Green synthesis of (CS/OLE) AgNPs and evaluation of their physico-chemical characteristic

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Abstract
The present article involves the bio-synthesis of (Chitosan/olive leaf extract) silver nanoparticles (CS/OLE) AgNPs using a simple green electrochemical procedure followed by UV-irradiation time. The properties and structure of the resulting (CS/OLE) AgNPs were characterized by employing several analytical techniques including, Infrared spectrum (FT-IR), UV–VIS spectroscopy, X-ray analysis (XRD), energy-dispersive X-ray (EDX) and degradation. Besides, the studying of the thermal characteristics of the (CS/OLE) AgNPs electrets were also investigated. Formation of Ag nanoparticles was observed upon varying the solution color from faint yellow into yellowish brown and was achieved by the appearance of absorption peak at about ~ 410 nm of the resulting AgNPs corresponding to the surface plasmon resonance (SPR). The sharp peaks appear at 32.16°, 46.19°, 54.75°, 57.59°, and 76.7°, indicating the presence of AgNPs as shown from XRD. With comparing the anti-bacterial efficiency of (CS/OLE) AgNPs and (CS/OLE) we found that the AgNPs display a relatively high anti-bacterial activity than in plant extract and chitosan alone. The electrical properties of (CS/OLE) AgNPs films were studied by global thermally stimulated depolarization current (TSDC) spectra for explaining the relaxation phenomena of the samples. In addition, the molecular parameters (The activation energy $E_a$ and pre-exponential time $\tau_0$), have been evaluated by the Arrhenius equation. The $E_a$ was found in ~ (0.39–0.62 eV) for (CS/OLE).

Keywords Anti-bacterial activity · (CS/OLE) AgNPs · Energy-dispersive X-ray (EDX) · Relaxation time · Thermal characteristics

