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Ionic Liquid Mediated Synthesis of ZnO Microspheres via Hydrothermal Method

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A B S T R A C T

Metal oxide microspheres have potential applications in various fields. In this work, zinc oxide microspheres were synthesized using 1-butyl 3-methyl imidazolium hexaflourophosphate($BMIMPF_6$)ionic liquid as a medium via a hydrothermal method. The morphology and structure of the samples were characterized by UV-Vis spectroscopy, FTIR, X-ray diffraction (XRD), photoluminescence spectroscopy and Scanning electron microscopy (SEM). Results revealed the formation of spherical morphology which confirms the formation of ZnO microspheres. The room temperature photoluminescence (PL) spectra showed broad and strong visible emission spectra.

1. Introduction

Metal oxide microspheres have shown great deal of attention because of their attractive properties and applications in distinctive area, for example, gas sensors, catalysis, photoelectron devices, highly functional and effective devices.[1-3] These nanomaterials have novel electronic, and structural properties which are of high importance in fundamental and connected fields. One such promosing metal oxide semiconductor materials is Zinc oxide (ZnO) comprising of a band gap 3.37eV and large exciton binding energy of 60meV[4,5]. Its remarkable electrical, optical, photoelectronic and electrochemical properties have empower applications in solar cells, transparent anodes, sensors, antimicrobial agent and drug delivery systems[6-8]. In literature, there are many techniques which are available for synthesis of metal oxide. Synthesis methods available for ZnO are laser ablation,[9] hydrothermal methods,[10] electrochemical depositions[11] sol–gel method,[12] chemical vapor deposition, [13] thermal decomposition,[14] and combustion method[15]. Some of the latest methods are ultrasound[16], microwave assisted combustion method[17], electrophoretic deposition[18].

Latest exploration demonstrated that ionic liquids (IL) can give a potential device to the generation of another era of synthetic nanostructures. This is because that ionic liquid contains extended hydrogen bonds frameworks and are highly polar solvent and are subsequently enriched with preorganized structures.[19] Ionic liquid have other specified properties due to which they act as a soft template media for synthesis of semiconductor materials, such as high vapor pressure, high melting point temperature and high liquidous range. These properties of ionic liquid may furnish materials with fascinating morphologies and properties which are not acquired by utilizing traditional solvents and strategies.[20] In this regard, few reports have focused on the synthesis of ZnO microspheres using ionic liquid via solvothermal method and solgel method.[21,22] Intrigued by this, we sought to investigate the use of room temperature ionic liquid as a tempalate for the synthesis of ZnO microspheres using a hydrothermal method. We have chosen hydrothermal process as it has several

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advantages over other growth processes, such as use of simple equipment, catalyst-free growth, low cost, large area uniform production, environmental friendliness and less hazardous[23]. Till now, no literature is available for the synthesis of ZnO via hydrothermal method using $BMIMPF_6$ ionic liquid .

In the present work,ZnO microspheres were synthesized using hydrothermal method. Hydrothermal technique is a promising synthetic method because of the low process temperature and easy control of the particle size. In this work ethylene glycol has been used as a solvent media and imidazolium hexafluorophosphate as a soft template. Zinc nitrate was used as a precursor for synthesis of ZnO microstructure. The resultant product were characterized by using FTIR, UV-vis spectroscopy, the morphology study was done using scanning electron microscopy (SEM), and phase of the prepared sample was confirmed using X-ray diffraction study (XRD).The room-temperature photoluminescence (PL) spectroscopic study carried out enables to determine the electronic energy levels of ZnO microspheres.

2. Materials and methods.

1-methylimidazole (99%) and 1-chlorobutane (99.5%) were purchased from Sigma-Aldrich and were distilled over KOH and P_2O_5,respectively. Hexafluorophosphoric acid (ca. 65% solution in water), zinc nitrate and zinc acetate, were purchased from Aldrich. Sodium hydroxide, ethanol and methanol were purchased from Himedia. Ethylene glycol (99%). Milli-Q water (Millipore, 18 MΩ) was used throughout the work.

