

Synthesis of polymeric CdS and its optical properties investigation

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Producing of polymeric cadmium sulfide in polyvinyl alcohol matrix is reported. The result was achieved through solid state sulfurization of hybrid interpolymeric complex of polyvinyl alcohol with cadmium chloride. In this process CdS inherits polymeric chain structure of CdCl₂ complexing with polyvinyl alcohol due to diffusion restriction. One-dimensional structure of CdS was verified by high degree of luminescence polarization and Raman spectra behavior. It was observed that Raman spectrum of produced material is similar to spectrum of polyacetylene. This similarity disappears at impurities addition. Appearance of Raman band at 228 cm⁻¹ indicates formation of CdS chain structure. Resulting polyvinyl alcohol — CdS system has a structure of Little's high temperature superconductor.

Keywords: one-dimensional structures, inorganic polymers, conjugated polymers, hybrid polymeric complexes, polyvinyl alcohol, CdS.

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1. Introduction

Polymers possess of some valuable properties in comparison with other types of materials. Unfortunately, linear chain structure is peculiar mainly for organic compounds. It would be desirable to produce inorganic polymeric structures with highly anisotropic properties. It is commonly accepted that decrease of inorganic particles' size to atomic level brings possibility to produce materials with unusual properties. Discoveries of fullerenes, nanotubes and graphene are regarded as important scientific achievements. Particular attention of scientists is directed to low-dimensional systems. But creation of inorganic true one-dimensional structures still remains unresolved problem due to insufficient localization of molecular bonds with few exceptions.

The method of inorganic polymeric structures creation based on template synthesis approach [1] was earlier suggested [2]. Complexing organic polymer can serve as template for inorganic polymeric chain synthesis. Resulting structure represents hybrid interpolymeric complex like DNA double helix. Polyvinyl alcohol (PVA) -(CH₂CHOH)_n- is a compound suitable as a template due to high content of hydroxylic groups. Following usage of solid state treatment (predecessor technique) gives opportunity to produce inorganic polymers stabilized in organic matrix. Such a way has been already used for producing of polymeric CdS in PVA [3]. The presence of polymeric CdS was indicated by appearance of a new band in Raman spectrum at 220 cm⁻¹ in addition to a common band of crystalline CdS at 300 cm⁻¹. So, a mixture of polymeric and crystalline CdS in PVA was actually produced and additional investigations were needed to polymeric structure of produced CdS confirmation.

In this research polymeric CdS was produced in PVA matrix by treatment of PVA-CdCl₂ hybrid interpolymeric complex with gaseous H₂S. Polymeric structure of this material was verified by luminescence polarization and Raman spectra behavior. Structure of PVA-CdCl₂ hybrid interpolymeric complex was investigated earlier [4].

2. Experimental

We used 18–88 grade PVA, produced by BDH Chemicals Ltd. and CdCl₂ · 2.5H₂O „analytically pure“ grade. Doping compounds were AlCl₃H₂O „analytically pure“, and MnCl₂ · 4H₂O „pure“. Sulfurization was carried out with H₂S produced from Na₂S · 9H₂O „analytically pure“ and HCl „pure“ interaction. For comparison we used CdS powder „chemically pure“ grade.

We prepared films with the nearly same sizes and different concentrations of the dopants. Firstly we produced 10% water solution of PVA. Then, 0.65 g of CdCl₂ · 2.5H₂O (and dopants) was mixed with 5 ml of 10% PVA solution. These mixtures were spilled and left on a flat fluoroplastic surface until completely dryness of the samples at room conditions. After the samples become dry they were placed in glass vessel with H₂S atmosphere for several days to convert halides into sulfides. After sulfurization and additional drying the samples were ready for measurements. Finally, we expect that dopants are included homogeneously in CdS and make nearly 10⁻³–10⁻² mass ratio. The ratio of PVA to CdS units was 4 to 1. XRD analysis indicated absence of crystalline phases. For comparison purpose we used the reference sample which was produced by mixing of PVA solution with CdS powder (5 ml of 10% PVA to 0.2 g CdS). This sample was opaque in opposite to other transparent

samples. Dehydration of PVA was carried out 15 hours at 200°C in vacuum (residual pressure approximately 1 Pa).

It should be emphasized that we don't regard our final samples as true hybrid interpolymeric complexes of PVA and CdS but rather as polymeric CdS fixed in PVA. They were produced from real hybrid interpolymeric complex PVA-CdCl₂ using solid state chemistry approach. In this way product inherits structure of reagents due to diffusion impediment. There is interaction between CdCl₂ and PVA's -OH groups indicating in Raman spectrum [4] which is absent in PVA-CdS system [3].

