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Synthesis of gold nanorods using concentrated aerosol OT in hexane and its application as catalyst for the reduction of eosin

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ABSTRACT

The microemulsion method for the preparation of nanoparticles is well known. We have used the aqueous core of highly concentrated aerosol OT in hexane solution to synthesize gold nanorod by utilizing the aqueous core of surfactant aggregates as host nanoreactor. The shape and size of the aqueous core as well as the particles formed inside the core can be controlled by changing the parameter W_0 (water to surfactant ratio), concentration of gold salt and the concentration of surfactant. When the concentration of the surfactant is very high the shape of the aqueous droplet does not remain spherical but take the shape of prolate. In our study we have made gold nanorods by the reduction of gold chloride with sodium borohydride in the aqueous core of 1 M AOT hexane at a W_0 of 10. The rods are highly monodispersed with a diameter of about 20 nm and a length of 200 nm with an aspect ratio of 10. The absorption spectra of the gold nanorods show two different peaks one at 535 nm and the other at 965 nm. The particles were used as a catalyst for the reduction of eosin with sodium borohydride. The rate constant comes out be very large in comparison with that of uncatalysed reaction. The reaction was carried out at various temperatures between 20 and 60 °C and the activation energy of the reaction was calculated using Arrhenius plot between $-\ln k$ and $1/T$. The activation energy of the gold nanorods catalysed reaction comes out to be more than two times as compared to uncatalysed reaction.

1. Introduction

The progressive decrease in size of metal and semiconductor nanoparticles has been observed to be significant from both fundamental and application points of view. There is widespread interest in understanding the shape and size-dependent properties of nanomaterials for the development of various applications. Many characteristic properties of the nanoscale materials including optical, electronic and catalytic activity are shape and size dependant [1–3]. The catalytic activity of nanoparticulate materials is because of the enormous number of active sites available for the reactants [4–6]. Of course, the efficacy of nanoparticle catalysts depends on various other factors [7–10] such as morphology, average size distribution, porosity, and phase composition. Therefore the technique of fabrication of nanomaterials with controlled size and morphology is required so as to tailor their properties. In recent years, a great deal of progress has been made in the synthesis of various nanostructures with controllable morphology and properties, including one dimensional structure such as nanorods and nanowires [11–14]. These are important class of the nanomaterials due to their promising applications in both fundamental research and nanodevice fabrication [15–17] and have compelled scientists to devise direct and simple methods to accomplish synthesis with high yield [18–21]. Growth of nanostructures having different morphologies can result in the modification of its physical properties and improvement in performance characteristics. By tuning the aspect ratio of nanorods one can follow the transition from zero to one dimensional structure such as nanorods and nanowires. Those structures can also be used as building blocks for anisotropic nanostructured materials and devices like high density data storage devices [22]. Nanoparticles with specific shapes display more particular and valuable characters in optical properties than spherical ones [23,24]. There is an increase in research activities on gold nanorods, to a large extent, is a result of the unique nature of these nanostructures. Gold nanorods are particularly suitable for photonic, optoelectronic, and biotechnological applications in the NIR region [25]. Among many other nonspherical nanostructures, gold nanorods are more directed to advanced uses such as anticancer agent, near-infrared (IR) filter, and storage media, since nanorods have a longitudinal plasmon band at near-infrared region, [26–28].

In the present study we have synthesized gold nanorods in highly concentrated AOT solution in hexane by the reduction of chloroauric acid with sodium borohydride. The particles were prepared at a high concentration of surfactant and the transmission

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electron microscopy confirmed the formation of nanorods. Catalytic study of the gold nanorods-catalyzed reaction was followed by monitoring the absorbance of eosin in the visible spectrum of eosin. Reactions were also followed at different temperatures to measure the activation energy of the above reaction.

2. Materials and experimental procedure

2.1. Materials

All the chemicals used were of AR grade and were used without further purification. The aqueous solutions were prepared in double distilled water. The Chloroauric acid ($HAuCl_4$) and the dye eosin was purchased from Thomas Baker, Sodium borohydride was purchased from s d fine-chem limited. AOT (i.e., sodium bis(2-ethylhexyl)sulphosuccinate) was procured from ACROS organics. The solvent hexane and ethanol was procured from Spectrochem and Merck Ltd respectively.

2.2. Synthesis of gold Nanorods

Gold nanorods (GNRs) was prepared by the reduction of auric chloride by sodium borohydride in the aqueous core of concentrated solution of AOT in hexane. To 10 ml of 1 M AOT in hexane, 100 μl of 2% (w/v) $HAuCl_4$ and 1700 μl of water was added to maintain a W_0 of 10 (W_0 is the molar ratio of water to AOT). The solution was stirred till the clear solution 'A' is obtained. In another 10 ml of 1 M AOT in hexane solution, 100 μl of 2% sodium borohydride and 1700 μl of water was added to maintain a W_0 of 10. The solution was stirred to get a clear solution 'B'. When both the solutions A and B become clear, the solution B was added to solution A very slowly at 20 °C. After the complete addition of solution B to A the mixture was kept on stirring for another 2 h. To extract the nanorods 2 ml of distilled ethanol was added to the mixture and kept in cold overnight and decanting off the supernatant solution. The nanorods were washed 4–5 times with ethanol and water to remove AOT completely. The nanorods were then dispersed in distilled water by sonication for 10 min for characterization and further applications.