2.1 Synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF6) ionic liquid

Before the synthesis of $BMIMPF_6$, 1-Butyl 3-methyl imidazolium chloride (BMIMCl) was synthesized by the procedure stated earlier[24]. In a typical synthesis of $BMIMPF_6$, BMIMCl (0.17 mol) was transferred to a round bottom flask followed by the addition of 40 ml of deionised water. An aqueous solution of 65% HPF_6 in a 1.1:1 molar ratio was added slowly to minimize the amount of heat generated.

As HPF_6 was added two phases formed, where $BMIMPF_6$ was the bottom phase and the HCl was the upper phase.The upper phase was decanted and the remaining product was washed with water several times. Then the resulting product was dried at 70 °C in vacuum line for 4 h. ^1H NMR spectra are shown in Fig. 1.^1H-NMR($CDCl_3$, 400MHz): δ(ppm) = 8.29 (s, 1H, NCHN), 7.258 (d, 1H, $CH_3NCHCHN$), 7.22 (d, 1H, $CH_3NCHCHN$), 4.05 (m, 2H, $NCH_2(CH_2)_2CH_3$), 3.78 (s, 3H, NCH_3), 1.71 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.25 (m, 2H, $N(CH_2)_2CH_2CH_3$),0.816(t,3H,$N(CH_2)_3CH_3$).

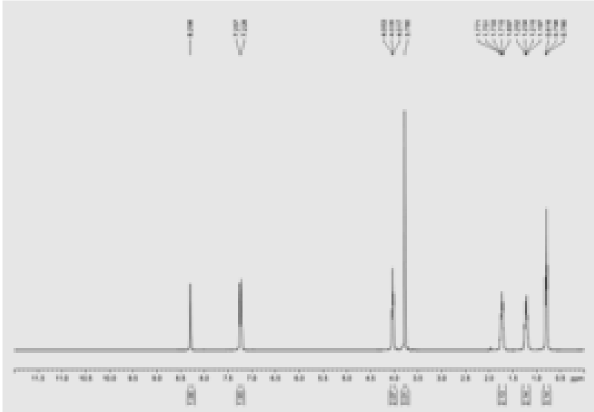

Fig.1. ^1H NMR spectra of $BMIMPF_6$ ionic liquid.

2.2 Synthesis of Zinc oxide microsphere in $BMIMPF_6$ ionic liquid

About 3 g of zinc nitrate (10.1 mmol) was dissolved in 35 ml of ethylene glycol and 5 ml of 1-butyl-3-methylimidazolium hexafluoro phosphate was added. The mixture was stirred for 24 h to form a clear solution. After getting the clear solution, it was transferred to a stainless steel autoclave. The reaction temperature was 180 °C. The resultant products were collected by centrifugation and then washed with distilled water and ethanol to remove ionic liquid and dried at 80°C in a vacuum oven to get ZnO microsphere. The samples were annealed at 500°C for 5h in tubular furnace for further characterization.

2.3 Material Characterization

The characterization of the synthesiszed ionic liquids was carried out using nuclear magnetic resonance spectrometer (Bruker-400 MHz) and UV-vis spectrophotometer (UV-2450 Shimadzu). Synthesiszed zinc oxide was charecterized using Fourier Transform Infrared Spectroscopy (FTIR) and the phase analysis of ZnO was carried out using X-ray diffractometer (PANalytical, Philips) using Ni-filtered Cu $K\alpha^1$ radiation in the 2θ range of 20-70° with a scan speed of 5° per minute. The XRD spectra were analyzed using the Philips X'pert Highscore Plus software. The morphologies of the sample were determined by using scanning electron microscopy (SEM) JEOL JSM-6480 LV microscope.

