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The Effects of Sodium Chloride in the Formation of Size and Shape of Gold (Au) Nanoparticles by Microwave-Polyol Method for Mercury Adsorption

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***Abstract*—** Mercury is a natural occurring element and present in various concentrations in the environment. Due to its toxic effects, it is desirable to research mercury sensitive materials to adsorb mercury. This paper describes the preparation of Au nanoparticles for mercury adsorption by using a microwave (MW)-polyol method in the presence of three different Sodium Chloride (NaCl) concentrations (10, 20 and 30 mM). Mixtures of spherical, triangular, octahedral, decahedral particles and 1-D product were obtained using this rapid method. Sizes and shapes was found strongly depend on the concentrations of NaCl. Without NaCl concentration, spherical, triangular plates, octahedral, decahedral nanoparticles and 1D product were produced. At the lower NaCl concentration (10 mM), spherical, octahedral and decahedral nanoparticles were present, while spherical and decahedral nanoparticles were preferentially form by using 20 mM of NaCl concentration. Spherical, triangular plates, octahedral and decahedral nanoparticles were obtained at the highest NaCl concentration (30 mM). The amount of mercury adsorbed using 20 ppm mercury solution is the highest (67.5 %) for NaCl concentration of 30 mM. The high yield of polygonal particles will increase the mercury adsorption. In addition, the adsorption of mercury is also due to the sizes of the particles. The sizes of particles become smaller with increasing NaCl concentrations (size ranges, 5-16 nm) than those synthesized without addition of NaCl (size ranges 11-32 nm). It is concluded that NaCl concentrations affects the formation of sizes and shapes of Au nanoparticles thus affects the mercury adsorption.

***Keywords*—** Adsorption, Au Nanoparticles, Mercury, Sodium Chloride.

I. Introduction

ENVIRONMENTAL mercury levels have increased considerably in recent years. Mercury is a very volatile element and its vapors can be a dangerous source of air pollution, thus representing a serious risk for human health [1]. Exposure to high mercury levels can be harmful to the brain, heart, kidneys, lungs and immune system of humans of all ages [2]. An increasing awareness of mercury and volatile mercury compounds contamination in the environment has been responsible for intense research of mercury sensitive materials.

The ability of gold (Au) to adsorb and amalgamate mercury is well known. Since the reactions strongly depend on sizes and shapes, the polyol method is one of the typical techniques to prepare Au nanoparticles of different sizes and shapes by reducing their ionic salts. In general, a mixture of reagent and polymer surfactant in ethylene glycol (EG) is heated in an oil bath for several hours and spherical nanoparticles are prepared. Recently microwave (MW) heating has been coupled with the polyol method for rapid preparation of Au nanoparticles [3]. When Au^{3+} in $AuCl^{-}$ ions is reduced in EG in the presence of polyvinylpyrrolidone (PVP) under MW heating for 2-3 min, mixtures of triangular, square, rhombic and hexagonal nanoparticles are produced. In addition, small numbers of one-dimensional (1-D) nanorods and nanowires are produced.

To determine optimum experimental conditions for the synthesis of Au nanoparticles, dependences of the sizes and shapes on such experimental parameters as concentrations of PVP and molecular weights of PVP (10 and 58 k) have been examined [4], [5]. It was found that the sizes and shapes of Au nanoparticles depended strongly on these experimental parameters. For the mercury adsorption result, we have especially studied preparation of Au nanoparticles solution from mixtures of $HAuCl_4.3H_2O$/PVP/EG solutions [4], [5]. In our systematic studies on sizes and shapes of Au nanoparticles, we found that Au nanoparticles from mixture of $HAuCl_4.3H_2O$ (2.539 mM)/PVP (11.1 mM)/EG produced high yield of polygonal particles and the solution adsorbed more mercury. It is important to note that, the amount of mercury adsorbed is inversely proportional to the sizes of Au nanoparticles. However, further detailed studies were required in order to determine optimum experimental condition for size and shape controlling synthesis for the mercury adsorption performances.

