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A simple microemulsion based method for the synthesis of gold nanoparticles

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ABSTRACT

The production of gold nanoparticles and nanoplates by enzymatically-synthesized lauroyl glucose, lauroyl fructose and lauroyl ascorbate is described. These emulsifiers formed oil-in-water microemulsions with toluene and the available reducing groups brought about a rapid reduction of chloroauric acid ($HAuCl_4$). Gold nanoparticles could thus be synthesized without the use of an additional reducing agent. Optical images, UV–visible spectroscopy, scanning electron microscopy, energy dispersive spectra (SEM–EDS) and X-ray diffraction (XRD) analysis revealed the presence of gold nanoparticles, which on further incubation aggregated into nanoplates. This paper thus describes a novel application of the enzymatically-synthesized esters.

1. Introduction

Nanoparticles have become significant in the recent years and have created an impact in the areas of electronic, energy, chemical and biological sciences [1]. In particular, biological synthesis of nanoparticles has become a popular alternative [2]. Several organisms produce enzymes such as lipases, proteases and β-glucosidases that have been used for the production of a variety of surfactants [3]. Amongst these, lipases play a special role in the synthesis of different types of emulsifiers including sugar fatty acid esters [4]. Such sugar esters are synthetic amphipathic molecules that have both polar (sugar) and non-polar (fatty acid) moieties. They exhibit a variety of biological activities [4–7] and display emulsifying, solubilizing as well as foaming properties [8–10]. Ascorbate fatty acid esters are also important surfactants that have several applications [11].

The reducing capabilities of glucose, fructose and ascorbate are retained in lauroyl glucose, lauroyl fructose and lauroyl ascorbate as the esterification generally occurs at 6-O-positions [12–14]. We have hypothesized that these esters could play a dual role in nanoparticle synthesis (i) by stabilizing oil-in-water emulsions thereby aligning the reducing groups on the outer side (ii) by reducing $HAuCl_4$ to Au°. Conventionally, water-in-oil emulsions are used to reduce metal salts in a controlled manner. The process involves the making and mixing of two types of emulsions (i) containing the metal and (ii) containing the reducing agent. The present paper describes a simple procedure for the synthesis of gold nanoparticles using oil-in-water emulsions of lauroyl sugars or ascorbate wherein, the emulsifiers themselves bring about a reduction of the gold salt thus saving energy as well as raw materials.

2. Experiment

2.1. Enzymatic synthesis of emulsifiers

The enzymatic production of lauroyl glucose and its subsequent purification were carried out as described earlier [10]. Lauroyl fructose and ascorbate were also prepared in a similar manner by substituting glucose with fructose or ascorbic acid. The esters were purified and monitored by using the protocols described earlier [10,14,15].

2.2. Synthesis and characterization of gold nanoparticles

The esters equivalent to one unit of emulsification activity [10], $HAuCl_4$ (3 mM gold) and toluene (0.1% final concentration) were added to Milli-Q water (reaction mixture volume was 5.0 ml). The tubes were sealed; vortexed for 1 min, incubated at 70 °C for 1 h and the synthesis of nanoparticles was monitored. Three controls (i) without the esters, (ii) without toluene and (iii) without the vortexing step were maintained for understanding the significance of each step. Standard protocols and equipment described earlier [16,17] were used to characterize the nanoparticles. The particle size was analyzed

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by using dynamic light scattering equipment (25 °C at a fixed angle of 90°) and the Brookhaven 90plus particle sizing software.

3. Results and discussion

In the literature, there are a large number of reports on the use of water-in-oil microemulsions for nanoparticle synthesis. Such microemulsions are transparent, isotropic liquid media having nanosized water droplets (reverse micelles) dispersed in the bulk organic phase that are stabilized by surfactant molecules [18]. These water pools offer unique microenvironments for nanoparticle synthesis [19]. These nano-reactors continuously collide, a fraction of droplets form short-lived dimers and they exchange their water contents [20,21]. If two emulsions: one with the metal and the other containing a reducing agent are used, the drops collide; an exchange takes place and the metal gets reduced. Nickel nanoparticles have thus been synthesized by using water-in-oil microemulsions of water/cetyltrimethylammonium bromide/n-hexanol. These nanoparticles were synthesized by rapidly mixing equal volumes of two water-in-oil microemulsions (i) with solubilized $NiCl_2$ and (ii) with hydrazine (reducing agent) [22]. We describe a unique method of nanoparticle synthesis based on oil-in-water emulsions wherein, the emulsifiers themselves brought about the reduction of $HAuCl_4$ to gold nanoparticles and nanoplates.

