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Two-step fabrication of ZnO-PVP composites with tunable visible emissions

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ABSTRACT

We report a two-step fabrication of zinc oxide-polyvinylpyrrolidone (ZnO-PVP) composites for potential phosphor-based applications. The composites are fabricated by initially preparing ZnO microrods using hydrothermal growth method and then dip-coating the microrods into aqueous PVP solutions with varying molar concentrations. The as-prepared ZnO microrods exhibit smooth surfaces and broad visible emissions, while the ZnO-PVP composites have pitted surfaces with shifted and reduced visible emissions. These changes in the structural and optical properties, which are found to depend on the PVP concentration, are attributed to the adsorption of PVP on the microrod surface. Although the surface morphology and visible emission are modified by PVP, the composites still maintain a hexagonal wurtzite crystal structure and near-band-edge ultraviolet (UV) emission similar with the as-prepared microrods. Our results therefore suggest that the ZnO-PVP composites can be used as phosphors that offer not only properties found in both ZnO and PVP but also tunable visible emissions which can be controlled during material fabrication.

1. Introduction

Composites made of polymers and inorganic compounds have the combined properties of both materials such as processability, flexibility, high mechanical strength, thermal stability, and chemical resistance. The poor thermal, mechanical, and electrical properties of the polymer constituent are compensated by the use of inorganic fillers possessing good optical, electrical, and magnetic characteristics. In general, the resulting properties of the composite strongly depend on the nature of its constituents as well as the shape, size, distribution, and crystallinity of the incorporated fillers [1–3]. Because of their improved properties, polymer-inorganic composites are useful in optical and magnetic applications [4,5], electronic devices [6], and biotechnology [7], to name a few.

Zinc oxide (ZnO) nanostructures are notable reinforcement materials for the fabrication of polymer-inorganic composites because of their biocompatibility, high surface-to-volume ratio, high ultraviolet (UV) absorption, good optical transparency, high electron mobility, and room-temperature stability. Several reports have investigated the development of ZnO-polymer composites for different practical applications. Polyaniline-ZnO (PANI-ZnO) composites prepared by direct thermal oxidation and in-situ polymerization exhibit increased current density and high UV absorption and therefore have a potential solar cell application [8]. UV-blocking ZnO quantum dots have been incorporated in a transparent poly(methyl methacrylate) (PMMA) matrix through a sol-gel route, and the resulting transparent composite film, which can completely absorb UV radiation with wavelengths less than 340 nm, can be used as a UV-shielding organic glass [9].

There are some challenges that need to be addressed in the fabrication of polymer-inorganic composites. For composites with oxides, a common problem is the incompatibility at the interface between the hydrophobic polymer matrix and the hydrophilic oxide surface [10]. This incompatibility causes aggregation of the

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incorporated particles leading to the degradation of the composite properties. Another drawback for composites with ZnO is the presence of defects in the ZnO crystal. These defects such as interstitials and vacancies compromise the optical emission processes related to most ZnO applications. Surface treatment of the inorganic oxide material is then a widely explored technique to address the aforementioned challenges. Surface modification can be done through chemical treatment (surface pretreatment of particles by a coupling agent or grafting polymerization) or physical treatment (surfactant treatment or polymer encapsulation of particles) [11,12]. Polyvinylpyrrolidone (PVP), a non-toxic and water-soluble polymer with film-forming characteristics, is a popular encapsulating agent of ZnO particles because of its excellent adsorption ability and surface passivation [13–16]. Numerous studies report the effect of PVP on the optical properties of ZnO. Recently, ZnO nanorods fabricated via wet chemical methods without PVP exhibit green visible emission, while ZnO nanorods with PVP exhibit blue visible emission [17]. In addition, ZnO hexagonal nanoprisms synthesized by employing PVP exhibit intense UV emission centered at about 370 nm and have quenched visible emission [18]. Tunable luminescence from blue to yellow wavelengths of undoped ZnO nanowires prepared by microwave irradiation has also been achieved by using PVP as capping agent [19]. Moreover, ZnO rods fabricated using hydrothermal method exhibit UV emission centered at 378 nm and visible emission extending from about 500 to 700 nm, and the UV to visible emission intensity ratio increases with increasing PVP concentration of up to 1 mM in the hydrothermal growth solution [15]. By investigating and redesigning polymer-inorganic composites based on PVP and ZnO nanomaterials, novel industrial applications can be developed. For example, using a surface-modified ZnO-PVP composite as an electron-transporting layer has recently been demonstrated to enhance charge collection in inverted polymer solar cells compared to using a pure ZnO film [20].

In this study, we investigate the two-step fabrication of ZnO-PVP composites for potential phosphor-based applications. The composites are fabricated by initially preparing ZnO microrods using hydrothermal growth method and then dip-coating the microrods into aqueous PVP solutions with varying molar concentrations. Hydrothermal growth method is employed to synthesize the ZnO microrods because of its simplicity and versatility. On the other hand, dip-coating is used to incorporate PVP because of its simplicity, low cost, and high coating quality [21]. Compared to previous investigations, this study employs a fabrication process in which PVP is incorporated to the ZnO rods after the hydrothermal growth and the obtained ZnO-PVP composites exhibit tunable luminescence from red to green wavelengths. This report specifically aims to characterize the structural and optical properties of the composites, to compare the composites' properties with the as-prepared microrods, and to provide some insights on the composites' potential phosphor-based applications.

