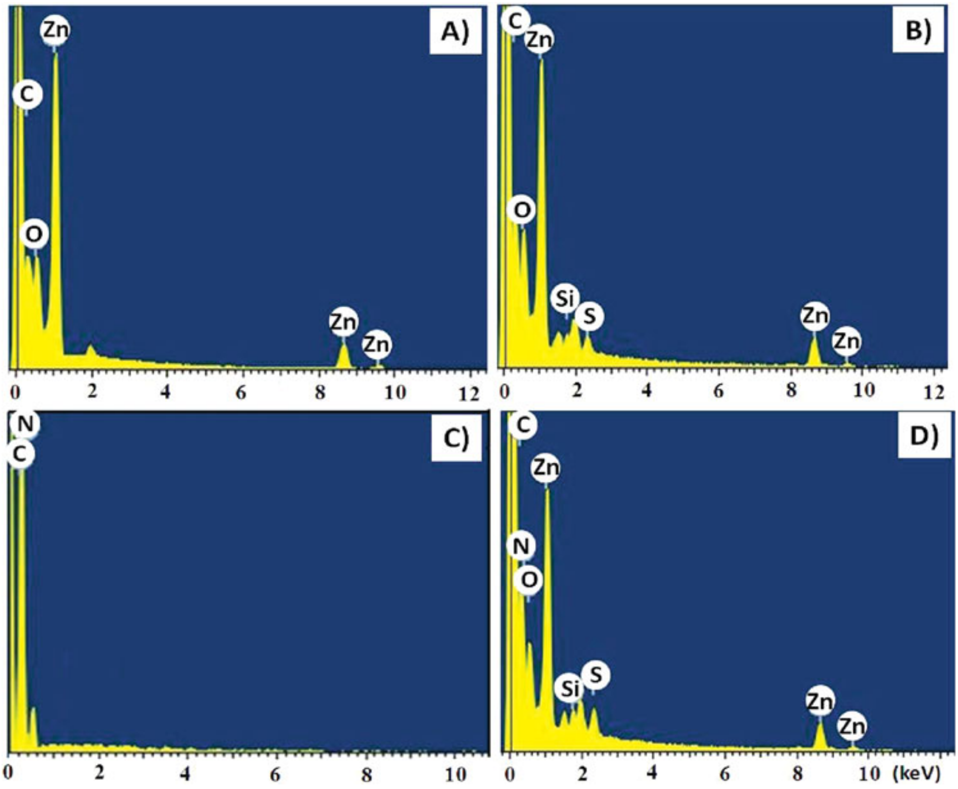

Figure 3. EDX analysis of (A) ZnO nanoparticles, (B) ZnO-RAFT, (C) PVP and (D) PVP-*g*-ZnO.

the PVP-*g*-ZnO of maximum intensity slightly shifted to a higher binding energy, indicating that the polymeric chains were directly grafted from the surfaces of ZnO nanoparticles.

Furthermore, the immobilization of RAFT agent and grafting of PVP on the surface of ZnO nanoparticles were investigated by EDX analysis. The EDX spectrum of ZnO-RAFT shows C, O, Zn, S, and Si which indicate the anchoring of RAFT agent on the surface of ZnO (Fig. 3B). The elemental mapping of the PVP-*g*-ZnO demonstrated the presence of C, O, Zn, S, Si and N elements (Fig. 3D). These results clearly indicate that the successful grafting of PVP from the surface of ZnO *via* RAFT polymerization.

The crystal and physical changes of ZnO nanoparticles PVP grafted ZnO nanoparticles were investigated using XRD analysis. The pristine ZnO nanoparticles exhibits sharp peaks centered at $2\theta = 31.8$, 34.5, 36.4, 47.6, 56.7, 62.9, 66.4, 68.0, 69.2, 72.6 and 77.0, which correspond to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1), (0 0 4) and (2 0 2) reflections, respectively (Fig. 4A). After the surface modification by RAFT agent, the characteristic peaks of ZnO-RAFT (Fig. 4B) and ZnO nanoparticles (Fig. 4A) can be observed at the same positions. Futhermore, the RAFT polymerization of 4-VP on ZnO nanoparticles surface generated PVP-*g*-ZnO nanocomposites (Fig. 4C), which are similar to the main peaks of the pure ZnO nanoparticles. These XRD results confirmed that the grafting of polymer did not alter the crystallinity of ZnO nanoparticles.

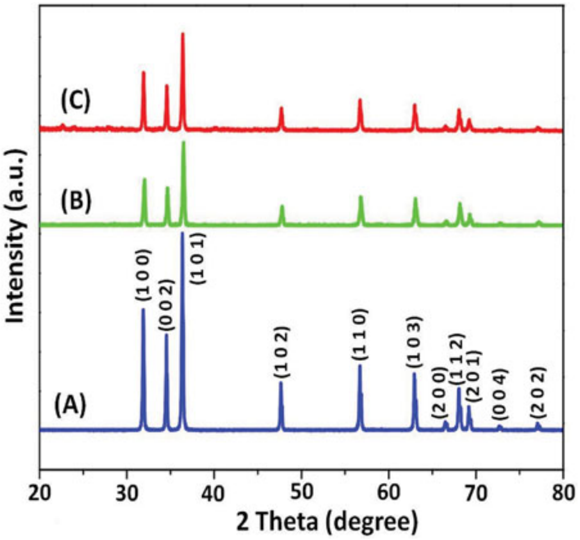

Figure 4. X-ray diffraction patterns of (A) ZnO nanoparticles, (B) ZnO-RAFT, and (C) PVP-*g*-ZnO.

