

Short Communication

Investigation of Metallic Silver Nanoparticles through UV-Vis and Optical Micrograph Techniques

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Received: 6 September 2016 / Accepted: 29 October 2016 / Published: 12 December 2016

In this work, UV-Vis and optical micrograph techniques were used to characterize the reduced silver nanoparticles in chitosan polymer doped with AgNO₃ salt. The UV-Vis spectrum shows distinguishable surface plasmonic resonance (SPR) absorption peaks at about 430 nm for the samples containing different amount of silver salt. The SPR peaks indicate the existence of silver nanoparticles. Upon the increase of silver nitrate salt concentration, the SPR peak intensity is enhanced, indicating the reduction of large amount of silver ions to the metallic silver nanoparticles in chitosan (CS) host polymer. Optical micrograph results show that silver nanoparticles are well dispersed at low silver salt concentrations. A leakage of large white spots of silver nanoparticles was observed at a higher silver salt concentration. The effect of lattice energy of silver salts on silver ion reduction and its distribution is interpreted. The FE-SEM image shows small white spots of silver nanoparticles on the surface of the sample. The observed shift in the Fourier transform infrared (FTIR) bands of CS:AgNO₃ relative to that of pure CS indicates the complexation between the chitosan polymer and the silver nitrate salt.

Keywords: natural polymers electrolyte; UV-Vis; Optical micrographs; SEM; FTIR

1. INTRODUCTION

Solid polymer nanocomposites with exceptional properties have become promising materials due to their applications in photonics, electronic and high-energy electrochemical devices [1-4]. The main advantage of metal nanoparticles is that their optical, electronic, and structural properties can be modified by controlling the particle dimensions without changing the chemical composition [5,6].

Among all metal nanoparticles, silver nanoparticles possess many outstanding properties, such as catalytic effect, antimicrobial activity, and high electrical and thermal conductivities [7-9]. The unique property of metallic silver nanoparticles is that they can exhibit a surface plasmonic resonance (SPR) peak when interacting with the photons of visible light [10]. It was reported that the SPR peaks and line widths are sensitive to the size and shape of the metallic nanoparticles [11-13], and their height gives information on the concentration of metal nanoparticles [14,15]. Recently natural polymers have attracted an increasing amount of attention, mainly due to their abundance and environmental concerns [16-18]. Among the natural polymers, chitosan (CS) is a promising polymer due to its non-toxicity, biodegradability, biocompatibility and antibacterial, excellent film forming characteristics, as well as ease of modification by various techniques [19-22]. Chitosan is a natural biocompatible cationic polysaccharide made from alkaline N-deacetylation of chitin [23-25]. CS consists primarily of repeating units of $\beta(1\rightarrow4)$ linked 2-amino-2-deoxy-D-glucopyranose [26-27]. The main features which separate CS structure from other biopolymers are the presence of hydroxyl (OH) and amine (NH_2) functional groups on its backbone and thus CS meets a necessary requirement for preparation of solid polymer electrolytes [28-30]. In the present work the reduction of silver ions to silver nanoparticles were investigated through the UV-Visible and optical micrograph techniques in CS: AgNO_3 based solid polymer electrolyte. The FTIR was also used to confirm the complex formation between the chitosan host polymer and silver nitrate salt.

2. EXPERIMENTAL DETAILS

2.1 Raw Materials

Chitosan (CS) powder from crab shells ($\geq 75\%$ deacetylated, average molecular weight 1.1×10^5 g/mol) procured from Sigma-Aldrich, silver nitrate (AgNO_3) with a molecular weight 169.87 g/mol supplied by Sigma-Aldrich. A 1% of acetic acid (CH_3COOH) was prepared with glacial acetic acid solution and utilized as the solvent to prepare the solid polymer electrolytes. All chemicals were used without further treatment or purification.

2.2 Preparation of nanocomposite polymer electrolytes

In this work solid polymer electrolyte films based on chitosan (CS) were prepared by solution casting technique. One gram of CS powder was dissolved in 100 ml of 1% acetic acid. The solution was stirred continuously using a magnetic stirrer for more than 24 hours at ambient temperature. Once the polymer was completely dissolved a clear viscous solutions were obtained. Different amounts of silver nitrate (AgNO_3) (4, 8, 12, 16, 20, and 24 wt%) were added separately to this solution with continues stirring to prepare the various composition of CS/ AgNO_3 solid polymer electrolyte system. The homogenous mixture solutions were then cast into plastic Petri dish and allowed to dry at room temperature. After the film has formed, it was transferred into desiccator with silica gel desiccants for additional drying. Table I summarizes the concentration of the prepared samples.

