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Review

Polysaccharides templates for assembly of nanosilver

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ABSTRACT

Polysaccharides are particularly attractive in biomedical applications due to its biodegradability and biocompatibility. In addition to its ecofriendly effects and easy processing into different hydrogel shapes, made polysaccharides used on a large scale as suitable media for preparation of silver nanoparticles (AgNPs). In spite of, most of polysaccharides are water insoluble, but it has shown to be quite efficient capping agents and/or nanoreactor matrices for production of AgNPs. Several methods have been developed to get the benefit of multi-functionality for polysaccharides' macromolecules in preparation of AgNPs. Therefore, recently, preparation of nanosilver using different polysaccharides have been the focus of an exponentially increasing number of works devoted to develop nanocomposites by blending AgNPs with different polysaccharides matrices. The current review represents a wide survey for the published studies which interested in using of polysaccharides in nanosilver preparations.

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1. Introduction

Noble metal nanoparticles are characterized by unique electronic, optical, mechanical, magnetic and chemical properties rather than the bulk materials become recently the subject of focused research in the last decade. These unique properties are attributed to large volume to surface area ratio which leads manifold applications in solar energy conversion, catalysis, medicine and water treatment for instance (Hutchinson, 2008; Kamat, 2002; Li, Liu, Wang, & Wang, 2001).

Generation of metal nanoparticles includes three main stages, namely the reduction reaction of metal ions to free atoms, nucleation and growth. Recent studies showed that, the reaction kinetics and experimental conditions play important roles for the nucleation and growth stages. Reduction of metal salt precursors to the elemental metal nanoparticles plays a crucial role, and generally requires a reducing agent and a stabilizer one, in order to obtain shape and size controlled metal nanoparticles (MNPs). Therefore, all of afore mentioned methods in the literatures used for synthesis of nanometals become an attractive field for research in order to transform the sized controllable nanoparticles potential

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applications to reality (Knoll & Keilmann, 1999; Sengupta et al., 2005; Wiley, Sun, & Xia, 2007).

A fact has been achieved that the size, morphology, despersibility, and physicochemical properties of the metal NPs are strongly affected by the experimental conditions, reaction kinetics between metal ions with reducer, and stabilizer (Sengupta et al., 2005). Some commonly used chemical reductants for preparation of nanosilver are borohydride, ascorbate, hydrazine, and elemental hydrogen (Ahmadi, Wang, Green, Henglein, & El-Sayed, 1996; Chou & Ren, 2000; Evanoff & Chumanov, 2004; Merga, Wilson, Lynn, Milosavljevic, & Meisel, 2007; Nickel, Castell, Poppl, & Schneider, 2000; Shirtcliffe, Nickel, & Schneider, 1999; Sondi, Goia, & Matijevic, 2003). Some of the commonly used methods for surface protection of MNPs are self-assembled monolayers, as the most popular is citrate and thiol-functionalized organic substrates (Ullman, 1996), encapsulation in H_2O pools of reverse microemulsions (Petit, Lixon, & Pileni, 1993) and dispersion in polymeric matrixes (Hebeish, El-Rafie, Abdel-Mohdy, Abdel-Halim, & Emam, 2010; Zahran, Ahmed, & El-Rafie, 2014a, 2014b).

Polysaccharides, due to their ability for chelating different metal ions it could act as stabilizing agents. The polymer–metal ion complex can then be reduced under different experimental conditions, to produce MNPs with small size and narrow size distribution. Additionally, polysaccharides could also be characterized by good reducibility, as its building blocks contain different functional groups and thus can play the dual roles of NPs generators and protecting agents. This dual function of the polysaccharide can be an advantage in the green and cost effective syntheses of MNPs since it avoids the usage of harmful and toxic chemicals which limited the use of MNPs for biological or medical applications.

1.1. *Silver nanoparticles (AgNPs)*

Different metal nanoparticles (i.e., Ag, Au, Pd, Pt, Rh, Ir, etc.) with diameter more than 10 nm are characterized by high stability due to their chemical inertness, however, when the size decreased to 2–4, they become easily oxidized in air. Different metal nanoparticles could be physically, biologically or chemically prepared in suitable solvent, in the presence of protective/capping/stabilizing agent such like polymers, surfactants or strong coordination ligands.

