SYNTHESIS AND CHARACTERIZATION OF GOLD NANOPARTICLES FOR MERCURY ADSORPTION

MAWARNI FAZLIANA BINTI MOHAMAD

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Dedicated to my beloved family…

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ABSTRACT

This research was carried out to synthesize and characterize different sizes and shapes of gold (Au) nanoparticles in order to find the optimum synthesis parameters for maximum mercury adsorption. The different sizes and shapes of Au nanoparticles were prepared using microwave (MW) polyol method. By using different polyvinylpyrrolidone (PVP) concentrations (1.9-33.3 mM), different concentration of sodium chloride (NaCl) (10-30 mM) and different amount of $[Au]_{1/}[Au]_0$ molar ratio (1-9), different sizes and shapes of Au nanoparticles were obtained. The Au nanoparticles were characterized using ultra violet-visible (UV-Vis) absorption spectroscopy and transmission electron microscopy (TEM). The different sizes and various mixtures of spherical, triangular, cubic, hexagonal, octahedral, decahedral, icosahedral and one-dimension (1-D) particles were obtained using those methods. Mercury adsorption was determined based on different sizes and shapes of Au nanoparticles and measured using atomic absorption spectrophotometer (AAS). The optimum PVP concentration is 22.2 mM for 92 % spherical particles of a size in range less than 10 nm. It was found that, using 11.1 mM of PVP solution, the sizes and shapes can be further reduced in the presence of chloride ions. It was also found that, 20 mM of NaCl is sufficient to produce stable Au nanoparticles with most of the particles are spherical in which 97 % of particles diameter is less than 10 nm. The different of $[Au]_1/[Au]_0$ molar ratio led to the high yield of polygonal nanoparticles and the size is increase with increasing $[Au]_1/[Au]_0$ molar ratio. However, the optimum values of $[Au]_1/[Au]_0$ molar ratio cannot be determined because the sizes and shapes are irregular. High mercury adsorption was obtained for spherical nanoparticles (263.18 mg/g) with 99 % particles size less than 10 nm. The defect on spherical nanoparticles surface contributes to high mercury adsorption. In addition, smaller sizes of Au nanoparticles increase the total surface area available for mercury adsorption. It was found that the formation of sizes and shapes of Au nanoparticles was depend on parameters such as the concentration of PVP, NaCl, as well as $[Au]_1/[Au]_0$ molar ratio, and thus affects the mercury adsorption.

ABSTRAK

Kajian ini telah dijalankan untuk mensintesis dan mencirikan saiz dan bentuk nanopartikel emas (Au) yang berbeza bagi mencari nilai parameter sintesis yang optimum untuk penjerapan merkuri yang maksimum. Saiz dan bentuk nanopartikel Au yang berbeza telah disediakan mengikut kaedah poliol gelombang mikro (MW). Dengan menggunakan kepekatan polyvinylprrolidone (PVP) (1.9-33.3 mM) yang berlainan, kepekatan natrium klorida (NaCl) (10-30 mM) yang berlainan dan pelbagai jumlah nisbah $[Au]_1/[Au]_0$ (1-9), pelbagai saiz dan bentuk nanopartikel Au yang berbeza telah diperolehi. Pencirian nanopartikel Au telah dilakukan dengan menggunakan spektroskopi IR (UV-Vis) dan mikroskop elektron penghantaran (TEM). Pelbagai saiz dan campuran partikel yang berbeza seperti sfera, segi tiga, kubik, heksagon, oktahedral, decahedral, icosahedral dan satu dimensi (1-D) partikel telah deperolehi menggunakan kaedah ini. Keputusan jerapan merkuri telah ditentukan berdasarkan saiz dan bentuk nanopartikel Au yang berbeza dan disukat menggunakan spektrofotometer penyerapan atom (AAS). Kepekatan PVP yang optimum ialah 22.2 mM dengan 92% zarah adalah sfera dengan julat saiz yang kurang daripada 10 nm. Didapati bahawa, dengan menggunakan larutan kepekatan PVP 11.1 mM, saiz dan bentuk boleh diturunkan lagi dengan wujudnya ion klorida. Didapati juga bahawa, 20 mM NaCl adalah mencukupi untuk menghasilkan Au nanopartikel yang stabil. Kebanyakan zarah sfera adalah 97% diameter adalah lebih kurang daripada 10 nm. Kepelbagaian nisbah molar $[Au]_1/[Au]_0$ membawa kepada hasil nanopartikel poligon yang tinggi dan saiz partikel yang lebih besar dengan peningkatan nisbah molar $[Au]_1/[Au]_{0.}$ Walau bagaimanapun, nilai optimum nisbah molar $[Au]_1/[Au]_0$ tidak dapat ditentukan kerana saiz dan bentuk yang tidak menentu. Merkuri penjerapan yang tinggi telah diperolehi untuk nanopartikel sfera (263.18 mg/g) dengan 99% zarah saiz adalah kurang daripada 10 nm. Kecacatan permukaan pada nanopartikel sfera menyumbang kepada penjerapan merkuri yang tinggi. Di samping itu, saiz Au nanopartikel yang lebih kecil meningkatkan jumlah luas permukaan yang tersedia untuk penjerapan merkuri. Didapati bahawa pembentukan saiz dan bentuk Au nanopartikel bergantung kepada parameter seperti kepekatan PVP, NaCI, serta nisbah molar $[Au]_1/[Au]_0$, sekali gus memberi kesan kepada penjerapan merkuri.

