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Electrochemical Synthesis of New Silver-Chitosan/Polyvinyl Alcohol Hybrid Nanoparticles and Evaluation of Their Antibacterial Activities

E. Salih[1,*], F.M. Reicha[1], I.M. El-Sherbiny[2]

[1]*Biological Advanced Materials, Physics Department, Mansoura University, Mansoura, ET-35516, Egypt.*
[2]*Chemistry Department, Mansoura University, Mansoura, ET-35516, Egypt.*

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ABSTRACT

In the current study new antibacterial densely dispersed silver nanoparticles (AgNPs) have been synthesized using a facile electrochemical approach in the presence of chitosan (Cs)/polyvinyl alcohol (PVA) semi-interpenetrating (semi-IPN) NPs. Formation of the AgNPs was confirmed by appearance of surface plasmon resonance peaks at 405 nm. The intensities of the absorption increased with increasing the time of both electrochemical process and the reduction time up to 2 h. The prepared Cs/PVA semi-IPN NPs were uniform and spherical with average size of 150 nm. The AgNPs were formed mostly on the surface of Cs/PVA semi-IPN NPs in addition to a portion formed in the suspension with average size in the range of 3 - 8 nm. The antibacterial activity of the Cs/PVA NPs and the newly developed Ag-Cs/PVA hybrid NPs was evaluated against *P. aeruginosa*, *Klebsiella*, *E. coli*, and *S. epidermidus* bacteria. It was found that the green synthesized Ag-Cs/PVA hybrid NPs exhibited a stronger antibacterial activity as compared with Cs/PVA NPs especially for *S. epidermidus*.

1. Introduction

A significant body of research has focused recently on the development and study of metal nanoparticle (NPs) because of their potential applications in different fields such as optics, optoelectronics, biomedical, biochemical sensing and catalysis [1]. One of the most important classes of metal NPs is that made of noble metals such as gold (Au), silver (Ag) and platinum (Pt) [2]. From the noble metal NPs, AgNPs have been used as antimicrobial, electrical conducting, and in various sensing purposes [3, 4].

Although different techniques such as laser ablation, lithography and photochemical reduction have been used effectively to synthesis different types of metal NPs, these techniques showed many shortcomings to be seriously considered. For instance, some of them involve the use of hazardous chemicals [5, 6]. Therefore, the eco-friendly synthesis of NPs has recently received growing attention. For example, several biological systems including bacteria, fungi, yeast and plant extracts have been used in this regard [7-10].

Preparation of metal NPs using the electrochemical technique was described for the first time in literature by Reetz and Helbig [11]. In their reported study, a metal sheet was anodically dissolved and the resulting intermediate metal ions were reduced at the cathode, forming metallic particles stabilized by tetra-alkyl ammonium salts. This was then adopted for the electrochemical preparation of the AgNPs in acetonitrile containing tetra-butyl ammonium salts [12, 13]. In our previous study [14], AgNPs were synthesized via electrochemical oxidation of Ag metal into Ag^+ with in situ complexation with the chitosan (Cs) followed by UV irradiation reduction.

The study reported herein describes a facile electrochemical synthesis of new Ag-Cs/polyvinyl alcohol (PVA) hybrid NPs and the assessment of their antibacterial activities. The Cs/PVA semi-interpenetrating (semi-IPN) NPs were firstly prepared through ionotropic gelation of Cs chains in the presence of sodium triphosphate pentabasic (STPP) with in situ incorporation of free PVA chains. The prepared Cs/PVA semi-IPN NPs were then used for the first time in literature as a platform for the synthesis of AgNPs through electrochemical complexation technique. Cs was selected in this study due to its various significant biological properties such as non-toxicity, biodegradability, biocompatibility and particularly its antibacterial capability [15], which would further enhance the antibacterial activities of the developed AgNPs.

2. Experimental Methods

2.1 Materials

Chitosan (Cs) of low MW, polyvinyl alcohol (PVA) with average MW of 84 kDa, and sodium triphosphate pentabasic (STPP) of practical grade 90-95% were provided by Sigma-Aldrich (Germany). Acetic acid was provided by Fisher (UK). The silver plates (20 mm × 40 mm × 5 mm) of purity 99.99% were purchased from Algom Co. (Cairo, Egypt). The silver plates were well polished before use with the aid of a very fine emery paper, cleaned by acetone, ethanol (90%) and de-ionized water. All other reagents were of analytical grade and used as received.

