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Gamma irradiation induced in situ synthesis of lead sulfide nanoparticles in poly(vinyl alcohol) hydrogel

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HIGHLIGHTS

- PbS-PVA hydrogel nanocomposite was prepared by gamma irradiation.
- PbS nanoparticles are around 5 nm in diameter, with band-gap energy of 1.84 eV.
- PbS nanoparticles are positively strained and under tensile stress (lattice expansion occurs).
- Hydrogels shows non-Fickian diffusion with typical values for water diffusion in polymers (10^{-9} cm^2/s).
- Thermal stability of PbS-PVA xerogel nanocomposite is slightly enhanced compared to PVA xerogel.

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ABSTRACT

In this study, the nanocomposites based on semiconductor lead sulfide (PbS) nanoparticles and poly (vinyl alcohol) (PVA) were investigated. The gamma irradiation induced in situ incorporation of PbS nanoparticles in crosslinked polymer network i.e. PVA hydrogel was performed. PVA hydrogel was previously obtained also under the influence of gamma irradiation. UV–Vis absorption and X-ray diffraction measurements were employed to investigate optical and structural properties of PbS nanoparticles, respectively, and obtained results indicates the presence of nanoparticles with approximately 6 nm in diameter and face centered cubic rock-salt crystal structure. The porous morphology was confirmed by scanning electron microscopy. Swelling data revealed that investigated hydrogels (PVA and PbS-PVA nanocomposite) shows non-Fickian diffusion, indicating that both diffusion and polymer relaxation processes controlled the fluid transport. The values of diffusion coefficients have an order of magnitude 10^{-9} cm^2/s (typical values for water diffusion in polymers) and the best fit with the experimental results showed the Etters approximation. Comparing the thermal properties of PbS-PVA xerogel nanocomposite with PVA xerogel it was observed that incorporation of PbS nanoparticles in crosslinked PVA matrix just slightly enhanced the thermal stability of nanocomposite.

1. Introduction

The synthesis of the meso- and nanostructured "soft" materials, which can be used as a carrier for the incorporation and organization of nanoparticles, is an important step in the development of functional nanoscale devices. Organic polymers, especially hydrogels are an attractive class of such soft materials because their properties can be tuned according to the required functions. The mesoporous network of hydrogels as a matrix is a suitable template for the in situ synthesis, stabilization and distribution of metal nanoparticles (Ag, Au) (Jayaramudu et al., 2013; Krklješ et al., 2007a; Krstić et al., 2014), magnetic particles (Fe_3O_4) (Marinović-Cincović et al., 2014) as well as semiconductor nanoparticles (CdS, PbS) (Gattás-Asfura et al., 2003). 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 nanoparticles can be tuned for optimum photovoltaic efficiency. In particular, in situ growth PbS nanoparticles in PVA 3D hydrogels matrix could produce soft 3D material nanocomposite with optical nonlinearity (metamaterials), opening perspectives for its application in special optical devices requiring small band gap semiconductors embedded almost in water (optical properties of PVA

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are similar to water) (Buso et al., 2005; Segal et al., 2015).

It is well known that the properties of nanocomposites are dependent on the method of synthesis (Kuljanin et al., 2006; Wu et al., 2008), and that the radiolytic method is particularly suitable for generation of nanoparticles in a solution (Hayes et al., 1989; Krklješ et al., 2007a). On the other hand, radiolytic method is also highly suitable way for formation of three-dimensional polymer network i.e. hydrogels. The radiation induced synthesis offers a number of advantages over the conventional physical and chemical methods. Some of them are the easiness of process control, there is no need to use the initiators and crosslinkers (clean synthesis), and probably most important, from the biomedical point of view, is the possibility of simultaneous hydrogel formation and its sterilization in one technological step (Rosiak, 1991; Rosiak and Ulanski, 1999). Despite all the mentioned advantages of radiolytic method, there is not so many investigations related to synthesis of nanocomposites based on nanoparticles incorporated in a hydrogel matrix.

In colloidal chemistry, the process of particles growth usually occurs through the Oswald ripening mechanism. As a result, the particle size increases continuously during growth because the larger particles grow on account of dissolution of smaller ones (Qiao et al., 1999). A convenient procedure to restrict their growth is the in situ synthesis of nanoparticles within the polymer matrix with an improved architecture i.e. within the three-dimensional network of hydrophilic polymers. Thus formed nanoparticles are entrapped in polymer network (Fig. 1). As a result, a novel inorganic/organic hybrid crosslinked nanocomposite was obtained.

In this work, to the best of our knowledge, the first results of a new method of synthesis of PbS-PVA hydrogel nanocomposite were presented. Namely, the radiolytic in situ synthesis of PbS nanoparticles within the PVA hydrogel, previously crosslinked also by gamma irradiation, was successfully performed. The liquid-filled cavities within the PVA hydrogel were used as nanoreactors for the formation of PbS nanoparticles (template synthesis). The optical and structural properties of radiolytically synthesized PbS nanoparticles in PVA hydrogel as well as morphology of obtained crosslinked PbS-PVA nanocomposite were investigated. Moreover, as one of the main physico-chemical properties of crosslinked polymer systems, the swelling behavior was analyzed. In addition, the thermal stability analysis of crosslinked systems, pure PVA and PbS-PVA nanocomposites, was conducted.

