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Optical Properties of Polyvinyl Alcohol (PVA) Thin Films Doped with Tungsten Disulfide (WS_2) Nanoparticles

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الخصائص البصرية لأغشية البولي فينيل الكحولية الرقيقة (PVA) المشوبة بجسيمات نانوية من ثنائي كبريتيد التنغستن(WS_2)

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ABSTRACT

Background:

Polyvinyl alcohol (PVA) is a versatile synthetic polymer with excellent optical and mechanical properties, making it suitable choice for a range of applications. The incorporation of tungsten disulfide (WS_2) nanoparticles into PVA offers the potential to enhance these properties, enabling applications in flexible electronics and optoelectronic devices.

Materials and Methods:

Thin films of PVA doped with WS_2 nanoparticles at concentrations of 0.5%, 1%, and 2% were prepared using the casting method. The films were deposited with a thickness of 150 nm on glass substrates. Structural and optical characterizations were performed using X-ray diffraction (XRD) and UV-Vis spectroscopy to study the semi-crystalline nature and optical behavior of the composites.

Results:

The XRD analysis revealed that the semi-crystalline nature of pure PVA and the formation of crystalline WS_2 phases with increased doping ratio. UV-Vis measurement showed enhanced light absorption in the visible region, with a consistent red shift in the absorption edge. The direct band gap decreased from 4.1 eV for pure PVA to 4.03 eV for 2% WS_2-doped films, while the Urbach Energy increased, indicating higher structural disorder with increasing doping.

Conclusions:

The incorporation of the WS_2 nanoparticles into PVA significantly alters its structural and optical properties, reducing the band gap and enhancing light absorption. Results highlight the potential of PVA/WS_2 Nano-composites for use in photonic and optoelectronic applications.

Key words: Polyvinyl alcohol, tungsten disulfide, optical properties, thin films, X-ray diffraction, UV-Vis spectroscopy, band gap, Urbach energy, Nano-composites.

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INTRODUCTION

The PVA is very unique synthetic polymer, it is also versatile due to its peculiar properties that have made it useful in quite a large number of scientific and industrial applications. The PVA properties are to be water-soluble, as well as an excellent film-forming, adhesive, and emulsifying capability-a subject in material science [1]. Among the most valued advantages of PVA have excellent optical properties: highly transparent in the visible region and with a controllable refractive index. Because of these features, the PVA represents an ideal matrix for optical applications. In this respect, such features allow the enhancement of light absorption and scattering upon doping with Nano-materials by making PVA an extremely suitable choice for the fabrication of value-added composite materials [2]. The good tensile strength and flexibility of the mechanical properties of the PVA make it an effective matrix polymer for embedding various Nano-particles by proper improvement of the composite functional performance. Hydroxyl groups in the structure of PVA ensure strong interaction with different Nano-materials and thus improve their dispersion and stability within the polymer matrix. This attribute is more important for enhancement of the optical and electronic properties of the composite films [3].

Tungsten disulfide indeed represents an inorganic transition metal dichalcogenide TMD with superior electronic, mechanical, and optical properties. Inorganic Nano-materials WS_2 share the same layered structure as graphene: the hexagonally arranged tungsten atoms are sandwiched between the layers consisting of sulfur atoms. The given structure enables WS_2 to demonstrate strong anisotropy and tunable band gaps, which change from indirect to direct depending on the number of layers [4]. Used as a filler material incorporated in polymer matrices like PVA, WS_2 has the potential to dramatically enhance some optical and electric properties of composites. The addition of Nano-particles to PVA can enhance its light absorption capability, shifting the optical band gap and giving better performance in composite films for photonic and optoelectronic applications [5].

While the integration of WS_2 with the PVA realizes the characteristic features of both, an approach to develop hybrid materials with tailored characteristics becomes feasible. The synergy from the PVA matrix and WS_2 filler contributes to enhance structural stability, improved mechanical strength, and superior optical performance-highly desirable features for flexible electronics, sensors, and optoelectronic devices. Accordingly, researching PVA/WS_2 composites holds the potential to contribute considerably to the advancement of Nano-composite material-based research in various high-performance optical and electronic applications [6].

