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Acetanilide mediated reversible assembly and disassembly of Au nanoparticles

A. Murugadoss [a], Manoranjan Kar [b], Arun Chattopadhyay [a,b,*]

[a] Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, India
[b] Centre for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati 781039, India

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ABSTRACT

Herein we report the generation of Au nanoparticles (NPs) by sparingly soluble acetanilide in water. We also report the formation of linear chain-like superstructures of self-assembled Au NPs, in the presence of excess acetanilide. This was achieved in two different ways. In the first method, acetanilide was added, with increasing concentration, into aqueous $HAuCl_4$ to produce Au NPs as well as for the formation of assembly, which varied according to the concentration of acetanilide. The other route involved formation of spherical Au NPs at the lowest concentration of acetanilide, which was followed by the formation of assembly of various lengths upon further addition of variable amount of acetanilide. The assemblies were stable in aqueous solution for days with characteristic UV–vis absorption spectra consisting of two peaks. While the wavelength of the first peak remained the same, the position of the second peak changed to longer wavelength with increasing acetanilide concentration. Interestingly, the linear chain-like arrays could be broken into individual particles by first dilution of the solution concentration followed by treatment with ultrasonic waves. The individual Au NPs again formed linear chain-like arrays upon addition of excess acetanilide.

1. Introduction

Systematic organizations of nanoscale particles into well-defined superstructures are currently being addressed by self-assembly using electrostatic forces or molecular bonds and by using template-based approaches [1–5]. Interestingly, assembly of nanoparticles (NPs) and the associated physical property changes have been used in sensing heavy metal ions, DNA hybridization and other biomolecular events [6–11]. Molecularly programmed assembly of NPs would be key to further applications encompassing chemistry, biology, material science and optoelectronics. Chemistry, especially the use of 'soft' interactions, offers the possibility of molecular level control over reversible assembly and disassembly of NPs in solution [12–17], which remains much to be explored. Molecularly controlled assembled NPs would not only offer newer materials with tunable properties but may also reveal a great deal about the nature of molecular interactions between the NPs and the assembling molecules.

Herein, we report the use of sparingly soluble acetanilide in the reversible assembly and disassembly of Au NPs in water. Also, acetanilide has concurrently been used for the synthesis of Au NPs from $HAuCl_4$. The primary control parameter, in the assembly formation, is the concentration of acetanilide in the medium, which also acted as the reducing agent as well as the stabilizer for the NPs. We have used two different ways to achieve the assembly formation. The first method involved simultaneous synthesis and assembly of spherical NPs using various amount of acetanilide during synthesis. In the other method minimum acetanilide concentration was first used in the preparation of spherical Au NPs. This was followed by addition of various amount of acetanilide in order to obtain controlled organization. The results obtained were similar. The optical properties of the NPs and their assemblies were commensurate with the amount of acetanilide present in the medium. Interestingly, the assemblies of NPs could be disassembled into individual NPs using ultrasonic waves and further reassembled into superstructures by concentrating the redispersed particles. The studies here indicate the possibility of molecular level control on the organization of NPs in aqueous media.

2. Materials and methods

Hydrogen tetrachloroauraurate ($HAuCl_4$, 17% Au in HCl as purchased from Sigma–Aldrich), and acetanilide (99%, from Merck), were used as received without further purification. Milli-Q grade water was used in all the experiments.

2.1. Synthesis of Au nanoparticles using acetanilide

2.1.1. Method-I

The method involved the use of various amounts of acetanilide at the time of synthesis. Typically, to five 30 mL vials—each con-

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[*] Corresponding author at: Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, India. Fax: +91 361 258 2349.
E-mail address: arun@iitg.ernet.in (A. Chattopadhyay).

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taining 10 mL of Milli-Q grade water—10, 20, 30, 40 and 50 mg acetanilide were added. The concentrations of acetanilide in the vial were thus 7.29, 14.58, 21.87, 29.16 and 36.45 mM respectively. The vials were then heated to 90 °C in order to dissolve acetanilide. This was followed by addition of 20 µL of 17.26 mM of $HAuCl_4$ to each solution while they were still being heated. These reaction mixtures were then kept on a hot plate under slow boiling condition for 5 min. The resulting solutions appeared red in color. This indicated possible formation of Au nanoparticles (NPs). The red colored solutions were taken out from the hot plate and cooled to room temperature. The solutions were used for further characterization studies. The pH of all of the resulting solutions was measured to be 3.5. It was also observed that while the solutions containing initially 7.29, 14.58, 21.87 mM of acetanilide were stable for 3–4 days, those containing 29.16 and 36.45 mM of acetanilide were stable for only a day after which visible precipitation could be observed. However, if the pH of the solutions were changed to 7.0—after synthesis—they were stable for a couple of weeks without occurrence of observable precipitations.

2.1.2. Method-II

This method involved the synthesis of Au NPs with minimum amount of acetanilide followed by addition of various excess amounts of acetanilide. Five 30 mL vials, each containing 20 mg of acetanilide (14.58 mM) in 10 mL Milli-Q water, were kept on hot plates at 90 °C. To each of the solutions, 20 µL of 17.26 mM of $HAuCl_4$ was then added. This was followed by keeping the reaction mixtures on the hot plate under slow boiling condition for 5 min, after which the solutions turned red. The solutions were then taken out of the hot plate, immediately followed by addition of appropriate amount of acetanilide so that the total concentrations of acetanilide in the vials were 18.95, 23.30, 27.71, 32.07 and 36.45 mM respectively. These solutions were then kept at room temperature for 30 min before use. The pH of the resulting solution was found to be 3.5. The solutions, as such, were used for further characterization studies.

