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RADIOLYTIC INCORPORATION OF GOLD NANOPARTICLES INTO PVA HYDROGEL

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ABSTRACT

This work describes the Au-PVA hydrogel nanocomposites synthesized by radiolytic *in situ* incorporation of gold nanoparticles (Au NPs) into poly(vinyl alcohol) (PVA) hydrogel. Synthesis of nanocomposites was conducted as two-step gamma irradiation induced process. In the first step, the crosslinking of polymer chains occurs and PVA hydrogel with a large number of pores was obtained. In the second step, these pores serve as nanoreactors for the formation of Au NPs. The presence of Au NPs was confirmed by absorption spectra, while morphological and structural analysis reveals the spherical shape of Au NPs, with the diameter around 15 nm and *fcc* crystal structure. The structural parameters of xerogels indicate that incorporation of Au NPs induce the expansion of polymer network. Long-time stability of Au-PVA hydrogel nanocomposites is caused by interactions between the surface of Au NPs and OH groups of PVA chains.

INTRODUCTION

Hydrogel nanocomposites are a new class of hybrid materials which can be defined as swollen crosslinked polymer networks with incorporated nanoparticles or some other nanostructures [1]. This crosslinked structures are capable to absorb significant amounts of water or biological liquids without dissolving or losing their structural integrity [2]. In recent years, numerous studies have been focused on the hydrogel nanocomposites, because the crosslinked polymer networks (hydrogels) represent a promising solution for stabilization, size control and uniform distribution of NPs. The presence of NPs can improve the existing properties of hydrogels and/or add them new unique physical properties, which make the hydrogel nanocomposites as ideal candidates for application in the electronics, optics, sensors, catalysis, drug delivery and other biotechnological areas [2,3].

In this study, PVA hydrogel (previously obtained by gamma irradiation) was used as template for stabilization of Au NPs, during their *in situ* gamma irradiation induced synthesis. PVA is water-soluble transparent polymer, biocompatible and biodegradable, while Au NPs have received great interests

due to attractive thermal, catalytic, optical, electronic and antimicrobial properties. The radiolytic synthesis was chosen because it is suitable for both formation of polymer network and metal NPs. It has many advantages over conventional methods: the process is easily controlled, do not leave any toxic residues, and promote simultaneous synthesis and sterilization of materials [4].

EXPERIMENTAL

The 5 wt% PVA solution was exposed to gamma irradiation (^{60}Co source, absorbed dose 25 kGy, dose rate 0.5 kGy/h) to induce crosslinking and formation of polymer network. PVA hydrogel was extracted in water for 7 days and dried to the constant mass. The obtained PVA xerogel was swelled by Ar-saturated solutions containing 3.5×10^{-3} M and 7.0×10^{-3} M of HAuCl_4 , with addition of 0.2 M 2-propanol, and exposed to gamma irradiation (dose rate 10 kGy/h) up to 17 kGy and 34 kGy, respectively, to perform *in situ* reduction of gold ions and formation of Au NPs. Optical properties of Au-PVA hydrogel nanocomposites were investigated by Thermo Fisher Scientific Evolution 600 UV-Vis spectrophotometer. Morphology of lyophilized PVA hydrogel as a matrix was analyzed by SEM (JEOL JSM-6610LV, operated at 20 kV). The size and shape of Au NPs were investigated by TEM (Philips EM 400, operated at 120 kV). Au-PVA xerogel nanocomposite was grinded in ball mill, dispersed in distilled water and deposited on C-coated copper grid. Microstructural properties of nanocomposites were examined by XRD (Bruker D8 Advance Diffractometer, $\text{Cu K}\alpha_1$ radiation, $\lambda = 0.1541$ nm), while the interaction between incorporated Au NPs and PVA hydrogel was investigated by FTIR spectroscopy (Thermo Electron Corporation Nicolet 380 spectrophotometer, ATR mode). Macroscopic properties of xerogels (xerogel density (ρ_{xg}) and equilibrium swelling degree (SD_{eq}) and their primary structural properties (average molar mass between crosslinks (M_c), crosslinking density (ρ_c) and pore size (ξ)) were determined as described in the literature [5].

