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Optical and structural properties of radiolytically *in situ* synthesized silver nanoparticles stabilized by chitosan/poly(vinyl alcohol) blends

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HIGHLIGHTS

- Ag NPs were synthesized by γ-irradiation and stabilized by CS/PVA blends.
- Composition of CS/PVA blends has influence on the size of spherical Ag NPs.
- simulation based on Mie theory was used to calculate the parameters of Ag NPs.
- Ag NPs are stabilized through interactions with -OH and -NH_2 groups of polymers.
- Optical band gap energy was calculated from UV–vis spectra by Tauc's expression.

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ABSTRACT

In this study, the potential of chitosan/poly(vinyl alcohol) (CS/PVA) blends as capping agent for stabilization of Ag-nanoparticles (Ag NPs) during their *in situ* gamma irradiation induced synthesis was investigated. The UV–vis absorption spectra show the surface plasmon absorption band around 410 nm, which confirms the formation of Ag-nanoparticles. It was found that the composition of CS/PVA blend affected the size of the obtained Ag-nanoparticles, as well as the parameters such as density, molar concentration and effective surface area, calculated from the experimentally obtained UV–vis absorption spectra and spectra obtained by simulation according to the Mie theory. SEM micrograph and XRD measurement indicated a spherical morphology and face centered cubic crystal structure of Ag-nanoparticles, with diameter around 12 nm. The values of optical band gap energy between valence and conduction bands (E_g), calculated from the UV–vis absorption spectra, also show dependence on the blend composition for Ag–CS/PVA colloids as well as for Ag–CS/PVA nanocomposites.

1. Introduction

One of the major challenges in designing of polymer nanocomposites is the ability to control the size and the morphology of nanoparticles, as well as to achieve their homogeneous distribution through the polymer. Methods for the preparation of polymer nanocomposites are mostly based on *in situ* polymerization in the presence of nanoparticles (Džunuzović et al., 2009a, 2009b) or on incorporation of previously synthesized nanoparticles in the polymer (Pandey et al., 2011; Vodnik et al., 2012). However, by these methods, sometimes is too difficult to achieve homogeneous distribution of nanoparticles and prevent their agglomeration in the polymer. Therefore, the method of *in situ* synthesis of nanoparticles within polymer matrix was investigated in many studies (Agnihotri et al., 2012; Chahal et al., 2011; Krklješ et al., 2007a; Luo et al., 2009; Mohan et al., 2007; Radosavljević et al., 2012).

The gamma irradiation induced reduction of metal ions in polymer solutions i.e., radiolytic *in situ* synthesis of metal nanoparticles in the presence of polymers such as chitosan (CS) and poly(vinyl alcohol) (PVA) or other bio- and synthetic polymers, is particularly suitable for preparation of nanocomposites based on Ag-nanoparticles (Ag NPs) incorporated in polymer matrix (Gerasimov, 2011; Huang et al., 2009; Kumar et al., 2005; Naghavi et al., 2010; Phu et al., 2010, Rao et al., 2010; Temgire and Joshi, 2004; Zhou et al., 2012). The advantage of *in situ* radiolytic method, over the other methods, is possibility to obtain a homogeneous distribution of synthesized Ag-nanoparticles within the polymer matrix as well as to control their size by changing the experimental conditions. The obtained material is clean and sterilized at the same time, which is very important in the case of their potential biomedical applications. The presence of

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polymer molecules during the radiolytic *in situ* synthesis of Ag-nanoparticles significantly suppresses the process of their agglomeration and further growth, by interaction of polymer's functional groups with a high affinity for the metal with atoms on the surface of metal clusters. In the previous research, the radiolytically synthesized Ag-nanoparticles were successfully stabilized by using poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP), poly (N-isopropylacrylamide) (PNiPAAm) and poly(bis-co-2-hydroxyethyl methacrylate-co-itaconic acid) poly(bis-co-HEMA-co-IA) (Cvetićanin et al., 2010; Jovanović et al., 2011, 2012; Kačarević-Popović et al., 2007, 2010; Krklješ et al., 2007a, 2007b).

On the other hand, polymer blending is simple and convenient procedure to obtain new material with required properties especially in the bioapplication when blend components are synthetic and natural polymers. In particular, blending the CS with PVA improves tensile strength, flexibility, bulk and surface hydrophilicity of the blended films. Moreover, water uptake in CS/PVA blend films as well as the selective protein immobilization can be controlled by variation of their contents and the pH of solution. Therefore, combination of CS with PVA as blend stabilizer of Ag-nanoparticles creates materials which will be useful in the range of applications from electronics to chemo/bio-sensing platforms, tissue engineering systems or antibacterial materials (Bahrami et al., 2003).

