Fructose-mediated gold nanoparticles synthesis

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Abstract: Gold nanoparticles were synthesized at room temperature and atmospheric pressure using fructose, a common and non-toxic monosaccharide. The nanoparticles were mostly spherical, with a homogenous shape and a small size distribution. Fructose was a reducing and stabilizing agent, and the stability of the nanoparticles depended on its concentration.

Subjects: Organic Chemistry; Materials Chemistry; Nanoscience & Nanotechnology

Keywords: gold nanoparticles; nanoparticles synthesis; fructose

1. Introduction

Gold nanoparticles have been studied for a long time due to their interesting properties (1, 2), and they have been recently characterized in a comprehensive way by researchers. As gold is a non-toxic material, it has attracted the attention of researchers for biomedical applications, especially in the field of nanomedicine (2), the properties of noble metal nanoparticles, such as SERS (3, 4) have also applications on the field of medicine (2); however, some synthesis involve the use of toxic or noxious materials, such as toxic organic solvents, thus those gold nanoparticles need to be carefully purified before using, propitiating aggregation of the nanoparticles. Researchers have been working on synthesis methods that do not use toxic materials (5, 6); in this way the purification is very easy and sometimes is not needed; among the materials used for this kind of synthesis are polysaccharides (7) and monosaccharides (8). Gold nanoparticles conduct electricity, and they can be used also to turn isolating materials into conductive materials. In this short communication, we describe the synthesis of gold nanoparticles using fructose, a non-toxic monosaccharide that is cheap and abundant and that with glucose forms sucrose, common sugar; this synthesis is also environmental friendly. As some sugars, fructose is a reducing agent, the reducing character is reached when the sugar is in its open form and is maximized when the sugar is ionized, this can be completed changing

ABOUT THE AUTHORS

Our research group interest is in the synthesis of nanocomposites for several applications, specially for high power applications. Our research group works with polymers and several nanoparticles, among them metallic oxides, metallic nanoparticles and organic nanoparticles, such as cellulose nanocrystals. With the aforementioned materials, we make composites for high power applications; those applications include energy storage and dielectric materials.

PUBLIC INTEREST STATEMENT

In this work, we synthesized gold nanoparticles using fructose, a common sugar. The gold nanoparticles were spherical with a uniform size. We did not use sodium borohydrate as reducing agent; instead of it, fructose was used as reducing and stabilizing agent. The reactions were carried out at room temperature and atmospheric pressure. Potassium hydroxide was used to make for an alkaline pH and to maximize the reducing potential of fructose. We found that the nanoparticles were more stable when less gold precursor was used and when fructose was used in higher concentrations. We made this procedure because gold, citric acid and fructose are non-toxic, so the nanoparticles may be used for medical applications.
the pH to alkaline, fructose usually ionizes when the pK is 11.99 to 12.5 (9); it also has the advantage of being more soluble than other sugars; here fructose is used as reducing and stabilizing agent. The synthesis of the gold nanoparticles described in this work is easy and convenient as is carried out at room temperature and atmospheric pressure.

2. Methodology

2.1. Materials
All reagents were used as received. D-Fructose (U. S. p ≥ 98%) was purchased from Fermont. Chloroauric acid (HAuCl₄, 99.999%) and citric acid (≥99%) were purchased from Sigma-Aldrich. Potassium Hydroxide (KOH, 87.4%) was obtained from J. T. Baker.

2.2. Experimental
Stock solutions were prepared for HAuCl₄ and citric acid, the concentration of the first solution was 0.1 M and the solution for the latter reactant had a concentration of 0.05 M; both stock solutions were prepared in deionized (DI) water. A stock solution of KOH was prepared in DI water having a concentration of 1.0 N.

The gold nanoparticles were synthesized using fructose as reducing agent and as stabilizing agent; some synthesis were made using citric acid as co-reducing agent. All syntheses were made at room temperature. 10 mL of DI water were added to a round-bottom flask and then the HAuCl₄ solution was injected and it was left to dissolve for 10 min. Two HAuCl₄ quantities of gold precursor were tested in the reaction: 250 and 82 μmol; for the former, 25 μL of the HAuCl₄ were added, and for the latter concentration, 8.2 μL of the same solution were added. After the addition of gold, 1.5 mL of citric acid 0.05 M was added. Then, fructose was added, the amount of this compound was calculated and weighed for the desired concentration and added to the solution; several concentrations of fructose were tested, the concentrations are all listed on Table 1. Then, 50 μL of the KOH solution was added and the solution was left to react. The reaction was completed usually in 30 min.

