Transparent and flexible thin films of ZnO-polystyrene nanocomposite for UV-shielding applications†

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A solution casting approach was developed to obtain flexible and self-supporting ZnO-polystyrene (PS) nanocomposite thin films (ca. 360 μm) which were highly transparent in the visible region and exhibited excellent UV-absorbing properties. The nanocomposite films were prepared from homogeneous solutions of ligand-modified ZnO nanocrystals and PS. UV-Vis spectra, transmission electron microscopy (TEM), thermogravimetric analysis (TGA), X-ray diffraction (XRD) and photoluminescence (PL) characterization techniques were employed to study optical and structural properties, as well as thermal stabilities of the nanocomposite films. Results revealed the high UV-shielding efficiency of the composites: for a film containing 1.0 wt. % of ZnO nanocrystals, over 99% of UV light at wavelengths between 200 and 360 nm was absorbed while the optical transparency in the visible region was slightly below that of a neat PS film. Minute amounts of organic ligands minimized aggregation of the ZnO nanocrystals, leading to the homogeneous blend solutions and eventually the well dispersed ZnO-PS nanocomposite films with stable optical properties. The present work is of interest for developing transparent UV-shielding materials and should help in the understanding and design of inorganic-polymer nanocomposites with desired properties.

Introduction

Despite many useful applications, UV light may be harmful for human health. For instance, an overexposure to UVB light (280–320 nm in wavelength) leads to some forms of skin cancer, since the radiation directly damages DNA molecules in skin cells.[1–4] UV light also has degradation effects on various materials, such as polymers, dyes, pigments and semiconductor devices.[5–7] Due to its higher energy, light in the UVB range generally causes more serious damage than that in the UVA range (320–400 nm in wavelength). Therefore, extensive research efforts have been devoted to developing transparent UV-shielding materials which are ideal for applications such as UV-protecting coatings, contact lenses, optical filters etc.[8–13]

Inorganic-polymer nanocomposites, which exhibit an ensemble of properties of both inorganic nanoparticles and polymers, are excellent candidates for UV-shielding applications. Such composites benefit from physical flexibility and ease of processing, which are typical characteristics of polymers. The UV-shielding efficiency of the composites can be improved by incorporated wide bandgap semiconductors (TiO$_2$, ZnS, CeO$_2$, ZnO, and etc.)[14–22] Among the wide bandgap semiconductors, ZnO is attractive due to its remarkable optical properties and environmentally friendly nature.[23] A significant number of studies have reported on the preparation of ZnO-polymer nanocomposites.[24–30] Two general strategies were applied: in situ synthesis of nanocrystals by sol–gel polymerization and ex-situ synthesis of ZnO nanoparticles and their incorporation into the polymer matrix by mechanical blending, polymer melt intercalation or solution processing. The in situ strategy generally results in highly homogeneous nanocomposites with no phase separations at the molecular level.[29] Nevertheless, the in situ strategy requires good control over both the sol–gel process to obtain ZnO nanocrystals with desired properties and the polymerization process in the same reaction media, which only applies to limited systems. In addition, the complexity of the in situ approach limits its industrial applications. In contrast, the ex-situ approach is straightforward and provides the flexibility of selecting inorganic and polymer components with well defined properties.[24–27] However, simple blending of ZnO nanocrystals with a polymer often leads to inhomogeneous and usually opaque materials that suffer from nanoparticle agglomeration and phase separation.[30] Methods aiming to improve the dispersion of ZnO nanocrystals in the polymer matrix are critical to fabricate practical transparent UV-shielding materials. For instance, Demir et al. prepared ZnO–polymethylmethacrylate (PMMA) nanocomposites by polymerization of dispersions of surface-modified ZnO nanoparticles in the monomer.[31] In another study, exfoliated ZrP nanoplatelets were utilized to control the dispersion of ZnO

