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A simple synthesis route for preparation and optical properties of PMMA-g-ZnO nanocomposites through surface-initiated radical polymerization

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Abstract. An effortless chemisorption access for the planning of nanocomposites containing a semiconductor ZnO nanoparticles and poly(methyl methacrylate) (PMMA) is demonstrated. First, thiol-functionalized ZnO (ZnO-SH) were prepared by a silanization reaction between ZnO nanoparticles and (3-mercaptopropyl) trimethoxysilane. Then, a reserved radical polymerization of methyl methacrylate in the attendance of Zinc oxide-thiol (ZnO-SH) and butyrolactam produced PMMA-g-ZnO nanocomposites. DSC were used to examine the weight decline of glass transition temperature of nanocomposites. The ocular characteristics of the nanocomposites were studied by Ultraviolet-visible (UV-vis) absorption spectroscopy and photoluminescence spectroscopy (PL). The results accentuate the role of the grafted PMMA polymer segments in augmenting the strength of dispersal and near-band edge (NBE) emission of ZnO nanoparticles.

1. Introduction

The size dependent optoelectronic properties of semiconductor nanocrystals has attracted attention of scientists. The ongoing research and development of nano-sized Zinc oxide (ZnO) nanoparticles has led to widespread applications such as a light-emitting diode, photodetector, field-effect transistors, biological and chemical sensors, transducers, nanocantilevers, thermal transport elements and new types of solar cells, etc. [1-4]. The advantage of ZnO when used in biological applications such as bio-imaging and cancer detection lies in its environmental friendliness. However, ZnO nanoparticles, when dispersed in organic solvent and matrices, may cause particle agglomeration due to their high surface energy. Thus, to overcome the above limitations, the ZnO-polymer polymer nanoparticles was implanted in a small number of inorganic nanoparticles [5-7]. In addition, the composite nanoparticles (inorganic core/ organic shell) are widely used in scientific fields due to their unique optical, mechanical, thermal and electrical characteristics.

To improve the surface characteristics of the substrate, studies have shown that tethering of polymer brushes on a solid substrate is an effectual method. In particular, the ‘living’/controlled



radical polymerization played an important role in grafting polymerization of the surface of inorganic nanoparticles because of the presence of covalent bonds with a series of dense polymer chains [8-14]. Although there are advances in this method, most of them have their inherent bottlenecks such as difficulties in removing all the metallic catalyst from the products and complexities in reaction paces to introduce functional species and chain transfer agent to the inorganic surface for polymerization.

Given the aforementioned background, our aim is to develop a facile chemical strategy to deliver ZnO based nanocomposites with suitable processability and dispersibility by altering the inorganic surface by a one-pace immediate attaching of initiator moiety, preferably thiol groups. Recently, Butyrolactam (BL) has been found to be an important factor, acting as a stabilizer for the radical and a reversible capping agent, in supporting the polymerization of surface bonded thiol groups. [15-17]. A successful creation of PMMA-g-ZnO oxide nanocomposites through the surface initiated grafting polymerization of methylmethacrylate (MMA) from thiol functionalized ZnO nanoparticles has been demonstrated in this work.

2. Materials and testing methods

2.1. Materials

Before using, methylmethacrylate was purified of inhibitor with a neutral alumina column. ZnO nanoparticle, (3-mercaptopropyl) trimethoxysilane (MPTMS), butyrolactam (BL) and all the chemicals used were provided by Aldrich. Modification of ZnO nanoparticles with MPTMS was presented in the report [18].

2.2. Combination of PMMA-g-ZnO nanocomposites through surface-initiated radical polymerization

2g of MMA, 0.2 g of ZnO-SH, 0.2 g of BL, 4 mL of THF and using a Teflon-covered propulsion rod was placed in a 25 mL circle bottle decorated with a restore condenser. The bottle was washed with nitrogen, heated to 90 °C and stirred continuously. At the end of the desired time, the bottle temperature was reduced to 35 °C and the reaction blend was precipitated with methanol. The resulting product had dregs removed and was dried in a vacuum oven. Toluene was used to dilute the mixture and the mixture was centrifuged to collect the PMMA-g-ZnO freed from the unlinked polymer. Hereafter, this strategy will be denoted as thiol-lactam initiated radical polymerization (TLIRP).

