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STRUCTURE AND OPTICAL PROPERTY OF GOLD NANOPARTICLES SYNTHESIZED BY MODIFIED POLYOL METHOD

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Abstract. *In this research, Au nanoparticles were successfully synthesized by modified polyol method with commercial precursors to be gold (III) chloride trihydrate ($HAuCl_4{\cdot}3H_2O$), ethylene glycol (EG), poly(vinylpyrrolidone) (PVP), sodium borohydride ($NaBH_4$). The structure and properties of as-prepared Au nanoparticles have been investigated by X ray diffraction (XRD), transmission electron microscopy (TEM), and UV-vis-NIR spectroscopy. As a result, Au nanoparticles with the average particle size of 28.80 nm were successfully synthesized in the range of about 50 nm. It is evidenced that the assembly of gold nanoparticles was presented in their nucleation, growth, and formation.*

Keywords: polyol method; $NaBH_4$; PVP; Au nanoparticles.

Classification numbers: 67.30.ef.

I. INTRODUCTION

So far, there have been the various physical and chemical synthetic methods of metal nanoparticles [1]. It is known that the as-prepared Au nanoparticles have very potential applications for catalysis, biology, medicine, and nanomedicine [2, 3]. In controlled synthesis of Au-based nanoparticles, the critical issues of their size, shape, morphology, and nanostructure have been intensively investigated in modified polyol methods [4–6]. Researchers have focused in an understanding of the relationships between concentration of the precursors for the formation of nanoparticles, EG or PEG solvents for the formation of nanosystem, reducing agents as $NaBH_4$, concentrations of protecting agents as poly(vinylpyrrolidone) (PVP), cetyltrimethyl ammonnium bromide (CTAB), dendrimers, and ligands for the stabilization of nanoparticles, and their controlling-structure agents [1–3]. In plasmonic sensing, Au-based nanoparticles have studied for the investigation of surface plasmon resonance (SPR), surface enhanced Raman spectroscopy (SER), and tip-enhanced Raman spectroscopy (TER), and their promising applications for next-generation SPR, SER, and TER sensor devices [2, 3].

In recent years, the functional Au metal and alloy nanoparticles have been studied for cancer therapy, drug delivery, antimicrobial application, biosensors (glucose, nucleic acid, and protein biosensors), energy, environment, and food industry [4–6]. It is known that the modified polyol methods are effectively used to synthesize the metal, bimetal, oxide, and alloy nanoparticles in many reviewed works with the good utilization of ethylene glycol (EG) and polyethylene glycol (PEG) [4–6]. Therefore, our modified polyol methods with $NaBH_4$ and structure controlling agents open new ways of controlled sythesis of Au nanomaterials for the above potential applications. In the synthesis of metal nanoparticles, it is proved that EG is an industrial solvent, perfectly suited for the controlled synthesis of nanomaterial systems of metal, oxide, and alloy [4–8]. Additionally, EG is readily available and completely safe for the controlled synthesis of Au nanomaterials.

To meet the sufficient amount of Au nanoparticles needed for research, we have synthesized Au nanoparticles using a modified polyol process with $NaBH_4$. The size, the shape, and the structure of Au nanoparticles were investigated in the range of 50 nm. The prepared Au nanoparticles have various shapes, sizes, and morphologies in the range of 50 nm. The existence of the various sizes of Au nanoparticles, which was due to the assembly of the as-prepared nanoparticles in solution, was shown in TEM investigation.

II. EXPERIMENT

II.1. Materials and synthesis

Chemicals from Sigma-Aldrich were utilized with the purity including poly (vinylpyrrolidone) (PVP) as a stabilizer, gold (III) chloride trihydrate ($HAuCl_4{\cdot}3H_2O$), sodium borohydride ($NaBH_4$) as strong reducing agent for the formation of Au nanoparticles from $HAuCl_4{\cdot}3H_2O$, ethylene glycol (EG) as both solvent and weak reducing agent, ethanol, acetone, and hexane, which is the same as mentioned in recent works [9–12]. Here, all chemicals were of analytical high standard grade**,** and were used without any further purification. In one typical process, 10 mL of EG, 10 mL of 0.375M PVP, 4 mL of 0.0625 M $HAuCl_4$ and $NaBH_4$ were added in a flask. The addition of $HAuCl_4$ and PVP was done many times until 4 mL of $HAuCl_4$were used. The complete reduction of $[AuCl_4]^{-1}$ by both EG and $NaBH_4$occurred over a short period of around 30 min. The samples were successfully prepared by the polyol method.