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† Electronic supplementary information (ESI) available: Experimental details of characterization techniques and procedures. Typical UV-Vis absorption spectrum, PL spectrum and XRD pattern of the ZnO-PS composite films. See DOI: 10.1039/b914156a
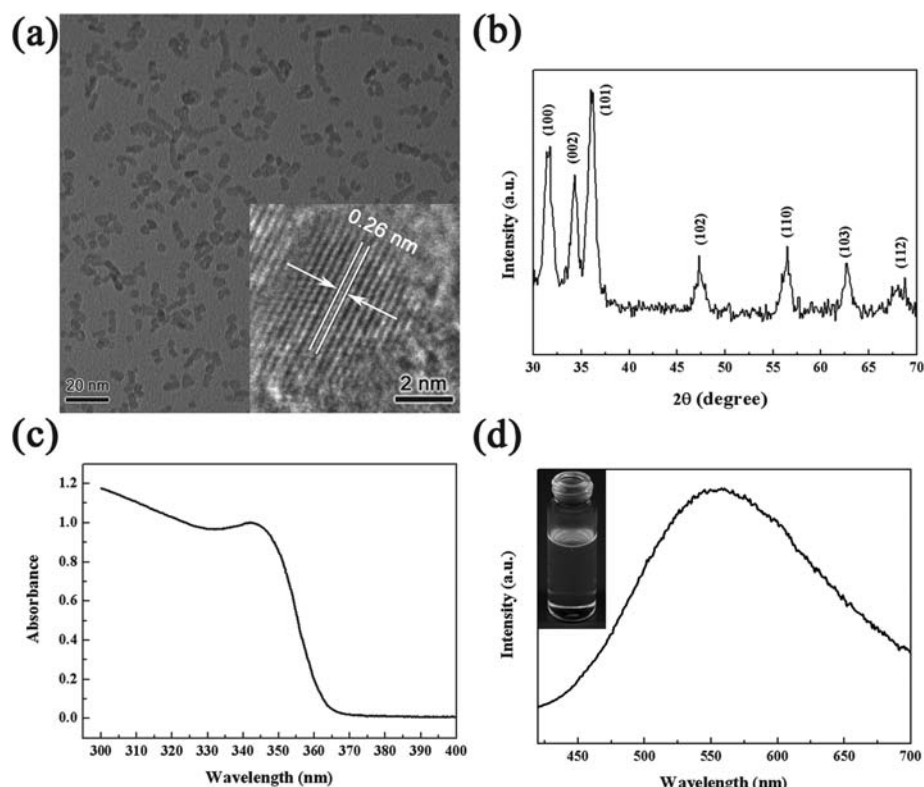
Fig. 1 (a) TEM and HRTEM (inset) image of the as-prepared ZnO nanocrystals. (b) XRD pattern of the as-prepared ZnO nanocrystals. (c) UV absorption of the as-prepared ZnO nanocrystals. (d) PL spectrum of the as-prepared ZnO nanocrystals. Inset: digital photograph of a chloroform solution of the ZnO nanocrystals under irradiation from a UV lamp (λ = 254 nm) in which a bright yellow emission is evident.

nanoparticles in epoxy resin.[12] Nevertheless, a simple and effective approach, which is suitable for production of transparent UV-shielding materials at industrial scale, is still a challenge and requires further efforts.

In this report, we describe the fabrication of ZnO-PS nanocomposite thin films by casting homogeneous solutions of ligand-modified ZnO nanocrystals and PS. Organic ligands have been extensively studied in the field of colloidal nanocrystals in terms of stabilizing the inorganic cores and controlling the surface properties.[32] Less is known regarding the effects of organic ligands on the dispersion of ZnO nanoparticles into the polymer matrix. In this study, octylamine and oleic acid were employed as typical examples of alkyl-amines and fatty acids, two kinds of widely used ligands, to examine the impact of the ligands on the optical properties of the composite films. On the other hand, PS is chosen as a host matrix because it is colorless and flexible as thin films, which are ideal for investigating the optical properties. In addition, PS is one of the most widely used kinds of plastic. Products from PS, such as disposable cutlery, packaging materials, and plastic models, *etc.*, are nearly ubiquitous. It is of actual interest to develop transparent and UV-absorbing PS composite materials. However, only few reports are available on the preparation of PS-ZnO nanocomposites.[33,34] The goal of transparent and UV-shielding ZnO-PS composite materials is yet to be achieved. Considering the simplicity of the fabrication of the composite materials, as shown in the experimental section, this work may shed light on the creation of transparent ZnO-PS composite materials with excellent UV-shielding properties.

