Journal of Luminescence 196 (2018) 64–68

Contents lists available at ScienceDirect

Journal of Luminescence

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

Sensitization of ZnO nanoparticles by metal–free phthalocyanine

Mehrnaz Gharagozlou[a,*], Sanaz Naghibi[b]

[a] Department of Nanomaterials and Nanocoatings, Institute for Color Science and Technology, PO. Box: 16765-654, Tehran, Iran
[b] Young Researchers and Elite Club, Shahreza Branch, Islamic Azad University, Po. Box 311-86145, Shahreza, Iran

ARTICLE INFO

Keywords:
ZnO
Phthalocyanine
UV–vis. spectroscopy
Photoluminescence spectroscopy
Sensitizing

ABSTRACT

Metal–free phthalocyanine (PC) as an efficient dye sensitizer was successfully used to prepare a hybrid compound based on ZnO nanoparticles. The PC/ZnO sample is synthesized via a simple solution method and characterized by XRD, TGA, FTIR, PL, TEM, and UV–visible spectroscopy. The results show that the phase component and morphology do not change due to the modification process. The weight ratio of ZnO to PC in the PC/ZnO sample is estimated to be about 9, based on the TG analysis. The FTIR spectroscopy shows that (i) a new band appears at 749 cm^{-1} (assigned to the C–H bending vibration) and (ii) the hydroxyl stretching vibrations is intensified (due to the increase in surface defects and approved by PL spectroscopy). Both are evidences for the creation of conjugate between ZnO NPs and PC molecules.

The main influence of this process is to change in the UV–visible absorption behavior of the sample. The UV–visible spectrum shows a wide peak in the wavelength range of 280–320 nm, with the maximum peak at 274 nm (assigned to the Soret band), approving enhancement of its photoactivity.

1. Introduction

Phthalocyanines (PC) are aromatic and planar π–electron macroheterocycles. The chemical structure of this substance consists of extensive delocalized π–electron in which four isoindole subunits are connected to each other. This unique chemistry results in interesting applications in dyeing [1]. On the other hand, due to the redox and light–harvesting characteristics of the molecules, PC becomes a more interesting agent for sensitization [2]. Hodak et al. have reported the sensitization of TiO_2 with PC. They showed that the redox potential of the modified TiO_2 particles caused to enhance the oxidation performance. On the other hand, immobilization on the particles surface led to the reusability of the synthesized photocatalysts [3]. Mahmiani et al. have studied modified TiO_2 NPs with M–phthalocyanines and investigated the influence of this procedure on photodegradation of 4–chlorophenol. They showed that M–PCs are anchored on the TiO_2 surface without any effect on the phase component, whereas the optical properties and photoactivity have been improved in the visible light region [4]. Mattioli et al. prepared the hybrid ZnPC/ZnO system. They showed that the molecular conjugation could be formed without any anchoring agents and their improved structural and electronic characteristics give them a the high potential interest for photovoltaic applications [5]. Mari et al. and Ghosh et al. fabricated the hybrid film of CuPC/ZnO. They showed the photoelectrical characteristics have been improved via this procedure, enabling the as–sensitized specimens in view of solar cell applications [6,7]. The main aim of using PC as the sensitizing agent is to provide high–performance in photovoltaic applications [2,4–7]. The other applications of the sensitization process include photodynamic therapy [8] and pollution degradation [9].

The present study focuses on sensitizing the as–prepared ZnO NPs by PC to synthesize metal–free PC/ZnO nanohybrid and to improve their optical characteristics. This research team has published some investigations about the sensitization of TiO_2 and ZnO NPs by vitamin B12 [10–12]. The observed results of this work would be compared with those of the pervious one [12], which showed the influences of sensitizing agents (vitamin B12 or PC) on the mentioned properties.