II.2. Measurements and methods

In the experimental methods, UV-vis-NIR spectroscopy, XRD, and TEM were used for the study of the as-prepared Au nanoparticles. The final products can also be studied by a spectrometer in the range of wavelength of 250-1000 nm for an analysis of the formation of Au nanoparticles. Lamda spectrometer was connected with personal computer with software (PerkinElmer UV WinLab and UV WinLab Data Processor & Viewer) for data analysis. The X-ray diffraction patterns were recorded by X-ray diffractometer (Rigaku D/max 2550V) at 40kV/200 mA and using Cu Kα radiation (1.54056 Å). In addition, TEM (JEM-2100F) with acceleration voltage of 200kV, around 0.1 nm lattice resolution, and around 0.19 nm point resolution was used in order to analyze the size and shape of the Au nanoparticles.

III. RESULTS AND DISCUSSION

III.1. Crystal structure of Au nanoparticles

The XRD result of a typical sample was recorded at 2θ angle in the range of 25° to 95° of Au nanoparticles presented (Fig. 1). Consequently, the crystal of as-prepared nanoparticles was very good. XRD was used to quickly identify the crystalline nanomaterial of all samples. The results showed no appearance of strange peaks. It indicated that all the as-synthesized Au nanoparticles have high purity and fine crystal structure. Here, we only presented the results of one typical sample for random selection. After the XRD survey of one sample corresponding to the fast phase identification in our measurements, Au metal nanoparticles of importance have face centered cubic (fcc) lattice, with ions arranged in a cubic close-packed arrangement [9].

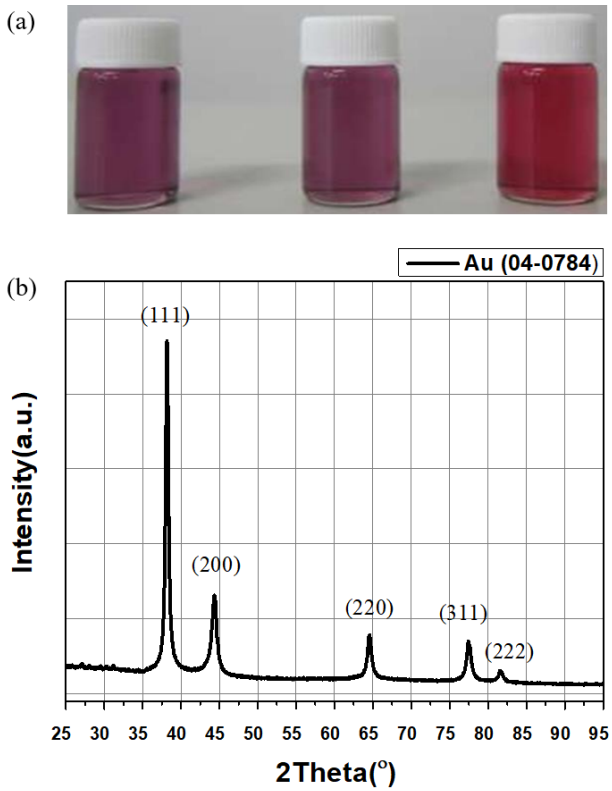

Fig. 1. (a) Three samples of as-prepared Au nanoparticles. (b) Crystal structure of Au nanoparticles by XRD.

The sample was measured by XRD showing diffraction peaks at 2θ angles of XRD of Au particles with the fcc structure consistent with the recent work [9, 13]. The XRD results of the Au nanoparticles show that the peaks at different angles characterize the structural aspects of Au nanoparticles with high crystallization corresponding to the fine crystal planes at 38.20° (111), 44.40° (200), 64.60°, (220), 77.54° (311), and 81.72° (222), respectively. Au nanoparticles show that crystal parameters were found in the coincidence with the pattern of Au (PDF-04-0784). It is

known that the values of the distances between atomic planes in Au nanoparticles were estimated to be 2.35, 2.03, 1.44, 1.23, and 1.17 Å corresponding to (111), (200), (220), (311), and (222) planes, respectively. The intensity of the strongest line on XRD diagram is the (111) crystal plane. Our result of crystallization of Au nanoparticles is consistent with published works [14–16]. Therefore, the fine crystal phase of the as-prepared Au nanoparticles by our modified polyol methods was confirmed via experimental.

