

Raman Spectroscopic Study of CdS, PVA Composite Films

Y. A. Badr,¹ K. M. Abd El-Kader,² Rasha M. Khafagy³

¹National Institute of Laser Enhanced Sciences (NILES), Cairo University, Cairo, Egypt

²Faculty of Science, Physics Department, Suez Canal University, Ismaillia, Egypt

³Faculty of Women for Art, Science and Education, Physics Department, Ain Shams University, Cairo, Egypt

Received 21 July 2003; accepted 14 October 2003

ABSTRACT: A new material, which can be used in solar energy utilization, is obtained here by adding different weights of poly(vinyl alcohol) (PVA) to the semiconducting material CdS. The effect of this addition was studied by using FT-Raman spectrometer (based on 1500 mW Nd:YAG laser at 1064 nm), UV-Vis-IR (190–800 nm) spectrophotometer, and X-ray diffractometer. Our experimental results indicated the appearance of several new Raman bands, which have not existed in both CdS and PVA. Some of the bands which are already existing in the Raman spectra of PVA showed an unexpected systematic increase in their intensities after the addition of CdS to the matrix. On the other hand, some of the new Raman bands appeared in special concentrations of PVA only, whereas some of the Raman bands of CdS were found to disappear after adding PVA. Finally, shifts in some bands associated with random increase in their intensities after adding PVA to CdS was

detected in the FT-Raman analysis. The experimental evidence given here might be attributed to the occurrence of new bonds, indicating that the produced mixture is a new material. The assignment of the new bands as well as an interpretation of the obtained variations is given here. Our X-ray diffraction data confirmed the interpretation introduced here. Moreover, the UV-Vis spectra confirmed the existence of new absorption bands in the Visible region. The I-V characteristic curve was measured for a selected concentration of the new composite material, showing a remarkable increase in the values of the conduction current of about two orders of magnitude as compared with the pure PVA material. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1984–1992, 2004

Key words: Raman spectroscopy; UV-Vis spectroscopy; WAXS; composites

INTRODUCTION

The possibility of operation by optoelectronic parameters by using the nanocrystallites (NC_s) incorporated within polymer matrices is a new promising way of creating nonlinear optical composites.^{1–5} Particular interest is connected to semiconducting NC_s because theoretical simulations^{6–8} predicted the possibility of an increase of the second-order nonlinear optical susceptibilities in this type of NC and because of their other unique properties, which are not present in bulk materials,^{9,10} where these nanoparticles exhibit size-dependent properties (size-quantization effects). Unfortunately, for a wide application of NC_s in optoelectronics, there appears to be a complication because of the necessity of preparation of high-quality homogeneous specimens. Usually the specimens are prepared similar to films deposited on a dielectric substrate; in this case, a major problem appears to be a high light-scattering background. To eliminate this problem, the guest–host polymer technique of NC-polymer composite production^{11,12} was suggested. Such a technique was applied for a Sn₂P₂S₆ semiconductor NC

incorporated in the photopolymer matrix.¹² Another reason for using the guest–host polymer technique is that semiconductor nanoparticles are themselves highly unstable, and in the absence of a trapping media or some other form of encapsulation, they agglomerate or coalesce extremely quickly.^{13,14} For this reason, bonding of capping agents to nanoparticles is necessary to provide chemical passivation, and also, to improve the surface state which has significant influence on the optical and electronic properties of nanoparticles.¹⁵ Polymers may be a good choice as stabilizers, because they can interact with the metal ions by complex or ion-pair formation and can be designed to vary certain physical properties of semiconductor nanoparticles.¹⁶ In the present work, poly(vinyl alcohol) (PVA), which is a water-soluble polymer, was used as capping polymer molecules to stabilize the CdS nanoparticles.¹³ Moreover, the calculated charge density distributions in the PVA photopolymers^{17–19} indicated a good complementary of the PVA polymers to the CdS nano-semiconducting crystallites because the appropriate matrix dipole moments are almost collinear. Another important advantage of the PVA matrices is their good mechanical and acousto-optical properties,¹⁷ where this parameter determines the photoinduced response in the newly suggested composite.

Correspondence to: Y. A. Badr (ybadr@hotmail.com).

On the other hand, CdS is one of the most studied materials, with a band gap of about 2.43 eV.^{20–23} It is an efficient window layer for the fabrication of solar cell structures because of its high transmittivity and low resistivity. Furthermore, CdS thin films have been considered for application in heterojunction solar cells^{24,25} and optoacoustic transducers.²⁶ Also, PVA has been used in a wide variety of fields since its discovery in 1924.^{27–34} The optical uses of PVA are concerned with the retardation, polarization, and filtration of light, as well as with photography³⁵ and related imaging fields. PVA can be also used in medical applications such as artificial blood vessels, artificial intestines, contact lenses, and drug-delivery systems.^{36–38} Different additives are usually added to polymers to modify and improve their properties. Inorganic additives such as transition metals salts have considerable effect on the optical and electrical properties of the PVA polymer.^{26,39}

