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GAMMA IRRADIATION INDUCED SYNTHESIS OF PbS/PVA HYDROGEL NANOCOMPOSITE

J. Kuljanin-Jakovljević, A. Radosavljević*,
J. Spasojević and Z. Kačarević-Popović

*Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522,
11001 Belgrade, Serbia (*krkljes@vinca.rs)*

ABSTRACT

This work describes radiolytic *in situ* incorporation of lead sulfide nanoparticles (PbS NPs) in poly(vinyl alcohol) (PVA) hydrogel. Optical, structural, swelling and diffusion properties of prepared PbS/PVA hydrogel nanocomposite were investigated. Obtained results indicate formation of PbS NPs with a cubic crystal structure and diameter around 3 nm. Incorporation of PbS NPs in PVA hydrogel causes a change in the swelling and diffusion properties.

INTRODUCTION

In the last decade, the preparation of nanoparticles and nanomaterials has been very interesting subject in nanotechnology science. Organic polymers, especially hydrogels, are an attractive class of materials due to unique properties, and represent a good platform for nucleation and growth of NPs due to free space between the polymer chains that serve like nanoreactors in hydrogel swollen state (template synthesis). The mesoporous network of hydrogels as a matrix is a suitable template for the *in situ* synthesis, stabilization and distribution of metal NPs (Ag, Au) as well as semiconductor NPs (CdS, PbS). These nanocomposite materials have potential biomedical application, but also can be used for the fabrication of novel photonic materials and “solid state” solar devices where the spacing between NPs can be tuned for optimum photovoltaic efficiency.

The properties of nanocomposites are strongly dependent on the method of preparation and experimental conditions. Among a number of techniques reported for the synthesis of nanocomposite systems, the radiolytic method is one of the most promising strategies due to several advantages compared to conventional methods. The aim of this work was to investigate the possibility of the radiolytic *in situ* incorporation of PbS NPs within the PVA hydrogel, previously crosslinked also by gamma irradiation, as well as to explore the influence of PbS NPs on swelling and diffusion properties of polymer network.

EXPERIMENTAL

PVA solution (5 wt.%) was exposed to gamma irradiation (^{60}Co source, dose rate 0.5 kGy/h, absorbed dose 25 kGy) to induce crosslinking of polymer chains, and PVA hydrogel with 86% weight fraction of gel was obtained. Then, PVA xerogel was immersed in water solution of lead nitrate ($\text{Pb}(\text{CH}_3\text{CO}_2)_2$, $5 \cdot 10^{-4}$ M) and 1-dodecanethiol ($\text{CH}_3(\text{CH}_2)_{11}\text{SH}$, $1 \cdot 10^{-2}$ M), previously saturated with Ar in order to remove oxygen. The swelling of polymer network was carried out at room temperature for 24 h, and then the sample was gamma irradiated (dose rate 12.3 kGy/h, absorbed dose 3.2 kGy). The obtained PbS/PVA nanocomposite was characterized by UV-Vis, XRD, SEM and swelling measurement in water at 25°C. The crystalline domain size was determined from XRD by Sherrer formula ($D = k\lambda/\beta \cos\theta$, where $k=0.9$ is a constant for cubic structure, $\lambda=0.1541$ nm is the X-ray wavelength, β is the full width at half maximum, and θ is the diffraction angle), while the lattice constant was calculated as $a = d_{hkl}(h^2 + k^2 + l^2)^{1/2}$ (d_{hkl} is space between the planes in the atomic lattice, while h , k , and l are Miller indices). Swelling process was monitored gravimetrically by measuring mass of swollen hydrogel at predetermined time intervals (m_t), until the initial mass of xerogel (m_0) was equilibrated (m_{eq}). The swelling degree was calculated as $SD = (m_t - m_0)/m_0$, and the equilibrium swelling degree (SD_{eq}) was determined by replacing m_t with m_{eq} . Power law approach ($SD/SD_{eq} = kt^n$, where k is the kinetic constant related to the structure of the network, t is the time and n is the diffusion exponent) was used to determine the diffusion model and to calculate the kinetic parameters of diffusion. The values of the kinetic parameters k and n were determined from the intercept and slope, respectively, of the curves of $\ln(SD/SD_{eq})$ versus $\ln t$ by linear fitting at the initial stage of swelling ($SD/SD_{eq} \leq 0.6$). Diffusion coefficient was calculated as $D = k^{1/n} \pi \delta^2 / 16$, where δ is the sample thickness.

RESULTS AND DISCUSSION

The mechanisms of the formation of nanocrystalline sulfides under the gamma irradiation are not very clear up to now. However, when the solution containing Pb^{2+} ions and appropriate sulfur source is irradiated, a series of reaction will happen. It is well known that some radiolytic species, including e_{aq}^- , H_3O^+ , OH^\bullet , H^\bullet , H_2 and H_2O_2 are generated when water is γ -irradiated. The solvated electrons (e_{aq}^-) has so strong reducing capability that $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ can be reduced to S^- and further to S^{2-} . Then, the S^{2-} anion combines with Pb^{2+} cation to generate PbS NPs [1]. Thus formed PbS NPs are entrapped in the PVA network, and prepared PbS/PVA hydrogel nanocomposite is insoluble in water.

