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GOLD NANOPARTICLES-ARSENIC TRISULFIDE COMPLEX FORMATION AND PHOTOINDUCED TRANSFORMATION

Alkhalil G. (ITMO University)
Supervisor - Associate Professor, Burunkova J.A. (ITMO University)

Using FTIR spectroscopy it was confirmed that when mixing two solutions of arsenic trisulfide As_2S_3 and gold nanoparticles AuNPs they interact and form a complex. The reversable photoinduced transformations of the composite material were studied using Raman spectroscopy.

Introduction. Composite materials based on chalcogenide glasses (ChGs) represent an important growing class of materials due to their promising physical and optical characteristics as well as a broad range of applications. Moreover, ChGs possess unique metastability, which means they are susceptible to photo structural changes induced by bandgap energy illumination. These structural changes are accompanied by changes in the optical properties, such as the optical absorption edge and refractive index, and they can be reversible or irreversible. The photoinduced changes of As_2S_3 were extensively investigated as both bulk glass and thin films. However, the effect of plasmonic field of metals nanoparticles on these changes has not been studied so far. Therefore, in this work we present the effect of AuNPs on the photoinduced transformations of As_2S_3 studied by several spectroscopic techniques.

Main part. The preparation method was based on impregnating pieces of porous glass PG in solution that contained the composite and it included the following steps:
1- Dissolving As_2S_3 in propylamin.
2- Adding dodecanthiol functionalized AuNPs dissolved in toluene to the As_2S_3 solution.
3- Impregnating small pieces of PG in the obtained solution.
4- After 3-4 days the samples were taken out of the solution and left to air dry for several hours and then they were thermally treated for 2 hours at $140C^0$.
To understand the interaction between AuNPs and As_2S_3, solutions of both of them and for the mixtures were studied using FTIR spectroscopy. We observed in the FTIR spectra several indications of AuNPs-As_2S_3 complex formation. These indications proved that the ions in the As_2S_3 salt replaced the thiol group in the dodecanthiol functionalized AuNPs.
To study the photoinduced transformations of PG-As_2S_3 and PG AuNPs-As_2S_3 composites, the transmission spectra and Raman spectra of the samples were recorded before and after irradiation with 532nm laser light and then after annealing at $150C^0$ for one hour. Also, the band gap energy of the samples was calculated from the transmission spectra at each stage. Although for both samples we observed a photobleaching effect (blue shift in the transmission spectrum), for the samples with AuNPs they were not accompanied by any change in the band gap energy, unlike PG-As_2S_3 which had an increase in the band gap energy by 0.2 eV.
For AuNPs-As_2S_3 we observed more structured Raman spectra with several relatively narrow bands comparing to the spectra of PG-As_2S_3 which have the typical broad band of As_2S_3.
In results, the photoinduced changes of PG-As_2S_3 can be attributed to the decrease of the amorphous state and the related density of localized band gap states within the As2S3 phase in PG. Introducing the AuNPs, we believe, resulted in nanocrystals formation and therefore the photoinduced transformations in this case has different mechanism than changing in the amorphous state of the material.

Conclusion. The fabrication route of new composite material based on AuNPs-As_2S_3 doped in porous glass was presented. Several light-induced changes in the optical properties, such as the change in transmission spectra and Raman spectra have been observed and discussed. This composite exhibits

a reversible photoinduced bleaching effect. The initial state of the PG-AuNPs-As_2S_3 composite can be restored by annealing. Introducing the AuNPs, resulted in a stable band gap energy and this can be attributed to a nanocrystals formation in the presence of AuNPs.
Developing and optimizing the optical properties of the PG-AuNPs-As_2S_3 composites can be useful for creating 3D optical-structural patterns with various optical parameters for different applications such as holographic data storage or functional optical elements for visible-infrared optics.

Alkhalil. G. (author)	Signature
Burunkova J.A. (supervisor)	Signature