Table I. The composition of CS:AgNO₃ solid polymer electrolyte films.

Designation	AgNO ₃ (wt.%)	Chitosan (g)	AgNO ₃ (g)
CSPE-0	0	1.00	0.0000
CSPE-1	4	1.00	0.0416
CSPE-2	8	1.00	0.0869
CSPE-3	12	1.00	0.1363
CSPE-4	16	1.00	0.1904
CSPE-5	20	1.00	0.2500
CSPE-6	24	1.00	0.3157

2.3 Characterization techniques

The UV-Visible spectra of the prepared films were recorded using a Jasco V-570, UV-Vis-NIR spectrophotometer (Jasco SLM-468, Japan) in the absorbance mode, and in the wavelength range between 190 to 1500 nm. The optical micrograph images of the prepared nanocomposites films were realized by Optical Microscope. The image of the film surface of the samples was taken using an optical microscope (MEIJI) attached with digital camera and software from DINO-LITE at adjusted magnification. A scanning electron micrograph was taken using the (FEI Quanta 200) field emission scanning electron microscope (FE-SEM) to study the morphological characteristics. FTIR spectra were recorded using Thermo Scientific/Nicolet iS10 spectrometer with 1 cm⁻¹ resolution in the transmission mode from wave numbers 500 to 5000 cm⁻¹.

3. RESULTS AND DISCUSSIONS

3.1 UV-Visible and morphological study

UV-Visible spectroscopy is a simple and quite a sensitive technique that can be used to detect the formation of silver nanoparticles [10,31]. Figures 1 and 2, shows the obtained UV-Visible absorption spectra of pure CS and CS:AgNO₃ solid electrolyte samples. As can be seen in the Figure 1 the pure CS film does not show any appreciable absorption peak in the wavelength region 400 nm to 1500 nm, however a broad absorption band centered at 430 nm was observed for CS:AgNO₃ solid electrolyte samples (Figure 2). This absorption band is called a localized surface plasmon resonance (SPR) [32]. Other researchers also observed the SPR peak in the same region for spherical silver nanoparticles produced in PVA [33], and PVP [34] host polymers. Thus, the observed SPR in CS:AgNO₃ samples reveals the reduction of silver ions (Ag⁺) to the metallic silver nanoparticles (Ag⁰) in the present system. The present of lone pair electrons in functional groups of CS are responsible for complexation as well as reduction of silver ions to silver nanoparticles [35,36]. The interaction between silver ions and polar groups of chitosan can be more understood in FTIR section. The increment of the relative intensity of the SPR peaks with increasing silver salt concentration, implying an increasing amount of Ag⁰ nanoparticles due to the increase of silver ions' reduction in the system [37-40].

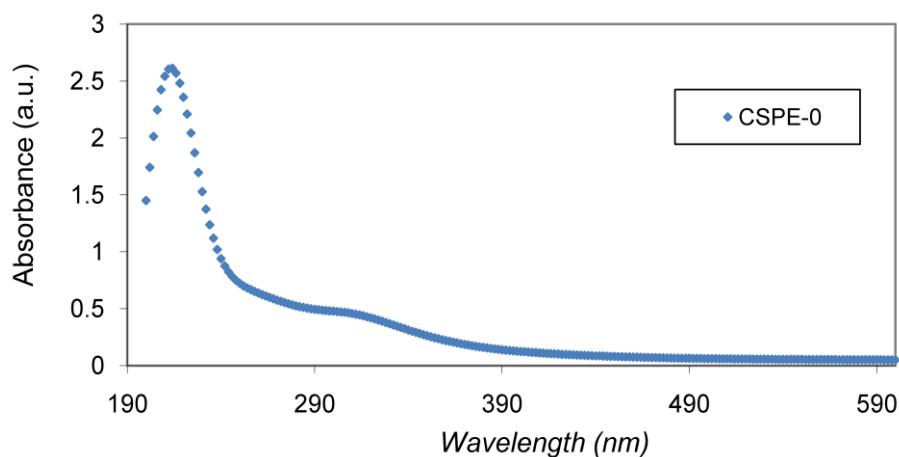


Figure 1. UV-Visible absorption spectrum for pure chitosan (CSPE-0) film.

