Photochemical Synthesis of Gold Nanoparticles with Interesting Shapes

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Abstract:

Our research focused on gold nanoparticle synthesis using UV irradiation to form interesting shapes. Xenon lamp irradiation with a band pass filter selecting wavelengths 250 nm to 350 nm was used to excite the gold precursor, hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4(3H_2O)$) in ethylene glycol (EG). The excited gold precursor is then reduced to gold metal atoms by the solvent, ethylene glycol (EG) and through disproportionation. Polymer polyvinylpyrrolidone (PVP) was used as the surfactant. Optical spectroscopy and transmission electron microscopy were used to characterize the particles. Particle sizes with triangular, pentagonal, and hexagonal shapes were fabricated with various sizes.

It was demonstrated that this convenient method is versatile to fabricate gold nanoparticles with controlled size and shape.

Introduction:

Nano-scaled materials are of great interest due to their optical and catalytic properties varying with their sizes and shapes [1, 2]. This dependence comes from the spatial confinement of the electrons. In gold metal nanoparticles, strong light absorption in the visible region is shown. The strong absorption results from nanoparticles' coherent oscillation of the free electrons on the particle surface called the surface plasmon resonance. The surface plasmon resonance of gold nanoparticles has broad application and has drawn great attention in recent years [1, 2]. Herein, we report a photochemical gold nanoparticle synthesis method.

In the reaction, the gold salt, $HAuCl_4$ absorbs the UV light to generate an excited electronic state, and then reacts with ethylene glycol (EG), which serves as both the solvent and the reducing agent. The gold salt is gradually reduced to Au^+. Au^+ then disproportionates to form gold atoms. The gold atoms serve as nucleation sites for further growth of nanoparticles. The surface regulating polymers (PVP) are expected to bind on the gold surface, insulate the particles from gold ions and further aggregation, therefore stopping growth and stabilizing the particles. Further, PVP is believed to have selective interaction between different planes of the gold crystal, thus enhancing the growth along one direction while reducing the growth along another direction [3]. Therefore, with different PVP and gold salt concentrations, we can control the shapes and sizes of the particles.

Results and Discussion:

The effects of altering gold salt concentration, PVP/Au ratio and light intensity on the particles formed were studied. In gold concentration studies, samples were prepared by adding different gold salt volumes, while maintaining constant PVP/Au molecular ratio. Based on TEM images, higher gold salt concentration, lower PVP concentration and lower irradiation power produce larger particles. These images are shown in Figure 1 (a)-(d) with; (a) low gold salt concentration, (b) high gold concentration, (c) high PVP concentration, and (d) low PVP concentration. This trend was also observed in the optical spectra as a red shift of the plasmon resonance absorbance peak around 540 nm and an increase in the infrared absorption

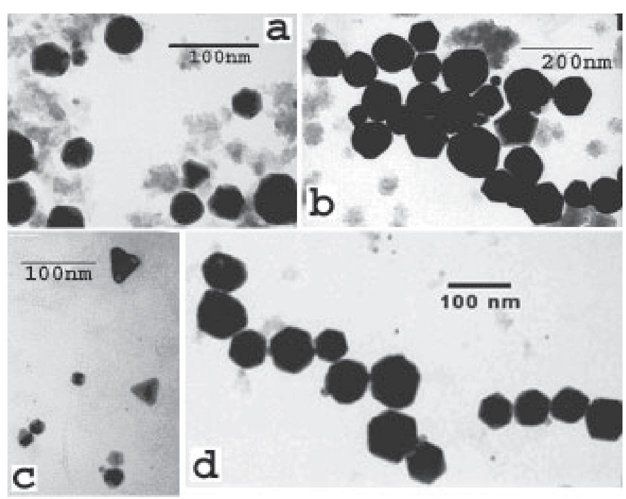

Figure 1: TEM images of gold nanoparticles generated with different parameters.

region. Typical optical absorption spectra are shown in Figure 2.

In typical samples, hexagonal shapes presented about 30% of the particles. Triangles, pentagons represented about 10% and 5% respectively, and the other 50% were spheres and random shapes. For hexagons, the highest yield of 50% can be achieved by using 54 µl PVP, 70 µl gold salt, and 2.7 ml EG with 8 aluminum screening layers. The statistics were obtained from TEM images. Generally, the triangular particles percentage was higher in the samples with smaller particles. Reactions have been carried out both with and without stirring. It was found that particles exhibit better uniformity in size and better yield of interesting shapes without stirring.

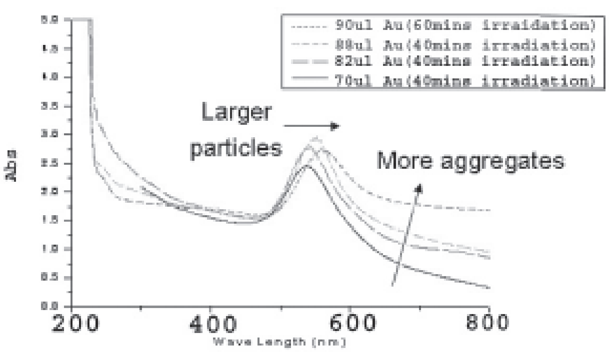

Figure 2: Optical spectra with samples generated with different gold salt concentration.

Experimental Procedure:

Solutions of 0.375M PVP, 0.083M $HAuCl_4$ were prepared in ethylene glycol for use in all experiments. Samples with different combinations of EG, PVP, and $HAuCl_4$ were placed in a 1 centimeter path length quartz cuvette for irradiation. A typical sample consisted of a homogenized solution of 2.7 ml EG, 68 µl PVP, and 70 µl $HAuCl_4$. Samples were fixed and not stirred. An 88 watts xenon lamp was used for irradiation with a band pass filter selecting wavelengths 230 nm to 380 nm, with layers of closely packed aluminum screening used to adjust the irradiation power. The setup is illustrated in Figure 3. Absorption spectra were measured on a Shimadzu UV-3103-PC spectrophotometer. For the TEM sample preparation, a drop of sample was placed on a carbon coated copper grid, left overnight in the dark, and dried with a heat gun. Alternatively, a drop of sample solution was attached on one side of the copper grid, which then was gently placed on filter paper with the opposite site facing down. The grids were washed with small volume of water to remove excess PVP prior to viewing in the TEM.

Future Works:

Future work should be focused on further optimizing the yield. Some possible parameters are to provide uniform UV-irradiation across the sample, to use other surfactants, and to use narrower bandwidth filters.

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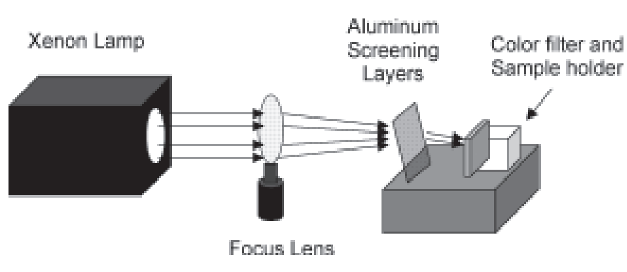

Figure 3: Diagram of the experimental set-up