III.2. Size and shape of Au nanoparticles

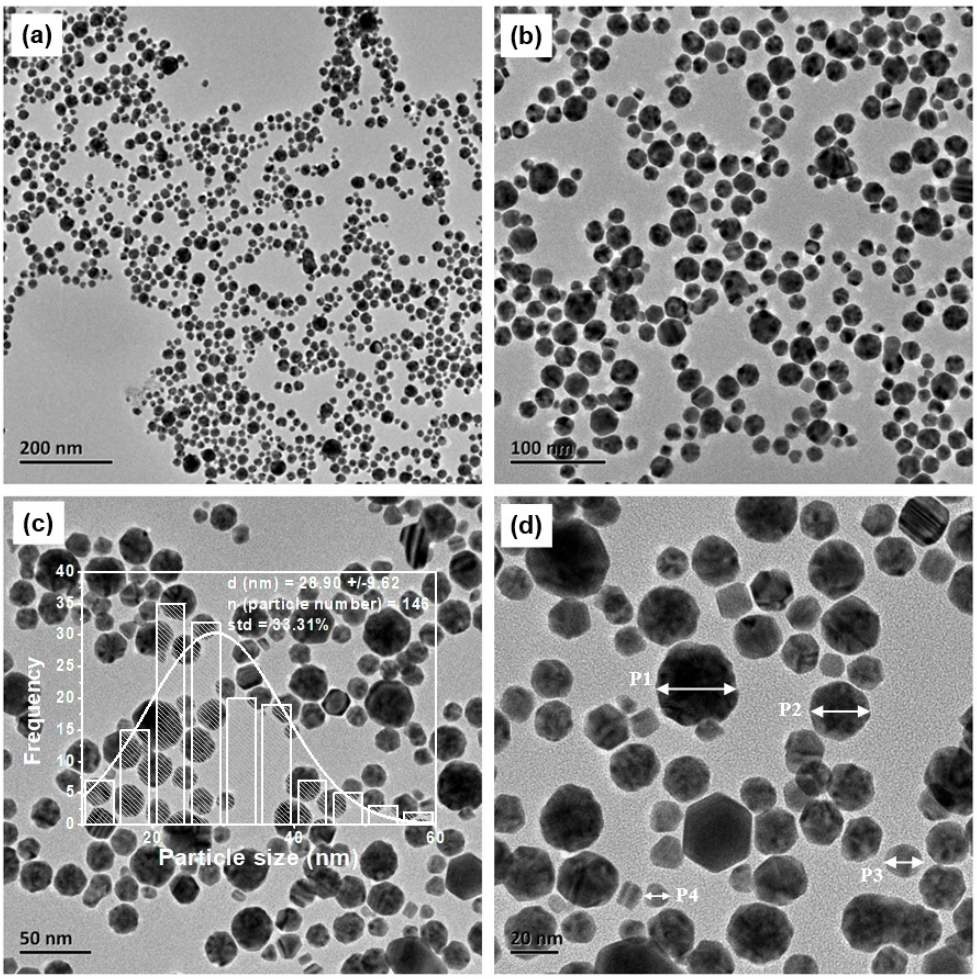

Fig. 2. TEM image of the as-prepared Au nanoparticles. Scale bar: (a) 200 nm; (b) 100 nm; (c) 50 nm; (d) 20 nm. The large Au nanoparticles were possibly formed by attachment, aggregation, self-assembly of the small Au nanoparticles.