Introduction
Recently, nanoscience and nanotechnology are exciting research fields for various reasons. The branch of nanotechnology has a dimension below 100 nm, which leads to the significance of the physicochemical at this scale compared to the large scale (El-Sherbiny et al. 2013). The matrix must be biodegradable, biocompatible, and nontoxic to be used in biomedical applications. Traditional industries usually consist of toxic and polluted ingredients, resulting in the pollution to the environment (Zhang et al. 2020; Liao et al. 2021). To solve this challenge, nanoparticles are employed to develop green slurries used in industries and manufacturing (Zhang et al. 2018; Zhang et al. 2019). In addition, nanoparticles are also applied to fabricate high performance surfaces by nanoscience and nanotechnology for the use in semiconductor, optoelectronics and aerospace industries (Zhang et al. 2015). This is extremely difficult to be performed by traditional industries and manufacturing (Zhang et al. 2017). The most important is that these developed green slurries, methods and nanotechnology are a great contribution to the conventional manufacturing and industries, dramatically reducing the pollution to the environment (Wang et al. 2018). Chitin, the second most common organic component following cellulose, is used to make Chitosan (CS) (Billmeyer 1984; Zhang et al. 2010). Chitosan fulfills all biomedical standards and can be considered a great matrix. Because of its exclusion characteristics, superior capacity to create films, biological, biocompatibility, environmental friendliness, lipophilicity, antibacterial properties, bio-functionality, and a strong affinity for proteins are all characteristics that should be considered CS has attracted attention. (Billmeyer 1984; Zhang et al. 2010; Alkire et al. 2012; Fahmy and Sarhan 2021). The
both amino and hydroxyl groups have reactivity that can improve CS, changing their characteristics to accommodate unique application (Saba et al. 2010). Owing to these distinctive characteristics, CS has found numerous applications in both biomedical and industrial sectors. Recently, CS has been used in gene therapy (Huang and Liu 2013; Acosta et al. 2015), drug delivery (Chen et al. 2014; Gupta et al. 2018), and wound healing (Fan et al. 2016; Ali et al. 2018; Hu et al. 2018). The recent study has concentrated on the analysis and improvement of nanoparticles (silver Ag, gold Au, platinum Pt, and lead Pd) due to its another features and prospective utilises in a variety of fields, including electrical, magnetic, catalytic, optical, and sensing technologies to bulk metals (He et al. 2003). Elemental silver Ag is a ductile and malleable transition metal with a white metallic luminosity appearance. The (Ag) metal has the highest thermal, electrical conductivity and has the lowest connect resistance. Alongside, (Ag) has a broad optical reflection compared to the other metals (Kaur et al. 2013). Silver nanoparticles have many applications in various fields, from therapeutics, antimicrobial to diagnostics and electronic (Mittal et al. 2012). Silver nanoparticles are a universal antibacterial material with excellent antibacterial activity at low concentration levels (Omran and Taghavinia 2012). The Ag NPs have biological and chemical characteristics that allow appealing consumer manufacture, medical industries, and food technology. In addition, Ag NPs have individual optical and physical factors that do not exist in bulk Ag, which leads to the vast potential for medical applications (Heer 1993). Several strategies are used to produce the Ag NPs by the chemical and physical techniques, such as photochemical reduction (Wang et al. 2009), lithography (Murphy et al. 2015), and laser ablation (Lukman et al. 2011). Still, because of the expensive and the toxicity of the chemicals, it not used commonly. Consequently, it is essential to utilize a biosynthesis technique that included microorganisms, such as fungi, yeast, and bacteria. Interestingly, the preparation of Ag NPs by plant extract has a significant advantage in protecting the environment. The uses of the biosynthesis method have various benefits, such as simple, reliable, low cost, eco-friendly, and enhance nanostructured materials (El-Sherbiny et al. 2013). Olive leaves (OLE) have a robust antioxidant characteristic. In addition, OLE included both reduction and stabilising agents in the Ag NPs equipment process. Olive tree leaves consider agricultural waste, which contains flavonoids and a large amount of phenolic acid, the most prevalent of which is oleuropein (Goldsmith et al. 2014). Olive leaves benefit from the treatment of conditions caused by a virus, bacterium, and protozoan, because it has antimicrobial activity, antioxidant properties, anti-HIV properties, vasodilation effect, hypoglycemic effect and anticancer properties (Leonardis et al. 2008; Fares et al. 2011; Goldsmith et al. 2015). Antibacterial activity appears to be mediated by phenolic structures comparable to oleuropein destroying bacterial membranes and breaking cell peptidoglycans.

The easy synthesis methodology (the electrochemical method) described in the gift study isn’t just a cheap and quick way to make (CS/OLE) AgNPs. However, because all of the structure materials in the project are regenerative and environmentally friendly, it may be used for a variety of biological applications and provides a wide range of bioactivity and environmental benefits.

In our previous work (Reicha et al. 2012; Ahmed et al. 2019), we explained (CS/OLE) AgNPs using the electrochemical method. The goal of this study is devoted to investigate the bio-synthesis of relatively stable and highly dispersed (CS/OLE) AgNPs utilizing a simple electrochemical technique followed by the exposed to UV-light irradiation for different irradiation time. In addition, study the change of antibacterial effect against gram positive (Staphylococcus aureus) and gram negative (Escherichia coli) bacteria of the improve (CS/OLE) AgNPs as compared to CS, OLE, and CS/OLE alone. Structural and optical of the resulting (CS/OLE) AgNPs were described by FTIR spectroscopy, UV–vis spectrophotometry, EDX, and XRD. In addition, the impact of Ag nanoparticles on the bandgap energy are investigated. Moreover, the TSDC spectrum have been investigated to demonstrate the impact of the relaxation behavior for (CS/OLE) and (CS/OLE) AgNPs samples and then the activation energy and relaxation time have been evaluated.

Experimental techniques

Materials

Oxford lab provided commercial chitosan (CS) powder with a degree of deacetylation (DD) of 93 percent (Thani, India). EL-Naser Pharmaceutical Co., Egypt, provided Tween 80, ethanol, glycerol, and acetic acid. The olive leaves (OLE) were taken from a campus in Mansoura, Egypt. OLE was obtained from a local market in Mansoura, Egypt. Sigma-Aldrich (St Louis, USA), provided a 99.99 percent pure silver plate with (20×40×5) mm. The cathode was a platinum (Pt) sheet (20×40×2) mm acquired from the Sigma. De-ionized water was also utilised to prepare the samples.

