



Optical properties of incorporating of ZnO nano-particles on the dopant poly(o-toluidine)

Rawnaq A. Talib^{a,*}, Dalal K. Thbayh^a, Kareema M. Ziadan^b

^a Polymer Research Center, University of Basra, Basra, Iraq

^b University of Basra, College Science, Department of Physics, Basra, Iraq

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ABSTRACT

This work submit a study of the optical characteristic and EDX of nano ZnO/poly (o-toluidine) (POT) doping with organic acids dodecylbenzene sulfonate acid (DBSA) composites were synthesized by in-situ chemical oxidative polymerization method of (o-toluidine) monomer in existence of different ZnO nanoparticles concentration (weight ratio OT/ZnO:1/0.05, 1/0.1, 1/0.15), the products were washed by the centrifugation method, in order to avoid a higher loss of ZnO. Those POT-DBSA/ZnO composite films were intended by spin coating procedure. The optical properties of the prepared films were examined by Fourier transform infrared (FT-IR), UV-Visible. The structural properties of composite films were tested by energy-dispersive X-ray spectroscopy (EDX). The results of the FTIR indicate that ZnO were successfully embedded in the POT via chemical interactions between ZnO and OT monomer. The results of UV-Visible showed a sharp increase in the band gap from (2.55to2.68) eV with increasing the percentage ratio of ZnO nanoparticles in POT-DBSA matrix. The EDX spectrum showed the presence of element Zn in POT-DBSA/ZnO composites, it is absent in POT-DBSA, which was consistent with the results FTIR.

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1. Introduction

The potential of synthesizing and doping of the POT with inorganic and organic acid such as HCl, H₂SO₄, CSA, HNO₃, DBSA and HClO₄ is one of the electronic key factors responsible for many uses [1–3]. Poly (o-toluidine) is one of the most promising replace polyaniline [4–6] due to its excellent chemical stability with a high level of conductivity, easily polymerization and polyaniline poor solubility in a plurality of solvents. Therefore, POT doped with organic acids dodecylbenzene sulfonate (DBSA) containing long alkyl chains could be dissoluble in collective common solvents, such as toluene, xylene, m-cresol and chloroform [7–9]. DBSA has many industrial applications like as an emulsifier for agricultural herbicides, in emulsion polymerization and as a coupling agent [10]. To solve the problem of poor chemical, thermal and mechanical possession of conducting polymers in applications and system formation is limited, a great quantity of study has been performed

to prepare composites/ nanocomposites of conducting polymer with other nanoparticles [11–16]. POT has been probably the most widely studied one. Indeed, have studied the chemical polymerization of (O-toluidine)(OT) and its application in solar cell [17,18]. The electro polymerization of OT was studied by other authors using various electrolytes with different weight ratios, these works revealed that POTs have interesting electro-optical properties and can be used as electrochromic and electronic devices [19]. There are three major preparations methods which can be used to get inorganic-polymer composites, direct blending of more components insolvent, in-situ polymerization of monomer units in existence of inorganic-particles and dissolve blending of inorganic particles with polymer [20,21]. Nano structure materials with a diversity of forms, such as nanofibers, nanoparticles, nanobelts, and nanowire, are large interest due to their interesting applications in many fields. ZnO an important semi-conductive oxide, is a II–VI set compound semiconductor with a direct band gap and a large exciton binding energy (3.37) eV and (about 60 meV) at room temperature [22]. The great interaction of POT–DBSA/ ZnO composite is instituted on the roof area as the magnitude of ZnO NPs diminution, the surface to volume proportion and specific area

* Corresponding author.

E-mail addresses: Rounq4@gmail.com (R.A. Talib), dalal.thebayh@uobasrah.edu.iq (D.K. Thbayh).

safely increase. The relatively high particle surface area is highly beneficial for the better employ of POT–DBSA/ZnO nanocomposite. In the current work, the synthesis of composites of soluble POT

doped with dodecylbenzene sulfonate (POT–DBSA) was used to compositeness with different weight ratios of ZnO nanoparticles structural by in-situ chemical oxidative polymerization method