MATERIALS AND METHODS

The PVA thin films were prepared by dissolving 25 g PVA in 200 ml of water and stirring for 40 min. Then, WS_2 nanoparticles were dispersed in the liquid PVA solution at various WS_2 concentrations: 1 g of WS_2 was dissolved in 20 ml of prepared PVA solution and stirred for 30 min; Then, 2 g of WS_2 - in 20 ml of prepared PVA solution and stirred for 30 min; and 0.5 g of WS_2 was dissolved in prepared PVA solution. The liquid PVA-WS_2 solutions obtained were then cast onto a glass substrate, using a casting technique. The films obtained were dried under ambient conditions for further characterization.

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RESULTS AND DISCUSSION

1 - X-Ray Diffraction (XRD) Analysis of PVA and WS_2-Doped PVA Composites

Figure 1 shows the XRD patterns of pure polyvinyl alcohol and the PVA impregnated with various weight percentages of tungsten disulfide, such as 0.5, 1, and 2 wt.%. In summary, these diffraction patterns provide essential information on the structural evolution in PVA due to the increased addition of WS_2. The XRD pattern of pure PVA exhibited a broad peak centered at approximately 20°, which confirmed its semi crystalline nature. There are no sharp peaks to indicate long-range crystalline order for the pure PVA matrix [7].

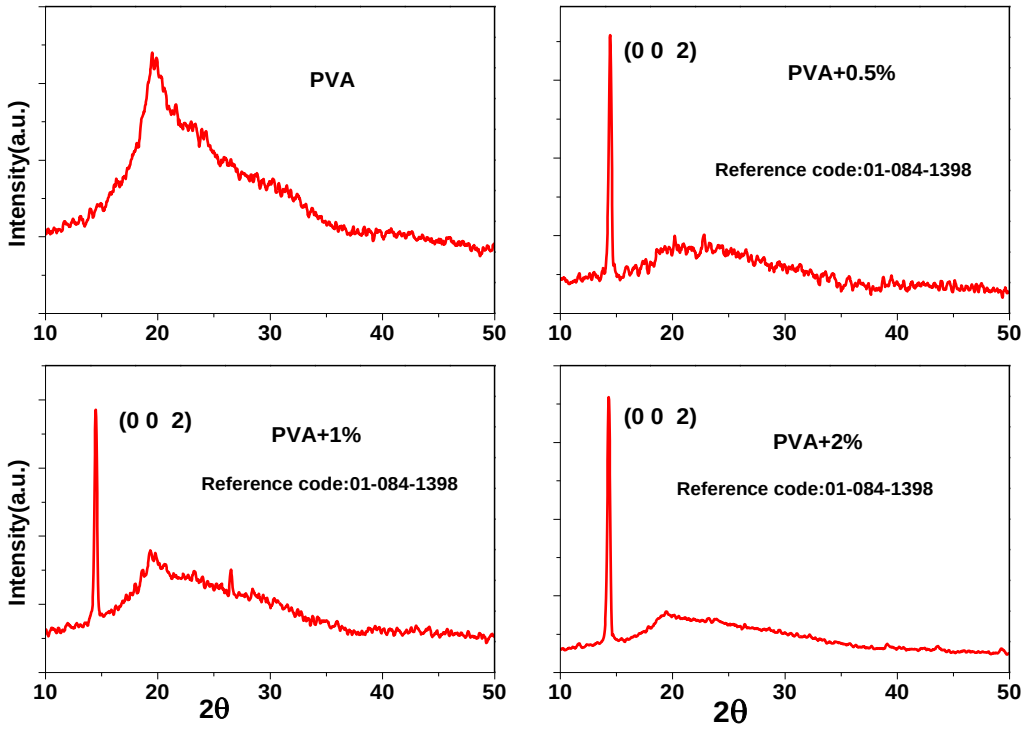

Figure 1: The XRD patterns of pure PVA and PVA doped with WS_2 at different concentrations (0.5%, 1%, and 2%).