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LIST OF SYMBOL

^{O}C	-	Celcius
D	-	Dimension
^{O}F	-	Fahrenheit
g	-	Gram
$g{\cdot}mol^{-1}$	-	Gram per mole
J	-	Joule
k	-	Kilo (10^{3})
K	-	Kelvin
L	-	Liter
m	-	Meter
m	-	Mili (10^{-3})
min	-	Minute
M	-	Mega (10^{6})
M	-	Molar
MM	-	Molar mass
N	-	Nano (10^{-9})
N	-	Normal
μ	-	Micro (10^{-6})

LIST OF ABBREVATIONS

AAS	-	Atomic absorption spectrophotometer
Ag	-	Silver
Al	-	Aluminium
Au	-	Gold
EG	-	Ethylene glycol
EtHg	-	Ethyl mercury
$HAuCl_4 . 4H_2O$	-	Hydrogen tetrachloroaurate (III) tetrahydrate
Hg	-	Mercury
$HgCl_2$	-	Mercury chloride
LNG	-	Liquefied Natural Gas
MeHg	-	Methyl mercury
MW	-	Microwave
NaCl	-	Sodium chloride
Pa	-	Pascal
Phe-Hg	-	Phenyl mercury
ppb	-	Part per billion
ppm	-	Part per million
ppt	-	Part per trillion
PSA	-	Pressure swing adsorption
PVP	-	Polyvinylprrolidone
SEM	-	Scanning electron microscopy
TEM	-	Transmission Electron Microscopy
US EPA	-	United State Environmental Protection Agency
UV	-	Ultraviolet
Zn	-	Zink

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CHAPTER 1

INTRODUCTION

1.1 Background

Mercury is present in nature and in most natural gas and natural gas condensate at varying levels (Ebinghaus et al., 1999). In Malaysia, the mercury concentration in natural gas and natural gas condensate are between 1 and 200 $\mu g/Nm^3$ and 10 and 100 $\mu g/Nm^3$ of gas, respectively (Shafawi et al., 1999). Mercury in natural gas condensate could be present in a variety of forms (elemental, organometallic and inorganic salt), depending on the origin of the condensates. Although the concentrations of mercury in a given natural gas may be considered very low, but the consequence is cumulative as it amalgamates. In the gas processing plant, mercury accumulates in sufficient quantities to cause severe attack and failure of cryogenic aluminum heat exchangers resulting in a mechanical failure and gas leakage (Wilhelm, 2000). Another reason for removing mercury is because mercury is a very volatile element. Its vapors become a dangerous source of air pollution, thus contributing a serious risk for human health (Ebinghaus et al., 1999). Mercury is considered as hazardous to human health. The strong bonds formed between this metal and sulfur in the body will interfere with the functions and synthesis of both enzymes and proteins. Exposure to high mercury levels can be harmful to the heart, lungs, kidneys, brain and immune system of humans of all ages (Darbha et al., 2007).

1.2 Problem Statement

Mercury has caused numerous aluminum exchanger failures. To avoid potential equipment failure, strict limits were placed on the permitted level of mercury in natural gas through the aluminum heat exchanger. The level of mercury removal needed is below detectable level of 0.01 $\mu g/Nm^3$ of natural gas transferred to the cryogenic processing plant.

In providing the typical level of mercury, several approaches have been developed for the removal of mercury content in natural gas processing plant. A variety of methods have been reported by previous researchers concerning removal of mercury included carbon adsorption, ion exchange, chemical precipitation, membrane filtration, adsorption and photoreduction (Kadirvelu et al., 2004). Among all these reasons, the majority of the effectiveness and economic methods are based on adsorption process (Arakaki et al., 2003). However, even after mercury has been detected and removed, they must be constantly tested to ensure that they are performing effectively. But accurate measurements of the type and quantity of mercury present in natural gas are critical because of the presence of mercury in variety of physical and chemical species that feature different solubility, chemical reactivity, volatility and toxicity (Wilhem and Bloom, 2000; Frech et al., 1996).

Several techniques have been applied for the determination of mercury content by the analytical technique such as cold vapor atomic absorption spectroscopy, cold vapor atomic fluorescence spectrometry, atomic emission spectrometry and inductively coupled plasma-mass spectrometry. However, mercury must be collected from a gas sample before proceeding with the measurement techniques. The determination of mercury in natural gas is difficult because of the very low concentrations involved, the nature of mercury that is very volatile and the difficulty of the sample matrix. This shows that either a highly sensitive detector or a large sample volume, or both is needed.

In light of this constraint, preferred mercury sampling methods by using gold as a collector was used before they were shipped from the processing plant to the laboratory for analysis. However, these applications are costly, unwieldy and are not suitable for mobile used. In addition, a research has been done to develop a mini mercury sensor by using amalgam procedure between mercury and gold. The use of this gold is based on thin film in which the gold must be very thin to achieve a reasonable sensitivity. Due to that reason, gold nanoparticles can be used to fulfill the requirement mentioned.

