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Irradiated chitosan nanoparticle as a water-based antioxidant and reducing agent for a green synthesis of gold nanoplatforms

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HIGHLIGHTS

- WSCS-NPs was successfully prepared under irradiation.
- WSCS-NPs are spherical with nanoscaled size as small as 15 nm.
- WSCS-NPs show effective antioxidant and reducing power than CS in acetic acid.
- WSCS-NPs have lower toxicity than CS in acetic acid.
- WSCS-NPs display efficacy for green synthesis of monodispersed AuNPs (20 nm).

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ABSTRACT

The idea of preparing water-soluble chitosan and observing its nanostructural morphology are proposed using irradiation process. The water-soluble chitosan nanoparticles (WSCS-NPs) properties were assessed for a possible use as an antioxidant and reducing agent for a green synthesis of gold nanoparticles (AuNPs). The characteristics of WSCS-NPs were verified using FT-IR, XRD, C H N analyzer and TGA. The nanostructural morphology was investigated using SEM and TEM. The number average molecular weight of WSCS-NPs was as low as 3800 g/mol with narrow polydispersity of 1.26. The average hydrodynamic diameter of WSCS-NPs was 15.40 ± 0.47 nm. The 1,1-diphenyl-2-picryl-hydrazyl (DPPH) free radical scavenging activity of WSCS-NPs at 0.1 mg/mL was up to 80%, while the original CS exhibited no antioxidant activity. An effective concentration of WSCS-NPs to reduce DPPH free radicals (150 μM) by 50% is as low as 0.025 mg/mL. The *in vitro* cytotoxicity test by MTT assay demonstrated that WSCS-NPs are non-toxic with an IC_{50} of 2000 μg/mL. The WSCS-NPs are efficient reducing and stabilizing agent for producing stable colloidal AuNPs. The achievement of the WSCS-NPs and its ability to create AuNPs would be a part of growing interest of green nanotechnology in biomedicine.

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1. Introduction

Synthesis of gold nanoparticles (AuNPs) is one of the expanding research areas in nanotechnology. With their novel properties, they have been applied in many applications particularly biomedicine and other bio-related applications, such as drug delivery (Agasti et al., 2009), photothermal therapy (Hainfeld et al., 2010), diagnosis (McMahon et al., 2008) and biosensor (Carlo et al., 2012). Several methods such as chemical reduction (Murphy et al., 2008; Brown et al., 2010), sonochemical (Naeini et al., 2010), and photochemical reduction (Stern et al., 2008) have been developed to synthesize metal NPs including AuNPs. In the past decade, with some hazardous chemicals remaining in the products, the alternative green synthesis has been emerged. The green synthesis of AuNPs has been performed using natural reducing and stabilizing agents. Biomolecules from plant extracts have been widely proposed as green synthesis of AuNPs (Mittal et al., 2013) as a result of their antioxidant and reducing properties. However, small molecular natural products still lack of the

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stability including chelating and stabilizing efficiencies. Biomacromolecules, e.g., starch, chitosan, gelatin and alginate, have been the most widely used as capping agents for the synthesis of metal NPs (Vasileva et al., 2011; Huang and Yang, 2004; Anh et al., 2010). Unlike the small molecular reducing agents, the biopolymers themselves exhibit low reactivity to reduce metal ion to metal atom because of their inherent high molecular weight, low solubility or lack of reducing power function.

Chitosan (CS), a deacetylated form of chitin, makes up the second-most naturally abundant copolysaccharides next to cellulose. It is one of the biodegradable carbohydrate polymers consisting of pyranose ring of β-(1,4)-2-acetamido-2-deoxy-β-D-glucose (chitin) and β-(1,4)-2-amino-2-deoxy-β-D-glucose (chitosan) linked with a glycosidic linkage. It dictates numerous advantage properties, such as biodegradability (Shigemasa et al., 1994), biocompatibility (Risbud and Bhonde, 2000), bioactivity (Dumitriu et al., 1989) and non-toxicity (Denkbas and Odabasi, 2002). Several studies have proposed CS as a biomaterial for pharmaceutics (Kim et al., 2008), tissue engineering (Li et al., 2005), cosmetics (Kim et al., 2006), food preservation (Kanatt et al., 2008) and dietary (Anraku et al., 2009). The amino ($-NH_2$) and hydroxyl (–OH) groups of CS at C-2 and C-6 positions not only provide reactive sites for functionalization but also exhibit strong metal ion chelation (Guibal, 2004), oil absorption (Sokkera et al., 2011), antimicrobial (Park et al., 2004), and antioxidant activities (Yang and Mau, 2008). Regarding to the antioxidants, many researchers have focused on the extraction, identification, modification and application of alternative natural antioxidants to use in numerous purposes in order to avoid pathogenic risk of the synthetic antioxidants (Wu et al., 2011). It is also known that the most common chemical species, which act as antioxidant or reducing agents are hydroxyl, –OH (e.g. phenolics), sulfhydryl, –SH (e.g. cysteine and glutathione) and amino, $-NH_2$ groups (e.g. uric acid, spermine and proteins) (Decker, 1998). Therefore, CS has attracted much attention to develop as natural antioxidant and reducing agent since it has plenty of –OH and $-NH_2$ groups as H-atom donation (Castagnino et al., 2008; Guo et al., 2006; Sun et al., 2008; Gue et al., 2008). Feng et al. (2008) have concluded that the –OH group in the saccharide units can react with free radicals by the H-abstraction reaction and the $-NH_2$ group of CS can react with free radicals to form additional stable macroradicals. Although the –OH and $-NH_2$ groups of CS exhibit many unique properties including antioxidant and reducing power, CS has its inherent drawback of non-reactivity and insolubility because of strong inter- and intra-molecular hydrogen bonding. The $-NH_2$ group ($pKa = 6.2 - 7.0$) is completely protonated in acids with p*K*a less than 6.2 making CS soluble. Thus, CS is insoluble in water, aqueous bases and organic solvents (Kubota et al., 2000; Kurita, 2006, Rinaudo, 2006). This is a vastest limitation to use CS in aqueous solution at neutral pH to apply in a wide range of applications particularly biological media.