The addition of WS_2 gives a way to significant changes in the XRD patterns. A prevailing diffraction peak at around 14° was readily observable with 0.5% doping of WS_2, corresponding to the (002) plane of WS_2 [8], confirming the crystalline phases of WS_2 within the PVA matrix. This peak becomes sharper and more pronounced for 1% and 2% of WS_2, which signifies the increase in crystallinity after the incorporation of more crystalline WS_2 particles. The appearance of the reflection in the (002) plane signifies the formation of hexagonal WS_2 and confirms its incorporation in the polymer matrix [8].

As shown in Figure 1, the diffraction peaks corresponding to WS_2 grow stronger with higher doping concentrations, reflecting an increase in the density of WS_2 crystals embedded in the PVA matrix. Beyond this, the WS_2 nanoparticles appear to actively reorganize the PVA's molecular structure supported by XRD data. Notably, the broad peak typically associated with PVA's

amorphous regions becomes sharper in composites with WS_2, signaling that the nanoparticles promote structural alignment and suppress disordered arrangements in the polymer [9].

These results show that WS_2 doping of PVA has an important implication for the structure, given that it transforms the initially main amorphous material to a composite with detectable crystalline characteristics due to the imbedded WS_2 Nano-particles [10].

The crystallographic parameters for WS_2 analyzed in this study were derived from a standard crystallographic database. WS_2 adopts a hexagonal crystal structure (space group *P63/mmc*, No. 194) with unit cell dimensions of $a = b = 3.1532$ Å and $c = 12.3230$ Å, along with angles $\alpha = \beta = 90°$ and $\gamma = 120°$. The calculated density of the material is 7.76 g/cm³, and the unit cell volume is 106.11×10^6 pm³, containing two formula units (Z = 2). Additionally, the reference intensity ratio (RIR) for WS_2 was determined to be 14.73, reflecting its relative diffraction strength in the composite system[10].

2- OPTICAL PROPERTIES

Figure 2 shows the absorbance spectrum of PVA and PVA-WS_2 thin films, respectively. These absorption spectra give some key insights into the interaction between the polymer matrix and the WS_2 nanoparticles within the PVA thin films and the WS_2-doped PVA films. It can be seen that there is a variation in the absorbance characteristics with an increase in the concentration of WS_2, hence proving that doping alters the optical behavior of the composite films. Pure PVA films exhibit an absorbance peak in the UV region (band gap ~4.1 eV [11]), attributed to their intrinsic optical transitions. However, introducing WS_2 nanoparticles significantly enhances the composite's absorbance across the visible and near-UV spectrum as the WS_2 concentration increases. This enhancement arises from the strong light-matter interactions characteristic of transition metal dichalcogenides (TMDCs) such as WS_2, which exhibit high absorbance due to their layered electronic structure and excitonic effects [12].

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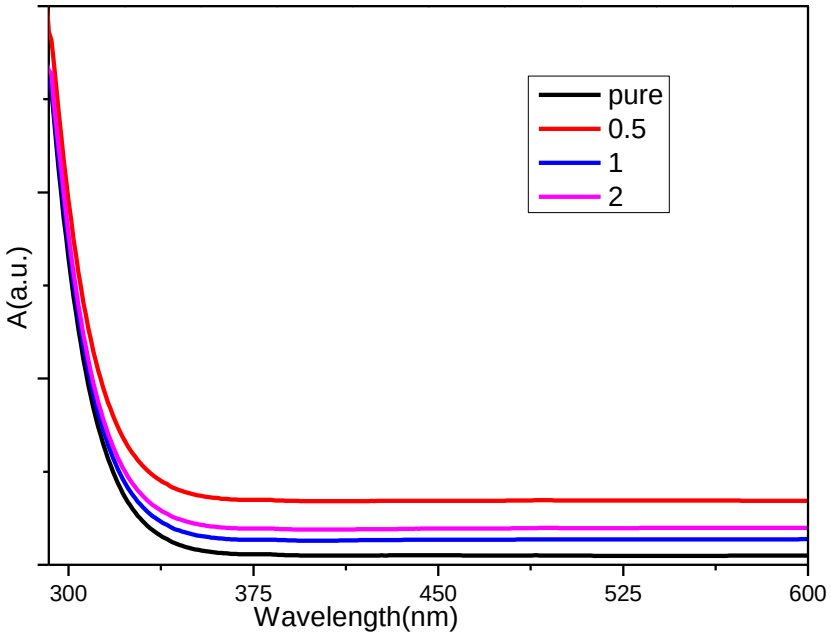

Figure 2: Absorbance spectrum of pure PVA and PVA doped with WS_2 at various concentrations.