Method and preparation

Olive leaf extract preparation

Fresh olive leaf portions were collected and rinsed repeatedly with tap water, distilled water, and de-ionized water before being sliced into fine pieces. The dried olive leaves powder was then weighted and mixed with 80 percent
ethanol for 2 h at 60 °C utilizing mixer grinder with about 200 g piece of thoroughly washed, finely ground of finely olive leaves were weighted and mixed with Ultrasonic bath for 10 min. To form crude, the extract was passed over filter paper (Waterman, No.1), and then nightly dried in electric oven at 323 K. Finally, this crude was maintained at ~ 4 °C even another investigation.

**Chitosan (CS) and olive leaf extract (OLE) film preparation**

The solution of CS was made by dissolving 1 wt% chitosan in 1 percent acetic acid and shaking it overnight to ensure complete dissolution. To eliminate any bubbles, the resulting viscous solution was stored overnight. The Tween 80 and (glycerol/CS = 0.5 w/w) were then mixed, and agitated for 1/2 h. The olive leaves extracts were then inserted to CS solution (10 g/L), stirred to overnight and any insoluble particles were removed using a centrifuge (1500rps) (Model: PLC-012E). The solution was poured into the glass -petri dishes and baked for 24 h at 50 degrees Celsius.

**(CS/OLE) AgNPs preparation**

The electrochemical oxidation/complexation approach was used to make AgNPs for 2 h at a constant voltage of 1.5 V. Two electrodes (Ag as anode and Pt as cathode) were immersed in electrolytic solution (CS/OLE) and reduced through UV- irradiation (max wavelength = 254 nm at ~ 303 K for varying irradiation times) (Ahmed et al. 2019).

**Instrumentation**

At room temperature, the experiment was conducted with quartz cuvettes with (one cm optical path), a blank of (100 ml) water, and (1 ml) acetic acid. FT-IR measurements for the samples were carried out and analyzed on Mattson (5000) FT-IR spectrometer into range from 400–4000 cm⁻¹ at the resolution of 8 cm⁻¹ at 303 K. All samples were placed in the spectrometer's sample holder. Using a Philips PW 1390 X-ray diffractometer, the XRD patterns of the CS, (CS/OLE), and (CS/OLE) Ag NPs films were obtained. The X-ray diffraction produces a monochromatic beam with CuK radiation at a temperature of = (1.5406) A°. The applied potential is 40 kV and with current intensity ~ 40 mA per second. X-ray runs were carried out at scanning rates of 2θ = 2° /min, with the 20 scanned between (4 and 70)°. The microstructure of the (CS/OLE) AgNPs was also investigated by an energy-dispersive X-ray (EDX) unit.

**Antibacterial assay of (CS/OLE) AgNPs**

Antibacterial activity of aqueous OLE plants extracts and synthesized (CS/OLE) AgNPs were evaluated by the agar well diffusion method against two harmful pathogens; Gram-negative Escherichia coli and Gram-positive Staphylococcus aureus. Bacterial strains were cultured on a nutrient broth medium for 24 h at 37 °C. One hundred microliters of bacterial cultures (10⁶ CFU/ml) were inoculated in Mueller–Hinton agar plate. Then, the wells were made using a sterile cork-borer. About one hundred microliters of CS/OLE, (CS/OLE) AgNPs, pure CS, and control (OLE) were pipetted into each well. The plates were incubated for 24 h at 37 °C. The diameter of the inhibitory zone was measured after incubation.