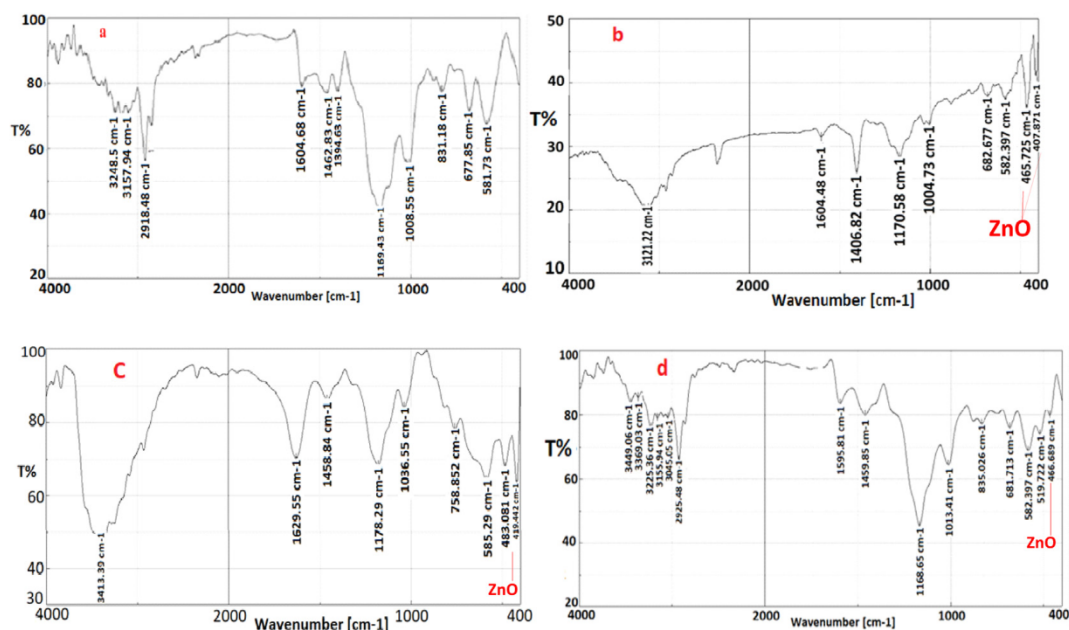


Fig. 1. FTIR spectra of (a) dopant POT, (b) POT-DBSA/5% ZnO, (c) POT-DBSA/10% ZnO, and (d) POT-DBSA/15% ZnO nanocomposites.

Table 1

Characteristic frequencies of chemically synthesized modes of the dopant POT and POT-DBSA/ZnO nanocomposites.

Assignment	Wave number (cm ⁻¹)POT-DBSA	Wave number (cm ⁻¹)POT-DBSA/5%ZnO	Wave number (cm ⁻¹)POT-DBSA/10%ZnO	Wave number (cm ⁻¹)POT-DBSA/15%ZnO
Zn–O	–	407	419	466
C–N–C bonding mode of aromatic ring	581	465	483	519
C–H out of plane bonding in benzenoid ring	677	582	586	582
C–H in plane bonding	1008	682	756	681
Vibration band of the dopant ion	1169	1004	1036	1013
C=C stretching mode of the benzenoid rings	1462	1170	1178	1168
C=C stretching mode of the quinoid rings	1604	1406	1458	1459
H–N stretching vibration	3248	1629	1595	1595
		3121	3413	3449

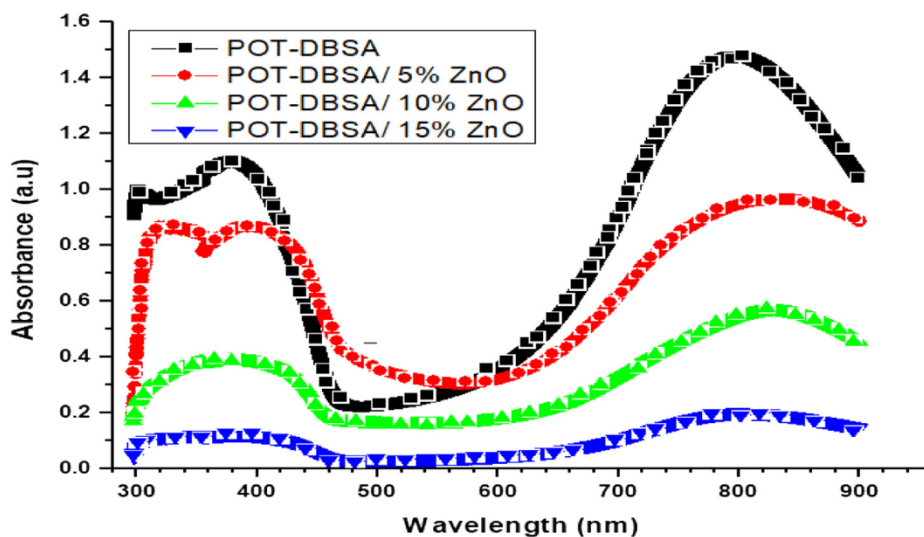


Fig. 2. UV–Visible spectra of POT-DBSA, and POT-DBSA/ (5, 10, and 15 wt%) ZnO nano composites using chloroform as solvent.

is presented, which has not been reported so far. The effect of various weight ratios of ZnO nanoparticles on the optical properties of the polymer has been studied by using various analytical optical techniques.