2.3. Characterization of Gold nanorods

Au nanorods prepared in H_2O/AOT/hexane solution was characterized by TEM and UV–Vis spectophotometrically. Transmission electron microscopic (TEM) pictures were taken with a Technai G2 30 U-Twin, Technai 300 kv ultra twin microscope. The gold nanorods after extraction were redispersed in ethanol by sonication for 15 min. A drop of the dilute ethanolic solution was put on the polymer coated grid and dried. This step was repeated for a couple of times after complete drying of the grid, a TEM picture of the particles was taken.

The UV–visible spectra of the particles was taken after dispersing the particles in water by sonication and was recorded in the wave length range of 300–1100 nm using Shimadzu-1601 UV–Vis spectrophotometer.

2.4. Kinetic studies of the reduction of eosin

To 2 ml of distilled water taken in a 3 ml cuvette, 40 μl of 10^{-2} M eosin, 60 μl of 0.2%(w/v) aqueous dispersion was added. The reaction was started by adding 400 μl of 0.5 M sodium borohydride solution to the reaction mixture. The reaction was studied spectrophotometerically by measuring the decrease in absorbance of eosin at 535 nm with time in the temperature range of 20–60 °C. The temperature of the reaction mixture was kept constant by circulating water of desired temperature around the sample holder from a thermostatted water bath. For the uncatalyzed reaction 60 μl of 0.2% (w/v) gold nanorods was replaced by an equal volume of double-distilled water.

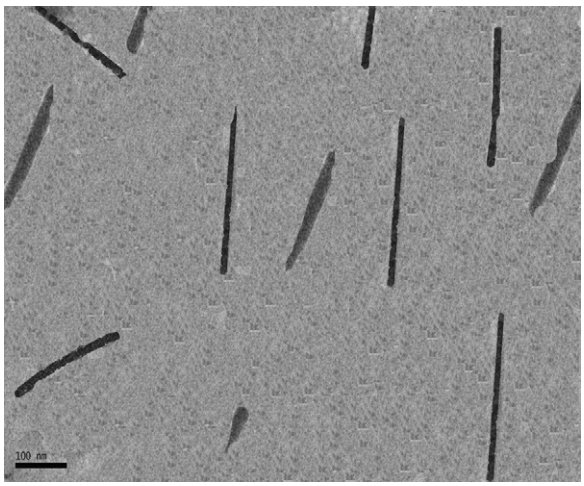

Fig. 1. TEM picture of gold nanorods having a length of around 200 nm and a diameter of about 20 nm, prepared using concentrated AOT in hexane solution.

3. Results and discussion

Various methods [29–36] have been reported in the literature for the preparation of nanorods. We have used the aqueous core of water/aerosol OT/hexane solution as a host nanoreactor to make gold nanorods. It is already known that water, AOT and oil mixed together at different proportion represented by a triangular phase diagram [37], which generally include both solution phases (isotropic phase) and liquid crystalline phases. In a three or four component system there are usually two isotropic solution phases, one rich in water generally termed as L1 and other in oil continuous phase termed as L2. At a higher concentration of AOT where the solution crosses the L2 phase, the spherical droplets take the shape of prolate. It was further observed that at a particular point in the triangular phase diagram the aspect ratio of rod shaped gold nanoparticles remains constant even on repeated synthesis. We used the same principle in our synthesis procedure i.e. the reduction of gold chloride to metallic gold takes the shape of non-spherical rod types inside the prolate shaped droplets. The shape and size of the nanorods can be controlled by varying the shape and size of the aqueous droplets of the ternary system. We have prepared gold nanorods at 1 M concentration of AOT and at a W_0 of 10. Maintaining these parameters of the ternary water/AOT/hexane system it was observed that the aspect ratio of the nanorods remain constant at 10 which has been confirmed from TEM pictures. Fig. 1 shows the transmission electron microscopic picture of the gold nanorods prepared using 1 M AOT in hexane solution and at a W_0 of 10. The nanorods are reasonably monodispersed and are around 200 nm long and about 20 nm in diameter and having an aspect ratio of 10.

Fig. 2 shows the UV–Vis spectra of gold nanorods. Au nanorods possess two characteristic absorption bands [38], a transverse band, similar to that of gold nanospheres, in the visible region corresponding to electron oscillations along the short axis (at 530 nm) and another longitudinal band in the near-infrared region corresponding to electron oscillation along the long axis (at 967 nm) which undergoes a shift with increasing aspect ratio. The latter is particularly sensitive toward the size and the organization of the NRS.

The gold nanorod catalyzed reduction of eosin by $NaBH_4$ involves the reduction of double bond in the eosin molecule to single bond and was studied spectrophotometrically. In the gold