Carbohydrate Polymers 86 (2011) 1615–1622

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Utilization of hydroxypropyl cellulose for green and efficient synthesis of silver nanoparticles

E.S. Abdel-Halim[a,b,*], Salem S. Al-Deyab[a]

[a] Petrochemical Research Chair, Chemistry Department, College of Science, King Saud University, Riyadh 11451, P.O. Box 2455, Saudi Arabia
[b] Textile Research Division, National Research Center, Dokki, Cairo, Egypt

ARTICLE INFO

Article history:
Received 8 June 2011
Received in revised form 25 June 2011
Accepted 27 June 2011
Available online 5 July 2011

Keywords:
Hydroxypropyl cellulose
Propylene oxide
Etherification reaction
Silver nanoparticles

ABSTRACT

Hydroxypropyl cellulose samples having different molar substitution were prepared through alkalization of cellulose followed by etherification reaction with propylene oxide. Factors affecting hydroxypropyl cellulose preparation like alkali concentration, propylene oxide concentration as well as etherification reaction temperature and duration were extensively studied. The prepared hydroxypropyl cellulose samples were characterized by measuring their molar substitution and then were tried for their water solubility which showed that samples having molar substitution of 0.4 or higher are completely water soluble. The obtained hydroxypropyl cellulose samples were used in the preparation of silver nanoparticles through reduction of silver nitrate. UV–vis spectra of the prepared silver nanoparticles reveal that full reduction of silver ions to silver nanoparticles takes place at pH 12.5. Optimum conditions for conversion of silver ions to silver nanoparticles are to use 0.3% solution of hydroxypropyl cellulose having molar substitution of 0.42, carrying out the reaction at 90 °C for 90 min.

1. Introduction

In recent years the term metal nanoparticles has arisen and metal nanoparticles have attracted great attention due to their large surface area to volume ratio as well as their unique optical, electronic, and catalytic properties, which make them find applications in many different fields (Abdel-Halim, El-Rafie, & Al-Deyab, 2011; Babu, Kim, Kim, Ahn, & Lee, 2010; Hebeish, El-Rafie, Abdel-Mohdy, Abdel-Halim, & Emam, 2010; Vimala, Sivudu, Mohan, Sreedhar, & Raju, 2009). The use of organic polymers as templates is considered as one of the most powerful and effective methods used to synthesize metal nanoparticles (Božanić, Dimitrijević-Branković, Bibić, Luyt, & Djoković, 2011; Hang, Tae, & Park, 2010; Hebeish, El-Shafei, Sharaf, & Zaghloul, 2011; Konwarh, Karak, Sawian, Baruah, & Mandal, 2011; Kora, Sashidhar, & Arunachalam, 2010; Zhuang, Cheng, Kang, & Xu, 2010). In addition to producing stable and dispersed nanoparticles with controlled size, shape and distribution, this method also enables one to combine the desired properties of the template polymers together with the novel properties of the metal nanoparticles, which make the resulting composite suitable for different unique applications (Du, Niu, Xu, Xu, & Fan, 2009; Du, Xu, Wang, Yuan, & Hu, 2009; Li et al., 2009; Maneerung, Tokura, & Rujiravanit, 2008; Tomšič et al., 2009). Particularly, using natural polymers such as polysaccharides as templates for preparation of metal nanoparticles has attracted much interest; because composites composed of natural polymers and metal nanoparticle provide great potential for biomedical applications such as in biosensing, therapy and bioimaging. Recently, much effort is focused on the biomimetic self-assembly of natural polymers. The self-assembled natural polymer nanostructures may be good choices as templates, since it cannot only inherit the advantages of individual natural polymer as a template for the metal nanoparticles synthesis, but also guide and control the assembly of metal nanoparticles.

Metal nanoparticles are mainly utilized in many applications such as water purification, catalysis of chemical reactions and hydrogen storage. For example, a wide range of applications have been found for metal nanoparticles in catalysis (Biffis, Orlandi, & Corain, 2003; Daniel and Astrue, 2004), electronics (Kiesow, Morris, Radehaus, & Heilmann, 2003), sensors and high density information storage (Ross, 2001; Vaseashta and D-Malinovska, 2005), luminescence devices (Colvin, Schlamp, & Alivisatos, 1994), photonics (Xu, Zhang, Paquet, Lin, & Kumacheva, 2003), pharmaceuticals, biotechnology and medicine (Xu, Zeng, Lu, & Yu, 2006). Due to their high active surface area, metal nanoparticles generally tend to agglomerate to form larger particles. To prevent this agglomeration action and to stabilize and control the nanoparticles structures,

* Corresponding author at: National Research Center, Dokki, Cairo, Egypt. Tel.: +20 108113477.
E-mail address: essamya@yahoo.com (E.S. Abdel-Halim).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.06.072

various biological templates, dendrimers, synthetic polymers, natural polymers and surfactants have been used (Bajpai, Mohan, Bajpai, Tankhiwale, & Thomas, 2007; Chen, Serizawa, & Akashi, 1999; Chen and Hsieh, 2002; Esumi, Suzuki, Yamahira, & Torigoe, 2000; Esumi, Isono, & Yoshimura, 2004). Some biological systems have natural complicated mesoscopic and macroscopic structures with tremendous control over the placement of nanoscopic building blocks within extended architectures (Mandal, Phadtare, & Sastry, 2005). The concept of green synthesis of nanoparticles was first promoted by Raveendran, Fu, and Wallen (2003) in which glucose acted as reducing agent and starch played the role of particles stabilizer. Silver nanoparticles were prepared in another study by means of using the carbohydrate polymer, sodium carboxymethyl cellulose for the nanoparticle preparation and in that case, sodium carboxymethyl cellulose was found to work effectively as both reducing and stabilizing agent (Chen, Wang, Zhang, & Jin, 2008; Hebeish et al., 2010). In presence of sodium carboxymethyl cellulose, mono-disperse self assembly of ordered arrays of platinum nanoparticles were successfully prepared (Liu, Sutton, & Roberts, 2007). Green synthesis of cadmium nanoparticles has been achieved through a very simple route by means of using the natural polymer starch as an efficient capping agent (Wei, Kang, & Mu, 2004). In another study, starch acted dual role as both reducing and stabilizing agent in the green production of silver nanoparticles having average diameter of 10–34 nm, in an autoclave reaction at 15 psi, 121 °C for 5 min. Silver nanoparticles prepared using this technique were found to be highly stable in aqueous solution over a period of more than three months (Vigneshwaran, Nachane, Balasubramanya, & Varadarajan, 2006). Moreover, starch modified with mercapto was used as a successful template in fabricating hollow silver nanospheres (Wang and Chen, 2007). In addition, to the above reported methods, several approaches have been carried out to prepare silver nanocomposites with well-defined size and morphology (Zhang, Zhang, Wang, Chen, & Lei, 2001; Zhao et al., 2005).

