# Effect Of Cobalt’s Chloride On The Optical Properties Of Poly (O-Toluidine) And Study Of It’s Organic/Inorganic Solar Cell

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## Abstract

Preparation of poly (o-toluidine) was doped by different volume ratios of cobalt chloride and characterized by (FT-IR, XRD and SEM). The results showed that the intensity of absorption increased while energy gaps of the prepared polymer decreased with respect to increasing ratio of the dopant where the direct and indirect energy gaps were calculated, in addition to edge of the absorption. Photovoltaic device was fabricated by deposit the prepared polymer on the n-type silicon by spin coating method, so the batter efficiency of the prepared devices was 3.02% which was tested under dark and illumination with intensity of 100mW/cm².

**Keywords:** Poly (o-toluidine), cobalt’s chloride, solar cell

## Introduction

In the last years, the conductive polymers had the attention of researchers to fabricate many electronical devices and other applications such as schottky diodes, LED, FET, sensors and inhibitor for carbon steel (Yu-Kai Han et al, 2014; A. Elmansouri et al, 2009; T. P. Nguyen et al, 2009; Jeongwoo Lee et al, 2010; A. Benchikh et al, 2009). One of the conducting polymers was poly aniline and its derivative such as poly (o-ansidine) (POA) and poly (o- toluidine) (POT). The polymer (POT) was used in this study because it has many important characteristics, like optical and electrical properties, inexpensiveness and environmental stability (Anand Kumar et al, 2011) besides another more advantage which is synthesis of the POT by chemical polymerization mothed considered as a common attention mothed. (Kareema. M. Ziadan et al, 2012; K. M. Zaidan et al, 2012; Vasant Chabukswar et al, 2011). In spite of the above advantages but many researchers still make enhancement to (POT) to get better properties according to urgent need to use it in different application fields. One of the manners used to enhance properties of the polymer is it’s doping by different dopants (organic and inorganic dopants) (L. Skjolding et al, 2008; Shihai Ding et al, 2006; D.D. Borole et al, 2002). The Cobalt chloride ($CoCl_2.6H_2o$) which was considered as the important dopants to modify the acidity of NaY zeolite (M. ZENDEHDEL et al, 2007). The organic solar cells have a large area of researchers attention in the field of renew energy due to their properties such as solution processability, organic thin film devices which can be fabricated with low cost manufacturing techniques, modifying the chemical structure of the compounds (organic semiconductors) in endless combinations and furthermore, the organic molecules have reduced costs compared with traditional photovoltaics and ecological significant advantage (Yunlong Guo et al, 2014; Youjun He et al, 2012; Chen Zhao et al, 2013; Marianne Strange et al, 2008; F.C. Krebs, 2009; G. Hadziioannou et al, 1999; C. Winder et al, 2004). In previous studies which were reported as success attempts to fabricate the photovoltaic devices where POT polymer used as active layer whereas the better power conversion efficiency, open voltage circuit ($V_{oc}$), short circuit current ($J_{sc}$) and full factor (FF) were 2.55%, 0.46V, 13 mA/cm$^2$and 0.426 respectively after doped it by para – toluene sulfonic acid (PTSA) (KAREEMA.M.ZIADAN et al, 2013). This article included the synthesis of POT and it’s doping by different volume ratios of the cobalt’s chloride and study of the optical properties and tested as active layers for solar cell applications. The charge separation process at the Donor:Acceptor interface in an organic/inorganic solar cell included the main photovoltaic steps: (1) photo-excitation into excitons , (2) excitons migration to interfaces, (3) charge transfer from the donor to the acceptor at the interface and (4) the charge collected by electrodes (Blom et al, 2007).

