

Research Article

Synthesis and Self-Assembly of Gold Nanoparticles by Chemically Modified Polyol Methods under Experimental Control

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In our present research, bottom-up self-assembly of gold (Au) nanoparticles on a flat copper (Cu) substrate is performed by a facile method. The very interesting evidence of self-assembly of Au nanoparticles on the top of the thin assembled layer was observed by scanning electron microscopy (SEM). We had discovered one of the most general and simple methods for the self-assembly of metal nanoparticles. The general physical and chemical mechanisms of the evaporation process of the solvents can be used for self-assembly of the as-prepared nanoparticles. The important roles of molecules of the used solvents are very critical to self-assembly of the as-prepared Au nanoparticles in the case without using any polymers for those processes. It is clear that self-assembly of such one nanosystem of the uniform Au nanoparticles is fully examined. Finally, an exciting surface plasmon resonance (SPR) phenomenon of the pure Au nanoparticles in the solvent was fully discovered in their exciting changes of the narrow and large SPR bands according to synthesis time. The SPR was considered as the collective oscillation of valence electrons of the surfaces of the pure Au nanoparticles in the solvent by incident ultraviolet-visible light. Then, the frequency of light photons matches the frequency of the oscillation of surface electrons of the Au nanoparticles that are excited.

1. Introduction

At present, the bottom-up assembly of precious metal nanoparticles, such as gold (Au), silver (Ag), and copper (Cu) with and without control under suitable experimental conditions is very of importance [1–4]. In the popular cases, we can think that it is self-assembly of the as-prepared nanoparticles

without control or self-assembly of the as-prepared nanoparticles with control. Scientists have intensively investigated the self-assembly of nanoparticles involving in temperature, pressure, chemical reaction, mechanism, time, types of solvents or liquids used, additives, capping polymers and ligands used, mixture of solvents, by external weak and strong electromagnetic fields, by the weak and strong optical excitation

of light sources, methods of excitation sources through their chemical synthesis by sono-chemistry method or microwave or ultrasound processes, and so forth. In particular, the self-assembly of the cheap and precious metal nanoparticles can lead to build completely new nanotextures, and functional nanostructures or new nanoorganizations from nanoscale to microscale on their entire sized ranges with potential applications in photonics, catalysis, biology and medicine as well as nanomedicine. In new nanotextures containing nanoparticles, the most desirable optical properties as so-called surface plasmon resonance (SPR) or the specific oscillation of conducting electrons at surface interface of the Au nanoparticles and medium in their ultraviolet-visible (UV) spectrum can be realized in optical biosensors. Clearly, the visible-region plasmon bands are usefully exploited in photonics applications. In particular, Au nanoparticles can be used an agent for dangerous cancer diagnosis and therapy due to SPR [3]. In addition, self-assembly of the nanoparticles can occur at room temperature with biomolecules, or hydrogen-hydrogen interactions, or with the widespread use of typical homogeneous solvents and homogeneous nanosystems, such as ethylene glycol. The directed self-assembly of nanoparticles by various chemical and physical methods was discussed. However, self-assembly of nanoparticles or one nanosystem has become a big challenge with various recent discoveries [5–8]. As a result, we suggested that self-assembly method could lead to create the new blocks from nanocrystals. However, self-assembly has a wide and deep meaning in new nanostructures to be controlled or new phenomena of the behavior of specific common interactions among nanoparticles through various assembled media [7]. According to the XRD analysis reported, it was found that $(h k l)$ planes of the Au nanoparticles are different from various polyhedral shapes and morphologies, such as typically $(1 1 1)$, $(2 0 0)$, $(2 2 0)$, and $(3 1 1)$ of various shapes such as octahedra, truncated octahedra, cuboctahedra, truncated cube, cube, and trisotahedra [9].

In one good work, the SPR of spherical Au nanoparticles was studied in the use of cetyltrimethylammonium bromide (CTAB) with a very low concentration. The functional groups of CTAB were the linkers among the as-prepared Au nanoparticles. In our research, we suggested that molecules of ethanol or other liquids and solvents are the main causes of the wonderful self-assembly of the prepared nanoparticles in optical absorption spectra observed [10, 11]. In our previous works, it turns out that the novel issues of morphology, size, and structure of Pt nanoparticles according to self-aggregation, self-agglomerate, self-assembly, and internal structural changes were confirmed. In this context, self-assembly of the as-prepared nanoparticles of interest after evaporation of the solvents or heat treatment can be clearly and transparently understood [12, 13]. In our viewpoints, we suggested that self-assembly in building of new nanostructures occurs easily via surface attachments among them in order or disorder with the connections at surfaces, edges, and corners or all combinations. Here, typical collisions among nanoparticles need to be intensively studied in detail at nanoscale of the nanosized ranges of 10 nm, 100 nm, 1000 nm, and 10 μm as classical collisions in the various media, such as