The chemical modification of cellulose fibers with the etherifying agent, propylene oxide, results in the introduction of side chains of hydroxypropyl groups into the polymeric backbone of cellulose. This chemical modification is known as etherification reaction and is mainly done to convert the water insoluble cellulose to water soluble derivative (cellulose ether), namely hydroxypropyl cellulose (Du, Niu, et al., 2009; Du, Xu, et al., 2009; Pal, Singhal, & Kulkarni, 2000, 2002). As a three-membered cyclic ether, propylene oxide is known to be a very reactive reagent and this is due to its highly strained three-membered epoxide ring.. In substitution reactions by etherification, the cellulose molecule should first be activated to make the O–H bond nucleophilic and to facilitate the formation of alkali cellulose (cellulose-O^-). Alkaline reagents in this regard are excellent as catalysts for the formation of alkali cellulose. This alkalization step is to be followed by reaction of cellulose-O^- with propylene oxide which results in formation of hydroxypropyl cellulose through bimolecular substitution reaction (Hjärtstam and Hjertberg, 1998). The efficiency of hydroxypropylation reaction is greatly influenced by the reagents used as well as the reaction conditions. Etherification reaction occurs mainly in the amorphous region of the cellulose fiber due to its accessible structure. The reaction efficiency is quantified by the percentage of the etherifying reagent reacted or substituted upon cellulose. The rest of the etherifying reagent that does not react with cellulose is consumed to form by-products. The etherification reaction efficiency depends greatly upon the diffusion or penetration of the alkali catalyst and the etherifying agent into cellulose fibers and the chances of collisions of the cellulose alcoholate nucleophile with the propylene oxide molecule. The elevated temperature of reaction helps in diffusion of alkaline catalyst and penetration of etherifying reagent more readily into the reaction point inside the cellulose fiber and thus economizes the reagent consumption. A number of processes have been developed for the preparation of low substituted hydroxyalkyl cellulose ethers in aqueous phase.. High levels of substitution can be obtained in carbohydrates by using non-aqueous media (Drummond, Albers, & Furlong, 1992; Keates, Mitchell, & Peuvrel, 1992) or in dry conditions (Weiβ, Knoch, Laicher, Stanislaus, & Daniels, 1995). The molar substitution (Heinämäki, Lehtola, Nikupaavo, & Yliruusi, 1994; Larsson, Hjärtstam, Berndtsson, Stading, & Larsson, 2010; Suto and Suzuki, 1997; Wollenweber, Makievski, Miller, & Daniels, 2000), average molecular weight (Matsuo & Yanagida, 1991) and distribution of substituent (Skuse, Norris-Jones, Yalpani, & Brooks, 1992; Suto, Ohshiro, Ito, & Karasawa, 1987) determine the properties of the prepared hydroxypropyl cellulose.

The aim of the present study is to tailor hydroxypropyl cellulose molecules having certain molar substitution just enough for achieving complete water solubility. This can be achieved by optimizing the different reaction conditions, like alkali concentration, propylene oxide concentration and reaction duration and temperature. The prepared hydroxylpropyl cellulose will be used as a template for the green synthesis of silver nanoparticles.

2. Experimental

2.1. Materials

Cellulose powder was supplied by Sigma–Aldrich, propylene oxide was supplied by Sigma–Aldrich. Isopropyl alcohol, sodium hydroxide, silver nitrate, and acetone were all laboratory grade reagents.

2.2. Hydroxypropylation

Hydroxypropylation of cellulose was carried out by a two-steps method (A and B) (Zahran, Abdel-Halim, & El-Rafie, 1998).

Step A. Formation of alkali celluloseCellulose samples were dispersed individually in sodium hydroxide solutions containing 5–40% NaOH (based on weight of cellulose) for 1 h at room temperature using material to liquor ratio 1:20. The formed alkali cellulose was filtered under suction using a sintered glass funnel until the ratio of cellulose to the alkali solution reaches 1:3 (w/w).

Step B. Etherification reactionCold isopropyl alcohol was added to the formed alkali cellulose (4 ml for each 1 g cellulose), finally cold propylene oxide (0 °C) was added and the reaction cup was tightly closed. The reaction mixture was homogenized by well shaking then the cups are batched in a thermostatic water bath at the desired reaction temperature. At the end of reaction duration, the resultant product was neutralized with hydrochloric acid then precipitated by washing several times with acetone, and finally dried and crushed.

2.3. Preparation of silver nanoparticles

Silver nanoparticles were prepared by means of simple chemical reduction of silver nitrate with hydroxypropyl cellulose in an aqueous solution. Certain weight of the so-prepared hydroxypropyl cellulose having molar substitution of 0.42 was dissolved in 100 ml distilled water and brought to heating at different temperatures. Definite volume of $AgNO_3$ solution was added drop-wise to the hydroxypropyl cellulose solution keeping continuous vigorous stirring for certain durations. Short time after addition of silver nitrate solution, the hydroxypropyl cellulose solution acquires light yellow color indicating the reduction of silver nitrate to nanometalic

silver. The light yellow color turns to dark yellow then brown as the reaction proceeds. Factors affecting the reduction efficiency and nanoparticles stability as well as shape and size of the formed silver nanoparticles are given in the text.

2.4. Testing and analysis

2.4.1. Assessment of hydroxypropyl cellulose molar substitution

The propoxyl content of the hydroxypropyl cellulose expressed as molar substitution was measured according to a reported method (Chen, Wu, Miao, Luo, & Jiang, 2010).

2.4.2. Characterization of silver nanoparticles

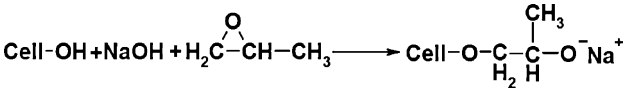
2.4.2.1. Ultra violet–visible (UV–vis) spectra. Ultra violet–visible (UV–vis) spectra have been proved to be quite sensitive to the formation of silver colloids because silver nanoparticles exhibit an intense absorption peak due to the surface plasmon excitation (it describes the collective excitation of conduction electrons in a metal). UV–vis spectra of silver nanoparticles embedded in hydroxypropyl cellulose were recorded using Spectra 50 ANALYTIKA JENA Spectrophotometer from 300 to 550 nm. A solution containing hydroxypropyl cellulose alone (without silver nitrate) dissolved in distilled water was used as the blank.

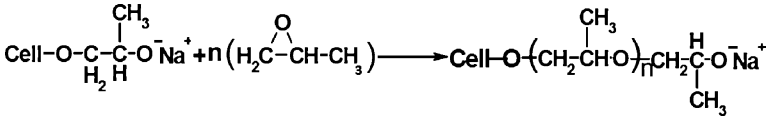
2.4.2.2. Transmission electron microscopy (TEM). Particle shape and size were recorded by means of using a JEOL-JEM-1200 Transmission Electron Microscope. Specimens for TEM measurements were prepared by dissolving a drop of colloid solution on a 400 mesh copper grid coated by an amorphous carbon film and evaporating the solvent in air at room temperature. The average diameter of the silver nanoparticles was determined from the diameter of 100 nanoparticles found in several arbitrarily chosen areas in enlarged microphotographs.