2.2 Preparation of Cs/PVA Semi-IPN NPs

The aqueous suspensions of Cs/PVA semi-IPN NPs were prepared using ionotropic gelation technique as illustrated in Scheme 1. Briefly, a predetermined weight of Cs was dissolved in 0.8% w/v acetic acid to yield a Cs solution with a final concentration of 1% w/v. Then, 45 mL of the prepared Cs solution (1% w/v) was mixed with equal volume of PVA (1% w/v) with continuous stirring. Afterwards, 10 mL of STPP (0.25% w/v) aqueous solution was added drop wise to the mixture under sonication for 5 min with 20 seconds pulse on and 5 seconds pulse off.

2.3 Electrochemical Synthesis of Ag-Cs/PVA Hybrid NPs

The Ag-Cs/PVA hybrid NPs were prepared through electrochemical oxidation/complexation followed by UV-irradiation reduction (Scheme 1). The electrochemical oxidation process was carried out using a potentiostatic method in a one compartment electrochemical cell at a constant potential of 5 V. The used cell consists of two polished silver plates (20 mm × 40 mm × 5 mm) as anode and cathode, being vertically placed face-to-face 20 mm apart. The two electrodes were immersed vertically in the prepared aqueous suspension of Cs/PVA semi-IPN NPs. The electrochemical process was carried out for different time intervals (0.5, 1, 1.5, and 2 h). Afterwards, the reduction process of the resulting

*Corresponding Author
Email Address: ehabsalih89@gmail.com (Ehab Salih)

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suspension was completed via UV-irradiation with the aid of a UV-lamp at λmax = 254 nm at 25 °C with a constant stirring for different irradiation times (0.5, 1, 1.5 and 2 h).

2.4 Characterization

The synthesis of Ag-Cs/PVA hybrid NPs was confirmed using UV-Vis spectrophotometer (Thermo Scientific Evolution 600 UV-Vis spectrophotometer). The analysis was performed at room temperature using quartz cuvettes (1 cm optical path) and the blank was the corresponding solvent. The possible functional groups in both Cs and PVA that can participate in the reduction process of Ag^+ ions and capping of the resulting AgNPs were identified using attenuated total reflectance (ATR) spectroscopy (NECOLET iS10). The size of the prepared Cs/PVA semi-IPN NPs and the Ag-Cs/PVA hybrid NPs was measured by dynamic light scattering, DLS (Malvern nanosizer, Malvern Instruments Ltd., Worcestershire, UK). Morphology of the NPs was investigated by HRTEM (JEOL-JEM-2100). Samples were prepared by placing few drops of the NPs suspension on carbon-coated copper grids, followed by allowing the solvent to slowly evaporate before recording the TEM images.

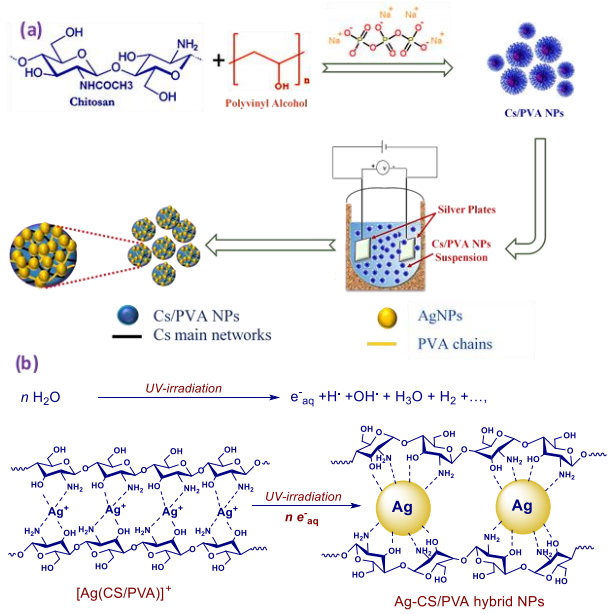
2.5 Antibacterial Studies

The antibacterial activity of Cs/PVA semi-IPN NPs and the developed Ag-Cs/PVA hybrid NPs was evaluated against *P. aeruginosa*, *Klebsiella*, *E. coli*, and *S. epidermidus* bacteria. Nutrient agar was used as a medium to grow bacteria. The bacterial suspension was obtained by making a saline suspension of isolated colonies selected from 18 to 24 h of nutrient agar plating. 200 µL of the samples on agar plates were inoculated with *P. aeruginosa*, *Klebsiella*, *E. coli*, and *S. epidermidus*. These plates were then incubated at 37 °C for 24 h and the inhibition zones were measured.