Luminescence measurements were carried out at room temperature using spectrometric complex produced by „OKB Spectr“ company, Russia. Luminescence was immediately excited by polarized full UV LED radiation with wavelength $\lambda_{\max} \sim 405$ nm. Registration was performed in 0° configuration relative to excitation direction at analyzer axis parallel (||) or perpendicular (⊥) to polarizer one. Raman spectra were obtained with Bruker RFS100 spectrometer at 1064 nm excitation.

3. Results and discussion

Polarized luminescence spectrum of synthesized PVA-CdS is represented at Fig. 1. Luminescence of synthesized PVA-CdS was turned out highly polarized contrary to depolarized luminescence of PVA-CdS mixture. Its intensity is order of magnitude higher and maximum is shifted to shorter wavelength. The ratio of luminescence intensities of different polarizations $I_{||}/I_{\perp}$ is approximately 90. Such high rate of luminescence polarization is common for polymers [5–8]. Depolarization of luminescence of CdS microcrystals can be explained by migration of excited charge carriers [9,10]. Such migration is impossible in one-dimensional CdS polymeric chains. Therefore, polarization of luminescence confirms polymeric chain structure of CdS in our materials.

Raman spectra of pristine PVA, dehydrated PVA and synthesized PVA-CdS are presented at Fig. 2. Dehydrated PVA is a kind of polyacetylene (with the same primary structure: $-(C_2H_2)_n-$). Its Raman spectra were investigated earlier [11]. It was established that two bands (at 1110 and 1490 cm^{-1}) of oscillations transversal to polymeric chain are enhanced and other PVA Raman bands (corresponding to oscillations along the chain) are suppressed. It has been explained by the effect similar to SERS (Surface Enhanced Raman Scattering) which takes place at the presence of conducting particles [12]. Significant increase of background signal was also observed. Reported Raman spectra of common trans- and cis-polyacetylenes also have similar two intensive main bands with lower background [13]. Surprisingly, similar Raman spectrum was observed for synthesized PVA-CdS. It can be explained based on the conception of PVA-CdCl₂ hybrid interpolymeric complex formation and inheriting of its structure by final PVA-CdS material. In this case PVA chains lie along CdS chains with high longitudinal

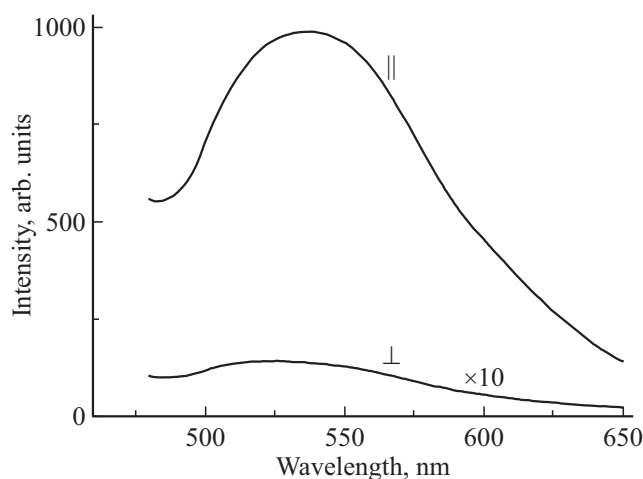


Figure 1. Luminescence spectra of synthesized PVA-CdS with parallel and perpendicular positions of analyzer relatively to polarizer.

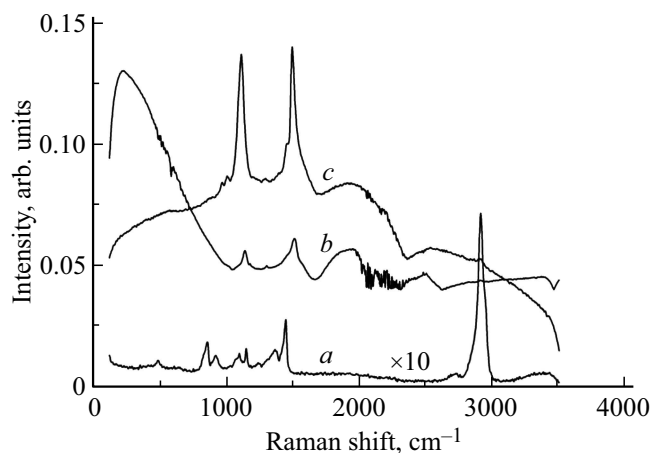


Figure 2. Raman spectra of pristine PVA (a), synthesized PVA-CdS (b) and dehydrated PVA (c).

polarizability (conditioned by molecular conductivity) and again SERS-like effect determines Raman spectrum similar to dehydrated PVA one. In addition, luminescence band around ~ 225 cm^{-1} Raman shift presents in PVA-CdS spectrum.

