Carbohydrate Polymers 98 (2013) 290–294

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

# Green synthesis of silver nanoparticles using cellulose extracted from an aquatic weed; water hyacinth

Tanki Mochochoko, Oluwatobi S. Oluwafemi*, Denis N. Jumbam, Sandile P. Songca

*Department of Chemistry and Chemical Technology, Walter Sisulu University, Mthatha Campus, Private Bag XI, Mthatha 5117, Eastern Cape, South Africa*

ARTICLE INFO

*Article history:*
Received 12 December 2012
Received in revised form 29 April 2013
Accepted 19 May 2013
Available online xxx

*Keywords:*
Silver nanoparticles
Water hyacinth
*Echhornia crassipes*
Cellulose
Capping agent
pH

ABSTRACT

As part of the desire to save the environment through "green" chemistry practices, we herein report an environmentally benign synthesis of silver nanoparticles (Ag-NPs) using cellulose extracted from an environmentally problematic aquatic weed, water hyacinth (WH), as both reducing and capping agent in an aqueous medium. By varying the pH of the solution and reaction time, the temporal evolutions of the optical and morphological properties of the as-synthesised Ag-NPs were investigated. The as-synthesised cellulose capped silver nanoparticles (C–Ag-NPs) were characterised using Fourier transform infrared spectroscopy (FTIR), ultraviolet–visible spectroscopy (UV–vis), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). The maximum surface plasmon resonance (SPR) peak decreased as the pH increased indicating that an increase in the pH of the solution favoured the formation of smaller particles. In addition, instantaneous change in the colour of the solution from colourless to brown within 5 min at pH 11 showed that the rate of reduction is faster at this pH compared to those at lower pH. The TEM micrographs showed that the materials are small, highly monodispersed and spherical in shape. The average particle mean diameters were calculated to be $5.69 \pm 5.89$ nm, $4.53 \pm 1.36$ nm and $2.68 \pm 0.69$ nm nm at pH 4, 8 and 11 respectively. The HRTEM confirmed the crystallinity of the material while the FTIR spectra confirmed the capping of the as-synthesised Ag-NPs by the cellulose. It has been shown therefore that based on this synthetic method, this aquatic plant can be used to the advantage of mankind.



## 1. Introduction

Metal nanoparticles have received a lot of attention in the recent years due to their unique optical, electrical, and biological properties which make them central to numerous applications such as in catalysis, bio-sensing, imaging, drug delivery and optical spectroscopy including surface-enhanced Raman scattering (SERS) (Abdel-Halim & Al-Deyab, 2011; Bankar, Joshi, Kumar, & Zinjarde, 2010; Hebeish, El-Rafie, Abdel-Mohdy, Abdel-Halim, & Emam, 2010). Amongst different types of metal nanoparticles such as copper, zinc, titanium, magnesium and gold, Ag-NPs are of particular interest because of their potent antimicrobial activity against different types of pathogens such as *Bacillus subtilis*, *Staphylococcus aureus*, *Klebsiella pneumonia* and so on (Li, Ma, Zhang, Liu, & Sun, 2011; Rai, Yadav, & Gade, 2009; Shameli et al., 2012). This extends their application to medicine, dental materials, coating of stainless steel materials, water treatment, sunscreen lotions, and elimination of microorganisms on textile fabrics (Oluwafemi et al., 2013; Rai et al., 2009). The smaller the particles, the greater the antimicrobial effect (Baker, Pradhan, Pakstis, Pochan, & Shah, 2005; Morones et al., 2005). However, these smaller particles are very reactive and consequently form aggregates thus losing their fundamental properties (Chen, Wang, Zhang, & Jin, 2008). To circumvent this challenge, passivating agents such as polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), hyperbranched polyurethane (HP), and polyacrylonitrile (PAN) with reducing agents such as sodium borohydride, hydrazine, hydroxylamine, n-hexadecyltrimethylammonium bromide (HTAB) to mention a few, have been used successfully in the synthesis and stabilisation of silver nanoparticles (Abu Bakar, Ismail, & Abu Bakar, 2007; Hasell, Yang, Wang, Brown, & Howdle, 2007; Maria et al., 2009; Sharma, Yngard, & Lin, 2009). The utilisation of some of these passivating and reducing agents introduced yet another challenge of high cost and toxicity therefore threatening environmental sustainability and limiting the biological applications of these noble materials. These challenges have undoubtedly led to the current drive towards integrating the basic principles of 'green chemistry' – a concept that promotes the use of non-toxic chemicals, environmentally benign solvents, and renewable materials (Raveendran, Fu, & Wallen, 2003; Sharma et al., 2009; Vigneshwaran, Nachane, Balasubramanya, & Varadarajan, 2006; Wegner & Jones, 2009) into synthetic chemistry in general and in this case into the synthesis of

* Corresponding author. Tel.: +27 765110322.
*E-mail address:* Oluwafemi.oluwatobi@gmail.com (O.S. Oluwafemi).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.05.038

nanomaterials. Reveendran et al., in 2003, reported the first completely green synthesis of Ag-NPs using starch as stabilising agent and glucose as reducing agent (Sharma et al., 2009). These materials are environmentally benign, non-toxic, abundant, renewable, and biodegradable. Several syntheses based on this modification have been reported (Darroudi, Ahmad, Abdullah, & Ibrahim, 2011; Darroudi, Ahmad, Zamiri, et al., 2011; García-Serrano, Pal, Herrera, Salas, & Ángeles-Chávez, 2008; Giuffrida, Ventimiglia, & Sortino, 2009; Hu, Wang, Wang, Zhang, & Yu, 2008; Oluwafemi et al., 2013). Li, Jia, et al. (2011) also prepared cellulose–silver nanocomposites using cellulose dispersed in N,N-dimethylacetamide (DMAc) as the stabilising agent and ascorbic acid as the reducing agent. The same group further reported the microwave synthesis of cellulose–silver nanocomposites using ethylene glycol (EG) as reducing agent (Li, Ma, et al., 2011). However, EG and DMAc are organic solvents and are not environmentally friendly. Therefore, preparation of Ag-NPs using water – a more environmentally benign solvent will be most preferable for a completely green chemistry approach (Raveendran et al., 2003).