3. Results and Discussion

3.1 Formation of Ag-Cs/PVA Hybrid NPs

Cs/PVA semi-IPN NPs were used in the current study as an active platform for the synthesis of AgNPs through electrochemical oxidation of Ag anode into Ag^+ ions followed by a UV-irradiation reduction as illustrated in Scheme 1a. During the synthesis process as illustrated in Scheme 1b, both the free Ag^+ ions and the resulting ionic complexes (Ag^+-Cs/PVA) are reduced by the hydrated electrons (e_{aq}^-) which formed upon UV-irradiation of the aqueous solution [16, 17]. Then, the Ag atoms undergo aggregation through metallic bonding to form the Ag core of the NPs [18]. Presence of Cs/PVA NPs is important for the stabilization of the formed AgNPs on their surfaces as they prevents the Ag clusters from further aggregation at the macroscopic level due to the ion-dipole intermolecular forces [19].



Scheme 1 A schematic illustration of (a) the synthesis procedures of Cs/PVA semi-IPN NPs and Ag-Cs/PVA hybrid NPs, and (b) the suggested synthesis mechanism of the Ag-Cs/PVA hybrid NPs

Formation of Ag-Cs/PVA NPs was confirmed using UV-Vis spectrophotometry through the appearance of absorption peaks at around 405 nm as shown in Fig. 1a and b. These peaks are corresponding to the characteristic surface plasmon resonance (SPR) of the formed AgNPs [20]. The effects of parameters such as the electrochemical complexation time and UV-irradiation time onto the physicochemical characteristics of the developed Ag-Cs/PVA NPs were also studied. For instance the intensities of the absorption peaks were found to increase with increasing the time of both the electrochemical process and the reduction step indicating that the concentration of the obtained Ag hybrid NPs increases with time [21].

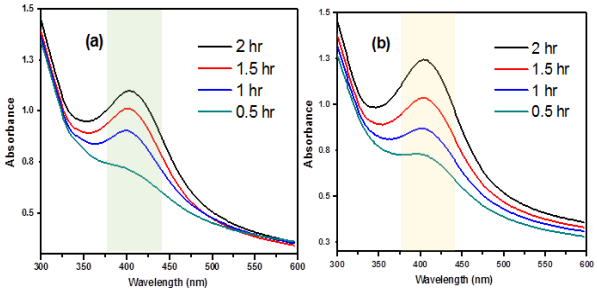


Fig. 1 UV-Vis spectra of the Ag-Cs/PVA hybrid NPs resulting from electrochemical oxidation/complexation of Ag^+ ions with Cs/PVA NPs at (a) different time intervals of complexation (0.5, 1, 1.5 and 2 h) followed by UV-irradiation reduction for 1 h, (b) different time of UV-irradiation reduction (0.5, 1, 1.5 and 2 h) with the complexation time kept constant at 1 h

3.2 FTIR Characterization

Fig. 2 shows the ATR–FTIR spectra of Cs, PVA, Cs/PVA NPs and the Ag-Cs/PVA hybrid NPs. In the case of Cs (Fig. 2a), the spectrum shows a peak at about 3320-3450 cm^{-1} which can be assigned for the O-H stretching vibration and the N-H extension vibration of the polysaccharide moieties of Cs molecules. The signal appeared around 2876 cm^{-1} is attributed to the stretching vibrations of the aliphatic C-H bonds whereas the absorption band noted at 1638 cm^{-1} is due to the stretching vibration of the C=O bond. In the case of PVA (Fig. 2b), the spectrum demonstrated absorption peaks at about 3250 cm^{-1} (–OH stretching) and at about 1441 and 1081.5 cm^{-1} corresponding to the –C–O group [22]. Comparing the FTIR spectrum of the resulting Ag-Cs/PVA hybrid NPs (Fig. 2d) with that of the Cs/PVA NPs (Fig. 2c) reveals a reduction in the intensity of the peak at about 3320-3450 cm^{-1}, which confirms the formation of AgNPs upon interaction with the terminal hydroxyl groups of PVA, and both the amino and hydroxyl groups of the Cs.

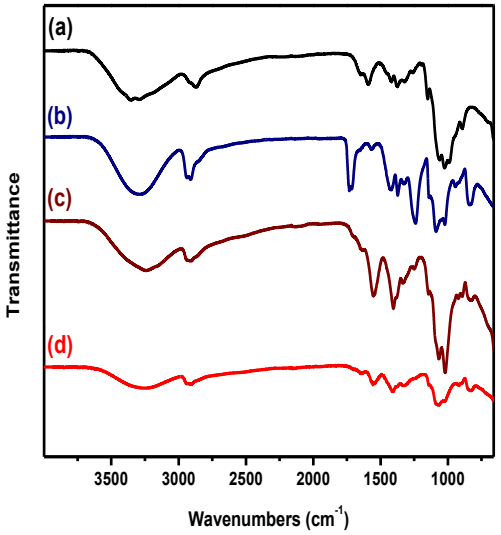


Fig. 2 FTIR spectra of (a) Cs, (b) PVA, (c) Cs/PVA NPs and (d) Ag-Cs/PVA hybrid NPs.

