

Investigation of Chitosan Embedded with Silver Vanadate Nanorods and their Optical Properties

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CHITOSAN is a natural polysaccharide polymer which is non-toxic, biodegradable, cationic and biocompatible. Present work study physical and chemical characteristics of pure chitosan thin film and other samples that modified through embedding different concentration of silver vanadate nanorods prepared via solution casting route. Casting route was employed for preparation of chitosan thin films and other sample containing gradient increase of synthesized silver vanadate nanorods. The optical properties have been investigated through ultraviolet–visible (UV/Vis) optical absorption spectroscopy. Experimental data reveals an observable decrease in the values of optical energy gap with increasing content of silver vanadate nanorods which result in enhancement of the sensitivity for all prepared thin films.

Keywords: Nanocomposites; Chitosan; Semiconductors; Silver vanadate; UV/Vis

Introduction

Lately, the nanostructural process, which depends on the utilization of distinctive features of the nanostructural ranges from 1 to ~100 nm, the size of the different structural constituents such as layers, grains, pores and so on is utilized always for production of new materials and determine the physicochemical, non-equilibrium nature and the physic-mechanical characteristics of nanostructural materials. It is obvious from general searches that radiation, thermal and deformation impact, bringing about homogenization, recrystallization and other phenomena could be accompanied by the change in the nanostructure through the deterioration of its characteristics [1-2].

Chitosan is considered as a natural polymer (cationic polysaccharide) that extracted from chitin through the deacetylation process. Chitosan's ability to treat thin films or porous structures for use in diverse applications is one of the most characteristic features of chitosan [3-4]. Chitosan is used in pharmaceutical and medical applications

such as surgical Sutures, sponges, artificial skin, drugs release, membranes and contact lenses and etc ... The characteristic of chitosan can be modified through the addition of inorganic material, organic substance, nanomaterial or another polymer [4-6]. The characteristics of chitosan can be adjusted through UV irradiation, heating and mechanical remediation. There are three steps occur during ultraviolet irradiation of polymer matrices. In the first step, the excited chitosan molecules are created, in the second step, a scission of the chain and the cross-link occurs then finally the oxidation state take place [7].

Many semiconductor nanomaterials such as ZnO, Fe₂O₃, TiO₂, WO₃, CuO, and SnO have considerable special attention in various applications [8]. Unfortunately, most of them have various disadvantages, which limit their use in practical applications such as heterogeneity on its structures, have a large particle size, inactive below the visible light and contain a high value in its band gap (for example TiO₂ is nearly 3.2 eV), as a result of the conventional methods of

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preparation. Thus, the evolution and synthesis of new material are to reinforce the activation and utilization below visible light (solar light) [9-10].

Among those photocatalytic materials, silver vanadates are significant materials because they have an efficient photophysical properties under solar light irradiation, electrochemical, chemical sensing properties, controlled nanocrystallinity, morphology and a narrow band gap. Previously, AgVO₃ nanomaterials have been synthesized by different techniques including co-precipitation, biomimetic method, sonochemical synthesis and hydrothermal process. Silver vanadate (β -AgVO₃) nanorods are used in various applications such as antibacterial agents, in lithium-ion batteries as cathode substance, photocatalysts and in the electrochemical cells [11-13]. Recently, hybrid components based on chitosan have been progressed, including metal nanoparticles, conducting polymers and metal oxide nanoparticles because of their excellent characteristics of individual materials and simultaneous biocompatibility effects. Hence, the incorporation of metal oxide nanomaterials into chitosan to produce materials of outstanding photocatalytic effect and stable in both acidic and basic solvents attracted much attention of many researchers [14-16]. Organic and inorganic blockers are used to protect from UV radiation, but organic blockers absorb UV rays. The inorganic blockers such as TiO₂, AgVO₃ and ZnO are common choices to scatter UVA and UVB radiation. Then, inorganic blockers can be used as a sun protection cream to prevent the skin cancer [17].

Chitosan and silver vanadate nanorods can form the synthetic composites due to their specific characteristic of both components. The prepared composites confer specific chemical, mechanical and structural characteristics. The production of new biomaterials with relatively low pollution, unique properties and low cost has a great possibility to be used in various applications [15].

