



Spectroscopic Studies of Polypyrrole - PVA Reinforced Iraqi Bentonite Clay Composites

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Abstract

The mixture of Polypyrrole solution with polyvinyl alcohol reinforced Iraqi Bentonite clay are used for preparing a composite that investigated in this study. The weight percentage of bentonite used is 5, 10, 15, and 20 and the particle size selected is less than 75 μm . Composite samples prepared has a thickness of 0.15mm and dimensions of 2.6 \times 2.8 cm². The optical properties of polymer composites were studied using UV-Vis spectroscopy. The values of optical energy gap decreased from 5.44, 5.41, 5.38 and 5.28 eV for the 5, 10, 15, and 20 wt% of bentonite respectively, and the absorption coefficient increased. The extinction coefficient increases with increasing additive bentonite and decreases as the incident wave length increase. The present work is very important for tailoring the optical response of Polypyrrole – bentonite composites according to specific requirements.

Key Words: Polypyrrole, Polyvinyl Alcohol, Composite, Bentonite Clay, UV-Vis Light.

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Introduction

Composite materials were first introduced in the 1960s. From both a practical and fundamental standpoint, the study of mixtures of composite materials that consisting of at least two phases of different chemical compositions has captivated interest. The macroscopic physical properties of the composite materials can be utilized to develop materials with a desired average response (Emidio et al, 2015). Oxides, activated carbon, phenolic resins, Kaolin clay, cotton stalks, and rice husk are just a few of the materials being utilized to remove colors from industrial colored effluents. Bentonite is a rock made primarily of clay minerals, most often montmorillonite. Hectorite, nontronite, and saponite are other sematic group minerals. A variety of fillers for reinforcing polymeric materials were investigated. However, there are just a few studies that show each filler's

reinforcement effects in each matrix system (Pattabi et al, 2007). Polymer optical characteristics, on the other hand, are designed to improve reflection, polarization, antireflection, and interference properties (El-Kader et al, 2002). PPy is one of the most essential polymeric materials since it has a wide range of applications in industry and is relatively inexpensive to make (Hadi et al, 2011).

PVA is a crystalline polymer that is highly soluble in water; nevertheless, dissolving it necessitates the breakdown of the crystal structure, which must be done at a high temperature (Noor et al, 2020). Wave guides and photonic integrated circuits can be made with PVA with a controlled refractive index ranging from extremely low to very high values.

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Conducting polymers, in particular, have been extensively researched due to their one-dimensional conjugated structures, surface reactivity, and tunable conductivity. Nanostructured conducting polymers, such as nanoparticles (Eman, et al, 2020), nanofibers, nanotubes, and nanowires, have also attracted a lot of attention, owing to their potential applications in batteries (Huang et al, 2005), conducting paints, electrochemical sensors, and field emission applications (Long et al, 2011; Grim, 1970). Because of its high electrical conductivity, relatively low toxicity, good air stability, and ease of manufacture, polypyrrole (PPy) is one of the most studied conducting polymers (Pailleret et al, 2011). In general, two methods for preparing polypyrrole can be used (Jang, 2006), namely chemical and electrochemical polymerizations. During the polymerization of pyrrole, both can use a template to produce polypyrrole nanostructures (Hien et al, 2005).

For many years, researchers have been interested in studying the effects of UV light on polymers. Spectroscopy is an important aspect of this type of investigation (Liu et al, 2005). Due to the interaction between the ground and excited state aromatic groups, i.e. the creation of intermolecular excimers, polymers with pendant aromatic ring groups, such as Polypyrrole, are known to introduce a different fluorescence band at longer wavelength under irradiation. This phenomenon has long been recognized as a useful tool in the study of polymer structure (Kapil et al, 2019). The effects of Bentonite on the optical characteristics of polypyrrole and polyvinyl alcohol as fillers are discussed in this paper (Huang et al, 2004; Vetter et al, 2006).