Since the reactions of Au nanoparticles are strongly dependent on sizes and shapes, many studies on the syntheses of Au nanoparticles have been carried out to control the formation of size and shape (Ahmadi et al., 1996; Belloni, 1996; Henglein, 1993; Pal et al., 1997; Jana et al., 1996; Schmid, 1994; Whitten et al., 1999). By understanding the properties and the mechanism of formation of these Au nanoparticles, a better control of their size and shape and applications can be achieved. The polyol method is one of the typical techniques to prepare Au nanoparticles of different sizes and shapes by reducing their ionic salts. 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 (Fievet et al., 1989; Silver et al., 1996 & 1997; Hedge et al., 1997). For the rapid preparation of Au nanoparticles, microwave (MW) heating has been coupled with the polyol method (Tsuji et al. 2003). When Au^{3+} in $AuCl^{-}$ ions is reduced in EG in the presence of polyvinylpyrrolidone (PVP) under microwave (MW) heating for 2-3 min, mixtures of square, triangular, rhombic and hexagonal nanoparticles are produced. In addition, small numbers of one-dimensional (1-D) nanorods and nanowires are also produced. But so far, there is no details study has been done on the effect of size and shape of Au nanoparticles on mercury adsorption.

Thus, this research was focused on synthesis and characterization of Au nanoparticles using various polyvinylpyrrolidone (PVP), hydrogen tetrachloroaurate (III) ($HAuCl_4.3H_2O$) and chloride ions (NaCl) to find the optimum values of synthesis parameters for producing different sizes and shapes of Au nanoparticles and to determine the suitable size and shape of Au nanoparticles for mercury adsorption. Mercury adsorption on Au nanoparticles is the initial step in understanding on the interaction between different size and shape of Au nanoparticles and mercury that will provide design criteria for a new highly sensitive mercury sensor.

1.3 Objective and Scopes

Based on the research background, the objectives of this research are:

1. To synthesize the different sizes and shapes of gold nanoparticles using various amount of PVP, NaCl and $[Au]_1/[Au]_0$.

2. To characterize and determine the optimum values of synthesis parameters of gold nanoparticles

3. To determine the optimum size and shape of gold nanoparticles for maximum mercury adsorption

In order to achieve the aforementioned objectives, the research is divided into following scopes:

1. Synthesis of Au nanoparticles was carried out by using MW-polyol method with different amounts of PVP in order to obtain different sizes and shapes of Au nanoparticles. The formation and growth of Au nanoparticles was controlled using different amount of NaCl and $[Au]_0/[Au]_1$ and gold in MW-polyol method.

2. Characterization of Au nanoparticles was carried out by using ultra violet-visible (UV-Vis) absorption spectroscopy and transmission electron microscopy (TEM) to observe the sizes and shapes of Au nanoparticles. The size and shape of each particle were measured to determine the distribution of Au nanoparticles formed.

3. Measurement of mercury adsorption onto different sizes and shapes of Au nanoparticles were determined by analyzing the concentration of mercury solution before and after the contacts with Au nanoparticles by using atomic absorption spectrophotometer (AAS).

1.4 Thesis Outline

This report contains five chapters. Chapter 1 presents general introduction, problem background, objectives and scopes, thesis outline and chapter summary. A review on mercury in environment, sources of mercury emissions, mercury in natural gas, problem of mercury in processing plant, potential adsorbent for mercury removal, technique to monitor mercury and potential gold to detect mercury is presented in Chapter 2. Chapter 3 discusses about research methodology which comprised of chemicals used and experimental procedures for synthesis, characterization and mercury adsorption measurement. The results and discussions of the study are presented in Chapter 4, while Chapter 5 presents the conclusion of this research and future work recommendations.

1.5 Summary

The ability of gold to form amalgam with mercury is the main reason to carry out this study. The development of Au nanoparticles as a new highly sensitive mercury detector is to enhance the performance of the existing mercury collector and sensor in order to make the process more effective and cost valuable. However, insufficient knowledge to determine suitable size and shape of Au nanoparticles as well as their effect on mercury adsorption may limit the function of the Au nanoparticles. Therefore, this preliminary work will address the effect of different size and shape of Au nanoparticles on mercury adsorption performances to get suitable sizes and shapes for the optimum mercury adsorption. It was expected that Au nanoparticles could provide a design criteria for a new highly sensitive mercury sensor.

REFERENCES

ACAP. (2004). Artic Council Action Plan to Eliminate Pollution of the Artic. Assestment of Mercury Releases from the Russian Federation: Reduction of Atmospheric Mercury Releases from Arctic States. Russian Federal Service for Environmental, Technological and Atomic Supervision Danish Environmental Protection Agency, COWI A/S.

Ahmadi, T. S., Wang, Z. L., Green, T. C., Henglein, A. and El-Sayed, M. A. (1996). Shape-Controlled Synthesis of Colloidal Platinum Nanoparticles. *Sci*. 272: 1924–1926.

Amirbahman, A., Ruck, P. L. Fernandez, I. J., Haines, T. A. and Kahl, J. S. (2004). The Effect of Fire on Mercury Cycling in the Soils of Forested Watersheds: Acadia National Park, Maine, U.S.A. *Water, Air, Soil Pollut.* 152: 313-331.

Arakaki, L. N. H., Filha, V. L. S. A., Espinola, J. G. P., da Fonseca, M. G., de Oliveria, S. F., Arakaki, T., and Airoldi, C. (2003). New Thiol Adsorbent Grafted on Silica Gel: Synthesis, Characterization and Employment for Heavy Metal Adsorption, *J. Environ. Monit.* 5: 366-370.

Atwood, D. A. and Zaman, M. K. (2006). Mercury Removal from Water. *Struct. Bond.* 120: 163-182.