2. Experimental

The required ZnO NPs were prepared using green chemistry method, which was previously detailed elsewhere [13]. In this procedure, zinc (II) acetate dehydrate [$Zn(O_2CCH_3)_2{\cdot}(H_2O)_2$], L-leucine [$C_6H_{13}NO_2$] and 5-sulfosalicylaldehyde sodium salt [5NaO5S] were used as the raw chemicals. Three solutions were prepared: (I) 50 mmol of L-leucine in 100 cc of water at the temperature of 70 °C; (II) 50 mmol of 5-sulfosalicylaldehyde sodium salt in 100 cc of water; (III) 50 mmol of zinc acetate dehydrate in 200 cc of water. The solutions of L-leucine and 5-sulfosalicylaldehyde sodium salt were mixed and allowed to stir for 30 min, then the third solution was added dropwise under stirring. The pH value and temperature of the obtained solution were adjusted to

* Corresponding author.
E-mail address: gharagozlou@icrc.ac.ir (M. Gharagozlou).

https://doi.org/10.1016/j.jlumin.2017.12.020
Received 22 May 2017; Received in revised form 10 December 2017; Accepted 11 December 2017
Available online 12 December 2017
0022-2313/

7 and 70 °C, respectively. After vigorous stirring for 1 h, the resulted solution was aged for 24 h to form a white precipitate. This was filtered, washed, dried, heat treated at 500 °C, and crushed to achieve ZnO NPs.

The sensitization process was accomplished as described before [12]. For this purpose, a suspension of NPs in water with a concentration of 25 g/L was prepared and sonicated for 15 min. The water based PC solution was fabricated at a concentration of 0.25 g/L. Then, equal amounts of the mixtures were mixed and stirred at reflux for 24 h. The obtained suspension was centrifuged at 4500 RPM for 10 min to separate the solid part. The obtained powder was washed with ethanol and dried. It is expected that PC/ZnO nanohybrid could be synthesized by this procedure.

The phase components of the samples were recorded by an X-ray diffractometer (XRD, PANalytical, Philips, Netherlands) using Cu-Kα radiation (λ = 1.5418 angstroms).

The weight loss amount of the modified sample due to heating to 1200 °C was calculated by a thermogravimeter (TGA: Pyris Diamond, PerkinElmer, USA). ZnO as an inorganic compound does not show any weight loss till 1200 °C, whereas PC is not stable at temperatures above 500 °C and leaves only a trace of residual ash after burning out [14]. Accordingly, the residual mass after heat treatment at 1200 °C is related to the inorganic part and the percentage of the organic part could be achieved from the weight loss amount [15].

The conjugation between ZnO NPs and PC molecules was examined by Fourier transform infrared spectroscopy (FTIR: Jasco 460, Japan) in KBr disk and transmission mode.

Photoluminescence spectra (PL) were recorded using a spectrophotometer (LS 55, PerkinElmer, USA).

Transmission electron microscopy (TEM: CM200 FEG, Philips, Netherlands) at an acceleration voltage of 100 kV was used to obtain microscopic images

The absorbance of the solutions was measured at 200 − 800 nm by a spectrometer (Lambda, EQ–OC1, PerkinElmer, USA).

3. Results and discussion

Modification of an inorganic ceramic compound such as ZnO with an organic molecule such as PC could lead to change some characteristics of the as-synthesized compound. This phenomenon may be due to the planar geometry of PC molecules and their aggregation tendency. There are two types of aggregation arrangement: *head to tail* and/or *head to head* stacking, which determine the properties changes [7].

3.1. XRD analysis

Fig. 1 shows the XRD patterns of the ZnO NPs [13] and as–synthesized PC/ZnO sample. Both of them matched with the standard diffraction patterns of hexagonal ZnO (JCPDS: 01-076-0704 and space group: *P*63*mc* 186). The phase component and peaks positions did not changed through the sensitizing procedure. It is important to retain the crystalline state of ZnO NPs after the PC loading process, whereas the polycrystalline feature of PC is not seen in the composite compound. Further, the comparative height of the peaks in the 2θ range of 30–40° decreased due to the decrease in ZnO concentration. Contrary to what is mentioned by Ghosh [7], this procedure did not lead to the preferentially oriented growth of ZnO NPs. This difference is probably due to the difference in the preparation methods. They have synthesized ZnO NPs in a solution of PC, whereas this work was mainly based on the physical mixture of ZnO and PC. The results confirm this subject, so the obtained compound could be considered as a ZnO containing system.