The main goal of present study devoted for preparation and characterization of chitosan filled AgVO₃ nanorods using a simple casting method and determines the effect of variable filler concentrations on the optical and surface characteristics of prepared samples for different optical and industrial applications.

Experimental

Materials and Methods

Chitosan was obtained from (Aldrich Co.). Silver vanadate was obtained from the reaction of

0.01 M ammonium trioxovanadate (NH₄VO₃) that purchased from Sigma–Aldrich, Germany and 0.01 M silver nitrate (AgNO₃) that obtained from Bio Basic Canada Inc.

The accurate amount of AgNO₃ (0.01 M) was dissolved in 200 ml distilled water and added drop by drop to NH₄VO₃ (0.01 M) that dissolved in 200 ml distilled water. The mixture of the solution was stirred at ambient temperature and controlled pH from 4.6 to 5.8. AgVO₃ was observed by the production of a yellow precipitate. Silver vanadate nanorods were washed by using ethanol and distilled water several times and kept thermally in the oven at 50°C.

Polymeric composites were prepared through the mixing of different concentrations of silver vanadate with 1g chitosan that dissolved in 2% acetic acid. The latest composition of the prepared films was (0.01, 0.02, 0.03, 0.04, 0.05, 0.06 Wt. %) of silver vanadate in the polymer composite.

The prepared films were obtained by casting the solutions into plastic Petri-dishes. Polymer films were submitted to the ultra-high sonication instrument at room temperature for 15 min. After solvent evaporation, the prepared thin films were kept thermally in the oven at 50°C and placed in a vacuum desiccator at room temperature until use. Table (1) summarizes the different concentration of the prepared films.

Characterization

The spectrophotometer (V-570 UV/Vis-NIR, JASCO, Japan) was employed to measure Ultraviolet/visible (UV/Vis) absorption spectra in the wavelength region of 190–1100 nm.

Results and Discussion

Ultra violet –visible radiation

UV-Vis spectroscopy is an important analytical method that consists of an absorption range

TABLE 1. The composition of chitosan filled with AgVO₃ polymer films.

Samples	Chitosan (wt. %)	AgVO ₃ (wt.%)
Cs	100.0	0.00
Cs1	99.99	0.01
Cs2	99.98	0.02
Cs3	99.97	0.03
Cs4	99.96	0.04
Cs5	99.95	0.05
Cs6	99.04	0.06

from the 190-1100 nm to identify the functional groups in molecules due to excitation of electrons according to molecular orbital theory.

The UV–visible spectroscopy of the prepared AgVO₃ nanorods is shown in Fig. (1). The steep curve of the spectra analysis observes that the visible light absorption that because of the band-gap transition. The absorption band of prepared silver vanadate nanorods at room temperature is equal 376 nm. In AgVO₃, the valence band has consisted of Ag 4d and O 2p orbitals. The properties of absorption edge indicated for AgVO₃ is due to the hybrid orbital of Ag 4d and O 2p or (the transition of electrons from the Ag 4d and O 2p) in valence band orbitals to vacant 3d conduction band of V⁵⁺, which observe a high donating of V 3d and Ag 5s orbitals that located in the lower section of the conduction band.

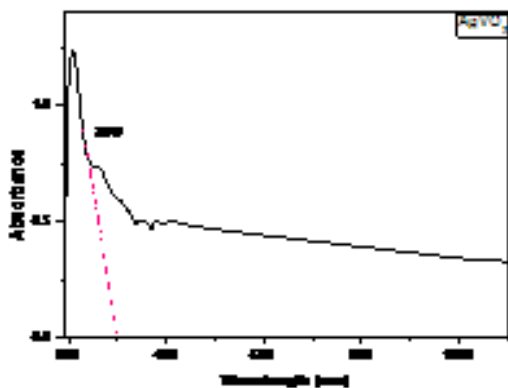


Fig. 1. UV/Vis analysis of synthesized AgVO₃.