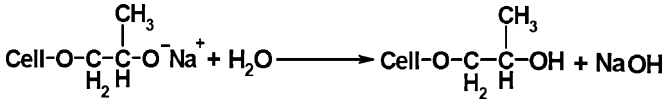
3. Results and discussion

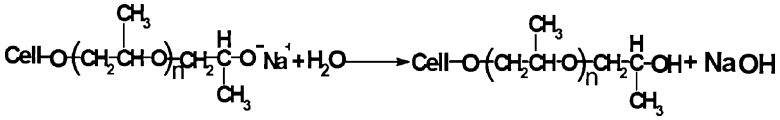
3.1. Preparation of hydroxypropyl cellulose

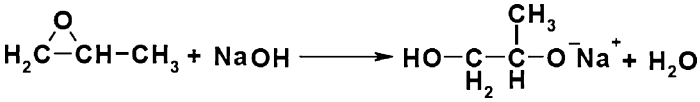
Hydroxypropyl cellulose is one of the most important commercially produced water soluble polymers, which have many industrial uses. A systematic study was designed to find the optimum conditions for the preparation of water soluble hydroxypropyl cellulose keeping in mind that the resultant product should have certain molar substitution suitable for reduction of silver nanoparticles. The hydroxypropylation reaction was carried out under different conditions including alkali concentration, concentration of propylene oxide, temperature and reaction duration. Cellulose samples were subjected to alkali treatment followed by addition of isopropyl alcohol as diluent and propylene oxide as the etherifying agent. Given below the equations which illustrate the reaction mechanism and the by-products formed during etherification reaction.

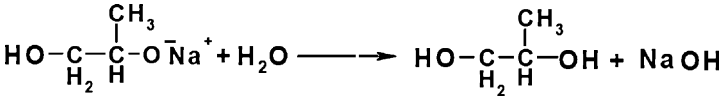

(1)

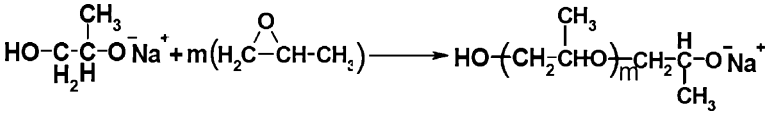

(2)

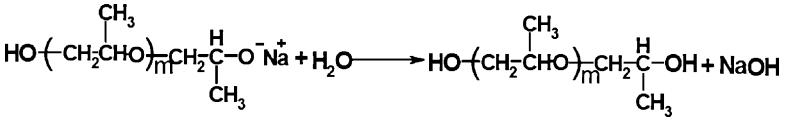

(3)


(4)


(5)


(6)


(7)


(8)

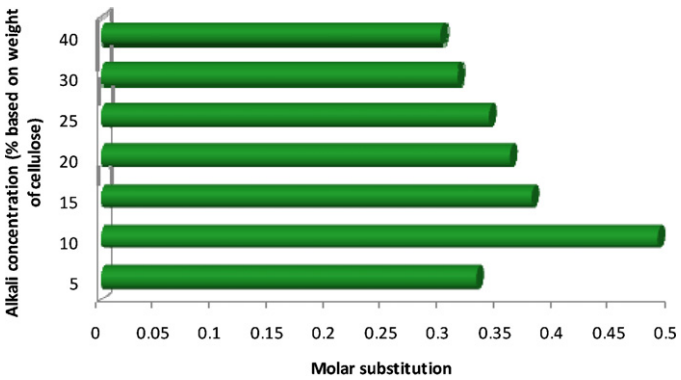


Fig. 1. Effect of alkali concentration on the molar substitution. Cellulose:alkali solution, 1:20; [propylene oxide], 115 g/100 g cellulose; alkali cellulose:isopropyl alcohol, 1:4; temperature, 60 °C; duration, 2 h.

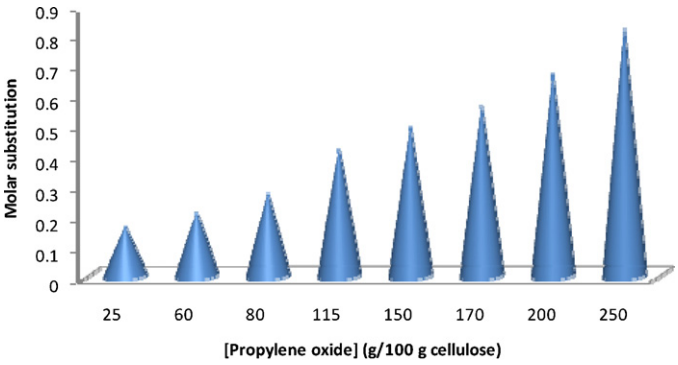


Fig. 2. Effect of propylene oxide concentration on the molar substitution. [Alkali], 10% NaOH (on weight of cellulose); cellulose:alkali solution, 1:20; alkali cellulose:isopropyl alcohol, 1:4; temperature, 60 °C; duration, 2 h.

3.2. Effect of alkali concentration on the hydroxypropylation reaction

Cellulose was dispersed in sodium hydroxide solutions containing 5–40% NaOH (based on weight of cellulose) using material to liquor ratio of 1:20, filtered until the ratio of cellulose to the alkali solution reaches 1:3 (w/w). Isopropyl alcohol was then added to the alkali cellulose followed by addition of calculated amount of cold propylene oxide 115 g/100 g cellulose. The reaction temperature was raised to 60 °C and the reaction mixture was kept at this temperature for 2 h. The resultant product was neutralized, precipitated and dried as mentioned in Section 2. The resultant product was evaluated via determining the molar substitution.

Fig. 1 shows the effect of NaOH concentration used in alkali pretreatment prior to the hydroxypropylation reaction on the molar substitution of the resultant hydroxypropyl cellulose. The data indicates that the molar substitution of the resultant hydroxypropyl cellulose is enhanced significantly by increasing NaOH concentration, during the alkali treatment step; up to 10% of the weight of cellulose, further increase above this limit is accompanied by gradual decrement in the molar substitution. The enhancement in the molar substitution could be attributed to the increased cellulose swellability and thereby the accessibility of the cellulose structure towards hydroxypropylation reaction. The decrement in the molar substitution at higher alkali concentration reflects the formation of reaction by-products resulting from homopolymerization of propylene oxide (Eqs. (5)–(8)) rather than the etherification reaction between propylene oxide and cellulose.

3.3. Effect of propylene oxide concentration on the molar substitution

Fig. 2 shows the effect of the amount of propylene oxide incorporated in the reaction medium on the molar substitution of the resultant hydroxypropyl cellulose. The hydroxypropylation reaction was carried out using 10% NaOH during the alkali treatment step followed by incorporation of different concentrations (25–250%) from propylene oxide (based on dry weight of cellulose). It is clear from the data in Fig. 2 that increasing the amount of propylene oxide incorporated in the reaction medium is accompanied by drastic enhancement in the molar substitution. It is understandable that the cellulose hydroxyls are immobile, so the reaction of hydroxyl groups with propylene oxide should depend on the availability of propylene oxide molecules in their vicinity, that is why as the amount of propylene oxide increases the extent of hydroxypropylation reaction increases accordingly.

