

Synthesis of Gold (Au) Nanoparticles for Mercury Adsorption

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Abstract: **Problem statement:** Mercury is not only hazardous to human health and the environment but could also attack equipment components resulting in a mechanical failure and gas leakage. **Approach:** Describes the preparation of various sizes and shapes of Au nanoparticles for mercury adsorption by using polyol method under MW heating. Au nanoparticles have been synthesized by a polyol method under Microwave (MW) heating in the presence of Au seed ($[Au]_1/[Au]_0 = 6$ of molar ratio) and different Polyvinylpyrrolidone (PVP) concentrations (11.1, 22.2 and 33.3 mM). The amount of mercury adsorbed was determined by analyzing the concentration of mercury solution before and after the contacts with various sizes and shapes of Au nanoparticles. **Results:** When the lower PVP concentration (11.1 mM) was used, polygonal and spherical nanoparticles were dominantly present, while spherical nanoparticles were preferentially formed by using higher PVP concentrations (22.2 and 33.3 mM). It was found that the diameter and length of Au nanoparticles decreased with increasing PVP concentrations. When Au nanoparticles solution was prepared using Au seed, significant changes in sizes and shapes of Au seed occurred. Spherical nanoparticles in the Au seed (22.2 mM) were completely changed to polygonal nanoparticles. The amount of mercury adsorbed using 9 ppm mercury solution on polygonal nanoparticles is higher (64.88%) than spherical nanoparticles (18.77%). **Conclusion:** These results indicated that mercury adsorption strongly depends on the sizes and shapes of Au nanoparticles. Polygonal nanoparticles adsorbed more mercury than spherical nanoparticles but the amount mercury adsorbed is inversely proportional to their size.

Key words: Au nanoparticles, polyol method, microwave heating, mercury adsorption

INTRODUCTION

Mercury is present in nature and is also present in most natural gas and natural gas condensate at varying levels (Ebinghaus *et al.*, 1999). The typical mercury concentration in natural gas and natural gas condensate is between 1 and 200 $\mu\text{g Nm}^{-3}$ of gas (Shafawi *et al.*, 1999). Mercury in natural gas condensate could be present in various forms (elemental, organometallic and inorganic salt), depending on the origin of the condensates.

Mercury extraction and purification of gases, as well as reworking the products of gas deposits, which involve mercury separating as a fairly toxic element, is very important for the environment protection (Spiric and Mashyanov, 2000). It is important even in cases when mercury is not an industrial component; the huge amounts of world annual reworking gas should be taken into account (Ozerova *et al.*, 1999).

Previous study stated that the purpose of removing mercury from natural gas is to protect downstream aluminum heat exchangers in natural gas plants. Mercury has caused numerous aluminum exchanger failures. It amalgamates with aluminum, resulting in a mechanical failure and gas leakage (Wilhem and Bloom, 2000). Another reason for removing mercury is that mercury is a very volatile element. Its vapors can be a dangerous source of air pollution, thus representing a serious risk for human health (Ebinghaus *et al.*, 1999). Exposure to high mercury levels can be harmful to the brain, heart, kidneys, lungs and immune system of humans of all ages (Darbha *et al.*, 2007).

Among various metallic nanoparticles, 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 a typical technique to prepare Au nanoparticles of different sizes and shapes by reducing their ionic salts. In general, a mixture of

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reagent and polymer surfactant in Ethylene Glycol (EG) was heated in an oil bath for several hours and spherical nanoparticles were prepared. Recently Microwave (MW) heating has been coupled with the polyol method for rapid preparation of Au nanoparticles (Tsuji *et al.*, 2003; 2004). This study describes the preparation of various sizes and shapes of Au nanoparticles for mercury adsorption by using polyol method under MW heating.

MATERIALS AND METHODS

Hydrogen tetrachloroaurate (III) hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), is a source of Au nanoparticles, Ethylene Glycol (EG) is used as solvent and reducing agent, Polyvinylpyrrolidone (PVP) as a protecting or capping agent and Mercury Chloride (HgCl_2) is a source of mercury.