Because PVA is water soluble, it is important to understand the chemical mechanisms involved in the reaction of this material with water.⁴⁰ Vibrational spectroscopies (infrared and Raman) are important techniques in the characterization of molecular structure and the mechanisms of chemical reactions in which chemical species are involved. Because the IR absorption by water molecules is very strong, it is thought here that the Raman spectroscopic studies can provide a better insight into the solubilization mechanism not only for the PVA films, but also for the CdS+PVA films, where this issue could be more important because of the addition of PVA to the soluble material CdS during the preparation of the new complex in the form of thin films. Furthermore, Raman spectroscopy of crystalline semiconductors is a fast and nondestructive technique to assess sample qualities such as microcrystallinity, homogeneity, and surface conditions.⁴¹ Raman spectra of crystalline samples are known to give rise to sharp peaks, whereas that of amorphous or polycrystalline samples show very broad peaks. Tensile and compressive stresses affect the Raman spectrum by a shift. For nanocrystallites, the confinement effect induces a broadening and downward shift of the Raman peaks.^{42,43} We analyze the Raman spectra of the samples (Fig. 1), keeping these aspects in mind. In an ideal bulk crystal, the phonons can be represented by plane-wave-like functions having a spatial extension over the whole crystal, which can be considered infinite. However, in nanocrystals, the phonon cannot penetrate significantly beyond the crystallite surface surrounded by the dielectric matrix. The confinement of the phonon to the volume of the microcrystal results in the relaxation of the conservation of crystal momentum in the process of creation and decay of phonons leading to the asymmetric broadening and low frequency shift of the longitudinal optical phonons (1LO)-Raman peaks. More-

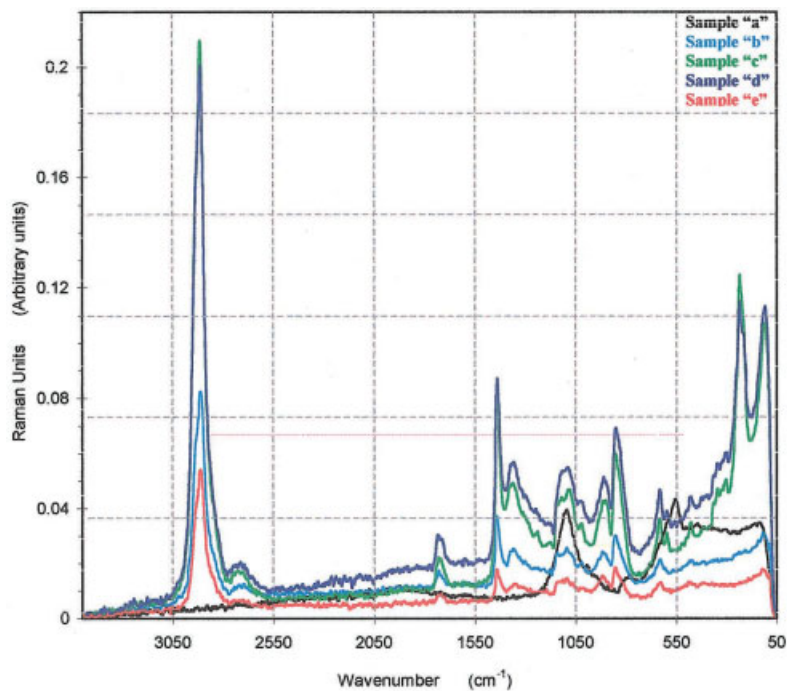
over, none of the reported Raman spectra for PVA in the new compound were analyzed⁴⁰ in detail for the problem of dissolution. Consequently, it is aimed in this work to consider the changes in the Raman spectra of CdS due to the addition of different concentrations of PVA to account for the effect of dissolution on the CdS+PVA films obtained here because we consider that mixing CdS with PVA might lead to a new material that has several advantages and new properties, which make its applications in the production of simple and cheap types of solar cells quite possible.

EXPERIMENTAL

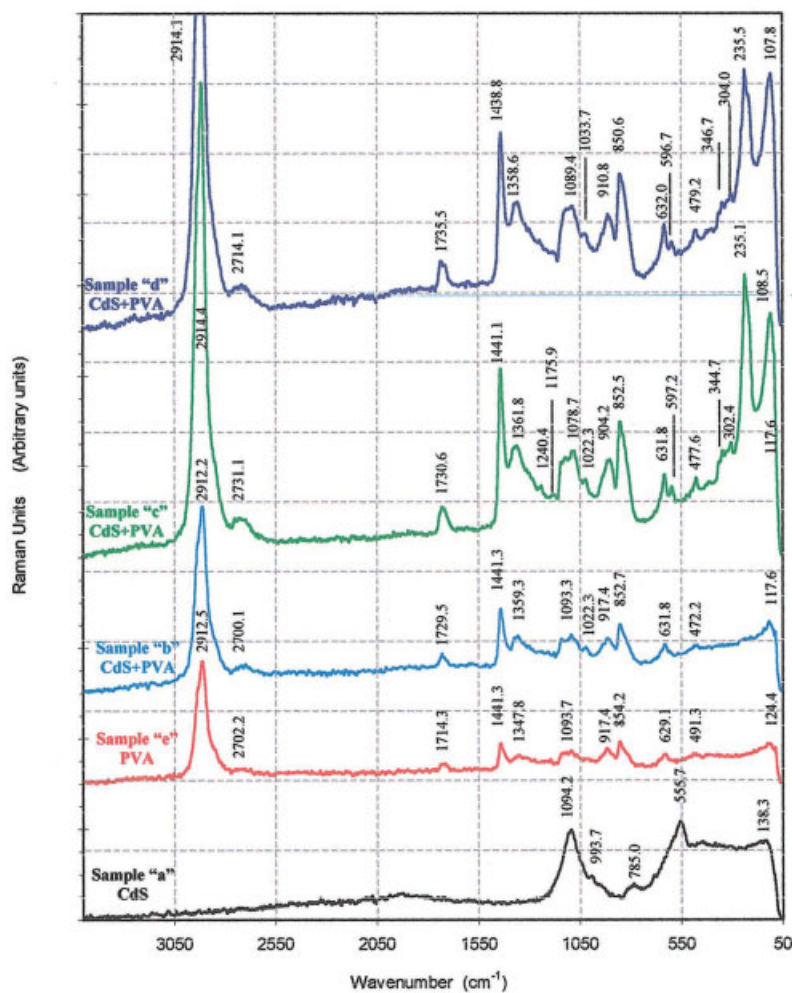
PVA with a molecular weight of 17,000 g/mol (sample e; BDH, UK) was used as a basic polymeric material in this work. PVA films were prepared by using a casting technique. PVA solution was prepared by dissolving 3 g PVA in 50 mL of distilled water and maintained for 24 h at room temperature to swell. The solution was then warmed up to 333 K and thoroughly stirred by using a magnetic stirrer for 4 h until the polymer became completely soluble. The solution was poured into flat glass plate dishes. Homogeneous films were obtained after drying in an air oven for 48 h at 313 K. The thickness of the produced films was 200 μm . The mechanism of preparing the CdS-PVA composite films is illustrated in Table I, at which the following steps are indicated:

- Step 1: Addition of CdCl₂ to CdS + 20 mL of distilled water
- Step 2: Addition of PVA to 30 mL of distilled water
- Step 3: Step 1 is added to step 2
- Step 4: The final solution was poured into flat glass plate dishes
- Step 5: Homogeneous films were obtained after drying in an air oven for 48 h at 313 K.

The FT-Raman spectra were measured by using a Bruker FT-Raman spectrometer of type RFS 100/S, which is attached to a Bruker-IFS 66/S spectrometer, which provides high resolution to better than 0.10 cm^{-1} . Bruker's patented frictionless interferometer with its Rocksolid alignment provides high sensitivity and stability. The diode-pumped, air-cooled Nd:YAG laser source with maximum laser power of 1500 mW at 1064 nm is controlled completely through software. The standard RFS 100/S configuration provides a spectral range of 70–3600 cm^{-1} (Stokes shift) and –100 to –2000 cm^{-1} (anti-Stokes shift). To measure the I-V characteristic curve, a pure PVA sample in addition to sample b were used after evaporating Au electrodes with an area of about 3 mm^2 and a thickness of 100 nm. Measurements were taken for different voltages up to 60 V by using a Keithley electrometer model 616.



(a)



(b)

Figure 1 (a) FT-Raman scattering spectra for the samples without any separation of the curves; (b) FT-Raman scattering spectra. (All the spectra are shifted vertically for clarity.) [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
The Percentage of Each Sample as Used in the Samples Preparation

Sample No.	CdCl ₂ (g)	CdS (g)	Weight of PVA (g)
a	—	Pure CdS	—
b	1	0.5 + 20 mL Water	2.5 + 30 mL Water
c	1	0.27 + 20 mL Water	1.5 + 30 mL Water
d	1	0.125 + 20 mL Water	2.875 + 30 mL Water
e	—	—	Pure PVA

RESULTS AND DISCUSSION

Raman spectra

It is well known that the vibrational spectra of PVA are related to the vibrational modes of (—CH₂—CHOH—) monomer, which is expected to have 17N modes of vibrations.⁴⁴ Because this monomer lacks a center of symmetry, the 17 modes are expected to be active in both Raman and IR. Moreover, PVA is considered as disordered, and consequently, the degree of disorder and polymerization may cause small shifts in band positions between IR and Raman spectra. The Raman spectra of pure CdS (sample a), Pure PVA (sample e), and three different mixtures of CdS+PVA (samples b, c, and d, respectively) are given in Figure 1(a, b). Table II summarizes the most pronounced Raman peaks and the corresponding assignments given in literature.⁴⁵ This table showed that some of the bands obtained here were not detected before and not given any assignments.

The Raman spectra of pure PVA film showed only 11 bands, and as mentioned above, the dissolution might have a strong effect on the position of the Raman bands. We considered the data given⁴⁰ for dry, wet, and films of PVA⁴⁵ for comparison and to account for the variations occurring because of the addition of the polymeric material PVA to the semiconducting material CdS. On the other hand, Pure CdS showed six vibrational bands, as given in Table II. Adding PVA (with different concentrations) to CdS resulted in several changes in the spectrum such as the increase in the number of Raman bands obtained for CdS+PVA (e.g., sample b showed 13 bands; sample c showed 18 bands, while sample d showed 17 bands). This might mean that adding PVA to CdS resulted in the appearance of new vibrational bands, which are not present in both PVA and CdS Raman spectra. This observation might lead to the conclusion that new bonds occurred because of this addition (i.e., a new material is obtained). Also, Raman spectra of the present samples contain relatively sharp crystalline-like peaks originating from the fixed surface boundary conditions of CdS nanocrystals surrounded by the polymer matrix.⁴¹ Some of the newly appearing bands appeared only in sample c such as the very weak band at 1240.4, which is not appearing in any other form of PVA. Other

bands are appearing in sample c and d only, as follows: 108.5, 235.1, 302.4, 344.7, 597.2 cm⁻¹. Hexagonal CdS exhibits a first-order Raman band at 304 cm⁻¹ and a second-order band around 600 cm⁻¹, which corresponds to the first-order (LO) and second-order 2(LO) vibrations of hexagonal CdS, respectively.⁴⁶⁻⁴⁸ This band appeared here only after adding PVA to CdS. Also, in the CdS-PVA composites, bands above 300 and 600 cm⁻¹ are associated with the formation of CdS particles in the PVA host. When the CdS concentration increases, the Raman spectra strongly reflects the CdS particle growth. The crystallite quality in samples c and d is better than in sample b. The bands observed around 600 cm⁻¹ can be associated to a second-order of the LO mode, which could be understood as a resonant Raman effect, because of the limited size of the CdS particles or as transitions from the cluster system. More experimental data are necessary to confirm one of these hypotheses. Finally, the obtained Raman bands are suffering from several abnormal behaviors, including the following:

1. The Raman band at 2912.5 cm⁻¹ of pure PVA, which is assigned as $\nu_s(\text{CH}_2)$,⁴⁰ showed an abnormal behavior for the CdS-PVA composite samples, where its intensity was found to increase with the increase of the amount of CdS added to PVA. It was expected that this band would suffer some kind of reduction in its intensity as the PVA matrix is diluted by CdS. It is thought here that the addition of PVA to the CdS matrix caused the CH₂ to form some kind of clustering, and the size of these clusters increases as the concentration of CdS in the matrix increases. On the other hand, at certain concentrations, repulsion between clusters occurs, leading to a slight decrease in the intensity of this band.

