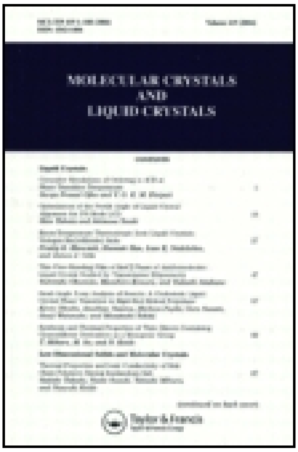

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Structure, Electrical and Luminescent Properties of the Polyaniline-GaSe Hybrid Nanocomposites

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Version of record first published: 03 Mar 2011

To cite this article: O. I. Aksimentyeva, P. Yu. Demchenko, V. P. Savchyn & O. A. Balitskii (2011): Structure, Electrical and Luminescent Properties of the Polyaniline-GaSe Hybrid Nanocomposites, Molecular Crystals and Liquid Crystals, 536:1, 65/[297]-71/[303]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.538345

Mol. Cryst. Liq. Cryst., Vol. 536: pp. 65/[297]–71/[303], 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.538345

Structure, Electrical and Luminescent Properties of the Polyaniline–GaSe Hybrid Nanocomposites

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A connection between the structure and the electrical and luminescent properties of polyaniline (PANI)–GaSe hybrid nanocomposites is investigated.

By XRD and conductivity measurements, we have found that the nanocomposite is formed only in the interval of GaSe contents 8–22.5%. The addition of GaSe decreases the conductivity by 5–7 orders, by preserving the semiconductor behavior. The emission bands in GaSe–PANI nanocomposites are essentially shifted as compared with those in pure GaSe. The XRD investigation indicates a decrease in the average size of GaSe crystallites during the formation of the composite. A mechanism of interaction of polyaniline with gallium selenide nanoplates is proposed.

Keywords Cathode luminescence; conductivity; GaSe; nanocomposite; polyaniline; X-ray diffraction

Introduction

Hybrid composites based on a semiconductor and polymer nanoparticles have a potential application as materials for electrooptical and sensor devices and alternative energy sources [1–4]. These composites can be fabricated by simple, safe, and energy-saving methods without vacuum technologies. Semiconductor nanocrystals embedded in a polymer matrix and conducting polymers integrated with porous semiconductor media can significantly affect the luminescent properties causing a shift of the spectrum and an increase in its intensity [3]. Among different types of organic solar sells, the organic-inorganic hybrid elements seem more promising, because they provide both a large-area interface, where the efficient exciton dissociation may proceed, and two separate channels for the efficient electron and hole transport [4].

Gallium selenide is a layered semiconductor crystal characterized by a high photosensitivity in the visible and near IR regions and manifests strong luminescent properties under various conditions of excitation [5,6]. Peculiarities of the crystalline

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structure do not require a precise mechanical or chemical processing of the surface. These crystals are of high inertness to the adsorption of foreign atoms and molecules. The absence of dangling bonds on the selenium terminated face of GaSe ensures a very low rate of surface recombination. However, a large specific resistance of GaSe, only the low-temperature luminescence, and the rigidity of its singe crystals limit the application of this semiconductor in flexible elements of electrooptics and nanophotonics like GaSe nanodisks self-organized into objects similar to organic *J*-aggregates [5]. The modification of GaSe by conducting polymers, especially by polyaniline (PANI), can lead to a significant improvement of the conductivity and the flexibility of GaSe – polymer composites. In the present paper, the connection between the structure and the electrical and luminescent properties of GaSe-PANI nanocomposites is investigated.

Experimental

Materials

Aniline monomer, toluene sulphonic acid (TSA), ammonium persulphate as an oxidant were purchased from Aldrich Chemical Co. Nanodispersed GaSe powder was obtained by the mechanical and ultrasonic dispersions of GaSe crystals in butyl alcohol and by the centrifuging separation as described in [7]. The fraction with particles with an average size of 60–70 nm was employed for the composite formation.