Preparation of Au nanoparticles: The MW-polyol method used in this study was similar to that reported previously (Tsuji *et al.*, 2003; 2004). The following two procedures have been used for the preparation of Au nanoparticles solution. No Au seed are used in first procedures, while they are used in the second procedure:

- Procedure 1: This procedure was used for the study of fundamental effects of the different PVP concentration. Au nanoparticles solution were prepared by reduction of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.02 g: 0.0559 mmol) in 20 mL ethylene glycol in the presence of various mixtures of PVP (average molecular weight: 10,000, 2.22-6.66 g: Corresponding to 0.222-0.666 mmol). The solution was rapidly heated by MW irradiation from room temperature to the boiling point of EG (198°C) for 3 min. The product solution of PVP (4.44 g: 0.444 mmol) was used as Au seed.
- Procedure 2: This procedure was used to observe the growth of Au nanoparticles. Here, we define $[\text{Au}]_0$ as a initial concentration of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ used for Au seed in the first step, while $[\text{Au}]_1$ denotes a concentration of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in the second step. Then, the $[\text{Au}]_1/[\text{Au}]_0$ molar ratio used in this study corresponded to 6. The solution was heated again by MW irradiation for 3 min

Preparation of mercury solution: The initial mercury standard solution was prepared by dissolving 0.01354 g of HgCl_2 in 1 L deionized water. This solution was further diluted whenever necessary for the analysis.

Characterization of Au nanoparticles: After MW irradiation, products solutions of Au nanoparticles were centrifuged at 10,000 rpm for 2 h. 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.

Mercury adsorption measurement: After Au nanoparticles solution was centrifuged, the precipitate (0.001 g) was added in 10 ml mercury solution. The percentage Au nanoparticles to adsorb mercury were determined by analyzing the concentration of mercury solution before and after the contacts with Au nanoparticles. The absorbance measurements were carried out by the atomic absorption spectrophotometer. (AAS, AAnalyst 400).

RESULTS

Synthesis of Au nanoparticles: Figure 1 shows TEM photographs of Au nanoparticles prepared from procedure 1 and procedure 2. Various mixtures of spherical and polygonal nanoparticles were prepared. To obtain information on optical of Au nanostructures, absorption spectra of reagent and product solution in Procedures 1 and 2 were measured in UV-Vis spectra (Fig. 2).

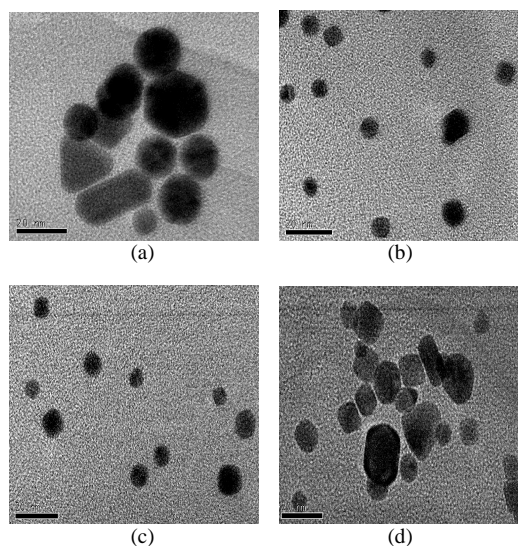


Fig. 1: TEM photographs of Au nanoparticles prepared from Procedure 1 (a-c) with PVP concentration (11.1-33.3 mM) and (d) from Procedure 2 with $[\text{Au}]_1/[\text{Au}]_0$ molar ratio corresponded to 6. (a) 11.1 mM; (b) 22.2 mM; (c) 33.3 mM; (d) $[\text{Au}]_1/[\text{Au}]_0 = 6$

