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Synthesis, characterization and optical properties of gelatin doped with silver nanoparticles



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Silver nanoparticles were synthesized by chemical reduction method.
- TEM studies showed that the average particle size of Ag NPs was about 55 nm.
- Reduction of optical band gap of gelatin was achieved under addition of silver nanoparticles.
- There is noticeable color gradient between gelatin and doped samples.

A R T I C L E I N F O

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ABSTRACT

In this study, silver nanoparticles were synthesized by chemical reduction of silver salt (AgNO₃) solution. Formation of nanoparticles was confirmed by UV-visible spectrometry. The surface plasmon resonance peak is located at 430 nm. Doping of silver nanoparticles (Ag NPs) with gelatin biopolymer was studied. The silver content in the polymer matrix was in the range of 0.4–1 wt%. The formation of nanoparticles disappeared for silver content higher than 1 wt%. The morphology and interaction of gelatin doped with Ag NPs was examined by transmission electron microscopy and FTIR spectroscopy. The content of Ag NPs has a pronounced effect on optical and structural properties of gelatin. Optical parameters such as refractive index, complex dielectric constant were calculated. The dispersion of the refractive index was discussed in terms of the single – oscillator Wemple–DiDomenico model. Color properties of the prepared samples were discussed in the framework of CIE $L^*u^*v^*$ color space.

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Introduction

Nanosized metal particles posses unique electronic, optical, magnetic, thermal and catalytic properties that are different considerably from that of the bulk phase [1–3]. It comes from small sizes and high surface/volume ratios. Doping of polymers with nanoparticles is an attractive process to take advantage of these

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properties. The doped polymer matrices have long time stability [4,5], potential applications in nanoelectronic devices, sensors, molecular optical devices [6–8], optoelectronic applications and engineering nanocomposites with well defined properties. Silver nanoparticles (Ag NPs) have received considerable attention due to its chemical stability, good thermal, electrical conductivity and catalytic properties. Silver nanoparticles can be synthesized using various methods such as chemical, electrical [9], γ -radiation [10], photochemical [11], and laser ablation [12]. The most popular preparation technique of Ag NPs is the chemical reduction of silver salts by sodium borohydrate or sodium citrate. This preparation is

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simple but great care must be exercised to make stable and reproducible colloid. The size-induced properties of nanoparticles enable the development of new applications or the addition of flexibility to existing systems in many areas, such as catalysis, optics, microelectronics, antimicrobial materials, and molecular labeling [13,14].

Gelatin is a biopolymer with an attractive feature is that it has not shown any antigenicity and is completely resorbable in vivo [15]. It is widely used in pharmaceutical industry and for medical device applications. It is used also for regenerative medicine as a candidate material for obtaining scaffolds with similar qualities of natural media for a wide range of tissues [16,17]. Gelatin can act as a protective medium in the synthesis of monodisperse colloidal particles in aqueous solution system [18]. Some other applications of gelatin include hair care products, cosmetics, electroplating, food industry, and paper textile sizing [19].

In this work, we have attempted the preparation of Ag NPs. The influence of the silver content on the optical properties of gelatin biopolymer is studied with the support morphological analysis.

Experimental

Preparation of samples

Gelatin (BDH) (from cold water fish skin with Mwt. about 60 kD), silver nitrate and sodium citrate (Fisher) were used as received. All glassware were thoroughly cleaned in aqua-regia and rinsed copiously with triply distilled water. All solutions of the salts and polymer were prepared in triply distilled water. Colloidal silver solutions were prepared according to Graber [20] with some modification. Approximately 90 mg of AgNO₃ was dissolved in 500 mL of triply distilled water and brought to boiling while being vigorously stirred. Reduction of the silver salt was accomplished by adding in a single step of 10 mL of 1% sodium citrate. The solution was kept on boiling for about 1 h. After the end of reaction, the color of the colloids was greenish-yellow.

Weighed amounts of gelatin were dissolved in triply distilled water using a magnetic stirrer at 60 °C. Solutions of silver colloids and gelatin were mixed using magnetic stirrer at 60 °C with different weight percentages (0 wt%, 0.4, 0.6 and 1 wt% silver colloids). The solid samples were made by casting technique. Films of suitable thickness (\approx 30 µm) were casted onto stainless steel Petri dishes, and then dried in an open air at room temperature (30 °C) for 6 days until solvent was completely evaporated.

Spectroscopic measurements

Transmission electron microscopy (TEM) was performed using Joel "JEM-1011" electron microscope operated at 80 kV. The IR spectra were measured using PYE spectrophotometer in the range of 4000–400 cm⁻¹. The absorption measurements of the samples were performed using V-670 spectrophotometer. The tristimulus transmittance values (*X*, *Y*, *Z*) were calculated using the transmittance data obtained in the visible range according to CIEL**u***v** system. Also, the CIE three dimensional (*L**, *U**, *V**) color constants, whiteness (*W*), yellowness (*Y*), chroma (*C**), hue and color difference (ΔE) were performed.

Results and discussion

Morphology and IR analysis

Fig. 1(a) shows TEM micrograph of silver nanoperticles colloidal solution with spherical three dimensional distributions and average particle size 55 nm. For 1 wt% Ag NPs-gelatin composite



Fig. 1. TEM images of the (a) Ag colloids, (b) 1 wt% Ag NPs doped gelatin sample.

sample (Fig. 1(b)), the nanoparticles are more dispersed in gelatin and the particle size increased up to \approx 70 nm. The polymer functions as a binder, prevents the process of agglomeration of Ag NPs [21] and finally limits the diameter of nanoparticles formed. Gelatin has hydrophilic nature that protects the surface of fabricated nanoparticles. The electrostatic interactions between gelatin and silver nanoparticles were analyzed by FTIR spectroscopy. Gelatin is a polyamide protein so the infrared spectra of it (Fig. 2) exhibited a pronounced amide and hydrogen bonding characteristic absorption bands at 1634 cm⁻¹ (Amide I), 1525 cm⁻¹ (Amide II), 1237 cm⁻¹ (Amide III), and 3288 cm⁻¹ (Amide A) [22–24]. Among these absorption bands, the amide I vibration mode is mainly a C=O stretching vibration coupled to contributions from the C–N



Fig. 2. FTIR spectra of Ag NPs doped gelatin samples.

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