solvents and liquids. However, molecular forces of solvents containing the prepared nanoparticles can show extreme importance in self-assembly of the prepared nanoparticles [14–17]. It is known that self-assembly of the nanoparticles has naturally various origins from various forces, typically Van der Waals, surface and interfacial interactions, electrostatic forces of the as-prepared nanoparticles and capping agents, capillary forces, hydrodynamic forces, interfacial interaction in the closely-directed connections between the solutions of the as-prepared nanoparticles and substrates. Certainly, we can develop various simple conjugation methods with self-assembly of the defined nanoparticles using positive or negative electrostatic attractions at molecular level with biomolecules for engineering new sensor devices. Thus, the self-aggregation of the nanoparticles in solvents used is crucial to the self-assembly. The colloidal self-assembly of precious metal nanoparticles occurs in the evaporation of the solvent containing the nanoparticles, which will also lead to create potential optical applications in the large nanosized blocks. In most of the cases, surface stabilizers, such as polymers and surfactants, play important roles in self-assembly of engineered nanoparticles in various solutions when we use them at a low concentration. The self-arrangements of the as-prepared Au nanoparticles on the substrates as well as patterns and templates or self-assembled masks and frameworks are very exciting to the clear mechanisms of self-assembly of nanoparticles in the various solutions, especially in the previously as-prepared templates. For the case of self-assembly of Pt nanoparticles, we found that the phenomena of particle-particle attachment, aggregation, agglomeration, and assembly of as-prepared Pt nanoparticles [12, 13]. Thus, ethanol evaporation and the interactions of the pure Au nanoparticles after the complete evaporation are important to the self-assembly of the pure Au nanoparticles on the flat Cu substrate. At the same time, we also discovered that the possible self-attachments between two particles, and among many nanoparticles in the bondings originating from the corners, the edges, the surfaces, and other arbitrary attachments are very crucial to self-assembly of the as-prepared nanoparticles with and without control. This is the truth in our present research of the self-assembly of the as-prepared Au nanoparticles in a comparison with self-assembly of the as-prepared Pt nanoparticles [12, 13, 18]. Therefore, the as-prepared Au nanoparticles can be combined through the particle-particle attachments, typically important corner-corner, edge-edge, surface-surface, surface-corner, and surface-edge attachments in the self-assembly of homogeneous nanosystems for new and attractive nanostructures with or without control [19, 20]. This is the nanoparticle self-assembly. The mechanisms of nucleation, growth, and formation of the metal nanoparticle in the solution with the capping agent are self-aggregation or agglomeration, and self-assembly as well as random and direct self-collisions among clusters, nanoclusters, and nanoparticles in various size ranges according to synthesis time and experimental conditions in various liquid media [18, 19]. The experimental processes of self-assembly of the nanoparticles usually take a lot of time in the solvents and polymers. Thus, the self-assembly of the nanoparticles can

occur at room temperature without the surface modifications with the use of linkers or connections of polymers and surfactants. Moreover, self-assembly of nanoparticles for large controlled nanotextures is a good way of the design of functional nanosized materials and devices. Recently, magnetic assembly has been intensively developed by researchers and scientists [1–6, 10, 11, 16, 17]. Therefore, we suggest that the surface modification of the as-prepared Au nanoparticles with functional molecules, polymers, and surfactants can be done in the standard patterns and templates using building blocks that lead to create many potential applications in biomedical engineering. However, the key challenge is to obtain the methods and processes of the self-assembly of the known nanoparticles with high reliability, durability, and stability. In principle, our results can lead to develop novel synthesis methods with the highest control level for nanoparticle assembly.

In this research, the highly uniform Au nanoparticles of around 100–250 nm were successfully synthesized by polyol method using NaBH_4 as a strong reducing agent. It was discovered that the self-arrangements of the as-prepared Au nanoparticles were observed in the flat Cu substrate after the complete evaporation of ethanol at room temperature. In addition, the as-prepared Au nanoparticles exhibit the intriguingly strong SPR band for potential applications of SPR sensors.