2. Experimental

ZnO-PVP composites were fabricated using a two-step process: the hydrothermal growth of ZnO microrods and the dip-coating in a PVP solution. The ZnO microrods were initially prepared using the hydrothermal growth method similarly described in Refs. [22–24]. Aqueous 8.0-mM solutions of zinc acetate dihydrate [99.5%, $Zn(CH_3COO)_2 \cdot 2H_2O$] and hexamethylenetetramine or hexamine [99.0%, $(CH_2)_6N_4$] were mixed in a glass beaker containing bare glass substrates which initially underwent standard degreasing procedures. After heating at 90 °C for 120 min, the substrates were removed from the solution, washed with deionized water (DI H_2O), and dried in air without any additional heat treatment. The as-prepared ZnO samples were then dip-coated in an aqueous PVP solution (10,000 M_W) for 60 min while being heated at 50 °C. Such preparation of composite is similar to the procedure described in Ref. [25]. After dip-coating, the samples were harvested from the solution, rinsed with DI H_2O, and were also dried in air without any additional heat treatment. Different ZnO-PVP composites were fabricated by varying the PVP concentration from 0.8 to 4.0 mM.

Different structural and optical characterization techniques were implemented to investigate the ZnO-PVP composites. The structural properties of the composites were studied using scanning electron microscopy (SEM) and x-ray diffraction (XRD) spectroscopy. Sample images were taken using a field emission scanning electron microscope (Philips FEG SEM XL30), while sample crystallinity was examined using a Bragg-Brentano type x-ray diffractometer (Shimadzu MAXima X XRD-7000, 0.15406 nm Cu Kα radiation). The optical properties of the composites were also characterized using Raman, time-integrated photoluminescence (TIPL), and Fourier transform infrared (FTIR) spectroscopies. Raman spectroscopy was done using the 514.5-nm line of an argon-ion (Ar^+) laser (Spectra-Physics Modu-Laser). The laser was focused on the sample through a custom-built micro-Raman setup, and the sample emission was fiber-fed through backscattering geometry to a spectrometer (Horiba Jobin Yvon iHR550) equipped with a silicon (Si) charge-coupled device (CCD) detector (Horiba Jobin Yvon Synapse). Moreover, TIPL spectroscopy was implemented using the frequency-tripled output (3ω, 290 nm) of a Ti:sapphire laser system (Spectra-Physics Tsunami 3941-M1S and Spitfire). The laser was focused on the sample at an angle of 45° from the normal, and the sample emission was collected normal to the sample and was fiber-fed to a handheld spectrometer (StellarNet BLUE-Wave UVNb-50) with a spectral resolution of 1 nm. The TIPL spectroscopy measurements were also carried out using different excitation energy densities from 0.5 to 1.0 mJ cm^{-2} and different exposure times from 0 to 25 min to assess the stability of the samples with respect to the laser beam. Furthermore, FTIR spectroscopy was performed using an FTIR spectrometer (Shimadzu IRPrestige-21). The scans were obtained with a single-reflection horizontal attenuated total reflectance (ATR) accessory (PIKE MIRacle ATR), and the final FTIR spectra were processed using ATR correction. In addition, dynamic laser light scattering (DLS) measurements were obtained using a particle size analyzer (Horiba LB-550) with 650-nm, 5-mW laser diode to investigate the composite size distribution and light scattering. All characterizations and measurements were done at room temperature.

3. Results and discussions

Fig. 1 shows the XRD spectrum of the ZnO microrods prepared using hydrothermal method. All peaks can be indexed to the reflections of hexagonal wurtzite ZnO. The peaks at 31.7, 34.4, 36.2, 47.5, 56.5, 66.3, 67.9, and 69.1° correspond to the (100), (002), (101), (102), (110), (200), (112), and (201) reflections, respectively. No characteristic peaks from other ZnO phases or impurities can be observed. From the XRD pattern, the lattice constants and unit cell volume of the as-prepared ZnO microrods are computed. The ZnO microrods have a 3.25 Å a-axis lattice parameter, a 5.20 Å c-axis lattice parameter, and a 47.6 $Å^3$ unit cell volume. All values are in good agreement with the theoretical and experimental values for hexagonal wurtzite ZnO [26] and with the JCPDS reference [27].

Fig. 2 shows the SEM images of the ZnO microrods prepared using hydrothermal method and the ZnO-PVP composites fabricated using different PVP concentrations. The as-prepared ZnO microrods exhibit distinct hexagonal facets and uniform lengths and widths ranging from 8.5 to 11.1 μm and 1.3 to 1.9 μm, respectively. On the other hand, the fabricated ZnO-PVP composites have