**TSDC system**

TSDC spectrum was examined by utilizing a (home-made) cell at a range of temperature around K (300–400). The parallel plate electrodes were employed, mostly with upper plate being spring-loaded to maintain the electrical link intact even during temperature cycling. The polarisation of samples was carried by a fixed electric field (E_p) by obtain a global of (TSDC) spectra, the polarising temperature (T_p) was reduced to the freezing temperature and subsequently refrigerated to frozen in dipolar orientation. Once the sample short-circuited, the depolarization current produced from segmental orientation was then listed as the temperature increase. The current was gauged with (a Keithley electrometer 610C) at fixed β=(3 K/min), and temperature was calculated by a temperature controller unit (Digi-sence, 2186-25A, Cole-Parmer system Co, USA), the final temperature producing in TSDC spectra.

**Results and discussion**

**X-ray diffraction (XRD)**

XRD analysis was utilized to examine the crystalline structure of the green synthesized (Ag NPs) with biosynthesized (CS/OLE) extract. As demonstrated in Fig. 1, the diffraction of pure olive leave extract commutated an amorphous nature with broadband at 2θ = 21°. Chitosan, on the other hand, displays four weak peaks with degrees of crystallinity of 26.21% at 2(°) values of (8.08, 11.47, 18.17, and 22.53)°, this value increases to 30.99% for (CS/OLE) extract. The increase in the degree of crystallinity (X_c% = 46.96%) of improved (CS/OLE) AgNPs due to the appearance of Ag NPs by using the electrochemical method (Acosta et al. 2015). Comparatively, the diffractograms of CS/OLE and the CS indicate that variant
bands for chitosan was disappeared in (CS/OLE). The diffractograms of the enhanced Ag NPs appeared a reflectivity at the value of 2θ appear at 27.77°, 32.16°, 46.19°, 54.75°, 57.59°, and 76.7°, which attribute the existence of silver nanoparticles (Loo et al. 2012). These peaks may also contribute to the crystallographic planes (111), (200), (220), (311), (222), and (311). Utilizing Scherrer equation ($D = \frac{n\lambda}{\beta \cos \theta}$), where $D$, is the crystallite size, $n$ is constant = 0.9 assuming spherical particles, $\lambda$ is the X-ray wavelength, $\beta$ is the line width after compensation for experimental broadening, and $\theta$ is a diffraction angle (Bombicz 2019), silver nanoparticles have an average crystal size of 36.8 nm. The Williamson-Hall plot (Ismail et al. 2014) was used to calculate the ($\varepsilon$), and average grain size ($t$) of Ag NPs, as shown in Fig. 2 (Mote et al. 2012):

$$\beta \cos \theta = \frac{c\lambda}{t} + 4\varepsilon \sin \theta$$

where $c$ is the shape factor (0.9), it was observed that the ($\varepsilon$) = $10.4 \times 10^{-3}$, and average grain size (46.3 nm). As shown in the (Table 1), lattice strain at each peak position has been calculated from the equation:

$$Latticestrain = \frac{\beta \cos \theta}{4\varepsilon \sin \theta}$$

As noticed from Table 2, the degree of crystallinity, interplanar spacing ($d$), and interchain separation ($R$) for all samples have been calculated. In addition, the crystallinity of the (CS/OLE) AgNPs was improved by enhancing the time of electrochemical; this was achieved by utilizing the Material Studio Vision software 7.

Table 1 Lattice strain and crystal size of (CS/OLE) AgNPs at each peak position

| Peak position ($2\theta$) | Lattice strain ($\varepsilon$) | Crystal size ($D$) of AgNPs (nm) |
|--------------------------|-----------------------------|---------------------------------|
| 27.7751                  | 0.0038                      | 35.95                           |
| 32.1688                  | 0.0067                      | 38.72                           |
| 46.1903                  | 0.0084                      | 21.53                           |
| 54.7526                  | 0.0085                      | 18.09                           |
| 57.59                    | 0.0015                      | 95.22                           |
| 76.7428                  | 0.0144                      | 7.63                            |