2. Experimental

2.1. Synthesis

2.1.1. Chemical. Chemicals (Aldrich, Sigma-Aldrich) used are the following: poly(vinylpyrrolidone) (PVP) as a stabilizer, gold (III) chloride trihydrate, ACS reagent (Chemical kinds according to the specifications of the American Chemical Society), NaBH_4 as strong reducing agent, ethylene glycol (EG) as both solvent and weak reducing agent, ethanol, acetone, and hexane. Here, all chemicals used were of analytical standard grade and were used without any further purification. Moreover, ionized and distilled water with very high purity was prepared by MilliPore purification system available in our laboratory for washing and cleaning during experimental processes.

2.1.2. Synthesis of Gold Nanoparticles

(1) *Synthesis of Au Nanoparticles in Ethylene Glycol.* In the present process, chemicals including EG, HAuCl_4 , NaBH_4 , NaOH, and PVP were used for synthesis of Au nanoparticles. In order to synthesize Au nanoparticles, 10 mL of EG, 10 mL of 0.375 M PVP, 6 mL of 0.0625 M HAuCl_4 , and 0.55 g of NaBH_4 were used. To begin with, 50 μL of HAuCl_4 and 100 μL of PVP were added in the flask many times after every 60 s interval until 6 mL of HAuCl_4 were thoroughly used. Typically, the reduction of $[\text{AuCl}_4]^{-1}$ by EG and NaBH_4 occurred for a short time of 10–30 min. The resultant mixture was heated and refluxed at 200–220°C. The yellow colour of the mixture of HAuCl_4 , EG, and NaBH_4 precursors was changed into the

violet or deep purple colour of the product of the as-prepared Au nanoparticles. To obtain Au nanoparticles, washing and centrifugations are similar to the preparation procedure of pure Pt nanoparticles. This was centrifuged using the Kubota 3740 centrifuge for 15 min. The supernatant was separated and precipitated by adding a triple volume of acetone for washing, cleaning, and removing PVP polymer and any impurities to obtain the pure Au nanoparticles. Then, it was centrifuged for 30 min in the corresponding procedures of removing remaining PVP and impurities on the surfaces of the prepared Au nanoparticles with the use of a mixture of ethanol and hexane. In most of the cases, the prepared Au nanoparticles were homogeneously dispersed in ethanol by ultrasonication method (US-2 Model, 38 KHz). Finally, the small fixed volumes (μL) of the drops containing the pure Au nanoparticles of about 100–250 nm were placed onto a copper substrate. The fixed volume of a mixture of ethanol and the pure Au nanoparticles was gradually evaporated at room temperature for several hours from 5 to 7 h to receive the pure Au nanoparticles in the self-assembly on a copper substrate.

(2) *Self-Assembly of Au Nanoparticles.* In the self-assembly of Au nanoparticles, the evaporation control of ethanol solvent is important. The homogeneous solvents (e.g., ethanol or hexane, etc.) were used for the dispersion of Au nanoparticles of around 100–250 nm after complete removal of PVP polymer. Here, 1 mL of ethanol containing the pure Au nanoparticles is used for the self-assembly of Au nanoparticles. Every stop of the mixture of the as-prepared Au nanoparticles and ethanol solvent (10 μL) was fallen freely on the flat Cu substrate. After complete evaporation of ethanol, the second stop was set on flat Cu substrate, and so on. Gradually, the next drops of the solvent containing the Au nanoparticles were continuously set on the substrate for making a thin layer of Au nanoparticles after evaporation. After that, we had completely utilized 1 mL of a mixture of ethanol containing the as-prepared Au nanoparticles. Finally, the samples were kept overnight for free evaporation in air at room temperature.

2.2. Characterization

2.2.1. UV-Vis-NIR Spectroscopy. In order to investigate the formation mechanism of Au nanoparticles prepared by the reduction of HAuCl_4 precursor by ethylene glycol, 20 μL of the stock solution of 0.0625 M HAuCl_4 , and 20 μL of the solution of the as-prepared product containing PVP protected Au nanoparticles were used in the solvent of around 3 mL ethanol in the analysis of UV-Vis spectroscopy after centrifugation process by the centrifuge (Kubota 3740) many times with plastic bottles, typically as Nalgene centrifuge ware of very high quality. Every volume from 1 mL to 2 mL of reaction mixtures was collected during synthesis for UV-Vis investigations of the formation mechanism of the Au nanoparticles in ethylene glycol. The final solution products containing Au nanoparticles were also studied by UV-Vis-NIR spectroscopy (Ubest 570 UVVis-NIR spectrometer) in the range of wavelength of 200–1100 nm for an analysis of the final formation of the Au nanoparticles by the reduction