2.3. The dispersion stability of PMMA-g-ZnO nanocomposites

The dispersion steadiness of polymer-grafted nanocomposites in toluene was evaluated after standing at 35 °C temperature for the required time. 2.0 g of PMMA-g-ZnO nanocomposites dissolved in 100 ml toluene was kept in a pipette and the pipette was stored at 35 °C temperature. After a period of time, the depth of sedimentation from the surface of suspension was recorded. The steadiness of nanocomposites is shown through the lack of depth of the surface of suspension. The following equation shows the sedimentation rate of dispersed nanocomposites in toluene:

The sedimentation percentage of composite particle (%) = $H/H_0 \times 100\%$, where H (cm) is the depth of sedimentation from the surface of suspension and H_0 (cm) is the total depth of suspension.

2.4. Characterization

Fourier-transformed infrared (BOMEM Hartman & Braun FT-IR spectrometer) spectra were recorded to characterize the chemical changes in the surface functionalities of ZnO. GPC was performed using an Agilent 1200 Series equipped with PLgel 5 μm MIXED-C columns. Tetrahydrofuran was used as the solvent and calibration was carried out following PS standards. The differential scanning calorimetry (DSC) measurements were conducted using a Perkin Elmer calorimeter (DSC6200). We used an F-4500 spectrofluorometer (Hitachi, Japan) with a 352-nm excitation source to record the photoluminescence (PL) spectra.

3. Results and discussion

The FT-IR spectra of ZnO nanoparticles, ZnO-SH and PMMA-g-ZnO nanocomposites are used to investigate the bonding nature in nanocomposites. For the FT-IR spectrum of ZnO nanoparticles, the strip at 488 cm^{-1} is the feature absorption of Zn–O link and the broad absorption strip at 3427 cm^{-1} can be ascribed to the absorption of -OH species. The absorption strip at 2823 and 2928 cm^{-1} , assigned to CH_2 -moiety, and a weak strip at 2572 cm^{-1} , assigned to S–H stretching band of the MPTMS indicated that the MPTMS was attached to the surface of the Zinc oxide nanoparticles *via* the silane coupling response. The FT-IR spectra of PMMA-g-ZnO nanocomposites show an adsorption strip at 1732 cm^{-1} which is determined by the C=O stretching of PMMA. The strips in the region from 3000 to 2850 cm^{-1} correspond to the C–H stretching of the CH_3 and CH_2 species of attached poly(methylmethacrylate). It can be concluded that PMMA was covalently grafted onto the surface of ZnO nanoparticles.

Polymerization on the surface of ZnO-SH nanoparticles were surveyed in different response times (5h, 10h and 15h). The grafted polymers were separated from PMMA-g-ZnO nanocomposites with HCl solution to determine the living nature of the TLIRP and estimate the molecular weight (M_n) of the grafted PMMA. Properties of the PMMA chains separated from the solution were analyzed with GPC. From GPC results, M_n of the PMMA was found to be proportionally increasing with monomer conversion and the polymerization time. The GPC analysis of the cleaved PMMA reveals that the M_n is ranged from 57, 68, and to 105 kg/mol with relatively narrow PDI of 1.65, 1.71 and 1.74, respectively. All these results explicitly suggest that the TLIRP was occurred in living and controlled manner.

Figure 1 shows the glass transition temperature (T_g) of the grafted PMMA series on the outer of Zinc oxide nanoparticles. The T_g of PMMA-g-ZnO nanocomposites are $114.5\text{ }^\circ\text{C}$, $118.3\text{ }^\circ\text{C}$ and $123.4\text{ }^\circ\text{C}$, which correspond to reaction times of 5h, 10h and 15h, respectively. It was observed that T_g of PMMA-g-ZnO nanocomposites was enhanced by 6–15 $^\circ\text{C}$ in comparison with free PMMA. The explanation for this is that restricting of one end of the polymer series on the Zinc oxide nanoparticles would prevent the motion and vibration of the entire chain and led to a greater T_g .

To investigate the effect of surface modification, the sedimentation behavior of PMMA-g-ZnO nanocomposites and bare ZnO nanoparticles in acetone was compared (Figure 2). PMMA-g-ZnO gave a steady colloidal dispersal in the acetone, while bare Zinc oxide (ZnO) nanoparticles precipitated easily with a higher rate. It was observed that Zinc oxide nanoparticles with a higher attaching density were steadier than that of a lower attaching density. This phenomenon signifies that the grafted polymer series raises the compatibility with organic solvent and reduces the combination of Zinc oxide nanoparticles.

