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Synthesis of gold nanoparticle necklaces using linear–dendritic copolymers

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ABSTRACT

Linear–dendritic copolymers containing hyperbranched poly(citric acid) and linear poly(ethylene glycol) blocks (PCA–PEG–PCA) were used as reducing and capping agents to synthesize and support gold nanoparticles (AuNPs). PCA–PEG–PCA copolymers with 1758, 1889 and 3446 molecular weights, called A1, A2 and A3 through this work, respectively, were synthesized using 2, 5, and 10 citric acid/PEG molar ratios. The diameter of A1, A2 and A3 in a fresh water solution was investigated using dynamic light scattering (DLS) and it was between 1.8 and 2.8 nm. AuNPs were simply synthesized and supported by addition a boiling aqueous solution of $HAuCl_4$ to aqueous solutions of A1, A2 and A3. Supported AuNPs were stable in water for several months and agglomeration was not occurred. The loading capacity of A1, A2 and A3 and the size of synthesized AuNPs were investigated using UV spectroscopy and transmission electron microscopy (TEM). It was found that the loading capacity of PCA–PEG–PCA copolymers depend on the concentration of copolymers and the size of their poly(citric acid) parts directly. For example average loading capacities for 400 μM concentration of A1, A2 and A3 were 32.24, 37.4 and 41.52 μM, respectively, and average loading capacities for 400, 200 and 100 μM concentration of A1 were 32.24, 20.28 and 9.1 μM, respectively. Interestingly there was a reverse relation between the size of synthesized AuNPs and size of poly(citric acid) parts of PCA–PEG–PCA copolymers.

1. Introduction

Nanogold or gold nanoparticles (AuNPs) have been widely studied in the past 10 years because of their unique properties, such as catalysis, quantum size effect, and optical properties [1]. Due to the requirements for control of nanoparticle size and surface functionalization for this broad range of applications, different synthetic methods have been developed to generate monodisperse AuNPs. One of the most widely used methods is the reduction of tetrachloroaurate ions $AuCl_4^-$ in aqueous medium using sodium citrate to generate particles with diameters typically ranging from 10 to 100 nm [2]. Although this method has good control over producing a particular particle size, it is limited to the synthesis of larger particles. The Brust method and various modifications are useful for the generation of AuNPs having core sizes ranging from 1 to 4 nm [3–5]. In the Brust method, the transfer of $AuCl_4^-$ into toluene or chloroform is performed using tetraalkylammonium bromide followed by reduction with sodium borohydride in the presence of alkylthiols. Disadvantages of this method include contamination of the synthesized particles with boride [6] and potential presence of impurities introduced by the use of capping ligands which also hinder the surface modification and functionalization of particles for particular applications. A few other single-