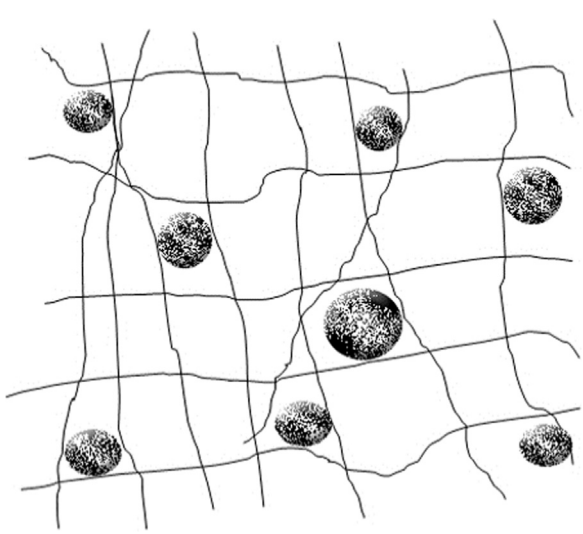

Fig. 1. Schematic presentation of the immobilization of nanoparticles in a crosslinked polymer matrix.

2. Experimental

2.1. Materials

All chemicals were commercial products of analytical grade and were used without additional purification. Poly(vinyl alcohol) (PVA), with $M_w = 72$ kDa and 99% of minimal degree of hydrolysis, and lead acetate ($Pb(CH_3CO_2)_2$) were products of Merck (Germany), while 1-dodecanethiol ($CH_3(CH_2)_{11}SH$) was obtained from Sigma-Aldrich (USA). Water from Millipore Milli-Q system (Millipore Corporations, USA) was used in all experiments, while the high purity argon gas (99.5%) from Messer Tehnogas (Serbia) was used for removing the oxygen from solutions.

2.2. Synthesis of PbS-PVA nanocomposites

PVA solution (5 wt%) was prepared by dissolving the polymer in distilled water at 90 °C for 6 h, under the constant stirring. In order to remove oxygen, the PVA solution was bubbled with Ar for 30 min, poured into specially designed mould (two glass plates separated by rubber spacer) and exposed to gamma irradiation (^{60}Co source, dose rate 0.5 kGy/h, total absorbed dose 25 kGy) to induce crosslinking of polymer chains. The obtained PVA hydrogel was extracted in distilled water for 8 h at the 80 °C, in order to remove the residual of non-crosslinked polymer, and dried at the vacuum oven at 25 °C to the constant weight.

Synthesis of PbS-PVA nanocomposites was carried out by radiolytic in situ incorporation of PbS nanoparticles into previously obtained PVA network. PVA xerogel (dried gel) was immersed in a water solution of $Pb(CH_3CO_2)_2$ ($5 \cdot 10^{-4}$ mol/dm^3) and $CH_3(CH_2)_{11}SH$ ($1 \cdot 10^{-2}$ mol/dm^3), which is previously saturated with Ar. The swelling of polymer network was conducted in sealed cell at room temperature for 24 h, and then the sample was exposed to gamma irradiation at the dose rate of 12.3 kGy/h up to the total absorbed dose of 3.2 kGy. After irradiation, the formed PbS nanoparticles are entrapped in the PVA network, and crosslinked PbS-PVA hydrogel nanocomposite was obtained.

2.3. Methods of characterization

Weight fraction of the gel (%) was determined by gravimetric method as

$$W_g(\%) = (W_{ae}/W_{be}) \times 100 \quad (1)$$

where W_{ae} is the weight of the dry gel after extraction and W_{be} is the initial weight of the dry gel before extraction.

The UV–Vis absorption spectra were recorded by Perkin-Elmer Lambda 5 spectrophotometer, in the wavelength range of 200–800 nm.

Microstructural properties of crosslinked PbS-PVA nanocomposites were investigated by X-ray diffraction (XRD) measurements performed on Philips PW 1710 diffractometer (Cu Kα1 radiation, $\lambda = 0.1541$ nm).

Scanning electron microscopy (SEM) analysis of the morphology of crosslinked PbS-PVA nanocomposite was performed on JEOL JSM-6610LV instrument, operated at an accelerating voltage of 20 kV. The sample was prepared by freeze-drying method and prior to the analysis was coated with thin layer of gold (around 15 nm).

Swelling behavior of crosslinked samples, pure PVA and PbS-PVA nanocomposite, was investigated in excess of distilled water at 25 ± 1 °C. Xerogel discs (diameter $d = 3.8 \pm 0.2$ mm, thickness $\delta = 1.4 \pm 0.1$ mm) were immersed in distilled water, and process of swelling was monitored gravimetrically by measuring weights of swollen hydrogel at predetermined time intervals. Swelling degree