Synthesis and characterization of silver-aqueous polymer (Cts/Dx) nanocomposite

K M Prabu1*, G Venkatesh2, R Amaravel2, P Agalya1, G Kalayan1, S Kanimozi1 and S. Suresh1
1PG & Research Department of Physics, Sri Vidya Mandir Arts & Science College, Katteri, Uthangarai – 636 902, Tamil Nadu, India
2PG & Research Department of Physics, AVS College of Arts and Science, Salem – 636 106, Tamil Nadu, India
*E-mail: svmprabu@gmail.com

Abstract: Silver nanoparticles (Ag NPs) are prepared with an aid of a facile chemical route. The prepared Ag NPs are stabilized by making nanocomposite with aqueous polymer in view of its practical application. In the present study, polymers, such as chitosan and dextran (Cts/Dx) are used for making composite owing to their immense applications in pharmaceutical, chemical, food and drug industries as emulsifier, carrier and stabilizer. The synthesized silver-Cts/Dx copolymer nanocomposites (Ag-Cts/Dx) are characterized by UV-visible spectrophotometer, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), atomic force microscopy (AFM), dynamic light scattering and Zeta potential analyzer. The results are in good agreement with the calculated and experimental results of previous research works.

Keywords: Silver nanoparticles; Aqueous polymer; Stabilizer; Nanocomposite

1. Introduction

The formulation of metal nanoparticles incorporated polymer nanocomposites has been elicited immense research interest, owing to their peculiar antibacterial activity and photoelectrical properties and as a consequence, they find potential application prospects in the areas of biomedical photocatalysis and food packaging [1–5]. In such kind of nanocomposites the polymer principally acts as an excellent host material for embedding metal nanoparticles, nevertheless it hinders the nanoparticles growth by controlling nanoparticles nucleation [6]. Among the diverse metal nanoparticles (Ag, Au, Cu, Ti and Zn) with biocidal properties, the Ag NPs hold most peculiar bactericidal features against diverse microorganisms of pathogenic nature, such as bacteria, viruses, yeasts and fungi [7, 8]. The Ag NPs exhibited superior antimicrobial properties over metallic silver because of their high surface area that facilitates better interaction with microorganisms [9]. The Ag NPs can be introduced in different mediums, viz. stabilizing agents and polymers by different strategies [8]. In view of the prospective of such polymer nanocomposites towards biological applications [10], it is greatly astonishing that numerous research works emerged out pertaining to the metal nanoparticles incorporated biopolymer networks till date is meager. Certainly, this unusual incidence sturdily contrasts with profusion of previous literature data pertaining to biopolymer network preparation in pharmaceutical science [11].

Chitosan, a deacetylated chitin form is regarded as a natural polysaccharide that has been proposed potential substitute towards synthetic stabilizers. Chitosan contains linked units of glucosamine and N-acetyl glucosamine by β-1,4-glucosidic bonds. It exhibits distinctive chelating, polycationic and film forming capabilities owing to its linear polysaccharide with rich oxygen that holds active groups of amino and hydroxyl [12]. Hence, chitosan holds several attractive biological characteristics, viz. biodegradability, biocompatibility, non-antigenicity and adsorption. On the other hand, the natural polymer, dextran, a hydrophilic, colloidal, biocompatible and harmless polysaccharide is composed of linear α-1, 6-linked D-glucopyranose residues, including a low proportion of α-1,2, α-1,3 and α-1,4 linked side chains [13]. Moreover, its biodegradation can be accomplished by dextranase that is an integral part of mammalian tissue. It has hydroxyl groups that

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd
create hydrogels through photochemical crosslinking. Because of its natural resistant capability of cell adhesion and protein adsorption, its polymer backbone modification facilitates generation of a hydrogel with unique properties.

The present work involves synthesis of silver nanoparticles (Ag NPs) using polymers containing AgNO$_3$ as precursor. As far as we know the use of these biodegradable and natural polymers towards the synthesis of Ag NPs has not been reported elsewhere. In this work, a method towards the synthesis of Ag NPs by natural polymers is established. The structure and morphology of the prepared Ag NPs is analyzed by spectroscopic techniques.

2. Experimental
2.1. Materials and Methods
Silver nitrate (AgNO$_3$) and polymers (Cts and Dx) were procured from SD Fine Chemicals. All the chemicals received were used as they belong to analytical regent grade with high purity ($\geq$ 99%). The glassware’s used in the work were washed thoroughly with aqua regia solution (HCl and HNO$_3$ with 3:1 (v/v)) and rinsed comprehensively using double distilled water before use. Sample preparations and dilutions were performed using ultrapure water.