Table 2 Values of peak position ($2\theta$), degree of crystallinity $X_c\%$, interplanar spacing ($d$), and interchain separation ($R$)

| Sample       | $2\theta$ (°) | Degree of crystallinity ($X_c\%$) | $d$ (nm) | $R$ (nm) |
|--------------|---------------|----------------------------------|---------|---------|
| CS           | 22.41         | 26.21                            | 20.20   | 25.26   |
| OLE          | –             | –                                | –       | –       |
| CS/OLE       | 22.32         | 30.99                            | 20.29   | 25.36   |
| (CS/OLE) AgNPs | 21.67       | 46.96                            | 20.86   | 26.61   |

EDX

The production of the (CS/OLE) AgNPs was also achieved by using EDX, as demonstrated in Fig. 3 and Table 3. It was seen that significant evidence from the appearance of Ag content approach to 0.56% in the EDX spectra of the (CS/OLE) AgNPs occurred after 2 h of electrochemical process. This amount of silver nanoparticles could be causes suitable antibacterial activity.
FTIR analysis

FT-IR analysis was utilized to identify and describe the functional groups, between the CS molecules and (Ag⁺) ions during the electrochemical technique, as well as reduce and stabilize biomolecules, for the characterization of the olive leave extract and the resulting nanoparticles to examine the impact that occurs as a result of UV irradiation. Figure 4 shows the FTIR spectra of (CS/OLE) AgNPs before irradiation, as well as (CS/OLE) AgNPs after (1, 2, 3, and 4) h of radiation. As shown from Fig. 4, there is an increase in all peak absorption after first-hour radiation and hydrogen bond at peak at 3440 shifted to 3446 cm⁻¹ (Ismail et al. 2014) which is attributed to the (hydroxyl group, O–H) and (amine group, NH₂), the modest widening and peak at 860 cm⁻¹ suggested that the metal and polymer were interacting well. All of these suggested that UV irradiating samples improves the interaction between CS/OLE and silver nanoparticles. After the second hour, FTIR show that there is a reduced in strength of the peaks appears at ~3446, 2923, 1414, and 1550 cm⁻¹ so, this means the sample starts degradation at the second hour. After the third hour, there’s an increase in the intensity of 2923 and 2854 cm⁻¹, which refer to the symmetric and asymmetric C-H, a slight decrease in intensity of peak appear at 1640 cm⁻¹ refer to carbonyl group C=O and in silver nanoparticle (this may happen due to degradation of the sample). The peaks at ~ (1550, 1414, 1252 and 1034) cm⁻¹ refers to the N–H bending (amide‖), aromatic ring, C–O–H and C–O stretching (Ahmed et al. 2019). After the fourth hour, there is an increase in the intensity of 2923, 2854, 1640 and 1550 cm⁻¹; this significant change may occur due to the formation of the new structure.
UV spectra

UV–vis spectra is one of the most important tools has been utilized to detect the electronic transitions between orbitals/bands of atoms and molecules presence in polymeric materials. In addition, the UV–Vis spectra were used to confirm the synthesis and formation of the Ag NPs of the reaction media at electrochemical time and various times of UV light-irradiation reduction, as demonstrated in Fig. 5. Production of the prepared Ag nanoparticles was observed upon varying the solution color from faint yellow into brown and was achieved by the absorption peak appeared at about ~410 nm of the resulting Ag NPs corresponding to the surface plasmon resonance (SPR). The impact of UV-irradiation upon the prepared (CS/OLE) AgNPs, also were investigated, as shown in Fig. 5. The spectra demonstrate absorption peak in the visible region attributed to the SPR. By increasing the UV-irradiation reduction time, more Ag NPs were formed and the OLE extract acts as a good stabilizing agent for the developed Ag NPs. In addition, there was an increase in all peak absorption after the first-hour radiation; this means interaction between components was enhanced. After the second hour, UV shows a decrease in peaks at (250, 280, and 340) nm and this is a significant change that may be carried out due to degradation. The Ag NPs formation was also proved by the color alter of the plant extract and the occurrence of surface resonance (SPR) at ~410 nm with an increase in peak intensity in most cases in the UV–Vis spectra. All bands invariability increased in their intensity with a prominent peak around (250, 280, 340, and 410) nm with a blue relativity shift by increasing the UV irradiation time at ~470 nm. The variation of color and intensity could occur with increasing time of radiation due to the alteration in the obtaining Ag NPs (Usha Rani and Rajasekharreddy 2011).