Synthesis of Composites

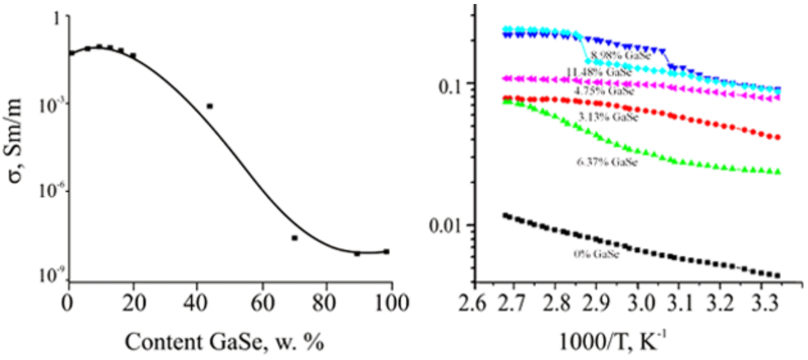
For the composite fabrication, we developed a method of self-assembling of GaSe nanoparticles during the oxidative polymerization of aniline on the surface of GaSe nanoparticles in a TSA solution used both as a surfactant for GaSe and a doping agent for polyaniline with means of the ultrasonic dispersing. The content of the inorganic phase (GaSe) was varied from 0 to 100 wt.%.

Measurements

X-ray powder diffraction data were collected on an automatic diffractometer STOE STADI P with a linear PSD detector (transmission mode; Cu $K_{\alpha 1}$ radiation, a curved germanium (111) monochromator; 2θ-range: $4 \leq 2\theta \leq 110$. A preliminary data processing and the X-ray profile and phase analyses were performed as in [8]. The molecular structure of composites has been studied by Fourier Transform Infrared Spectroscopy (FTIR) using an AVATAR-320 N spectrophotometer in the wave number range 400–4000 cm^{-1}. Measurements of the specific volume conductivity and the temperature dependence of the conductivity were carried out at a dynamic temperature change (5 K/min). A powder sample was placed in a quartz cylinder ($d = 5$ mm, $h = 2$ mm) between two nickel disk contacts with built-in thermocouple and at a pressure of 10 N/cm^2. Emissive properties of hybrid layers were examined by cathodoluminescence (CL) at $T = 77$ K at the excitation by a pulse electron beam with the energy $E_{\mathrm{p}} = 9$ keV, the pulse frequency $f = 20$ Hz, and the pulse duration $\tau_{\mathrm{p}} = 3$ µs.

Results and Discussion

It was found that the conductivity (σ) of the obtained GaSe–PANI(TSA) composites is similar to that of pure PANI(TSA) polymer with some increase at the GaSe content



(a) (b)

Figure 1. Effect of the GaSe content on the conductivity of GaSe-PANI(TSA) composites at $T = 295$ K (a) and the temperature dependence of the conductivity of GaSe-PANI(TSA) composites at different contents of gallium selenide (b).

in the interval of 8–22.5 wt.%. At the GaSe content more than 30%, a value of specific volume conductivity of composites falls by a factor of 6 orders and approaches the conductivity of pure GaSe at the GaSe content exceeding 70% (Fig. 1a).

The temperature dependence of the conductivity satisfies the activation law in the interval of 293–453 K (Fig. 1b). On the basis of the obtained dependences, we calculated the effective values of activation energy E_σ for the charge transport. It increases with the GaSe content in composites from $E_\sigma = 0.17$–0.25 eV (0–22.5% GaSe) to $E_\sigma = 0.40$–0.76 eV (50–100% GaSe).

The XRD powder pattern of PANI-TSA with a few broad diffraction peaks indicates the presence of a practically amorphous phase with an average apparent crystallite size of 26 Å, which is in good agreement with [8].

We established that synthesized pure GaSe crystallizes in the hexagonal β-modification (space group $P6_3/mmc$) with the refined lattice parameters $a = 3.7526(2)$ and $c = 15.9815(10)$ Å. However, its microstructure is complicated due to the high texture and the cleavage of the material. The diffraction peaks with *hkl* indices such as (103), (104), (105), (107), (203), (207), etc., are strongly broadened and reduced in intensity, while peaks (101) and (102) have higher intensity in comparison with their theoretical intensity. In addition, there are weak diffraction peaks from pure trigonal Se (space group $P3_121$) as a synthesis residue.