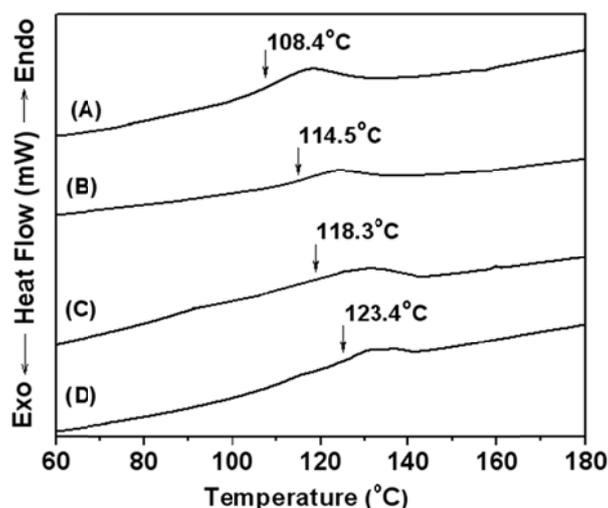


Figure 1. DSC curves of (A) cleaved PMMA from PMMA-g-ZnO nanocomposites, and PMMA-g-ZnO nanocomposites after polymerization for (B) 5 h, (C) 10 h, and (D) 15 h, respectively.

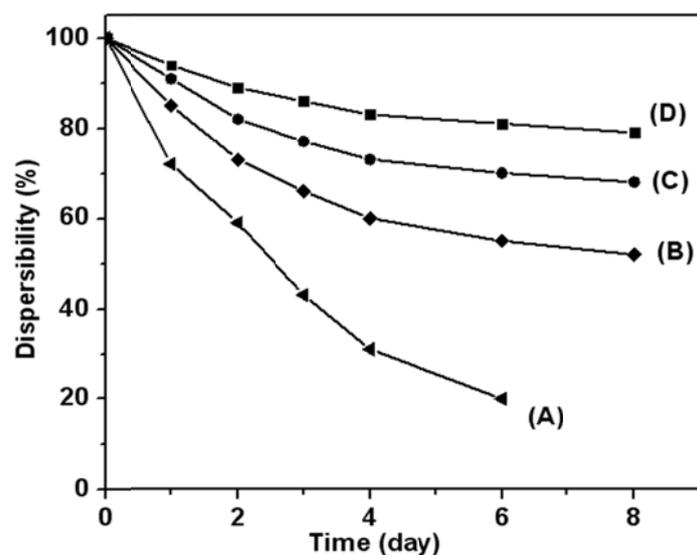


Figure 2. Sedimentation curves of (A) ZnO nanoparticles, and PMMA-g-ZnO nanocomposites after polymerization for (B) 5 h, (C) 10 h, and (D) 15 h, respectively.

The surface states of Zinc oxide is exhibited *via* its optical characteristics. The influence of PMMA grafting on ZnO nanoparticles was examined by UV-vis absorption spectroscopy and photoluminescence (PL) spectroscopy. The absorption spectra of ZnO nanoparticles and PMMA-g-ZnO nanocomposite are shown in Figure 3. Figure 3A demonstrates the onset of absorbance in the region from 380 to 400 nm, which are assigned to the excitement of electrons from the valance strip to the conduction band of Zinc oxide nanoparticles. A red shift with enhanced absorption has been sighted when combining Zinc oxide nanoparticles in the PMMA network, which can be explained by the attendance of Zinc oxide nanoparticle in PMMA network. The absorption of the PMMA-g-ZnO nanocomposites lasts throughout the Ultraviolet-visible region while the bare Zinc oxide nanoparticles indicate absorption in Ultraviolet region (<400 nm).

Optical characteristics of ZnO based nanohybrids are interesting for a typical semiconductor. Generally, photoluminescence spectroscopy of Zinc oxide nanoparticles has two components. The first one is typical excitation emission (TEE) or near-band-edge (NBE) emission. At the standard conditions, ZnO material gives emission band at 370 nm corresponding to 3.37 eV band gap energy. The second component is deep-level emission (DLE) related to oxygen vacancies. Figure 4 shows the photoluminescence spectroscopy spectra of the Zinc oxide nanoparticles and PMMA-g-ZnO nanocomposites as made by TLIRP for 5, 10 and 15 h, correspondingly, with excitement at 325 nm. Figure 4A showed that there is no conspicuous photoluminescence spectroscopy in clean PMMA when a potent absorption peak at 360 nm may be sighted in ZnO nanoparticles in Figure 4B, which indicates a well-determined excitonic emission characteristic. From Figure 4C-E, it is showed that the intensity of emission peak increases along with grafting density. The result indicates that the covalent grafting of PMMA on ZnO nanoparticles can enhance the PL property of ZnO nanoparticles. The phenomenon could be explained by the change of the local structure of ZnO nanoparticle surface by a different dielectric constant of the surrounding material, initiated by a surface modification by PMMA. This consequently causes screening effects to occur, reducing surface traps. As a result, fewer holes can be kept at the surface trap which quenches unwanted deep-level emission, and consequently intensify NBE emission which is pre-requisite for optical applications.