The optical bandgap energy can be obtained by an equation, which is based on the onset of UV – vis (Ahmed et al. 2019), which calculated, as shown in Table 4:

\[ E(\text{ev}) = h\frac{c}{\lambda_{\text{edge}}} = \frac{1240}{\lambda_{\text{edge}}(\text{nm})} \]

where \( (E) \), energy = bandgap, \( (h) \), Planks constant = $6.626 \times 10^{-34}$ J.s, \( (c) \), speed of light = $2.99 \times 10^8$ m/s and \( (\lambda) \), wavelength = absorption peak value. The optical energy gap have been evaluated from the maximum UV vis spectroscopy and it is found that, \( E \) varies from 3.59608 for (Cs/OLE) AgNPs to 3.49148 eV for (Cs/OLE) AgNPs after 4 h irradiation, this decrease result from the formation of silver nanoparticles.

Antibacterial assay

The antimicrobial activity for various samples revealed that different solutions inhibited both gram positive and gram negative bacteria. Figure 6 and Table 5 show the results of the antibacterial properties. This result revealed that (CS/OLE) AgNPs have a relatively wide antibacterial efficiency via the two examined bacterial isolates in comparison with control OLE and pristine chitosan. This good result of antibacterial activities of small-sized Ag NPs may be compatible with their large surface area (Lok et al. 2007; Kaur et al. 2013) which provides more surface contact with the cell wall of bacteria. Bacterial growth inhibition may be linked to interactions with lipophilic bacterial membrane components, which may result in alterations in H\(^+\) and K\(^+\) permeability, ultimately causing damage to essential functions and cell death. Furthermore, there is a synergistic effect between Ag particles and natural compounds in olive leaves extract. Furthermore, the antibacterial efficacy against \( (S. \text{aureus}) \) in the solution incorporating (10 g/L) OLE was substantially larger than in the solution incorporating chitosan or extract alone, implying a synergistic action. (CS/OLE) AgNPs can inhibit
growth more significantly than chitosan and olive leaves extract. Antibacterial chemicals are thought to be more active against Gram-positive bacteria than Gram-negative bacteria (Cao et al. 2010; Kaur et al. 2013; Aldosary and Abd El-Rahman 2019).

The degradation of samples

The elution procedure was used to degrade or release a component from the CS-olive leaf and silver nanoparticle in aqueous medium with varying PH values (7 and 10) while continuously stirring at 30 °C. In an acidic media, there is no release; however, there is a release at PH values of 7 and 10. Figures 7 and 8 show that the component released the most during the first two days, and that after those two days, there is a modest shift in the strength of peaks and a rise in absorbance with an increase in PH aqueous solution.

Table 5 Antibacterial activity given as the diameter of the inhibitory zone (mm)

| Samples       | E. coli | S. Aurous |
|---------------|---------|-----------|
| (CS)          | –       | 2         |
| (OLE)         | –       | 1         |
| (CS/OLE)      | 10      | 8         |
| (CS/OLE) Ag NPs | 15      | 12        |

Thermal stimulated depolarized current (TSDC) technique

The well-known thermal poling technique have been applied during electrets formation of CS/OLE and (CS/OLE) AgNPs samples have been interpreted by TSDC techniques. All samples were studied under the influence of the experimental parameter, such as poling field \( E_p \) and poling temperature \( T_p \).

