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Short Communication

Solid-state synthesis of silver nanowires using biopolymer thin films

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ABSTRACT

In this paper, we describe a novel method of silver nanowire (AgNW) synthesis. Silver nanoparticles (AgNPs) were synthesized under ambient conditions by a chitosan/chitin-based method. These crystalline AgNPs then served as seeds for the solid-state formation of AgNWs within a drop-cast chitosan/chitin thin film. To the best of our knowledge, this is the first report of AgNW growth on a bio-polymer thin film. Chemical analysis demonstrated that AgNPs and AgNWs produced by this synthetic process have distinct interactions with polysaccharide polymers, and unlike AgNWs produced by other methods, the AgNWs formed in the chitin/chitosan matrix display an irregular twisted morphology. The flexible AgNW/chitosan nanocomposite material is conductive, and we incorporate this new material into a peroxide sensor to demonstrate of its potential applications in chemical sensing devices.

1. Introduction

Metallic nanoparticles have enhanced and often unique catalytic [1–3] and physical properties [4,5]. Silver and other noble metal nanomaterials are of particular interest and importance because of their unique electronic, optical, and biological activities [6–9]. Silver nanomaterials are synthesized by various methods including photochemical approaches that utilize the light-sensitive aspects of precursor materials, standard chemical approaches using citrate or borate reducing agents, and "green" approaches that use a biological material in at least one step of the synthesis process [10–12]. Nanoparticle synthetic processes involve several steps that include the reduction of a metal ion in solution into an insoluble precipitate; the formation of a nucleation site either from individual precipitated nanoparticles or by the aggregation of these particles; and the stabilization of the nascent particle, which is followed by the nanoparticle growth [10,11,13,14]. Control of each step enables the control over the size, crystallinity, and morphology of the nanomaterial products from specific synthetic reactions [9–11,14,15].

Several green synthetic methods for generating silver nanoparticles (AgNPs) have also been developed, which use biomolecules such as proteins and polysaccharides to stabilize and promote nucleation [14,16]. Environmentally friendly "green" methods of nanoparticle synthesis often take advantage of biomimetic self-assembling systems or use catalytic elements such as living cells or biopolymers [13,17,18]. A polysaccharide AgNP synthetic method uses starch as the capping agent and monomeric β-D-glucose as the reducing agent in an aqueous solution. Extracts of various plants and microorganisms have also been demonstrated to promote the formation of AgNPs by the participation of protein/peptides in the reduction, nucleation, and stabilization steps [13,17]. Recently, a chitosan photochemical synthetic method has been described that enables the formation of AgNPs of different morphologies and crystallinities in a wavelength-dependent manner [10]. Synthetic processes that produce highly anisotropically shaped particles are especially desirable in many applications because of the enhancement of specific optical properties such as surface plasmon resonance [9,12].

Silver nanowires (AgNWs) are synthesized primarily by polyol methods, which are energetically and environmentally costly [13,16,19,20]. Recently, there has been an increased interest in the identification and fabrication of novel nanocomposite materials, which consist of metallic or metal oxide nanoparticles and another nanoscale material [13,21]. By combining the properties of two nanomaterials, there is often a synergetic effect that extends, enhances, and/or increases the properties of one or more of the constituents of the nanocomposite [22–24]. However, fabrication methods of such multicomponent nanomaterials often rely on a multistep process, relying on post-fabrication mixing or the combination of individual nanoscale components, which often results in a product that is not ideal in composition and/or non-scalable

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[25,26]. In this paper, we describe a novel, single-step process that promotes the self-growth of AgNWs within thin films of the polysaccharide chitin/chitosan. To the best of our knowledge, this is the first report on AgNW growth in solid state. The resulting material is a flexible, conductive biopolymer nanocomposite that has potential in several applications including chemical sensors. Here, we demonstrate the detection of hydrogen peroxide on AgNW/chitosan films by non-enzymatic electrochemistry.

2. Results and discussion

2.1. AgNP synthesis in a chitosan solution

The polysaccharide chitosan is a polymer of β (1 → 4)-linked D-glucosamine subunits [27–29] that has been demonstrated to synthesize AgNPs in aqueous solutions [10,30]. To synthesize our AgNPs, we produced 5-mM $AgNO_3$ in a 1% chitosan aqueous solution containing 1% acetic acid; this solution was sonicated for 4 h resulting in a characteristic color change from clear to opaque solution with a purple/pink hue (Fig. 1A). The pH of the chitosan/$AgNO_3$ solution was 5 during the AgNP synthesis reaction. The maintenance of pH at above 5 is crucial for the synthesis of AgNPs; chitosan/$AgNO_3$ solutions with a pH of 3 or lower had no AgNP formation (Fig. 2A, left); however, the increase in the pH of the chitosan/$AgNO_3$ solution to 9 resulted in the formation of a gel state of the chitosan mixture that had the characteristic purple hue of AgNP formation (Fig. 2A, right). SEM analysis of these AgNPs showed the formation of rod-shaped AgNPs instead of cuboidal AgNPs (Fig. 2B). We confirmed the presence of AgNPs by UV–Vis spectrometry, in which a characteristic AgNP absorption peak appeared at 400–550 nm (Fig. 1B) [13,15].