3. Results and Discussion

Fig. 2 shows the UV-Vis spectra of synthesized $BMIMPF_6$ ionic liquid. To minimize the effect of impurity on ionic liquid, it was washed several times with water. No absorption peak was observed which confirmed the formation of colourless impurity free ionic liquid. The X-ray diffraction data were recorded by using Cu Kα radiation (1.54Å). The intensity data were recorded over a 2θ range of 20-80º. The diffraction pattern was indexed to the XRD patterns of the wurtzite-type ZnO which indicated the presence of wurtzite-type structure after annealing at 500 °C.

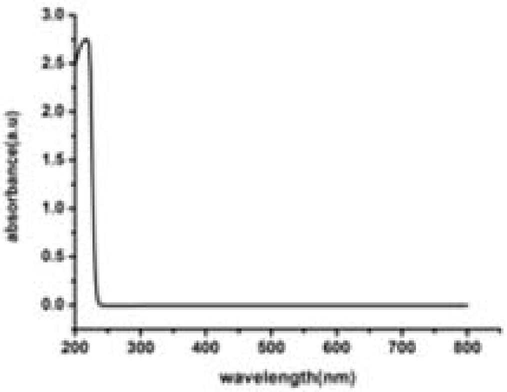

Fig.2. UV-Vis spectra of 1-butyl-3-methylimidazolium hexafluorophosphate.

Fig. 3(a) shows the XRD pattern of ZnO microspheres in presence of ionic liquid after annealation (JCPDS file No. 79-0207) and Fig 3 (b) shows before annealation. XRD pattern indicates that ZnO microspheres synthesized in presence of ionic liquid matches the zinc phosphate which transforms into wurtzite structure of ZnO after annealing it at 500 ºC for 2 hours.

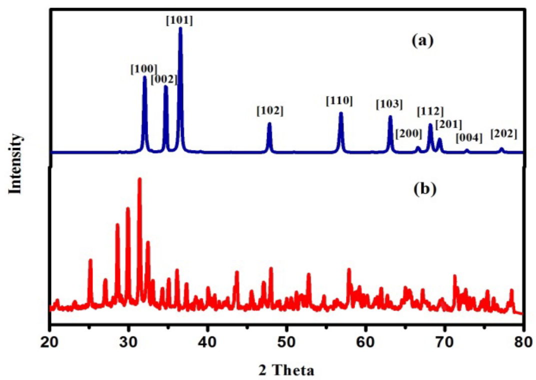

Fig.3. XRD pattern of ZnO (a) after annealing and (b) before annealing.

The sharp and narrow peaks also illustrate that ZnO microspheres has high crystallinity and purity. Diffraction peaks corresponding to the impurity were not found after annelation in the XRD patterns, confirming the high purity of the synthesized products.

The FTIR spectrum of pure ZnO microspheres synthesized by hydrothermal method was analysed in the spectral region 400-4000 cm^{-1}. Fig. 4 shows the FTIR spectrum of the ZnO microspheres.

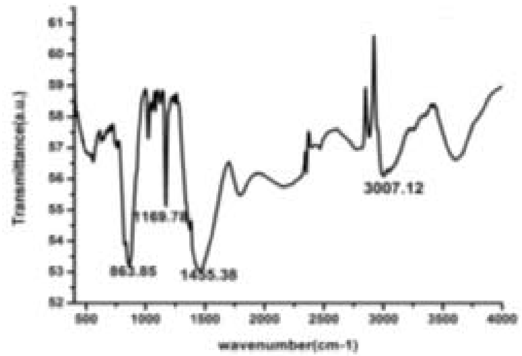

Fig.4. FTIR spectra of ZnO microspheres.

