Structural Morphology and Optical Properties of Nanocomposites based Conducting Polymer

Manal A. Saleh, Mohammed K. Jawad
Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq
E-mail corresponding auther: mohamedkadhom66@gmail.com

Abstract: A simple, inexpensive, pulsed laser deposition (PLD) technique excimer source Nd:YAG laser was used for the preparation of the all films irradiation targets and deposite of nickel oxide NiO, polypyrrole PPy, carboxylic functionalized multi-walled carbon nanotubes (f-MWCNT), [PPy:(f-MWCNT)] nanocomposite, [NiO/PPy:(f-MWCNT)] and [PPy:(f-MWCNT)/ NiO] films on fluorine-doped tin oxide (FTO) substrates. Surface morphology of all films and nanocomposite was investigated by Scanning Electron microscopy (SEM) display various morphology on the surface of the all films and nanocomposites, but the predominant structure is granular morphology, x-ray diffraction (XRD) indicates that the peaks of all films are broadening expect for PPy are sharp peaks, the optical absorbance spectra for the studied all films showed the maximum values around (425, 333, 347, and 397) nm refer to type transitions (π*-π) and (polaron-π*) and the maximum value of NiO around 346 nm. The optical energy gap of all films was determined and values around (2.2, 2.6, 2.8, 3.2) eV. It has been observed that the measurements for films [NiO/PPy:(f-MWCNT)] and [PPy:(f-MWCNT)/NiO] may be identical and NiO nanoparticles are a good adhesion to nanocomposite films and interconnected in structure.

Keywords: Polypyrrole, functionalized Multi-walled carbon nanotubes, nanocomposites , (PLD) technique, films deposition, nickel oxide.

I. INTRODUCTION

Polypyrrole (PPy) has a considerable interest of scientists because of its distinctive features as large conductance, easy procedure of preparation, promising mechanical properties, stability, and simple fabricated as a composite matrix. Polypyrrole has large potential applications in electronics, corrosion protection, drug delivery, supercapacitors, and sensors [1]. In last year’s laser deposition of polymers gained attention due to its used in the electronics field. Besides the conductive polymers, have been utilization in composites constituent by including with nanoparticles like carbon
nanotubes (CNT) [2]. The multiwall carbon nanotubes (MWCNTs) have special features like high given area and aspect ratio which made them active as conductive fillers in polymers [3]. Furthermore, MWCNTs is famous for their rapid electron-transmitting architecture, as well possesses an electrocatalytic activity for the $I_3^-$ reduction in the electrolyte [4]. Nickel oxide NiO is recognized antiferromagnetic substance [5], and a metal imperfect p-type semiconductor [6] with a 3.6 eV band gap [7]. NiO films have a wide extent of applications because to their superior chemical fastness. They have been utilized as electrochromic devices, catalysts, and fuel cells. The goal of this research, obtained quality films from polypyrrole-functionalize multi-walled carbon nanotubes and NiO thin-film layers (PPy:f-MWCNT/NiO) nanocomposite on FTO glass by using pulsed laser deposition (PLD).

2. Experimental Part

2.1 Materials

Polypyrrole (PPy) (purity 99%, conductivity 10-50 S m$^{-1}$, D=0.99 g/ml Sigma–Aldrich), dry powder, f-MWCNT, (purity of >98%, D=0.28 g/cm$^3$ with 20 to 30 nm diameter, 10-30 μm length) were purchased from Neutrino, dry powder, FTO conductive glass (8–12 - sq$^{-1}$, Sigma–Aldrich), a thickness of 2.2mm. NiO nanoparticle powder (99% purity, MW=74.6928 g/mol) (D=6.67 g/cm$^3$) Black powder USA.