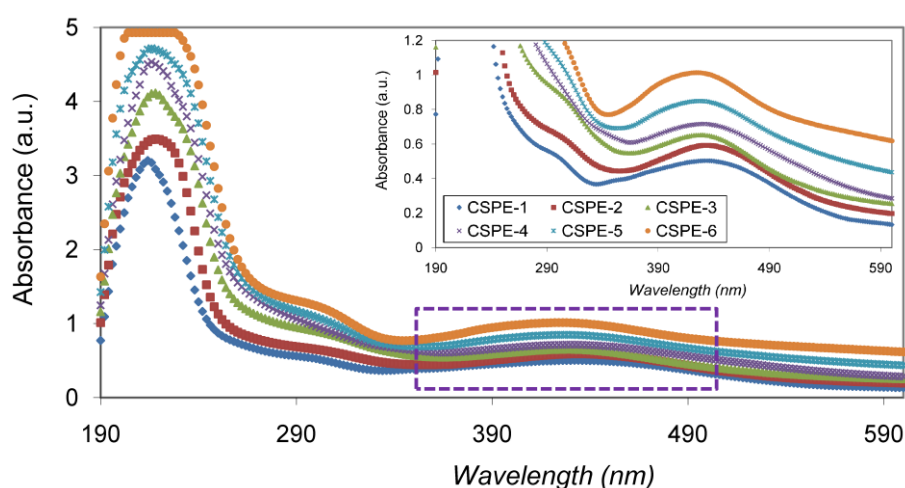


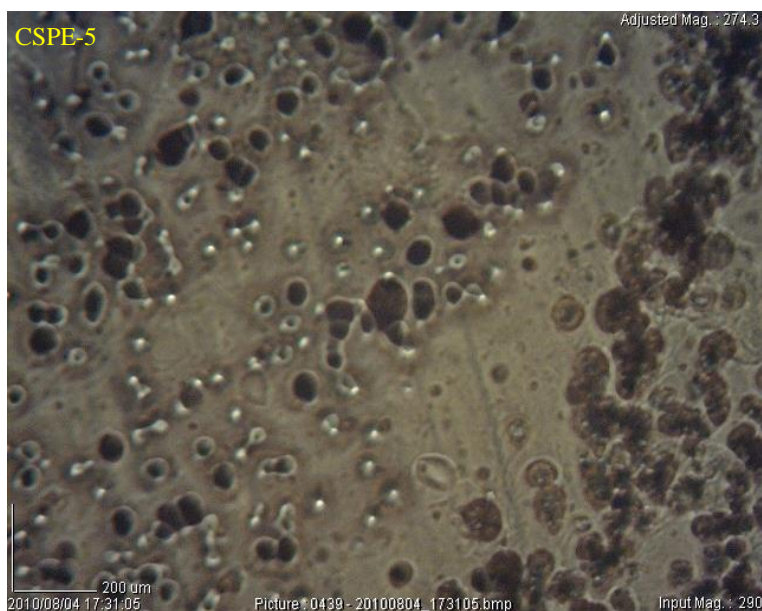
Figure 2. UV-Visible absorption spectra for CS:AgNO₃ solid films with different silver salt concentration.

The formation of metallic silver nanoparticles in the investigated systems is also indicated from the change in the color of the polymer electrolyte solution from yellow to dark brown. Kang et al., [41], also observed the color change in poly (ethylene phthalate) (PEP) and poly (2-ethyl-2-oxazoline) (POZ) polymer electrolyte containing silver tetrafluoroborate (AgBF₄) salt as a result of silver ion reduction. It is interesting to note that the SPR peak shifted to higher wavelength with increasing silver salt concentration. At higher AgNO₃ content, the synthesized silver nanoparticles combined with each other to create a group of aggregations. Thus, the particle size of silver nanoparticles increases with increasing silver salt content. The formation of metallic silver clusters or aggregates can be more understood in optical micrographs section.

The morphology of CS:AgNO₃ polymer electrolyte films were characterized by optical microscopy to observe the formation of silver nanoparticles. Figure 3 show the surface morphology of different compositions of CS:AgNO₃ solid polymer electrolytes. The optical images show some clusters and aggregated particles, which can be attributed to the leakage of the silver nanoparticles to the membrane surface [26]. The silver nanoparticles are formed as a consequence of chemical

reduction of silver ions by lone pair electrons of polar (NH_2 and OH) groups of chitosan biopolymer [42]. It can be seen that the size of aggregated metallic silver particles which appeared on the surface of $\text{CS}:\text{AgNO}_3$ polymer electrolyte membrane increased with increasing the concentration of AgNO_3 slat. In our previous work distinguishable white chains and a percolative path was observed for the reduced silver particles in $\text{CS}:\text{AgCF}_3\text{SO}_3$ solid electrolyte system [42]. The formation of white chains is related to the fact that silver salts with the larger CF_3SO_3^- (0.256 nm) anions have a much stronger tendency to form complexes with polar groups that have lone pair electrons than those with the smaller anions such as NO_3^- (0.189 nm) [43]. As well as the lattice-energy of silver salts significantly influences the rates of silver ion reductions [43,44].