One of the abundant aquatic weed species is the water hyacinth *(Eichhornia crassipes)*. This deadly aquatic weed (Fig. 1) found in tropical and subtropical regions such as Asia, South America, North America, Central America, Africa, and Oceania is a major problem to the environment (Wissel, Mayr, & Lücke, 2008). It is known to impede navigation through waters, blocking river waters and canals, clogging irrigation and hydropower systems. It also provides favourable breeding zones for disease-causing insects, quickens evapotranspiration and reduces biodiversity. Huge amounts of money are spent worldwide to remove this weed using chemical, biological, and mechanical methods which are aimed at its total eradication without making good use of it. In addition to this fact, some of these methods of removal also cause havoc like environmental pollution and destruction of other useful plants. Thus, its eradication and utilisation towards the advantage of mankind have become a major interest. Recent reports have shown that this weed has a high fibre content and contains a high percentage of cellulose in its shoot and roots (Sundari & Ramesh, 2012; Zhou et al., 2009). However, there are no studies indicating the use of this aquatic weed in the synthesis of silver nanoparticles. In this study, as part of the quest for a completely green synthesis of Ag-NPs and finding an economical and hazard-free method of disposing this weed, we report the first synthesis of silver nanoparticles using the cellulose extracted from the shoot of this plant (water hyacinth) as both the reducing and stabilising agent without any accelerator. By varying the pH of the solution and reaction time, control over monodispersity, size and shape of the as-synthesised C–Ag-NPs was investigated.

## 2. Materials and methods

### 2.1. Materials

Water hyacinth plant shoot collected from a local river in the Mthatha area (South Africa) was used as a source of cellulose. Toluene (Sigma–Aldrich), ethanol (Shalom Lab Supplies cc), sodium hydroxide pellets, hydrogen peroxide and silver nitrate (Sigma–Aldrich). All of these reagents were of analytical-grade and were used as received without further purification. The reaction was carried out in the dark to avoid any photochemical reactions

### 2.2. Extraction of cellulose from water hyacinth

The cellulose from the plant was extracted based on the method by Teixeira et al. (2011), with slight modification. Briefly, the water hyacinth shoot was washed, oven dried and cryocrushed in a mortar with a pestle followed by particle separation using 500 μm sieve. The resultant powder (10 g) was soxhlet extracted for 6 h with a 450 mL toluene/ethanol mixture in the ratio 2:1 (v/v) at 80 °C. The powder was then oven dried at 60 °C for 16 h after which it was dissolved in 400 mL distilled water. The resultant solution was stirred vigorously with a high energy homogeniser for about 30 min and filtered. The filtration was followed by bleaching the residue in a mixture of 100 mL 5% sodium hydroxide and 100 mL 11% hydrogen peroxide at 60 °C for 1 h and then re-filtered. The process of bleaching and filtration was repeated twice. The final residue was washed with distilled water to obtain a neutral pH and oven dried at 60 °C until constant weight.

### 2.3. Synthesis of silver nanoparticles

45 mL of Cellulose solution (0.5 g/100 mL of distilled water, homogenised at 60 °C for 1 h) was put in three separate flasks. The pHs of two out of the three solutions were adjusted from its original value of 8.0 to the desired pH (4 and 11) by the dropwise addition of dilute solutions of hydrochloric acid (0.5 M) or sodium hydroxide (0.5 M). To each of the solutions above, at the different pH values of 4, 8 and 11, 2.5 mL of 1 M silver nitrate solution was added at 75 °C. Aliquots were taken at different reaction times to monitor the reactions. Each aliquot was diluted using distilled water in the ratio 1:15 for characterisation.

## 3. Characterisation

### 3.1. UV–vis spectroscopy

The absorption spectra of the synthesised samples were obtained using Perkin Elmer lambda 25 UV–vis spectrophotometer in the 200–700 nm wavelength ranges.

### 3.2. Transmission electron microscopy (TEM)

Transmission electron microscopy was used to observe the size, shape, and morphology of the synthesised nanoparticles. A drop of a diluted specimen was mounted on carbon coated copper grid and placed in a JOEL JEM 2100 (TEM) operating at the voltage of 200 KV.

### 3.3. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra were measured using a Perkin Elmer spectrum, one FTIR spectrometer equipped with the universal ATR sampling accessory. The measurements were done in the transmission mode within a 4000–400 $cm^{-1}$ range and 4 $cm^{-1}$ resolution maintaining a total of 50 scans for each sample analysed.

## 4. Results and discussion

### 4.1. UV–vis spectroscopic analysis

In this reaction, cellulose extracted from water hyacinth shoot acted as both reducing and stabilising agent. The colour of the solution in the reaction flask changed from white to intense brown within 5 min for the reaction at pH 11 (Fig. 1a inset). However, for the reaction at pH 8 and 4, a gradual development of the brown colour was observed within 30 min and 6 h respectively. The instant change in the colour of the solution at pH 11 indicated that the rate of reduction was faster at this pH compared to those at lower pHs. The UV–vis spectra shown in Figs. 2–4 depict the surface plasmon resonance (SPR) peaks of the as-synthesised C–Ag-NPs at pH 4, 8, and 11 respectively. The spectra confirmed that the rate of the silver nanoparticles is slowest in the acidic medium. At pH 4 (Fig. 2)