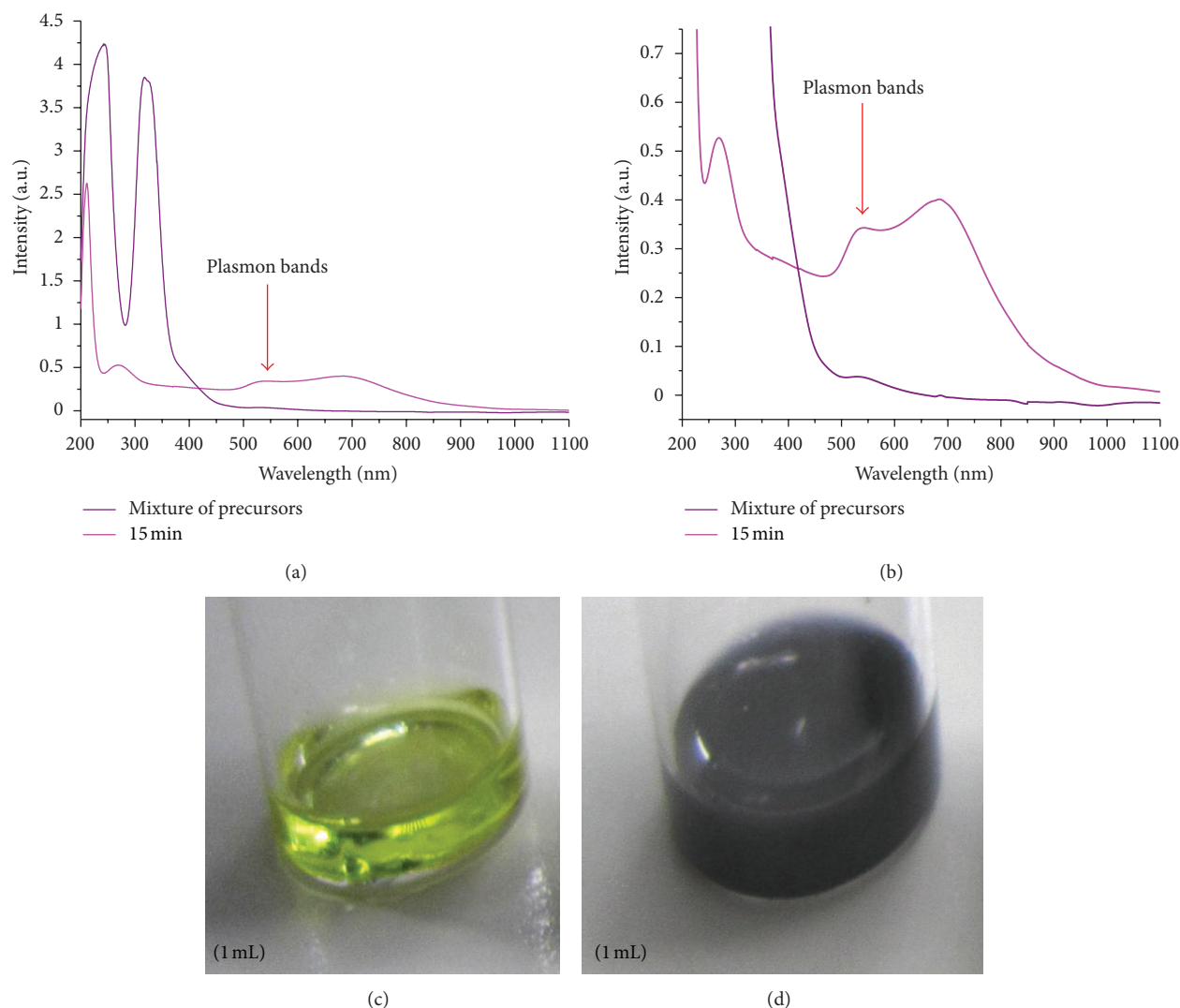


FIGURE 1: (a) UV-Vis spectra of the mixture of the solution of the precursors, and (b) UV-Vis spectra of the product solution containing Au nanoparticles with surface plasmon resonance bands. (c) Yellow color of the stock solution of precursors in ethylene glycol. (d) Violet color of the prepared product of the Au nanoparticles.

of HAuCl_4 by ethylene glycol as a weak reducing agent, and NaBH_4 as a strong reducing agent during synthesis.