2. The new band appearing at about 1022 cm⁻¹ only after adding PVA to CdS, and which is attributed to S=O symmetric ring vibration, might lead to the conclusion that addition of PVA to CdS resulted in a new vibrational band combining the sulfur in CdS to O and OH from PVA, indicating that a new compound is obtained. Similar interpretation can be applied to the bands at 629.1, 1093.3, 1359.3, and 1441.3 cm⁻¹.

3. CdS was found to have two pronounced bands at 555.7 and 1094.2 cm⁻¹ in addition to several shoulders at 138.3, 785.0, and 993.7, and a hallow at 1924.0 cm⁻¹. The first pronounced band at 555.7 cm⁻¹ (S—S valence) was found to disappear completely in the composites of CdS+PVA. The second band at 1094.2 cm⁻¹ (—SO—OH) cannot be distinguished from that band of PVA at 1093.7 cm⁻¹ (νCO). However, generally it is existing but shifted toward lower wave number in other samples.

4. A shift of more than 15 cm⁻¹ in some PVA bands was associated with a remarkable increase in the intensity due to the addition of PVA to the CdS matrix.

- The shift is mostly toward the low frequency side, for example,

TABLE II
Comparison between the Obtained FT-Raman Bands for PVA as well as the Corresponding Assignments as Compared with Literature [44, 45], in Addition to the FT-Raman Bands Obtained for Different Composites

Assignment	Raman bands as given in literature			Raman bands as given in our experimental data				
	PVOH dry	PVOH wet	PVOH film	PVA e	Sample b	Sample c	Sample d	CdS a
—	—	—	—	124.4 vw	117.6 w	108.5 s	107.8 s	—
—	—	—	—	—	—	—	—	138.3 vw
CC torsion and bending [45]	Freq. decrease as chain length increase			—	—	235.1 s	235.5 s	—
—	—	—	—	—	—	302.4 w	304.0 w	—
Monosubstituted acetylenes (also at 630) [45]	—	—	—	—	—	344.7 w	346.7 w	—
Disubstituted acetylenes [45]	369 w	372 w	367 w	—	—	—	—	—
$\gamma_w(\text{CO})$ [44]	413 w	423 w	412 w	—	—	—	—	—
$\delta(\text{CO})$ [44], CH out-of-plane [45]	480 w	475 w	475 w	—	—	—	—	—
CICHCHCI out-of-plane [45]	—	—	—	491.3 vw	472.2 vw	477.6 w	479.2 w	—
CH out-of-plane [45]	521 vw	522 vw	524 vw	—	—	—	—	—
S—S valence [45] (alkyl disulfides)	—	—	—	—	—	—	558.6 vvw	555.7 s
$\gamma_w(\text{OH})$ [44]	592 vw, sh	603 vw, sh	580 vw, sh	—	—	597.2 w, sh	596.7 vw, sh	—
$\gamma_w(\text{OH})$, $\gamma_t(\text{OH})$ [44], CS stretch [45]	628 m	633 m	627 m	629.1 w	631.8 w	631.9 m	632.0 m	—
—	—	—	—	—	—	—	—	785.0 w
$\gamma_r(\text{CH}_2)$ [44]	—	810 w, sh	807 w, sh	—	—	—	—	—
$\gamma(\text{CC})$, Skel [44]	853 s	853 s	852 s	854.2 m	852.7 m	852.5 s	850.6 s	—
Ring vib. [45]	891 m, sh	—	—	—	—	—	—	—
$\gamma_r(\text{CH}_2)$, Skel [44]	915 m	909 s	914 s	917.4 w	917.5 w	904.2 m	910.8 m	993.7 vw, sh
Symmetric ring vib., S=O [45]	1023 w	1025 w	1020 w	—	1022.3 vw, sh	1022.2 vw, sh	1033.7 vw, sh	—
$\nu(\text{CO})$ [44], —SO—OH [45],	1070 w, sh	1074 w, sh	1068 w, sh	1093.7 w	1093.7 w, sh	1078.7 m, sh	1089.4 s	1094.2 s
$\nu(\text{CO})$, $\delta(\text{CO}+\text{OH})$ [44]	1093 m	—	—	—	—	—	—	—
C—OH valence asymmetric ring vibration [45]	1125 vw	1125 s	1124 m	—	—	—	—	—
$\nu(\text{C—O—C})$, $\nu(\text{CC}+\text{CO})$ [44]	1146 m	—	1141 vw	—	1141.7 w, sh	1121.4 m, sh	—	—
Ring vib. cyclopropane derivatives [45]	—	1189 vw	1181 vw	—	—	—	—	—
$\gamma_w(\text{CH})$ [44]	1237 w	1229 vw	1233 w	—	—	1240.4 vw, sh	—	—
$\delta(\text{CH}+\text{OH})$ [44]	—	—	1295 vw	—	—	—	—	—
$\delta(\text{CH}+\text{OH})$ [44] R—SO ₂ —R [45]	1356 m	1346 m	1351 m	1347.8 vw	1359.3 w	1361.8 m, sh	1358.6 m, sh	—
$\gamma_w(\text{CH}_2)$ [44]	1371 m	1376 m	1372 m	—	—	—	—	—
$\delta(\text{CH}_2)$ [44], —O—SO ₂ —O [45]	1441 s	1435 s	1435 s	1441.3 m	1441.4 m	1441.1 s	1438.8 s	—
C=O residual acetate [44]	1711 m	1711 m	—	1714.3 w	1729.5 w	1730.6 m	1735.5 m	—
C=O [45]	1727 m	—	1721 bd	—	—	—	—	—
—	—	—	—	—	—	—	—	1924.2 hallow
—	2245 vw, bd	2235 w, bd	2250 vvw	—	—	—	—	—
—	2712 w	2736 w	2715 w	2702.2 vw	2700.1 w	2731.1 w	2714.1 w	—
$\nu(\text{CH})$ [44]	2835 w, sh	2851 w, sh	2838 w, sh	—	—	—	—	—
$\nu_s(\text{CH}_2)$, $\nu(\text{CH})$ [44]	2910 s	2918 s	2911 s	2912.5 s	2912.2 s	2914.4 vs	2914.1 vs	—
$\nu_a(\text{CH}_2)$, $\nu(\text{CH})$ [44]	2934 m, sh	—	2933 m, sh	—	—	—	—	—
—	3025 vw	—	3025 vw	—	—	—	—	—
$\nu(\text{OH})$ [44]	3380 w, bd	obsc	3335 w, bd	—	—	—	—	—