In the present study, sizes and shapes of Au nanoparticles were prepared by using MW-polyol method in the presence of NaCl with various concentrations for the optimum mercury

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adsorption. Among various experimental parameters, we focused and studied upon the concentrations of chloride ion from NaCl. It was found that these parameters played a significant role in the formation of sizes and shapes of Au nanoparticles.

II. Materials and Methods

Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4.3H_2O$) as a source of Au nanoparticles, polyvinylpyrrolidone (PVP) as a protecting agent or capping agent, sodium chloride (NaCl) as a source of chloride ions and ethylene glycol (EG) as both solvent and reductant. Mercury chloride ($HgCl_2$) is used as a source of mercury.

A. Preparation of Au Nanoparticles

The MW-polyol method used in this study was similar to that reported previously [3], [6]. To study the effects of NaCl concentrations, Au nanoparticles solutions were prepared by reduction of $HAuCl_4.3H_2O$ (0.02 g: 0.0508 mmol) in 20 ml ethylene glycol in the presence of PVP (average molecular weight: 10,000, 2.22g). The solution was added with various concentrations of chloride ion (10-30 mM) and the solutions were rapidly heated by MW irradiation from room temperature to the boiling point of EG (198^oC) for 3 minutes. PVP acts as a stabilizer of small Au nanoparticles.

B. Preparation of Mercury Solution

The initial mercury standard solution was prepared by dissolving 0.027 g of $HgCl_2$ in 1 liter deionized water. This solution was further diluted whenever necessary for the analysis.

C. Characterization of Au Nanoparticles

After MW irradiation, products solutions of Au nanoparticles were centrifuged at 10,000 rpm for 2 hours. The relative centrifugal force was 9503 G in the centrifugal separation. The centrifugal step was carried out twice. The precipitate was collected and dispersed on ethanol for transmission electron microscopy (JEOL JEM-2010 TEM) observation. Absorption spectra of reagent and product solutions were measured in ultra violet-visible (UV-Vis) absorption spectroscopy using Jenway 6305 spectrometer. Original product solutions were diluted in ethanol by factor of 25 before the spectral measurements.

D. Mercury Adsorption Measurement

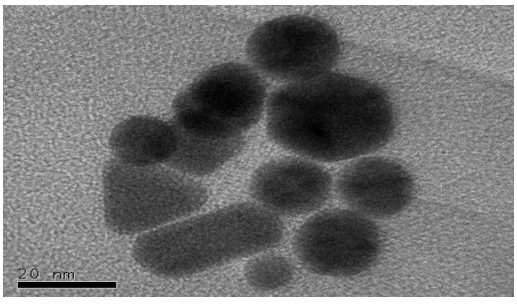
After Au nanoparticles solution was centrifuged, the precipitate (0.001 g) was added in 20 ml mercury solution. The percentage Au nanoparticles to adsorb mercury were determined by analyzing the concentration mercury solution before and after the contacts with Au nanoparticles. The absorbance measurements were carried out by the atomic absorption spectrophotometer. (AAS, AAnalyst 400).

