Carbohydrate Polymers 92 (2013) 1402–1407

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Stabilisation of silver and copper nanoparticles in a chemically modified chitosan matrix

Anand D. Tiwari, Ajay K. Mishra*, Shivani B. Mishra, Alex T. Kuvarega, Bhekie B. Mamba

Department of Applied Chemistry, University of Johannesburg, P.O. Box 17011, Doornfontein 2028, South Africa

ARTICLE INFO

Article history:
Received 3 August 2012
Received in revised form 3 October 2012
Accepted 4 October 2012
Available online 12 October 2012

Keywords:
Stabilisation
Silver
Copper
Nanoparticle
Chitosan
Optical property

ABSTRACT

This work describes the stabilisation of silver and copper nanoparticles in chemically modified chitosan colloidal solution. Chitosan-N-2-methylidene-hydroxy-pyridine-6-methylidene hydroxy thiocarbohydrazide (CSPTH) was used as a stabilising and reducing agent for silver and copper nanoparticles. The modified chitosan derivatives and the synthesised nanoparticles were characterised by Fourier transform infrared (FT-IR) spectroscopy, Ultraviolet–visible (UV–Vis) spectroscopy and X-ray diffraction (XRD). Particle size, morphology and segregation of the nanoparticles were determined by transmission electron microscopy (TEM). The size of the nanoparticles was found to be less than 20 nm and 50 nm for silver and copper nanoparticles, respectively. These nanoparticles were stabilised in a chemically modified chitosan solution and their properties were studied using fluorescence spectroscopy, photoluminescence spectroscopy and surface-enhanced Raman scattering (SERS). The optical properties of silver nanoparticles in surface plasmon band (SPB) were enhanced at 407 nm compared to those of copper nanoparticles. Fluorescence (400 nm and 756 nm), photoluminescence (450 and 504 nm) and Raman scattering (1382 and 1581 cm^{-1}) properties for the copper nanoparticles were superior to those of the silver nanoparticles.

1. Introduction

The synthesis of metal nanoparticles is a subject of current interest due to their unique properties and promising applications (Cobley, Rycenga, Zhou, Li, & Xia, 2009; Li, Camargo, Lu, & Xia, 2009; Sharma et al., 2009; Sun & Xia, 2002; Yavuz et al., 2009). The synthetic procedure for fabricating metal nanoparticles can be divided into two stages: the reduction of metal salts and the capping by a protective agent. Capping prevents the nanoparticles from aggregation thus allowing segregation of the metal nanoparticles (Quiros et al., 2002). Among the many metal nanoparticles, silver nanoparticles (AgNPs) have received considerable attention due to their attractive physico-chemical properties and their proven antibacterial properties against a wide range of microorganisms (Oka, Tomioka, Tomita, Mishino, & Veda, 1994; Oloffs et al., 1994).

Nano-silver can be modified for better efficiency in diverse medicine and life sciences applications such as drug manufacturing advancement, protein detection and gene delivery (Geddes et al., 2003; Mahmoudi, Simchi, Imani, Milani, & Stroeve, 2008). The copper metal fabrication of miniaturised nano-devices that integrate electronic, photonic, chemical and biological features is important for future electronic and sensing devices (Sashiwa & Aiba, 2004). Surface plasmon band (SPB) sensors are widely used for biosensing, especially as affinity biosensors (Kadir, Patrick, & Geddes, 2006). The intrinsic properties of metal nanoparticles are mainly governed by their sizes, shape, composition, crystallinity, and structure. The requirement for LSPR (localised surface plasmon resonance) is a large negative real and a small imaginary dielectric function. A number of metals (i.e. Li, Na, Al, In, Ga, and Cu) meet this criterion and in theory should support plasmon resonances for at least part of the UV–Vis–NIR region (Bohren & Huffman, 1983; Zeman & Schatz, 1987). However, most of these metals are either unstable, or prone to surface oxidation that can significantly affect their optical properties. As a result of surface oxidation, the plasmonic properties of copper nanoparticles (CuNPs) have not received much attention compared to silver plasmonic properties.