PVOH Dry, PVOH wet, and PVOH film refer to Raman experiments on initial pellet, aqueous solution, and precipitated film, respectively. Abbreviations: s: strong; m: medium; w: weak; vw: very weak; vvw: very very weak; sh: shoulder; bd: broad; skel: skeletal; obsc: obscured by overlapping H₂O band; vib: vibration. Symbols: ν : stretch; ν_a : asymmetric stretch; δ : bend; γ_w : wag; γ_r : rock; γ_t : twist.

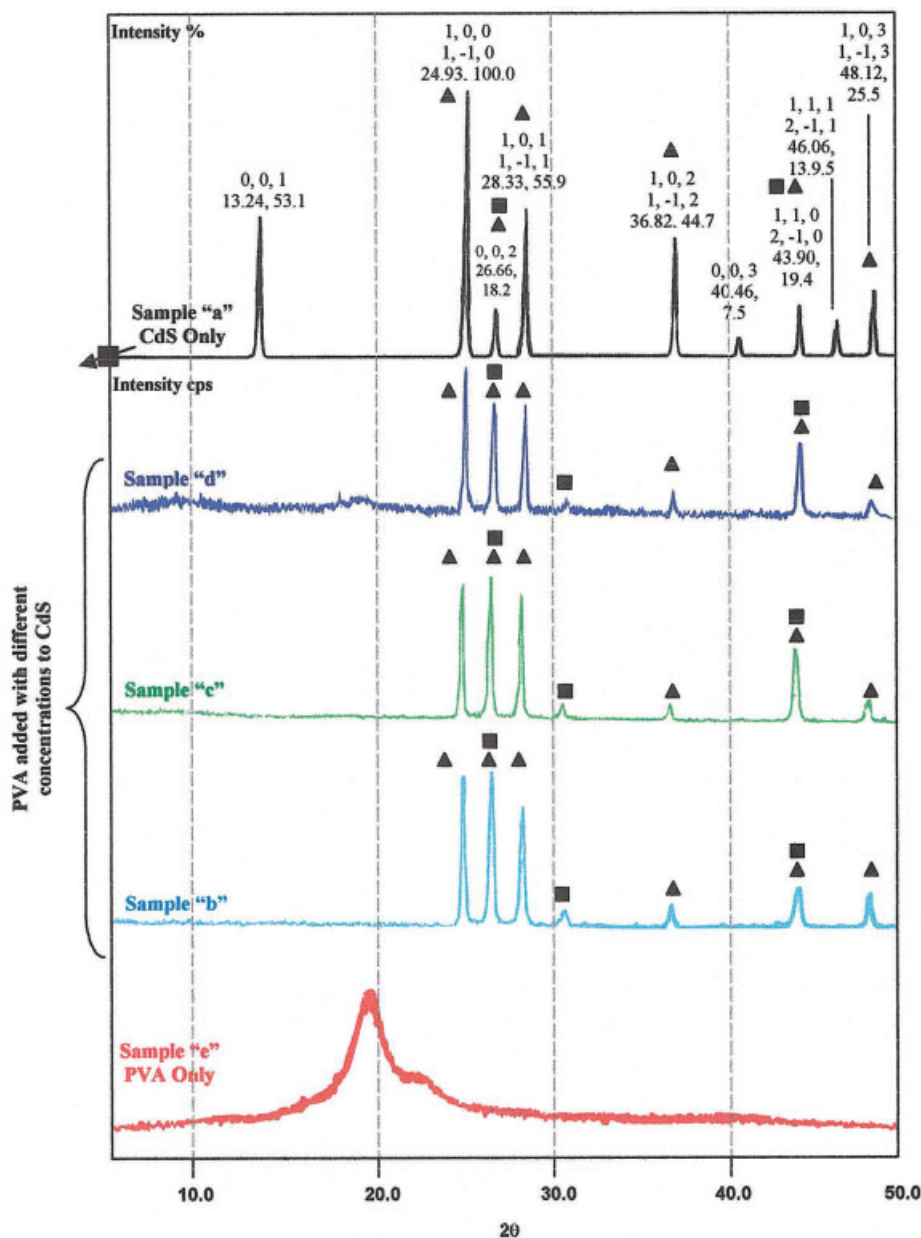


Figure 2 XRD patterns for pure CdS (sample a), PVA (sample e), and the different mixtures of CdS+PVA. ▲: hexagonal; ■: cubic. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

