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Facile and green synthesis of silver nanoparticles using oxidized pectin

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ABSTRACT

In the current work, an alternative route for facile synthesis of nanosilver is reported. Oxidized pectin has been used as the reducing agent as well as the stabilizing agent, resulting in the formation of oxidized pectin-nanosilver (OP-NS) core sheath nanohydrogels. The effect of reaction parameters on the synthesized nanoparticles is investigated. The structural and morphological features have been analyzed using X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) respectively. The crystal size of the synthesized nanosilver was calculated to be 28.76 nm. While the average size of the core sheath structure varied from 289 nm to 540 nm, the size of the silver nanoparticle entities at the core varied from 100 nm to 180 nm, with variation in reaction time. From the morphological examination, it could be seen that flower like nanostructures are formed with nanosilver in the core surrounded by a polymeric halo.

1. Introduction

In recent years, nanotechnology has become a by-word in all walks of life. Nanocomposites constituting of polymers and metals, especially silver, have an important role to play in this aspect. Interest has veered towards the development of silver nanocomposites due to their diverse range of applications, e.g. in healthcare, sensors [1], catalysis [2], plasmonic devices [3], conducting materials [4,5], and food packaging [6,7]. Nanosilver is particularly useful in preventing wound infection due to its excellent antimicrobial activity [8,9]. Indeed, silver and its compounds have traditionally been used through the millennia to treat wounds [10,11].

Polysaccharides are abundant in nature and have found application in a wide range of industries. Pectin is an anionic polysaccharide, poly(1,4-galacturonic acid), found in the cell walls of terrestrial plants. It is a hydrogel by nature and is therefore attractive for use as a gelling agent [12] and in wound care devices. The presence of groups like $-OH$, $-COOH$ and $-COOCH_3$ on the backbone of the pectin chain renders it readily susceptible to functionalization. Pectin and alkenyl succinic anhydride were used for the controlled deposition of nanoparticles that led to a high impact on the substrate surface properties of paper [13]. Pectin/chitosan/Eudragit® RS ternary films were developed for sigmoidal drug delivery [14]. Takei et al. oxidized citrus pectin and coupled it with an anticancer drug, doxorubicin [15]. It was suggested by Cipriani & co-workers that chemically sulfated citrus pectin possesses good antithrombogenic properties and could be used as wound dressings [16]. Coacervation between pectin and gelatin could be helpful for controlled drug delivery [17]. In our previous work, we reported the in-situ crosslinking between oxidized citrus pectin and gelatin and these matrices could potentially be used in wound dressings [18].

The synthesis of nanosilver has been a subject of enormous interest in recent years. Eid & Azzazy reported the controlled synthesis of hollow flower like silver nanostructures from $AgNO_3$ with the aid of dextrose, trisodium citrate and sodium hydroxide [19]. Various reducing sugars like glucose, fructose and sucrose have been used to synthesize silver nanoparticles, both with and without stabilizing agents [20–22]. The fungus *Trichoderma viride* was used to reduce $AgNO_3$ to AgNPs through an extracellular biosynthesis method [23]. Hydrazine hydrate was employed as the reducing agent by several researchers to synthesize AgNPs from $AgNO_3$ [3,24]. Radiolytic synthesis of AgNPs has also been reported. Kristić et al. investigated the efficacy of chitosan/PVA blends as capping agents for AgNPs synthesized by gamma irradiation [25]. Carboxymethyl chitosan (CMCTS)/gelatin/nanosilver hydrogels were developed by radiation induced reduction and crosslinking [26]. These gels could potentially be used as wound dressings. CMCTS serves as a reducing agent as well as a stabilizing agent. Gamma radiation has been used to prepare nanosilver nanohydrogels of poly(methacrylic acid) where the radiation performs two functions — polymerization of the monomer and reduction of silver ions to nanosilver [27]. In our previous work, we reported the fabrication of OP and gelatin crosslinked matrices [18]. Incorporation of silver nanoparticles into these matrices can lead to the development of potential wound care devices. Obviating the ex situ reduction of silver salt to silver as reported in other methods, we aim to develop an in situ reduction approach wherein the silver nanoparticles would be synthesized within the system, thus reducing the cytotoxicity.