## Experimental work

Poly (O-Toluidine) was prepared by using chemical polymerization of O-Toluidine monomers. 0.27M of o-Toluidine monomer in 0.25M HCL by using constant stirrer at (0-5) ℃ for 30 min. 10 gm of ammonium per sulphate was dissolved in distilled water which was added to the dissolved monomer as drop by drop for ~20 min. to keep a ratio of the monomer to oxidizing agent as (1:2). After completing dropping ammonium per sulphate, the mixture continued in stirrer for 24hr´s more to obtain a greenish-black precipitate of the polymer which was filtered and washed three times by distilled water, methanol and acetone respectively. The resulted polymer was characterized by FT-IR and XRD techniques as explained in detail in our previous study (R.K.Fakher Alfahed et al, 2015). The process of doping has been made by dissolve 10mg of POT per 1ml of formic acid, and also cobalt chloride was dissolved in formic acid with concentration of (0.042M).The different volume ratios (5%, 10%, 20%, 30%, 40% V/V) was added to the dissolved POT and permitted to be mixed by used magnetic stirrer for 5hr´s, then the doped POT solution deposited on the different substrates for study. The class substrate is used to study the optical properties, XRD analysis and test the morphology of the POT by SEM as well as silicon wafer (Si-n) used as substrate to fabrication solar cell which was etched by Hydrofluoric acid (HF) before deposit the POT on it, then gold and Aluminum was deposited as electrodes on the top and back of solar cell respectively as shown in figure (1) and the thickness of the prepared samples was measured by Ellipsometry instrument to be (45.86, 55.7, 55.75, 55.94, 56.69, 58.2) nm for pure and 5%doped, 10%doped, 20%doped, 30%doped, 40%doped respectively.

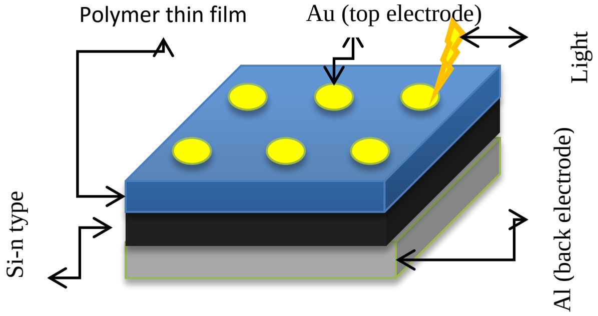


Fig. (1): structure of photovoltaic device.

## Results and discussions

### SEM Characterizations

The morphology images of the POT and doped POT were illustrated in figure (2). It show that the roughness's of the surfaces of these samples increase with increasing the dopants which were POT/salt composite films are well dispersed in POT matrix and displayed surfaces without pin holes , high roughness and more compact because of the present of HCL. At the volume ratio of dopant (20%), the surface has less roughness because of the dopant and polymer reaching to complete mixed (D. J. Walsh et al, 1985).

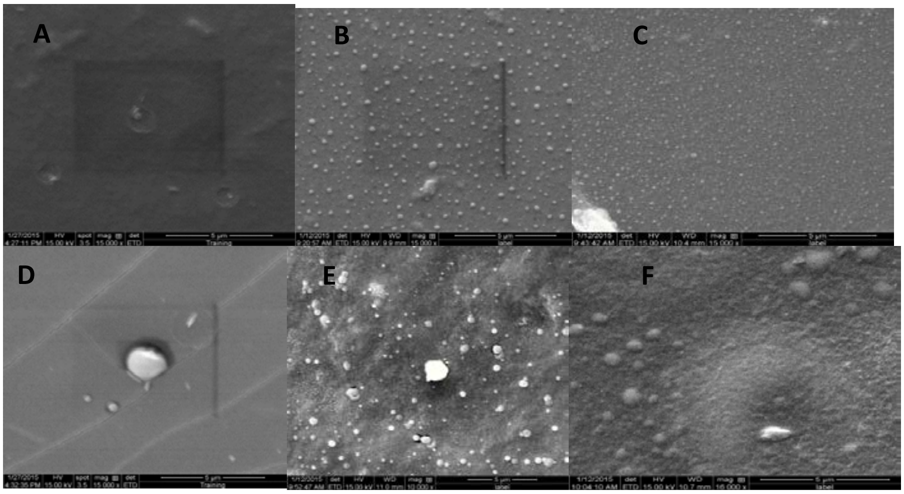
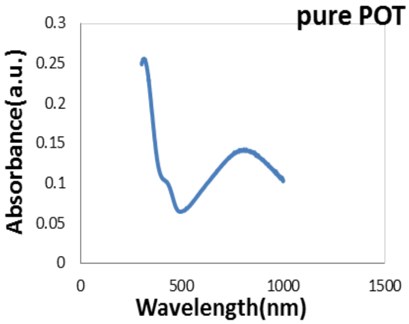


Fig. 2: SEM image of POT and doped POT: (A) pure POT, (B) 5%doped, (C) 10% doped, (D) 20% doped, (E) 30% doped, (F) 40% doped.