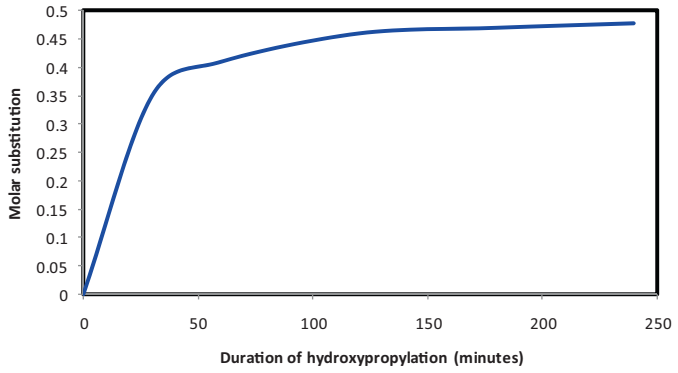


Fig. 3. Effect of hydroxypropylation duration on the molar substitution. [Propylene oxide], 115 g/100 g cellulose; [alkali], 10% NaOH (on weight of cellulose); cellulose:alkali solution, 1:20; alkali cellulose:isopropyl alcohol, 1:4; temperature, 60 °C.

3.4. Effect of the reaction duration on molar substitution

Fig. 3 shows the effect of reaction duration on the extent of hydroxypropylation expressed as molar substitution. The data in Fig. 3 reveal that the rate of hydroxypropylation tremendously increases by increasing the reaction duration up to 120 min, further increase above this limit is accompanied by marginal increments. It could be concluded that soluble hydroxypropyl cellulose is obtained when the value of molar substitution exceeds 0.4.

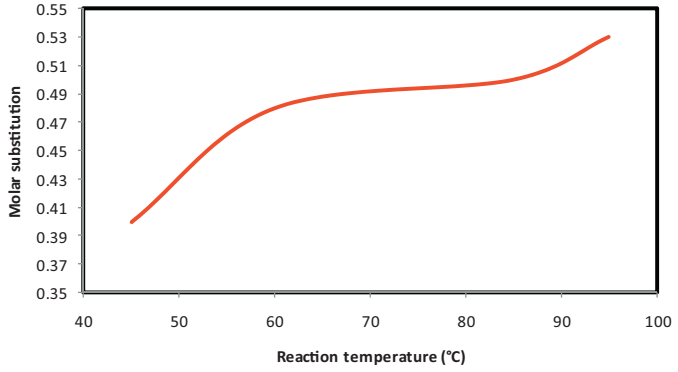


Fig. 4. Effect of hydroxypropylation temperature on the molar substitution. [Propylene oxide], 115 g/100 g cellulose; [alkali], 10% NaOH (on weight of cellulose); cellulose:alkali solution, 1:20; alkali cellulose:isopropyl alcohol, 1:4; duration, 2 h.

3.5. Effect of hydroxypropylation temperature

Fig. 4 shows the effect of reaction temperature on the molar substitution values of the hydroxypropyl cellulose. It is seen from the data that significant enhancement in the extent of hydroxypropylation occurs by raising the reaction temperature. This can be explained in terms of the favorable effect of temperature in increasing the swellability of cellulose in addition to increasing the kinetic energy of the propylene oxide molecules, thus giving rise to more chances for molecular collisions and accordingly higher reaction rates.

3.6. Water solubility of the prepared hydroxypropyl cellulose

Prepared hydroxypropyl cellulose samples having different molar substitution were tried for their complete water solubility. Based on the noticed solubility behavior it was concluded that complete water solubility is associated with molar substitution exceeding 0.4. Accordingly, the optimum conditions for preparation of completely water soluble hydroxypropyl cellulose from cellulose are, performing the alkali pretreatment step using 10% NaOH (based on weight of cellulose), *M*/*L* ratio 1:20, temperature 30 °C and duration 60 min. For the hydroxypropylation step, the alkali treated cellulose is to be mixed with 2-propanol in a material to liquor ratio of 1:4, and then propylene oxide 115 g/100 g cellulose is added and the hydroxypropylation reaction is run at 60 °C for 120 min.

3.7. Synthesis of silver nanoparticles

The current study reports the green synthesis of silver nanoparticles using hydroxypropyl cellulose. The synthesis method is based on using tailored hydroxypropyl cellulose which functions as both reducing and stabilizing agent during synthesis.

3.7.1. Proposed mechanism of reduction

The silver ions interact with the available functional groups of the hydroxypropyl cellulose, as reported earlier for starch (Vigneshwaran et al., 2006). Hydroxypropyl cellulose is known to be rich in hydroxyl functional groups present originally in the cellulose backbone in addition to those introduced at the ends of the side chains due to hydroxypropylation. The large number of hydroxyl groups on this natural polymer facilitates the complexation of silver ions. Subsequently, these silver ions oxidize the hydroxyl groups of hydroxylpropyl cellulose to carbonyl groups, and as a result the silver ions are reduced to elemental silver. Also during the preparation of hydroxypropyl cellulose oxidation of the existing hydroxyl groups to carbonyl groups such as aldehydes can happen. In turn, these powerful reducing aldehyde groups reduce more and more of silver ions to elemental silver. Further, these nanoparticles are probably capped and stabilized by the polysaccharide matrix. The structure of carbohydrate polymers is very complex, it is most likely that more than one mechanism is involved in the complexation and subsequent reduction of silver ions. Silver ion complexation by hydroxyl groups and its subsequent reduction by aldehyde groups are reported for starch (Vigneshwaran et al., 2006). Silver nanoparticles produced using gum acacia, carboxylate groups involving complexation of silver ions and its subsequent reduction by hydroxyl groups were reported (Mohan, Lee, Premkumar, & Geckeler, 2007).

3.7.2. Effect of pH on silver nanoparticles formation

Fig. 5 shows the UV–vis spectra of the silver nanoparticles prepared using hydroxypropyl cellulose as reducing and stabilizing agent at different pHs. 0.3 g hydroxypropyl cellulose of molar substitution of 0.42 was dissolved in distilled water using heating magnetic stirrer. After complete dissolution, the pH was adjusted to pH values of 4, 7, 10 and 12.5 using dilute sulphuric acid or sodium hydroxide. The solution temperature was raised to 70 °C. At this end, silver nitrate (0.1 N) was added drop wise (1 ml each), keeping in mind that the total volume of the reaction medium is 100 ml. The reaction was allowed to proceed under continuous stirring for 2 h whereby silver colloid was formed. The information obtained from the UV–vis spectra of the silver nanoparticles prepared at different pH values reveal that much changes in the electronic absorption spectra accompanies the change in pH of the solution that as the pH increases up to 10, a band at 405 nm starts to appear and reaches its maximum intensity at pH 12.5. This is the band characteristic for silver nanoparticles and its absence at pH 4 and pH 7 means that acid to neutral range is not ideal for silver nanoparticle formation and the nanoparticles formation is more favored in the alkaline range. At pH 12.5 the band becomes stronger and symmetrical, with a pronounced bell shape at λ_{max} 405 nm. This band could be assigned to the plasmon resonance of silver nanoparticles. The behavior caused by the observations stated above could be attributed to: (i) the formation of various ionic states of silver such as Ag^{+}, Ag^{2+} and Ag^{3+} bound to negatively charged surface of hydroxyethyl cellulose polymer and this was confirmed by simple chloride test, that at low pH values, chloride test gave white precipitate indicating lack of reduction of silver ion to silver metal in acidic–neutral range. When the pH increases the reduction of silver ions to Ag° is enhanced and the maximum intensity of the plasmon peak (405 nm) at pH 12.5 indicate full reduction of Ag ions to silver nanoparticles and, therefore, reflecting the dual role of hydroxypropyl cellulose as stabilizing and efficient reducing agent in alkaline medium.

