Synthesis of Gold Dendrites in a Green Chemistry Approach Using Hydroxyethyl Cellulose

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Abstract. In this work we report a simple method of preparation of gold dendrites using hydroxyethyl cellulose (HEC) in a green chemistry approach using only water as the solvent. Here HAuCl₄ is reduced to nanodendrites using HEC, which acts as a reducing as well as stabilizing agent. Depending on the reaction conditions gold nanoparticles, snake shaped gold nanostructures and gold dendrites were formed. The gold nanostructures were characterized using transmission electron microscopy. These gold nanostructures are biocompatible and biodegradable.

Keywords: gold dendrites, hydroxyethyl cellulose, green chemistry approach.

1. Introduction

Tremendous interest in research on gold nanostructures is motivated by their fascinating properties with different morphology leading to new functional materials with novel electronic, mechanical and biological properties [1-3]. The size and shape of metal nanoparticles strongly influence their optical, electronic and magnetic properties [4]. Noble metal nanoparticles play an important role in a wide variety of fields such as catalysis [5] photonics [6] optoelectronics [7] information storage [8] photography [9] and surface enhanced Raman scattering [10].

Gold have unique distinctiveness in the field of nanoscience and nanotechnology due to their high electrical and thermal conductivity, high ductility and chemical inertness. It is a great challenge to have control over the morphology of noble metal nanostructures. Recently fabulous efforts have been made to synthesize anisotropic gold nanoparticles.

Various methods are reported for the fabrication of microsized gold structures, which includes photolithography [11], microcontact printing [12], micromanipulator [13] micromachining [14], directional freezing of Au nanoparticles [15], assembly of colloidal particles using an alternating electric field [16], assembly of gold colloidal particles into nano and micro wires using the time averaged dielectrophoretic force from an applied electric field [17] and sequential deposition of materials in capillaries [18]. In the synthetic route for gold nanostructures various reductants have been used including pyrrole, aniline and thiophene [19].

Recently, great interest is being shown for the creation of nanoscale materials using environmentally benign, ‘green’ conditions rather than the extreme conditions needed for conventional chemical synthesis [20]. Herein a modified natural polymer, hydroxyethyl cellulose is selected for the synthesis of gold dendrites.

2. Experimental

2.1. Chemicals

Hydroxyethyl cellulose (average molecular weight, 250000) were obtained from Aldrich chemicals and used as received. Millipore water was used throughout the experiment. Stock solutions of 15wt % of
hydroxyethyl cellulose and 50mM gold chloride solutions were prepared in Millipore water and the test solutions were diluted from these stock solutions, using Millipore water.

### 2.2. Preparation of gold dendrites using hydroxyethyl cellulose

In a typical experiment, 200µl of the gold chloride stock solution was added to 10ml of 15 wt% hydroxyethyl cellulose solution, the reaction mixture was heated to 75°C with stirring for four hours, then cooled to room temperature. Within 5-10 minutes the colour changed from pale yellow to purple, indicating the reduction of the metal ions to nanoparticles.

### 2.3. Transmission electron measurements

TEM images were obtained using JEM 3010 operating at an accelerating voltage of 300 KV. Samples for TEM analyses were prepared by placing a drop of the particle solution on the 400 mesh carbon coated copper TEM grids and blotting out the excess solution with a blotting paper followed by drying at room temperature. The particles were highly stable under the electron beam without any sign of degradation.

### 3. Results and discussion

The chemical structure of hydroxyethyl cellulose is shown in fig. 1.

![Chemical structure of hydroxyethyl cellulose.](image)

Fig. 1: Chemical structure of hydroxyethyl cellulose.

Fig. 2 (A) shows the TEM image of the gold dendrites. Structurally distinct, well-defined dendrites show sharp primary, secondary and tertiary branches. The size of the dendrites was in the range of 5-10 µm. The selected area electron diffraction (SAED) pattern of the gold dendrites is shown in Fig. 2 (B), indicating the crystallinity.

The EDX spectrum of the gold dendrites is shown in fig. 2(C). The pattern indicates that the Au dendrites are pure and free from impurities, the Cu peaks arise from the Cu grids used to obtain the spectrum. The photograph of the gold dendrite solution is shown in fig. 2(D). The color of the solution was purple.

It was very interesting to find that when the same reaction mixture was heated at high temperature above 200 °C, the dendritic structure was destroyed and separate nanoparticles were observed. The TEM image of the gold nanoparticles at higher temperature is shown in fig. 3 (A) and the HRTEM of the gold nanoparticles is shown in fig. 3(B). From the HRTEM it can be concluded that the gold nanoparticles are polycrystalline. The HRTEM showed lattice fringes at 0.206 nm and 0.144 nm which correspond to \{200\} and \{220\} lattice spacing of the fcc gold.

Under the same reaction condition with shorter reaction time, less the 120 min the reaction mixture produced snake shaped gold nanoparticles, the results are published elsewhere [21].

Depending on the reaction condition, time and temperature the reaction mixture can be used to form gold nanoparticles or snake shaped gold nanostructures or gold dendrites.

The mechanism for the formation of snake-shaped gold nanostructures and the gold dendrites may be explained as follows. The mechanism proposed for the formation of snake shaped gold nanoparticles involving the formation of the nanoparticles, brownian motion of these nanoparticles and local oswald ripening are presented elsewhere [21]. There are different models to explain the phenomena of dendritic growth of the nanostructures, which includes the diffusion limited aggregation (DLA) model, deposition, diffusion and aggregation (DDA) model and cluster-cluster aggregation (CCA) model [22].
It is reported that non-equilibrium growth and molecular anisotropy are the main factors governing the formation of dendritic structures apart from the other factors like templates, absorbates and solvents. The microscopic interfacial dynamics (involving surface tension, surface kinetics and anisotropy) and the macroscopic external forces (involving solvents, templates, diffusion and surfactants) are essential for these dendrites [23]. The HEC molecule must act as a template to assemble the nanoparticles and is considered to accelerate the fusion of nanoparticles to form snake-shaped structure and finally the gold dendrites.

4. Conclusion

In summary, we have used a simple aqueous-phase chemical method to synthesize gold dendritic nanostructures using hydroxyethyl cellulose and gold chloride, in a fast way. Here HEC is used as a reducing as well as stabilizing agent for the gold dendritic nanostructures. Thus gold dendrites are produced in a green chemistry way and without any template. The time and temperature of the reaction has significant effect on the morphology of the gold nanostructures. The gold dendritic nanostructures in HEC showed extremely high stability over a long period of time more than several months. These gold dendrites have important applications in microelectronic devices and nanometer-scale electrodes. Only the preliminary results are presented here. The gold dendrites are biocompatible. Applications of these gold dendrites as substrates for surface enhanced raman spectroscopy for biomolecules are being carried out and will be discussed in future.

5. Acknowledgements

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6. References


Fig. 2: TEM image of the gold dendrite (A), the SAED pattern for the gold dendrite (B), EDX spectrum of a gold dendrite (C) and photograph of the gold dendrite solution (D).

Fig. 3: TEM image of the gold nanoparticles (A), the HRTEM image for the gold nanoparticle (B).