124.4 cm^{-1} \rightarrow 117.6, 107.8, and 108.5 cm^{-1}
 491.3 cm^{-1} [$\delta(\text{CO})$] \rightarrow 472.2, 477.6, and 479.2 cm^{-1}
 917.4 cm^{-1} [$\gamma_r(\text{CH}_2)$, Skel] \rightarrow 917.5, 904.2, and 910.8 cm^{-1}

- The shift toward higher frequency such as in the bands

2702.2 cm^{-1} \rightarrow 2700.1, 2731.1, and 2714.1 cm^{-1}
 1347.8 cm^{-1} [$\delta(\text{CH} + \text{OH})$] \rightarrow 1359.3, 1361.8, and 1358.6 cm^{-1}
 1714.3 cm^{-1} [C=O] residual acetate \rightarrow 1729.5, 1730.6, and 1735.5 cm^{-1}

629.1 cm^{-1} [$\gamma_w(\text{OH})$, $\gamma_t(\text{OH})$] \rightarrow 631.8, 631.9, and 632.0 cm^{-1}

The band at 1714 cm^{-1} (C=O), which is thought to be associated with the acetate residuals, suffered from a shift in addition to an increase in the intensity; this could be attributed to the effect of dissolution as confirmed by Krimm et al.⁴⁴ in their analysis and conclusions concerning PVA films, which has vibrational bands lying between dry and wet PVA bands. In addition to the remarkable shifts of some of the bands belonging to CdS and PVA due to mixing, clear change in the intensities of some of the PVA bands due to the addition of CdS were also observed, where

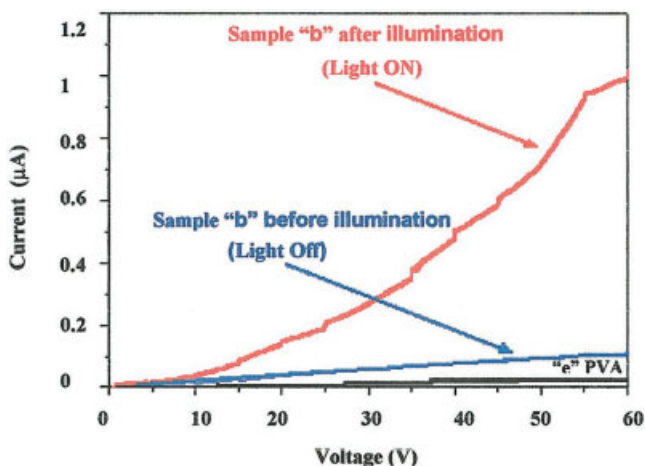


Figure 3 The I-V characteristic curve for pure PVA sample in addition to sample b before and after illumination with white light. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PVA vibrational modes were found to have frequencies very close to those obtained for dry PVOH before being mixed with CdS, whereas after mixing the solubility was found to be improved as the frequencies become closer to the wet PVOH.⁴⁴ Moreover, our X-ray diffraction patterns showed the disappearance of some bands in CdS and the appearance of a new diffraction pattern not existing in either CdS or PVA. These experimental evidences might lead us to the conclusion that the CdS–PVA composites represent some kind of new materials.

WAXS patterns

Our X-ray diffraction data for pure CdS (sample a), PVA (sample e), and the different mixtures of CdS–PVA composites as given in Figure 2 showed that PVA, which is well known to be as a crystalline polymer,⁴⁹ has only two diffraction patterns at 2θ : 19.15° , 19.76° representing the crystalline phase,⁴⁹ followed by a nearby shoulder (hallow) representing the non-crystalline (amorphous) part of the sample. The crystalline nature of PVA results from the strong intermolecular interaction between PVA chains through the intermolecular hydrogen bonding.⁴⁹ The intensity of the diffraction and also the size of the crystals in PVA are determined by the number of PVA chains packing together.⁴⁹ CdS has nine lines, as shown in Figure 2, together with the corresponding h k l layers. After being complexed with sulfides, the PVA lines disappeared totally. This is because the interactions between PVA with CdS led to the decrease of the intermolecular interaction between the PVA chains and thus the crystalline degree.⁴⁹ CdS–PVA composite samples showed a fewer number of patterns, whereas three lines of CdS at $2\theta = 13.24^\circ$, 40.46° , 46.06° also

disappeared. On the other hand, the relative intensities of the bands showed abnormal behavior with the increase of the amount of CdS in the matrix. Finally, a new small diffraction pattern at about $2\theta = 30.7^\circ$ appeared only after adding PVA to CdS, which did not show up in either pure CdS or pure PVA and the intensity of this band is minimum at higher concentrations of PVA in CdS. It is well known that CdS can exist in either cubic or hexagonal phase or as a mixture of both phases. Recently, a transition from the cubic phase to the stable hexagonal phase can be achieved under certain conditions.⁵⁰ Also, Lui et al.⁵¹ showed the coexistence of both the cubic and the hexagonal phases of CdS in some samples and pure hexagonal phase in other CdS samples, depending on the reaction time consumed during the sample preparation. The band at $2\theta = 30.61^\circ$, which characterizes the cubic phase,⁹ appeared in our case only after adding PVA to CdS, while the intensity of all the peaks characterizing the hexagonal phase only such as the peaks at $2\theta = 48.12^\circ$, 36.82° , and 24.93° suffered a remarkable reduction after mixing with PVA. On the other hand, the intensity of the peaks belonging to both phases increased upon mixing, indicating that mixing CdS with PVA caused a change from the hexagonal phase to the cubic one. Again, this experimental remark confirms the anomalous behavior reported here of the Raman band at 2914.1 cm^{-1} , the intensity of which was found to be increasing as the concentration of CdS is increased (i.e., its intensity decreases as the concentration of PVA is increased). These two experimental facts might confirm the clustering processes proposed here in PVA as the concentration of CdS increases. The disappearance of the PVA bands in the matrix together with the irregular change in the relative intensities might reflect the fact that the existence of CdS caused some kind of clustering of the PVA segments leading to an irregular distribution of the CdS in the matrix. This might confirm the unexpected increase of the Raman band at 2912.5 cm^{-1} with the increase of CdS in the matrix.

