Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 138 (2015) 434–440

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis, characterization, optical and antimicrobial studies of polyvinyl alcohol–silver nanocomposites

K.H. Mahmoud *

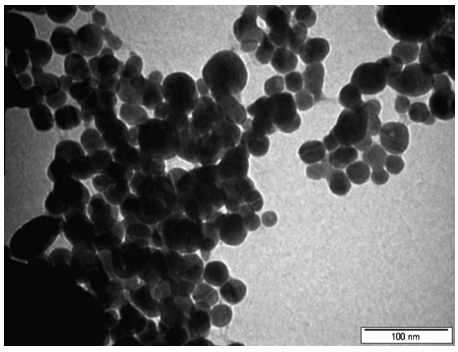
Physics Department, Faculty of Science, Taif University, Taif, Saudi Arabia
Physics Department, Faculty of Science, Cairo University, Cairo, Egypt

HIGHLIGHTS

- Silver nanoparticles were synthesized by chemical reduction method.
- TEM studies showed that the average particle size of Ag NPs was about 19 nm.
- Optical band gap of PVA was reduced under addition of Ag NPs.
- The antimicrobial activity of PVA was enhanced under addition of Ag NPs.

GRAPHICAL ABSTRACT

TEM image of the Ag colloids.



ARTICLE INFO

Article history:
Received 9 August 2014
Received in revised form 23 October 2014
Accepted 24 November 2014
Available online 28 November 2014

Keywords:
Silver nanoparticles
PVA
Optical properties
Antimicrobial activity

ABSTRACT

Silver nanoparticles (Ag NPs) were synthesized by chemical reduction of silver salt ($AgNO_3$) through sodium borohydride. The characteristic surface plasmon resonance band located at around 400 nm in the UV–Visible absorption spectrum confirmed the formation of Ag nanoparticles. Polyvinyl alcohol–silver (PVA–Ag) nanocomposite films were prepared by the casting technique. The morphology and interaction of PVA with Ag NPs were examined by transmission electron microscopy and FTIR spectroscopy. Optical studies show that PVA exhibited indirect allowed optical transition with optical energy gap of 4.8 eV, which reduced to 4.45 eV under addition of Ag NPs. Optical parameters such as refractive index, complex dielectric constant and their dispersions have been analyzed using Wemple and DiDomenco model. Color properties of the nanocomposites are discussed in the framework of CIE L*u*v* color space. The antimicrobial activity of the nanocomposite samples was tested against Gram positive bacteria (*Staphylococcus aureus* NCTC 7447 & *Bacillus subtillis* NCIB 3610), Gram negative bacteria (*Escherichia coli*, NTC10416 & *Pseudomonas aeruginosa* NCIB 9016) and fungi (*Aspergillus niger* Ferm – BAM C-21) using the agar diffusion technique. The antimicrobial study showed that PVA has moderate antibacterial activity against *B. subtillis* and the 0.04 wt% Ag NPs composite sample effect was strong against *S. aureus*.

Introduction

Metal nanoparticles particles posses peerless electronic, optical, magnetic, thermal and catalytic properties that differ extremely

* Address: Physics Department, Faculty of Science, Taif University, Taif, Saudi Arabia. Tel.: +966 530175838.
E-mail address: cairouni1@yahoo.com

http://dx.doi.org/10.1016/j.saa.2014.11.074
1386-1425/

from that of the bulk phase [1–3]. Polymer based nanocomposites are being considered as versatile materials in many scientific applications leading to technological progress [4,5]. This is due to the fact that incorporation of the nanoparticles into the polymer matrix significantly affects its optical, thermal and electrical properties [6,7] while retaining its ingrained characteristics. It opens a new gateway in developing the materials for improved performance [8] in many potential applications like optical devices, biomedical science, the efficient integration of such nanocomposites for technological applications, the pre-requisites include the selection of host matrix and embedded nanoparticles along with the control on their size, shape, concentration and distribution within the matrix [9–11].

Silver nanoparticles (Ag NPs) have received considerable attention due to its chemical stability, good thermal, electrical conductivity and catalytic properties. Different methods can be used for Silver nanoparticles synthesis such as chmical, electrical [9], γ- radiation [12], photochemical [13], laser ablation [14].

Polyvinyl alcohol polymer is a suitable host matrix due to its high mechanical strength, water-solubility, good environmental stability, easy processability, Besides, it is semicrystalline, fully biodegradable, bio compatible, non toxic. Moreover, it contains a carbon backbone with hydroxyl groups, which can be used as a source of hydrogen bonding and assist in the formation of polymer nanocomposites [15–18].