## UV-Visible spectra of POT and doped POT

Absorption spectra of the prepared polymers were recorded at room temperature in the wavelength range (250-1000) nm by using UV-visible spectrophotometer (Cary 50 scan VARIAN). Absorption spectra of the pure POT showed three absorbance peaks at ( 312 , 426 , 803 ) as illustrated in figure (3) which were represented as the $\pi$-$\pi^*$ , polaron- $\pi^*$ and $\pi$-polaron transition respectively, this result was agreed with previous studies (Shihai Ding et al, 2006; D.D. Borole et al, 2002). The appearance of these peaks was produced due to presenting the Hydrochloric acid (HCL) as result as increases degree of the polymerization which led to increase in the molecular weight of the synthesized polymer at low temperature degree (0-5) °C. This result was agreed with previous studies (D. Geethalakshmia et al, 2014).



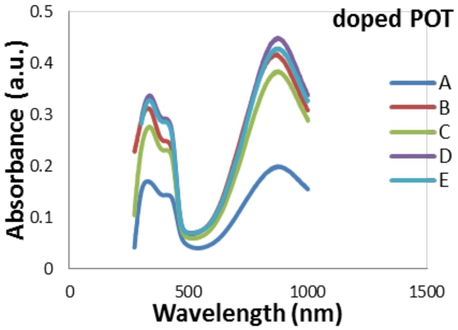


Fig. 3: absorption spectrum of pure POT.

Fig. 4: absorption spectra of doped POT by different volume ratios of cobalt chloride:- (A) POT-5%cobalt chloride, (B)POT 10%cobalt chloride, (C) POT- 20%cobalt's chloride, (D) POT-30%cobalt chloride, (E) POT- 40%cobalt chloride.

The important features for influence of doping process on the absorption polymer spectra by cobalt chloride are shifting third peaks to high wavelength in addition to have high intensity and at same time the intensity of first peaks were decreased. The absorption spectra of POT doped by different volume ratios (5%, 10%, 20%, 30%, 40% V/V) as illustrated in figure (4) they showed three absorption peaks have positions as tabulated in table (1), the first peaks denoted to $\pi$-$\pi^*$ electronic transition (benzenoid ring) and its position attributed to degree of the conjugation between the neighboring phenylene rings in polymer chain. These peaks displayed a hypochromic shift (change of spectral band site in absorption of a molecule to the shorter wavelengths) with respect to transition in POT due to steric effects of $-CH_3$ groups which led to reduce the conjugation length in POT. The second peaks referred to polaron-$\pi^*$ (bipolaronic transition) because of the protonation of the polymer main chain was occurred and the electron transferred from benzenoid to quinoid rings. While the third peaks assigned to polaron-$\pi$ transition which suggests that the free carriers were presented. The intensity of the polymer absorption peaks before and after doping process were different, it was suggested that when the intensity of third peaks are higher than first peaks that refer to predominance quinoid rings rather than benzenoid rings and also when comparing third peaks with second peaks it's clear that the polarons rather than bipolarons [D.D. Borole et al, 2002; D. Geethalakshmia et al, 2014; Z. Mucuk et al, 2009).

Table 1: absorption peaks positions of doped POT.

| material | 1st. peak | 2nd. peaks | 3rd. peaks |
|---|---|---|---|
| POT-5% $CoCl_2.6H_2o$ | 327 | 415 | 871 |
| POT-10% $CoCl_2.6H_2o$ | 322 | 426 | 874 |
| POT-20% $CoCl_2.6H_2o$ | 334 | 434 | 882 |
| POT-30% $CoCl_2.6H_2o$ | 337 | 409 | 876 |
| POT-40% $CoCl_2.6H_2o$ | 332 | 407 | 876 |