The optical band gap (*Eg*) is determined from the Tauc plot using the relation:

$$(\alpha h\nu)^n = A(h\nu - Eg) \qquad (1)$$

where α is the absorption coefficient, h is Planck's constant, ν is the frequency of light, Eg is the optical bandgap, and n is a constant that depends on the type of electronic transition, n=2 for direct allowed transitions, and n=1/2 for indirect allowed transitions.

As shown in Figure 3 (allowed direct transition), in the case of pure PVA, the measured band gap is 4.1 eV, and that characterizes an insulator. With doping by various WS_2 concentrations: 0.5% WS_2 doping: It reduces the band gap to 4.08 eV, showing a slight decrease. 1% WS_2 doping: The band gap further decreases down to 4.06 eV. 2%WS_2 doping: This shows the merit of lowest band gap, 4.03 eV, among the samples tested.

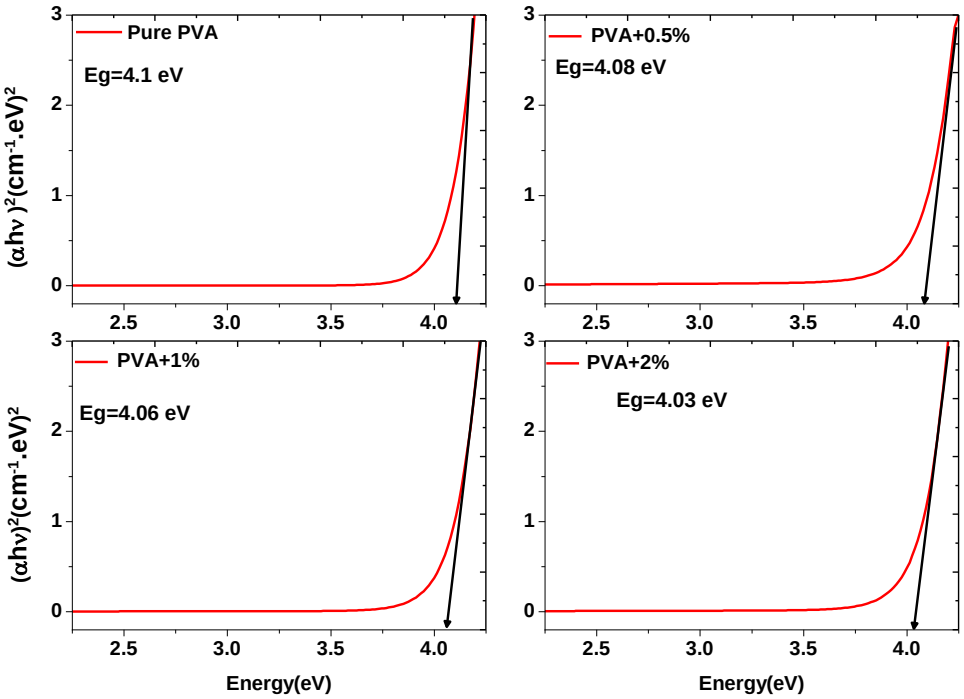

Figure 3: Plot of $(\alpha h\nu)^2$ versus energy (hν) for direct transitions in pure PVA and WS_2-doped PVA.

The band gap reduction progressively with the increment of the WS_2 content signifies the red shift in the absorption edge. This red shift [13] indicates that the incorporation of WS_2 introduces extra energy levels around the conduction band of the PVA matrix, which reduces the energy needed for electronic transitions to take place. This could be due to strong interaction between the nanoparticles of WS_2 and the PVA matrix, modifying the electronic structure to provide easier transitions at lower energies.

The red shift in the band gap with increasing WS_2 concentration provides strong evidence [14] that metal selenide nanoparticles influence the optical properties of PVA. The observed band gap reduction indicates that WS_2 lowers the energy barrier for electronic transitions, thereby enhancing optical activity in the visible region. It can be associated with the localized states created by WS_2, which allow enhanced absorption at extended wavelengths-like lower energies.