The XRD powder patterns of PANI–GaSe (6.7%) and PANI-GaSe (10.0%) (Fig. 2) obtained by polymerization show the formation of PANI–GaSe nanocomposites. As one can see, their powder patterns show a combination of the diffraction maxima of PANI-TSA with the diffraction peaks of GaSe. The average apparent crystallite size of PANI is approximately equal to 97 Å, which is larger than that for pure PANI-TSA, while the average apparent crystallite size of GaSe (~450 Å) is reduced in comparison with that of pure GaSe. However, there are also the diffraction peaks of pure trigonal Se in a considerable amount. This means that a part of selenium ions of GaSe oxidizes to elemental selenium during the polymerization with oxidant $(NH_4)_2S_2O_8$.

Contrary to that, a mechanical mixture of PANI and GaSe reveals in fact only the diffraction peaks of GaSe, as those in a pure sample, and a very weak diffraction

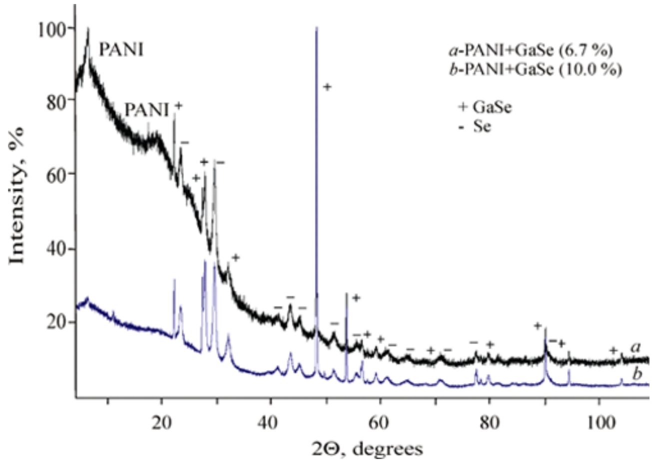


Figure 2. XRD powder patterns of PANI–GaSe nanocomposites.

halo of PANI [8]. So, the X-ray diffraction data confirm a nanocrystalline structure of composites obtained at the GaSe content in the interval 8–22.5 wt.%.

The FTIR spectrum of PANI (TSA) presented in Figure 3 well confirms the formation of polyaniline [9,10]: the peak near 1490 cm^{-1} is characteristic of a benzene ring, whereas the double absorption line at 1090–1100 cm^{-1} is due to bending-mode vibrations in the C-H plane. The other intense lines (1378 and 1565 cm^{-1}) are due to the stretching of C-N and C = N bonds, respectively. The tracks of the doping agent (toluene sulphonic acid) are clearly marked by two lines at 1035 and 695 cm^{-1}.

The above-mentioned absorbances remain in the FTIR spectrum of PANI (GaSe) (Fig. 3b). The additives to the absorbance spectrum are manifested as the rather weak (due to a low content of GaSe in the nanocomposite) lines at 526 and

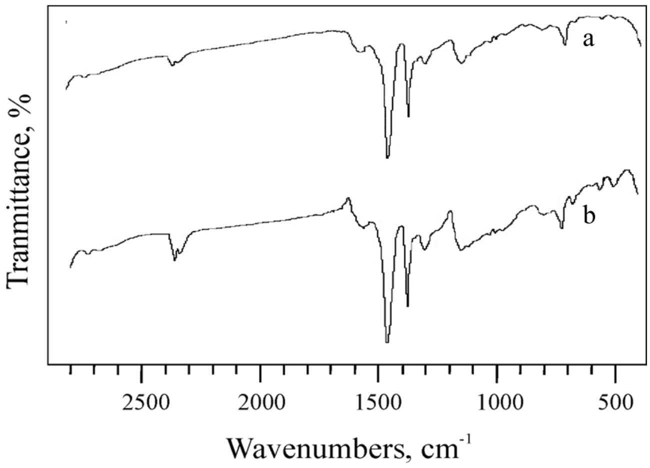


Figure 3. FTIR spectra of polymer PANI(TSA) (a) and GaSe-PANI(TSA) nanocomposites (b). The content of GaSe in the composite is 10 wt.%.