The values of absorption edge of pour POT and doped POT by different volume ratios of cobalt chloride were determined by plotting absorption coefficient (which calculated according to equation 1 (Omed Gh. Abdullah et al, 2013)) versus photon energy and then extrapolating the linear portion of curves to zero. The values of absorption edge are tabulated in table (2) were decreased with increasing the volume amount of dopants (cobalt chloride) due to localized states were created in the band gap of polymers (O.G. Abdullah et al, 2013) as shown in figure (5).

$$\alpha = \frac{2.3o3}{d}\log\left(\frac{I_0}{I}\right) = \frac{2.303}{d}\,A \qquad (1)$$

Where $I_0$and $I$ are the intensities of incident and transmitted radiation respectively, $d$ is the thickness of the sample. In addition, the absorbance (A) was determined by subtracting the value of less absorption from the absorption spectrum.

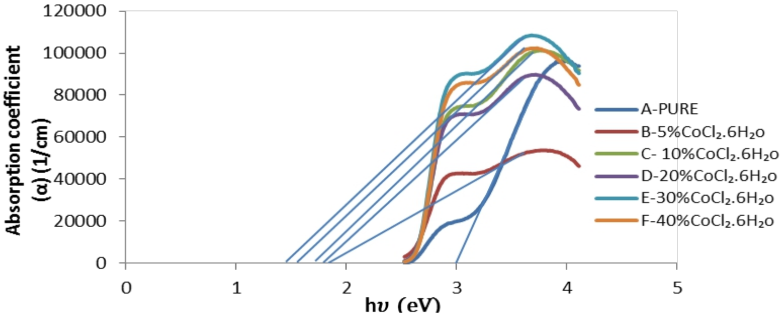


Fig. 5: Relation of absorbance coefficient ($\alpha$) versus ($h\nu$) for doped POT.

The optical energy gap of POT and doped POT by different volume ratios (5%, 10%, 20%, 30%, and 40%) cobalt's chloride were determined according to Tauc's relation (Youjun He et al, 2012).

$$\alpha h\gamma = A(h\gamma - E_g)^{1/n} \qquad (2)$$

Where hγ is the photon energy, α is absorption coefficient, A is a proportional constant and the value of n equal to (1/2, 3/2, 2, 3) for direct allowed, direct forbidden, indirect allowed and indirect forbidden transition respectively.

| material | Direct Energy gap | | Indirect Energy gap | | Absorption edge |
|---|---|---|---|---|---|
| | allowed | forbidden | allowed | forbidden | |
| Pure POT | 3.25 | 3.32 | 2.6 | 2.62 | 3 |
| POT-5% CoCl$_2$.6H$_2$o | 2.81 | 2.96 | 2.51 | 2.56 | 1.9 |
| POT-10% CoCl$_2$.6H$_2$o | 2.79 | 2.9 | 2.57 | 2.59 | 1.82 |
| POT-20% CoCl$_2$.6H$_2$o | 2.69 | 2.85 | 2.58 | 2.6 | 1.75 |
| POT-30% CoCl$_2$.6H$_2$o | 2.66 | 2.8 | 2.58 | 2.59 | 1.5 |
| POT-40% CoCl$_2$.6H$_2$o | 2.72 | 2.89 | 2.8 | 2.6 | 1.68 |

The value of energy gaps was decreased as result of increasing the amount of dopant (cobalt chloride) in which the reduced in energy gap was due to creation of polaron and bipolaron states between valance (V-B) and conduction band (B-V) of the polymers which means the cobalt chloride formed charge transfer complexes in polymer matrix and also led to increase the electrical conductivity due to increase the charges in lattice (Omed Gh. Abdullah et al, 2013; V. Raja et al, 2003). All the direct and indirect energy gaps were determined and listed in table (2).