Belloni, J. (1996). Metal Nanocolloids. *Curr. Opin. Colloid Interface Sci*. 1: 184-196.

Bennet, J. E. and Pinnel, M. R. (1973). Reactions between Mercury-Wetted Aluminum and Liquid Water. *J. Mater. Sci*. 8: 1189-1193.

Bloom, N. S. (2000). Analysis and Stability of Mercury Speciation in Petroleum Hydrocarbon. *Fresenius J. Anal. Chem.* 366: 438-443.

Boening, D. W. (2000) Ecological Effects, Transport and Fate of Mercury: A General Review. *Chemosphere.* 40: 1335-1351.

Boening, V. M., Abburi, K. Talbott, J. L. and Smith, E. D. (2003). Removal of Hexavalent from Wastewater using a New Composite Chitosan Biosorbent. *Environ. Sci. Technol*. 37:4449-4459.

Bouyssiere, B., Szpunar, J., Lespes, G. and Lobinski, R. (2003). Gas Chromatography with Inductively Coupled Plasma Mass Spectrometric Detection (GC-ICP MS). *Advances in Chromatography*. 42: 107-137.

Bruce, L. and Wise, G. (1974). Comments on-Voluminous Oxidation of Aluminum by Continuous Distribution in a Wetting Mercury Film. *J. Mater. Sci*. 9: 335.

Cathum, S., Velicogna, D., Obenauf, A., Dumouchel, A., Punt, M., Brown, C. E. and Ridal, J. (2005). Detoxification of Mercury in the Environment. *Anal. Bional. Chem*. 381: 1491-1498.

Clarkson, T. W., Magos, L. (2006). The Toxicology of Mercury and Its Chemical Compound. *Crit. Rev. In Toxicology*. 36: 609-662.

Clarkson, T. W., Magos, L., Myers,G. J., Eng, l. N. and Med. J. (2003). The Toxicology of Mercury Current Exposures and Clinical Manifestations. 349: 1731-1737.

Clevenger, W. L., Smith, B. W. and Winefoedner, J. D. (1997). Trace Determination of Mercury: A Review. *Crit. Rev. Anal. Chem.* 27: 1-26.

Coade, R. and Coldham, D. (2006). The Interaction of Mercury and Aluminium in Heat Exchanger in Natural Gas Plant. *International Journal of Pressure Vessels And Piping*. 83: 336-342.

Corvini, G., Stiltner, J. and Clark, K. (2002). Mercury Removal from Natural Gas and Liquid Streams, Texas, USA: UOP LLC.

Darbha, G. K., Ray, A. and Ray, P. C. (2007). Gold Nanoparticle-Based Miniaturized Nanomaterial Surface Energy Transfer Probe for Rapid and Ultrasensitive Detection of Mercury in Soil, Water and Fish. *Am. Chem. Soc.* 1: 208-214.

der Vaart, R. V., Akkerhuis, J., Feron, P. and Jansen, B. (2001). Removal of Mercury from Gas Streams by Oxidative Membrane Gas Absorption. *J. Membr. Sci.* 187: 151-157.

Ebinghaus, R., Tripathi, R. M., Wallschlager, D., Lindberg, S. E. in: Ebinghaus, R., Turner, R. R., de Lacerda, L. D., Solomons, W. (Eds.). (1999). Risk Assessment and Remediation. *Springer-Verlag.* Berlin. Chapter 1: 3–50.

El-Ela, M. A., Mahgoub, I., Nabawi, M. and Aziem, M. A. (2006). Eqytian Gas Plant Employs Adsorbents for Hg Removal. *J. Oil. Gas*. 104: 52-58.

English, J. J. and Duquette, D. J. (1993). Mercury Liquid Embrittlement Failure of 5083-0 Aluminum Alloy Piping. *Handbook of Case Histories in Failure Analysis*. 2: 207-213.

Fernandes, P. J. L., Clegg, R. E. and Jones, D. R. H. (1994). Failure by Liquid Metal Induced Embrittlement. *Eng. Fail. Anal.* 1: 51-63.

Fievet, F., Lagier, J.P. and Figlarz, M. (1989). Preparing Monodisperse Metal Powders in Micrometer and Submicrometer Sizes by the Polyol Process. *MRS Bull*. 14: 29.

Fievet, J., Lagier, J. P., Blin, B., Beaudoin, B. and Figlarz, M. (1989). Homogeneous and Heterogeneous Nucleations in the Polyol Process for the Preparation of Micron and Submicron Size Metal Particles. *Solid State Ionics*. 32/33: 198.

Frech, W., Baxter, D. C., Dyvik, G. and Dybdahl, B. (1995). On the Determination of Total Mercury in Natural Gases using the Amalgamation Technique and Cold Vapour Atomic Absorption Spectrometry. *J. Anal. At. Spectrom*. 10: 769-775.

Frens, G. (1973). Controlled Nucleation for the Regulation of the Particle Size in Monodisperse Gold Suspensions. *Phys. Sci*. 241: 20-22.

Fthenakis, V. M., Lipfert, F. W., Moskowitz, P. D. and Saroff, L. (1995). An Assesstment of Mercury Emissions and Health Risks from a Coal-Fired Power Plant. *J. Hazard. Matter*. 44: 267-283.

