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Investigation on a facile one-pot rapid synthesis approach for developing modestly monodispersed and stable spherical gold nanoparticles

Belina Xavier[1], A. Ramanand[2] and P. Sagayaraj[2*]

[1]Department of Physics, Stella Maris College (Autonomous), Chennai-600 086
[2]Department of Physics, Loyola College (Autonomous), Chennai-600 034

ABSTRACT

We report the rapid synthesis of gold (Au) nanoparticles by mixing an aqueous solution of $HAuCl_4$, CTAB and ascorbic acid by appropriate ratio, followed by the addition suitable amount of NaOH to maintain the pH of the solution. We have studied the formation of nanosized Au particles by both microscopic and spectroscopic characterization. The UV-Vis absorption spectrum of the sample shows the appearance of absorption band at 529 nm, which proves the quantum confinement of gold particles at the nanometer range. TEM image suggests that the as synthesized Au nanoparticles are spherical in shape and the particle size is in the range of 7-20 nm. The synthesized particles are found to be stable and hence suitable for potential application in various fields.

Keywords: gold nanoparticles, noble metals, wet chemical methods.

INTRODUCTION

Metal nanostructured materials have been the subject of much scientific research due to their characteristic properties that are distinctly different from their bulk counterparts, and considerable attention from both fundamental and applied research has been paid to the synthesis and characterization of these materials [1]. Particular interest has been focused on the noble metal nanoparticles because they are technologically important in many fields such as catalysis, optics, medical diagnostics, therapeutics, biomedical imaging, chemical and biochemical sensing, nanomedicines and nanoelectronics [2-6]. Among the known metal nanoparticles, gold nanoparticles (AuNPs) are extensively studied because of their unique optical properties originating from the excitation of surface plasmon resonance (SPR). Interestingly gold nanoparticles are promising candidates in HIV therapeutics due to their facile synthesis, ease of functionalization, biocompatibility and inherent non-toxicity. The unique chemical and physical properties of AuNPs also make them potential alternative to be looked upon for treatment against HIV [7]. Key nanoparticle parameters, which determine their physical and chemical properties, are their size and shape. A much sought after property is the ability to control the size and shape and also the uniformity of the nanoparticles formed. A size-shape monodisperse sample allows the properties of a nanoparticle dispersion to be considered as a summation of the properties of an individual nanoparticle. [8-16]

Precise control of size, shape, structure and morphology of nanoparticles has been one of the most attractive goals for the synthetic chemists in this field [17-19]. Common methods for size control employ capping agents, [20] such as surfactants, ligands, polymers,or dendrimers, to confine the growth in the nanometer regime. But in general these methods commonly produce spherical particles due to the low surface energy associated with such particles. Gold

nanoparticles have been the subject of intense research, culminating in preparative techniques in both aqueous [21-24] and organic media, [25-30]. The first, and older one, involves the reduction of tetrachloroaurate ions in aqueous media, employing reducing agents such as sodium citrate [21] or sodium borohydride.

The second concept involves the synthesis in organic solvents. The most popular method is the two phase synthesis reported by Brust et al [25] which involves the transfer of tetrachloroaurate ions into toluene with the use of tetraalkylammonium bromide and subsequent reduction with sodium borohydride in the presence of thiols.

In this article, we describe a simple and effective, one step method to synthesize spherical gold nanoparticles. The particle size in this method is controlled to a larger extent. The synthesis relies on the reduction of metal salt by a mild reducing agent. The pH of the mixture was controlled to enhance the formation of gold nanoparticles. The as-prepared nanoparticles have been characterized by UV–vis spectroscopy and, high Resolution transmission electron microscopy (TEM). It is evident from TEM that the size of these nanoparticles is in the range of 7-20 nm.

2. Experimental

2.1. Materials

Hydrogen tetrachloroaurate(I)hydrate ($HAuCl_4.H_2O$, 99.9+%),L-ascorbic acid (99+%), cetyl trimethylammonium bromide (CTAB, 98%) were purchased from Loba Chemi and NaOH was purchased from Fisher scientific. All chemicals were used as received. DeionisedMilli-Qwater (18MΩ cm) was used to prepare all solutions.

2.2. Synthesis procedure

45 ml of $2.5x10^{-4}$M $HAuCl_4.H_2O$ aqueous solution was taken and $4.5x10^{-3}$ mol of CTAB powder was added to the aqueous solution of $HAuCl_4$. The solution turned into light yellow colour. Then 250µl of 0.1 M L(+) ascorbic acid was added to the above mixture. The solution became colourless due to the reduction of Au^{3+}ions to Au^{+} ions. Then to the above mixture 600µl of 0.5 M NaOH was added to maintain the pH at 12. The colour of the mixture turned into blue within 1 minute after the addition of NaOH. The solution became purplish blue, and finally converted into purplish red within 10 minutes after the addition of NaOH. The mixture is left undisturbed for 48 hours. The collected sample was studied employing the UV-vis spectroscopy. The sample was also characterized with transmission electron microscopy (TEM) analysis. High resolution TEM characterization of the samples was performed with a JEOL JEM 3010 electron microscope operated at 200 kV. The UV-vis absorption spectrum was recorded using a JASCO V-570 spectrophotometer.