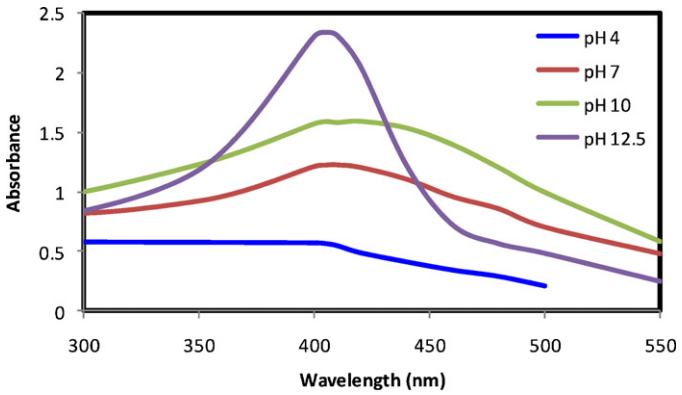


Fig. 5. Dependence of silver nanoparticles formation on the pH of the preparation medium. *Reaction conditions*: 0.3% (w/v) hydroxypropyl cellulose (molar substitution of 0.42); 1 ml (0.1 N) $AgNO_3$; temperature, 70 °C; duration, 120 min.

3.7.3. Effect of reaction duration and temperature on silver nanoparticles formation

Preparation of silver nanoparticles was carried out at 70 °C and samples from the reaction medium were withdrawn at different time intervals, namely, 15, 30, 60, 90 and 120 min for recording the UV–vis absorption spectra of the formed silver nanoparticles at these time intervals (Fig. 6a). The data in Fig. 6a reveal several important findings which can be presented as follows: (i) at the early stage reaction duration (after 15 min) the plasmon band is broaden and simple test for silver ion using NaCl solution indicates low conversion of silver ions to metallic silver nanoparticles at this duration; (ii) prolonging the reaction duration up to 30 min, then 60 min leads to outstanding enhancement in the plasmon intensity indicating that large amounts of silver ions are reduced and used for cluster formation; (iii) further increase in the reaction duration up to 90 min, the peak corresponding to silver nanoparticles

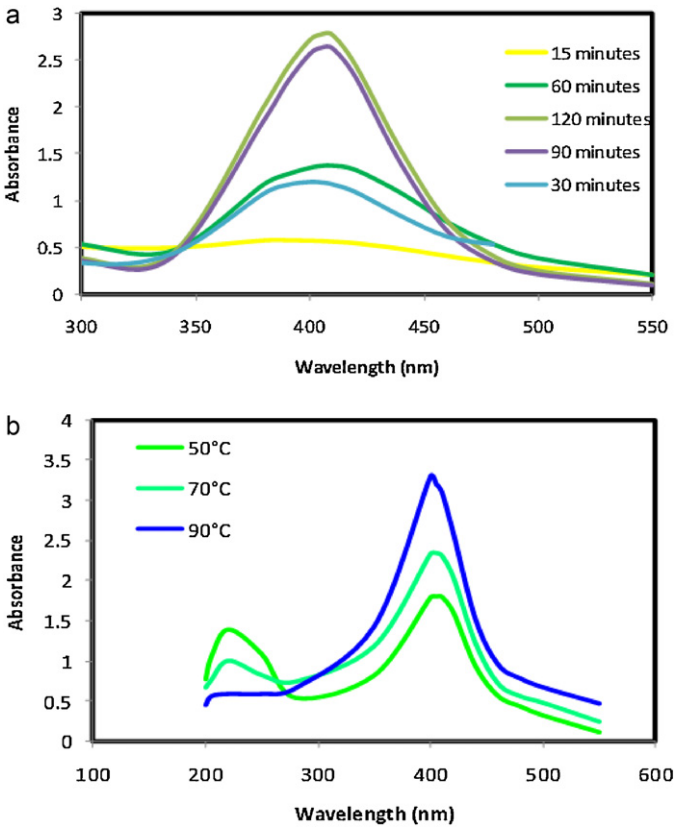


Fig. 6. Dependence of silver nanoparticles formation on reaction duration (a) and reaction temperature (b). *Reaction conditions* (a): 0.3% (w/v) hydroxypropyl cellulose (molar substitution of 0.42); 1 ml (0.1 N) $AgNO_3$; temperature, 70 °C; pH 12.5. *Reaction conditions* (b): 0.3% (w/v) hydroxypropyl cellulose (molar substitution of 0.42); 1 ml (0.1 N) $AgNO_3$; duration, 120 min; pH 12.5.

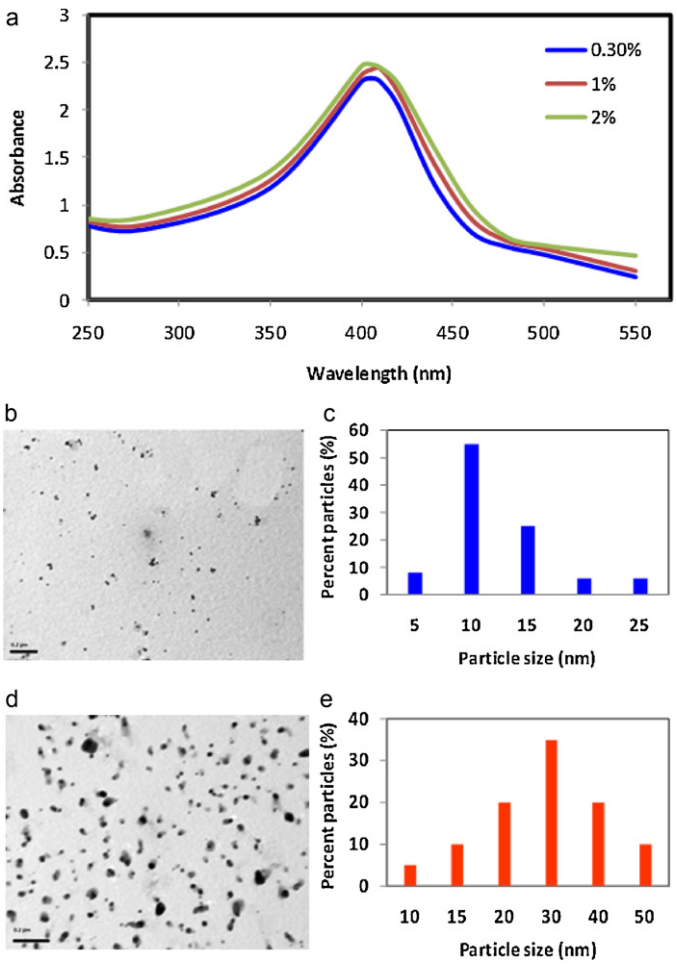


Fig. 7. UV–vis spectra, TEM micrographs and particle size distribution histograms of silver nanoparticles prepared using different hydroxypropyl cellulose concentrations. *Reaction conditions*: Hydroxypropyl cellulose with molar substitution of 0.42; 1 ml (0.1 N) $AgNO_3$; temperature, 70 °C; duration, 90 min; pH 12.5.

becomes more sharp and acquires an ideal bell shape. No marked improvement in the peak was noticed upon prolonging the reaction duration up to 120 min and this means that 90 min is optimum duration for complete reduction of silver ions to silver nanoparticles.