UV-vis spectra

To account for the performance of PVA before and after the addition of CdS and the improvement in its electrical conductivity, we measured the I-V characteristic curve for pure PVA sample in addition to sample b before and after illumination with white light, as shown in Figure 3. The curve of pure PVA remained constant after illumination, whereas that of sample b showed drastic changes, indicating an increase in the current of about two orders of magnitude. This might be attributed to the creation of free radicals and electrons in the composite because of the existence of the *n*-type CdS semiconducting material, which is enriched with free electrons in the

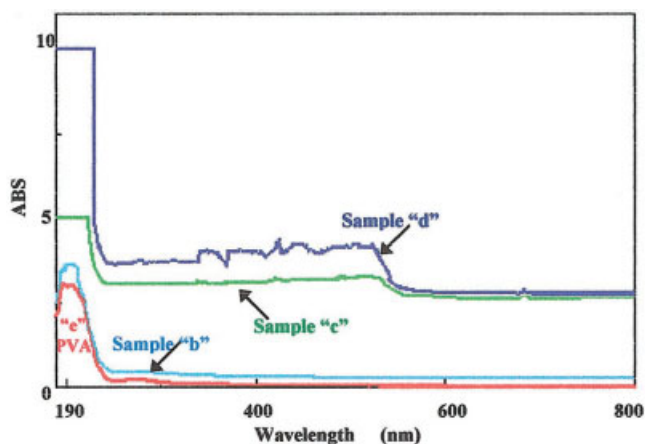


Figure 4 The optical absorption of PVA (sample e) and CdS–PVA mixtures (samples b, c, and d) in the UV–visible region (190–800 nm) by using the spectrophotometer Jasco model V-570. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PVA matrix. On the other hand, PVA might contain new free radicals resulting from the new bonds as proposed here, indicated by the appearance of new vibrational modes together with the disappearance of others.

As mentioned above, the new CdS–PVA composite showed an improvement in the optical properties of both CdS and PVA and consequently their performance. Such an improvement of the optical response of the composite due to the existence of PVA was detected before by Jorkaala and Stenonen,⁵² who used PVA photopolymer as a matrix to improve the optical properties and response of the semiconducting material ZnSe. It was thought worthwhile here to consider the optical absorption of PVA and CdS+PVA in the UV–visible region (190–2500 nm) by using the spectrophotometer Jasco model V-570. Our data showed that in the visible region (190–800 nm) several absorption bands show up in the new composites that are not appearing in PVA, as seen in Figure 4, while the UV and IR regions did not show any variations after adding PVA to CdS. In conclusion, the results obtained here showed that adding PVA to CdS resulted in the appearance of new bands in Raman, UV–vis, and X-ray diffraction patterns, together with the disappearance of original bands existing in pure PVA and CdS, confirming the production of new material (composite) with modified optical and electrical properties, which is thought here to be a good step toward the production of an organic material to be utilized as solar cells that is much cheaper and simple as compared with solar cells produced by spray pyrolysis, for example, or single-crystal substrates such as CdTe.