2. Experimental

2.1. Materials

O-Toluidine monomer (Fisher scientific company, USA), Dodecylbenzene sulfonate (DBSA) (Sigma Aldrich, USA), Ammonium peroxydisulphate (APS) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Sigma Aldrich, USA), Hydrochloric acid (Fluka company, USA), Zinc dioxide (Spadana Nano Pars Co.) from Iran, and Chloroform was bought from Sigma-Aldrich company, USA.

2.2. Preparation of POT doped with dodecyl benzene sulfonic acid (POT-DBSA)

Poly(o-toluidine) doped with DBSA was synthesized by blending in the same volume ratios of the 5.2 gm $(\text{NH}_4)_2\text{S}_2\text{O}_8$ prepared in 1 M HCl into 1.7 gm OT monomer prepared in HCl with weighted 5.8 gm DBSA. Stirring by a magnetic stirrer for a period of 24 h, a green gel was acquired [16,23,24] which was filtered, frequently washed by distilled water to take off the excess impurities and dried at 70 °C for 6 h. The resultant was a green powder (POT-DBSA).

2.3. Synthesis of POT-DBSA/ ZnO nanocomposite

POT-DBSA/ZnO nanocomposite which was prepared by in-situ oxidative polymerization of OT in the existence of ZnO nanoparticles utilizing $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidizing agent. The ZnO (5, 10, and 15 wt%) nanoparticles were pouring them to sol of OT-DBSA and polymerization was affected by the collection of solution of oxidant $(\text{NH}_4)_2\text{S}_2\text{O}_8$ synthetic in 1 M HCl. The collection of oxidant sol led to the polymerization of adsorbed OT on ZnO NPs resulting in the greenish precipitate colored solution and was preserved under stirring for a period of 24 h. The interaction blend was filtered, after that, washed with double distilled water to take off

surplus acid. The composite prepared was dried at the 70 °C, which was changed into powders. Thin films of POT-DBSA (dopant polymer) and POT-DBSA/ZnO (nanocomposites) on glass substrate were synthesized by using the spin coating method (Backer laboratory equipment, VE135N Model). In this method, the dopant polymer and nano composites dissolved in chloroform, the solution was then spread on a rotating substrate at a speed 1000 rpm for 30 s. When the solvent is evaporated, the thin polymer and nanocomposites layer is remaining.

Table 2

Summary of energy gap of POT-DBSA and POT-DBSA(5, 10, and 15 wt%) composites from optical absorption spectra.

Wt% ZnO in POT-DBSA	Eg (ev)
0	2.55
0.05	2.6
0.1	2.64
0.15	2.68

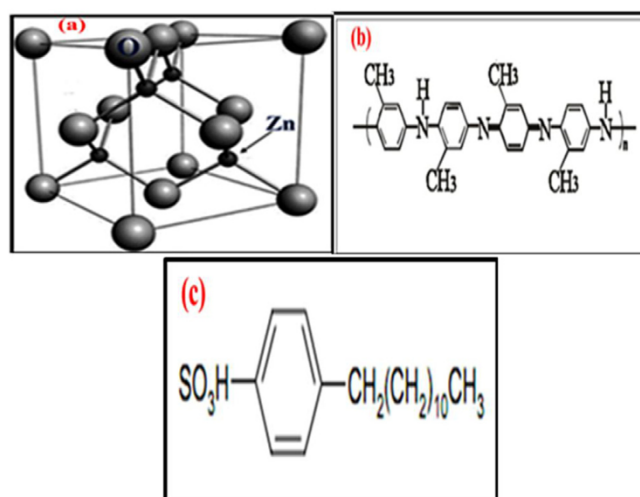


Fig. 4. The basic chemical structure of (a) ZnO (b) POT, and (c) DBSA [40,41].

