



Treatment of Waste Water using PB Doped nano Materials

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ABSTRACT

This article deals with the structural and optical characterization of lead-doped zinc oxide nanoparticles synthesized by precipitation method. X-ray diffraction study confirmed the substitution of Pb dopant without disturbing the basic wurtzite structure of zinc oxide. The average crystallite size, lattice constants, and unit cell volume also increased up to 10% of lead doping. The energy gap of the samples was determined from the ultraviolet-visible absorption spectrum as well as Tauc's plot which infers that the energy gap decreases with the increase of lead content. Fourier Transformation Infra-Red spectrum confirmed the lead dopant through peak shifting from 437-549 cm⁻¹. Photoluminescence spectrum also defines the lead dopant by means of intensity increase. Scanning electron microscope study also confirmed the existence of particles in nanometre size and it witnessed the microstructure transformation from nanoparticles to the rod-like structure on 10 (wt.%) lead doping.

KEYWORDS: Synthesized, morphology, diffraction, Photocatalytic, Ultraviolet-visible,

INTRODUCTION

Water is an important resource for life. However, due to population growth, industrialization, and the threat of climate change, water quality and adequacy have become serious concerns. Poor water quality affects many areas of human's welfare and has many economic and social implications.

Water is the most valued and important resource in the world and the lack of it has become a serious problem. Industrialization, urbanization, and climate change have created an urgent demand for the clean water that is so essential to human health. Lack of water can cause diseases such as typhoid fever, dysentery, cholera, and diarrhea, resulting in many deaths worldwide. Countless freshwater sources in the world are contaminated because of industrial activities and human negligence and they need to be purified. Water purification involves removing undesirable chemicals, biological contaminants, or even suspended solids from water systems to produce clean, safe water for human consumption and other purposes. There are traditional methods that include processes such as filtration, sedimentation, distillation, and chlorination, but these have limitations and can be resistant to antibiotics. Researchers are trying to overcome these limitations by developing alternative methods.

MATERIALS AND METHOD

Literature survey shows that different synthesis methods have been adopted for the synthesis of Pb doped ZnO nanoparticles, including sol-gel technique, microemulsion synthesis, mechanochemical processing, spray pyrolysis and drying, thermal decomposition of organic precursor, RF plasma synthesis, supercritical-water processing, self-assembling, hydrothermal processing, vapour transport process, sonochemical or microwave-assisted synthesis, direct precipitation and homogeneous precipitation method. For instance, has investigated Pb doped ZnO nanowires synthesized by a thermal evaporation method and studied their morphology and optical properties. They found that Pb doping lowers the crystalline quality of the ZnO nanowires. Similarly, also investigated Pb doped ZnO nanowires synthesized by the same thermal evaporation method. They found that the morphology of doped nanowires is like a cantilever however they observed a red shift in the UV-Vis spectrum due to the merge of impurity levels with the edge of the conduction band. Likewise, has synthesized Pb doped ZnO nanocrystals by simple chemical precipitation method and studied their

optical and electrochemical characteristics. They found that Pb has some influences on controlling the size and morphology of ZnO. Following this, has studied the characteristics of Pb doped ZnO thin film deposited by Spray Pyrolysis method.

They found the optical and structural properties of ZnO are modified by Pb doping and the transmittance increases in the near infrared region (800-1100 cm) as the doping percentage is increased. Also, they claimed the increase in the energy gap of ZnO from 3.27 to 3.36 eV. These literature surveys clearly reveal three major things (i) the reports available on Pb doping in ZnO nanoparticles using chemical route is scanty. (ii) Pb doping in ZnO is very difficult due to *p*-type impurity and (iii) we need to use some expensive method like discussed above. As a challenge, we preferred one of the versatile method, solution combustion method for both synthesis and doping of Pb in ZnO. In this report, we focus on the synthesis of Pb doped ZnO nanoparticles by chemical precipitation method. Zn_{1-x}Pb_xO samples were synthesized with different 'x' values ranging from 0, 2, 5, 8 and 10 (wt.%). Influence of Pb doping on structural and optical properties of ZnO nanoparticles have been studied by x-ray diffraction (XRD) method, Fourier transform infrared (FTIR) spectroscopy, Ultraviolet-visible (UV-Vis) spectroscopy, Scanning electron microscopy (SEM) with compositional analysis and We found that the crystallite size reduced from 32 nm to 24 nm with Pb doping.