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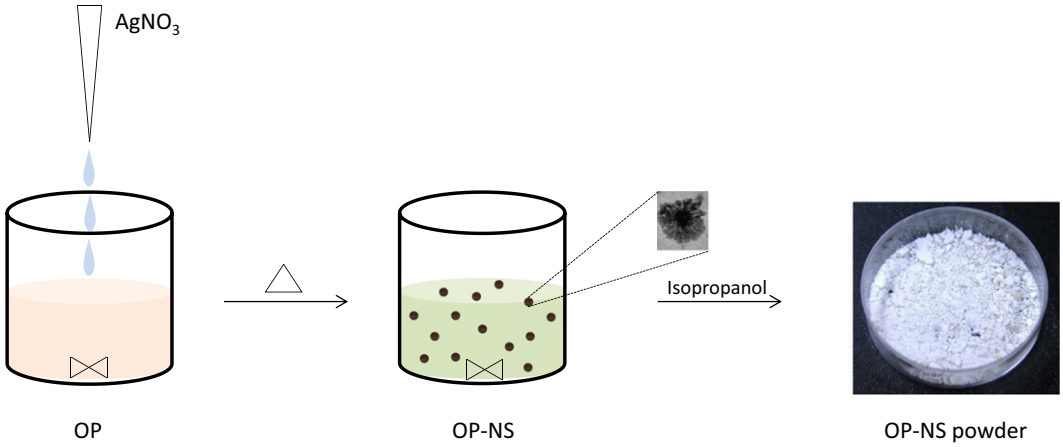

Fig. 1. Schematic representation of OP-NS nanohydrogel synthesis.

This sort of approach has not been reported earlier to the best of the authors' knowledge.

In the present study, we report the synthesis and characterization of stable silver nanoparticles by reduction of silver nitrate with oxidized pectin. These nanoparticles are embedded in the oxidized pectin matrix and therefore can be termed as nanohydrogels. Core sheath structures with silver nanoparticles at the core and oxidized pectin as the sheath are produced.

2. Experimental

2.1. Materials

Citrus pectin (M_w ~ 30,000 g/mol, degree of esterification ~ 72%) and isopropanol were purchased from CDH Fine Chemicals, India and Fisher Scientific, India, respectively. Silver nitrate and periodic acid were procured from Merck Chemicals, India. All other chemicals used were of analytical grade. Millipore water was used for all the experiments.

2.2. Oxidation of pectin by periodic acid

The periodate oxidation of pectin was carried out according to the procedure reported in our earlier work [9]. 3 mL of 0.5 M periodic acid was added to a 2% solution of pectin in distilled water. The pH of the medium was adjusted to 3.5 using dilute hydrochloric acid and sodium bicarbonate solution. The reaction was allowed to take place at 40°C under constant stirring for 16 h. To prevent autooxidation due to light, the reaction vessel was wrapped in several layers of aluminum foil and the reaction was carried out in the dark. At the end of the reaction, oxidized pectin (OP) was precipitated out using excess isopropanol, separated by vacuum filtration and dried in vacuum at 60 °C. The aldehyde content of OP thus prepared is 2.1 mmol/g [9].

2.3. Reduction of silver nitrate by oxidized pectin

1 wt.% of $AgNO_3$ was added to a 2.8% solution of OP (initial aldehyde content 2.1 mmol/g). The reaction was allowed to continue for predetermined intervals of time under constant stirring. The temperature was maintained at 60 °C. The reaction vessel was wrapped in several layers of aluminum foil to prevent autooxidation of $AgNO_3$ due to light. At the end of the reaction, oxidized pectin-nanosilver (OP-NS) was precipitated from the solution using excess isopropanol. Subsequently, it was separated out by vacuum filtration and dried in vacuum at 60 °C.

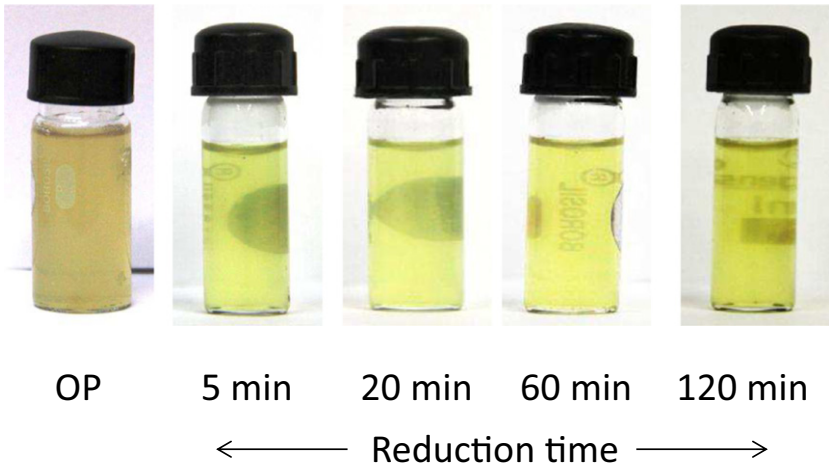

Fig. 2. Appearance of OP-NS solutions with varying reaction time. (a) 5 min; (b) 20 min; (c) 60 min; (d) 120 min. Initial aldehyde content 2.1 mmol/g; reaction temperature 60 °C; pH 4.