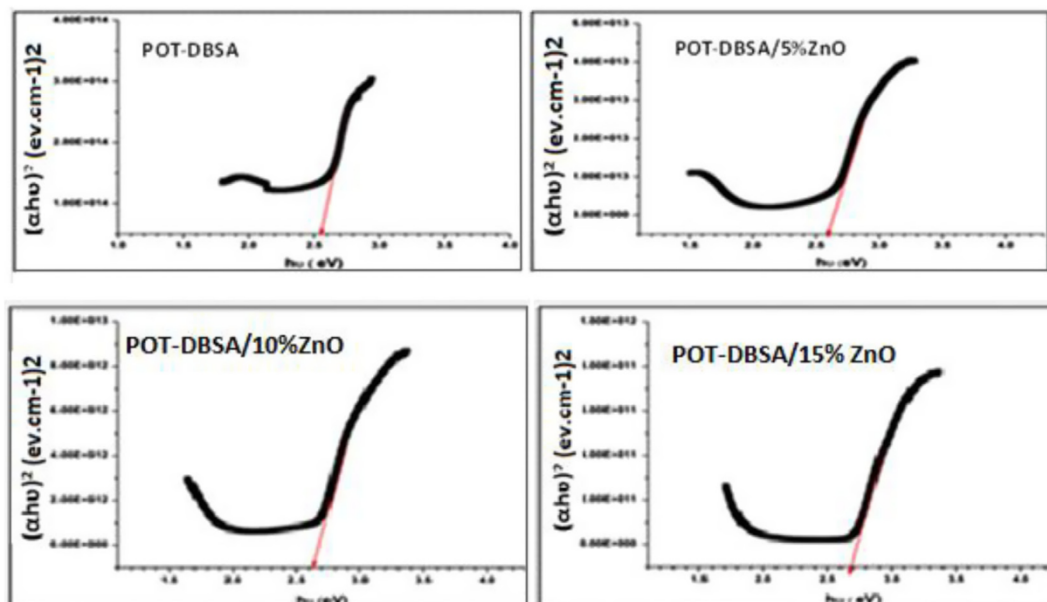


Fig. 3. Plot of $(\alpha hv)^2$ vs (hv) for POT-DBSA, and POT-DBSA/(5, 10, and 15 wt%) ZnO nanocomposites.

Fourier transform infrared (FT-IR) spectra were obtained the result on FT-IR 4200, Jasco. UV-visible spectra (CECIL(CE-7200), Aquarius) at wavelengths of 300–900 nm. EDX was performed on (FEI, Nova Nano SEM 450).

3. Results and discussion

3.1. FTIR spectroscopy test

The FT-IR spectra of the dopant POT and POT-DBSA/ (5, 10, and 15 wt% ZnO) nanocomposites are shown in Fig. 1 (a, b, c & d). Table 1

gives the special bands and their position. All of the FTIR spectra, Fig. 1, exhibit the POT characteristic peaks such as the vibration of quinoid rings at 1598 cm^{-1} while, the lower frequency mode at 1462 cm^{-1} describes the existence of benzenoid ring units [10,25]. The existence of these two peaks shows that the conducting polymer is possessed of the amine and imine units [26]. The band at 1169 cm^{-1} can be assigned to a vibration band of the dopant ion, which is created in protonation of DBSA with POT [25,27]. The band at 3248 cm^{-1} can be attributed to the N–H vibration [25]. There is another band present around 1008 cm^{-1} , corresponding to the C–H band [25]. 677 cm^{-1} (C–H out of plane bending vibration) [25],

Table 3
EDX data of (a) dopant POT, (b) POT-DBSA/5% ZnO, (c) POT-DBSA/ 10% ZnO, and (d) POT-DBSA/15% ZnO.

(a)

Element	Mass [%]	Atom [%]
Carbon	70.43	72.41
Nitrogen	3.74	3.29
Oxygen	24.20	18.68
Silicon	1.82	0.80
Sulfur	8.48	3.26
Molybdenum	12.08	1.56
	120.74	100.00

(b)

Elt	Line	W%	A%
C	Ka	62.02	75.49
O	Ka	17.77	16.23
Al	Ka	1.11	0.60
S	Ka	14.56	6.64
Fe	La	0.68	0.18
Zn	La	3.87	0.86
		100.00	100.00

Elt	Line	W%	A%
C	Ka	60.43	74.11
O	Ka	19.19	17.67
S	Ka	15.34	7.05
Fe	La	0.99	0.26
Zn	La	4.05	0.91
		100.00	100.00

(c)