References

- Norris, D. J.; Bavendi, M. G. *J Chem Phys* 1995, 103, 5260.
- Mews, A.; Kadavanich, A. V.; Banin, U.; Alivisatos, A. P. *Phys Rev B: Condens Matter* 1996, 53 (13), 242.
- Majchrowski, A.; Mefleh, A.; Lee, R.; Makowska-Janusik, M.; Kasperczyk, J.; Kityk, I. V.; Berdowski, J.; Benet, S. *Nonlinear Opt* 2000, 24, 335.
- Hill, N. A.; Whaley, K. B. *Phys Rev Lett* 1995, 75, 1130.
- Kityk, I. V.; Kassiba, A.; Benet, S. *J Cluster Sci* 2001, 12, 399.
- Schoenlein, R. W.; Mittelman, D. M.; Shiang, J. J.; Alivisatos, A. P.; Shank, C. V. *Phys Rev Lett* 1993, 70, 1014.
- Plucinski, K. J.; Kityk, I. V.; Kassiba, A. *Proc SPIE* 2000, 4182, 276.
- Li, Y.; Takata, M.; Nakamura, A. *Phys Rev B: Condens Matter* 1998, 57, 9193.
- He, S. T.; Yao, J. N.; Xie, S. S.; Pang, S. J.; Gao, H. J. *Chem Phys Lett* 2001, 343, 28.
- Fukuoka, A.; Sakamoto, Y.; Guan, S.; Inagaki, S.; Sugimoto, N.; Fukushima, Y.; Hirahara, K.; Iijima, S.; Ichikawa, M. *J Am Chem Soc* 2001, 123, 3373.
- Kuzyk, M.; Poga, C. *Molecular Nonlinear Optics*; Academic Press: New York, 1994; Chapter 7, p. 209.
- Kityk, I. V.; Mervinskii, R. I.; Kasperczyk, K. J.; Jossi, S. *Mater Lett* 1996, 27, 233.
- Liu, S. H.; Qian, X. F.; Yin, J.; Ma, X. D.; Yuan, J. Y.; Zhu, Z. K. *J Phys Chem Solids* 2003, 64 (3), 455.
- Winiarz, J. G.; Zhang, L.; Lal, M.; Friend, C. S.; Prasad, P. N. *Chem Phys* 1999, 245, 417.
- Qi, L.; Cölfen, H.; Antonietti, M. *Nano Lett* 2001, 1, 61.
- Yao, H.; Takada, Y.; Kitamura, N. *Langmuir* 1998, 14, 595.
- Kityk, I. V.; Kasperczyk, J.; Sahraoui, B.; Yasinskii, M. F.; Hollan, B. *Polymer* 1997, 38, 4803.
- Mervinskii, R. I.; Petrenko, O. G.; Kityk, I. V.; Lazarenko, E. T. *Opt Spectrosc* 1995, 78, 287.
- Petrnko, O. G.; Mervinskii, R. I.; Kityk, I. V. *J Opt Technol* 1995, 62, 26.
- Kitaev, G. A.; Urtskaya, A. A. *Russian J Appl Chem* 1992, 72 (4), 592.
- Vassiltsova, O. V.; Chuvilin, A. L.; Parmon, V. N. *J Photochem Photobiol, A* 1999, 125 (1–3), 127.
- Ellot, D. J.; Furlong, D. N.; Grieser, F. *Colloids Surf, A* 1999, 155 (1), 101.
- Battisha, I. K.; Afify, H. H.; Abd El Fattah, G.; Badr, Y. *Fizika A (Zagreb)* 2001, 10 (3), 33901.
- Matsuzaw, S. *Hand Book of Thermoplastics*; Marcel Dekker: New York, 1997.
- Kaetsu, I., Ed.; *Drug Delivery System*; CMC: Tokyo, 1986.
- Tawansi, A.; Oraby, A. H.; Zidan, H. M.; Dorgham, M. E. *Physica B* 1998, 254, 126.
- Abd El-Kader, K. M.; El-Lawindy, A. M. Y.; Mansour, A. F.; Abd Hamied, S. F. *J Appl Polym Sci* 2002, 84 (6), 1295.
- Abd El-Kader, K. M.; Orabi, A. S. *Polym Test* 2002, 21 (5), 591.
- Abd El-Kader, K. M.; Abdel Hamied, S. F. *J Appl Polym Sci*, 2002, 86, 1219.
- Abd El-Kader, K. M.; Abd Hamied, S. F.; Mansour, A. B.; El-Lawindy, A. M. Y.; El-Tantaway, F. *Polym Test* 2002, 21 (7), 849.
- Abd El-Kader, K. M. *J Appl Polym Sci* to appear.
- Lopez, D.; Cendoya, I.; Torres, F.; Tejada, J.; Mijangos, C. *J Appl Polym Sci* 2001, 82, 3215.
- Suzuki, M.; Yoshida, T.; Koyama, T.; Kobayashi, S.; Kimura, M.; Hanabusa, K.; Shirari, M. *Polymer* 2000, 41, 4531.
- Krumova, M.; Lopez, D.; Benavente, R.; Mijangos, C.; Perea, J. M. *Polymer* 2002, 42, 591.
- Finch, C. A. in *Polyvinyl Alcohol Properties and Applications*; Wiley: New York, 1973; p. 508.
- Horike, S.; Matsuzawa, S.; Yamaura, K. *J Appl Polym Sci* 2002, 84, 1178.

37. Matsuzaw, S. *Hand Book of Thermoplastics*; Marcel Dekker: New York, 1997.
38. Kaetsu, I., Ed.; *Drug Delivery System*; CMC: Tokyo, 1986.
39. Sengupta, A.; Holtz, M.; Quitevis, E. L. *Chem Phys Lett* 1996, 263, 25–32.
40. Cooney, T. F.; Wange, L.; Shaarma, S. K.; Gauldie, R. W.; Montana, A. J. *J Polym Sci, Part B: Polym Phys* 1994, 32, 1163–1174.
41. Nandakumar, P.; Vijayan, C.; Rajalakshmi, M.; Arora, A. K.; Murti, Y. V. G. S. *Physica E* 2001, 11 (4), 377.
42. Richter, H.; Wang, Z. P.; Ley, L. *Solid State Commun* 1981, 39, 625.
43. Campell, I. H.; Fauchet, P. M. *Solid State Commun* 1986, 58, 739.
44. Krimm, S.; Liang, C. V.; Sutherland, B. B. M. *J Polym Sci* 1956, 22, 227.
45. Tobin, M. C., *Laser Raman Spectroscopy*; Wiley-Interscience: New York, 1970.
46. Villavicencio García, H.; Hernández Vélez, M.; Sánchez Garrido, O.; Martínez Duart, J. M.; Jiménez, J. *Solid-State Electron* 1999, 43 (6), 1171.
47. Pechar, F.; Rykl, D. *Zeolites* 1983, 3, 329.
48. Landot, B. *Numerical Data and Functional Relationships in Science and Technology*; New series group III V. 17. *Semiconductor*; Springer Verlag: Berlin, 1988.
49. Qian, Xue-Feng; Yin, Jie; Huang, Jun-Chao; Yang, Xiao-Xia Guo, Yan-Fei; Zhu, Zi-Kang *Mater Chem Phys* 2001, 68 (1–3), 95.
50. Senthil, K.; Mangalaraj, D.; Narayandass, Sa. K. *Appl Surf Sci* 2001, 169–170, 476.
51. Liu, S. H.; Qian, X. F.; Yin, J.; Xi, H. A.; Huang, Z. H.; Zhu, Z. K. *Mater Sci Eng, B* 2003, 98 (2), 99.
52. Jorkaala, H.; Stenonen, H. *J Opt A* 2002, 4, 366.