In this study, the chitosan/poly(vinyl alcohol) (CS/PVA) blends were used as capping agent for stabilization of Ag-nanoparticles, during their *in situ* gamma irradiation induced synthesis. Chitosan is a linear polysaccharide primarily composed of β-(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units and partially of β-(1,4)-linked 2-deoxy-2-acetamido-D-glucopyranose units. It is prepared by the N-deacetylation of chitin, the most abundant natural polymer after cellulose. Chitin is not easily soluble in any solvent. Nevertheless, unlike chitin, chitosan is dissolved in aqueous solutions of some organic and inorganic acids and becomes cationic polymer because of protonation of amino groups on the C-2 position of the pyranose ring. Chitosan consists of a large number of functional amino groups and hydroxyl groups. Since chitosan is non-toxic and biocompatible with the human physiological system, it has been investigated as biomaterial in the fields such as biomedicine, pharmacology and biotechnology. Chitin and chitosan have already been used in agricultural, food, industrial and medical fields (Tuhin et al., 2012). In addition, the antibacterial properties of chitosan are suitable for use as wound dressings, and further improvement of wound healing is achieved by incorporation of Ag-nanoparticles, which also exhibit antibacterial properties. Chitosan also can be applied in the process of reducing radiation damage to the radiation workers or radiation cured patients as well as in other areas of oncology (Chmielewski, 2010). Poly(vinyl alcohol) is a vinyl type polymer, produced by free radical polymerization of vinyl acetate monomers. The degree of hydrolysis, i.e. the content of acetate groups in the polymer, has a comprehensive impact on its physico-chemical properties. Poly (vinyl alcohol) is non-toxic, water-soluble, biocompatible and biodegradable polymer that is widely used in biochemical and biomedical applications (Bahrami et al., 2003; Finch, 1973; Yang et al., 2010).

On the other hand, many nanomaterials such as titanium dioxide, zinc oxide, magnesium oxide or copper exhibit significant antibacterial properties, but nanocrystalline silver has proved as most effective antimicrobial agent. Ag-nanoparticles exhibits strong antimicrobial activity and a wide biocide inhibitory spectrum against microbes, both bacteria and viruses, and even eukaryotic microorganisms, *in vitro* and *in vivo* (Kemp et al., 2009; Pattabi et al., 2010; Rujitanaroj et al., 2008; Secinti et al., 2008). In addition, Ag-nanoparticles have high optical absorption efficiency, which is very suitable for biomedical diagnostics, biosensors and heat absorption in special devices (Jovanović et al., 2012).

Ag-nanoparticles in CS/PVA blends as a stabilizer can be obtained by reduction of Ag^+ ions by using sodium borohydride or by using the functional groups of polymers themselves ($-COOH$, $-NH_2$, $-OH$) (Agnihotri et al., 2012; Vimala et al., 2011). In this study, Ag-nanoparticles were *in situ* synthesized by gamma irradiation, using CS/PVA blends as a capping agent. Reduction of Ag^+ ions was performed by radiolytically formed reduction species. The influence of composition of CS/PVA blends on optical and structural properties of obtained Ag–CS/PVA nanocomposite systems was investigated using UV–vis spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD). Finally, the optical properties of synthesized Ag–CS/PVA nanosystems were analyzed by the optical band gap energy (E_g), calculated from the experimentally obtained UV–vis absorption spectra. In general, the band gap of a material is defined as the energy distance between the valence and conduction bands (Gasaymeh et al., 2010), and the most of a material's behaviors, such as intrinsic conductivity, optical transitions, or electronic transitions, depend on it. These properties of materials are important parameters in applied science.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (PVA) with molecular weight of 72 kDa and 99% of minimal degree of hydrolysis, silver nitrate ($AgNO_3$) and 2-propanol ($(CH_3)_2CHOH$) were products of Merck. A medium molecular weight chitosan (CS) with 200–800 cP viscosity (1% solution in 1% acetic acid) and 75–85% degree of deacetylation was obtained from Sigma-Aldrich, while acetic acid (CH_3COOH) was product of Zorka Pharma. All chemicals were commercial products of analytical grade and were used without additional purification. Water from Millipore Milli-Q system was used in all experiments, while the high purity argon gas (99.5%) from Messer Tehnogas was used for removing the oxygen from solutions.

2.2. Synthesis of Ag–CS/PVA nanocomposites

The solution of CS (2.5% (w/w)) was prepared by dissolving the CS in aqueous solution of CH_3COOH (5% (v/v)), at room temperature under the constant stirring for 3 h, while the aqueous solution of PVA (5% (w/w)) was prepared by dissolving PVA at 90 °C under the constant stirring for 6 h. Obtained solutions of CS and PVA were used to prepare solutions in which the mass ratios of CS/PVA were 100/0, 80/20, 60/40, 40/60, 20/80 and 0/100, while the total weight of polymers in the systems was constant. Then, in all prepared solutions, $AgNO_3$ and $(CH_3)_2CHOH$ were added up to the concentration of 5 mM and 0.2 M, respectively. In order to remove oxygen, solutions were bubbled with Ar for 30 min, and then exposed to gamma irradiation (^{60}Co radiation facility), at room temperature to the absorbed dose of 8.5 kGy for reduction of 5 mM Ag^+ ions, at a dose rate of 6 kGy/h. Ag–CS/PVA nanocomposites (10–30 μm thick films) were obtained after solvent evaporation from synthesized Ag–CS/PVA colloids, at room temperature.

2.3. Methods of characterization

The optical properties of synthesized Ag–CS/PVA systems, colloids and nanocomposites, were investigated by UV–vis absorption spectroscopy. Absorption spectra were recorded using Thermo Fisher Scientific Evolution 600 UV–vis spectrophotometer, in the wavelength range 300–800 nm. Theoretical calculations of