Based on the above conclusion, three trials for preparation of silver nanoparticles were carried out at three different temperatures, namely, 50 °C, 70 °C and 90 °C and the UV–vis absorption spectra were recorded in each case after fixed duration of 90 min (Fig. 6b). The data in Fig. 6b indicate that the reduction efficiency at 50 °C is not very good and no complete transformation of Ag^+ into silver nanopartricles is achieved at this temperature. This was evident by the presence of a strong peak characteristic for Ag^+ at wavelength 220 nm together with positive chloride ion test. Increasing the reaction temperature above this limit, 70–90 °C leads to the disappearance of the peak characteristic for Ag^+, indicating its complete transformation into Ag°. On the other hand, there is significant enhancement in the absorption band by rising the temperature up to 90 °C. Based on the above, the optimum temperature and duration for preparation of silver nanoparticles are 90 °C and 90 min, respectively.

3.7.4. Effect of hydroxypropyl cellulose concentration on silver nanoparticles formation

Different concentrations from hydroxylpropyl cellulose, namely, 0.3%, 1% and 2%, all of them having molar substitution of 0.42 were tried to reduce silver nitrate to silver nanoparticles at fixed temperature of 90 °C and the UV–vis absorption spectra of the so produced silver nanoparticles were recorded in each case after fixed duration of 90 min (Fig. 7a) The data in Fig. 7a reveal that regardless of the hydroxylpropyl cellulose concentration used, similar plasmon bands are formed at wavelength 405 nm with the formation of the ideal bell shape which is characteristic for the formation of Ag° nanoparticles. It is clear also that there is a small gradual increase in the absorption intensity, by increasing the hydroxypropyl cellulose concentration up to 2% which could be ascribed to the enhancement in the stabilization efficiency of the formed silver nanoparticles. It should be also mentioned that the least amount of hydroxypropyl cellulose in the reaction medium (0.3%) is enough for full reduction of the Ag^+ to Ag° nanoparticles.

TEM images and particle size distribution histograms of silver nanoparticles prepared using 0.3% hydroxypropyl cellulose (Fig. 7b and c) and 2% hydroxypropyl cellulose (Fig. 7d and e) indicate that 0.3% cellulose is an optimum hydroxypropyl concentration for preparation of silver nanoparticles. The obtained data illustrate that the number of nanoparticles formed in the range of 10–15 nm is 80% in case of using 0.3% hydroxypropyl cellulose, while in case of using 2% hydroxypropyl cellulose, the particles in the range of 10–15 nm represent only 15% of the total particles and the diameter of 85% of the particles fall in the range 20–50 nm.

3.7.5. Effect of molar substitution on silver nanoparticles formation

In addition to the trial made in the last section using hydroxypropyl cellulose of molar substitution of 0.42, another two samples having varying molar substitution, namely, 0.8 and 1

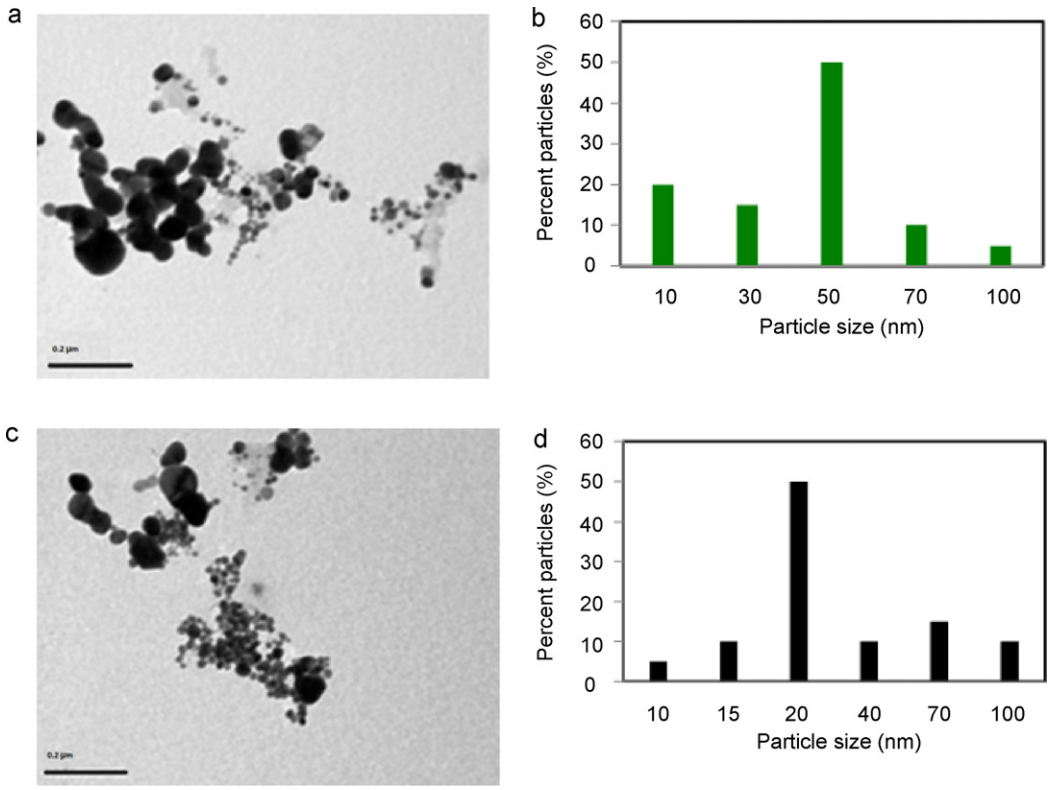


Fig. 8. TEM micrographs and particle size distribution histograms of silver nanoparticles prepared using hydroxypropyl cellulose having different molar substitution. *Reaction conditions*: 0.3% (w/v) hydroxypropyl cellulose; 1 ml (0.1 N) $AgNO_3$; temperature, 70 °C; pH 12.5; duration 90 min.

were used in this section separately in fixed concentration of 0.3% to prepare silver nanoparticles at 90 °C for reaction duration of 90 min. The couples of Figs. 7b and c, 8a and b, and 8c and d represent TEM images and particle size distribution histograms of silver nanoparticles prepared using 0.3% hydroxypropyl cellulose of molar substitution 0.42, 0.8 and 1, respectively. As is evident from TEM micrographs, regardless of the molar substitution, all hydroxypropyl cellulose samples could reduce silver ions to metallic silver in the nano size. As is evident from the histograms, the particle size distribution is affected by the molar substitution, that the higher the molar substitution, the larger the particle size and the higher is the scattering of particle size ranges.

