



In situ preparation of silver nanocomposites on cellulosic fibers – Microwave vs. conventional heating



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ABSTRACT

A green approach for the preparation of silver nanocomposites on viscose fibers using microwave and conventional heating is presented. Reduction of silver nitrate is induced by addition of 6-O chitosan sulfate (S-Chi) in aqueous media which provides steric protection and electrostatic stabilization to prevent agglomeration of the nanoparticles. The particles are formed in close spatial proximity to the fibers and adsorption of the particles via structural similarity takes place to create silver nanocomposites. All nanocomposites have been subjected to antimicrobial tests and high antimicrobial activity toward *Escherichia coli* bacteria has been determined. Further, the nanocomposites are characterized using different analytical techniques which reveal very similar results for both heating techniques. The only significant difference is observed concerning the shape of the nanoparticles on the viscose fibers which are slightly elongated for the microwave method in comparison to spheres observed by conventional heating. Therefore, detailed investigations on the formation of colloidal silver nanoparticles have been performed, comparing microwave dielectric and conventional heating at the exact same temperature and reaction times. These experiments resulted in nearly identical nanoparticle shape and size for both heating methods as demonstrated by dynamic light scattering, UV–vis spectroscopy and transmission electron microscopy. A wide range of parameters has been varied (temperature, AgNO₃ to S-Chi ratio, reaction time, and stirring speed) to study the nanoparticle formation under microwave and conventional conditions. No evidence for the existence of so-called specific microwave effects was obtained.

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1. Introduction

In the past decade, the demands on textile fibers have significantly increased. Large efforts have been made to implement additional functionalities on fibers which can be summarized by the term smart textiles. Such smart textiles can offer thermoresponsive behavior, conductivity, self cleaning effects, or magnetism to mention only a few (Daoud, Xin, & Zhang, 2005; Gonçalves, Marques, Tito Trindade, Neto, & Gandini, 2006; Malmström & Carlmark,

2012; Small & Johnston, 2009; Sun et al., 2008). While conducting fibers used in heating mats (Niemz, Riedel, & Knobelsdorf, 2009) provide a high degree of safety and durability in comparison to older devices based on iron wires, other approaches aim at modifying fibers with nanoparticles (NPs) exhibiting specific properties. For the treatment of chronic skin diseases for instance, fibers loaded with ZnO NPs have shown promising results (Boateng, Matthews, Stevens, & Eccleston, 2008) while the incorporation of silver NPs has proven to induce antimicrobial activity (Dastjerdi & Montazer, 2010; Hebeish et al., 2011; Johnston & Nilsson, 2012; Kelly & Johnston, 2011; Klemencic, Simoncic, Tomsic, & Orel, 2010; Lottermoser, 1903; Marambio-Jones & Hoek, 2010; Pivec et al., 2012; Ravindra, Mohan, Reddy, & Raju, 2010; Ristic et al., 2011; Sharma, Yngard, & Lin, 2009; Simoncic, 2010; Smiechowicz, Kulpinski, Niekraszewicz, & Bacciarelli, 2011; Tang et al., 2011; Travan et al., 2009; Vijayaraghavan & Nalini, 2010; Wendler, Meister, Montigny, & Wagener, 2007). Currently, there

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are numerous textiles on the market, in particular sportswear and socks, which have been treated with silver NPs in order to prevent bad odors stemming from bacterial growth as well as several medical products for wound care (e.g. AQUACEL[®], SILVERCEL[™]). In most of the cases, the manufacturing process involves a separate silver NP synthesis step followed by a loading of the particles onto the fibers using crosslinking agents or adsorption e.g. via electrostatic interactions. In the course of the silver NP synthesis, the reduction of silver (I) species is usually achieved using an excess amount of an external reducing agent such as NaBH₄, hydrazine or dimethylformamide using elevated temperatures (Dahl, Maddux, & Hutchison, 2007; Raveendran, Fua, & Wallen, 2006). The high costs and the environmental impact caused by the use of reducing agents can be avoided by replacement with reducing polysaccharides for silver NP synthesis (Donati et al., 2009; Kemp et al., 2009; Kemp & Linhardt, 2009; Raveendran, Fu, & Wallen, 2003; Sharma et al., 2009; Travan et al., 2009). In order to prevent aggregation, stabilizing and capping agents have to be employed which can be of environmental concern due to the toxic nature of the used stabilizers. Polysaccharides offer a wide range of structural diversity, they are renewable and many congeners are soluble in water; factors which are able to clearly improve the environmental performance. As a consequence, many different types of polysaccharides have been used for silver nanoparticle synthesis using conventional heating methods (Dahl et al., 2007; Donati et al., 2009; Kemp et al., 2009; Kemp & Linhardt, 2009; Sharma et al., 2009; Travan et al., 2009; Vijayaraghavan & Nalini, 2010). Nevertheless, these methods have proven to be inefficient in terms of energy input and have a quite modest life cycle assessment. A more elegant and efficient way is to use microwave heating in the course of the NP synthesis.