The optical energy band gap (E_g value) can be determined from plot photon energy ($h\nu$) versus $(\alpha h\nu)^2$. The optical energy band gap (E_g) can be estimated through the intercept of the tangent in the X-axis that shown in Fig.(2). E_g value is equal to 2 eV for AgVO₃. After the semiconductor is excited, the recombination processes are associated with distortions in the crystalline lattice. Therefore, the electronic characteristic can be altered due to the structural distortions. In our case, the emissions are very sentient to alter in the primary coordination sphere of V and Ag cations and observe different changes in the excitation spectra compared to their normal structural.

The photocatalytic activity depends on transfer, creation and segregation of photogenerated electron-hole pairs. The position of the band was calculated by the next empirical formulas:

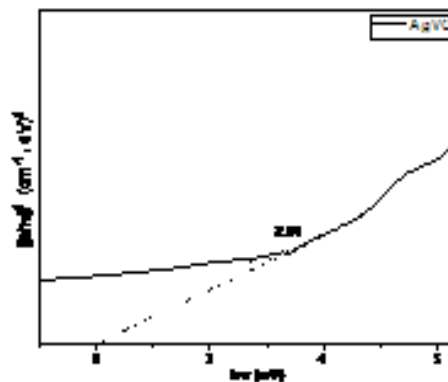


Fig. 2. Plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for the band gap energy of AgVO₃.

$$E_{VB} = X - E^e + 0.5E_g \quad (1)$$

$$E_{CB} = E_{VB} - E_g \quad (2)$$

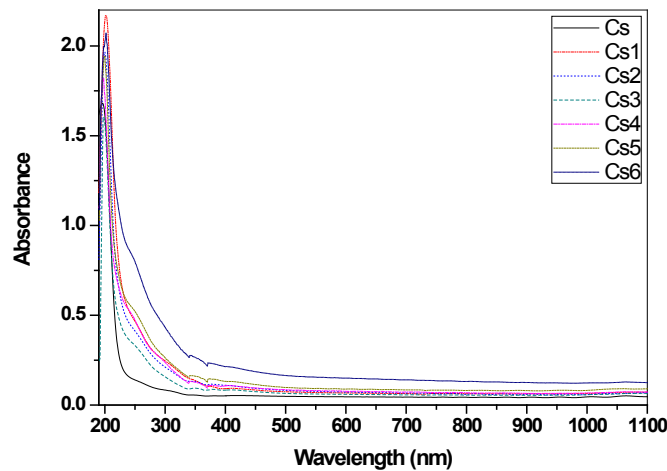
Where E_{VB} is the edge potential of valence band, X is the electronegativity of transition metal oxide semiconductor that the geometric signify to the electronegativity of atoms, E^e is the energy of free electrons on the hydrogen scale (approximately 4.5 eV), E_{CB} is the edge potential of conduction band and E_g is the energy of band gap for transition metal oxide semiconductor. The X value of AgVO₃ is 5.86 eV. As indicated in Table (2), according to the calculation, the values of E_g of the valence band and the conduction band of silver vanadate nanorods are 2.35 eV and 0.53 eV, respectively, which is comparable to the values described in the literature [18].

Figure (3) shows the absorption analysis of pure chitosan and prepared thin films. It can be observed that the pure chitosan presence in the invisible region at 226 nm due to its transparency. The absorption spectra indicated the transition of existed electrons form $n \rightarrow p^*$ d orbital due to the presence of auxochromes functional groups (NHCOR) and $\pi \rightarrow p^*$ transition due to the presence of chromophores groups (C=O) or (C=C) with a minimum excitation energy.

Whereas the prepared thin films that filled with a different concentration of silver vanadate nanorods indicate the shift of peaks to the longer wavelength in the range from 226 – 446 nm. Based on UV–visible analysis, the raising of the relative intensity is due to the incorporation of silver vanadate nanorods into pure chitosan matrix and the strong complexation and the interaction between AgVO₃ and polar group of pure chitosan matrix. In the prepared system, the formation of AgVO₃ nanorods can be observed from the change of color of the polymer composites from colorless to yellow.