Silver nanoparticles gained a great attention for its antimicrobial and beneficial properties toward health since ancient times [19]. These nanoparticles also are antimicrobial regarding a broad spectrum of Gram-negative and Gram-positive bacteria [20,21]. Moreover, silver nanoparticles show antifungal [22] and antiviral activity [23,24]. Recently, the attractive antibacterial activities of silver nanoparticles have retrieved importance due to an increase of bacterial resistance to antibiotics caused by their excessive use. The antibacterial activity of the silver-containing materials can be used, for example, in medicine to reduce infections as well as to prevent bacterial colonization on prostheses, dental materials, vascular grafts, catheters, human skin, and stainless steel materials [25].

As a result of coagulation of the metal colloids, they are usually unstable and difficult to use and consequently, their antibacterial activities are poor. This problem can be greatly solved by implanting or encapsulating the metal nanoparticles with polymer matrices [26,27]. PVA could be considered as a good host material for metal, due to its above foregoing properties [15–18] which make the silver nanoparticles can be easily prepared in aqueous medium and the preparation is virtually non-toxic.

In this work, we have attempted the preparation of PVA–Ag nanocomposites. We will focus our attention to enhance optical, structural, and antimicrobial properties of nanocomposites.

Experimental

Preparation of samples

Poly(vinyl)alcohol (PVA) with an approximate molecular weight of 17,000 was supplied by BDH chemical Ltd. Poole England. Silver nitrate and sodium borohydride (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. Hydrosol of silver nanoparticles has been chemically synthesized by chemical reduction of silver nitrate through sodium borohydride [28]. For this 10 mL volume of 1.0 mM $AgNO_3$ was added drop wise to 30 mL of 2.0 mM sodium borohydride solution that had been cooled in an ice bath. The reaction mixture was stirred vigorously on a magnetic stir plate. The solution turned light yellow after the addition of 2 mL of silver nitrate and a brighter yellow when all of the silver nitrate had been added. The entire addition took about three minutes, after which the stirring was stopped and the stir bar removed. The clear yellow colloidal silver is stable at room temperature stored in a transparent vial for as long as several weeks or months. Upon aggregation the colloidal silver solution turns darker yellow, violet and then grayish.

Weighed amounts of PVA were dissolved in triply distilled water using a magnetic stirrer at 60 °C. Solutions of silver colloids and PVA were mixed using a magnetic stirrer at 60 °C with different weight percentages (0, 0.04, 0.06 and 0.08 wt% silver colloids). The solid samples were made by casting technique. Films of suitable thickness (≈100 μm) were cast onto stainless steel Petri dishes, and then dried in an open air at room temperature (30 °C) for 3 days until solvent was nearly 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 400–4000 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 studied.

Antimicrobial activity

The antimicrobial activity of the nanocomposite samples was determined using the agar disc diffusion method as described by the National Committee for Clinical Laboratory Standards (NCCLS) [29–31]. The antibacterial activities were done by using 1 mg/ml solution in dimethyl formamide (DMF). The tested organisms were, Gram positive bacteria (*Staphylococcus aureus* NCTC 7447 & *Bacillus subtillis* NCIB 3610), Gram negative bacteria (*Escherichia coli*, NTC10416 & *Pseudomonas aeruginosa* NCIB 9016) and fungi (*Aspergillus niger* Ferm – BAM C-21). The bacteria and fungi were maintained on nutrient agar medium and Czapek Dox agar medium respectively. DMF showed no inhibition zones. The agar media were inoculated with different test microorganisms. After 24 h, of incubation at 30 °C for bacteria and 48 h of incubation at 28 °C for fungi, the diameter of inhibition zone (mm) was measured. We will Briefly, describe the agar well diffusion. With a sterile loop, pure colonies of the bacterial cultures were picked up; the colonies were suspended in 5 ml of sterile physiological saline. Well containing the biomaterial were placed a sterile forceps onto the agar surface and gently pressed down to ensure contact the plates were pre-incubated for 1 h, at refrigerator followed by incubation at 37 °C for 24 h, after incubation, the diameter of inhibition zone were measured (including the diameter of the hole).

Results and discussion

TEM profiles and IR spectra

Fig. 1(a) shows TEM image of silver nanoparticles colloidal solution with spherical three dimensional distributions and average particle size 19 nm. For 0.08 wt% Ag NPs- PVA composite sample (Fig. 1(b)) the nanoparticles are more dispersed in PVA and the particle size increased up to ≈33 nm. The polymer functions as a binder and also it prevents the process of agglomeration