2.2 Films Deposition

The focused Nd:YAG Q-switching laser beam at 1064 nm (pulse width 10 ns, repetition frequency 6 Hz) used to prepare films of PPy, f-MWCNT, and NiO. Each films were subjected to (140 shots and pulse energy of 200 mJ). The PPy, f-MWCNT and NiO powder films were prepared by using pulsed laser deposition on FTO conductive glass substrates keeping a distance of 1 cm from the target. An appropriate amount of the materials were compressed under 5 Ton to obtain the final pellet of 1.5 cm diameter and 0.2 cm thickness. It should be as intensive and homogeneous as much as possible to guarantee a best accuracy of the deposit the films. Also, PPy:f-MWCNT, nanocomposite film, was synthesized via a PLD method with a fixed amount (96 PPy:4 f-MWCNT)wt.%.
2.3. Preparation of (PPy:f-MWCNT/NiO), (NiO:PPy/(f-MWCNT)) Films:
After deposition [NiO, PPy, and (f-MWCNT)] films and getting [PPy:(f-MWCNT)] nanocomposite films according to the ratio and volume requirement, then NiO was deposited as a layer above and below [PPy:(f-MWCNT)] nanocomposite films in two ways: First, the nanocomposite [PPy:(f-MWCNT)] film was pulses as a first layer. Then NiO film was deposited above nanocomposite film as a second layer. The gained film of composing of two layers [PPy:(f-MWCNT)/ NiO]. Whereas the second procedure was done reverse to the first procedure to obtained films of two layers [NiO/PPy:(f-MWCNT)].

2.4. Films characterization
The morphology of the film samples was measurement by using (SEM-Sirion field emission). X-ray diffraction (XRD) was done using a Philips MRD diffractometer in the two modes. Optical reflectance measurements were carried FILMS diffraction patterns were recorded on a Panalytical Debye–Scherrer diffraction camera to examine the film crystallinity. The optical properties were survey by obtained the absorption spectra from the UV-VIS spectrophotometer with a range of 200-1100 nm.

3. Results and discussions
3.1. Structural Results
The XRD patterns of the influence of the Nd:YAG laser for each samples, NiO, PPy, [f-MWCNT], [PPy:f-MWCNT] nanocomposites, [NiO/PPy:f-MWCNT] , and [PPy:f-MWCNT/NiO] is indicated in Fig. (1 a, b, c, d, e, & f). It observes that the spectra of the grown NiO nanoparticles, showing in Fig (1a), the expanding of the line which is a feature of the formation of nanoparticles. It is found that NiO nanoparticles film display obvious one diffraction peaks, (111), (200), (220), appear at 2$\theta$ (13.35˚,18.60˚,40.85˚) respectively, which indicates NiO nanoparticles crystallization. The film deposited is assign to the (200) lattice plane reflection of the cubic NiO phase which identical to the (002) lattice plane reflection of the metallic Ni cubic phase [8], immediately output from the Ni target. The results of NiO agree with previous work [9-12]. From the structure and performance of f-MWCNT; is show in Fig (1b) it can be seen that the XRD patterns indicating the functionalized carbon nanotubes still have the same tubular structure represent the feature graphitic peak emerging due to exist of the tubular structure of the carbon atoms in the specimen with (002) planes. The peak can be attributed to the diffraction from the (002) planes of the CNTs which appears more
width. The functionalized carbon nanotubes have diffraction peaks at 23.85°. The XRD pattern of PPy shows in Fig (1c) a sharp and high intensity peak at 2θ 26.7° and lower intensity peaks at 2θ 28.55°, which are related to the periodicity parallel and vertical to the polymer chains [13, 15, 16].

The XRD pattern of [PPy:f-MWCNT] nanocomposites show in Fig. (1d), the peak at 2θ 24.25° and little dense peak display at 2θ 34.7°, can be attributed to the peak of PPy and graphite-like structure of f-MWCNT respectively. The [PPy:f-MWCNT] nanocomposite, show abroad and high intense peak appeared at around 2θ 24.25° that can be appointed as the assistance from the polymer backbone of PPy the nanocomposite film [17]. The peaks of nanocomposites are wider than the pure PPy due to the merged with the peak of PPy. [13, 14]. The interfere diffraction peaks of f-MWCNT with PPy describe the formation of [PPy:(f-MWCNT)] nanocomposite via PLD technique [18]. Fig (1e) indicates that the nanocomposites [NiO/PPy:(f-MWCNT)] and [PPy:(f-MWCNT)/NiO] display a small shift almost negligible, NiO/PPy:f-MWCNT peak appeared at 2θ = 24.35°. It was evident that the NiO nanoparticles were completely interlocked between the PPy:f-MWCNT nanocomposites and retain their identical structure.
Fig. (1): XRD patterns of, a-(NiO), b-(f-MWCNT), c- (PPy), d-(PPy:MWCNT) nanocomposite e-(PPy:f-MWCNT/NiO) and f-(NiO/PPy:f-MWCNT).
3.2 Optical Results