The energy red shift towards higher doping concentrations is consistent with a view that doping creates new states, thereby allowing transitions at lower energies. This minor reduction of the band gap can enable the use of such materials in optoelectronic applications, especially in areas where fine-tuning of the band gap is necessary [14].

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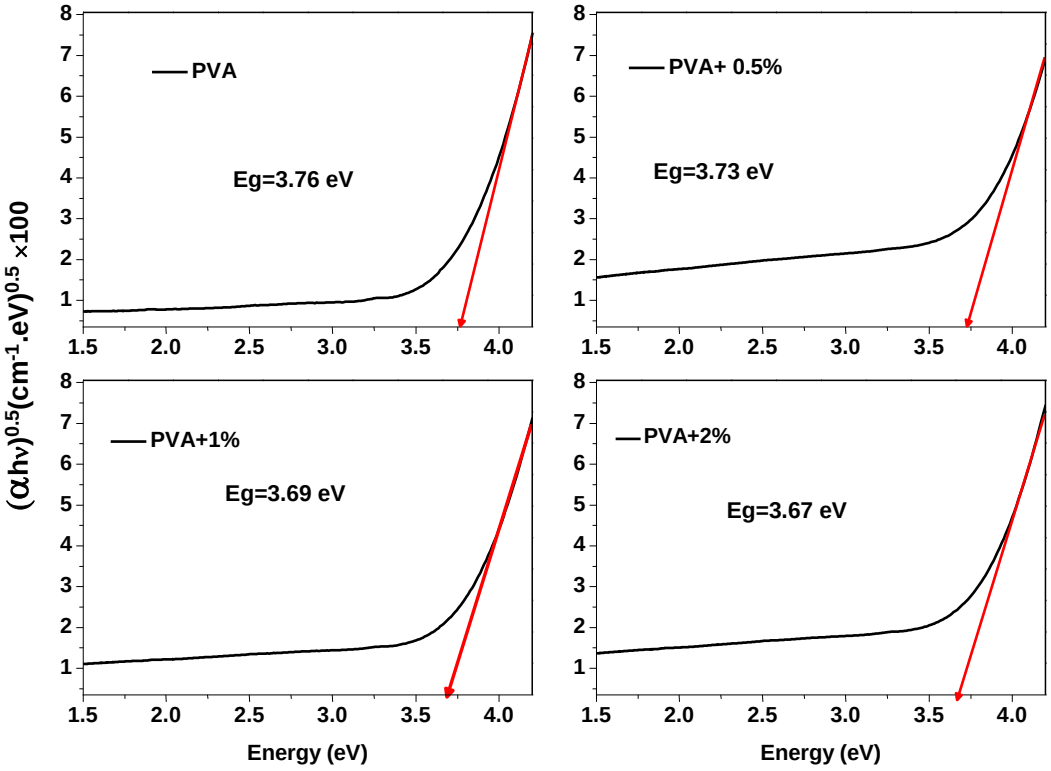

Figure 3: Plot of $(\alpha h\nu)^{0.5}$ versus energy (hν) for indirect transitions in pure PVA and WS_2-doped PVA.

Urbach Energy (E_u) is used to quantify the disorder in a material, where the relationship between the absorption coefficient (α) and photon energy (hν) follows the Urbach rule:

$$\alpha = \alpha_0 (h\nu - E_g)/E_u \qquad (2)$$

Here, α_0 is a pre-exponential factor, E_g is the energy band gap, and Eu directly reflects structural or thermal disorder. Higher Eu is associated with increased disorder, typically caused by defects or impurities. Pure PVA is characterized by a low Eu of 198 meV (Figure 4), consistent with its predominantly amorphous polymer structure containing inherent disorder. When 0.5% WS_2 is introduced, Eu is increased to 233 meV, indicating that even minimal amounts of WS_2 cause disruptions in the PVA structure, resulting in reduced ordering. At 1% WS_2, Eu is further elevated to 255 meV, suggesting the presence of additional defects and scattering sites. At 2% WS_2, the highest disorder is observed, with Eu reaching 289 meV. This is attributed to the aggregation of WS_2 nanoparticles, which leads to significant disruption of the PVA matrix.