2.2. Preparation of Silver Nanoparticles
A mixed polymer solution was prepared by dissolving Cts/Dx (1 wt%) in ultrapure water. Silver nitrate was used for preparing AgNO$_3$ solution (10$^{-2}$ M) in ultrapure water. Then, diverse concentrations (0.01, 0.02, 0.03 and 0.04 wt%) of AgNO$_3$ solution (1.2 ml) in ultrapure water was mixed with Cts/Dx solution at 80 °C. The change of colour from clear colorless to yellowish-brown color solution indicated the formation of Ag NPs.

3. Characterization Studies
UV-Vis absorption spectrum of the Cts/Dx/Ag nanocomposites was recorded using UV-Vis spectrophotometer (Lambda 35, Perkin Elmer) between wavelength range of 200 and 800 nm. Fourier transform infrared spectrum was taken in Perkin Elmer FTIR spectrophotometer. XRD pattern of the samples was recorded using X’PERT PRO diffractometer. Morphological analysis was carried out in scanning electron microscopy (JSM-6510 V, Japan). Elemental features of Ag-polymer nanocomposites was examined by EDS integrated with SEM. AFM images were recorded in Atomic Force microscope (XE-100E). The Ag NPs average size and zeta potential were calculated by Zetasizer Nano ZS instrument (Malvern International Ltd.). The sample dilutions were performed in ultrapure water in the ratio of 0.1 : 25 (v/v).

4. Results and Discussion
4.1. UV-Vis Absorption Analysis
Silver nanoparticles (Ag NPs) synthesized through the method of chemical reduction in Cts/Dx solution with diverse concentrations of AgNO$_3$ were examined using UV–Vis spectrophotometer and the resultant spectra are presented in figure 1 a-e. The solution colour was altered from white to yellowish-brown during the reaction. The distinctive colors of colloidal silver appeared could be attributed to the surface plasmon resonance (SPR) absorption nature of Ag NPs. The absorbed light energy from the incident electromagnetic radiation generates oscillation in the electrons present in the conduction band of Ag NPs [14]. The resultant solution colour and maximum absorbance are ascribed to size of the formed Ag NPs. This observation was confirmed by UV–vis spectra. The absorption spectrum of Cts/Dx copolymer exhibited characteristic peaks at 252 nm due to $\pi$ $\rightarrow$ $\pi^*$ transition [15, 16]. Likewise, the shift in absorption bands appear in the UV–vis spectrum of Cts/Dx/Ag nanocomposites (Figure 1 b-e) produced by resilient interaction between Cts/Dx and Ag NPs. UV–vis absorption spectrum of synthesized Ag NPs disclosed an absorption peak between 420 and 470 nm by $\pi^*$ $\leftrightarrow$ $\pi$ transition [17], which is the characteristic SPR band of Ag NPs (Figure 1 b-e). A
A considerable difference in absorption intensity of Ag NPs was noticed while AgNO$_3$ concentration was differed between 0.01 wt% to 0.04 wt%. The Ag NPs absorption intensity increases upon increasing AgNO$_3$ concentration that revealed production of higher number of Ag NPs [18]. The shift in SPR absorption peak belongs to Ag NPs towards lower wavelength region and its narrowing nature while AgNO$_3$ concentration was increased from 0.01 wt% to 0.04 wt% in the nanocomposite exhibited that there was a reduction in size of the Ag NPs when the concentration of AgNO$_3$ was increased.

Figure 1. UV-vis absorption spectra of (a) Cts/Dx and Cts/Dx/Ag nanocomposites with different AgNO$_3$ concentrations ((b) 0.01 wt%, (c) 0.02 wt%, (d) 0.03 wt% and (e) 0.04 wt%).