TSDC of chitosan and olive leaves extract (CS/OLE)

Impact of polarizing \( E_p \) electric field

Figure 9 shows the TSDC spectra of (CS/OLE) films at a constant polarising temperature 373 K, polarising period 15 min, and varied polarising fields (1, 3, 5, 7, and 10) \( 10^5 \) V/m. A single broad peak described all spectra with the exact position of maximum temperature, this peak assigned to the \( \alpha \)-relaxation (Sarhan 2018). Furthermore, the current strength rises as the polarising electric field rises, which could be related to an increase in dipole–dipole interaction. To examine the origin of this peak, the max. current \( I_m \) is calculated as a function of the \( E_p \). It was observed that the \( I_m \) of every peak is increased linearly with \( E_p \), as seen in the inset of Fig. 9. The activation energy can be obtained from the correlation between \( \ln I \) and 1000/T from the Arrhenius equation, \( I=I_o \exp \left( \frac{E_o}{KT} \right) \), whereby \( T \) is the absolute temperature and \( E_o \) is the activation energy, as represented in Fig. 10. Its values are illustrated in Table 6. Because of significant intramolecular coupling or contact, the co-operative
behaviour of molecular motion in ($T_g$) glass-transition temperature results in a high activation energy value.

**Impact of polarizing ($T_p$)**

The TSDC spectrum of CS/OLE were investigated for varied polarising temperatures (323, 346, 373, and 428) K, with a constant polarising time of 15 min, a constant polarising field of $1\times10^6$ V/m, and a constant polarising duration of 15 min. Figure 11 displays the TSDC of CS/OLE samples, it was noticed that the peak position of $\alpha$-relaxation was appreciably influenced by the variation of poling ($T_p$). Furthermore, increasing the polarisation temperature causes the ($I_{\text{max}}$), and ($T_{\text{max}}$) increases and the peak position also shift to a higher temperature, implying that heating causes a structural change that may change the degree of crystallinity and ($T_{\text{max}} > T_p$), related to a space charge contribution. In Fig. 12 and Table 7, the activation energy values are represented.
TSDC of (CS/OLE) AgNPs

Impact of polarizing electric Field

TSDC spectra are quite useful for determining the nature of a polymer’s transition. At a constant polarising temperature of 373 K, polarising period of 15 min, and varied polarising fields (3, 7, and 10) of $10^5$ V/m, TSDC spectra of (CS/OLE) Ag NPs were examined. The presence of two distinct relaxation peaks may be seen in Fig. 13. The dipolar relaxation attendant with the orientation of the polar side group was attributed to a first peak ~ 320 K (at lower Temp.), and more intense second peak at 390 K (at higher Temp.) was defined as relaxation (Heer 1993). Hence, this dipolar peak round $T_g$ is assumed to a dipole– depolarization. β- relaxation is always expected to be weaker than the α relaxation. Furthermore, the ($I_{max}$) of both α and β peaks was increased by increasing Ag content. In addition, the intensity of current increases by increasing the polarizing field, this may occur due to the rise in dipole–dipole interaction. The activation energy of the samples can be determined, as shown in Table 8. Because of significant intramolecular coupling or contact, the cooperative nature of molecular -motion in glass-transition temperature results in a high activation energy value.

**Table 6** CS/OLE molecular properties at various electric fields

| $E_p \times 10^5$ (V/m) | $T_{max}$ (K) | $I_{m}$ (10^{-11}Amper) | $E_a$ (eV) | Relaxation time $\tau$ |
|------------------------|--------------|-------------------------|-----------|-------------------------|
| 1                      | 377          | 4.7                     | 0.58      | $7.446 \times 10^{-6}$  |
| 3                      | 377          | 5.35                    | 0.47      | $2.715 \times 10^{-5}$  |
| 5                      | 377          | 5.75                    | 0.44      | $7.302 \times 10^{-5}$  |
| 7                      | 377          | 6.6                     | 0.39      | $3.83 \times 10^{-4}$   |
| 10                     | 377          | 7.25                    | 0.62      | $2.033 \times 10^{-3}$  |

**Table 7** Values of activation energy $E_a$ and Relaxation time $\tau$ of CS/OLE at various polarizing temperatures

| $T_p$ (K) | $T_{max}$ (K) | $I_{m}$ (10^{-11}Amper) | $E_a$ (eV) | Relaxation time $\tau$ |
|-----------|---------------|-------------------------|-----------|-------------------------|
| 323       | 343           | 5.1                     | 0.464     | $6.65 \times 10^{-5}$   |
| 348       | 355           | 5.7                     | 0.445     | $2.3 \times 10^{-4}$    |
| 373       | 369           | 6.5                     | 0.334     | $1.9 \times 10^{-3}$    |
| 423       | 383           | 8.7                     | 0.258     | $3.8 \times 10^{-2}$    |