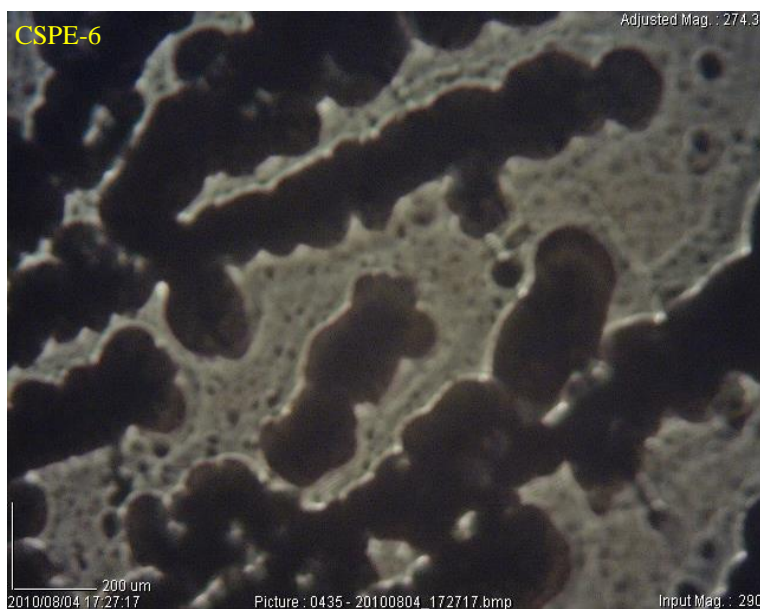


Figure 3. Surface image of CS:AgNO₃ solid electrolyte films with different silver salt concentration.

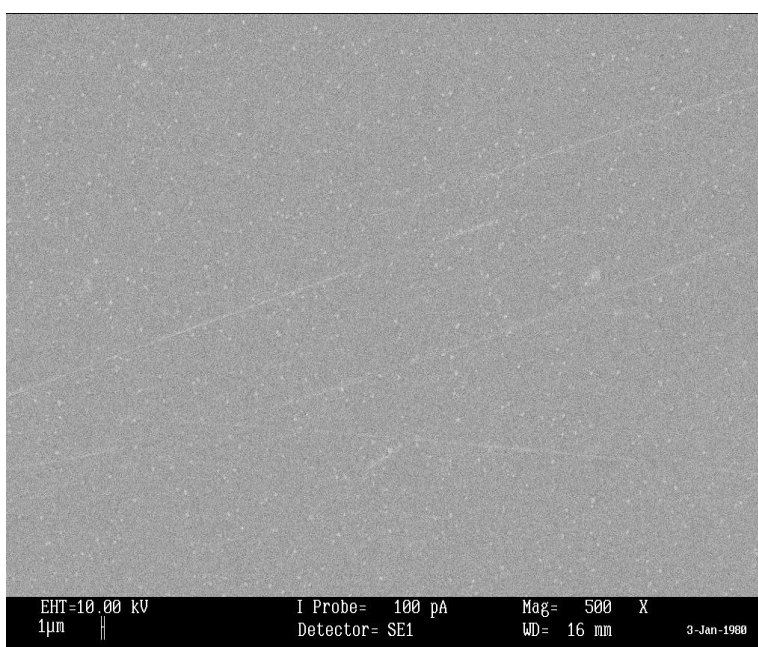


Figure 4. The field emission scanning electron microscopy (FE-SEM) image of CSPE-6 sample.

The lattice-energy of AgCF₃SO₃ (716 kJ/mol) is smaller than that of AgNO₃ (773 KJ/mol), and thus the interaction of silver ion with CF₃SO₃ is weaker than that with NO₃. Consequently, more silver ions can be reduced in CS:AgCF₃SO₃ system and white chains were observed [42], while this phenomenon is not appeared for CS:AgNO₃ system as depicted in Figure 4. As a whole, the distribution of silver nanoparticles was uniform and homogeneous when the amount of AgNt was less than 12 wt. %. The results of optical micrographs are supported the UV-Visible investigations. The occurrence of silver particle aggregation can be attributed to the phase separation of silver particles

from the host polymer because the aggregated silver nanoparticles are not consistent with the CS polymer matrix at higher salt content [45]. To confirm the complex formation of silver ions with ($-NH_2$) and ($-OH$) groups of CS matrix, the FTIR spectroscopy was carried out on CS:AgNO₃ samples.