During last decade microwave heating has received considerable attention as a promising method for the synthesis of nanomaterials (Klinowski, Paz, Silva, & Rocha, 2011; Polshettiwar, Nadagouda, & Varma, 2009; Tompsett, Conner, & Yngvesson, 2006; Vanetsev & Tretyakov, 2007). Among the different types of nanomaterials, the microwave-assisted synthesis of colloidal inorganic nanocrystals has become an area of intense interest, growing significantly over the past few years as a powerful alternative to more traditional synthetic methods (Baghbanzadeh, Carbone, Cozzoli, & Kappe, 2011; Bilecka & Niederberger, 2010; Tsuji, Hashimoto, Nishizawa, Kubokawa, & Tsuji, 2005). The motivation for the use of microwave energy has mainly been to design processes with dramatically reduced reaction times, higher yields, and improved materials properties. If efficient agitation can be ensured (Herrero, Kremsner, & Kappe, 2008), and the temperature is monitored/controlled by fast-responding internal probes (Herrero et al., 2008; Obermayer & Kappe, 2010), rapid “in core” volumetric heating without significant temperature gradients will occur. Similar to the situation for many other metallic NPs, microwave dielectric heating is a well established technique for the synthesis of silver NPs (Chen, Wang, Zhang, & Jin, 2008; Dzido & Jarzebski, 2011; Gao, Lu, & Komarneni, 2005; Komarneni, Li, Newalkar, Katsuki, & Bhalla, 2002; Kundu, Wang, & Liang, 2009; Li et al., 2012; Liu, Huang, Chu, & Ko, 2005; Liu, Tian, Wang, & Sun, 2011; Luo & Sun, 2007; Nadagouda, Speth, & Varma, 2011; Nadagouda & Varma, 2008; Tsuji et al., 2006, 2010; Zhu & Zhu, 2006). Simple reducing sugars such as glucose, maltose and sucrose have often been used for the microwave assisted synthesis of silver NPs; reports on polysaccharides involve carboxymethyl cellulose (CMC), starch and β -cyclodextrins which can act as stabilizers and reductants in the course of the silver NP preparation have also appeared in the literature (Virikutyte & Varma, 2011). Despite the large number of reports that have described the microwave-assisted synthesis of silver NPs, the real role of microwave irradiation in these processes is still a controversial question. In most of the

published examples, not only were the preparations more rapid using microwave technology, but in addition a significant difference between the materials obtained by microwave dielectric heating and conventional heating was observed. Unfortunately, in many of these reports a domestic microwave oven has been utilized, which makes controlling of reaction temperature virtually impossible. Independent of the employed microwave instrument, it has been suggested that these discrepancies were due to the occurrence of some type of “microwave effect”, including claims of selective heating (Nishioka et al., 2011a; Silva & Unali, 2011; Wada et al., 2007; Xia et al., 2008), the elimination of wall effects (Horikoshi, Abe, Torigoe, Abe, & Serpone, 2010; Nishioka et al., 2011b; Tsukahara, Nakamura, Kobayashi & Wada, 2006), or apparent nonthermal effects (Baruwati, Polshettiwar, & Varma, 2009).

In this manuscript we investigate the in situ preparation of silver NPs on cellulosic fibers to create silver cellulose nanocomposites. Toward this goal we utilized silver nitrate as silver precursor and 6-O chitosan sulfate (S-Chi) as a reducing and capping agent. The synthesis is performed in aqueous medium using controlled sealed vessel single-mode microwave technology. The formation of silver NPs under microwave dielectric heating has been studied in detail and an in-depth comparison between the materials obtained by conventional heating and microwave dielectric heating was performed.

2. Experimental

2.1. Materials

Sulfated chitosan (S-Chi) ($M_r \sim 20,000$ g/mol) was synthesized in our labs according to a published literature procedure (Fasl et al., 2010). The degree of deacetylation (DA) was determined conductometrically and yielded a DA of 82.5%. The degree of sulfate substitution (DS) was determined to be 0.86 based on sulfur content determinations using ICP/MS. IR (KBr, cm⁻¹): 3440 ν_s (O–H), 2800–2900 ν_s (C–H), 1625 ν_s (C=O), 1525 ν_s (NH₂), 1218 ν_{asym} (O=S=O), 1063 ν_{sym} (O=S=O), 796 ν_s (C–O–S), ¹³C NMR (D₂O, 75.4677 MHz, ppm): δ 55.18 (C-2), 66.54 (C-6), 72.67 (C-5), 73.02 (C-4), 74.76 (C-3), 101.72 (C-1).

Silver nitrate (99%) was purchased from Merck and used without further purification. Viscose fibers were obtained from Lenzing AG (Lenzing, Austria). Bidistilled water was used in all the experiments

2.2. Microwave instrumentation

Microwave irradiation experiments were performed using a dedicated single-mode microwave reactor (Monowave 300, Anton Paar, Graz, Austria) with 850 W maximum magnetron output power, allowing sealed vessel processing up to 300 °C and 30 bar of pressure in combination with an efficient magnetic stirring system. For the syntheses described herein, the reaction temperature is monitored by an internal fiber-optic (FO) temperature probe (ruby thermometer).

Some experiments were additionally conducted in a CEM Discover (Matthews, NC, USA) single mode microwave reactor equipped with a fiber-optic (FO) probe provided by the instrument manufacturer for directly controlling and monitoring the internal reaction temperature (Hosseini, Stiasni, Barbieri & Kappe, 2007). These experiments were performed in constant power mode under reflux conditions and magnetic stirring, monitoring the temperature of the reaction mixture by the FO sensor. A constant magnetron power of 28 W was used to achieve reflux temperature (100 °C) and also ensured a steady reflux of the reaction mixture for the duration of the experiment.

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