4.2. XRD Studies
The XRD pattern of Cts/Dx and Cts/Dx/Ag nanocomposites are shown in Figure 2 a-e. The broad diffraction maximum observed at 21° in the XRD pattern of Cts/Dx co-polymer composite (Figure 2 (a)) is related to amorphous phase of Cts/Dx and the sharp diffraction lines situated at 17° and 29° correspond to the (0 2 1) reflection of Cts and Dx [19]. The other diffraction peaks noticed at 38°, 44°, 64° and 77° in the Cts/Dx/Ag nanocomposites correspond to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) diffraction planes of the face centered cubic lattice belongs to silver which are in good reliance with corresponding standard values that support reduction and growth of Ag NPs (JCPDS: 04-0784) [20]. Moreover, the sharp and intense diffraction peaks located at 38.04° correspond to the diffraction plane of (1 1 1) indicated a highly organized Ag NPs crystal structure. Average crystalline size of Ag NPs was found out by adopting the following standard formula prescribed by Debye-Scherer [21].

\[
\text{Average crystal size (D)} = \frac{0.9 \lambda}{\beta \cos \theta}
\]

Here, \(\lambda\) is X-ray wavelength (1.540 Å), \(\beta\) is angular peak width at half maximum along (1 1 1) plane peak of Ag NPs and \(\theta\) is Bragg’s diffraction angle. Ag NPs grain size range was measured as 14 nm. The reflecting peak at \(2\theta = 38.04°\) was taken for calculating average diameter of Ag NPs. The calculated lattice constant by d-spacing of (1 1 1) plane (Figure 2e) and equation \(1/dg^2 = (h^2 + k^2 + l^2)/a^2\) was 0.1783 nm, which is in good reliability with the standard value (0.1786 nm). Moreover, the
sharp and intense diffraction peak situated at 38.04° (1 1 1) disclosed highly organized Ag NPs crystal structure.

Figure 2. XRD patterns of (a) Cts/Dx and Cts/Dx/Ag nanocomposites with different AgNO₃ concentrations ((b) 0.01 wt%, (c) 0.02 wt%, (d) 0.03 wt% and (e) 0.04 wt%).

Table 1 shows micro-strain (ε) value of Cts/Dx/Ag nanocomposites measured at 80 °C. The calculated grain size was in the range of 15.6, 15.1, 14.8 and 14 nm depending on the reaction condition. The calculated lattice parameters were also in accordance with previous reports. The micro-strain (ε) value was found out by the formula given below [22].

\[
\text{Micro strain (ε)} = \frac{\beta \cos \theta}{4}
\]

The micro-strain was found out to be \(4.1224 \times 10^{-3}\) for Ag NPs. The intrinsic stress varied monotonically with respect to micro structure, shape and size of Ag NPs. The dislocation density (δ) value was calculated by the following formula.

\[
\text{Dislocation density (δ)} = \frac{1}{D^2}
\]

Specific surface area (SSA) is a derived scientific value by which type of material and its properties can be determined. Its importance is highly useful during adsorption and surface reaction studies.

\[
\text{Specific surface area (SSA)} = \frac{S_{A_{\text{Part}}}}{V_{\text{Part}} \times \text{Density}}
\]
Table 1. The 2θ value, d-space, cell parameters, average crystal size (D), micro-strain (ε), dislocation density (δ) and specific surface area (SSA) of Cts/Dx/Ag nanocomposites with different AgNO₃ concentrations.

| Sample       | 2θ value | d-space value | Cell parameter a=b=c | Average crystalline size (D) | Micro-strain (ε) x 10¹⁴ | Dislocation density (δ) x 10⁻⁴ | Specific surface area (SSA) |
|--------------|----------|---------------|-----------------------|-------------------------------|--------------------------|-------------------------------|-----------------------------|
| Cts/Dx/Ag (0.01 wt%) | 38.02    | 2.3674        | 4.0876                | 15.6                          | 3.9975                   | 41.09                         | 31.20                       |
| Cts/Dx/Ag (0.02 wt%) | 38.01    | 2.3673        | 4.0911                | 15.1                          | 4.0392                   | 43.85                         | 30.21                       |
| Cts/Dx/Ag (0.03 wt%) | 38.03    | 2.3674        | 4.0945                | 14.8                          | 4.0714                   | 45.65                         | 29.63                       |
| Cts/Dx/Ag (0.04 wt%) | 38.04    | 2.3678        | 4.0976                | 14.0                          | 4.1224                   | 50.87                         | 28.04                       |

4.3. FTIR Studies
The FTIR spectra of Cts/Dx copolymer and Cts/Dx/Ag nanocomposites with different AgNO₃ concentrations are depicted in figure 3. The Cts/Dx copolymer formation can be demonstrated by FTIR spectroscopy. The FTIR spectrum of Cts/Dx shows characteristic peaks at 1764 cm⁻¹ due to C=O symmetric stretching band of anhydride groups, 1752 cm⁻¹ by C=O symmetric stretching band of Cts, 1256 cm⁻¹ owing to C-O-C stretching band of Dx and 1101 cm⁻¹ by COCH₃ stretching band of Dx [23]. Here, the absence of AgNO₃ band at 1390 and 1450 cm⁻¹ was observed in the spectra of both polymer dispersions containing Ag particles that confirmed the transformation of AgNO₃ into Ag [24]. The reduction of Ag⁺ to Ag⁰ can be accomplished by interaction with surroundings polymer dispersions.