4. Conclusion

Hydroxypropyl cellulose samples having different molar substitution were prepared through alkalization of cellulose followed by etherification reaction with propylene oxide. Factors affecting hydroxypropyl cellulose preparation like alkali concentration, propylene oxide concentration as well as etherification reaction temperature and duration were extensively studied. It was found that the molar substitution increases by increasing the concentration of sodium hydroxide during the alkalization step, up to 10% of the weight of cellulose and further increase above this limit is accompanied by gradual decrement in the molar substitution. Also it was found that increasing the amount of propylene oxide incorporated in the reaction medium is accompanied by drastic enhancement in the molar substitution. Prolonging the reaction duration or increasing reaction medium temperature was found to increase the molar substitution. The prepared hydroxypropyl cellulose samples were characterized by measuring their molar substitution and were tried for their water solubility and it was found that samples having molar substitution of 0.4 or higher are water soluble. The obtained hydroxypropyl cellulose samples were used in the preparation of silver nanoparticles through reduction of silver nitrate and the preparation reaction was carried out under different conditions including pH, temperature, duration as well as concentration of hydroxypropyl cellulose and its molar substitution. UV–vis spectra of the silver colloidal solution reveal that full reduction of silver ions occurs at pH 12.5. Prolonging the reaction time up to 90 min brings about reduction of larger amounts of silver ions. Complete transformation of silver ions into silver nanoparticles occurs at 90 °C. No marked improvement in the beak intensity was noticed on increasing hydroxypropyl cellulose concentration from 0.3% to 2%. Also increasing the molar substitution from 0.42 to 1 was found to have negative effect on the dispersion of silver nanoparticles, particle size distribution, and the stabilization effect of hydroxypropyl cellulose macromolecules.

Acknowledgement

The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding the work through the research group project No. RGP-VPP-029.

References

Abdel-Halim, E. S., El-Rafie, M. H., & Al-Deyab, S. S. (2011). Polyacrylamide/guar gum graft copolymer for preparation of silver nanoparticles. *Carbohydrate Polymers*, *85*, 692–697.

Babu, V. R., Kim, C., Kim, S., Ahn, C., & Lee, Y. (2010). Development of semi-interpenetrating carbohydrate polymeric hydrogels embedded silver nanoparticles and its facile studies on *E. coli*. *Carbohydrate Polymers*, *81*, 196–202.

Bajpai, S. K., Mohan, Y. M., Bajpai, M., Tankhiwale, R., & Thomas, V. (2007). Synthesis of polymer stabilized silver and gold nanostructures. *Journal of Nanoscience and Nanotechnology*, *7*, 2994–3010.

Biffis, A., Orlandi, N., & Corain, B. (2003). Microgel-stabilized metal nanoclusters: Size control by microgel nanomorphology. *Advanced Materials*, *15*, 1551–1555.

Božanić, D. K., Dimitrijević-Branković, S., Bibić, N., Luyt, A. S., & Djoković, V. (2011). Silver nanoparticles encapsulated in glycogen biopolymer: Morphology, optical and antimicrobial properties. *Carbohydrate Polymers*, *83*, 883–890.

Chen, D. H., & Hsieh, C. H. (2002). Synthesis of nickel nanoparticles in aqueous cationic surfactant solutions. *Journal of Materials Chemistry*, *12*, 2412–2415.

Chen, C. W., Serizawa, T., & Akashi, M. (1999). Synthesis and characterization of poly(N-isopropylacrylamide)-coated polystyrene microspheres with silver nanoparticles on their surfaces. *Langmuir*, *15*, 7998–8006.

Chen, J., Wang, J., Zhang, X., & Jin, Y. (2008). Microwave-assisted green synthesis of silver nanoparticles by carboxymethyl cellulose sodium and silver nitrate. *Materials Chemistry and Physics*, *108*, 421–424.

Chen, Y., Wu, X., Miao, X., Luo, J., & Jiang, B. (2010). Determination of the degree of substitution of hydroxypropyl guar gum at C-6 by pyrolysis-gas chromatography spectrometry. *Carbohydrate Polymers*, *82*, 829–832.

Colvin, V. L., Schlamp, M. C., & Alivisatos, A. P. (1994). Light-emitting-diodes made from cadmium selenide nanocrystals and a semiconducting polymer. *Nature*, *370*, 354–357.

Daniel, M. C., & Astrue, D. (2004). Gold nanoparticles: Assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chemical Reviews*, *104*, 293–346.

Drummond, C. J., Albers, S., & Furlong, N. D. (1992). Polymer–surfactant interactions: (Hydroxypropyl) cellulose with ionic and ion–ionic surfactants. *Colloids and Surfaces*, *62*, 75–85.

Du, W. L, Niu, S. S., Xu, Y. L., Xu, Z. R., & Fan, C. L. (2009). Antibacterial activity of chitosan tripolyphosphate nanoparticles loaded with various metal ions. *Carbohydrate Polymers*, *75*, 385–389.

Du, Y. Z., Xu, J. G., Wang, L., Yuan, H., & Hu, F. Q. (2009). Preparation and characteristics of hydroxypropyl-β-cyclodextrin polymeric nanocapsules loading nimodipine. *European Polymer Journal*, *45*, 1397–1402.

Esumi, K., Suzuki, A., Yamahira, A., & Torigoe, K. (2000). Role of poly(amidoamine) dendrimers for preparing nanoparticles of gold platinum and silver. *Langmuir*, *16*, 2604–2608.

Esumi, K., Isono, R., & Yoshimura, T. (2004). Preparation of PAMAM- and PPI-metal (silver, platinum, and palladium) nanocomposites and their catalytic activities for reduction of 4-nitrophenol. *Langmuir*, *20*, 237–243.

Hang, A. T., Tae, B., & Park, J. S. (2010). Non-woven mats of poly(vinyl alcohol)/chitosan blends containing silver nanoparticles: Fabrication and characterization. *Carbohydrate Polymers*, *82*, 472–479.

Hebeish, A. A., El-Rafie, M. H., Abdel-Mohdy, F. A., Abdel-Halim, E. S., & Emam, H. E. (2010). Carboxymethyl cellulose for green synthesis and stabilization of silver nanoparticles. *Carbohydrate Polymers*, *82*, 933–941.

Hebeish, A., El-Shafei, A., Sharaf, S., & Zaghloul, S. (2011). Novel precursors for green synthesis and application of silver nanoparticles in the realm of cotton finishing. *Carbohydrate Polymers*, *84*, 605–613.

Heinämäki, J. T., Lehtola, V. M., Nikupaavo, P. J., & Yliruusi, K. (1994). The mechanical and moisture permeability properties of aqueous-based hydroxypropyl methylcellulose coating systems plasticized with polyethylene glycol. *International Journal of Pharmaceutics*, *112*, 191–196.

Hjärtstam, J., & Hjertberg, T. (1998). Swelling of pellets coated with a composite film containing ethyl cellulose and hydroxypropyl methylcellulose. *International Journal of Pharmaceutics*, *161*, 23–28.

Keates, P., Mitchell, G. R., & Peuvrel, E. (1992). Local structural correlations in anisotropic aqueous solutions of hydroxypropyl cellulose. *Polymer*, *33*, 3298–3301.