TABLE 2. Summarizes the different the values of E_g of the valence band and the conduction band of silver vanadate nanorods.

Sample	Optical property (eV)		
	E_g	E_{VB}	E_{CB}
β -AgVO ₃	2	2.35	0.35

**Fig. 3.** UV-Visible absorption spectra for pure chitosan and prepared thin films.

From the equation of Einstein's photon energy, the energy of the conduction band (E_{cb}) can be estimated directly:

$$E_{cb} = hc / \lambda_{max} \quad (3)$$

Where λ_{max} is the maximum of UV-visible absorbance wavelength, c is the speed of light and h is the Planck constant. The results are tabulated in Table (3). From the UV-visible analysis, it can be observed a wide peak in some of the absorption spectra. Thus, the energy of the conduction band of all prepared samples can be estimated indirectly by the Tauc's equation:

$$(\alpha h\nu)^2 = C(h\nu - E_{cbd}) \quad (4)$$

$$(\alpha h\nu)^{\frac{1}{2}} = C(h\nu - E_{cbi}) \quad (5)$$

Where E_{cb} is the direct energy of the conduction band (E_{cb}), C is constants, h is Planck's constant, $h\nu$ is the photon energy and α is the absorption coefficient. The direct and indirect transition energy of the conduction band of all prepared samples can be shown in Figure (4) and Figure (5) respectively. It is evident from the Figure (4), by increasing the concentration of silver vanadate nanorods, the energy of the conduction band (E_{cb}) decreased from 5.82 to 4.16 eV for direct transition and from 5.28 to 1.84

for indirect transition respectively. This denotes that silver vanadate nanorods formed a localized state and the density of this state increased by increasing the concentration of AgVO₃ nanorods, thus the energy of band gap decreased.

Urbach energy can determine the degree of material imperfection such as amorphous materials with a low crystalline in nature as shown in Fig. (6) and Fig.(7). Urbach energy can be calculated through the following equation: $\ln(\alpha) = E_{cb} - E_{cbi} - E_{cbi} \exp(-E_{cbi}/kT)$ (6) is missing (6)

Where α is the absorption coefficient, C is a constant, $h\nu$ is the photon energy and E_u is the Urbach energy that listed in the Table (3).

Refractive index

Changes in the value in the refractive index of all prepared thin films are important for controlling the optical characteristics of materials. Refractive index is a crucial optical parameter for designing optical fibers, prisms and optical windows. The refractive index value of the polymer composites are calculated using [19]:

$$(n_2 - 1) / (n_2 + 2) = 1 - \quad (7)$$

Where n is the value of the refractive index and E_{cbi} is the indirect energy of the conduction band

TABLE 3. the optical properties of all prepared thin films.

Samples	edge	E_{cb} (eV)	E_{cbd} (eV)	E_{cbl} (eV)	U_{energy}
	(nm)	by equation (3)	by equation (4)	by equation (5)	ΔE (eV)
Cs	226	5.48	5.82	5.28	0.50
Cs1	259	4.78	5.68	5.08	0.60
Cs2	278	4.44	5.76	5.10	0.60
Cs3	289	4.28	5.85	5.23	0.80
Cs4	319	3.87	5.90	5.20	0.79
Cs5	322	3.85	5.86	5.20	0.85
Cs6	342	3.61	5.70	4.88	1.01