To increase the solubility, radical scavenging ability, reducing power including reactivity of CS, many derivatives prepared by chemical conjugation via quaternization, *N*- and *O*-derivatization and antioxidant molecular conjugation (Xue et al., 1998; Xie et al., 2001; Zhong et al., 2007; Pasanphan et al., 2008; Wang et al., 2011; Zhang et al., 2012). However, chemical modification is commonly not preferred for food and health care applications because of the formation of detrimental products (Kanatt et al., 2008). Therefore, developing water-soluble CS without any *N*-derivatization would be a promising way to maintain its own properties and reduce usage of coupling agents. Besides, molecular weight reduction is well known process to improve solubility, chemical reactivity and bioactivity of CS (Du et al., 2009; El-Rehim et al., 2012; Yoksan et al., 2004; Pugliese et al., 2011). Accordingly, irradiation would serve as a green process because of the reaction carrying out in additive free and at ambient temperature (Ulanski and Rosiak, 1992; Hai et al., 2003). It is well-known aspects of irradiation of CS and its derivatives (Chmielewski, 2010); however, less known aspects of radiation-induced nanostructural CS and its applications. In the past few years, the systematic preparation of colloidal CSNPs using γ-irradiation has been proposed (Pasanphan et al., 2010). The CSNPs were spherical shape; however, they were not soluble in water and became agglomerated within a few hours. Although several water-soluble CS (WSCS) derivatives and radiation-induced degradation of CS have been proposed, to the best of our knowledge the strategies to prepare WSCS-NPs via irradiation in order to use as a green antioxidant and reducing agent for green synthesis of AuNPs have not yet been demonstrated.

Herein, the goal of the present study is to prepare WSCS-NPs using high-energetic irradiation. The properties of the obtained WSCS-NPs were characterized by FT-IR, XRD and TGA. The molecular weight was determined by GPC. The morphological information and nanoscaled size were also verified using SEM, TEM and DLS. The article also assesses the antioxidant activity, reducing power and cytotoxicity information of the WSCS-NPs using *in vitro* DPPH radical scavenging activity, ferric reducing antioxidant power (FRAP) and MTT assays, respectively. An approach to create AuNPs via a simple and green synthesis using the obtained WSCS-NPs in one-pot procedure was also demonstrated.

2. Experimental

2.1. Chemicals

Chitosan (CS) from shrimp shell ($Mv = 700$ kDa, degree of deacetylation (DD = 90%) was supplied from Seafresh Chitosan (Lab) Co., Ltd. (Thailand). Acetic acid, ethanol and methanol (AR grade) were from Labscan, Co., Ltd. (Thailand). Sodium hydroxide (NaOH) was bought from Carlo Erba Reagents (Italy). 1,1-diphenyl-2-picrylhydrazyl (DPPH) was obtained from TCI (Japan). Dialysis membrane (MWCO = 1000 Da) was purchased from Membrane Filtration Products, Inc., USA. Poly (ethylene oxide) GPC standards were obtained from PSS Polymer Standards Service GmbH, Mainz, Germany. Ferric chloride anhydrous and trichloroacetic acid were bought from Carlo Erba Reagents (Italy). Potassium ferricyanide was purchased from Sigma-Aldrich (USA). All chemicals were used without further purification.

2.2. Instruments

The ^{60}Co from a Gammacell 220 irradiator was used as a γ-ray source with an absorbed dose rate of 4.2 kGy/h. A Red-dyed PMMA dosimeter type Red 4304 was supplied from Harwell Dosimeter Ltd. All samples were irradiated in air under ambient temperature and pressure. The measurement accuracy was ± 10%. Such accuracy is nevertheless sufficient for most radiation processing applications (Fernandez et al., 2005). Fourier transform-infrared (FT-IR) spectrometry analysis was carried outusing KBr pellet technique in a Bruker Tensor 27 (USA) with 32 scans at 2 cm^{-1} resolution in a frequency range of 4000–400 cm^{-1}. Elemental analysis was performed using a LECO CHNS-932 with a combustion temperature of 950 °C under air atmosphere with O_2 as a combustion gas (flow rate 20 mL/min) and He as a carrier (flow rate 200 mL/min). X-ray diffraction (XRD) patterns were taken on a Bruker AXS (Germany) using Cu*K* radiation as an X-ray source and operating at 50 kV and 100 mA. The diffraction intensities were recorded from 5° to 45° 2θ angle. Thermogravimetric analysis (TGA) was carried out with a Mettler Toledo TGA/SDTA851 Thermo gravimeter (Mettler Toledo Corp., Zurich, Switzerland). The samples were heated in the temperature range of 200 to 720 °C at a heating rate of 20 °C/min under N_2 during

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