Fig. (2) and (3) demonstrates the optical absorption spectra and the variation of $(\alpha h\nu)^2$ versus $h\nu$ of NiO, PPy, f-MWCNT, PPy:f-MWCNT nanocomposites, NiO/PPy:f-MWCNT and PPy: f-MWCNT/NiO. The absorption spectra appear that films grown have a little absorbance in the visible / near IR-region, whereas it is a maximal in the UV-region. Fig. (2) display the absorbance for NiO film has a best value at wavelengths in the near of the essential absorption edge 346 nm. In general, the observance of the film has minimum values in the visible and near-IR-region because at the high wavelength the fallen photons don’t have adequate energy to interact with atoms, the photon will be send. As the wavelengths the decreases, the interaction between fallen photon and material will happened, and then the absorbance will increment. The result is in good agreement with [9, 10, 19].

The PPy film shows absorption peak at 475 nm, is observed in Fig. (2) films show a high value wavelength in the visible region. This is due to the lower film absorption which results from the transition of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and is related to the $\pi^*-\pi$ electronic transition along the backbone of the polymer chain, which is in good agreement with reported [20].

The absorption peak at 333 nm, for the f-MWCNT film is shifted to high wavelengths in the UV region. The absorption peak of [PPy:(f-MWCNT)] nanocomposite at approximately 397 nm is shown in Fig. (2), the characteristic peaks assigned to the polaron-$\pi^*$ transition and $\pi-\pi^*$ transition of the polymer chain, indicating that PPy has successfully created on the surface on f-MWCNT and incorporation within the PPy matrix with significant interaction between polymer chain and f-MWCNT, and weak conjugation which changes PPy from quinoid structure with big conjugation to benzenoid structure with nearly no conjugation [21]. UV-Vis peak of [NiO/PPy:(f-MWCNT)], [PPy:(f-MWCNT)/NiO] was reported at around 347 nm peak is noticing towards the longer wavelength side, refer in Fig. (2), a symmetry is observed in [NiO/PPy:(f-MWCNT)] and [PPy:(f-MWCNT)/NiO], due to the tuning of the laser influence value incident onto the targets. Indicate the electronic transition occur and the existence of different electronic levels, because of its high oxygen ion conduction [22]. A huge overlay of optical transition occurred between [PPy:(f-MWCNT)] and extrinsic states of NiO nanoparticles [24].
Fig. (3) shows energy gap value of all films, in PPy film the absorbance decreased with increasing wavelength in this range of spectrum [25], but in f-MWCNT and NiO films the absorption will increase, and it may be due to increased optical energy gap values, the absorption edge shifts towards the short wavelength side, due decrease in particle size. The band gap energy values of [PPy:(f-MWCNT)] nanocomposite that there is an increase in band gap value of nanocomposite compared PPy film because the relocation of polaron levels in the band gap of PPy due to the interaction with f-MWNT [22]. As adding NiO layer above and below nanocomposite. It can be observed that $E_g$ increases from (2.6 to 2.8) eV and shifts towards to UV-region. This transfer in the absorption peak exposes a change in an electronic structure and transition of polaron levels in PPy due to the interaction with NiO nanoparticles [23]. This may be due to decrease in grain size, thus there was agreement with SEM results depending on the structure of the film and its component. (Table1) shows the value of wavelength of absorbance edge and energy gap value. To calculate the band gap of all films, the absorption coefficient ($\alpha$) was used by using the relation [26].

$$\alpha h\nu = A (h\nu - E_g)^m$$

Where ($A$) is a constant, $E_g$ is the energy band gap of films, $h\nu$ is the incident photon energy, and ($m=1/2$) for direct allowed transitions and ($m=2$) for the indirect allowed transition.

![Absorbance versus wavelength for PPy, f-MWCNT, NiO, PPy-f-MWCNT, NiO/PPy-f-MWCNT, f-MWCNT, and NiO films.](image1)

**Fig. (2):** Absorbance versus wavelength for PPy, (f:MWCNT), NiO, [PPy:(f-MWCNT)], [NiO/PPy:(f-MWCNT)], and [PPy:(f-MWCNT)/NiO films.
Fig. (3): Variation of \((\alpha h\nu)^2\) versus \(h\nu\ eV\) for, PPy, (f-MWCNT), NiO, [PPy:(f-MWCNT)], [NiO/ PPy:(f-MWCNT)], and [PPy:(f-MWCNT)/NiO] films.