Controlling the factors which influence shape and size of nanoparticles is of empirical significance to modulate the catalytic, optical and/or biological properties of the manufactured nanometals. Generally, there are two different ways for morphological controlling of precious nanoparticles:(i) template-directed preparation, in which metal ions are reduced and nanoparticles grow within the template, therefore, the shape and sizes of the so-obtained nanoparticles are controlled by the morphological properties of the template; (ii) growth-directed preparation, in which, shape-selective nanometals are prepared by using suitable metal precursor, reducing agent, protecting agent and controlling reaction kinetics.

Silver materials are any silver-containing materials with special activities due to their nano-sized characters. Also nano-silver referred to commercial products which contain metallic silver in size range of 5–50 nm or ionic silver with special medical applications (Panyala, Pena, & Havel, 2008).

An impressive number of methods for synthesizing AgNPs have been described in literatures, as generally AgNPs could be applicable in different medical purposes (medical textiles, cosmetics, pharmaceutical products, etc.) or in other industrial applications (electronics, catalysis, etc.). A new concept referred to green synthesis of AgNPs has recently been introduced, where the used reactants and solvents are described as non-toxic and benign compounds to the environment, and the so-obtained nanosilver colloids could be applicable in different biological purposes (El-Rafie, Ahmed, & Zahran, 2014; Emam, El-Rafie, Ahmed, & Zahran, 2015; Hebeish et al., 2010; Zahran et al., 2014a, 2014b). The chemical reduction of silver salts is one of the most widespread methods used for the synthesis of silver nanoparticles. In this way, the metal salts are dissociated to metal ions, and then reduced by a reducer to form metal nanoparticles that are stabilized by suitable capping agent.

Great numbers of reducing agents include salts such as sodium borohydride (Guoping et al., 2012) or sodium citrate (Harriman, Thomas, & Millward, 1987) and gases such as carbon monoxide and hydrogen (Ershov & Abkhalimov, 2007) have been studied in literatures. Silver nanoparticles with high surface energy and high surface are tuned to aggregate or agglomerate. Recently, preparation of stable AgNPs is accomplished using protective coordinates, which provide electrostatic and/or steric protection like polymers and surfactants (El-Rafie et al., 2014; Zahran et al., 2014a, 2014b). Also, stabilization of nanoparticles through immobilization is another demonstrated stabilization way (White, Bellfield, Ellis, & Vandendaele, 2010).

The stability of the particles depends on the method in which the stabilizers are anchored to the manufactured nanoparticles. According to the nature of capping agent used, stabilization anchorage proceeds through three main mechanisms: (i) steric stabilization due to the presence of bulky groups, (ii) electrostatic stabilization, which arises from electrostatic attraction between opposing charges, or (iii) stabilization by ligands (organo-metallic or covalent bonds) (Castonguay & Kakkar, 2010; Richter, Schüler, Thomann, Mülhaupt, & Ludwigs, 2009; Scott, Wilson, & Crooks, 2005).

2. Polysaccharides mediated for AgNPs

Silver salts are historically known as antimicrobial agent, and recently, it has been reported that, silver nanocrystals is distinguished by its excellent antimicrobial action rather than ionic form (Emam, Mowafi, Mashaly, & Rehan, 2014). Besides, silver has been used for ages in wound treatment. Recently, upcoming resistances of pathogens against antibiotics (especially in medical care) led to an increase of silver incorporation into medical matrices and nowadays a variety of applications are in different local and international markets.

In the view of the large numbers of available natural polymers, this review has focused on the usage of polysaccharides derived from natural sources, i.e., polymeric carbohydrate structures that have been intensely investigated in the context of medical applications. Recent years have witnessed the implementation of AgNPs using polysaccharides as biodegradable and biocompatible polymers that directly emerge in biocidal materials. Such polymers in solutions are considered as hydrogels and can be described as effective capping agents for AgNPs. Polysaccharides have been used as composite matrices due to several characteristics of relevance for biological and medical applications, namely: biocompatibility, bifunctionality, sensitivity to external stimuli. In addition to their ability for coordinating with metal ions, polysaccharides could be used as reducers and capping agents for preparation of AgNPs.

The polymer–metal ion complex can be reduced under controllable experimental conditions, resulting in small sized nanoparticles. Once metal ions reduced to produce nano-sized species; polysaccharide building blocks will impair nanoparticles clotting (Fig. 1). So, the net produced matrix can be designed to perform different functions, depending on the properties of the loaded inorganic nanoparticles and, on the other hand, this product can be easily adapted to bio-systems due to their potential biocompatibility and low-toxicity. Polysaccharides could be described as polyfunctional compounds, as it includes different functional groups, so, they can serve as a springboard for the creation of