Experimental

The synthesis of ZnO nanocrystals was based on literature methods.[35,36] 0.8192 g zinc acetate (Zn(Ac)$_2$, Aldrich, 99.99%) and 250 μl of deionized water were added into a flask containing 42 ml of methanol. The solution was heated to 60 °C with vigorous magnetic stirring. 0.496 g potassium hydroxide (KOH, Aldrich, 85%+, pellets) was dissolved into 22 ml of methanol as the stock solution that was then introduced into the flask within 15–20 min. At a constant temperature of 60 °C, it took 2 h and 30 min to obtain ZnO nanocrystals. When the reaction was finished, the upper fraction of the reaction solution was discarded after 30 min. 50 ml of methanol was added to the solution and stirred for 2 min. Again, the upper fraction of the solution was discarded after 30 min. The methanol washing process was repeated and the upper fraction of the solution was taken away after overnight staying. The isolated ZnO nanoparticles were dissolved in 10 ml of chloroform and filtered through 0.2 μm PTFE filters, leading to a solution with a concentration of *ca.*
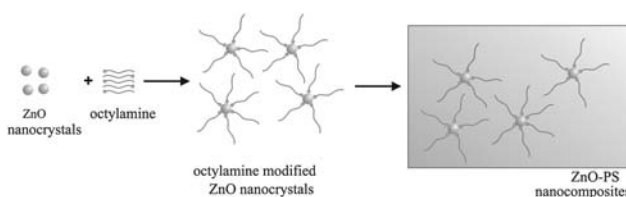

Fig. 2 Schematic illustration of the preparation of the ZnO-PS nanocomposite films.

31 mg/ml. The obtained ZnO nanocrystal samples were characterized by TEM, XRD, UV-Vis spectra and PL techniques. The results are shown in Fig. 1.

The processing of the ZnO-PS nanocomposite films was depicted in Fig. 2. A desired amount of octylamine, which acted as ligand, was introduced into the nanocrystal solution. 3 g PS (Alfa Aesar, M_w 100000) was dissolved in 40 ml of chloroform to form a homogeneous solution. The nanocrystal solution was mixed with a PS solution and stirred for 30 min. Then the intermixed solution of ZnO nanocrystals and PS was casted into a petri-dish, followed by solvent evaporation at ambient conditions to obtain ZnO-PS composite films (360 μm in thickness). In order to conduct a systemic study, composite films with different concentrations of ZnO nanocrystals (0.25, 0.5, 0.75, 0.93, 1.0 and 1.5 wt. %, respectively) were prepared. The optical, structural and other properties of the ZnO-PS nanocomposite films were
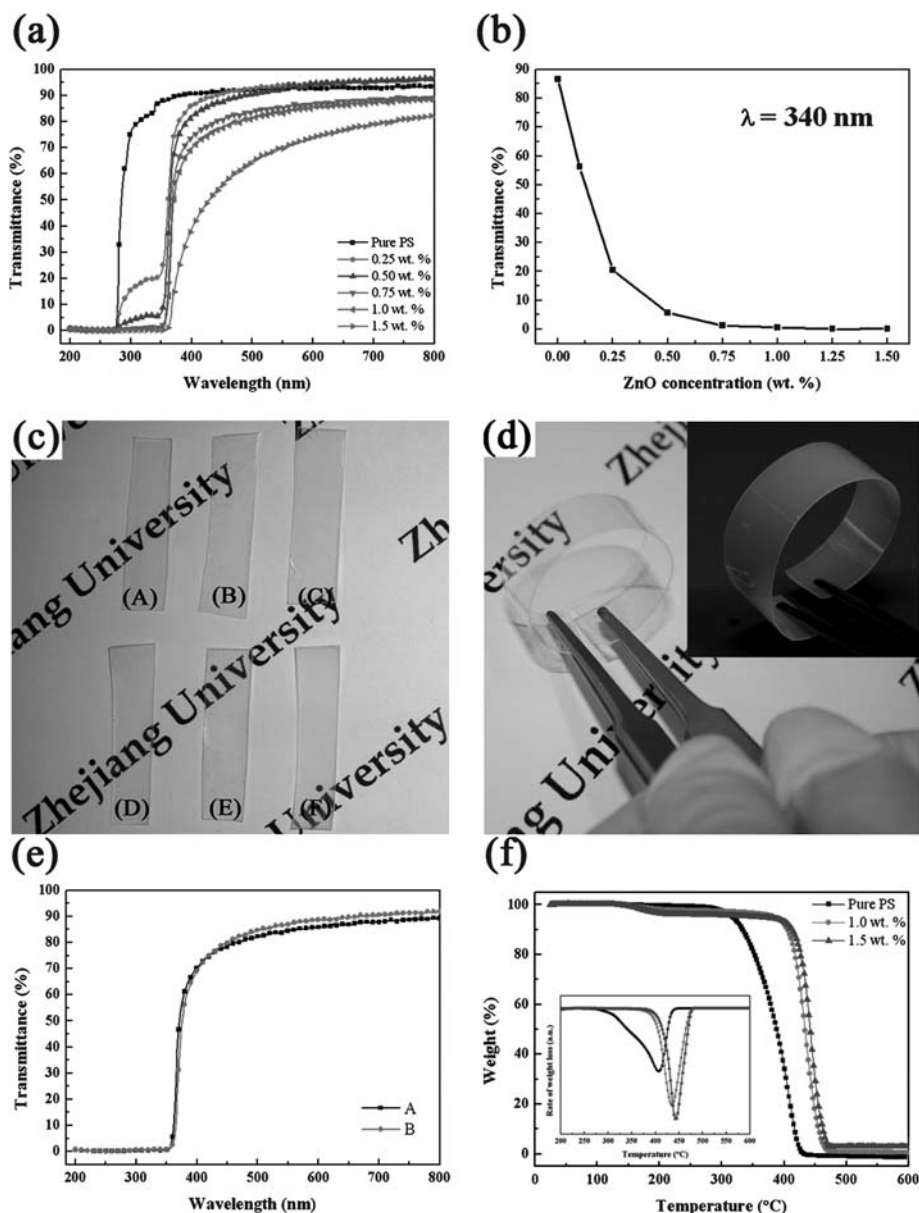