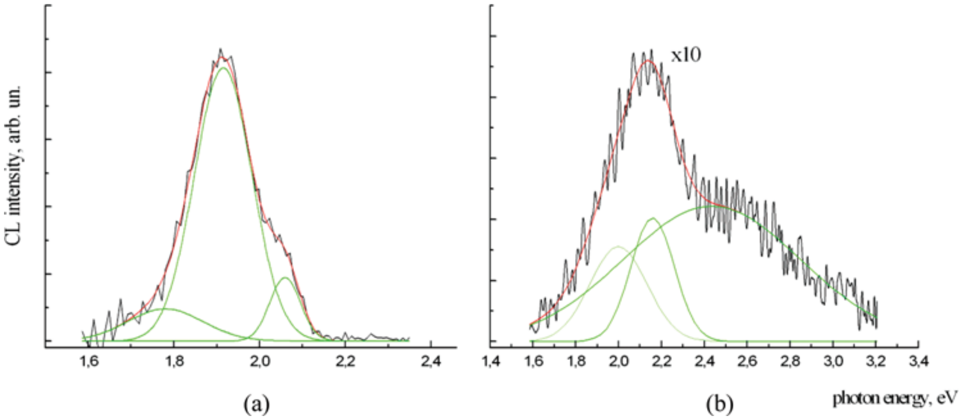


Figure 4. CL spectra of bare ultrasonically prepared GaSe particles (a) and GaSe-PANI(TSA) nanocomposites (b).

625 cm^{-1}, attributed to E'(LO) and A1' active phonon modes in a GaSe single crystal [11].

The formation of the nanocomposite causes a significant increase in the specific volume conductivity and changes in the CL spectra of composites as compared to those of the components (GaSe and nonluminescent PANI-TSA).

Figure 4 presents CL of GaSe nanoparticles formed by the ultrasonic treatment, as well as those capped by polyaniline chains. The CL spectrum of bare GaSe particles consists of two intense narrow bands at 1.9 and 2.06 eV. Those bands can be respectively attributed to the indirect and direct exciton recombinations in a GaSe single crystal which are polarized in the directions of the *c* and *a* crystallographic axes, respectively [12,13]. Note that a blue shifts in CL was observed, and the indirect transition band is more intense, which indicates a high rate of nonradiative recombination from the high-energy state.

In perfect GaSe single crystals, the direct transition intensity is at least one order higher than the indirect transition one. In addition, CL bands are essentially shifted by some tens of meV to the red side, but such phenomena are previously observed as comparing CL and PL excitation peculiarities [14]. The less intense band at about 1.77 eV is related to an intrinsic acceptor level. In our case, such level can be either from gallium vacancies [15], probably formed on the cleavage stairs in the process of ultrasonication in butyl alcohol or be an intrinsic acceptor level formed by extended defects like stacking faults [13]. Let us discuss the CL spectrum of polyaniline treated particles in more details. One can observe that the excitonic peaks became broader, as the direct transition band becomes more intense than the indirect one. Unambiguously, defects responsible for the direct exciton recombination extinguishing are now well passivated, since the low-energy defect band is also absent.

The higher energy band shifted to the blue side up to 2.5 eV can be explained only in terms of the quantum confinement effect for GaSe particles. Such an effect was studied up to date within two concurring models: GaSe nanospheres (quantum dots) [7] is rather controversial, since a strong anisotropy in the growth and the crystal structure of GaSe gives a little chance to form such isotropic objects and planar disks [16], with the quantum confinement mainly taking place along the *c*