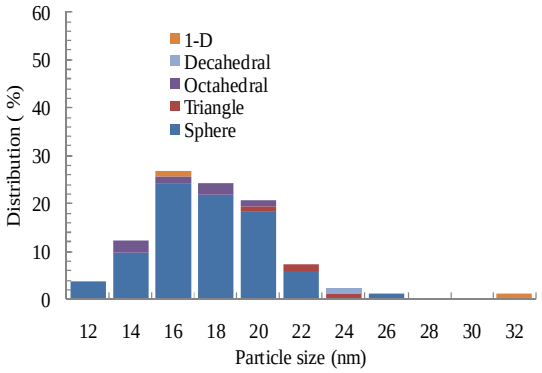
III. Results and Discussion

A. Synthesis of Au Nanoparticles

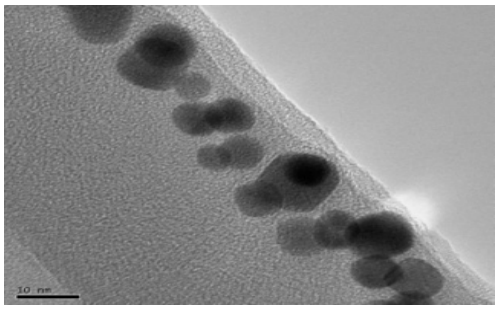
It is known that halogen anions such as Cl^- ions affect significantly morphologies and sizes of Ag nanparticles due to the selective etching by Cl^-/O_2 (dissolved in solvent) [7], [8], [9], [10]. Fig. 1 (a)-(d) shows TEM images of Au nanoparticles obtained without addition of NaCl [4] and at three different NaCl concentrations (10, 20 and 30 mM) and along with product distribution diagram of each particle that indicate the effect of NaCl concentration on the formation of size and shape of Au nanoparticles. It was found that sizes and shapes of products depend strongly on the NaCl concentrations. Various mixtures of spherical, triangular, octahedral, decahedral particles and 1-D product were produced. It should be noted that not only sizes but also yields of each product change with increasing NaCl concentration in Fig.1. The definition of sizes of each particle in this study is shown in Fig. S1 (Supplementary data). The average sizes of particles were measured from diameters and edge length of particles. The average sizes were estimated by measuring more than 100 particles.

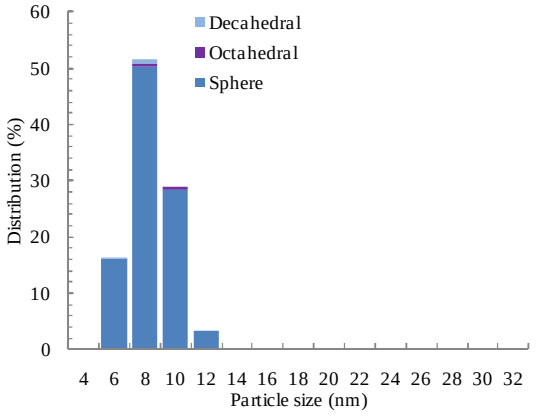
Without NaCl concentration, mixtures of the following particles were produced: spherical particles (yield 86 %, size ranges 11-25 nm), triangular plates (4 %, 20-24 nm), octahedral (7 %, 13-20 nm) decahedral (1 %, 24 nm) and 1 D product (2 %, 16-32 nm). At the lowest NaCl concentration of 10 mM, mixtures of the following particles were produced: spherical particles (yield 98 %, size ranges 5-13 nm), octahedral (1 %, 8-10 nm) and decahedral (1 %, 6-8 nm). At the medium NaCl concentration of 20 mM, mixtures of following nanoparticles were produced: spherical particles (yield 99 %, size ranges 4-15 nm) and decahedral (1%, 8 nm). At the higher NaCl concentration (30 mM), a mixture of following nanoparticles was obtained: spherical particles (yield 92 %, size ranges 7-16 nm), triangular plates (1 %, 10 nm), octahedral (6 %, 8-11 nm) and decahedral (1%, 7 nm). It should be noted that the sizes of particles smaller with addition of NaCl concentrations than those synthesized without addition of NaCl.