Fig. 3 (a) UV-Vis transmittance spectra of the composite films containing different concentrations of the ZnO nanocrystals. (b) Transmittances of the composite films containing different concentrations of the ZnO nanocrystals (340 nm radiation). (c) Digital photographs of the ZnO-PS nanocomposite thin films containing 0 wt. %, 0.25 wt. %, 0.5 wt. %, 0.75 wt. %, 1.0 wt. % and 1.5 wt. % of the ZnO nanocrystals, respectively (A–F). (d) Digital photograph showing the flexibility of a ZnO-PS nanocomposite film. Inset is a digital photograph of the ZnO-PS nanocomposite film under irradiation from a UV lamp (λ = 254 nm) in which a bright yellow emission of the film is evident. A typical PL spectrum of the ZnO-PS nanocomposite film is shown in the ESI.† (e) UV-Vis transmittance spectra of a composite film (0.93 wt. % of ZnO nanocrystals) recorded immediately after preparation (A) and after stored at ambient conditions for one month (B). (f) Thermogravimetric charts of a neat PS film and two ZnO-PS films (1.0 wt. % and 1.5 wt. % of ZnO, respectively). Inset shows the rate of weight loss of films during the heating process. The maximum rates of weight loss for neat PS film, the film with 1.0 wt. % of ZnO and the film with 1.5 wt. % of ZnO are 407 °C, 436 °C and 446 °C, respectively.

characterized by UV-Vis spectra, TEM, TGA, XRD and PL techniques. Details of characterization techniques and procedures are presented in the ESI.†