Details of the Experiment

Liquid pyrrole (Vpyrrole = 1.36 mL, 0.2 M) was injected into a beaker containing MnO2 powder (2 g) suspended in an aqueous solution of sulphuric acid (100 mL, 1 M) at room temperature to produce polypyrrole powders. The polymerization of pyrrole began almost soon after the monomer was added to the medium. At room temperature, the mixture was magnetically stirred for 4 hours. Filtration was used to collect the black polypyrrole precipitate 6, which was then rinsed several times with deionized water before being dried at 60 °C for 24 hours (Debiemme et al, 2009).

To remove salts and some contaminants that dissolved in water, the Bentonite particles were dispersed in distilled water and shaken vigorously for 24 hours at room temperature. Following filtering, the material was dried for 24 hours at 100 degrees Celsius using a dryer type (F.G. BODE&CO-Laboratory - Equipment - Hamburg-90), milled, and sieved to a particle size of fewer than 75 microns. Table (1) shows the chemical composition of Iraqi bentonite as supplied by the Iraqi state company of geological survey and miniry. Table (2) shows the results of the mineralogical examination of the final powder of Iraqi bentonite.

Table 1. Chemical composition of used bentonite

Oxide	Wt%	Oxide	Wt%	Oxide	Wt%
SiO ₂	56.77	MgO	3.42	SO ₃	0.59
Al ₂ O ₃	26.2	Na ₂ O	1.11	Cl	0.57
Fe ₂ O ₃	5.12	K ₂ O	0.6	L.O.I (loss of ignition)	0.49
CaO	4.48	P ₂ O ₅	0.65		

Table 2. Mineralogical analysis of used bentonite

Minerals	Percentage%
Montmorillonite [OH] ₂ Al ₂ SiO ₁₀	79
Attapulgite Mg ₅ Si ₈ O ₂₀ [OH] ₂ 8H ₂ O	7
Apatite Ca ₅ [Fe, Cl] P ₃ O ₁₃	5
Calcite CaCO ₃	5
Gypsum CaSO ₄ 2H ₂ O	2
Halite NaCl	1
Quartz SiO ₂	1

Before applying the bentonite as a filler, a coated layer of PVA solution (PH~3) was applied to cover it. Heat treatment (at 80 oC) was used to keep the Polypyrrole - modified bentonite mixture in slurry form and ensure high viscosity and homogeneity. Composite samples have been prepared with bentonite contents of 5, 10, 15, and 20 wt%, have a thickness of 0.15mm and 2.6×2.8 cm² in area. The method of preparation samples has been described elsewhere. Using a Shimadzu double-beam UV-Vis Spectrophotometer (UV-210 A) in the wavelength range 190-900 nm, all samples were subjected to UV-Vis transmission and reflection investigations. The measurement method has been detailed elsewhere.

Optical Calculations

In order to investigate the optical changes of the polymers - bentonite composite, the UV-Vis



absorbance spectra were recorded in the wave length 190–900 nm.

The variation of the absorption coefficient, α , can be described as a function photon energy as shown in figure (2). It can be given by the absorbance and sample thickness as (Hassan et al, 2018).

$$\alpha = 2.303 \frac{A}{d} \quad (1)$$

Where : A and d is the absorbance and sample thickness, respectively.

The absorption coefficient(α) and the attenuation coefficient (k) is directly proportional and can be described as:

$$k = \alpha \lambda / 4\pi \quad (2)$$

Where the symbol λ is the light free space wavelength.

In the investigated spectral range, the absorption coefficient values are less than 104cm^{-1} . The nature and value of the optical band gap is obtained using fundamental absorption, which corresponds to the excitation of the electron resulted from the valence to the conduction bands. The coefficient of absorption, α , and the energy, $h\nu$, can be expressed as

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (3)$$

where A is considered as a constant that depends on the probability of the transition and n is an optical absorption process index that is equal to $1/2, 2, 1/3$, or $2/3$ for indirect allowed, direct allowed, indirect forbidden, and direct forbidden transitions, respectively, from the theoretical point of view. The most common way for calculating the energy of band gap can be done by perform a graphical representation between $(\alpha h\nu)^n$ and photon energy, $h\nu$, and then choose the n number

that produces the best linear curve. The nature of the transition or the energy gap is determined by the value of n . The value of E_g will be supplied by the intercept on the $h\nu$ -axis if a suitable value of n is used to generate a linear plot, as shown in figures.