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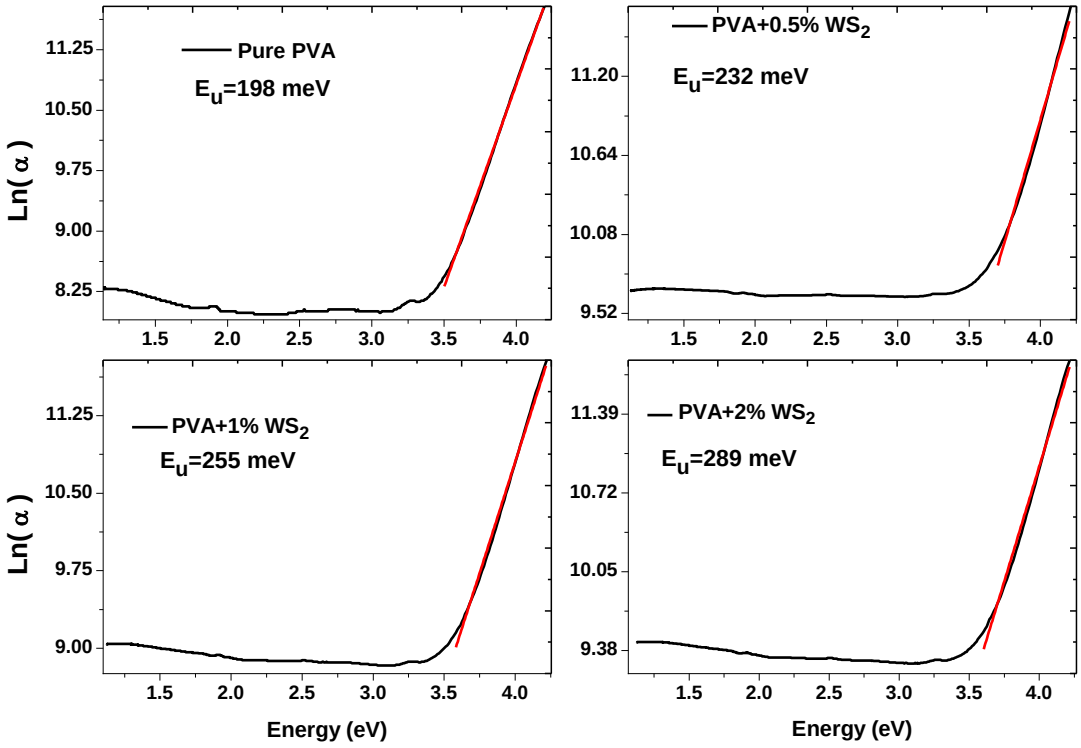

Figure4: Urbach energy for pure PVA and PVA doped with varying concentrations of WS_2.

Increased WS_2 doping is correlated with greater disorder, as reflected by higher Eu. The increased disorder is linked to a red shift in the absorption spectrum, facilitating electron transitions between states at lower energies. It is concluded that the structural disordering of PVA by WS_2 doping is responsible for the broadening of the absorption tail and alterations in optical properties, as evidenced by the rise in Urbach Energy [15].

Table 1 shows the direct band gap, indirect band gap, and normalized E_u of pure PVA and WS_2-doped PVA in different concentrations; the last three columns give the percentage change for each of those values, determined by using the following expression: $(E_1-E_i)/E_1$, where E_1 is the value for pure PVA and E_i is the value for the doped samples.

These data show that with changes in the doping ratio, the direct band gap changes. Within the range studied, the reduction of band gap energy is directly proportional to the doping concentration. However, the decrease in indirect band gap energy is roughly 1.5 times that of the direct gap. The difference might be due to the nature of the electronic transitions depending on whether the momentum changes are involved.

Also, the Urbach energy-that describes the band tail width-increases with increased doping. This is because of the increased disorder in the doped material, which is a result of the interactions between the polymer matrix and energy bands of the WS_2 dopant. Such interactions perturb the energy bands and yield a wider Urbach tail.