**TSDC of (CS/OLE) AgNPs**

Fig. 10 Relationship between Ln(I) and 1000/T(K), of CS/OLE at different $E_p$ with fixed $T_p = 373$ K and $t_p = 15$ min

Fig. 11 TSDC spectra of CS/OLE at various poling temperatures at (323, 348, 373, and 423) K with constant $E_p=1 \times 10^6$ V/m and $t_p=15$ min, $\beta = 4$K/min, carbon as electrode

Fig. 12 TSDC of (CS/OLE) depict the relationship between Ln(I) and 1000/T(K) with various $T_p$, $t_p=15$ min, and $E_p=1 \times 10^6$ V/m

Fig. 13 TSDC spectra of (CS/OLE) Ag NPs were examined.
Impact of polarizing temperature

Figure 14 shows the TSDC- spectra of (CS/OLE) Ag NPs for different polarising temperatures 323, 373, and 428 K, with a constant polarising field of $1 \times 10^6$ V/m, and a constant polarising time of 15 min. When the polarisation temperature ($T_p$) and ($T_{\text{max}}$) all rise and shifted to a higher place, it means that heating causes a structural variation and a shift in degree of crystallinity. Increasing the boiling temperature found that two peaks became one, and this may be ascribed to the motion of the main chain segment and trapping of the charge carrier in surface traps. The shift in behaviour is caused by changes in space-charge behaviour or the production of an interface between the polymer, and Ag NPs (Wang et al. 2009; Ahmed et al. 2017; Sarhan and Fahmy 2021). It can be observed that the peak position of relaxation depends basically on the $T_p$. Hence, one can notice that these peaks shift to a higher temperature as $T_p$ increases. The values of activation energy and relaxation time have been represented in Table 9.

Conclusions

The present study was carried out to synthesize the (CS/OLE) AgNPs, utilized the eco-friendly rapid green synthesis followed by the UV-irradiation reduction. The developed Ag NPs showed good stability and also, the antibacterial efficiency of the improved CS/OLE and (CS/OLE) AgNPs was investigated. The characteristic of the improved Ag NPs was examined by various techniques, such as UV/Vis, FTIR, EDX and XRD. UV Spectroscopy shows an increase and shift of the peak at $\sim$410 to 470 nm, following UV irradiation, the development of a massive cluster of AgNPs was observed. In addition, the optical energy varies from 3.59608 for (CS/OLE) AgNPs to 3.49148 eV for (CS/OLE) AgNPs after 4 h irradiation, this decrease result from the formation of silver nanoparticles. Furthermore, the relaxation phenomena of CS/
OLE and (CS/OLE) AgNPs samples have been investigated using TSDC technique, and the molecular parameters have been evaluated. TSDC of CS/OLE with varying $E_a$ represents a single peak at ~375 K; this peak refers to the alpha relaxation associated with the glass transition temperature $T_g$. The current increase in a linear relationship with the polling field. The $E_a$ was discovered in the 0.39–0.62 eV range. In addition, TSDC -spectra of (CS/OLE) Ag NPs with changing $E_a$ appear two major peaks, the first at 319 K attributed to dipolar relaxation- associated to polar side- group orientation and the second at 392 K attributed to relaxation. For the first peak, $E_a$ was determined to in the range ~ (0.3–0.47) eV, while second peak was in the range of (0.12–0.19) eV.

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**Data availability** The data sets generated and analyzed during the current study are included in this article and available from the corresponding author and other authors on a reasonable request.

**Declarations**

**Conflict of interest** The authors declare that they have no conflicts of interest.

**Human and animal rights** This article does not contain any studies involving animals performed by any of the authors.

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