Results and Discussion

The XRD patterns of a) Pure PPy, and b) PPy/Bentonite composite are shown in Fig. 1(a), and (b) respectively. XRD pattern of PPy exhibits abroad characteristic peak at $2\theta = 25^\circ$ broad characteristic peak at about 25° of pure PPy exhibits that pure PPy is amorphous., implying an amorphous structure (Lu et al, 2006). XRD patterns of Bentonite strong diffraction peaks are observed which are responsible for good crystalline nature other characteristic impurity peaks are not observed, resulting in high purity of Bentonite. According to sem pictures (Fig. 2c), the PPy particles seen in Fig. 2(a,b) are nanotubes. PPy nanotubes powder synthesized from nanostructured Bentonite powders have a typical outer diameter of ca. 70 nm, a length up to 400 nm, and an interior diameter of ca. 20 nm, which changes throughout the nanotube, according to typical SEM pictures. The SEM image (figure 2(a-c)) demonstrates this. We reasoned that the pyrrole took part in the self-assembly process of Bentonite and hence determined the production of nanotube (Jérôme et al, 2004) based on the generated Bentonite aggregates prior to working with a pyrrole monomer.

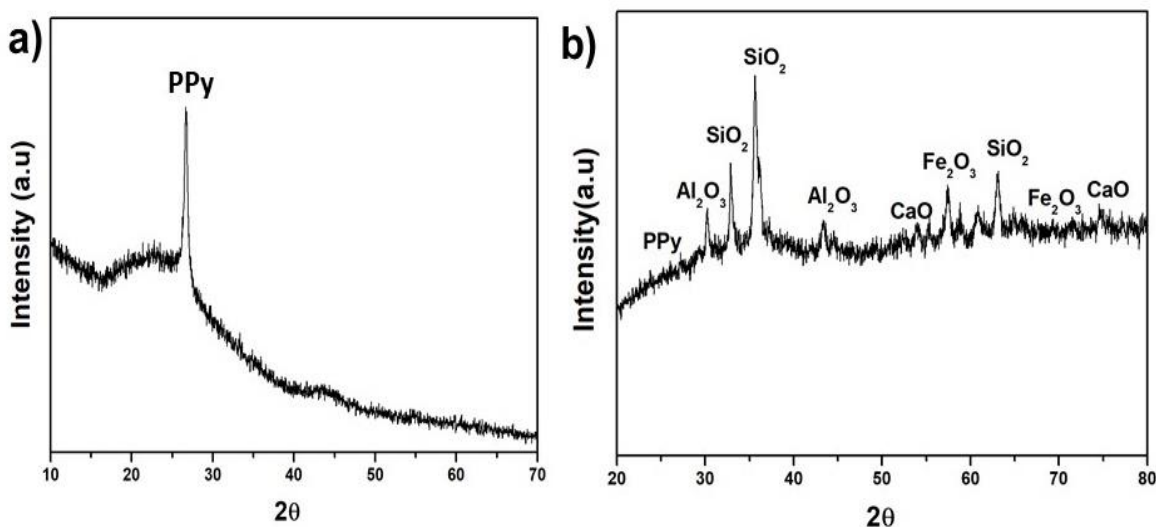


Figure 1. XRD patterns of pure PPy, and PPy/Bentonite composite