2.2.2. Scanning Electron Microscopy (SEM). In order to study the size, shape, and self-assembly of the as-prepared Au nanoparticles, we have used Field Emission scanning electron microscope (SEM), JEOL JSM-6340F operated at 5, 10, and 15 kV (5–15 kV), and probe current around $12 \mu\text{A}$. The SEM images of the self-assembly of the as-prepared Au nanoparticles were focused by suitably fine focus level and adjustment.

2.2.3. Energy-Dispersive X-Ray Spectroscopy (EDS). In our typical measurements, SEM system was interfaced with a typical Energy-dispersive X-ray spectroscopy (EDS) system for elemental analysis. In this system, EDS acquisition and

element analysis can be processed by Voyager software and Voyager environment for Spectral display. The EDS spectra of the as-prepared Au nanoparticles are snapped and viewed by Snapshot-V3.5.1 program. The connection for transferring image data was set up to the downloaded EDS spectra of the as-prepared Au nanoparticles from Spectral Voyager unit through EFTFP program to receive the EDS spectra with the results of element analysis. Therefore, the elemental composition of the prepared Au nanoparticles was measured by the EDS method.

3. Results and Discussion

3.1. Formation of PVP Protected Au Nanoparticles. Based on UV-Vis absorption spectra of PVP protected Au nanoparticles in Figures 1 and 2, we have evaluated the nucleation, growth, and formation of Au nanoparticles in a mixture

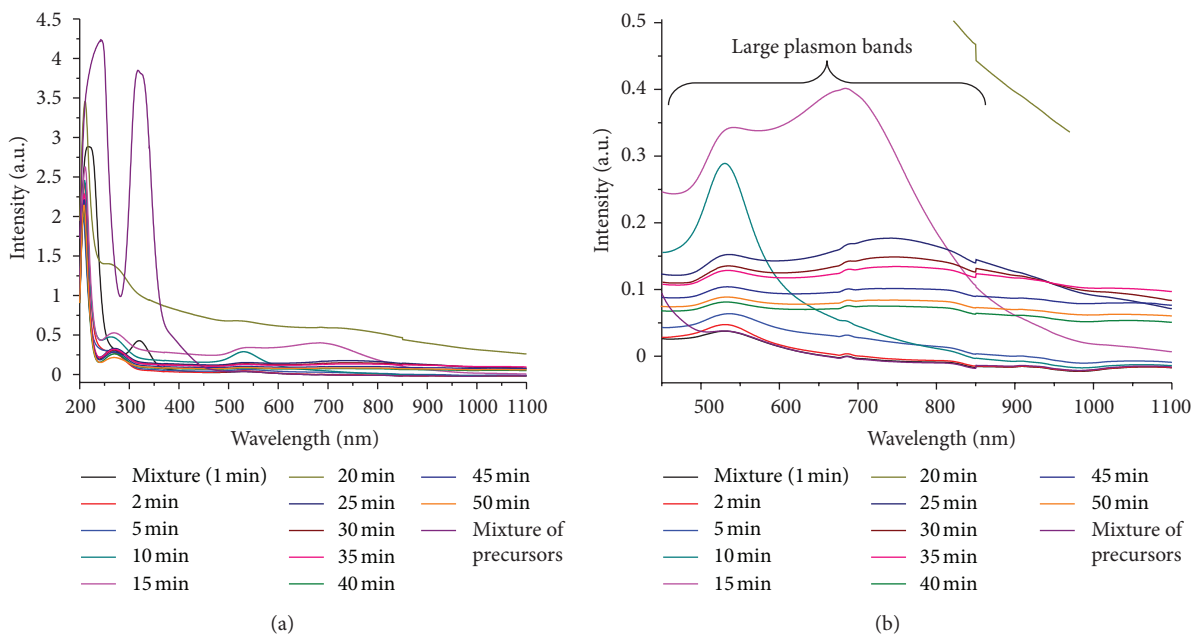


FIGURE 2: (a) UV-Vis spectra of Au nanoparticles with surface plasmon resonance bands. (b) The dependence of the surface plasmon resonance bands of Au nanoparticles on synthetic time in respective to the samples collected at different times.