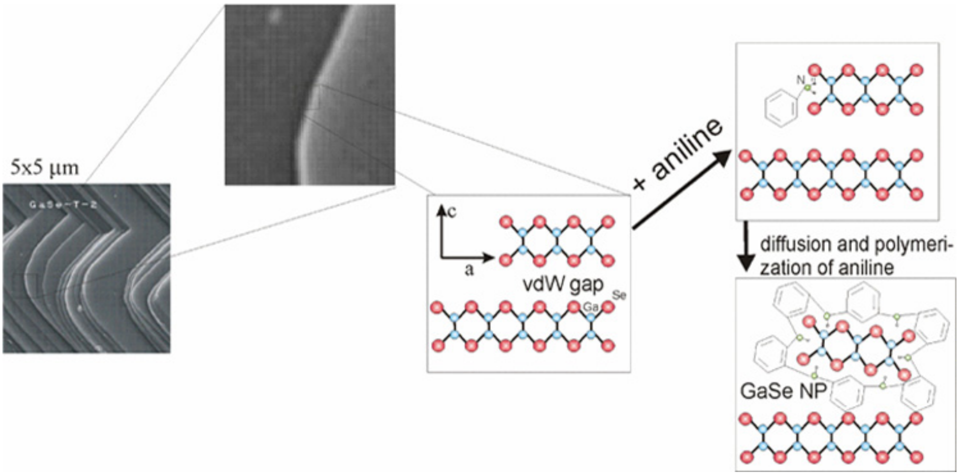


Figure 5. Schematic view of GaSe tetralayer particles capping stages by polyaniline.

crystallographic axis. In both models, the quantum confinement is essential at a linear parameter of about 1–2 nm and can be neglected for objects bigger than 5 nm, since the effective masses of electrons and holes are rather large. The observed shift (about 0.4 eV) is thus can be understood in terms of about 1.8-nm GaSe spheres or a single tetralayer GaSe sheet, in which, despite a linear real crystallographic height of about 0.8 nm, the wave functions significantly extend thought the potential barrier on both sides and are localized in almost the same (1.7 nm) linear space defined by the *c* crystallographic axis. As the second model got many successful confirmations [17,18], we propose the following sequence of the chemical interaction process between ultrasonically formed GaSe nanoparticles and polyaniline (see Fig. 5).

As usual, the surface of GaSe is characterized by such extended defects as cleavage stairs. Such defects are formed during the crystal growth which is strongly anisotropic with the sequential layer-by-layer formation. A much higher concentration of defects is produced during the fracture of such crystals [19] which is a technological step in the preparation of nanodispersed particles. The topology of those a surface is presented on the left-hand side of Figure 5. Let us consider what happens on the edge of such a cleavage stair. First of all, it has to be noticed that the edge of any GaSe tetralayer sandwich possesses a high adsorption activity due to unpaired gallium atoms in comparison to selenium terminated basal planes. Thus, gallium terminated edges on cleaved stairs act as a strong Lewis acid. On the contrary, amine groups are Lewis base species, which results in the adsorption of aniline on such cleavage stair. After adsorption, aniline molecules undergo diffusion into a van der Waals gap, whose linear size coincides with that of a benzene ring. Finally, the polymerization of aniline leads to the formation of free tetralayer GaSe planes capped by polyaniline chains providing a good passivation of gallium-containing edges of planes. We should admit that amine complexes act as satisfactory capping ligands for InSe and $CuGaSe_2$ nanoparticles [20,21]. The other proof of such hypotheses is the results of the XRD investigation indicating a decrease of the average size of GaSe crystallites.

Conclusions

The incapsulation of GaSe nanoparticles by polyaniline in a toluene sulphonic acid solution leads to the formation of nanocomposites in the interval of GaSe contents 8–22.5% which corresponds to the conductivity of composites higher by 5–7 orders than that of pure GaSe and reserves their semiconductor behavior. The XRD investigation indicates a decrease in the average size of GaSe crystallites during the composite formation.

Thus, the main advantage of polyaniline-modified GaSe particles is the formation of well-passivated inorganic nanocrystals capped by the bulky polymer which manifest the blue-shifted luminescence observed only in defect-free particles synthesized by metallorganic methods. As discussed above, bare uncapped GaSe particles do not reveal such properties. The low-energy defect luminescence also is not observed in aniline-treated particles, by confirming the "curing" of stacking faults and cleavage stairs. Such flattening surface process is a removal of inhomogeneities by one-by-one splitting off planar amine-capped tetralayer thick GaSe particles.

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