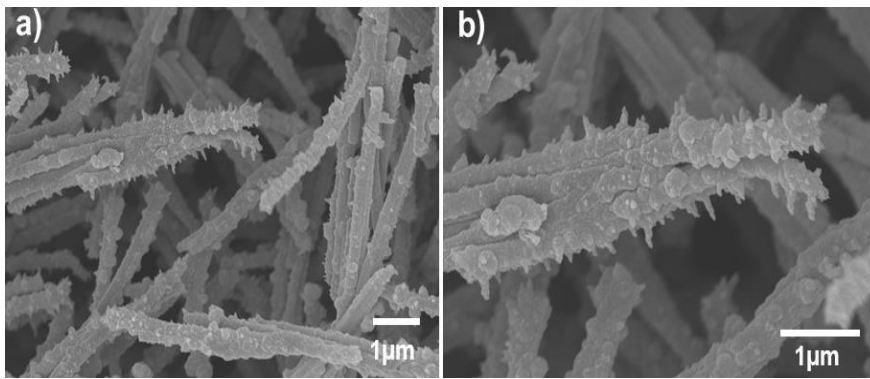


Figure 2. Different magnification - FESEM images of PPy/Bentonite composite

Fig. 3 shows the UV-Vis spectra of Polypyrrole - Bentonite composites. The spectrum shows the maximum absorbance peak occur at 190 nm. The transition of electrons in the n orbital from the ground state to the higher energy state s* is involved in the absorption of light energy by polymeric materials in the UV and Visible ranges. n → s* transitions are possible in saturated compounds comprising atoms with ion pairs (non-bonding electrons). The energy required for these transitions is frequently smaller than for s → s* transitions. They can be triggered by light

with a wavelength of 150 to 250 nm. In the UV region, the number of organic functional groups having n → s* peaks is limited. As can be seen in Fig.4 all the composites show an increase in absorbance with each additional of clay concentrations that suggests a uniform mixture of polymer with a slight difference in particle size. The result may be understood with interchange interaction in the outside of polymer coils (Janata et al, 2003).

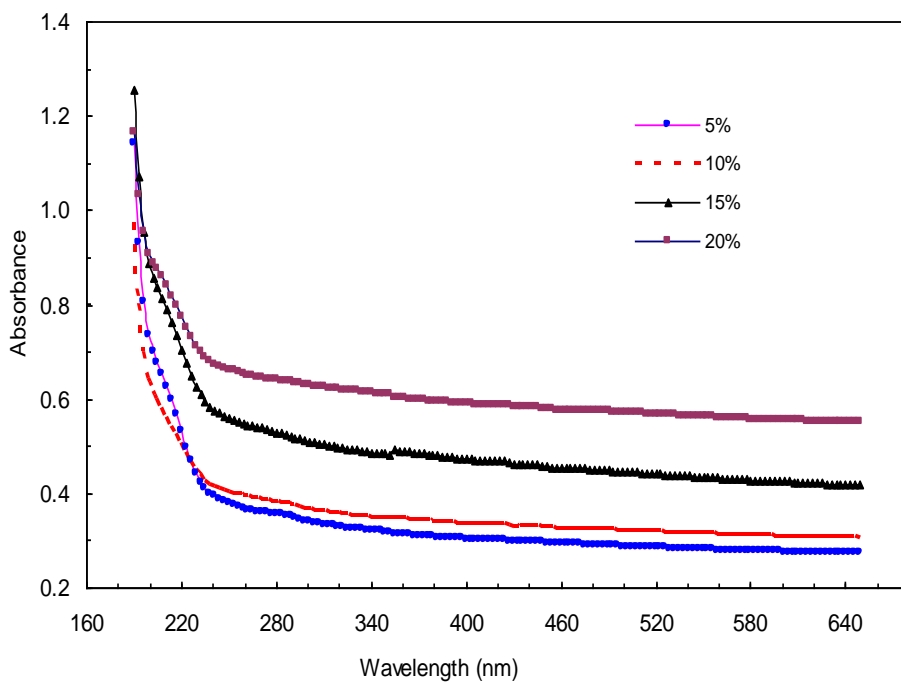


Figure 3. Variation of Optical Absorbance for Polypyrrole - Bentonite composites with wavelength