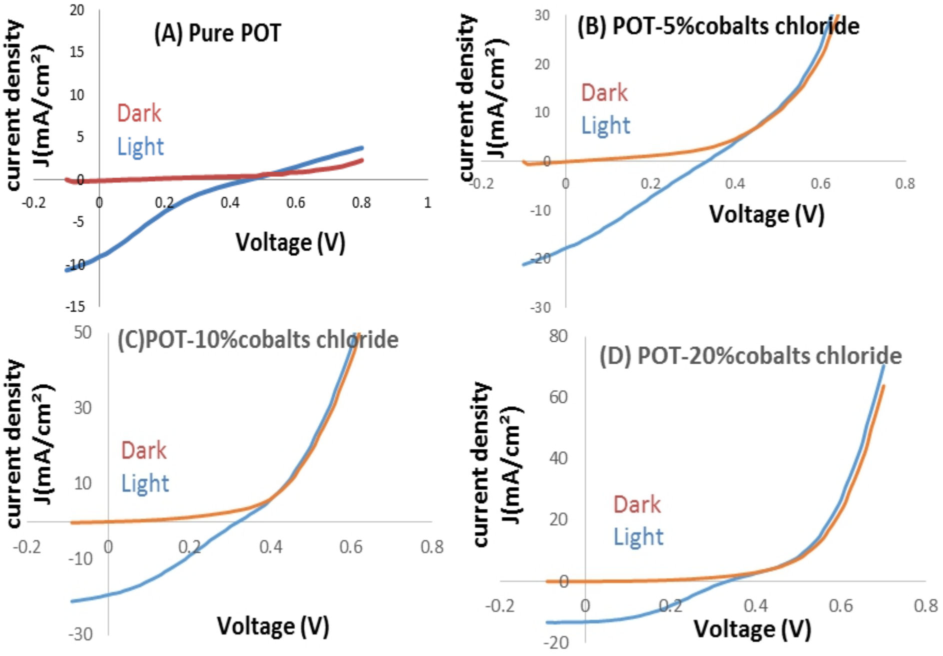
Table 2: The values of the absorption edge and band energy of POT and doped POT by different volume ratios of cobalt's chloride.

## J-V characterization of POT and doped POT solar cell devices

The J-V characterizations of poly (o-toluidine) (POT) and POT doped by different volume ratios of (5%, 10%, 20%, 30%, 40%) cobalt chloride ($CoCl_2.6H_2o$) for prepared photovoltaic devices in thickness (45.86, 55.7, 55.75, 55.94, 56.69, 58.2) nm as showed in figure (6). The performance of prepared devices for different volume ratios were studied according to these parameters as tabulated in table (3) in which the short circuit current ($J_{sc}$) and open circuit voltage ($V_{oc}$) were measured directly from the figures when applied voltage equal to zero and current of cell equal to zero respectively, while the series resistance ($R_s$) and shunt resistance ($R_{sh}$) were calculated according to inverse of the slope of I-V characteristics at V = 0 and I=0 in case of reverse and forward bias respectively, also full factor (FF) and power conversion efficiency (ƞ) were calculated according to equations (3 and 4), respectively [N. Khalifa et al, 2015; K. Y. Law et al, 1993; Teng Xiao et al, 2012).

$$FF = (V_{max}.J_{max})/(V_{oc}.J_{sc}) = P_{max}/(V_{oc}.J_{sc}) \qquad (3)$$

$$\eta = (P_{max}/P_{in}) = (V_{max}.J_{max})/P_{in} = (FF.V_{oc}.J_{sc})/P_{in} \qquad (4)$$



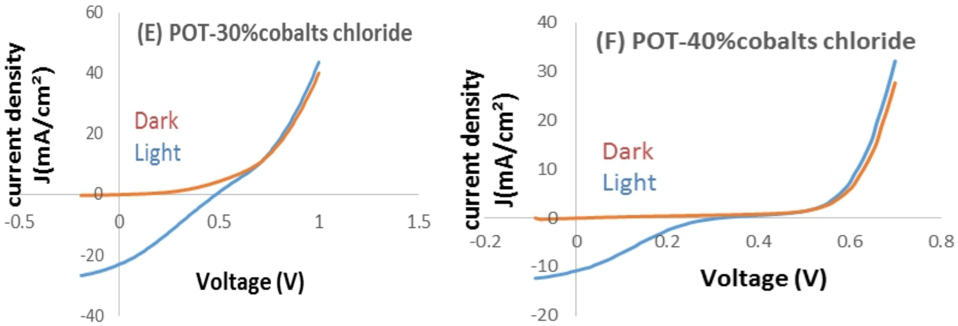


Fig. 6: J-V curves of POT and doped POT solar cell devices: (A) pure POT, (B) POT-5% cobalt chloride, (C) POT-10% cobalt chloride, (D) POT-20% cobalt chloride, (E) POT-30% cobalt chloride, (F) POT-40% cobalt chloride.