of PVP and ethylene glycol (EG) from molecules, atoms, clusters, nanoclusters to nanoparticles. The band at 384 nm becomes the band at 276 nm after the reduction of HAuCl_4 with NaBH_4 in EG. The band at about 243 nm becomes the band at about 210 nm after the reduction of HAuCl_4 with NaBH_4 in EG in the formation of the as-prepared Au nanoparticles with two main bands located at around 230 and 324 nm as collective electron excitation or strong localized surface plasmon resonance bands (SPR). Here, 384 nm and 243 nm were attributed to the ligand-to-metal charge-transfer transition of $[\text{AuCl}_4]^{1-}$ ions in a mixture of EG and ethanol. The remaining bands at 276 and 210 nm show the formation of the prepared Au nanoparticles. In our process, the pH degree of the mixtures studied was checked in the certain range of 6–8 during synthesis. The pH values of the reaction mixture can be suitably controlled by using the solution of 0.1M NaOH at various synthesis temperatures and experimental conditions. Here, UV-Vis spectra of a mixture of precursors (HAuCl_4 and EG) usually show the two strong absorption bands located at around 230.79 and 324.27 nm. In most of the UV-Vis measurements, the strong decrease in the peak intensity of the stock solution containing precursors at the absorption bands of 230 and 324 nm was clear experimental evidence of the final formation of the nanoparticle-solution products by the complete reduction of the $[\text{AuCl}_4]^{1-}$ ions by EG and NaBH_4 . However, there are various mechanisms of the final formation of Au nanoparticles. The desirable products are usually a nanosystem of the prepared Au nanoparticles with polyhedral and polyhedral-like morphologies and shapes as well as spherical and spherical-like morphologies and shapes. Eventually, the UV-Vis absorption spectra in the certain range of 200–1100 nm of a mixture taken at ~1, 2, 5, 10, 15, 20, 30, 35,

40, 45, and 50 minutes showed the two main bands located at around 230 and 324 nm as well as the two SPR bands or the localized SPR bands at 530 nm because of the phenomenon of collective oscillation of valence electrons of the prepared Au nanoparticles.

The strongest band at 230 nm was significantly decreased in the intensity according to the new bands at around 210–218 nm. On the other hand, the strong band at 324 nm was significantly decreased in the intensity according to the new band at around 320 nm after synthesis time of about 1 min, and the new stable bands at 269–273 nm.

This SPR peak is of very importance and interest in potential biosensor applications and biosensing. In our measurements, the samples of a lot of attention were specially paid, which are the samples collected at 1, 2, 5, 10, 15, and 20 min. The maximum intensity of SPR-phenomenon band was confirmed in the sample collected at 10 min at 530 nm. However, the samples collected at 15 and 20 min show significant changes of the SPR bands. The SPR band at 530 nm was enlarged in the much wider ranges of 450–1000 nm with the continuous shift. This is a new phenomenon in our research discoveries of SPR. However, the fixed position of SPR band at 530 nm was unchanged according to a high stability of SPR. We have suggested that surface plasmon resonance of the as-prepared Au nanoparticles was enhanced in the wider range of 450–1000 nm according to the wavelength range of biological tissues in spite of the SPR band of the narrow range of 450–600 nm with the strong SPR band at 530 nm of the samples collected at 10 and 15 min. The behaviour of the SPR was significantly changed in the samples collected at 15 and 20 min. After that, the intensity of SPR was reduced but the larger SPR bands of the sample collected at 20 min. This is an interestingly new observation of our research. It means