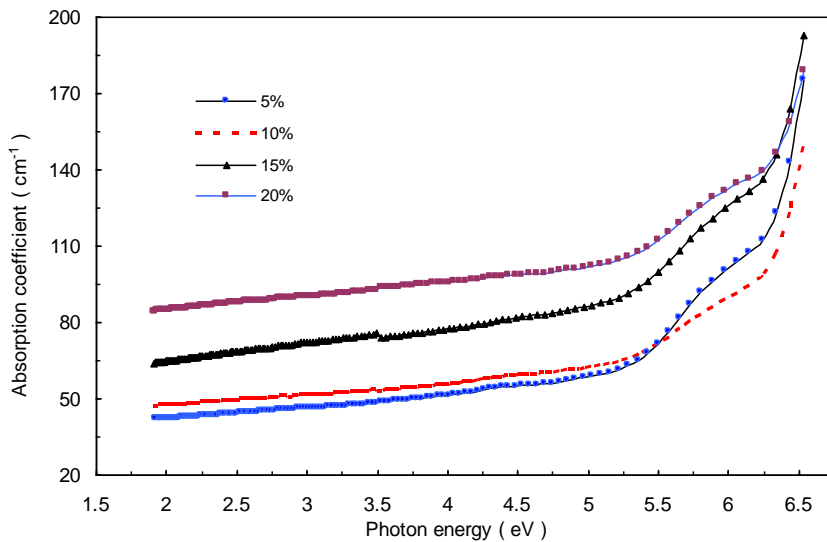


Figure 4. The relationship between the Absorption coefficient and Photon energy for Polypyrrole – Bentonite composites

It is clearly observable from Fig. 4 that for $h\nu < E_g$, no electron hole pairs can be shaped, α is small and the material is transparent. For $h\nu \geq E_g$, absorption should be strong. In order to obtain the optical energy gap (E_g) of the samples, the data of absorption consistent to the fundamental absorption edge along with the wavelength have been considered. These data have put in plots in the form of $(\alpha h\nu)^{1/2}$ as a function of photon energy $h\nu$. The optical energy gap values are obtained from the intercepts of

$(\alpha h\nu)^{1/2}$ plots versus $(h\nu)$ on the $h\nu$ axis as shown in Fig 5. It was noticed that as the clay content increase, the values of optical energy gap decreased from 5.44, 5.41, 5.38 and 5.28 eV for the 5, 10, 15, and 20 wt% of bentonite respectively. This is accredited to the defects increase that result in lower energy states formation that resulting from the increase in the charge carriers number in the conduction band (Mokrane et al, 2001).

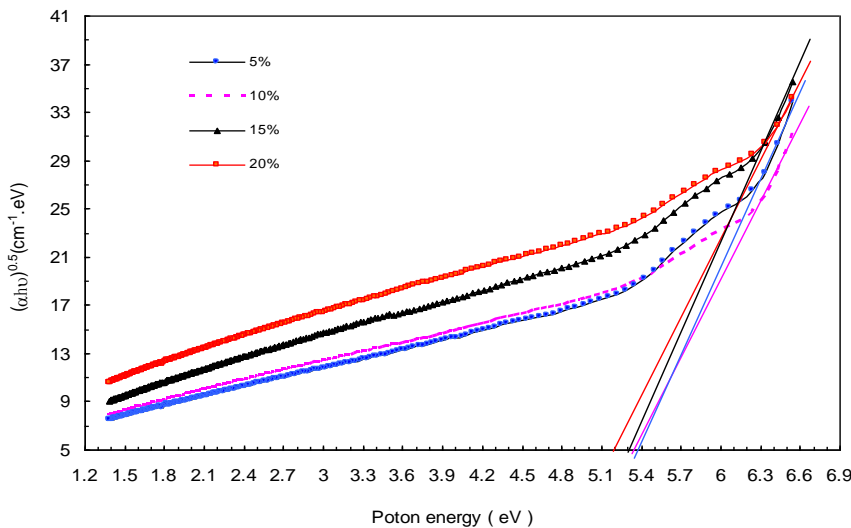


Figure 5. The relationship between $(\alpha h\nu)^{0.5}$ (cm⁻¹.eV) and Photon energy for Polypyrrole – Bentonite composites

The extinction coefficient (k) for Polypyrrole – bentonite composites varies with wavelength as

shown in Fig 6, demonstrating that the extinction coefficient increases as clay content increase and



decreases as incident wave length increase. According to several studies, the initiation of decomposition for polymer/clay composites increases dramatically as the clay content increases. We can clearly see that the

decomposition of polymer-bentonite composites occur in the ion fluence 275 eV. (Oukil et al, 2007; González et al, 2011).