RESULTS AND DISCUSSION

PVA hydrogel was obtained by gamma irradiation induced crosslinking of polymer chains. PVA^\bullet radicals, generated in the process of hydrogen abstraction from polymer chain by OH^\bullet and H^\bullet radicals (products of water radiolysis), interact with each other and finally form crosslinked polymer network [6]. The SEM micrograph (Fig. 1) clearly illustrates the porous

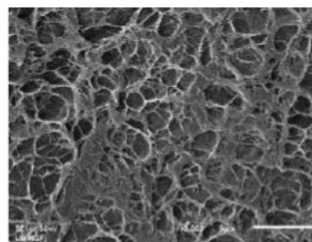


Figure 1. SEM micrograph of PVA hydrogel.

structure of obtained PVA hydrogel, with a large number of pores. Under the gamma irradiation, Au^{3+} ions are reduced by solvated electrons and 2-propanol radicals (primary and secondary reduction species) through the complex multi-step process. Formation of Au^0 atoms is followed by their aggregation into the clusters of higher nuclearity, and finally resulting in formation of Au NPs [7]. The obtained Au-PVA hydrogel nanocomposites have wine-red color which indicates the formation of Au NPs, while the UV-Vis absorption spectra (Fig. 2(a)) clearly show the characteristic surface plasmon resonance (SPR) band of Au NPs around 540 nm. The position, intensity and width of the SPR band depends on size, shape and surface structure of NPs as well as on dielectric constant and refractive index of medium in which NPs are embedded. Therefore, absorption spectra can be used to determine the size of metal NPs [8]. The mean diameter of Au NPs incorporated in PVA hydrogel is around 15 nm.

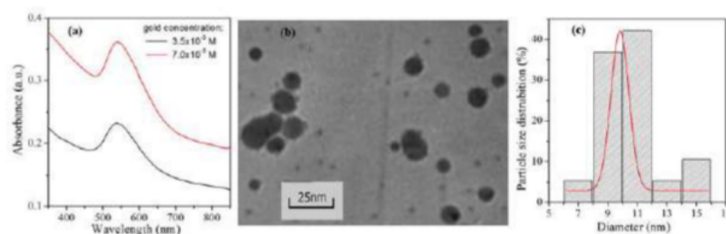


Figure 2. (a) UV-Vis absorption spectra of Au-PVA hydrogel nanocomposites, (b) TEM micrograph and (c) size distribution of Au NPs.

The shape and size distribution of the Au NPs were examined by TEM. Typical micrograph (Fig. 2(b)) reveals presence of spherical non-aggregated Au NPs in the size range from 6 nm to 16 nm, with the average diameter around 10 nm (Fig. 2(c)).

The XRD pattern of Au-PVA xerogel nanocomposite is shown in Fig. 3(a). The XRD peaks correspond to Bragg's reflections from the crystalline planes (111), (200) and (220) of Au NPs with the face centered cubic (*fcc*) crystal structure (JCPDS Card No. 04-0784). According to the Scherrer's equation [9], the crystalline domain size was found to be around 20 nm, which is slightly higher compared to size of Au NPs determined by UV-Vis spectroscopy and TEM analysis.

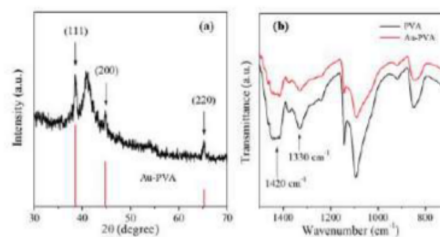


Figure 3. (a) XRD pattern and (b) FTIR spectra of investigated samples.

The primary structural properties of xerogels were calculated using equations given in the literature [5]. The increased values of SD_{eq} , M_c and ξ for nanocomposites indicate that incorporation of Au NPs induce the expansion of polymer network.

Table 1. The structural parameters for xerogels in distilled water at 25 °C.

Sample	ρ_{xg} (g/cm ³)	SD_{eq} (g/g)	M_c (g/mol)	$\rho_c \times 10^4$ (mol/cm ³)	ξ (nm)
PVA	1.27	16.4	3834	3.3	16.4
Au(3.5)-PVA	1.36	17.1	4879	2.8	19.1
Au(7.0)-PVA	1.43	17.9	5938	2.4	21.7

The interaction of Au NPs and PVA matrix was investigate by FTIR spectroscopy (Fig. 3(b)). The decrease in the intensity ratio between bands at 1420 cm⁻¹ (O–H in plane vibration) and 1330 cm⁻¹ (C–H wagging vibrations) with incorporation of Au NPs implies that decoupling between these vibrations takes place. These results indicate that main interaction between surface of Au NPs and PVA chains occurs over OH groups [9].

CONCLUSION

The gamma irradiation induced *in situ* incorporation of Au NPs into PVA hydrogel was successfully performed. The synthesized Au NPs are spherical in shape, with the mean diameter around 15 nm and *fcc* crystal structure. The structural parameters of xerogels indicate that incorporation of Au NPs induce the expansion of polymer network. Long-time stability of Au NPs and Au-PVA hydrogel nanocomposites occurs as a result of interactions between the surface of Au NPs and OH groups of PVA chains.

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