It is important that Raman spectra of synthesized PVA-CdS doped with Al and Mn are similar to pristine PVA Raman spectrum (Fig. 3) excluding intensive background signal. New band at 228 cm^{-1} appears in these spectra in addition to PVA bands. Such band was earlier attributed to polymeric CdS [3]. Obviously, it should be attributed to oscillations along polymeric chain because transversal oscillation is not Raman-active for linear chain structure. Evidently, this band is not observable in polymeric CdS due to high longitudinal polarizability. It appears in Al doped PVA-CdS because this impurity terminates CdS chains: $S = Al-S-Cd-$. This termination results in shorter CdS chains

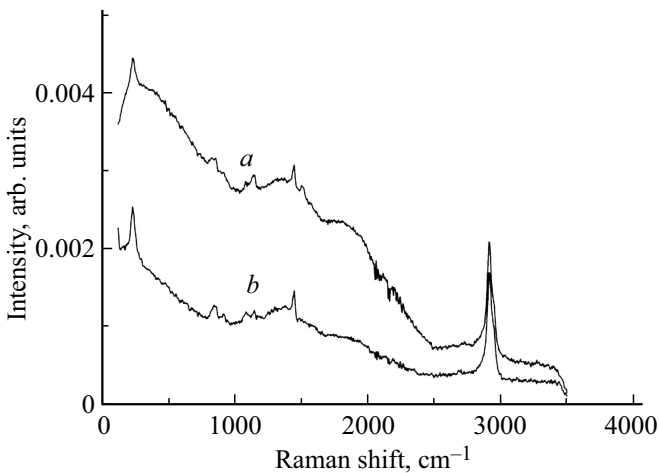


Figure 3. Raman spectra of synthesized PVA-CdS doped with Mn (2% from CdS) (a) and Al (1% from CdS) (b).

and loosing their high polarizability. Mn addition leads to similar effect on PVA-CdS Raman spectrum seemingly due to other reason. It increases resistivity of CdS chains to molecular electronic current which is responsible for high polarizability. Similar increase of resistivity is observed at doped metals due to electrons scattering on impurities.

It can be suggested that polymeric CdS has molecular-like polymeric structure: $-CdS-CdS-$ instead of: $-Cd-S-Cd-S-$ due to following reasons.

1) Raman signal should be intensive for molecular-like polymeric structure.

2) Dehydrated PVA (and polyacetylene) has similar (molecular-like) structure: $-C_2H_2-C_2H_2-$. It is supposed that its conjugated bonds are responsible for high longitudinal polarization and enhancement/suppression of Raman bands. Similarity of Raman spectra means that synthesized CdS has structure of conjugated polymers.

3) It is commonly accepted that in another well-known interpolymeric complex of PVA with iodine polymeric iodine also has molecular-like structure [14].

It should be mentioned that assumed structure of synthesized PVA-CdS material matches well to the structure of Little's high temperature superconductor which consists of conductive polymer with highly polarizing lateral groups [15]. In our case CdS can serve as conductive polymer oriented parallel to PVA chains containing polarizing hydroxilic groups. Though we did not find metallic-like macroscopic conductivity of our materials we can try to reach it using treatment by the similar way as it was done with polyacetylene. The first attempt of our material doping with iodine was not successful. In this process CdS changed its structure that was indicated by disappearance of 228 cm^{-1} Raman band and appearance of 300 cm^{-1} band. It is additional evidence of metastable polymeric CdS formation in PVA.

4. Conclusion

Data of polarized luminescence and Raman scattering indicate formation of CdS polymeric chains in polyvinyl alcohol matrix as a result of solid state conversion of hybrid interpolymeric PVA-CdCl₂ complex. This inorganic structure has electronic properties similar to polyacetylene ones. Used approach opens a new way to synthesis of one-dimensional structures and their properties investigations. It also allows designing of Little's high temperature superconductors.

Conflict of interest

The authors declare that they have no conflict of interest.

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