Gao Y., Jiang, P., Liu, D. F., Yuan, H. J., Yan, X. Q., Zhou, Z. P., Wang, J. X., Song, L., Liu, L. F., Zhou, W. Y., Wang, G., Wang, C. Y. and Xie, S. S. (2003). Synthesis,Characterization and Self-assembly of Silver Nanowires. *Chem. Phys. Lett*. 380: 146–149.

Gao, Y., Jiang, P., Liu, D. F., Yuan, H. J., Yan, X. Q., Zhou, Z. P., Wang, J. X., Song, L., Liu, L. F., Zhou, W. Y., Wang, G., Wang, C. Y., Xie, S. S., Zhang, J. M. and Shen, D. Y. (2004). Evidence for the Monolayer Assembly of Poly(vinylpyrrolidone) on the Surfaces of Silver Nanowires. *J. Phys. Chem. B*. 108: 12877–12881.

Gao, Y., Jiang, P., Song, L., Liu, L. F., Yan, X. Q., Zhou, Z. P., Liu, D. F., Wan, J. X., Yuan, H. J., Zhang, Z. X., Zhao X. W., Dou, X. Y., Zhou, W. Y., Wang, G. and Xie, S. S. (2005). Growth Mechanism of Ssilver Nanowires Synthesized by

Polyvinylpyrrolidone-Assisted Polyol Reduction. *J. Phys. D: Appl. Phys*. 38: 1061–1067.

Goodman, C. M., McCusker, C. D., Yilmaz, T. and Rotello, V. M. (2004). Toxicity of Gold Nanoparticles Functionalized with Cationic and Anionic Side Chains. *Bioconj. Chem*. 15: 897-900.

Gordon, P. (1978). Metal Induced Embrittlement of Metals-an evaluation of Embrittler Transport Mechanisms. *Metall. Trans. A*. 9A: 267-273.

Gordon, W. (1999). Assessing the Susceptibility of an LNG Plant to Mercury Induced Attack. *14th International Corrosion Congress Proceedings.* Cape Town, South Africa.

Havarinasab, S. and Hultman, P. (2005). Organic Mercury Compound and Autoimmunity. *Autoimmun. Rev*. 4(5): 270-275.

Hedge, M. S., Larcher, D., Dupont, L, Beaudoin, B., Tekaia-Elhsissen, K. and Tarascon, J. M. (1996). Synthesis and Chemical Reactivity of Polyol Prepared Monodisperse Nickel Powders. *Solid State Ionics*. 93: 33-50.

Henglein, A. (1993). Physicochemical Properties of Small Metal Particles in Solution:Microelectrode Reactions, Chemisorption, Composite Metal Particles, and the Atom-To Metal Transition. *J. Phys. Chem*. 97: 5457–5471.

Henglein, A. (1999). Radiolysis Preparation of Ultrafine Colloidal Gold Particles in Aqueous Solution. *Langmuir*. 15: 6738–6744.

Hunsberger, L. (1999). Experiment 13 UV-Vis Absorption Spectroscopy General Chemistry Laboratory Manual.

Hutchison, A. R. and Atwood, D. A. (2003). Mercury Pollution and Remediation: the Chemist´s Response to a Global Crisis. *J. Chem. Crystallogr*. 33: 1074-1542.

Ibano, D., Yokota, Y. and Tominaga, T. (2003). Preaparation of Gold Nanoplates Protected by an Anionic Phospholipid. *Chem. Lett*. 32: 574-575.

Im, S.H., Lee, Y.T., Wiley, B. and Xia, Y. (2005). Large-Scale Synthesis of Silver Nanocubes: The Role of HCl in Promoting Cube Perfection and Monodispersity. *Angew. Chem*. 44(14): 2154-2157.

Itoh, H., Tahara, A., Naka, K. and Chujo, Y. (2004). Photochemical Assembly of Gold Nanoparticles Utilizing the Photodimerization of Thymine. *Langmuir*. 20: 1972-1976.

Jana, N. R., Sau, T. K. and Pal, T. (1999). Growing Small Silver Particle as Redox Catalyst. *J. Phys. Chem*. B. 103: 115-121.

Jana, N. R., Gearheart, L. and Murphy, C. J. (2001). Wet Chemical Synthesis of Silver Nanorods and Nanowires of Controllable Aspect Ratio. *Chem. Commun.* 13: 617–618.

Jaramillo, T. F., Baeck, S.H., Cuenya, B. R. and McFarland, E. W. (2003). Catalytic Activity of Supported Au Nanoparticles Deposited from Block Copolymer Micelles *J. Am. Chem. Soc*. 125 (24): 7148-7149.

Jiang P., Li, S.Y., Xie, S.S., Gao, Y. and Song, L. (2004). Machinable Long PVP-Stabilized Silver Nanowires. *Chem. Eur. J.* 10: 4817–4821.

Jiang, Z. L., Feng, Z.W. and Shen, X. C. (2001). Microwave Synthesis of Au Nanoparticles with the System of $AuCl_4$-CH_3CH_2OH. *Chin. Chem. Lett.* 12: 551-554.

Kadirvelu, K., Kavipriya, M., Karthika, C., Vennilamani, N., and Pattabhi, S. (2004), Mercury (II) Adsorption by Activated Carbon Made from Sago Waste, *Carbon*, 42: 745-752.

Katz, D. L. and Lee, R. L. (1990). *Chemical Engineering Series*. United States of America: McGraw-Hill, Inc.