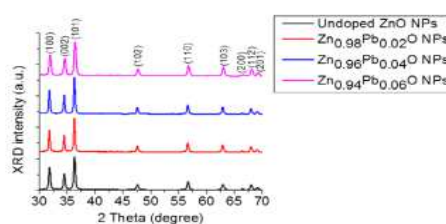
EXPERIMENTAL

To begin the synthesis of Pb-doped ZnO-NPs, analytical grade zinc nitrate hexahydrate Zn (NO₃)₂ · 6H₂O, lead nitrate dehydrate Pb (NO₃)₂ · 2H₂O, gelatin and distilled water were used as starting materials. All of the materials used were purchased from Sigma-Aldrich. The precursors were measured as Zn_{1-x}Pb_xO (x = 0, 0.02, 0.04, and 0.06) to obtain final products. First, a gelatin solution was prepared by adding gelatin (3.65 g) to distilled water at 60 °C. The metal nitrates were dissolved separately in a minimal amount of distilled water at room temperature, and then these were added to the gelatin solution. After that, the compound solutions were stirred and heated at 80 °C until gels were obtained. The gels were calcined at 550 °C for 5 h, at a heating rate of 2 °C/min. The resulting powders were characterized using several tools to check their quality.

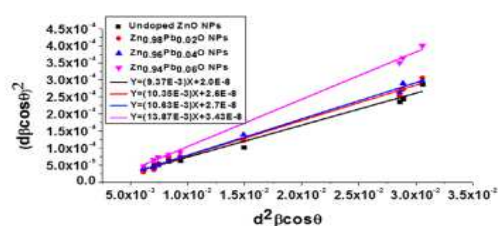
Powder X-ray diffraction (XRD) (Philips, X'Pert, CuKα) was used to evaluate the phase characteristics of the samples. Transmission electron microscopy (TEM) and selected area electron diffractometer (TEM/SAED, Hitachi H-7100) were employed to characterize the morphology and structure of the NPs. Elemental analyses of the products were conducted using an energy-dispersive X-ray spectroscope (EDX) and X-ray photoelectron spectroscopy (XPS; VG-Microtech ESCA2000). The XPS spectra were recorded using Mg-Kα radiation (1256.6 eV). The optical properties of the ZnO-NPs were characterized at room temperature using UV-vis (PerkinElmer, Inc.) and photoluminescence (PL, Jobin Yvon Horiba HR 800 UV) spectrometers. A He-Cd laser with an emission wavelength of 325 nm was used for the PL measurement.

RESULTS AND DISCUSSION

The XRD patterns of the NPs in the range of $2\theta = 30^\circ - 70^\circ$ are shown in Fig. 1. All of the detectable peaks could be indexed as belonging to the ZnO wurtzite structure (PDF card NO: 00-005-0664). No other peaks, such as those from Pb, PbO and ZnPbO, were detected. The ionic radius of the substitute Pb²⁺ ($R_{2+} \text{ Pb} = 1.19 \text{ \AA}$) is bigger than that of Zn²⁺ ($R_{2+} \text{ Zn} = 0.74 \text{ \AA}$). Thus, doping with Pb caused slight shift in the XRD.