3.2 FTIR analysis

FTIR spectroscopy was used to identify the chemical structure of the composite films and investigate the possible interactions between their components. Figure 5 represents the FTIR spectrum of different composition of CS:AgNO₃ complexes in the wave number region 400-5000 cm⁻¹. The main characteristic absorption peaks of CS are observed in all samples, such as vibration of the amino group (NH_2), $O=C-NHR$, and amine NH symmetric [46].

It can be noticed from Table II that there are a shifting towards lower wave number in the bands of amine (NH_2) and ($O-H$) groups. This significantly confirms that complexation has occurred between CS and AgNO₃ salt [47,48]. The shifting and decrease in the relative intensity of these bands are attributed to the electrostatic interaction between the ions and the functional groups of CS polymer [49-51]. Moreover, the shift of $N-H$ stretching vibration toward lower wavenumbers indicates that the inter- and intra-molecular hydrogen bonds of CS were weakened [6]. Recent studies confirmed that the hydroxyl ($-OH$), carboxyl ($-C=O$), and amine ($-NH$) groups have a critical role in the fabrication of silver nanoparticles [52].

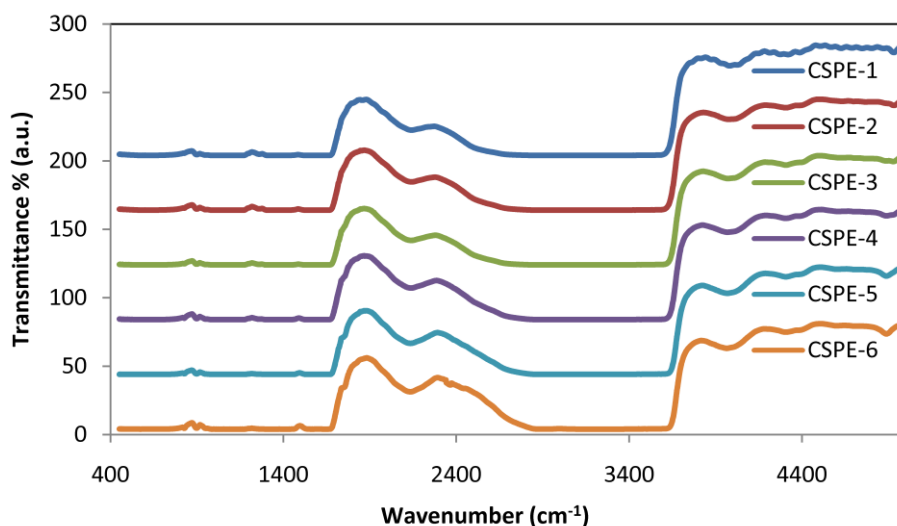


Figure 5. FTIR spectra of different composition CS:AgNO₃ solid polymer electrolyte films.

Table II. Assignments of FTIR bands for CS:AgNO₃ solid polymer electrolyte films.

Samples	Wavenumbers (cm ⁻¹)		
	NH ₂	O=C-NHR	O-H
CSPE-0	1559	1648	3358
CSPE-1	1562	1642	3242

CSPE-2	1562	1646	3217
CSPE-3	1564	1646	3213
CSPE-4	1568	1646	3210
CSPE-5	1572	1646	3192
CSPE-6	1560	1646	3185

4. CONCLUSIONS

The results of this work show that it is possible to use UV-Visible and optical micrograph techniques to characterize the reduced silver nanoparticles in chitosan:AgNO₃ polymer based solid electrolytes. The distinguishable surface plasmonic resonance (SPR) absorption peaks at about 430 nm are related to the existence of metallic silver nanoparticles. Upon the increase of silver nitrate salt concentration, the SPR peak intensity is enhanced, indicating the reduction of a large amount of silver ions to the metallic silver nanoparticles in chitosan (CS) host polymer. Optical micrograph results show that silver nanoparticles are completely dispersed at low silver salt concentrations. A leakage of large white spots of silver nanoparticles was observed at higher silver salt concentrations. The result of SEM image was explained on the basis of lattice energy of salts. From the SEM image, it is understood that it's hard to obtain white chains of silver nanoparticles for silver salts with high lattice energy. The observed shift in the Fourier transform infrared (FTIR) bands of CS:AgNO₃ relative to that of pure CS indicates the complexation between the chitosan and the silver nitrate salt.

Competing Interests

The authors declare that they have no competing interests.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from the University of Sulaimani-Ministry of Higher Education and Scientific Research-Kurdistan Regional Government and University of Human Development for this research work.

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