3.3 TEM Studies

TEM measurements were carried out to observe the size and morphology of the developed Cs/PVA semi-IPN NPs and Ag-Cs/PVA hybrid NPs. The obtained Cs/PVA NPs demonstrated compact, dense and spherical structure as apparent from the TEM micrograph (Fig. 3) with average size around 150 nm. As also apparent from the TEM micrograph, the synthesized AgNPs are well dispersed with uniform and spherical shapes and diameters ranging from 3 - 8 nm. It can also be noted that the AgNPs were formed on the surface of the Cs/PVA NPs in addition to a portion formed in the suspension.

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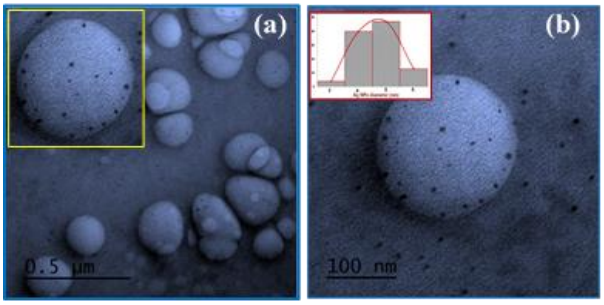

Fig. 3 Typical TEM images of the developed Ag-Cs/PVA hybrid NPs

3.4 Antibacterial Studies

The antibacterial activity of the prepared Ag-Cs/PVA hybrid NPs was evaluated against *P. aeruginosa*, *Klebsiella*, *E. coli*, and *S. epidermidus* bacteria and compared with Cs/PVA semi-IPN NPs (Fig. 4). The inhibition zones of Cs/PVA NPs and Ag-Cs/PVA NPs were found to be (17, 23 mm) for *P. aeruginosa*, (17, 19 mm) for *klebsiella*, (20, 23 mm) for *E. coli*, and (17, 25 mm) for *S. epidermidus* bacteria respectively. As can be also noted from Fig. 4, the Cs/PVA NPs mediated AgNPs showed stronger inhibition effect as compared to the Cs/PVA NPs. This relatively high antibacterial activity of the newly developed Ag-Cs/PVA hybrid NPs can be attributed to the small size and the high surface area of the NPs which allow them to reach easily the nuclear content of bacteria [8, 23, 24]. Also, it has been reported that the pathogenic effect of the NPs may be related to their stability in the medium as colloids, which modulates the phosphotyrosine pattern of the pathogen proteins and consequently arrests their growth [25]. Although the developed Ag-Cs/PVA NPs showed promising antibacterial activity against *P. aeruginosa*, *klebsiella*, *E. coli*, and *S. epidermidus,* further investigation are still required to study their antimicrobial effects on different types of microorganisms for potential widening of their applications.

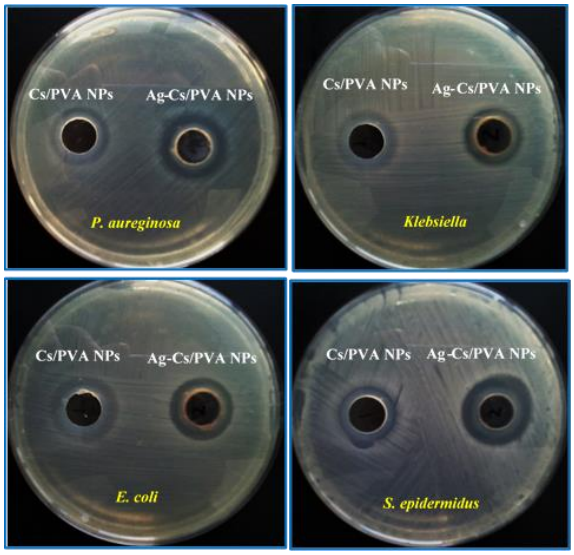

Fig. 4 Antibacterial activity of the developed Cs/PVA NPs and Ag-Cs/PVA hybrid NPs

4. Conclusion

The current study describes a successful eco-friendly synthesis of Ag-Cs/PVA hybrid NPs through electrochemical oxidation/complexation followed by UV irradiation reduction. The Cs/PVA semi-IPN NPs were used as a support during the synthesis and they found to be spherical with average size of 150 nm and the AgNPs were formed particularly on their surface in addition to a portion formed in the suspension with diameters ranging from 3 - 8 nm. The newly developed Ag-Cs/PVA hybrid NPs showed promising antibacterial activity against *P. aeruginosa*, *klebsiella*, *E. coli* and *S. epidermidus,* and could be tailored to act as good candidates for many biomedical applications.

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