Figure 3. FTIR spectra of (a) Cts/Dx and Cts/Dx/Ag nanocomposites with different AgNO₃ concentrations (b) 0.01 wt%, (c) 0.02 wt%, (d) 0.03 wt% and (e) 0.04 wt%.

4.4. SEM Analysis
The SEM images of Cts/Dx/Ag nanocomposites with different AgNO₃ concentrations ((b) 0.01 wt%, (c) 0.02 wt%, (d) 0.03 wt% and (e) 0.04 wt%) are given in Figure 4. As expected, the surface of Cts/Dx co-polymer microspheres shown in figure 4a is smooth and clean. The Cts/Dx/Ag nanocomposites surface structure reveals aggregated nature that is continuously distributed in the morphology of Ag/Cts/Dx nanocomposites. Nevertheless, while increasing the AgNO₃ concentration, some discontinuation in the morphology could be noticed. This phenomenon shows that under 0.03 wt% of AgNO₃, Ag/Cts/Dx NCs with better compatibility were formed.

![SEM images of Cts/Dx and Cts/Dx/Ag nanocomposites at different AgNO₃ concentrations](image)

**Figure 4.** SEM images of (a) Cts/Dx and Cts/Dx/Ag nanocomposites at different AgNO₃ concentrations ((b) 0.01 wt%, (c) 0.02 wt%, (d) 0.03 wt% and (e) 0.04 wt%).

4.5. **AFM Analysis**

Figure 5 exhibit topographic images of Cts/Dx/Ag nanocomposites. Size of the co-polymer capped Ag NPs was around 67 nm, which are distributed over an area of 1 μm². The AFM examination disclosed that the prepared Cts/Dx/Ag nanocomposites have very smooth surface. This characterization technique enables towards the examination of nanoparticles in contact mode. The AFM has significant advantage of probing high details about the surface topography qualitatively owing to its both lateral...
and vertical spatial resolution at nanometer scale. AFM analysis has evidenced towards the determination and verification of diverse morphological structures.

![Surface topography of Cts/Dx/Ag nanocomposite (0.04 wt %).](image)

**Figure 5.** Surface topography of Cts/Dx/Ag nanocomposite (0.04 wt %).

5. Conclusion
A facile route was established to prepare Cts/Dx/Ag nanocomposites. The results obviously revealed that the Ag NPs were produced not only on the surface of Cts/Dx matrices but also throughout the polymer network. The present study suggested that a number of morphologies of Ag colloids can be formed by modifying the capping and reducing agents. The capping agents Cts and Dx played a crucial role towards the synthesis of Ag NPs and the reduction in water-soluble co-polymer gave particles with spherical shape. This disclosed that the reducing agent is essential towards the reduction of precursor salt since the polymer worked both as reducing and stabilizing agent. The work facilitates a future direction towards the preparation of other metallic nanoparticles.

References
[1] Barbucci R, Consumi M, Lamponi S and Leone G 2003 Polysaccharides based hydrogels for biological applications. *Macromol. Symp.* 204 pp 37–58
[2] Chun KY, Oh Y, Rho J, Ahn JH, Kim YJ, Choi HR and Baik S 2010 Highly conductive, printable and stretchable composite films of carbon nanotubes and silver. *Nat. Nanotechnol.* 5 853–857
[3] Lightcap I V, Kosel TH and Kamat P V 2010 Anchoring semiconductor and metal nanoparticles on a two-dimensional catalyst mat. Storing and shuttling electrons with reduced graphene oxide. Nano Lett. 10 577–583

[4] Abreu A S, Oliveira M, Sa A, Rodrigues R M, Cerqueira M A, Vicente A A and Machado A V 2015 Antimicrobial nanostructured starch based films for packaging Carbohydr. Polym. 129 pp 127–134

[5] Zang L, Qiu J, Yang C and Sakai E 2016 Preparation and application of conducting polymer/Ag/clay composite nanoparticles formed by in situ UV-induced dispersion polymerization. Sci. Rep. 6:20470 pp 1–12