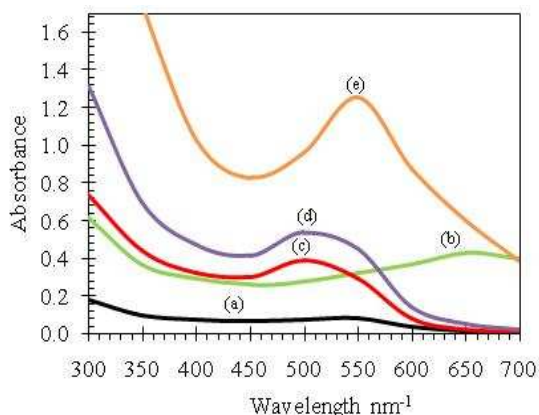


Fig. 2: Absorption spectra of original solution (a) and product solutions prepared from Procedure 1 with PVP concentration were (b) 11.1 mM, (c) 22.2 mM (d) 33.3 mM and (e) from Procedure (2) with $[Au]_1/[Au]_0$ molar ratio corresponded to 6

Table 1: AAS results of mercury adsorption mercury on Au nanoparticles solution

| Sample | Concentration (ppm) | | Amount mercury adsorbed (%) |
|---------------------|---------------------|-----------------|-----------------------------|
| | Initial, Ce | Equilibrium, Ci | |
| 11.1 mM | 9.071 | 4.094 | 54.87 |
| 22.2 mM | 9.071 | 7.368 | 18.77 |
| 33.3 mM | 9.071 | 6.406 | 29.38 |
| $[Au]_1/[Au]_0 = 6$ | 9.071 | 3.186 | 64.88 |

Mercury adsorption: Table 1 shows the concentrations of mercury solutions before and after the contacts with Au nanoparticles in order to determine the percentage of mercury adsorption on different sizes and shapes of Au nanoparticles.

DISCUSSION

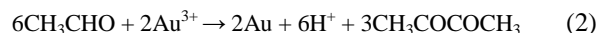
Synthesis of Au nanoparticles: Au nanoparticles were synthesized in order to examine the effects of PVP. It is known that without adding PVP, only large spherical Au nanoparticles with diameter 100-300 nm were produced in solution. These large spherical Au nanoparticles are formed by aggregation of small particles due to lack of surfactant PVP (Tsuji *et al.*, 2004).

Figure 1a-c shows TEM photographs of products obtained by using Procedure 1 at the three different PVP concentration and Fig. 1d shows TEM photographs using Procedure 2 with $[Au]_1/[Au]_0$ molar ratio corresponded to 6. At the lower PVP concentration (11.1 mM) larger triangular, square, hexagonal and spherical particles with diameter of 10-30 nm are

produced (Fig. 1a). It should be note that a nanorods with a diameter of 12 nm and length of 30 nm also produced. At higher PVP concentration (22.2 mM), spherical particles with diameter 6-10 nm was produced (Fig. 1b). At the highest PVP concentration (33.3 mM), hexagonal and spherical nanoparticles with diameter 5-10 nm were observed (Fig. 1c). These results indicated that the diameter and length of Au nanoparticles decreased with increasing PVP concentrations and thus, PVP concentration plays a significant role for the size and shape of Au nanoparticles.

When Au seed are used in Procedure 2 ($[Au]_1/[Au]_0$ molar ratio of 6), spherical nanoparticles changes to larger triangular, square and hexagonal particles with diameter of 8-20 nm. In addition, a few nanorods with diameter 8 nm and length of 20 nm was obtained. It was found that there is a growth from the Au seed to Au nanoparticles. It should be known that seeded medium synthesis is very effective for the size and shape controlled of Au nanoparticles (Jana *et al.*, 1999; 2001; Gole and Murphy, 2004).