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Table 1: Optical parameters of PVA and WS_2-doped PVA thin films, showing bandgap energies (direct and indirect) and Urbach energy with change ratios relative to pure PVA.

Thin film	Eg direct (eV)	Eg indirect (eV)	E_u (meV)	Change ratio of Direct	Change ratio of Indirect	Change ratio of E_u
PVA	4.1	3.76	198	0	0	0
0.5%	4.08	3.73	232	0.49%	0.80%	17%
1%	4.06	3.69	255	0.98%	1.86%	29%
2%	4.03	3.67	289	1.71%	2.39%	46%

CONCLUSIONS

This research demonstrates that incorporating WS_2 Nano-particles into the PVA thin films significantly affects the material's structural and optical properties. The XRD analysis confirmed the semi-crystalline nature of pure PVA and the emergence of crystalline WS_2 phases with increasing doping levels. Optical characterization revealed a consistent decrease in the optical band gap from 4.1 eV for pure PVA to 4.03 eV for films doped with 2% WS_2, indicating a red shift in the absorption edge due to the introduction of additional energy levels near the conduction band. The increase in E_u with higher doping concentrations suggests enhanced structural disorder, which contributes to broader optical absorption. These modifications in optical properties, facilitated by WS_2 doping, highlight the potential of PVA/WS_2 Nano-composites for applications in flexible electronics, photonic devices, and optoelectronics, where control over optical band gap and light absorption is crucial. Further studies on the electronic transport and photoluminescence properties could provide deeper insights into optimizing these composites for specific applications.

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Conflict of interests.

The authors declare that they have no conflicts of interest.

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الخلاصة

مقدمة:

يُعد كحول البولي فينيل (PVA) بوليمرًا صناعيًا متعدد الاستخدامات يتمتع بخصائص بصرية وميكانيكية ممتازة، مما يجعله اختيار مناسب لمجموعة من التطبيقات. يوفر دمج جسيمات نانوية من ثاني كبريتيد التنغستن (WS_2) في كحول البولي فينيل إمكانية تعزيز هذه الخصائص، مما يتيح تطبيقات في الإلكترونيات المرنة والأجهزة البصرية الإلكترونية.

طرق العمل:

تم تحضير أغشية رقيقة من PVA مشوبة بجسيمات نانوية WS_2 بتركيزات 0.5٪ و 1٪ و 2٪ باستخدام طريقة الصب. تم ترسيب الأغشية على ركائز زجاجية بسمك 150 نانومتر. تم إجراء التوصيف البنيوي والبصري باستخدام حيود الأشعة السينية (XRD) و UV–Vis لدراسة الطبيعة شبه البلورية والسلوك البصري للمركبات.

النتائج:

كشف تحليل XRD عن الطبيعة شبه البلورية لـ PVA النقي وتكوين أطوار WS_2 البلورية مع زيادة مستويات الشوائب. أظهر التحليل الطيفي للأشعة فوق البنفسجية والمرئية امتصاصًا معززًا للضوء في المنطقة المرئية، مع تحول أحمر ثابت في حافة الامتصاص. انخفضت فجوة النطاق المباشرة من 4.1 إلكترون فولت لـ PVA النقي إلى 4.03 إلكترون فولت للأغشية المشوبة بـ WS_2 بنسبة 2٪، بينما زادت طاقة Urbach، مما يشير إلى اضطراب هيكلي أعلى مع زيادة الشوائب.

الاستنتاجات:

يؤدي دمج جسيمات نانوية من WS_2 في PVA إلى تغيير خصائصها البنيوية والبصرية بشكل كبير، مما يقلل من فجوة النطاق ويعزز امتصاص الضوء. تسلط هذه النتائج الضوء على إمكانات مركبات PVA/WS_2 النانوية للاستخدام في التطبيقات الفوتونية والبصرية الإلكترونية.

الكلمات المفتاحية:

كحول البولي فينيل، ثاني كبريتيد التنغستن، الخواص البصرية، الأغشية الرقيقة، حيود الأشعة السينية، مطيافية الأشعة فوق البنفسجية والمرئية، فجوة الطاقة، طاقة أورباخ، المركبات النانوية.