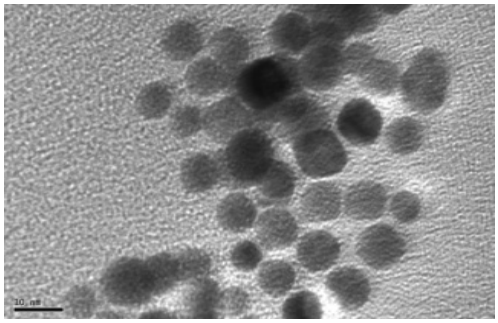


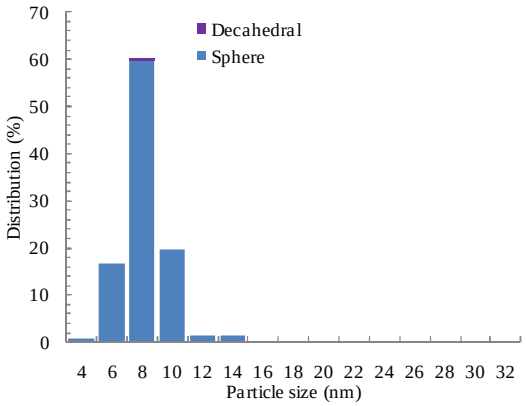
(a) Without NaCl



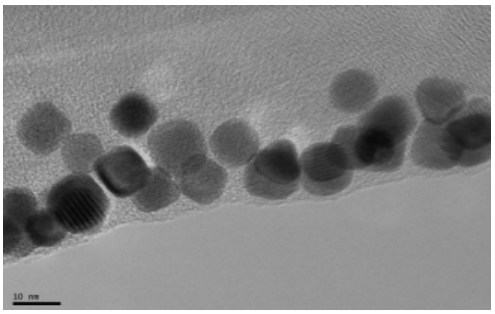


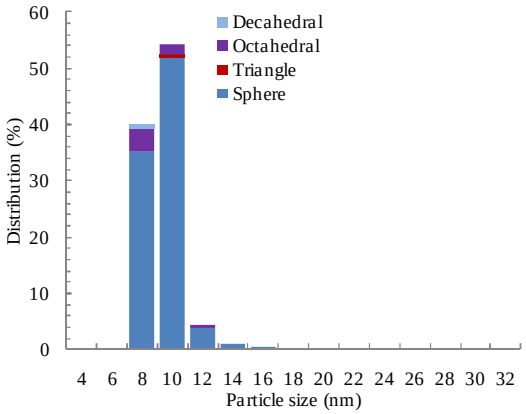
(b) 10 mM





(c) 20 mM





(d) 30 mM

Fig. 1 TEM photographs of Au nanoparticles obtained from different NaCl concentrations (a) without NaCl (b) 10 (c) 20 and (d) 30 mM along with product distribution diagram of each particle

Fig. 2 shows that the average size distribution of each product. The sizes of spherical, triangular, octahedral and decahedral nanoparticles prepared at the highest NaCl concentration (30 mM) were smaller than those synthesized without the addition of NaCl by factors of 1.9, 2.2, 1.8 and 3.4, respectively. The 1-D products were only produced by the solution without NaCl. These data indicate that the size for Au nanoparticles generally decreased with increasing the NaCl concentration.

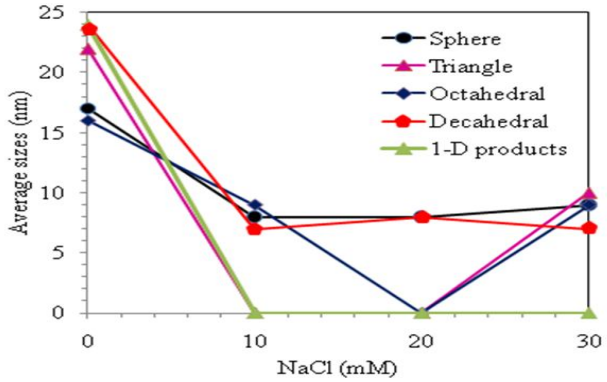


Fig. 2 Dependence of average size distribution of Au nanoparticles prepared from different NaCl concentrations (a) without NaCl (b) 10 (c) 20 and (d) 30 mM

The product solutions of Au nanoparticles were measured using UV-vis spectrometer. It is known that the wavelengths and absorbance of surface plasmon resonance (SPR) bands depend on their sizes and shapes of Au nanoparticles. In the product spectra (Fig. 3), SPR bands of Au nanoparticles appear in 500-700 nm regions. It is known that a SPR band of spherical Au nanoparticles appears in the 500-600 nm regions with a sharp peak at about 520 nm [11], [12], [13] while SPR bands of polygonal Au nanoparticles are observed in the 550-800 nm region [3].

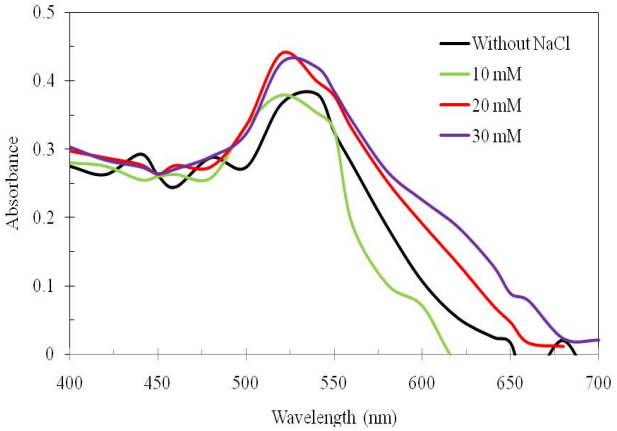


Fig. 3 Absorption spectra of product solutions with different NaCl concentrations