RESULTS AND DISCUSSION

The recipe for the formation of gold nanocrystals is similar to our preparation condition for the seed-mediated synthesis of gold nanorods. The concentrations of $HAuCl_4$ and CTAB used are the same as those of the growth solution prepared for nanorod formation. This is an attempt to synthesize gold nanoparticles of controlled size in a basic condition without the use of gold seed particles. We have discovered a route to make nearly spherical gold nanocrystals of diameter around 7.5 nm. The amount of NaOH added was selected to induce a reasonably fast growth of nanocrystals. Further the as-prepared gold nanoparticles showed high stability even after a few months of time. Deviated from the earlier work by Hsiang Yang Wu et al [31] the gold nanoparticles prepared in this work did not show any kind of branching or deterioration.

When a much smaller amount of NaOH was added, such that the solution was not sufficiently basic, the reduction of Au^{+} species to metallic gold was found to be quite slow. Fig. 1 shows the UV-vis absorption spectrum of the as-prepared Au NPs . A single absorption band at 529 nm was recorded after 48 h of reaction. The actual structure and size distribution of particles can be determined by TEM. Fig. 2 shows a typical TEM image of the sample. The image reveals that the nanoparticles have, in general, a spherical shape and there are e few particles showing polydispersity. These nanoparticles have fairly smooth surfaces, and the particle size is in the range of 7-20 nm. The obtained size of the nanoparticles is found to be smaller than the size reported by Hsiang Yang Wu et al [31] by employing wet chemical method. It is evident from optical absorption that the gold nanoparticles give rise to the single absorption band at 529 nm which confirms the quantum confinement of the sample. Et al showed that there was no formation of the gold nanoparticles when the pH of the solution was maintained at 12 [32]. In contrast we have the quantum confined gold nanoparticles formed when the pH of the solution was maintained at 12. To further examine the crystal structure of these spherical nanoparticles, the high-resolution TEM image of a single egg-shaped

nanoparticle was taken and is shown in Fig. 3. As can be seen, this nanoparticle is single crystalline with clear lattice fringes observable over the entire particle.

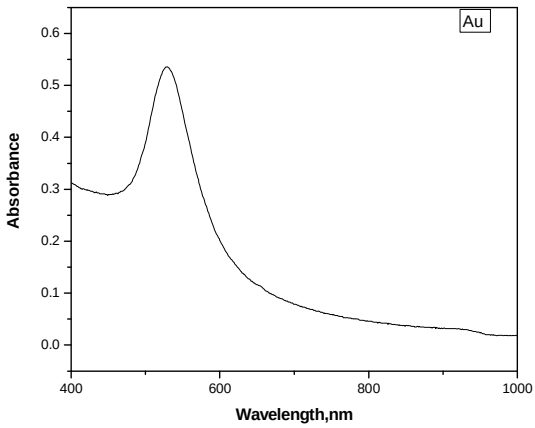

Fig. 1 UV-Vis absorption spectrum of the spherical gold nanocrystals

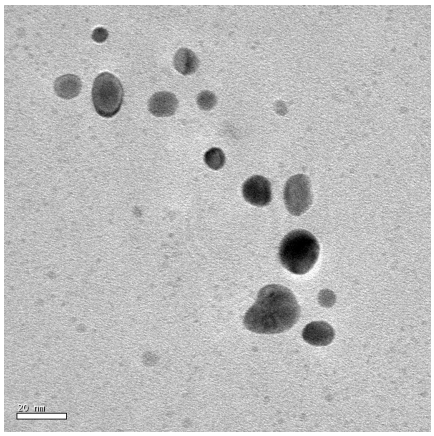

Fig. 2 TEM image of the spherical gold nanoparticles

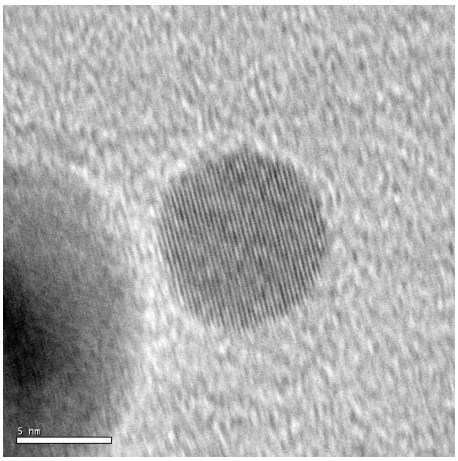

Fig. 3 High-resolution TEM image of a single spherical nanoparticle. Lattice fringes can be clearly seen over the entire nanoparticle.

CONCLUSION

We have demonstrated a simple one-step method for the rapid formation of spherical gold nanocrystal using ascorbic acid as a reducing agent. The resulting spherical nanoparticles are single crystalline and have a smooth surface structure. The particle size of the gold nanoparticles is controlled to a larger extent. These spherical nanocrystals are found to be stable over a longer period and are formed after 48 hours of reaction. This stable nature of the spherical gold nanoparticles is an added advantage to enhance and realize applications related to biological imaging, medical diagnostics and therapeutics.

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