Results and discussion

Fig. 3a shows the UV-Vis transmittance spectra of the films containing various concentrations of the ZnO nanocrystals (a typical UV-Vis absorption spectrum of the ZnO-PS films is shown in Fig. S1).† For neat PS films, UV lights with wavelengths longer than 280 nm cannot be filtered. In other words, neat PS films are transparent for UVB and UVA irradiations. By incorporating the ZnO nanocrystals into the polymer (as demonstrated by the XRD result shown in Fig. S1),† UV photons with wavelengths in the range from 280 to 360 nm are efficiently absorbed by the composite films. A high ZnO concentration in the film results in enhanced UV-shielding efficiency. For 340 nm UV irradiation, the transmittances of the films containing 0 wt. %, 0.25 wt. %, 0.50 wt. %, 0.75 wt. %, 1.0 wt. %, 1.25 wt. % and 1.5 wt. % of the ZnO nanocrystals are 87%, 20%, 5.7%, 1.2%, 0.62%, and 0.15%, respectively. Therefore, the ZnO-PS composite films exhibit high UV-shielding efficiency, especially for UVB irradiation. In the visible region, the composite films are fairly transparent with transmittances close to that of the neat PS film (Fig. 3a and 3c). These self-supporting composite films possess excellent flexibility, which can be demonstrated by digital photographs shown in Fig. 3d. The ZnO-PS films are stable under ambient conditions since no degradation of optical properties could be distinguished when the films were stored in air for one month (Fig. 3e). The thermal stabilities of films were tested by TGA with typical results shown in Fig. 3f. It is evident that the thermal stabilities of the composite films are improved compared with that of the neat PS film due to the incorporation of the ZnO nanocrystals.

The optical properties of the ZnO-PS composites are impressive: for a film containing 1.0 wt. % of ZnO, the film absorbs nearly 99% of UV light at wavelengths between 200 and 360 nm and exhibits optical transparency slightly below that of the neat PS film (ca. 85–90%) in the visible range. The appealing optical properties of the composites imply a good dispersion of the ZnO nanocrystals in the PS matrix. This can be confirmed by the TEM investigations (Fig. 4a) on the microtomed thin sections (ca. 80 nm) from the nanocomposite films where no large ZnO agglomerations were observed.

The high quality of the nanocomposites may be attributed to the well controlled synthesis that yields ZnO nanocrystals with diameters typically ca. 6 nm (Fig. 1), the addition of a specific amount of octylamine which binds to the nanocrystals surfaces, and the formation of the homogeneously intermixed solution of the ZnO nanocrystals and PS which results in a good dispersion
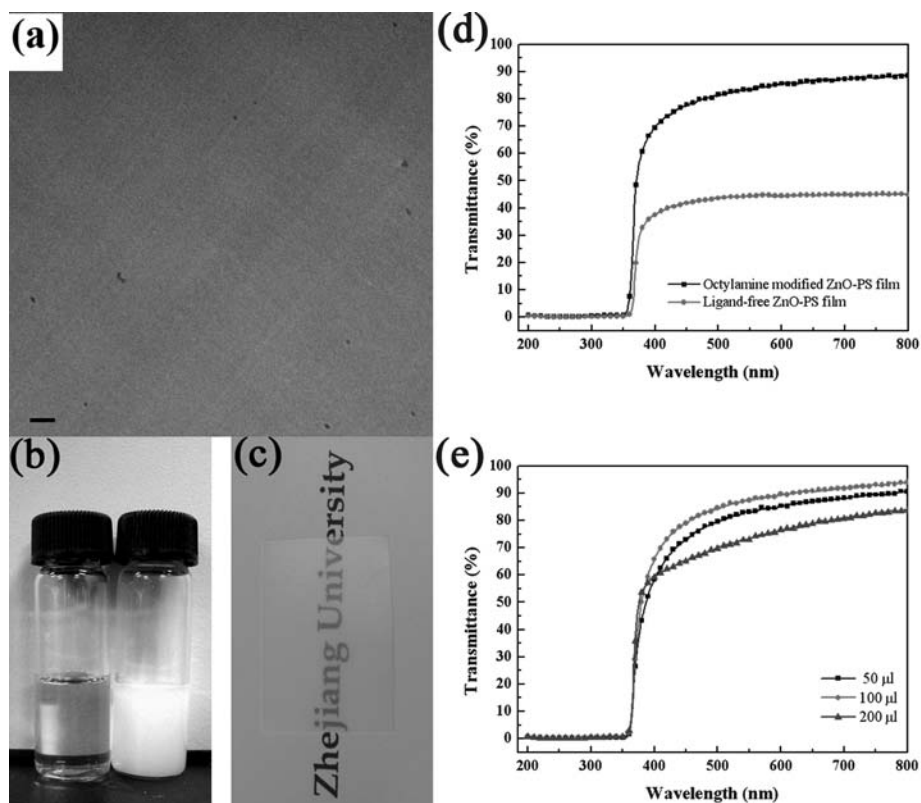