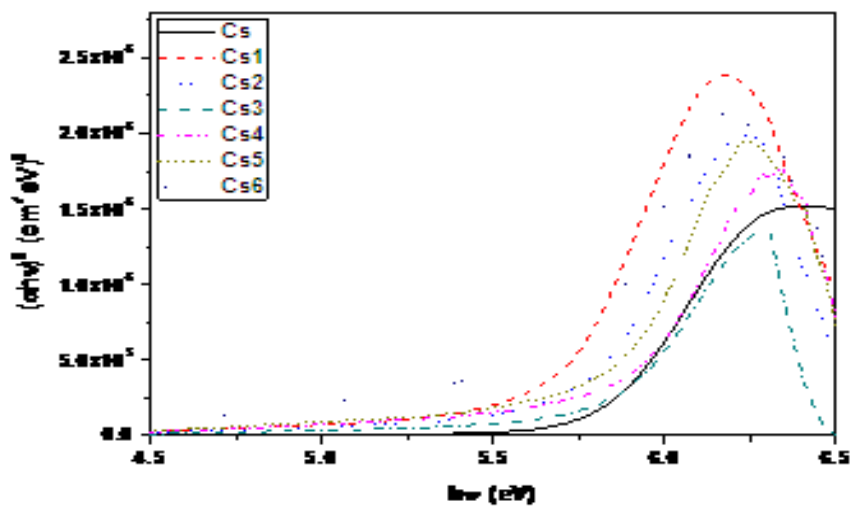


Fig. 4. The relation between $(h\nu)^2$ versus photon energy $(h\nu)$.

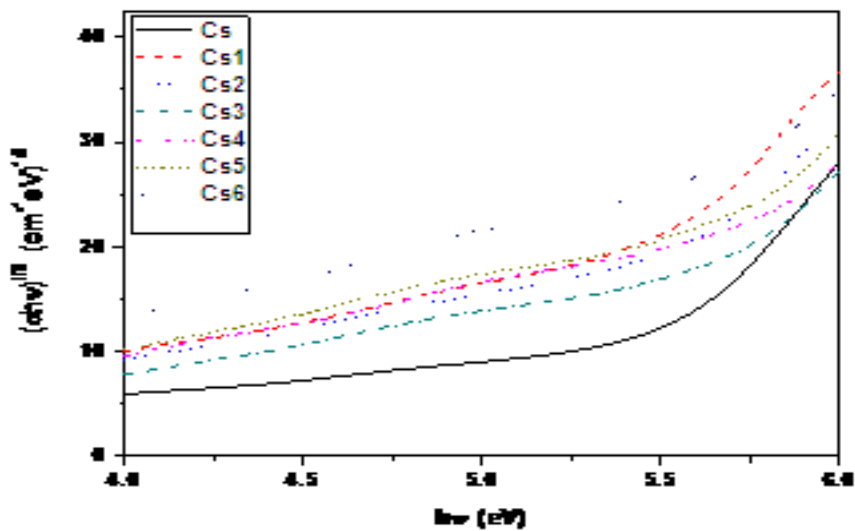


Fig. 5. The relation between $(h\nu)^{1/2}$ versus photon energy $(h\nu)$.

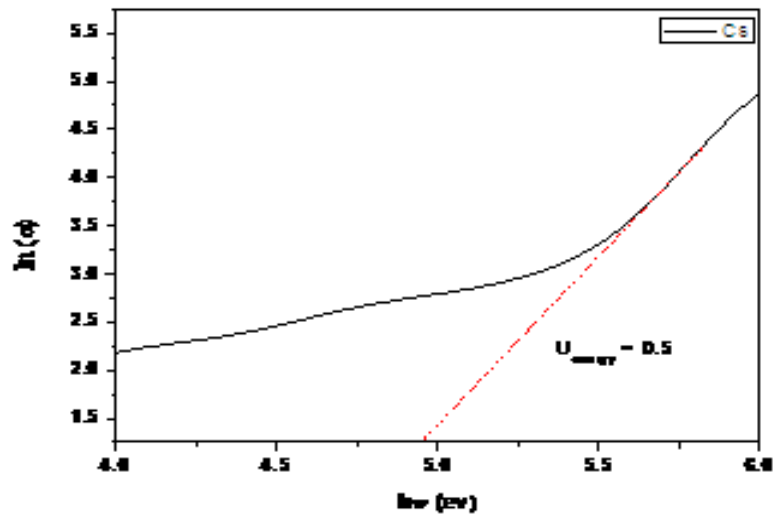


Fig. 6. Uenergy for pure chitosan.