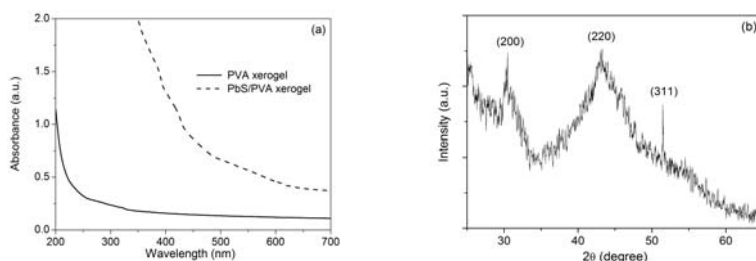


Figure 1. (a) UV-Vis absorption spectra of crosslinked systems and (b) XRD pattern of PbS/PVA xerogel nanocomposite.

Optical absorption spectra of PVA and PbS/PVA nanocomposite are presented in Fig. 1(a). The lack of excitonic peaks in the absorption spectra of nanocomposite is mainly explained by inhomogeneous broadening due to the size distribution of NPs, as well as by nature of polymer matrix. Moreover, the disappearance of the excitonic peak can be attributed to surface-related charge separation and polarization effects in PbS NPs, which were sensitive to the charges on the surfactant molecules [2]. In the case of investigated nanocomposite, the crosslinking of polymer chains induce the changes in the structure of polymer matrix, and probably thus leads to a change in the charge on the NPs surface.

The X-ray diffraction pattern of PbS-PVA nanocomposite is shown in Fig. 1(b). The XRD peaks correspond to Bragg's reflections from the crystalline planes (200), (220) and (311) of PbS NPs with the face centered cubic crystal structure (JCPDS Card File No. 5-592). The crystalline domain size (D) was found to be around 3 nm. Additionally, the lattice constant (a) was calculated and obtained value of 0.5917 nm for spacing $d_{220}=0.2092$ nm is close to the value from the JCPDS ($a_0=0.5937$ nm).

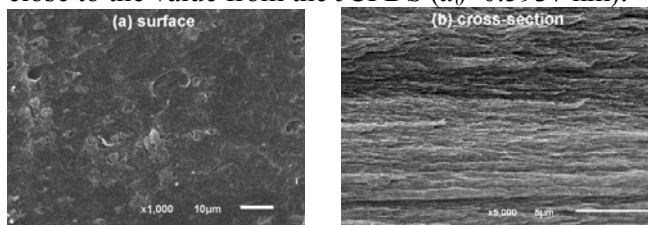


Figure 2. SEM micrographs of PbS/PVA xerogel nanocomposite

The SEM analysis shows that PbS/PVA nanocomposite has an uneven, partly open surface (Fig. 2(a)) with visible pores of different sizes, resulting from the evaporation of water from the sample during the lyophilization (process of sample preparation by freeze-drying). Fig. 2(b) indicates that the porous structure is a characteristic of the whole sample volume. Such a porous three-dimensional network structure is essential for the absorption and storage of large amounts of water within the hydrogel.

Swelling capacity is one of the most important parameters for evaluation the properties of hydrogels. Fig. 3 depicts the swelling curves of the PVA and PbS/PVA nanocomposite. It's clearly seen that isothermal kinetics swelling curves are similar in shape, but incorporation of PbS NPs in the PVA hydrogel induced the slightly decreased of swelling capacity and diffusion coefficient of PbS-PVA nanocomposite compared to pure PVA. Characteristic parameters of swelling process (SD_{eq} , k , n , D) for investigated systems are presented in Table 1. The obtained results indicate that hydrogel systems show non-Fickian or anomalous diffusion ($0.5 < n < 1$) when the rates of diffusion and polymer chain relaxation are comparable [3].

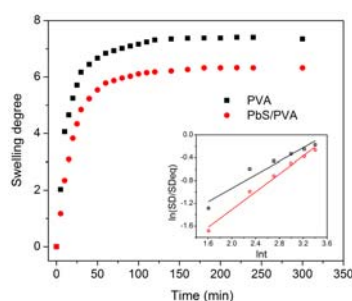


Table 1. Characteristic parameters obtained from swelling measurements.

Sample	SD_{eq}	k (1/min)	n	$D \times 10^7$ (cm^2/min)
PVA	7.35 ± 0.09	0.12	0.59	1.37
PbS/PV A	6.32 ± 0.06	0.06	0.78	1.25

Figure 3. Swelling curves of PVA and PbS/PVA nanocomposite in water at 25°C, and best linear fits of swelling curves (insert).

CONCLUSION

The PbS NPs, with diameter around 3 nm, have been successfully synthesized within the pores of PVA hydrogel using the gamma irradiation technique. Optical properties of PbS/PVA xerogel nanocomposite strongly depend on the structure of polymer matrix (crosslinked or uncrosslinked). Incorporation of PbS NPs into PVA hydrogel causes a slightly decrease in swelling capacity and diffusion coefficient compared to pure PVA, while non-Fickian diffusion transport mechanism remains unchanged.

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