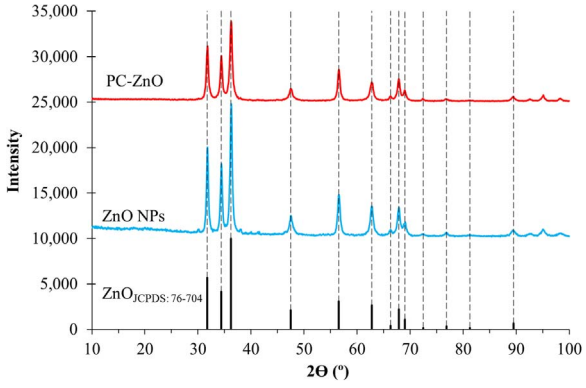

Fig. 1. XRD patterns of ZnO NPs [13] and PC/ZnO system. The black lines refer to the reference pattern of ZnO structure; JCPDS: 01-076-0704.

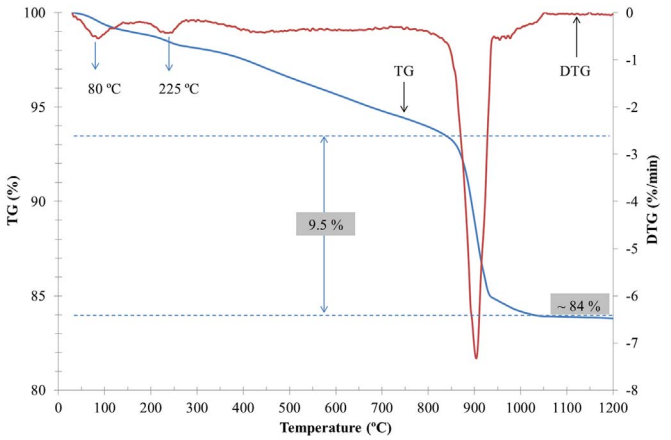

Fig. 2. TGA and DTG curves of the PC/ZnO system.

3.2. TG analysis

Fig. 2 exhibits the TGA and DTG results of the PC/ZnO sample. By forgoing the weight loss of the pristine ZnO powder and also the weight of remaining ash after PC heating [14], the weight loss of the sample could be considered as an index for determining the PC amount in the as–synthesized sample. The derivative curve shows two tiny shoulders at 80 and 225 °C and a main peak at ~ 900 °C. The TGA curve shows a distinct weight loss during heating till the temperature reaches around 850 °C. More increase in temperature led to intensify the weight loss. It seems that both peaks at < 300 °C are related to evaporation and/or burning out of water and other chemicals which were used as the starting materials. The weight loss at this step was calculated to be about 6%. At the second step, with increasing the temperature from 850 to 950 °C, the weight loss accelerated. This value was estimated to be about 9.5 wt%. This is attributed to the decomposition and combustion of the PC molecules. A weight loss of about 10% at this temperature is observed, specifying the weight percentage of the loaded PC on ZnO NPs.

3.3. FTIR analysis

In Fig. 3 the FTIR results of the samples were employed to evaluate the interaction of PC molecules and ZnO NPs. Theoretical calculation shows that there are 71 IR normal vibrational modes for the PC structure [16]. The experimental results show some of them as listed and assigned in Table 1. The main bands of this material are located in the fundamental range, i.e. 1800 − 400 cm^{-1}. The other peaks in the range of 4000 − 1800 cm^{-1} are weak and may not be of major importance. There are three intense and important peaks in the ZnO spectrum at 580, 1440, and 3430 cm^{-1}, which are originated from Zn–O, C–O, and –OH stretching vibrations, respectively. The results of the PC/ZnO conjugate shows that the main peaks of PC and ZnO remain after the sensitization process. This approves the existence of PC and also ZnO in