The thermal properties of ZnO nanoparticles, ZnO-RAFT and PVP-*g*-ZnO nanocomposites were studied by TGA, as shown in Fig 5. The weight loss of ZnO nanoparticles were assigned less than 2% when heated from 50 to 800°C, which was mostly due to the release of absorbed water (Fig. 5A). In the TGA curve of ZnO-RAFT, it showed that the organic

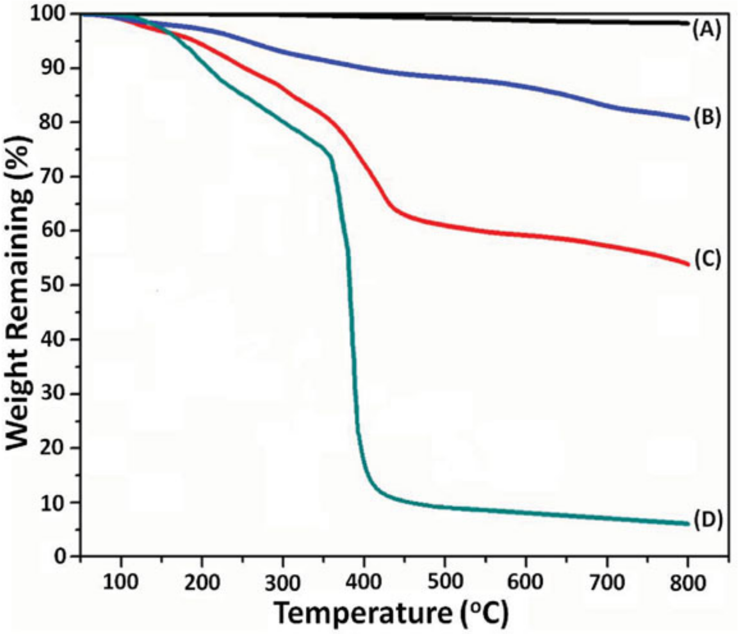

Figure 5. TGA spectra of (A) ZnO nanoparticles, (B) ZnO-RAFT, (C) PVP-*g*-ZnO and (D) PVP.

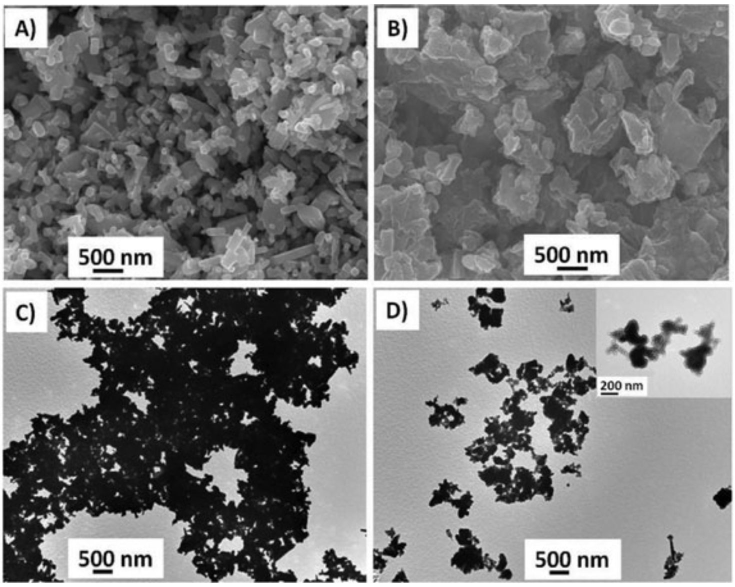

Figure 6. SEM pictures of (A) ZnO nanoparticles, (B) PVP-*g*-ZnO and TEM images of (C) ZnO nanoparticles (D) PVP-*g*-ZnO in DMF.

molecule encapsulation occured near 150 to 250 ºC and decamped due to the decomposition of the encapsulating organic molecules at high temperature. Also, it observed that the weight loss of ZnO-RAFT decreased 20% among 50 to 800 ºC (Fig. 5B). The as prepared PVP-*g*-ZnO nanocomposites showed thermal degradation at temperature range of 300 to 470°C, which is due to the decomposition of grafted PVP (Fig. 5C). Moreover, the weight fractions of organic moieties were observed to be 45% for PVP-*g*-ZnO nanocomposites. In the thermal degradation comparison of PVP-*g*-ZnO nanocomposites (Fig. 5C) to the neat PVP (Fig. 5D), the PVP-*g*-ZnO improved the thermal stability of material. The result suggests that upon inclusion of ZnO nanoparticles the thermal stability of PVP has been increased.

SEM and TEM analyses were used to investigate the morphology of ZnO and PVP-*g*-ZnO as shown in Fig 6. The SEM images of ZnO nanoparticles (Fig. 6A) and PVP-*g*-ZnO nanocomposites (Fig. 6B) demonstrated that PVP were prepared by RAFT from surfaces of ZnO nanoparticles. The covalent connection between PVP and ZnO nanoparticles leaded to the formation of PVP-*g*-ZnO nanocomposites, which prevented the agglomeration of ZnO nanoparticles dramatically in an organic solvent (Fig. 6C and 6D).

4. Conclusion

A facile chemisorption method for the preparation of PVP-*g*-ZnO was realized by RAFT technique, and the nanocomposites were characterized by FT-IR, XPS, XRD and EDX analyses. The TGA analysis indicates ca. 45% functionalization of ZnO nanoparticles with PVP. TEM and SEM images showed that ZnO nanoparticles were encapsulated in PVP. The nanocomposites exhibited better dispersion in DMF than un-grafted ZnO nanoparticles.

Acknowledgments

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