By performing Fourier-transform infrared (FTIR) spectroscopy, we defined the specific functional groups within the chitosan polymer that are engaged in the AgNP synthetic reaction. Chitosan had FTIR absorption peaks at 3447 and 3294 cm^{-1} due to the overlapping of hydroxyl (O–H) and amine (N–H) stretching bands, 1657 and 1584 cm^{-1} due to amine (N–H) bending, and 1374 cm^{-1} due to the C–H of the primary alcohol group in chitosan (Fig. 1C, blue line). In the FTIR spectrum of chitosan solution containing $AgNO_3$, the absorption bands at 1657 and 1584 cm^{-1} that represent chitosan $-NH_2$ groups disappeared and were replaced by a single peak at 1600 cm^{-1}, which demonstrates the reaction of the Ag^+ ion with the amine group (–NH) during and/or after the reduction to metallic silver (Fig. 1C, orange line); whether this represents a step in the nucleation process and/or a component of the stabilization of the nascent AgNPs remains unclear. However, we observed significant alteration in the shape and peak positions of $-NH_2$ and –OH groups at 3447 cm^{-1}, suggesting that there was an additional contribution of the amine group in this process, possibly in the stabilization of the nanoparticles [31]. TEM micrographs showed that the AgNPs produced by this method were cubical (Fig. 1D).

2.2. Chitosan thin film-supported AgNW synthesis

The chitosan/AgNP solution was drop cast onto a clean glass substrate, which upon drying produced a 10- to 20-μm purplish

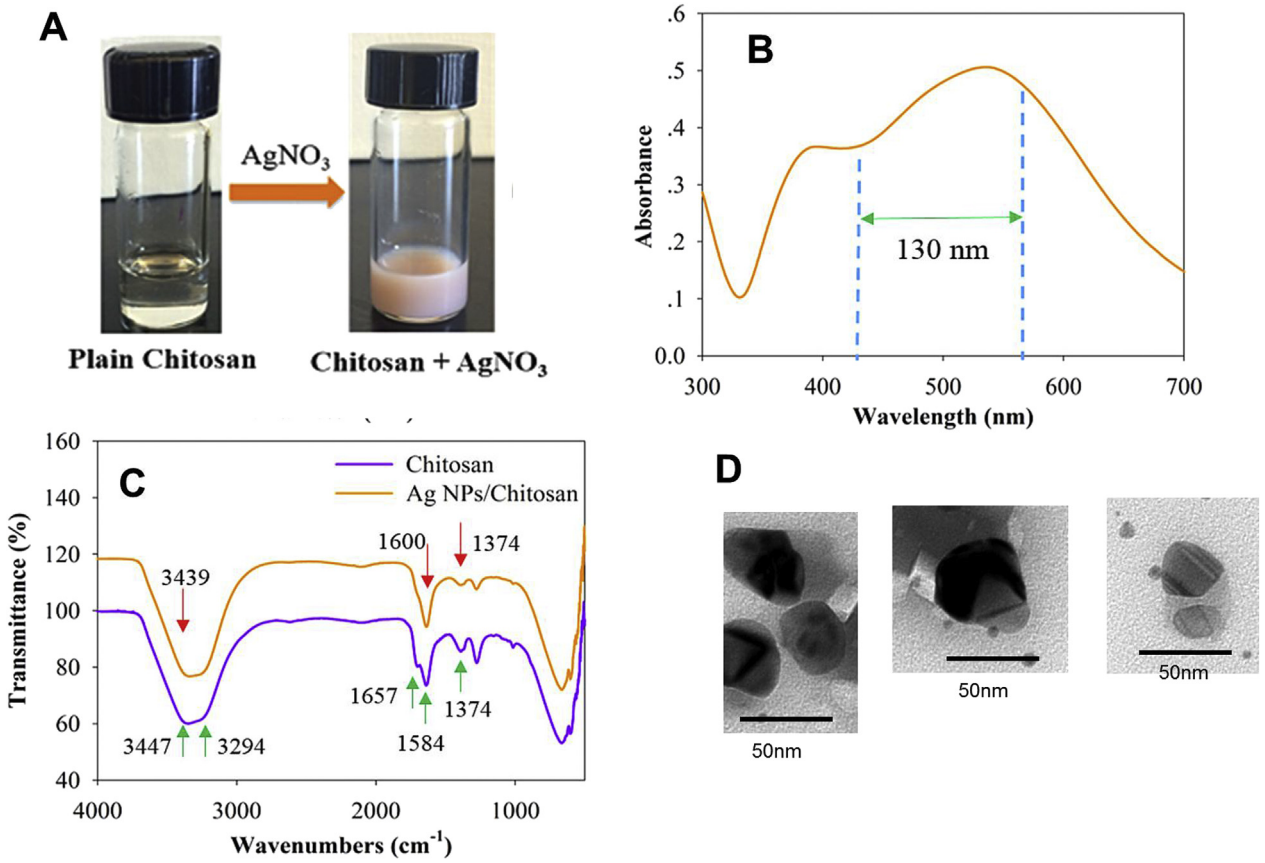

Fig. 1. (A) Vials containing chitin solution before (left) and after the addition of $AgNO_3$ (right), note the change in the color of the solution from clear to opaque with a purple hue. (B) UV–visible absorption spectra of AgNPs stabilized in chitosan. (C). FTIR spectra of AgNPs stabilized in chitosan (orange) and pure chitosan (blue). (D) TEM micrographs of cuboidal AgNPs produced by chitosan-based synthetic process.