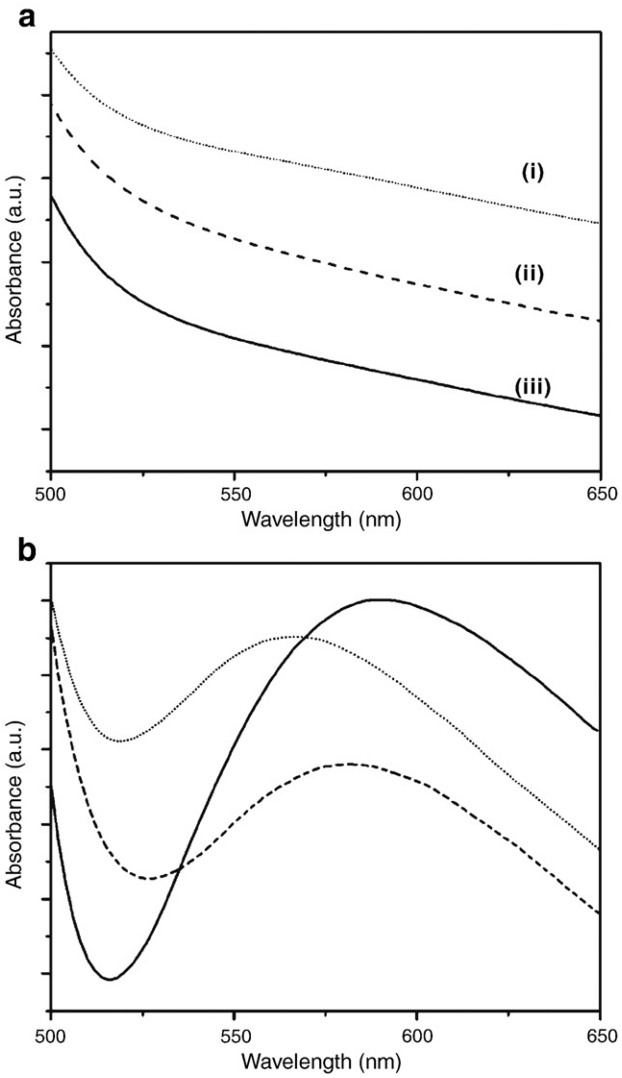

Fig. 1. UV–vis spectra of (a) control tubes (i) (ii) and (iii) described in the Experiment section and (b) spectra with lauroyl glucose (········), lauroyl fructose (- - -) and lauroyl ascorbate (—).

Fig. 1(a) shows the UV–visible spectra of the reaction mixtures in control tubes. As seen in the figure, there were no characteristic peaks in the range of 520–580 nm. The gold salt was not reduced in any of these tubes indicating that all the ingredients as well as the vortexing step were essential for nanoparticle synthesis. Fig. 1(b) shows the characteristic peaks observed when emulsions of lauroyl glucose, lauroyl fructose and lauroyl ascorbate were used in the reaction mixtures. All the esters were thus able to bring about a reduction of the chloroauric acid. Gold nanoparticles are known to display vivid colors as they absorb radiation in the visible region due to surface plasmon resonance, SPR [16,17]. Nanoparticle synthesis was rapid and within 20 min, the pinkish-red color and SPR were observed.

Fig. 2(a) shows SEM images of the spherical nanoparticles obtained (white arrows) with lauroyl glucose after 20 min. On further incubation, the reduced gold aggregated into larger hexagonal or triangular nanoplates as shown by white arrows [Fig. 2(b)]. With lauroyl fructose, a variety of forms (spheres, hexagons, triangles, rhomboids and rods) were obtained [Fig. 2(c)]. With lauroyl ascorbate (after 10 min of incubation), high magnification images (60,000×) indicated the presence of nanoparticles that were smaller than 100 nm. Their exact size could be estimated by dynamic light scattering studies as described later. Ascorbic acid is an efficient reducing agent and its ester also brought about a rapid reduction. Hexagonal and triangular nanoplates were formed after 1 h as against the 2 h incubation period required for sugar esters [Fig. 2(d), (e) and (f)]. The spot EDS attachment was used to determine the elemental composition and confirm the presence of gold in the nanoparticles and nanoplates. Fig. 2(g) is a representative EDS profile showing peaks that are characteristic of gold.

The XRD patterns of thin films of the emulsions that had synthesized nanoparticles were also obtained [Fig. 2(h)]. A broadening of the intense peaks due to (111), (200), (220) and (311) Bragg reflection at $2\theta = 38.36°$, 45.55°, 64.65° and 77.73°, respectively, confirmed the presence of gold nanoparticles.

The size distribution of nanoparticles was estimated by dynamic light scattering experiments. A representative multimodal size distribution graph for the nanoparticles that were obtained with lauroyl glucose after 20 min is shown in Fig. 3(a). The particle sizing software calculated the size of the nanoparticles to be in the range of 168 to 226 nm with an average size of 193 nm. These values are consistent with the observations made by using a SEM [Fig. 2(a)] wherein it can be seen that the average size is around 200 nm. The size distribution of the nanoplates (a small proportion) was in the range of 700 nm to 2000 nm after 20 min [indicated by black arrow in Fig. 3(a)]. On further incubation (after 2 h) the nanoplate size varied from 2750 nm to 5000 nm as also seen in the SEM observations [Fig. 2(e) and (f)]. A size range similar to that obtained with lauroyl glucose was also observed with lauroyl fructose after 20 min. However, the particle size after 2 h could not be estimated on account of the large size of the nanoplates as also seen in the SEM [Fig. 2(c)].

With lauroyl ascorbate, average size of the nanoparticles was much smaller (39 nm), the minimum and maximum being 35 nm and 48 nm, respectively, after 10 min [Fig. 3(b)]. The figure also shows that there was a small proportion of particles, in the range of 122 to 264 nm and 908 nm to 1970 nm (indicated by black arrows). On further incubation for 1 h, the size varied from 1820 to 5000 nm.

All the three esters were thus able to bring about a reduction of the chloroauric acid. The size and morphology of the nanoparticles thus formed were varied. With further fine-tuning of the protocol and with the use of appropriate capping agents such as thiols, chitosan, dodecanethiol or lysine [23–25] their size can be further regulated