Table 3: Parameters calculated from (J-V) characteristic of pure and doped POT.

| Material | $V_{oc}$ (V) | $J_{sc}$ $(\frac{mA}{cm^2})$ | $V_p$ (V) | $J_p$ $(\frac{mA}{cm^2})$ | $P_{max}$ $(\frac{mW}{cm^2})$ | FF (a.u.) | η (%) | $R_s$ (Ω) | $R_{sh}$ (Ω) |
|---|---|---|---|---|---|---|---|---|---|
| Pure POT | 0.44 | 9.09 | 0.18 | 4.326 | 778.6 | 0.19 | 0.78 | 2989.9 | 2119.3 |
| POT-5% $CoCl_2.6H_2o$ | 0.33 | 17.8 | 0.17 | 9.1666 | 1558.3 | 0.26 | 1.56 | 245.1 | 990.1 |
| POT-10% $CoCl_2.6H_2o$ | 0.31 | 19.38 | 0.17 | 11.328 | 1925.8 | 0.32 | 1.93 | 239.5 | 1840.6 |
| POT-20% $CoCl_2.6H_2o$ | 0.33 | 13.2 | 0.18 | 9.065 | 1631.7 | 0.37 | 1.6 | 192 | 17716.2 |
| POT-30% $CoCl_2.6H_2o$ | 0.43 | 24.2 | 0.23 | 13.127 | 3019.3 | 0.29 | 3.02 | 325 | 1512.9 |
| POT-40% $CoCl_2.6H_2o$ | 0.31 | 10.83 | 0.13 | 5.7733 | 750.5 | 0.22 | 0.75 | 529 | 2013.9 |

The efficiency of the prepared photovoltaic devices increased with increasing of dopants to be maximum value at the ratio of doping as 30% doped which exhibited the best photovoltaic performance, the value of Voc is 0.48 V, Jsc is 22.999 mA/cm², FF is 0.2842 and η is 3.0193% which reflected a better power conversion efficiency compared with other devices because of the absorption of incident light was slightly high furthermore, have excitation states which are increased the generated excitons (V. S. Arunachalam and E.L.Fleischer, 2008). The efficiency of the 20%doped decrease comparing with 10% and 30% that, was because surface morphology of the sample was smooth which led to less amount of the absorbed light and given low electron hopping transport, in other words, surface roughness of the active layer considered as important parameter because of its increase the photo-generated charge carriers near the site of contact between active layer and metallic electrode which support high efficient generation, extraction, collection of the photo-generated charge carriers and then the better power conversion efficiency was resulted (Yamamoto K et al, 1998; Riedel I. et al, 2004; Heejoo Kim et al, 2006; Heejoo Kim et al, 2007; Gang Li et al, 2005; Wanli Ma et al, 2005). Also the influence of shunt resistance on short circuit current was resulted due to increase the recombination of charge carrier near the dissociated site which was clear respect to doping process as 20% which led to decrease the power conversion efficiency (L.-M. Chen et al, 2009). The efficiency at ratio of dopant 40% was decreased due to decrease in short circuit current as result as to increase the shunt resistance to be (2013.91Ω) which resulted from recombination process in addition to properties of material at this ratio as like electrical and optical properties were decreased in conductivity and intensity of absorption respectively.

## Conclusion

Chemical polymerization method used to prepare poly (o-toluidine) and doping it by different volume ratios of cobalt's chloride which is characteristic with FTIR, XRD and SEM. POT and doped POT thin films have been prepared by spin coating method on different substrates. The absorption spectra of POT and doped POT were studied and showed three absorption peaks decreased in the energy gap with increasing the ratio of dopants in addition to absorption edge was calculated. The current density-voltage (J-V) characteristics of the prepared photovoltaic devices were studies which appeared increasing in the power conversion efficiency with increasing the ratio of dopants.

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