[6] Li H J, Zhang A Q, Hu Y, Sui L, Qian D J and Chen M 2012 Large-scale synthesis and self-organization of silver nanoparticles with tween 80 as a reductant and stabilizer Nanoscale Res. Lett. 7:612 pp 1–13

[7] Rai M, Yadav A and Gade A 2009 Silver nanoparticles as a new generation of antimicrobials. Biotechnol. Adv. 27 pp 76–83

[8] Martinez-Abad A, Lagaron J M and Ocio M J 2012 Development and characterization of silver based antimicrobial ethylene-vinyl alcohol copolymer (EVOH) films for food-packaging applications. J. Agric. Food Chem. 60 pp 5350–5359

[9] Toker R D, Kayaman-Apohan N and Kahraman M V 2013 UV-curable nano-silver containing polyurethane based organic-inorganic hybrid coatings. Prog. Org. Coat. 76 pp 1243–1250

[10] Dornish M, Aarnold M and Skaugrud O 1996 Alginate and chitosan: Biodegradable biopolymers in drug delivery systems. Eur. J. Pharm. Sci. 4 S153.

[11] Peppas N A 2004 Devices based on intelligent biopolymers for oral protein delivery Inter. J. Pharm. 277 pp 11–17

[12] Wei D, Sun W, Qian W, Ye Y and Ma X 2009 The synthesis of chitosan-based silver nanoparticles and their antibacterial activity Carbohydr. Res. 344 pp 2375–2382

[13] Rizwan M, Yahya R, Hassan A, Yar M, Azzahari A D, Selvanathan V, Sonsudin F and Abouloula CN 2017 pH sensitive hydrogels in drug delivery: Brief history, properties, swelling, and release mechanism, material selection and applications Polymers 9 pp 1–37

[14] Solomon S D, Bahadory M, Jeyarajasingam A V, Rutkowski S A, Boritz C and Mulfinger L 2007 Synthesis and study of silver nanoparticles J. Chem. Edu. 84 pp 322–325

[15] Kulkarni M V and Viswanath A K 2004 Comparative studies of chemically synthesized polyaniline and poly (o-toluidine) doped with p-toluene sulphonic acid. Eur. Polym. J. 40 pp 379–384

[16] Kohut-Svelko N, Reynaud S and François J 2005 Synthesis and characterization of polyaniline prepared in the presence of nonionic surfactants in an aqueous dispersion. Synth. Met. 150 pp 107–114

[17] Gasaymeh S S, Radiman S, Heng L Y, Saion E and Saeed G H M 2010 Synthesis and characterization of silver/polyvinilpirrolidone (Ag/PVP) nanoparticles using gamma irradiation techniques Am. J. Appl. Sci. 7 pp 892–901

[18] Huang N M, Lim H N, Radiman S, Khiew P S, Chiu W S, Hashim R and Chia CH 2010 Sucrose ester micellar-mediated synthesis of Ag nanoparticles and the antibacterial properties Colloids Surf. A: Physicochem. Eng. Asp. 353 pp 69–76

[19] Zhang Z, Zhang L, Wang S, Chen W and Lei Y 2001 A convenient route to polyacrylonitrile/silver nanoparticle composite by simultaneous polymerization–reduction approach. Polymer 42 pp 8315–8318

[20] Ndeh N T, Maensiri S and Maensiri D 2017 The effect of green synthesized gold nanoparticles on rice germination and roots. Adv. Nat. Sci.: Nanosci. Nanotechnol. 8:035008 pp 1–10

[21] Kathirvel P, Manoharan D, Mohan S M and Kumar S 2009 Spectral investigations of chemical bath deposited zinc oxide thin films – ammonia gas sensor J. Optoelectron. Biomed. Mater 1 pp 25–33
[22] Hankare P P, Chate P A, Sathe DJ, Chavan P A and Bhuse V M 2009 Effect of thermal annealing on properties of zinc selenide thin films deposited by chemical bath deposition. *J. Mater. Sci. Mater. Electron.* 20 pp 374–379

[23] Yoon K J, Woo J H and Seo Y S 2003 Formaldehyde free cross-linking agents based on maleic anhydride copolymers *Fiber. Polym.* 4 pp 182–187

[24] Jeon HJ, Yi SC and Oh SG 2003 Preparation and antibacterial effects of Ag–SiO2 thin films by sol–gel method *Biomaterials* 24 pp 4921–4928