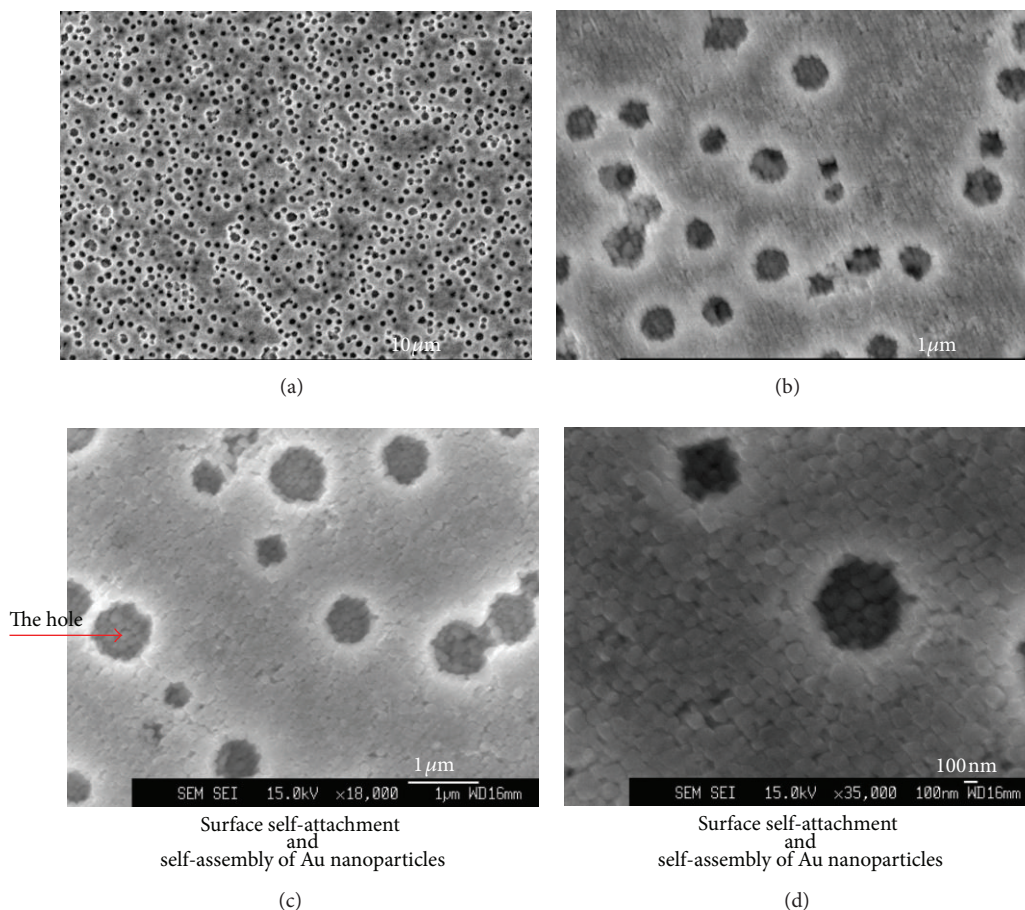


FIGURE 3: (a)–(d) SEM images of Au nanoparticles synthesized by polyol method with the use of HAuCl_4 (Precursor) and PVP (Capping agent) in respective to self-assembly of the pure as-prepared Au nanoparticles.

that the addition of SPR at around 682 nm was very strong to synthesis time of 15 min. Here, the additional SPR band did not appear in a period of 10 min but the strong SPR band was formed at 15 min during synthesis. The SPR band became stable in the range of 25–50 min with the weaker intensity. It is known that the precious nanoparticles have their own certain interaction with light when it is excited by the light source, which leads to the SPR band. It is known that SPR is the consequence of collective oscillations of conduction electrons of the as-prepared nanoparticles. So far, the SPR band has firmly found only in terms of the visible frequency regions for three metals including gold (Au), silver (Ag), and copper (Cu) [1, 8]. So far, Mie theory has used to study the characterization of precious metal nanoparticle in their optical properties [1, 3], especially in the phenomenon of SPR of Au nanoparticles. Mie theory is used as the good estimations of the SPR bands observed in the experimental UV-Vis spectra of the Au nanoparticles in the aqueous solutions or solvents according to their specific color.

When we have carried out the complete removal of PVP, Au nanoparticles were homogeneously dispersed in ethanol by using ultrasonication method. The SPR phenomenon was clearly observed in Figures 1 and 2 but the weaker

intensity comparable to the case of the PVP protected Au nanoparticles. Therefore, this is a very exciting evidence to the observed SPR effect.

The results of UV-Vis spectra of the as-prepared Au nanoparticles are in agreement with those of EDS analysis. In the case of the prepared Au nanoparticles, the Au element appeared with very strong peak at 2000 keV. Thus, both UV-Vis spectra and EDS analysis of the as-prepared Au nanoparticles present the evidence of the existence and formation of the Au nanoparticles by our simple polyol method.

3.2. Self-Assembly of the As-Prepared Au Nanoparticles. In our measurements, the Au nanoparticles show the size in the range of around 100–250 nm with spherical or spherical-like morphology and shape as well as polyhedral or polyhedral-like morphology and shape in Figure 3. They are homogeneous in size, shape, and morphology. Accordingly, Figure 4 shows the EDS spectrum of the evidence of the formation of the as-prepared Au nanoparticles according to their very exciting surface self-attachment and self-assembly. In our research, the self-assembly was discovered on the surface of the very thin layer of the prepared Au nanoparticles. The hard