Fig. 4 (a) A typical TEM image of thin sections of a ZnO-PS composite film (0.5 wt. % of ZnO). The scale bar is 100 nm. (b) Digital photographs of an octylamine modified ZnO nanocrystal solution 4 months after preparation (left) and a ligand-free ZnO nanocrystal solution a few days after preparation (right). (c) Digital photograph of a ZnO-PS composite film from the ligand-free ZnO nanocrystals (1.0 wt. % of ZnO). (d) UV transmittance spectra of the ZnO-PS films (1.0 wt. % of ZnO) incorporated with the octylamine modified ZnO and the ligand-free ZnO, respectively. (e) Transmittance spectra of ZnO-PS films (1.0 wt. % of ZnO) in which 50, 100, 200 μl of octylamine were used in the processing, respectively.
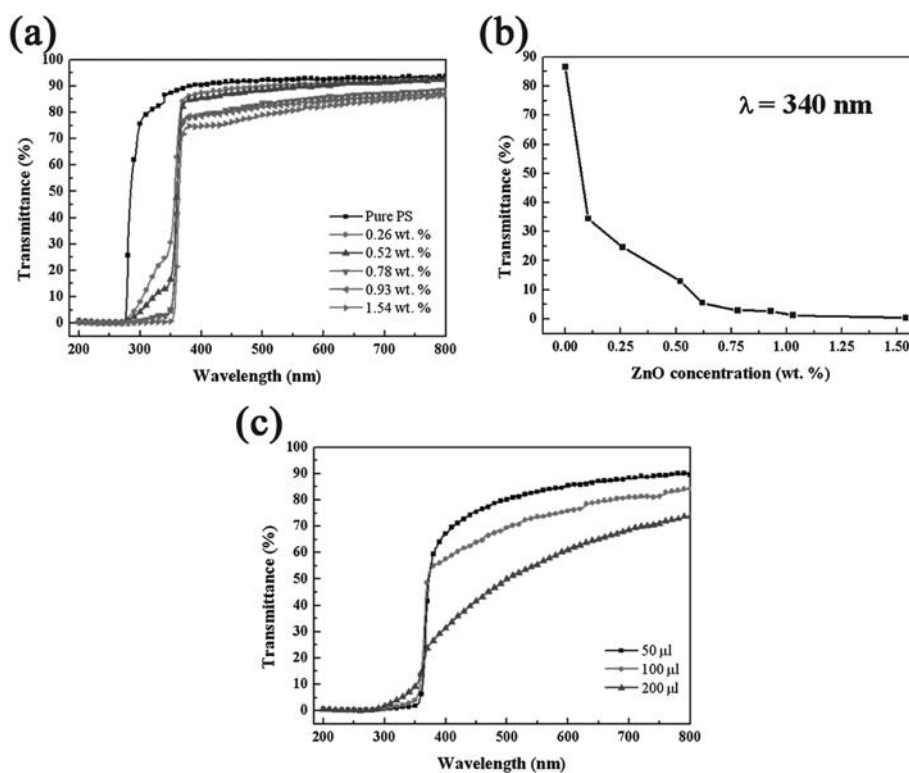
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Fig. 5 (a) UV-Vis transmittance spectra of the composite films containing different concentrations of the oleic acid modified ZnO nanocrystals. (b) Transmittances of the composite films containing different concentrations of the oleic acid modified ZnO nanocrystals (340 nm radiation). (c) Transmittance spectra of ZnO-PS films (0.93 wt. % of ZnO) in which 50, 100, 200 μl of oleic acid were used in the processing, respectively.