Table 1: shows the value of wavelength of absorbance edge and energy gap value

| Films            | \(\lambda\) (nm) | \(E_g\) (eV) |
|------------------|-------------------|--------------|
| NiO              | 346               | 3.2          |
| PPy              | 452               | 2.2          |
| f-MWCNT          | 333               | 3            |
| PPy: f-MWCNT     | 397               | 2.6          |
| NiO/PPy:f-MWCNT  | 347               | 2.8          |

3.3 Morphology Studies

The morphology of the samples were characterized by SEM for NiO, PPy, f-MWCNT, PPy: f-MWCNT, NiO/ PPy: f-MWCNT and PPy: f-MWCNT/NiO nanocomposites as shown in Fig. (4- a, b, c, d, & e). The photographic image for NiO of Fig. (4-a) display that the film is homogeneously distributed regular shaped, and each nanoparticle adopts a granular shape with average grain size is ~50 nm.

Fig. (4b) exhibited that the PPy film showed a spherical-like structure with concavo-convex aggregation and was disorderly. The PPy has a granular structure with a particle size in the range of ~20–50 nm. Such a structure could be inferred from that the rough surfaces coated on the FTO glass. Morphologically PPy shows the existence of small globules and porous surfaces which can beneficial for ion diffusion [27].
The SEM image for f-MWCNT is presented in Fig. (4c), which illustrate the one-dimensional structure of f-MWCNT appear as a continuous and rough meander-like film the presence of irregularly shaped flat. It can be observed a few hundreds of nm particulates quasi-spherical droplets with retaining its spherical granular structure. Moreover, a higher number of particulates also observed [28].

Experiments show that the presence of additive f-MWNTs causes a significant change in the PPy morphology. The SEM image in Fig. (4d) it can be observed that the PPy is regular coated onto the surface of (f-MWNT) structures, the PPy chains grow on the surface of (f-MWNT). [PPy:(f-MWCNT)] film was found to be covered the FTO glass resulting in spherical, cylindrical, tubular and interwoven surface structure illustrate that the outer surface of the composite is coarse. The (f-MWCNT) was included onto the PPy matrix which is expected to further enhance the conductivity and best adhesion with the substrate on the surface of the (f-MWCNT). The absorb PPy form [PPy:(f-MWCNT)] nanocomposite because possible interactions between PPy and f-MWCNT [29]. From Fig (4-e & f) display a uniform distributed and connected to the surface of the nanocomposite [PPy:(f-MWCNT)]. More active sites were available in this structure, and electron transport properties. The particle size was about 29 to 55 nm in Fig. (4e) and 29 to 45 nm in Fig. (4f) with orbicular morphology, the surface morphology considerably changed after adding NiO layer of the nanocomposite. It was observed from Fig. (4-e) porous structure has formed on the side of the film surface deposited on the substrate. Therefore, the nickel oxide film morphology changed with the deposition of the nanocomposite substrate. That producing from the propagation of the NiO at the grain frontier and the regular grain size of the film scale as seen in Fig.(4-e & f) [30].
Fig. (4): a-(NiO), b-(PPy), c-(f-MWCNT), d-[PPy:(f-MWCNT)] nanocomposite, e-[NiO/PPy:(f-MWCNT)], and f-[PPy:(f-MWCNT)/NiO] films.

4- Conclusion

In this work, films of [NiO, PPy, (f-MWCNT)], [PPy:(f-MWCNT)] [PPy:(f-MWCNT)/NiO] have been prepared by PLD method. XRD results reveals the combined broad peak and various peaks of all films expect for PPy are sharp peaks. NiO film illustrated the crystalline installation is crystallized in the cubic single phase with polycrystalline installation. Whereas optical properties show that when the absorption will increase, the optical energy gap values increased, due to decrease in particle size. It is noted for both XRD and UV measurements identification of [NiO/PPy:(f-MWCNT)] and [PPy:(f-
MWCNT)/NiO] films. The SEM of the obtained films indicates the orbicular morphology for all films.

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