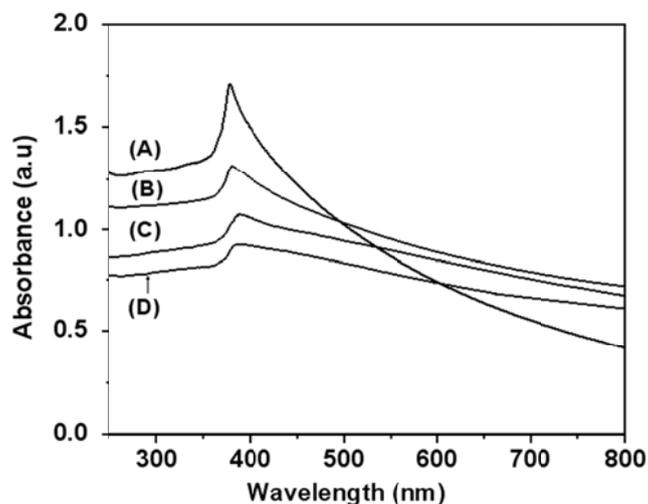


Figure 3. The UV–vis absorption spectra of (A) ZnO nanoparticles, and PMMA-*g*-ZnO nanocomposites prepared by TLIRP for (B) 5, (C) 10 and (D) 15 h, respectively.

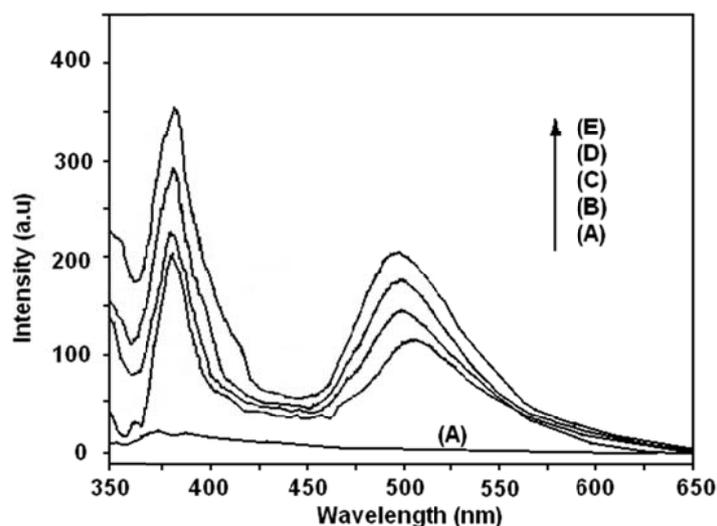


Figure 4. Room temperature PL spectra of (A) cleaved PMMA, (B) ZnO nanoparticles, and PMMA-*g*-ZnO nanocomposites prepared by TLIRP for (C) 5, (D) 10 and (E) 15 h, respectively.

4. Conclusions

In this study, PMMA-*g*-ZnO nanocomposites were prepared using surface TLIRP protocol. Initially, ZnO nanoparticles were functionalized by MPTMS. After that, surface initiated polymerization of MMA in the attendance of BL produced PMMA-*g*-ZnO nanocomposites. The analysis of FT-IR and EDS indicated that the surface of Zinc oxide nanoparticles was favourably grafted by PMMA *via* the covalent linkage between Zinc oxide and polymer. TGA and DSC analysis also showed that, in comparison with pure polymer, nanocomposites are more stable thermally. The dispersion stability of PMMA-*g*-ZnO nanocomposites in organic solvent was significantly improved. The Ultraviolet–visible absorption spectra confirmed that the PMMA-*g*-ZnO nanocomposite achieved a tall optical transmittance in close domain UV–vis. The PL spectra recommended that a stronger NBE excitonic emission peak of nanocomposites was developed upon covalent grafting of PMMA which reduces the surface traps.

Acknowledgments

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