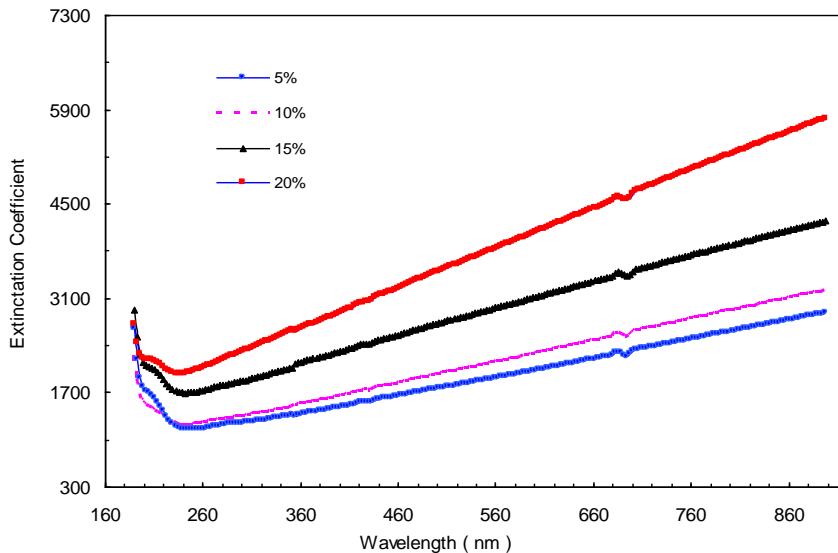


Figure 6. Variation of Extinction Coefficient for Polypyrrole – Bentonite composites with wavelength

Conclusions

The results showed that utilizing reinforced bentonite, the optical characteristics of composites could be altered. The absorption coefficient rises as the filler weight percent content rises. As the concentration of Bentonite in Polypyrrole was increased, the optical energy gap shrank. The extinction coefficient (k) rises as the weight percentage of bentonite added to the Polypyrrole rises and falls as the incident wave length rises. The findings suggest that the bentonite doping atoms will alter the structure of the host polymer.