2.3. Characterization
The gold sols were characterized using a Scanning Transmission Electron Microscope (STEM) JEOL 7600F. One drop of the tested gold sols was deposited in carbon-coated copper grid and let to dry overnight at room temperature in a powder free environment. The reaction was also monitored visually (8). The nanoparticles were measured using the Gatan Digital Micrograph software (Gatan Inc.), 100 nanoparticles were measured and averaged (10). The UV-vis spectra of the gold sols were observed using an Agilent Technologies Cary 60 UV-vis spectrophotometer.

| Table 1. Concentration of fructose |
|-----------------------------------|
| Concentration (mmol)              |
| 10                                |
| 20                                |
| 30                                |
| 40                                |
| 50                                |
| 75                                |
| 100                               |
| 150                               |
| 200                               |
3. Results
The reactions were completed usually in 30 min after the addition of KOH, if this step was omitted, no reaction was observed. The solution changed from transparent yellow to violet, blue and finally red, this indicates a reduction and a change in the diameter of the gold nanoparticles (11). Precipitation was observed in some samples, to correct this, the quantity of fructose was increased, until no precipitation was present, this happened when the concentration of fructose was 100 mM. The nanoparticles were more stable in the presence of citric acid; if only fructose was used, the stability was reduced, as there was precipitation observed in many samples, to reach stability the solutions had to have more fructose. The nanoparticles synthesized with the lower quantity of gold were more stable, the higher quantity had a tendency to produce aggregates; this is explained in terms of ionic strength of the solution, the samples synthesized with the higher quantity of gold were subjected to a high ionic strength, as there are more ions during the reaction, causing destabilization and aggregation of the nanoparticles. On the other hand, the nanoparticles with the lower quantity of gold were exposed to a lower ionic strength, thus the nanoparticles were not destabilized by the reaction environment.

The gold sols were observed with scanning electron microscopy. The morphology was uniform, with nanoparticles being mostly in spherical shape. Some other morphologies were observed, as triangular prisms. The diameter of the gold nanoparticles was 12 nm ± 0.54 nm; this shows that the size distribution is small and that the particles size is homogeneous. The gold nanoparticles can be seen in Figures 1–3. Figure 1 shows the gold nanoparticles after synthesis, it shows nanoparticles in the grid, the sols have a regular morphology. Figure 2 shows more gold nanoparticles; they are arranged in a wire-like manner, similar to gold nanoparticles synthesized using glucose (8) and other methods using citrate (2, 12). In Figure 3 is shown a region of the gold nanoparticles, in this micrograph the shape and size of the nanoparticles can be distinguished, and the image shows individual nanoparticles with no aggregation present. This suggests that the nanoparticles first form a mesh-like structure and then separate from these structures as they grow (12).

Figure 4 shows the UV-vis spectra of Au nanoparticles having citric acid and fructose. All samples show a peak at 520–550 nm, corresponding to the surface plasmon resonance of the gold nanoparticles (1, 8) The intensity of the peak at 300 nm decreases when the concentration of fructose is increased, this peak corresponds to the Au salt band, and the decreasing of intensity suggests that there is less unreacted gold in the sample and more Au nanoparticles. In the samples having a concentration of fructose higher than 100 mmol there is another peak present at 650 nm, interestingly, this peak has a maximum at 100 mmol of fructose concentration. The peaks at 550 and 650 nm suggest that there are present Au nanorods (13, 14); however, no other metal was used on the synthesis of the gold sols. The formation of Au nanorods could also be visually observed.
Figure 2. SEM micrograph of the gold nanoparticles showing a mesh-like structure.

Figure 3. SEM micrograph of non-aggregated gold nanoparticles showing their morphology.

Figure 4. UV-vis spectra of Au nanoparticles having citric acid and different concentrations of fructose: (a) 10 mmol, (b) 20 mmol, (c) 30 mmol, (d) 40 mmol, (e) 100 mmol, (f) 150 mmol.
Figure 5 shows the UV-vis spectra of the gold sols synthesized with only fructose. All of the spectra show a peak at around 550 nm, characteristic of gold nanoparticles. The peak blueshifts when the concentration of fructose is 75 mmol or higher, indicating that the size of the nanoparticles decreases. At a concentration of fructose of 50 mmol a peak at 680 nm started to show, this suggests that some gold nanorods are present (13, 14), as in the samples with citric acid. It is interesting to note that the peak of bulk gold is not present on these samples; however, aggregation was observed for the samples with lower concentration of fructose.

The characterization showed that gold nanoparticles were obtained, the presence of gold is confirmed by the UV-vis. The synthesis used for these gold nanoparticles makes them useful for several fields, among them the medicinal and electrical fields. Gold has been used in biomedical applications due to the non-toxic nature of this material; in this work we used fructose and citric acid as reducing, stabilizing and co-stabilizing agents; sodium borohydride was not used. The nanoparticles were synthesized with non-toxic materials, so they are able for biomedical applications. Gold is a conductive material, and gold nanoparticles are conductive too. These nanoparticles could be used for doping non-conductive materials and turning them conductive, or to improve the conductivity of other conductive materials. These gold nanoparticles are suitable for making composites and nanocomposites of several materials, among them polymeric materials for the electrical industry.

We hypothesized that during reduction of Au nanoparticles, fructose is oxidized to fructuronic acid (15). More information and discussion about the nanoparticles, the detailed results and the reaction mechanism will be published later.

4. Conclusions
Gold nanoparticles of different forms were synthesized. The nanoparticles have an average diameter of 12 nm, with spheres being the preferred form. The stability of the nanoparticles is increased with higher fructose concentrations, and with lower gold concentrations. The nanoparticles were more stable when citric acid was used in the synthesis. The UV-vis suggested that gold nanorods were also formed. These nanoparticles could be suitable for use in the electrical and/or biomedical fields.

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**Competing interests**
The authors declare no competing interest.
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