of the ZnO nanocrystals in the polymer matrix. Note that according to our synthesis approach, the bare ZnO nanocrystals are free of ligands with long alkyl chains. Therefore, the addition of ligands is essential so that the aggregation of nanocrystals in the solution processing can be minimized. This effect is confirmed by the fact that after the addition of octylamine, the chloroform solution of nanocrystals is stable in the time scale of several months while the ligand-free nanocrystal solutions become opalescent a few days after preparation due to precipitation of nanoparticle agglomerations (Fig. 4b). In another study, Sun *et al.* employed a solution casting method to fabricate ZnO-PMMA composites in which ZnO nanocrystals without any surface modification were used.[18] Aggregation of ZnO nanoparticles was observed in their experiments, which reflects the impact of ligands to the nanocrystals in terms of minimizing aggregations. Furthermore, ligands that bind to the nanocrystals surfaces can allow the nanocrystals to be dissolved in chloroform, ensuring the homogeneously intermixed solution of ZnO nanocrystals and PS. The ligands may modify the ZnO surfaces, making them more hydrophobic, which is beneficial in terms of improving the compatibility between the ZnO nanocrystals and the polymer matrix. In contrast, the optical properties of ZnO-PS composites from the ligand-free ZnO nanocrystals are difficult to control. Typically, for the ZnO-PS composites from ligand-free ZnO nanocrystals, the transmittances in the visible range significantly drop compared with that of the neat PS film (Fig. 4c–d), owing to the scattering by large aggregates formed during the processing. Thus, the addition of octylamine to the nanocrystal solutions is critical to improve the optical properties

of the composites. However, excessive amounts of ligands would have negative influences. As shown in Fig. 4e, for a composite film (1.0 wt. % of ZnO) from a ZnO nanocrystal solution (10 ml) with 200 μl of octylamine, although the absorbance in the UV range is identical, the transmittance in the visible range is significantly dropped comparing with that of the composite films from ZnO nanocrystal solutions with 50 or 100 μl of octylamine. We suspect that only a certain amount of octylamine is able to bind to the nanocrystal surfaces and act as ligand, leaving excessive octylamine unrestrained in the system. The free octylamine may crystallize around the octylamine capped ZnO nanocrystals in the amorphous PS matrix, causing phase segregation which makes the films less transparent. Investigations aimed at testing this hypothesis are under way.

It can be concluded that a suitable, but not excessive, amount of ligand is responsible for the good dispersion of the ZnO nanocrystals in the PS matrix. To further test this concept, we extended our approach to fatty acids, another important family of ligands that have been widely used for the dispersion of nanocrystals in organic solvents. Oleic acid was employed as an example. As demonstrated by Fig. 5a–b, ZnO-PS composite films from the oleic acid capped ZnO nanocrystals exhibit UV adsorbing and visible transparency properties similar to those of the films from the octylamine capped ZnO nanocrystals. An excessive amount of oleic acid leads to the degradation of optical properties, both in the UV range and in the visible range (Fig. 5c). Note that for the composite film prepared from excessive amounts of octylamine, only the optical transparency in the visible range of the composite film is affected. This is

attributed to that oleic acid can dissolve part of the ZnO nano-crystals whereas for octylamine that is not the case.

Conclusion

A simple and effective solution casting approach was developed to obtain ZnO-PS nanocomposite films. Owing to the surface modification by the ligands, the ZnO nanocrystals were able to be readily dissolved in solvents, homogeneously blended with the PS solutions and uniformly dispersed in the PS matrix. The ZnO-PS composite films possess appealing optical properties: a 360 μm thick film with ZnO content as low as 1.0 wt. % absorbs over 99% of UV lights (200–360 nm) and exhibits visible trans-mittance close to that of the neat PS film. Such a combination of excellent UV-shielding efficiency and high visible transparency indicates that the ZnO-PS composite films are one of the best candidates reported so far for UV-shielding applications. Considering their flexible and self-supporting nature, excellent stability in terms of optical properties, and improved thermal stabilities, the ZnO-PS nanocomposite films can be directly applied as transparent UV-shielding materials. Two kinds of organic agents, octylamine and oleic acid, were used as ligands and the role of ligands was investigated in detail. It was found that a suitable amount of ligand is critical for improving the dispersion of the ZnO nanocrystals in the composites and excessive amounts of ligands may degrade the optical properties of the composite films. This study not only presents a promising strategy for industrial production of UV-shielding nano-composites, but also contributes to the understanding and design of inorganic-polymer nanocomposites with desired properties.

Acknowledgements

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