European Polymer Journal 49 (2013) 630–636

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Polymerothermal Synthesis – A Facile and Versatile Method towards Functional Nanocomposites

Alok Chaurasia [a,1], Libo Wang [a,b,1], Leong Huat Gan [a], Ting Mei [b], Yongmei Li [a], Yen Nan Liang [a], Xiao Hu [a,*]

[a] School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore
[b] School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

ARTICLE INFO

Article history:
Received 17 November 2012
Accepted 13 December 2012
Available online 22 December 2012

Keywords:
Polymerothermal
Zinc oxide
Nanoparticle hybrids
Nanocomposites
Light emitting diode

ABSTRACT

This work discusses a facile and one-step method used for the preparation of functional nanoparticles (NPs)/polymer nanocomposite, based on regularly dispersed and zinc oxide (ZnO) quantum dot sized NPs in different polymer matrices without agglomeration. The synthesis was carried out in the absence of any organic additive or ligand. Readily available metal acetate precursor was employed and its conversion to NPs was achieved via low temperature heat treatment. Different self-assembled morphologies, obtainable and tailorable depending on selected polymers as the synthesis media, were elucidated in terms of specific coordination of the functionalities of the polymers towards metallic species, matching of polymer glass transition temperature (T_g) with precursor decomposition temperature, as well as the solid-state polymeric chain movement. This method is not only versatile for NP dispersion and morphological control, but also beneficial for functional device applications. Therefore, we also demonstrate the usage of ZnO NPs/poly(methyl methacrylate) (PMMA) nanocomposite thin film in a light emitting diode (LED) device, which emits bluish white light at relatively low turn-on voltage. Our new synthetic method is described as a 'polymerothermal' synthesis because the conversion to NPs took place in only polymer medium that is literally solvent-free.

1. Introduction

Zinc oxide (ZnO) is a non-toxic semiconductor with wide range of potential applications in the fields of electronics, photonics and biomedicine [1–5]. In particular, its ideal band gap and exciton dissociation energy make it favorable for specific functional devices. Promising results were constantly reported on incorporation of ZnO nanocrystals in polymer hybrid solar cell [3], transparent thin film transistors [4] and LEDs [6–9]. Although various methods were developed for ZnO nanoparticles (NPs) synthesis (e.g., precipitation, hydrothermal, solvothermal and sol–gel [10–14]), it is often challenging to purify the synthesized NPs and to re-disperse them into a polymer matrix [11,15,16]. These considerations are especially important for device fabrication from the aspects of processability and cost effectiveness. Moreover, many device applications require homogeneous NPs dispersion of particularly high concentration in a polymer matrix; this criterion demands practical technological solutions.

Incorporation of pre-synthesized nanoparticles including ZnO into polymer matrix via mechanical blending or solvent processing have met with limited success and often requires (i) tedious surface modification and/or

---

Abbreviations: NP, nanoparticle; ZnO, zinc oxide; T_g, glass transition temperature; LED, light emitting diode; MOCVD, metal organic chemical vapor deposition; $Zn(OAc)_2$, zinc acetate; PMMA, poly(methyl methacrylate); P4VP, poly(4-vinyl pyridine); PS, polystyrene; DBB, 1,4 dibromobutane; PL, photoluminescence; TEM, transmission electron microscopy; XRD, X-ray diffraction; EL, electroluminescence.

* Corresponding author. Tel.: +65 6790 4610; fax: +65 6790 9081.
E-mail address: asxhu@ntu.edu.sg (X. Hu).

[1] These authors are equally contributed.

0014-3057/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.eurpolymj.2012.12.004

(ii) the use of ligands that may deteriorate electro-optical properties of the hybrids [17]. Well-organized nanocrystals of noble metal such as Au and Pt could be synthesized in block copolymers [18–21]. However, previous attempt of preparing ZnO NPs using diethyl zinc as precursor in a block copolymer faced difficulty due to highly reactive and moisture-sensitive precursor, which was traditionally used for metal organic chemical vapor deposition (MOCVD) [22,23]. The interaction of the metallic species and polymer matrix as well as selection of suitable precursors are thus recognized to be critical. There is still lack of information in such context mainly due to vastness of material systems.

It is therefore highly desirable to develop a versatile and facile synthetic method for preparation of NPs or quantum dots (e.g., ZnO) that are well-dispersed in polymer matrix, at the same time, possessing well-defined nanostructures and morphologies. In this work, we explored a new 'polymerothermal' method: instead of high boiling point solvents, we used solid-state polymers as the synthetic media in which the precursors are converted to ZnO NPs. Although low boiling point solvents were used during thin film casting, the ZnO NPs only formed inside polymeric matrix during decomposition temperature; at the stage the solvent had fully evaporated. Recognizing the critical role of polymeric chain movement above T_g in solid state polymer, block copolymer was used to mediate the formation of various distinct assembled ZnO NP patterns. Using such ZnO NPs/polymer nanocomposite as the active layer, we successfully demonstrated a model single-layer bluish white-light LED. Our method is expected to widen the scope of using NPs/polymer hybrid systems for advanced functional devices as the method is by no means limited to one particular type of NP or polymer.