Kiesow, A., Morris, J. E., Radehaus, C., & Heilmann, A. (2003). Switching behavior of plasma polymer films containing silver nanoparticles. *Journal of Applied Physics*, *94*, 6988–6990.

Konwarh, R., Karak, N., Sawian, C. E., Baruah, S., & Mandal, M. (2011). Effect of sonication and aging on the templating attribute of starch for "green" silver nanoparticles and their interactions at bio-interface. *Carbohydrate Polymers*, *83*, 1245–1252.

Kora, A. J., Sashidhar, R. B., & Arunachalam, J. (2010). Gum kondagogu (Cochlospermum gossypium): A template for the green synthesis and stabilization of silver nanoparticles with antibacterial application. *Carbohydrate Polymers*, *82*, 670–679.

Larsson, M., Hjärtstam, J., Berndtsson, J., Stading, M., & Larsson, A. (2010). Effect of ethanol on the water permeability of controlled release films composed of ethyl cellulose and hydroxypropyl cellulose. *European Journal of Pharmaceutics and Biopharmaceutics*, *76*, 428–432.

Li, X., Chen, S., Hu, W., Shi, S., Shen, W., Zhang, X., et al. (2009). In situ synthesis of CdS nanoparticles on bacterial cellulose nanofibers. *Carbohydrate Polymers*, *76*, 509–512.

Liu, J., Sutton, J., & Roberts, C. B. (2007). Synthesis and extraction of monodisperse sodium carboxymethylcellulose-stabilized platinum nanoparticles for the selfassembly of ordered arrays. *Journal of Physical Chemistry C*, *111*, 11566–11576.

Mandal, S., Phadtare, S., & Sastry, M. (2005). Interfacing biology with nanoparticles. *Current Applied Physics*, *5*, 118–127.

Maneerung, T., Tokura, S., & Rujiravanit, R. (2008). Impregnation of silver nanoparticles into bacterial cellulose for antimicrobial wound dressing. *Carbohydrate Polymers*, *72*, 43–51.

Matsuo, M., & Yanagida, N. (1991). Molecular-weight dependence of morphology and mechanical properties of hydroxypropyl cellulose films cast from water. *Polymer*, *32*, 2561–2576.

Mohan, Y. M., Lee, K., Premkumar, T., & Geckeler, K. E. (2007). Hydrogel networks as nanoreactors: A novel approach to silver nanoparticles for antibacterial applications. *Polymer*, *48*, 158–164.

Pal, J., Singhal, R. S., & Kulkarni, P. R. (2000). A comparative account of conditions of synthesis of hydroxypropyl derivative from corn and amaranth starch. *Carbohydrate Polymers*, *43*, 155–162.

Pal, J., Singhal, R. S., & Kulkarni, P. R. (2002). Physicochemical properties of hydroxypropyl derivative from corn and amaranth starch. *Carbohydrate Polymers*, *48*, 49–53.

Raveendran, P., Fu, J., & Wallen, S. L. (2003). Completely "green" synthesis and stabilization of metal nanoparticles. *Journal of American Chemical Society*, *125*, 13940–13941.

Ross, C. A. (2001). Patterned magnetic recording media. *Annual Review of Materials Research*, *31*, 203–235.

Skuse, D. R., Norris-Jones, R., Yalpani, M., & Brooks, D. E. (1992). Hydroxypropyl cellulose/poly(ethylene glycol)-co-poly(propylene glycol) aqueous two-phase systems: System characterization and partition of cells and proteins. *Enzyme and Microbial Technology*, *14*, 785–790.

Suto, S., & Suzuki, K. (1997). Crosslinked hydroxypropyl cellulose films retaining cholesteric liquid crystalline order. 2. Anisotropic swelling behaviour in water. *Polymer*, *38*, 391–396.

Suto, S., Ohshiro, M., Ito, R., & Karasawa, M. (1987). Capillary rheometry of lyotropic liquid crystals of hydroxypropyl cellulose. *Polymer*, *28*, 23–32.

Tomšič, B., Simončič, B., Orel, B., Žerjav, M., Schroers, H., Simončič, A., et al. (2009). Antimicrobial activity of AgCl embedded in a silica matrix on cotton fabric. *Carbohydrate Polymers*, *75*, 618–626.

Vaseashta, A., & D-Malinovska, D. (2005). Nanostructured and nanoscale devices, sensors and detectors. *Science and Technology of Advanced Materials*, *6*, 312–318.

Vigneshwaran, N., Nachane, R. P., Balasubramanya, R. H., & Varadarajan, P. V. (2006). A novel one-pot 'green' synthesis of stable silver nanoparticles using soluble starch. *Carbohydrate Research*, *341*, 2012–2018.

Vimala, K., Sivudu, K. S., Mohan, Y. M., Sreedhar, B., & Raju, K. M. (2009). Controlled silver nanoparticles synthesis in semi-hydrogel networks of poly(acrylamide) and carbohydrates: A rational methodology for antibacterial application. *Carbohydrate Polymers*, *75*, 463–471.

Wang, L., & Chen, D. (2007). A facile method for the preparation of hollow silver spheres. *Materials Letters*, *61*, 2113–2116.

Weiβ, G., Knoch, A., Laicher, A., Stanislaus, F., & Daniels, R. (1995). Simple coacervation of hydroxypropyl methylcellulose phthalate (HPMCP). I. Temperature and pH dependency of coacervate formation. *International Journal of Pharmaceutics*, *124*, 87–96.

Wei, Q., Kang, S. Z., & Mu, J. (2004). "Green" synthesis of starch capped CdS nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *247*, 125–127.

Wollenweber, C., Makievski, A. V., Miller, R., & Daniels, R. (2000). Adsorption of hydroxypropyl methylcellulose at the liquid/liquid interface and the effect on emulsion stability. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *172*, 91–101.

Xu, S., Zhang, J., Paquet, C., Lin, Y., & Kumacheva, E. (2003). From hybrid microgels to photonic crystals. *Advanced Functional Materials*, *13*, 468–472.

Xu, Z. P., Zeng, Q. H., Lu, G. Q., & Yu, A. B. (2006). Inorganic nanoparticles as carriers for efficient cellular delivery. *Chemical Engineering Science*, *61*, 1027–1040.

Zahran, M. K., Abdel-Halim, E. S., & El-Rafie, M. H. (1998). Utilization of corn stalks for preparation of hydroxyethyl cellulose. *Colourage*, *45*, 19–26.

Zhang, Z., Zhang, L., Wang, S., Chen, W., & Lei, Y. (2001). A convenient route to polyacrylonitrile/silver nanoparticle composite by simultaneous polymerization–reduction approach. *Polymer*, *42*, 8315–8318.

Zhao, X., Ding, X., Deng, Z., Zheng, Z., Peng, Y., & Long, X. (2005). Thermoswitchable electronic properties of a gold nanoparticle/hydrogel composite. *Macromolecular Rapid Communications*, *26*, 1784–1787.

Zhuang, X., Cheng, B., Kang, W., & Xu, X. (2010). Electrospun chitosan/gelatin nanofibers containing silver nanoparticles. *Carbohydrate Polymers*, *82*, 524–527.