Kidnay, A.J. and Parrish, W. R. (2006). *Fundamentals of Natural Gas Processing.* United States of America: Taylor and Francis Group, LLC.

Kilgroe, J. D. (1996). Control of Dioxin, Furan and Mercury Emissions from Municipal Waste Combustors. *J. Hazard. Matter.* 47: 163-194.

Kinney, G. T. (1975). Skikda LNG Plant Solving Troubles. *Oil and Gas J*. Sept. 15th Issues. Kingston, H. M. and Haswell, S. J. (1997). Microwave-Enhanced Chemistry, Fundamentals, Sample Preparation and Apllications. *Am. Chem. Soc*. Wanshington. DC.

Kim F., Song, J.H. and Yang, P. (2002). Photochemical Synthesis of Gold Nanorods. *J. Am. Chem. Soc.* 124: 14316–14317.

Kim, K. H. and Kim, M.Y. (2002). A Decadal Shift in Total Gaseous Mercury Concentration Levels in Seoul, Korea: Changes between the late 1980s and the late 1990s. *Atmos. Environ*. 36: 663– 675.

LaMer, V. K. and Dinegar, R. H. (1950). Theory, Production and Mechanism of Formation of Monodispersed Hydrosols. *J. Am. Chem. Soc.* 72(11): 4847-4854.

Leeper, J. E. (1981). Mercury Corrosion in LNG Plant. *Energy Processing/Canada.* 46-51.

Leeper, J. E. (1980). Mercury- LNG Problem. *Hydroc. Proccs.* 237-240.

Li, H. X. and Rothberg, J. (2004). DNA Sequence Detection using Selective Fluorescence Quenching of Tagged Oligonucleotide Probes by Gold Nanoparticles. *Anal. Chem*. 76: 5414-5417.

Lindberg, R., Sundholm, G., Pettersen, B., Sjöblom, J. and Friberg, S. E. (1997), Multivariate Analysis of the Size Dependence of Monodisperse Silica Particles Prepared According to the Sol-Gel Technique. *Colloids Surf. A.* 123-124, 549-560.

Liu, F., Ker, C., Chang, Y., Ko, T., Chu, T. and Dai, B. (2003). Microwave Heating for the Preparation of Nanometer Gold Particles. *Jpn. J. Appl. Phys.* 42: 4152-4158.

Lobinski, R. and Adams, F. C. (1997). Speciation Analysis by Gas Chromatography with Plasma Source Spectrometric Detection. *Spectrochim Acta Part B*. 52 (13): 1865-1903.

Long, Nguyen Ngoc., Vu, Le Van., Kiem, Chu Dinh., Doanh, Sai Cong., Nguyet, Cao Tai., Hang, Pham Thi., Thien, Nguyen Duy. and Quynh, Luu Manh. (2009). Synthesis and Optical Properties of Colloid Gold Nanoparticles. *J. Phys.* 187: 1-8.

Lynch, S. P. (1992). Metal-Induced Embrittlement of Materials. *Materials Characterisation*. 28: 279-289.

Malikova, N., Pastoriza-Santos, I., Schierhorn, M., Kotov, N. A. and Liz-Marzán, L. M. (2002). Layer-by-Layer Assembled Mixed Spherical and Planar Gold Nanoparticles: Control of Interparticle Interactions. *Langmuir.* 18: 3694-3697.

Mazzolai, B., Mattoli, V., Raffa, V., Tripoli, G., Accoto, D., Menciassi, A. and Dario, P. (2004). A Microfabricated Physical Sensor for Atmospheric Mercury Monitoring. *Sens. Actuators*. 113: 282-287.

Muchlis, M. (1981). Analytical Methods for Determining Small Quantities of Mercury in Natural Gas. *Proc. Of the Annual Convention of the Indonesia Petroleum Association*. Jakarta. 401-421.

McNerney, J. J., Buseck, P. R. and Hanson, R. C. (1972). Mercury Detection by Means of Thin Gold Films. *Science*. 178: 611-612.

Mohr, C., Hofmeister, H., Radnik, J. and Claus, P. (2003). Identification of Active Sites in Gold-Catalyzed Hydrogenation of Acrolein. *J. Am. Chem. Soc.* 125: 1905-1911.

Mokhatab, S., Poe, W. A. and Speight, J. G. (2006). *Handbook of Natural Gas Trasmission and Processing*. United States of America: Elsevier, Inc.

Nasir, S. M. and Nur, H. (2008). Gold Nanoparticles Embedded on the Surface of Polyvinyl Alcohol Layer. *Journal of Fundamental Sciences*. 4: 245-252.

Pal, T., Sau, T. K. and Jana, N. R. (1997). Reversible Formation and Dissolution of Silver Nanoparticles in Aqueous Surfactant Media. *Langmuir*. 13: 1481-1485.

Park, K. S., Seo, Y. C., Lee, S. J. and Lee, J. H. (2008). Emission and Speciation of Mercury from Various Combustion Sources. *Powder Technol*. 180: 151-156.

Park, J. H., Lim, Y.T., Park, O. O., Kim, J. K., Yu, J. W. and Kim, Y.C. (2004). Polymer/Gold Nanoparticle Nanocomposite Light-Emitting Diodes: Enhancement of Electroluminescence Stability and Quantum Efficiency of Blue-Light-Emitting Polymers. *Chem. Mater*. 16: 688-692.