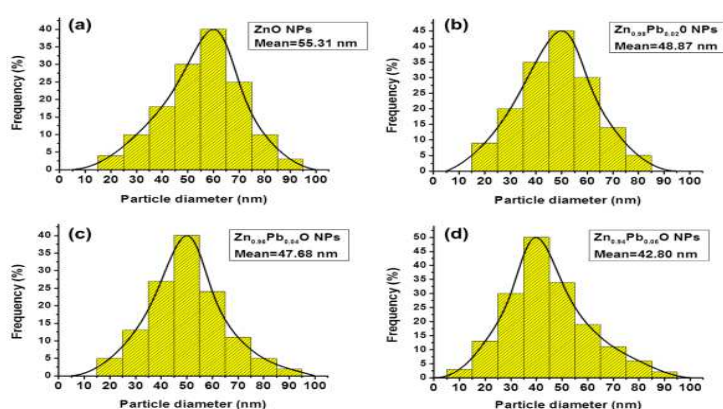


1 XRD patterns of undoped and Pb-doped ZnO NPs



2 SSP plot of the undoped and Pb-doped ZnO NPs

XRD results. In fact, Pb^{2+} ions play a passivation role. This passivation role causes the slow growth of the NPs. Therefore, under the same conditions, Pb-doped ZnO NPs size decreases with an increase in the Pb content. The EDX spectra are shown in Fig. 5a–d for undoped, Zn_{0.98}Pb_{0.02}O, Zn_{0.96}Pb_{0.04}O and Zn_{0.94}Pb_{0.06}O NPs, respectively. The EDX results are in good agreement with our calculation for Pb concentrations in the experimental part. The UV–vis absorption spectra of the ZnO NPs at room temperature are shown in Fig. 5e–h. The spectra reveal a characteristic absorption peak for ZnO, at wavelengths from around 373 nm for the undoped ZnO to around 400 nm for the samples that were synthesized with different concentrations of Pb. This can be attributed due to the intrinsic band gap absorption of ZnO, owing to the electronic transitions from the valence band (VB) to the conduction band (CB) ($O2p \rightarrow Zn3d$). In addition, the samples were characterized by PL. Figure 6b shows the PL spectra of the undoped and Pb-doped ZnO NPs. All of the PL spectra of the ZnO NPs show a peak in the ultraviolet (UV) region around 376 nm for the undoped ZnO NPs and around 400 nm for the Zn_{0.94}Pb_{0.06}O NPs, and a blue–green emission (deep-level emission [DLE]) peak in the visible region at 500–570 nm. It has been suggested that a visible emission is related to a singly ionized oxygen vacancy in ZnO, and results specifically from the recombination of a photo-generated hole with the singly ionized charge state of this defect.^{13–15} As can be seen, the PL spectrum of the undoped ZnO NPs shows a stronger UV peak than the DLE peak. The ratio of the UV to DLE peak is one of the main factors that is used for comparing the optical properties between samples. The UV/DLE ratio of the undoped ZnO NPs is bigger than the UV/DLE ratio of the Pb-doped ZnO NPs, and it decreases with increasing Pb content in the Pb-doped ZnO NPs. Therefore, Pb^{2+} ions generate more active defect sites in the ZnO lattice. As a result, more visible light is absorbed via these active defect sites, which may lead to a higher photocatalytic activity of the doped ZnO crystallites in visible.



CONCLUSION

Zn_{1-x}Pb_xO ($x = 0, 0.02, 0.04$ and 0.06) NPs were synthesized using a sol–gel method. The XRD and TEM results showed that crystallite and particle sizes of the Zn_{1-x}Pb_xO NPs decreased with an increase in the Pb content, without changing the wurtzite hexagonal single-phase structure of the ZnO. Optical characterization revealed that the band gap of ZnO NPs was decreased by increasing Pb concentration, compared to the undoped ZnO NPs. In addition, the PL results indicated more oxygen vacancies for the Pb-doped ZnO NPs than undoped ZnO NPs, which was further confirmed by the XPS results. In fact, the optical and XPS studies showed that the Pb-doped ZnO NPs had good potential to harvest visible light from the electromagnetic spectrum. The photocatalyst activity revealed a moderate MB removal efficiency for the Pb-doped ZnO NPs in comparison to the undoped ZnO NPs. In fact, it was observed that the stress and strain of the NPs are two factors, which have been considered in photocatalyst process.

References

1. M. Azarang, A. Shuhaimi, R. Yousefi and S. PilbanJahromi, One-pot sol–gel synthesis of reduced graphene oxide uniformly decorated zinc oxide nanoparticles in starch environment for highly efficient photodegradation of Methylene Blue RSC Adv., 2015, 5, 21888–21896.
2. R. Lamba, A. Umar, S. K. Mehta and S. K. Kansal, Well-crystalline porous ZnO–SnO₂ nanosheets: An effective visible-light driven photocatalyst and highly sensitive smart sensor material, Talanta, 2015, 131, 490–498.
3. R. Kumar, D. Rana, A. Umar, P. Sharma, S. Chauhan and M. S. Chauhan, Ag-doped ZnO nanoellipsoids: Potential scaffold for photocatalytic and sensing applications, Talanta, 2015, 137, 204–213.
4. R. Yousefi, F. Jamali-Sheini, M. Cheraghizade, S. Khosravi-Gandomani, A. Saaedi, N. M. Huang, W. J. Basirun and M. Azarang, Enhanced visible light photocatalytic activity of Sr-doped ZnO nanoparticles, Mat. Sci. Semicon. Proc., 2015, 32, 152–159.
5. F. Davar, A. Majedi, and A. Mirzaei, Green synthesis of ZnO nanoparticles and its application in the degradation of some dyes, J. Am. Ceram. Soc., 2015, 98, 1739–1746.
6. R. Yousefi, Effects of Sn atoms on formation of ZnO nanoring, Cryst. Eng. Comm., 2015, 17, 2698–2704.