The formations of anisotropic Au nanoparticles start by the following reactions according to reduction mechanism of metallic ions in EG (Fievet *et al.*, 1989):



As a result of the above reduction process, nucleation and growth processes of Au yield a mixture of polygonal and spherical nanoparticles. These nanoparticles were well dispersed because of the presence of a polymeric surfactant (PVP) that chemically absorb onto the surfaces of Au solid. The surface energies of large particles are lower than those of smaller one. It is therefore expected that some small nanoparticles are grown to a larger ones via an Ostwald ripening process (Roosen and Carter, 1998). With the assistance of PVP, some of the large nanoparticles were grown into anisotropic rod-shaped and wire structures. In this reaction, PVP kinetically acts as a controller of the growth rates of different crystalline faces through adsorption and desorption. The PVP adsorbed on specific crystalline surfaces and could significantly decrease their growth rates and lead to highly anisotropic growth (Almeida and Alcaccer, 1983).

The reagent and product solution of Au nanoparticles in procedure 1 and procedure 2 were measured using UV-Vis spectrometer. It is known that the wavelengths and absorbance of surface plasmon bands depend on their sizes and shapes of Au nanoparticles. The reactant spectrum composed without

an absorption peak. In the product spectra (Fig. 2), broad surface plasmon bands of Au nanoparticles appear in 500-700 nm regions. It is known that a surface plasmon band of spherical Au nanoparticles appears in the 500-600 nm regions with a sharp peak at about 520 nm (Henglein, 1999; Pastoriza-Santos and Liz-Marzan, 2002; Malikova *et al.*, 2002) while plasmon bands of polygonal Au nanoparticles are observed in the 550-800 nm region (Tsuji *et al.*, 2003).

Thus, strong band in the 500-600 nm region observed in spectra product solutions (Fig. 2c-d) are ascribed to a surface plasmon band of spherical Au nanoparticles while the longer wavelength bands above 600 nm is attributed to plasmon band of polygonal Au nanoparticles (Fig. 2b). The plasmon band of polygonal Au nanoparticles decreased with increasing the PVP concentration.

The spectrum for $[Au]_1/[Au]_0$ molar ratio of 6 is composed of a single peak at 550 nm. These observation are consistent with the fact that dominant product solution of 22.2 and 33.3 mM are spherical nanoparticles, while those product solution 11.1 mM and $[Au]_1/[Au]_0$ molar ratio corresponded to 6 are polygonal nanoparticles.

Mercury adsorption performance: Equation 3 was used to determine the percentage amount of mercury adsorbed:

$$\text{Percentage amount of mercury adsorbed} = \frac{C_i - C_e}{C_e} \times 100 \quad (3)$$

Where:

C_i = Initial mercury concentration (ppm)

C_e = Equilibrium mercury concentration (ppm)

Table 1 summarizes the AAS result of adsorption mercury in product solution in Procedures 1 and 2. In this study, 9.071 ppm initial concentration of mercury solution was prepared. At the low PVP concentration of 11.1 mM, 54.87% mercury was adsorbed. The adsorption mercury on Au nanoparticles prepared using 22.2 mM and 33.3 mM was 18.77 and 29.38%, respectively. At the $[Au]_1/[Au]_0$ of 6, the amount of mercury adsorbed was 64.88%.

The possible explanation of the adsorption is related to the sizes and shapes of Au nanoparticles. In this study, polygonal shape of Au nanoparticles adsorbed more mercury than spherical nanoparticles and the mercury adsorbed in Au nanoparticles is inversely proportional to their size.

CONCLUSION

In this study, MW-polyol method was applied to the rapid synthesis of Au nanoparticles. It was found that from TEM observation, sizes and shapes of Au nanoparticles strongly depend on experimental parameter such as concentration of PVP. The diameter and length of Au nanoparticles generally decreased with increasing the PVP concentration. The spectral observations from measurements in UV-visible absorption spectra are consistent with TEM observation of sizes and shapes of products solution. On the other hand, the growth from Au seed to Au nanoparticles changes from spherical to polygonal nanoparticles. The results show that mercury adsorption on the Au nanoparticles depends strongly on the sizes and shapes of Au nanoparticles. Polygonal nanoparticles adsorbed more mercury than spherical nanoparticles but the amount mercury adsorbed is inversely proportional to their size. A further study will be carried out to control the sizes and shapes of Au nanoparticles for optimum mercury adsorption.

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