Figure 2 shows the TEM images of Au nanoparticles in the range of 50 nm. It is observed that the various sizes of Au nanoparticles were calculated in Figs. 2c and 2d. For example, the

P1, P2, P3, and P4 particles show the particle sizes to be 9.13 nm, 14.32 nm, 24.93 nm and 34.07 nm, respectively. In the case of Au nanoparticles protected by a thin polymer layer of PVP synthesized by the improved polyol method with the addition of $NaBH_4$, a homogeneous system of Au nanoparticles has been obtained [3, 9]. Their shapes were found to be typical spherical and polyhedral. The very high roughness of the as-prepared Au nanoparticles was observed in their morphologies. Here, many Au nanoparticles have various large sizes and shapes but less than 50 nm. It is determined that the self-assembly of smaller Au nanoparticles less than 10 nm can lead the large nanoparticles [2, 3]. It is clear that the biggest particles were around 50 nm by self-assembly of smaller particles as shown in Fig. 2. The inset of Fig. 2(c) shows the particle size distribution of Au nanoparticles that are illustrated. It is clear that the average particle size (d) was 28.90 nm, the standard deviation (std) to be 33.31%, with the number of particles (n) to be 146 Au nanoparticles.

III.3. Optical property of Au nanoparticles

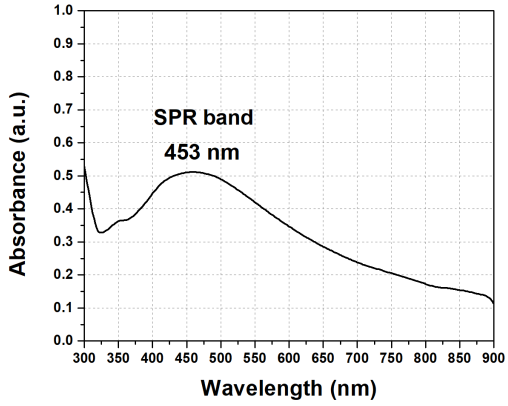

Fig. 3. UV-Vis spectrum of the as-prepared Au nanoparticles in solution exhibited a SPR band with a central peak at around 453 nm.

The optical property of the as-prepared Au nanoparticles with spherical and polyhedral-like shapes was found (Fig. 3). In general explanation, the plasmon oscillation for a sphere shows the displacement of the conduction electron charge cloud relative to the nuclei. This led that collective plasmon oscillation is measured to a system of particles [17, 18]. The stable SPR band at the central peak is important to potential biosensor applications and biosensing. The intensity of SPR band at around 453 nm was confirmed. The most exciting optical property of Au nanoparticles at a central peak around 530 nm was found in a plasmon band and the SPR peaks can be located in the much wider ranges from 450 nm to 1000 nm with the continuous shift, especially for Au nanorods [2,3,17,18]. Recently, many authors have also synthesized gold nanoparticles by seeded growth methods. In general, they have used CTAB as capping agent [14, 15] different from the use of PVP as capping agent [9, 13]. Recently, $NaBH_4$ been has used in a different way for controlled synthesis of Au nanoparticles, i.e., the reduction of Au precursor into Au nanoparticles [16]. It is obvious that researchers have used $NaBH_4$ reducing agent with the use of mechanosynthesis of Au nanoparticles [16]. It is certain that their TEM results are similar to the present results

when synthesis of Au nanoparticles by modified polyol methods don't need to use the mechanical method. Thus, SPR is an important phenomenon of the pure as-prepared Au nanoparticles in ethanol which was extensively studied according to various shapes and morphologies, which can be potentially used for next-generation SPR sensors [2, 3]. Today, the functional group of amino-NH_2 and thiol-SH groups can be used for bioconjugation to Au nanoparticles. In addition, Au nanoparticles are promisingly applied for molecular imaging, drug delivery, cancer diagnosis, and therapy [7].

IV. CONCLUSIONS

We have presented the successful synthesis of Au nanoparticles in the nanosized range of 50 nm with NaBH4 and EG by modified polyol method. As a result, there were the various particles with various spherical and polyhedral shapes in the range of 50 nm, respectively. Using the modified polyol method with $NaBH_4$, the size of Au nanoparticles was possibly controlled in the aforementioned ranges. We supposed that the large Au nanoparticles were formed by the assembly of a certain number of smaller nanoparticles. The variety in size and shape of nanoparticles is what researchers are concerned with rather than uniformity in size and shape. In addition, the SPR band of the as-prepared Au nanoparticles in ethanol was also found.

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