2.1.3. Disassembly of Au NPs

0.5 mL portion each of the Au NP solutions, containing the highest concentration of acetanilide (36.45 mM) and as prepared using *Method-I* and *Method-II* above, was taken in a 30 mL vial. To each of these two vials, 4.5 mL of Milli-Q water was added. The solution appeared nearly colorless with slight violet tint. UV–vis absorption spectra of the solutions were recorded. The solutions were then kept in an ultrasonication bath (Elma, with Model: D-78224, Singen/Htw at 35 KHz) for 3 h. The resulted solution shown violet in color and the UV–vis absorbance spectrum consisted of a single peak at 535 nm, with enhanced absorption value. On the other hand, the solution obtained from *Method-II* still did not show any color change. However, after sonication for a total of 8 h, the solution appeared violet (weak) in color and the UV–visible absorbance spectrum consisted of one major peak at 540 nm with a small hump at 650 nm. Both the solutions were used for further TEM analysis.

2.1.4. Reassembly of Au NPs

Twenty four, identically prepared solutions as reported above for the preparation of disassembly of Au NPs using *Method-I*, were mixed in a 30 mL vial, which was then subjected to ultracentrifugation at 70,000 rpm at 15 °C for 15 min. Finally, the pellet was collected and then washed with copious amount of water with centrifugation after each wash. This process was repeated for three times. The pellet was then redispersed in 3 mL water. The 0.8 mL of redispersed sample was diluted with 1.7 mL water. The pH of the solution was adjusted to 3.5 by adding 10 µL of ∼1 M hydrochloric acid. The total volume of the solution was made to be 2.5 mL. To this solution, 20 mg of acetanilide was added. The mixture was kept on a hot plate and slowly boiled for 3 min. The solution was brought to room temperature and further kept for 30 min before pursuing UV–visible absorption and TEM studies.

2.1.5. Analytical measurements

UV–vis absorption spectra of the samples were recorded using a HITACHI model U-2800 UV–visible spectrophotometer in the range of 300 to 1100 nm. The ^1H NMR spectra of acetanilide as well acetanilide capped Au NPs in $CDCl_3$ were recorded using a Varian 400 MHz spectrometer, with TMS as the internal reference. The dynamic light scattering (DLS) measurements of the liquid samples were performed with an LB-550 (HORIBA) DLS measurement system. Transmission electron microscopy (TEM) measurements were performed using JEOL-2100 equipment operating at an acceleration voltage of 200 kV. The TEM samples were prepared by placing a drop of liquid on carbon coated copper grid (400 mesh) followed by evaporation of the solvent at room temperature.

3. Results and discussion

When 34.5 µM $HAuCl_4$ was treated with 7.29 mM acetanilide (at boiling condition) UV–vis spectrum (Fig. 1A (a)) characteristic of spherical Au NPs was observed. A single peak with maximum at 551 nm was observed. Transmission electron microscopy (TEM) measurements of the sample indicated the presence of spherical NPs in the solution (Fig. 1B) with diameters of about 20 nm, although there was substantial number of NPs with diameters less than 10 nm. On the other hand, when increasing amount of acetanilide was used, the UV–vis spectra consisted of two surface plasmon resonance (SPR) peaks—the transverse one at 551 nm—while the longitudinal one appeared at increasingly higher wavelengths with the use of larger amounts of acetanilide (Fig. 1A (c)–(e)). For example, at the acetanilide concentrations of 21.87, 29.16 and 36.45 mM the second peak appeared at 698, 750 and 754 nm respectively. It is also important to mention that the peak at 551 nm remained constant for all of the above samples. TEM measurements (Figs. 1C and 1D) indicated the formation of necklace-like assemblies of NPs at higher acetanilide concentrations. The length of the chains increased with increasing acetanilide concentration. Also, branching of structures from a single head to several linear arrays could be observed. Interestingly, there was no formation of rods or other structures indicating that the extent of associations of NPs, which depended on the amount of acetanilide present in the medium, was responsible for the observed spectra in the present condition. X-ray diffraction (XRD) measurements also indicated the formation of Au NPs in the solution (refer to electronic Supplementary information—ESI—Fig. S1) as well as present in the assemblies. Further, dynamic light scattering (DLS) measurements of the above solutions showed that at the lowest concentration of acetanilide the particles formed were small with 30–40 nm in average diameter (Fig. 1E). On the other hand with increasing concentration of acetanilide the average sizes shifted to increasingly higher values (Figs. 1F–1I) of several microns. The observations indicate that in the presence of increasing amount of acetanilide longer assemblies in the medium were formed. In other words, as the acetanilide concentration was increased the number of particles involved in each assembly, which were responsible for the occurrence of the longitudinal plasmon resonance peak, had also increased. Thus with the increase of assembly size the longitudinal absorption maximum shifted to increasingly higher values. This is due to self-assembly of Au NPs into linear chain like arrays, where the length of the linear chain increases with increasing concentration of acetanilide (refer to ESI, Fig. S2). Also, Au NPs present in the each array were in close contact with each other and possibly were separated by acetanilide molecular layers, which lead to