The band between the 450-500 cm^{-1}corelated to metal oxide bond (Zn-O)[25]. After annelation, the peaks of ZnO becomes more sharpen suggesting the crystalline nature of ZnO microspheres. The peaks in the range of 1400-1500cm^{-1} corresponds to the C=O bonds. The adsorbed band at 1600 cm^{-1} is assigned O-H bending vibrations. The peaks in the range 1169 cm^{-1} and 3000cm^{-1} are due to O-H stretching and deformation, respectively, assigned to the water adsorption on the metal surface.

SEM micrograph was used to examine the topography and morphology of the samples. It provides essential information about shape, and size. Fig 5. displays the SEM micrograph of $BMIMPF_6$ ionic liquid mediated ZnO microspheres using hydrothermal method. SEM micrographs of the resultant ZnO shows the formation of spherical particles with an average diameter of 1.5 µm.

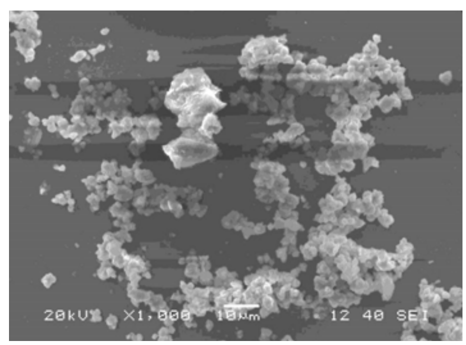

Fig.5.SEM image of ZnO microspheres.

The room-temperature photoluminescence (PL) spectroscopic study enables to determine the electronic energy levels from where emission is particularly observed which in turn helps to confirm the band structure of the metal oxides. Room-temperature photoluminescence (PL) spectra of the ZnO microspheres were shown in Fig.6 which was obtained with an excitation wavelength of 325 nm.The present spectra demonstrated visible emission. Visible emission generally influenced by the crystalline nature of ZnO microspheres. Large ZnO spheres with crystalline nature generally show stronger UV luminescence. However, smaller ZnO spheres with a large number of the defects show stronger defect-related to visible emission. In the present study two bands were observed in the PL spectrum: (1) a small band near 468 nm and (2) a broad band at around 562 nm.

A strong peak at around 468 nm is observed which corresponds to the blue emission. The blue emission band is related to intrinsic defect structures, in particular, oxygen vacancies and/or zinc deficiency.[26]

Broad band at 562 nm is related to the green emission which can be attributed to a deep level of trap-state emission. The green transition normally attributed to the singly ionized oxygen vacancy in ZnO and the emission results from the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy.

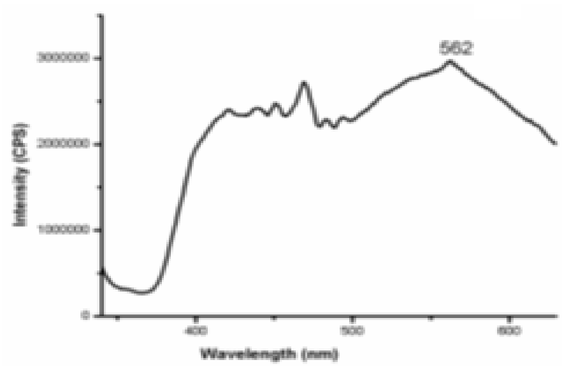

Fig.6. Photoluminescence spectra of ZnO microspheres.

The stronger intensity band suggests the presence of higher singly ionized oxygen vacancies in ZnO microspheres. The fluorescence strength is proportional to the number of vacancies and/or defects, so larger the axial dimension stronger is the emission[27]. These interesting photoluminescence properties can be used to control the optical properties of ZnO microspheres for variety of optical device applications.

4. Conclusion

ZnO microspheres have been successfully synthesized via hydrothermal method using $BMIMPF_6$ ionic liquid. The sample was characterized using different characterization techniques. XRD study confirms the wurtzite structure of ZnO microspheres. The SEM results showed the formation of spherical shape of ZnO microsphere having particle size of 1.5 µm. This method provides a really facile approach not only for different hierarchical microspheres but also for the design of new functional microspheres materials.

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