Pastoriza-Santos, I. and Liz-Marzan, L.M. (2002). Formation of PVP-Protected Metal Nanoparticles in DMF. *Langmuir*. 18: 2888-2894.

Petit, C., Lixon. P. and Pileni, M. (1993). In Situ Synthesis of Silver Nanocluster in AOT Reverse Mmicelles *J. Phys. Chem. B*. 97: 12974-12983.

Phannenstiel, L., Phannenstiel, L., McKinley, L. and Sorenson, J. (1975). Mercury in Natural Gas, Progress in Refrigeration Science and Technology. *Proceedings of the 14th International Congress of Refrigeration*. Moscow.

Pirronea, N., Costaa, P., Pacynab, J. M., Ferrara, R. (2001). Mercury Emissions to the Atmosphere from Natural and Anthropogenic Sources in the Mediterranean Region. *Atmos. Environ*. 35: 2997-3006.

Porel, S., Singh, S. and Radhakrishnan, T. P. (2005). Polygonal Gold Nanoplates in a Polymer Matrix. *Chem. Commun*. 18: 2378-2389.

Prange, A. and Jant-zen, E. (1995) Detemination of Organometallic Species using GC ICP MS. *J. Anal. At. Spectrom*. 10: 105-109.

Prasad, B. L. V., Stoeva, S. I., Sorensen, C. M. and Klabunde, K. J. (2002). Digestive Ripening of Thiolated Gold Nanoparticles: The Effect of Alkyl Chain Length. *Langmuir*. 18: 7515-7520.

Raffa, V., Mazzolai, B., Mattoli, V., Mondini, A. and Dario, P. (2006). Model Validation of a Mercury Sensor based on the Resistivity Variation of a Gold Thin Film. *Sens. Actuators*. 114: 513-521.

Rodhe, H. and Bergan, T. (2001). Oxidation of Elemental Mercury in the Atmosphere: Constraints Imposed by Global Scale Modeling. *J. Atmos. Chem*. 40: 191-212.

Rodríguez-Fernández, J., Pérez-Juste, J., Mulvaney, P. and Liz-Marzán, L.M. (2005). Spatially-Directed Oxidation of Gold Nanoparticles by Au(III)−CTAB Complexes. *J. Phys. Chem. B.* 109(30): 14257-14261

Roosen, A. R. and Carter. W. C. (1998). Simulations of Microstructural Evolution: Anisotropic Growth and Coarsening. *Physica A*. 261(1-2): 232-247.

Sanemasa, I. (1975). The solubility of Elemental Mercury Vapor in Water. *Bull. Chem. Soc. Jpn.* 48(6): 1795-1798.

Schambach, K., Eden, K., Schumacher, K. and Wiegleb, G. (2002). Micromachined Mercury Sensor. Proceeding of the 32nd European Solid-State Device Research Conference. September 24-26. Firenze, Italy: ESSDERC, 443-446.

Schmid, G. (1992). Clusters and Colloids – Metals in the Embryonic State. *Chem Rev*. 92: 1709–1727.

Schmid, G. (1994). In: Cluster and Colloids from Theory to Applications. VCH. New York.

Schmid, G. and Chi, L. F. (1998). Metal Clusters and Colloids. *Adv. Mater*. 10: 515.

Schroeder, W. H. and Munthe, J. (1998). Atmospheric Mercury-An Overview. *Atmos. Environ*. 32. 809-822.

Shafawi, A., Ebdon, L., Foulkes, M., Stockwell, P. and Corns, W. (1999). Determination of Total Mercury in Hydrocarbons and Natural Gas Condensate by Atomic Fluorescence Spectrometry. *Anal.*124: 788 –796.

Shafawi, A., Ebdon, L., Foulkes, M., Stockwell, P. and Corns, W. (2000). Preliminary Evaluation of Adsorbent-Based Mercury Removal Systems for Gas Condensate. *Anal. Chim. Acta*. 415: 21-32.

Shao, Y., Jin, Y. D. and Dong, S. J. (2004). Synthesis of Gold Nanoplates by Aspartate Reduction of Gold Chloride. *Chem. Commun*. 9: 1104-1105.

Silbergeld, E. K. And Devine, P. J. (2000). Mercury-Are We Studying the Right Endpoints and Mechanisms, *Fuel Process. Technol*. 65: 35-42.

Silver, P. Y., Herrera-Urbina, R., Duvauchelle, N., Vijayakrishnan, K. and Tekaia-Elhsissen, K. (1996). Preparation of Colloidal Silver Dispersions by the Polyol Process. 1. Synthesis and Characterization. *J. Mater. Chem*. 6: 573-577.

Silver, P. Y., Herrera-Urbina. and Tekaia-Elhsissen, K. (1997). Preparation of Colloidal Silver Dispersions by the Polyol Process. 2. Mechanism of Particle Formation. *J. Mater. Chem.* 7: 293-299.

Situmorang, M. S. M. and Muchlis, M. (1996). Mercury Problem in Arun LNG Plant. *Proceedings of the 8th International Gas Union.*

Speidel, M. O. (1994). The Theory of Stress Corrosion Cracking, NATO, 1971. *Proceedings of the 73rd GPA Annual Convention*. New Orleans, 389.

Sun, Y. and Xia, Y. (2002). Shape-Controlled Synthesis of Gold and Silver Nanoparticles. *Science.* 298: 2176-2179.