Polymer–metal nanoparticle composites research has received much attention in recent years due to an increased interest in their application in opto-electronics Korchev, Bozack, Slaten, and Mills (2004), nonlinear optical devices Inouye, Tanaka, Tanahashi, Hattori, and Nakatsuka (2000) and colour filters (Dirix, Bastiaansen, Caseri, & Smith, 1999). The size-dependent electronic and optical properties of the nanoparticles inbuilt with the optical transparency and mechanical stability of the polymer films signify their importance in many applications. Among the wide variety of polymer matrices, biopolymers are often the first choice as they are naturally available, cheaper as well as easy to synthesise and modify for various applications and more importantly, they are

---

* Corresponding author. Tel.: +27 011 559 6180; fax: +27 011 559 6425.
E-mail address: amishra@uj.ac.za (A.K. Mishra).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.10.008

environmentally friendly. Moreover, the availability of oxygen-rich functional groups of the biopolymers and their affinity towards metals make them an ideal matrix for the stabilisation of nanoparticles (Liu, He, Durham, Zhao, & Roberts, 2008). Biopolymers such as cellulose, starch and alginic acid have been previously used for the stabilisation of nanoparticles (Brayner, Vaulay, Fiévet, & Coradin, 2007; He, Kunitake, & Nakao, 2003; Raveendran, Fu, & Wallen, 2003). Chitosan, isolated from chitin, is the linear and partly acetylated (1–4)-2-amino-2-deoxy-<beta>-D-glucan (Muzzarelli, 1977, 2012), particularly well known for metal ion chelation (Muzzarelli, 2011) and for biological applications (Muzzarelli, 2009), as it is hydrophilic, biocompatible, biodegradable, non-antigenic and non-toxic (Muzzarelli, 2010).

In addition, chitosan is known to facilitate drug delivery across cellular barriers and transiently open the tight junctions between epithelial cells (Dodane, Khan, & Merwin, 1999). Few reports are available on synthesis of metal nanoparticles of smaller size in chemically modified chitosan matrices for various prominent applications (Bodnar, Hartmann, & Borbely, 2005; Ding, Xia, & Zhang, 2006; Sashiwa & Aiba, 2004). The green synthesis of gold nanoparticles has been used previously on the derivative of chitosan which has the functional group amine as reducing agent and thiocarbamide as stabiliser for the nanoparticles embedded in the film or as colloidal solution (Tiwari, Mishra, Mishra, Arotiba, & Mamba, 2011).

The objective of this study was to synthesise metal nanoparticles such as AgNPs and CuNPs in an aqueous solution. Chemically modified chitosan was used as a reducing and capping or stabilising agent for the metal nanoparticles. The morphology and stability of the metal nanoparticles were examined using transmission electron microscopy (TEM) and UV–Vis spectroscopy. The possible capping mechanism of the nanoparticle was monitored by the Fourier transform infra-red spectroscopy (FT-IR). Optical and spectroscopy properties such as SPB, fluorescence, photoluminescence and surface enhanced Raman scattering (SERS) of the nanoparticles were also studied.

2. Materials and methods

2.1. Materials

All compounds were of analytical grade and used as received. Acetic acid (99.7%), silver nitrate ($AgNO_3$) (99.9%) and copper dichloride ($CuCl_2{\cdot}2H_2O$) (99.0%) were purchased from Merck (South Africa) and thiocarbohydrazide (99.0% synthetic grade) was obtained from Sigma Aldrich (South Africa). Pyridine 2,6-dicarboxylic acid sourced from Merck (South Africa) was esterified using methanol to form pyridine 2,6-dimethylcarboxylate. Chitosan (75% deacetylated, low molecular weight) was purchased from Sigma–Aldrich (South Africa), and deionised (DI) water was used throughout the experiment.