2. Experimental section

2.1. Materials and synthesis procedures

Zinc acetate dihydrate, $Zn(O_2CCH_3)_2{\cdot}2H_2O$ ($Zn(OAc)_2{\cdot}2H_2O$), 1,4-dibromobutane (DBB), toluene (99.9%) and anhydrous methanol (99.8%) were obtained from Aldrich and used as received. Homopolymer of poly(methyl methacrylate) (PMMA) (MW = 120,000 g mol^{-1}) was obtained from Sigma–Aldrich whereas poly(4-vinyl pyridine) (P4VP) (MW = 9,800 g mol^{-1}, $M_w/M_n = 1.11$) and block copolymer of polystyrene-block-poly(4-vinylpyridine) (PS-*b*-P4VP), $M_{PS} = 11{,}800$ g mol^{-1}, $M_{P4VP} = 15{,}000$ g mol^{-1}, $M_w/M_n = 1.04$) were obtained from Polymer Source Inc. In a representative polymerothermal synthesis, polymer was dissolved in toluene (2 mg ml^{-1}) at room temperature and the solution was stirred for 24 h. Since $Zn(OAc)_2$ is insoluble in toluene, it was firstly dissolved in methanol (20 mg ml^{-1}) before being added into the polymer solution according to predetermined compositions. Methanol was selected as the co-solvent because of its miscibility with toluene and hence is able to facilitate homogeneous mixing of $Zn(OAc)_2$ with the polymer. After 24 h ageing, the polymer/$Zn(OAc)_2$ precursor solution was drop-cast on substrate, e.g., quartz or ITO coated glass. The air dried polymer/$Zn(OAc)_2$ mixture was subjected to heat treatment at temperatures up to 200 °C. The heat treatment conditions were determined through systematically monitoring the formation of ZnO NPs using UV–Vis absorption spectroscopy (the spectra are given in the appendix, Fig. S1). Similar procedures were used for PS-b-P4VP copolymers, and the molar ratio of 4VP:$Zn(OAc)_2$ was 1:0.8. Crosslinking could be introduced into the P4VP assemblies of the copolymer by adding 1,4 dibromobutane (DBB) into the pre-aged PS-*b*-P4VP/$Zn(OAc)_2$ precursor solution (4VP:DBB = 2:1). The solution was kept at room temperature for another 24 h during when P4VP cores were selectively crosslinked by DBB.

2.2. Characterizations

UV–Vis absorption and Photoluminescence (PL) spectra of the ZnO NP/Polymer nanocomposites were obtained using a Shimadzu UV2501PC spectrophotometer and a Shimadzu RF-5301 PC spectrofluorometer respectively. Transmission electron microscopy (TEM) was carried out by a JEOL 2010 microscope fitted with a LaB_6 filament under accelerating voltage of 200 kV. TEM samples were prepared by dropping the precursor solution onto TEM grids. Thin film X-ray Diffraction (XRD) patterns were collected with a Rigaku DMAX 2200 using Cu Kα radiation ($\lambda = 0.1542$ nm) operating at 40 kV and 40 mA. The scanning rate used was 2° min^{-1}.

2.3. Fabrication of LED device

The LEDs were fabricated by spin-coating $Zn(OAc)_2$/PMMA precursor solution onto glass substrates with patterned ITO. Prior to spin-coating, the substrates were cleaned by sonication in acetone and 2-isopropanol, followed by deionized water rinsing and oxygen plasma treatment. The thickness of ZnO NPs/PMMA hybrid thin film (after annealing) was about 30 nm at spin-coating speed of 2000 rpm. After annealing at 200 °C for 1 h, aluminium electrode of 100 nm thickness was deposited by using an Edwards Auto 306 electron beam evaporator. The electroluminescence (EL) spectra were recorded using a PDS-1 photomultiplier tube detector connected to a monochromator and the current–voltage (I–V) curve was measured using an HP 4155B semiconductor parameter analyzer.

3. Results and discussion

3.1. Polymers as synthetic media

To prepare homogeneously dispersed ZnO nano-particles (NPs) in polymer medium using polymerothermal method, the selection criteria for the polymers stem from the solubility, compatibility, precursor loading capacity, and also the targeted application. These attributes are governed by the polymer molecular structures. In this study, poly(methyl methacrylate) (PMMA), poly(4-vinyl pyridine) (P4VP) and di-block copolymer of styrene and 4-vinyl pyridine (PS-*b*-P4VP) were found suitable. Polystyrene (PS)