References

- Debiemme C. Template-free one-step electrochemical formation of polypyrrole nanowire array. *Electrochemistry communications* 2009; 11(2): 298-301.
- Emidio G, Mazzieri F, Verastegui-Flores RD, Van W, Bezuijen A. Polymer-treated bentonite clay for chemical-resistant geosynthetic clay liners. *Geosynthetics International* 2015; 22(1): 125-137.
- El-Kader KA, Orabi AS. Spectroscopic behavior of poly (vinyl alcohol) films with different molecular weights. *Polymer Testing* 2002; 21(5): 591-595.
- Awad EI, Al-Rubaye S, Jebur AL, Hadi AF, Awad NI. Measurement of Alpha Activity in Several Types of Iraqi Ceramic and Cement in the Iraqi Markets. *In IOP Conference Series: Materials Science and Engineering* 2020: 987(1).
- González MB, Saidman SB. Electrosynthesis of hollow polypyrrole microtubes with a rectangular cross-section. *Electrochemistry Communications* 2011; 13(5): 513-516.
- Hadi S, Hashim A, Jewad A. Optical properties of (PVA-LiF) composites. *Australian Journal of Basic and Applied Sciences* 2011; 5(9): 2192-2195.
- Hassan D, Hashim A. Preparation and Studying the Structural and Optical Properties of (Poly-Methyl Methacrylate-Lead Oxide) Nanocomposites for Bioenvironmental Applications. *Journal of Bionanoscience* 2018; 12(3): 346-349.
- Huang K, Wan M, Long Y, Chen Z, Wei Y. Multi-functional polypyrrole nanofibers via a functional dopant-introduced process. *Synthetic Metals* 2005; 155(3): 495-500.
- Hien NL, Garcia B, Pailleret A, Deslouis, C. Role of doping ions in the corrosion protection of iron by polypyrrole films. *Electrochimica Acta* 2005; 50(7-8): 1747-1755.
- Huang J, Kaner RB. Nanofiber formation in the chemical polymerization of aniline: a mechanistic study. *Angewandte Chemie International Edition* 2004; 43: 5817-5821.
- Jang J. Conducting polymer nanomaterials and their applications. *Emissive Materials Nanomaterials* 2006: 189-260.
- Jérôme C, Labaye DE, Jérôme R. Electrochemical formation of polypyrrole nanowires. *Synthetic metals* 2004; 142(1-3): 207-216.
- Janata J, Josowicz M. Conducting polymers in electronic chemical sensors. *Nature materials* 2003; 2(1): 19-24.
- Gulati K, Lal S, Diwan PK, Arora S. Investigation of thermal, mechanical, morphological and optical properties of polyvinyl alcohol films reinforced with buddha coconut (sterculia alata) leaf fiber. *International Journal of Applied Engineering Research* 2019; 14(1): 170-179.



- Long YZ, Li MM, Gu C, Wan M, Duvail JL, Liu Z, Fan Z. Recent advances in synthesis, physical properties and applications of conducting polymer nanotubes and nanofibers. *Progress in Polymer Science* 2011; 36(10): 1415-1442.
- Liu L, Zhao C, Zhao Y, Jia N, Zhou Q, Yan M, Jiang Z. Characteristics of polypyrrole (PPy) nano-tubules made by templated ac electropolymerization. *European Polymer Journal* 2005; 41(9): 2117-2121.
- Lu G, Li C, Shi G. Polypyrrole micro-and nanowires synthesized by electrochemical polymerization of pyrrole in the aqueous solutions of pyrenesulfonic acid. *Polymer* 2006; 47(6): 1778-1784.
- Mokrane S, Makhloufi L, Hammache H, Saidani B. Electropolymerization of polypyrrole, modified with germanium, on a passivated titanium electrode in aqueous nitrate solution: new results on catalytic reduction of protons and dissolved oxygen. *Journal of Solid State Electrochemistry* 2001; 5(5): 339-347.
- Noor HA, Al-Rubaye SH. Facile Synthesis of reduced graphene oxide wrapped on porous NiCo₂O₄ hexagonal nanoplates composite as electrode material for high performance supercapacitor 2020.
- Oukil D, Makhloufi L, Saidani B. Preparation of polypyrrole films containing ferrocyanide ions deposited onto thermally pre-treated and untreated iron substrate: Application in the electroanalytical determination of ascorbic acid. *Sensors and Actuators B: Chemical* 2007; 123(2): 1083-1089.
- Pattabi M, Amma BS, Manzoor K. Photoluminescence study of PVP capped CdS nanoparticles embedded in PVA matrix. *Materials Research Bulletin* 2007; 42(5): 828-835.
- Pailleret A, Hien NL, Thanh DM, Deslouis, C. Surface reactivity of polypyrrole/iron-oxide nanoparticles: electrochemical and CS-AFM investigations. *Journal of Solid State stable polypyrrole nanospheres using ozone* 2011; 27(22): 13719-13728.
- Zhang Z, Wang F, Chen FE, Shi G. Preparation of polythiophene coated gold nanoparticles. *Materials Letters* 2006; 60(8): 1039-1042.
- Aziz SA, Ali RS, Abd AN. Characterization studies of nickel oxide nanostructure films prepared by electrolysis method for photo detectors applications. *NeuroQuantology* 2020; 18(2): 45-49.