Elt	Line	W%	A%
C	Ka	44.51	56.54
O	Ka	35.58	33.93
Al	Ka	5.15	2.91
S	Ka	12.98	6.18
Fe	La	0.73	0.20
Zn	La	1.04	0.24
		100.00	100.00

(d)

581 cm⁻¹ (C–N–C bonding of aromatic ring). These outcomes are in perfect agreement with a prior spectroscopic description of POT [3,23]. With the addition of ZnO nanoparticles into POT in Fig. 1 (b, c, and d), ZnO peaks appear at approximately 413 and 471 cm⁻¹ is linked to the Zn–O stretching mode, It does not exist in POT-DBSA [28–32]. The apparent changes clearly in position of peaks and intensity of IR vibrational bands in composites due to the interaction amidst the ZnO NPs and POT in the polymer chain. This implies that POT and ZnO possibly from a hydrogen bonding via the interaction of imine group of POT with the surface defect of ZnO materials [33].

3.2. UV-Visible spectra

The optical absorption spectra of dopant POT and nanocomposites films are presented in Fig. 2, was listed in the wavelength domain of (250–900) nm. In all studied samples, the spectra reveal the existence of different peaks at 300, 400 and 800 nm. The first absorption peak denotes π - π^* transition of benzenoid rings appearing at 300 nm. Transformation of POT to the green colour (POT-DBSA) form led to significant expanding of the 300 nm peak with the look of second broadband at the region at and above 400 nm referencing a polaron–bipolaron transition [34]. The general doping polymer phase appearing at 800 nm, it is noted that emeraldine salt of POT-DBSA is stabilizing in chloroform [10]. The absorption spectrum of the POT-DBSA/ZnO is characterized by bands comparable to that of POT-DBSA, although, shifting in the wavelengths and a reduction in the intensity of absorption bands identical to that of POT-DBSA as the concentration of ZnO NPs was increased in the composites, the same result [35], showing that there occurs an intense interaction between the POT-DBSA with ZnO nanocomposite in the blend. The energy of band gap of the films has been studied using Eq. (1) [36]:

$$(\alpha hv) = A_0(hv - E_g)^{1/2} \quad (1)$$

where $h\nu$ is the optical photon, A_0 is a constant, E_g is the energy of band gap, and α is the absorption coefficient that is defined by the Beer-Lambert's law [37]:

$$\alpha = \frac{2.303A}{d} \quad (2)$$

where A is the absorbance and d is the film thickness. The optical band gap can be calculated via plotting $(\alpha hv)^2$ versus $h\nu$. A plot appearance of the relation between $h\nu$ and $(\alpha hv)^2$ is shown in Fig. 3. The E_g amount is gained using the linear segment of the curve to the optical photon $h\nu$ in the figure. The energy band-gap amount gained from the optical absorption spectra are registered in Table 2. The optical band gap is observed to increase with the addition of the ZnO nanoparticles. The increase in optical band gap amount from 2.55 eV to 2.68 eV is attributed to incorporation of ZnO nanoparticles, confirms the formation of POT-DBSA/ZnO hybrid nanocomposites [38], or because of is harmonious with the quantum confinement effects of ZnO nanoparticles [39].

3.3. EDX analysis

Fig. 4 display the basic chemical structure of POT, DBSA, and ZnO. The EDX spectrum shown in the Table 3, reveals the presence of Zn, O, S, and C elements (C, S peaks appear from POT-DBSA) in the dopant POT and composites. It can be concluded that the presence of Zn element in POT-DBSA/ ZnO composite in Table 3 (b, c, and d) the outcome from an interaction of POT-DBSA with ZnO nanoparticles, given it is absent in Table 3(a) for POT-DBSA. Moreover, the percentage of Zn, O elements noticeably increased with increasing ratio of ZnO to POT-DBSA.

4. Conclusion

POT dopant with DBSA/Nano ZnO composites were successfully prepared using in-situ polymerization of (o-toluidine) monomer in existence of different weight ratio of ZnO nanoparticles. Peaks of ZnO and POT-DBSA specified in the FTIR confirm the interaction amidst ZnO and polymer. The energy of band gap derived from the absorbance spectra increased from 2.55 eV to 2.68 eV with the increased of wt% ZnO in the POT-DBSA. The EDX spectrum reveals the presence of Zn element in POT-DBSA/ ZnO results from an interaction of POT-DBSA with ZnO nanoparticles, which was not the case in POT-DBSA.

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