Sun, Y. and Xia, Y. (2004). Mechanistic Study on the Replacement Reaction between Silver Nanostructures and Chloroauric Acid in Aqueous Medium. *J. Am. Chem. Soc.* 126: 3892-3901.

Suslick, K. S., Fang, M. and Hyeon, T. (1996). Sonochemical Synthesis of Iron Colloids. *J. Am. Chem. Soc*. 118: 11960-11961.

Tao, H., Murakami, T., Tominage, M. and Miyazaki, A. (1998). Mercury Speciation in Natural Gas Condensate by Gas Chromatography Inductively Coupled Plasma Mass Spectrometry. *J. Anal. At. Spectrom.* 13: 1085-1093.

Tkachenko, A. G., Xie, H., Liu, Y. L., Coleman, D., Ryan, J., Glomm, W. R., Shipton, M. K., Franzen, S. and Feldheim, D. L. (2004). Cellular Trajectories of Peptide-Modified Gold Particle Complexes: Comparison of Nuclear Localization Signals and Peptide Transduction Domains. *Bioconjugate Chem.*15: 482−490.

Tom, R.T., Suryanarayanan, V., Reddy, P.G., Baskaran, S. and Pradeep, T. (2004). Ciprofloxacin-Protected Gold Nanoparticles. *Langmuir*. 20: 1909-1914.

Tsuji, M., Hashimoto, M., Nishizawa, Y. and Tsuji, T. (2003). Preparation of Gold Nanoplates by a Microwave-polyol Method. *Chem. Lett.* 32: 1114.

Tsuji, M., Hashimoto, M., Nishizawa, Y. and Tsuji, T. (2004). Synthesis of Gold Nanorods and Nanowires by Microwave-polyol Method. *Mater. Lett.*58: 2326-2330.

Tsuji, M., Hashimoto, M., Nishizawa, Y., Kubokawa, M. and Tsuji, T. (2005). Microwave-Assisted Synthesis of Metallic Nanostructures in Solution. *Chem. Eur. J.* 11: 440.

Tsuji, M., Miyamae, N., Matsumoto, K., Hikino, S. and Tsuji, T. (2005). Rapid Formation of Novel Au Core–Ag Shell Nanostructures by a Microwave-polyol Method. *Chem. Lett.* 34: 1518-1519.

Tsuji, M., Matsumoto, K., Miyamae, N., Tsuji, T. and Zhang, X. (2007). Rapid Preparation of Silver Nanorods and Nanowires by a Microwave-Polyol Method in the Presence of Pt Catalyst and Polyvinylpyrrolidone. *Cryst. Growth. Des.* 7: 311-320.

Tu , W. and Liu, H. J. (2000). Rapid Synthesis of Nanoscale Colloidal Metalclusters by Microwave Irradiation *J. Mater. Chem.* 10: 2207-2211.

Ullman, A. (1996). Formation and Structure of Self-Assembled Monolayers. *Chem. Rev.* 96: 1533-1554.

US. EPA. (2001). Research and Development-Mercury in Petroleum and Natural Gas: Estimation of Emission from Production, Processing and Combustion.

Wang, Min-Hua., Hu, Jia-Wen. And Yeung, Edward S. (2010). Au nanoparticles Monolayer: Preparation, Structural Conversion and Surface-Enchanced Raman Scattering Effects. *Nanotechnology.* 21: 145608-145613.

Wiley, B., Herricks, T., Sun, Y. and Xia, Y. (2004). Polyol Synthesis of Silver Nanoparticles: Use of Chloride and Oxygen to Promote the Formation of Single-Crystal, Truncated Cubes and Tetrahedrons. *Nano Lett.* 4(9): 1733-1739.

Wiley, B., Sun, Y. and Xia, Y. (2005). Polyol Synthesis of Silver Nanostructures: Control of Product Morphology with Fe(II) or Fe(III) Species. *Langmuir.* 21(18): 8077-8080.

Wiley, B., Sun, Y. G., Chen, J. Y., Cang, H., Li, Z. Y., Li, X. D. and Xia, Y. N. (2005a). Shape-Controlled Synthesis of Silver and Gold Nanostructures. *MRS Bull.* 30: 356-361.

Wiley, B., Sun, Y. G., Mayers, B. and Xia, Y. N. (2005b). Shape-Controlled Synthesis of Metal Nanostructures: The Case of Silver. *Chem. Eur. J.* 11: 454-463.

Wilhelm, S. M. (1999). Design Mercury Removal Systems for Liquid Hydrocarbons. *Hydrocarbon Process.*78: 61 –71.

Wilhem, S. M. and Bloom, N. (2000). Mercury in Petroleum. *Fuel Process. Technol.* 63: 1-27.

Wilhem, S. M., Liang, L. and Kirchgesser, D. (2006). Identification and Properties of Mercury Species in Crude Oil. *Energy Fuels.* 20: 180-186.

Wilhelm, S. M., McArthur, A. and Kane, R. D. Method to Combat Liquid Metal Embrittlement in Cryogenic Aluminum Heat Exchangers. (1994). *Proceedings the 73rd GPA Annual Convention.* 62-71.

Whitten, R. L., Shafigullin, M. N., Khoury, J. T., Schaaff, T. G., Vezmar, I., Alvarez, M. M. and Wilkinson, A. (1999). Crystal Structures of Molecular Gold Nanocrystal Arrays. *In; Health J. R. ed. Nanoscale Materials Special Issues. Acc. Chem. Res.* 32: 387-445.