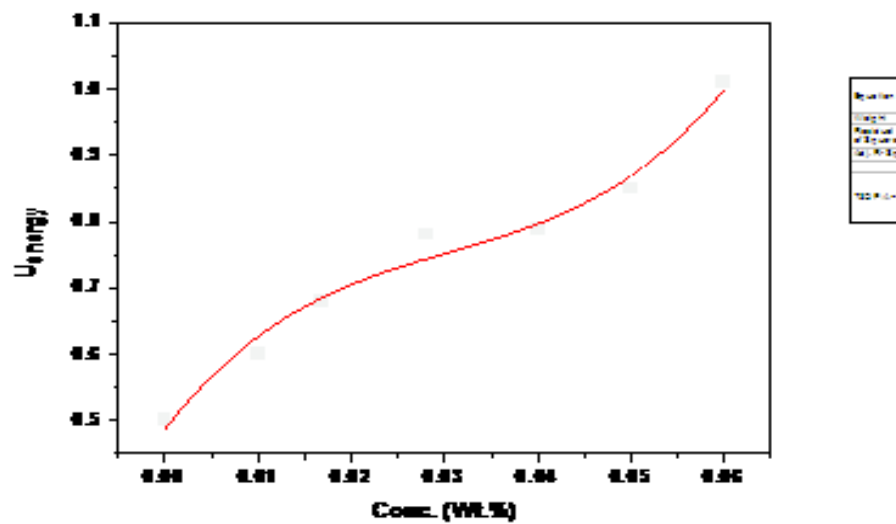


Fig. 7. The relation between Uenergy and different concentration of polymer nanocomposites.

TABLE 4. refractive index for all prepared samples.

Samples	Refractive index (n)
Cs	1.95
Cs1	1.97
Cs2	1.98
Cs3	1.94
Cs4	1.97
Cs5	1.97
Cs6	2.00

gap. The refractive index value of the polymer composites is listed in Table (4). It's clear that the value refractive index raised from 1.95 for pure chitosan to 2.77 for chitosan incorporated of the maximum concentration of AgVO₃ nanorods. The chitosan matrix becomes denser due to the incorporation of AgVO₃ nanorods and therefore display a high refractive index. Polymer composites with the high value of refractive index can be used in several applications involving light-emitting diodes, waveguides and antireflective coatings in optoelectronic and the optical instruments. It is obvious that the value of the refractive index is raised by increasing the concentration of AgVO₃ nanorods and indicated the homogeneous distribution of AgVO₃ nanorods within the chitosan matrix.

Conclusion

Silver vanadate nanorods have been successfully prepared via co-precipitation method by using deionized water, ammonium trioxovanadate and silver nitrate as the ingredients. Incorporation of AgVO₃ nanorods into pure chitosan film through solution casting method produced the chitosan - AgVO₃ thin film. The immobilized AgVO₃ showed the strong incorporation and the homogenous distribution within chitosan film. The UV absorption analysis is shown for polymer nanocomposites. The wavelength increases by the addition of AgVO₃ nanorods. Optical band gap decreases by the addition of silver vanadate nanorods loading. The enhancement in conducting properties is observed for all prepared thin films, which is illustrated from Tauc's plot.

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توصيف بوليمر الكيتوزان المدمج بعصيات نانومترية من فائيدات الفضة وخواصها الضوئية

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الكيتوزان عبارة عن بوليمر طبيعي متعدد السكريات وغير سام وقابل للتحلل كاتيوني ومتوافق حيويًا. العمل الحالي يقدم دراسة للخواص الفيزيائية والكيميائية لأفلام رقيقة من الكيتوزان النقي بالإضافة لعينات أخرى تم تعديلها من خلال أحجام تركيزات مختلفة من عصيات فانديت الفضة النانومترية. استخدمت تقنية صب المحلول لتحضير العينات النقية والمطعمة بعصيات الفضة النانومترية وبتراكيز مختلفة مع بوليمر الكيتوزان. وقد تم التحقق من الخصائص البصرية من خلال التحليل الطيفي للأشعة فوق البنفسجية والمرئية (UV / Vis). وتكشف البيانات التجريبية عن انخفاض ملحوظ في قيم فجوة الطاقة الضوئية مع زيادة محتوى فانديت الفضة النانومترية مما يؤدي إلى تعزيز حساسية جميع الأفلام.