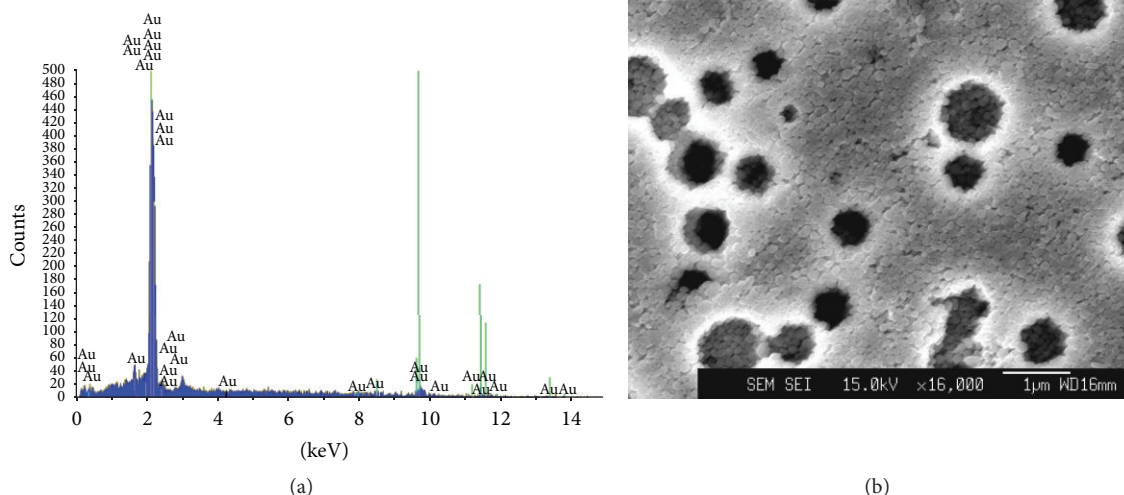


FIGURE 4: (a) EDS spectrum of the as-prepared Au nanoparticles. (b) Self-assembly of the pure as-prepared Au nanoparticles.

evidence of the self-assembly of Au nanoparticles on the flat Cu substrate for some hours were clearly observed in Figures 3 and 4(b). There are the different local areas on the substrate that were formed in the evaporation of the ethanol containing the prepared Au nanoparticles with the specific nanostructures. We can see that there are the local areas that are very similar to the interesting holes with the depth of hundred nanometers where the solvents are mainly stored during the ethanol evaporation. Then, the circle holes with their diameter in the ranges of around 1000 nm in size were formed in the certain forms as the exciting holes through nanoparticle self-assembly. The as-prepared Au nanoparticles were rearranged in order to build the holes during evaporation. In fact, the self-assembly of engineered nanoparticles is to create new nanotextures or nanoblocks with the use of some common polymers or linkers for the organic-metal connections among them. Therefore, they are not usually stable due to the simple and fast collapses of the assembled nanoblocks containing the prepared nanoparticles.

In general, colloids, colloidal clusters, and colloidal “molecules” can have the ability to bind directionally for the self-assembly [11]. In our present results, the as-prepared Au nanoparticles can clearly connect together via both short-range and long-range interactions in Figure 3. It should be stressed again that this process is the random and direct assembly of nanoparticles. The dense self-aggregation and dense self-assembly of the Au nanoparticles of around 100–250 nm with homogeneous size, shape, and morphology into a large array of the specific organized structures on the flat Cu substrates were performed only at room temperature during the slow evaporation process of ethanol solvent without the use of any polymers, block copolymer or surfactants, and so forth as well as without any surface modifications of these Au nanoparticles. In addition, the homogeneity of a nanosystem of Au nanoparticles is highly ordered. We suggested that surface attachment and self-assembly were well driven by thermodynamic processes of ethanol evaporation of a mixture of ethanol and the pure Au nanoparticles. These can lead to the mechanism of self-assembly of the prepared Au

nanoparticles via their self-attachment (... particle-contact-particle-contact ... particle) on the flat Cu substrate in Figure 3. Our present results can possibly lead to a general method of making self-assembly of the large 1D, 2D, and 3D organizations. In addition, we did not observe the Cu element (Figure 4) because the thin layer of the pure Au nanoparticles fully covered the surface area of the Cu substrate.

4. Conclusion

In this research, the interesting surface self-attachment and self-assembly of the as-prepared Au nanoparticles was observed during evaporation of the mixture of ethanol and Au nanoparticles without the use of any additives and polymers as well as biomolecule linkers. These showed that the specific collective interactions of the nanoparticles with liquid and evaporation of liquid can be controlled by the self-assembly of the arrangements of Au nanoparticles. The absorption spectra of the solutions of ethanol and the as-prepared Au nanoparticles show the strong SPR phenomenon. The SPR bands of the prepared Au nanoparticles become very stable with the as-prepared Au nanoparticles with synthesis time more than 20 min. However, their weaker intensity of SPR was observed.

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