2.2. Synthesis

2.2.1. Chitosan-N-2-methylidene-hydroxy-pyridine-6-methylidene-hydroxy-thiocarbohydrazide (CSPTH)

Modified chitosan (CSPTH) was synthesised, using a previously reported procedure (Tiwari, Mishra, Mishra, Arotiba, et al., 2011). The synthesis of CSPTH is summarised as follows: chitosan (3.0 g) was dissolved in 2% acetic acid (200 mL). A solution of pyridine-2,6 dimethylcarboxylate (12.5 g in 100 mL ethanol) was added to the chitosan solution and refluxed for 8 h. The mixture was kept overnight under ambient conditions. A gel was formed after neutralisation using 1 mM NaOH and this was completely precipitated in acetone. The filtered gel was dried in hot air (oven) at 60 °C for 3 h. The yield of the dried white solid product was 2.50 g (80%). The product was treated again with thiocarbohydrazide. The dried product (2.0 g) was dissolved in 4% acetic acid (100 mL) and 5.0 g thiocarbohydrazide in 2% acetic acid (200 mL). Both solutions were mixed and refluxed for 24 h. The product was neutralised using 1 mM NaOH and after this the gel formed was precipitated in acetone. The solid precipitate was dried in an oven at the 60 °C for 3 h. A brown yellowish solid product [1.25 g (75%)] was obtained. The structure of the produced modified chitosan derivative is shown in Fig. 1.

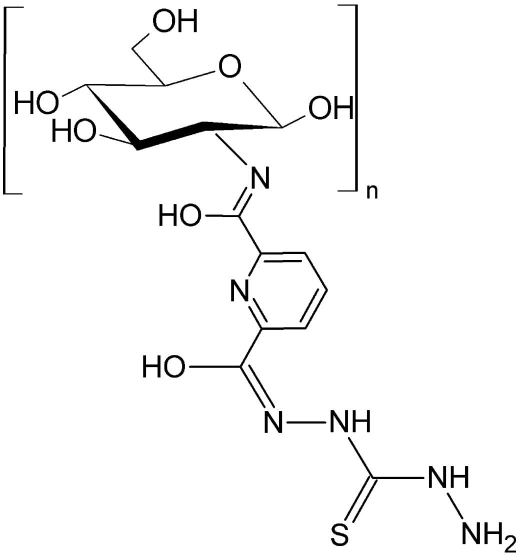

Fig. 1. Chemical structure of the chitosan-N-2-methylidene-hydroxy-pyridine-6-methylidene hydroxy thiocarbohydrazide (CSPTH).

2.2.2. Synthesis of silver and copper nanoparticles on the chemically modified chitosan biopolymer matrix (CSPTH-AgNPs/CuNPs)

Chemically modified chitosan (CSPTH) solutions (10 mg/mL) were prepared in 2% aqueous acetic acid w/v ratio. Silver nitrate and copper dichloride hydrate solutions (10 mM) were added to the modified chitosan biopolymer matrix (CSPTH) in 1:1 (v/v) ratio. The colloidal metal nanoparticle and modified chitosan biopolymer solution were heated at 60 °C for 2 h and then stirred for 1 h, after which the temperature was reduced to 30 °C. The acronyms CSPTH, CSPTH-AgNPs, and CSPTH-CuNPs were given to the modified chitosan biopolymers as stabilised silver and copper nanoparticles, respectively.

2.3. Characterisation

UV–Vis absorption spectroscopy measurements were performed on a Shimadzu UV-2450 PC dual-beam spectrophotometer using 1 cm path length quartz cuvettes. Spectra were collected for the aqueous solutions within the 200–800 nm spectral range. FTIR measurements of the biopolymer matrix with nanoparticles and their precursors were recorded on an FT-IR spectrophotometer (Perkin Elmer spectrum 100) equipped with a diamond/ZnSe universal ATR sampling accessory. Spectra were obtained in transmission mode over the 4000 cm^{-1} to 550 cm^{-1} wave-number region at a resolution of 4 cm^{-1} averaging 16 scans. The polymer film samples were prepared on glass slides and dried in the oven at 60 °C before being scraped off with a razor blade. Fluorescence spectroscopy was recorded on a Perkin Elmer LS 45 fluorescence spectrometer equipped with FL WinLab™ Software. An excitation