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step reduction processes also were developed to generate monodisperse gold nanoparticles, but these are limited to organic media [7–9]. In addition, the reduction of gold salt to form AuNPs using amine-containing organic molecules has been investigated [10–14], but most of the amine compounds used in those AuNPs syntheses are soluble in only organic solvents, and the reduction reactions must take place in an organic solvent or in a biphasic system. As a result, the nanoparticles prepared using those methods are not easily dispersed in aqueous solutions. To use the AuNPs in aqueous-based or biological systems, it is necessary to functionalize the particles with ligands which facilitate phase transfer from an organic to an aqueous medium. Alternative synthetic strategies based on using polymers as both the reducing and stabilizing agent for the generation of stable metal nanoparticles without the use of an additional stabilizing agent have been developed. The resulting nanoparticle-polymer composites have been shown to be useful in catalytic transformations [15] and they could be useful for nanostructured solar cells, photonic band gap materials, storage devices, and drug delivery. Some polymers can fulfill the required dual role as a reducer and stabilizer [16]. Examples include poly(methylhydrosiloxane) [17], poly(*N*-vinyl-2-pyrrolidone) [18], poly(sodium acrylate) [19], poly(ethylene oxide) [20], poly(vinyl alcohols) [21] and polyethylenimine [22]. However, even in the syntheses using those polymers, either the reduction reaction was carried out in organic solvents or polydisperse nanoparticles were produced. In both situations, the use of the nanoparticles is restricted, or at least complicated for aqueous-based (e.g., biological) applications or for applications that require monodisperse particles (e.g., electronics). The major advantage of using a polymer as a stabilizing agent is that it can be used to tailor the nanocomposite properties and also to provide long-term stability of the nanoparticles by preventing particle agglomeration [23–25]. Recently, the functionalized AuNPs were synthesized through different stabilizing and capping agents and showed the potential in several applications [26]. Although many block copolymers and dendrimers have been used as the stabilizing agents to synthesize AuNPs in the literatures [27], reports of the preparation and characterization of polymer–nanogold nanocomposites are occasional. In the literatures, many kinds of polymers such as poly(methylphenylphosphazene) (PMPP) [28], polyacrylamide [29], acrylic polymers [30–32], polyurethane (PU) [33], polystyrene (PS) [34], poly(ethylene glycol) (PEG) [35], poly(vinylphenol) (PVP) [36], poly(vinyl alcohol) (PVA) [37], poly(*o*-phenylenediamine) [38], poly(amic acid) (PAA) [39], polyimide (PI) [40], and polyfluorene (PF) [41–43] were used to prepare the polymer–AuNPs nanocomposite. Linear–dendritic macromolecules are hybrid large molecules containing dendrimers and linear polymers. Interesting properties of this type of dendritic macromolecules have stimulated investigation in this area [44–51]. Haba et al. reported preparation and encapsulation of gold nanoparticles using poly(ethylene glycol)-modified poly(amido amine) dendrimers. Encapsulated gold nanoparticles showed a heat-generating ability [52].

Synthesis of PCA–PEG–PCA linear–dendritic copolymers and their ability to encapsulate and release of organic guest molecules was reported previously [53–55]. Citric acid is a unique capping agent to cap and stabilize the metal nanoparticles such as gold nanoparticles, hence the PCA–PEG–PCA copolymers containing dendritic citric acid parts (which contain much more hydroxyl functional groups than citric acid molecule) and PEG as flexible part (which enhances the solubility) could be effective macromolecules to synthesize, protect, encapsulate and also stabilize AuNPs. On the other hand they are biocompatible materials and could be used to transport AuNPs in biological systems. In this work, PCA–PEG–PCA copolymers have been used to synthesize, encapsulate and stabilize AuNPs. The role of dendritic citric acid parts in the case of loading capacity and the size of AuNPs was investigated.

2. Experimental

2.1. Chemicals

Citric acid (extra pure anhydrous powder), $HAuCl_4$, $3H_2O$ (99.5%, for analysis) and poly(ethylene glycol) (M_n = 1500) were purchased from Merck. Dialyze bag (a semipermeable membrane cut off 2000) was obtained from Sigma, Aldrich.

2.2. Instrumental measurements and preparation of samples for analysis

The zeta potential and dynamic light scattering experiments were done by the commercially available instrument, Zetasizer, Nano series, ZEN 1600, laser 633 nm. Samples were dissolved in distilled water, and measurements were performed at 25 °C and started 10 min after the cuvette was placed in the DLS apparatus to allow the temperature to equilibrate. About 1 ml of the sample was transferred to a special dustfree light-scattering cell and the temperature was controlled within ±0.02 °C. Absorption spectra (300–800 nm) were recorded using a Perkin–Elmer Lambda 900 UV–vis/NIR spectrophotometer. Samples of linear–dendritic encapsulated nanoparticles (LDENP) were prepared and left at room temperature overnight. Then they were transferred to the spectrophotometer cell and spectra were recorded at 25 °C. Calibration curve was used to determine the loading capacities. TEM photos were recorded using Philips CH 200, LaB6-Cathode 160 kv.

2.3. Synthesis of PCA–PEG–PCA linear–dendritic copolymers

PCA–PEG–PCA linear–dendritic copolymers were synthesized according to the reported procedure in literature [56].

2.4. Preparation of linear–dendritic encapsulated nanoparticles (LDENPs)

Typically an aqueous solution of $HAuCl_4$ with a constant concentration (100 μM) was added to aqueous solutions of PCA–PEG–PCA copolymers in different concentrations