Thus, strong band in the 500-600 nm region observed in spectra product solutions are ascribed to a SPR band of spherical Au nanoparticles while the longer wavelength bands above 600 nm is attributed to SPR band of polygonal Au nanoparticles. Without NaCl concentration, a SPR band is composed with a peak at ~540 nm and a shoulder peaks at 680 nm are observed. At the lowest NaCl concentration (10 mM), SPR band is composed of a broad peak at 520 nm and a very weak shoulder peak at ~600 nm. By the addition 20 mM of NaCl concentration, the SPR band gives a peak at 520 nm and a very weak shoulder peak at ~680 nm. These results are consistent with the facts that the yield of polygonal particles is decreased in 10 and 20 mM of NaCl concentrations solution. At the highest NaCl concentration (30 mM), the SPR band with a peak ~520 nm and a shoulder peak at 660 nm are observed. These observation data are consistent with the sizes and shape changes observed in TEM images of Au nanoparticles (Fig. 1).

B. Mercury Adsorption

The concentration of mercury solution was measured before and after the contacts with Au nanoparticles in order to determine the performance of Au nanoparticles to adsorb mercury with different sizes and shapes of Au nanoparticles. Equation 1 was used to determine the percentage amount of mercury adsorbed:

$$\% \text{ amount mercury adsorbed} = \frac{C_i - C_e}{C_i} \text{ X } 100\ \% \qquad (1)$$

where Ci is initial mercury concentration (ppm) and Ce is equilibrium mercury concentration (ppm).

Table 1 summarizes the AAS result of mercury adsorbed on Au nanoparticles using 10 and 20 ppm mercury solution. Without NaCl concentration, 28.7 % mercury was adsorbed. The adsorption of mercury increased at 10 and 20 mM of NaCl concentrations with 65.8 and 66.7 %, respectively. The highest mercury adsorbed is 67.5 % by using 30 mM of NaCl concentration. The variation is due to the sizes and shapes of the Au nanoparticles produced. As discussed earlier, without NaCl concentration produced spherical, triangular plates, octahedral, decahedral nanoparticles and 1 D product (size ranges, 11-32 nm). By addition 10 and 20 mM of NaCl concentration, the yield of decahedral and octahedral particles decreased (size ranges, 5-15 nm). At the highest NaCl concentration (30 mM), the yield of decahedral and octahedral increased with addition of triangular shapes (size ranges, 7-16 nm). Thus, the high yield of polygonal particles will increase the mercury adsorption but the adsorption also depended strongly on the size of Au nanoparticles.

TABLE I
AAS RESULTS OF MERCURY ADSORPTION ON AU PRODUCTS SOLUTIONS

Sample	Concentration (ppm)		Amount mercury adsorbed (%)
	Initial, Ci	Equilibrium, Ce	
Without NaCl	19.7	14.05	28.7
10 mM	19.7	6.74	65.8
20 mM	19.7	6.56	66.7
30 mM	19.7	6.41	67.5

IV. CONCLUSION

In this study, MW-polyol method was applied for fast synthesis of Au nanoparticles. It was found that from TEM observation, different amount of NaCl concentration added has produced different sizes and shapes of Au nanoparticles.

The spectral observations from UV-visible absorption spectra are consistent with the TEM observation of sizes and shapes of products solution. From the mercury adsorption results, product with the high yield of polygonal particles adsorbed more mercury, but the amount of mercury adsorbed is also inversely proportional to the sizes of Au nanoparticles. It was concluded that NaCl concentrations affects the formation of shapes of Au nanoparticles thus affect the mercury adsorption. The present result provides new information about sizes and shapes controlled synthesis of Au nanoparticles for optimum mercury adsorption. In order to confirm the validity of this explanation, further detailed experimental and theoretical will also be necessary.

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