CHAPTER II

THEORETICAL BACKGROUND

2.1 Gold nanostructures synthesis

There are many methods for synthesizing metal nanostructures. Mostly, the fabrication methods of metal nanostructures can be divided into two main types, bottom-up and top-down approaches. Top-down approach was started from standard bulk materials and reduced to nanometer size with physical mechanization of those materials. Mostly bulk materials were evaporated at high temperature and dented to nanomaterials. But the bottom-up approaches started from atom or molecule and built up to nanometer size of materials using chemical reaction and physical interaction. Generally, methods of synthesis metal nanostructures have two important aspects, chemical and physical methods.

2.1.1 Physical method

2.1.1.1 Arc discharge method (ADM)

The large amount of energy estimated temperature of 1500-5000 K at gap distance between the electrodes was generated by stable pulse voltage about 135 volts [26-28]. The particle size of gold nanoparticles in the range of 2-40 nm with spherical shape on surface of electrode was melted and vaporized. Schematic diagram of the arc discharge system generated gold nanoparticles by plasma between gaps of electrode shown in Fig 2.1. The advantage of ADM method could be generated gold nanostructures without chemical surfactants and stabilizers at water or ethanol solution. Spherical structures were generated in this method. However, this method was applied to synthesize single-walled carbon nanotubes [28].

2.1.1.2 Aerosol method

Aerosol method produced gold nanoparticle by heating high purity gold placed inside a tube furnace at 1650 °C under carrier nitrogen gas. As the gold vapor at heated zone was condensed into particles and coagulated resulting in a wide size distribution. Charger device as UV light creating free electrons then charge the neutral particles to positive and negative particles. Finally, wide size distribution gold nanoparticle was classified by their aerodynamic diameter at differential mobility analyzer by balancing the force from an electric field [29].

2.1.1.3 Laser ablation/irradiation in liquid method

Laser ablation with gold plates in the liquid medium with stabilizer can be produced various gold nanostructures (nanoparticles, nanocubes, nanorods, nanocomposites, etc.). The fabrication and modification of nanomaterials in liquid based on laser irradiation has become a rapidly growing field .Fig 2.2 shows schematic diagram of the laser ablation method. The particles size can be controlled by changing the laser intensity and wavelength [30].

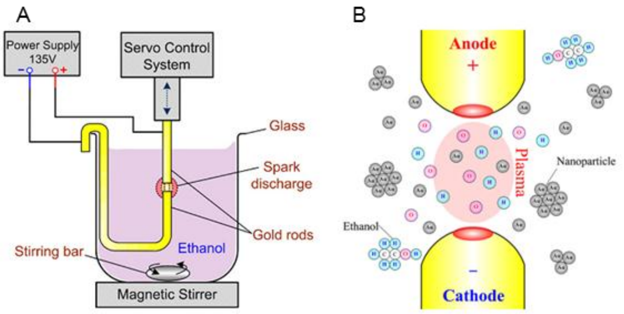


Figure 2.1 Schematic diagram of the arc discharge system (A) instrument component (B) mechanism of plasma generated gold nanoparticles [26].

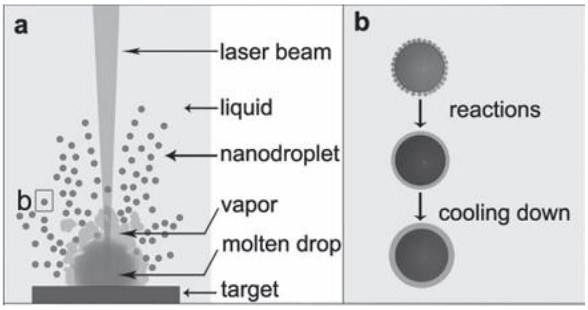


Figure 2.2 Schematic diagram of the laser ablation method [30].

2.1.2 Chemical method

The chemical method is mostly popular among chemists in the few years. The standard protocol for synthesis gold nanostructures using chemical method can be divided into chemical reaction and electrochemical reaction follows by type of reaction. The chemical reaction synthesized nanoparticles in liquid phase using metal salt and reducing agent. Borohydride reduction was classical method for synthesis of gold nanoparticles that the reactions occur rapidly causing the immediate nucleation of metal particles [31]. Recently, anisotropic noble nanomaterials (e.g., gold, silver, platinum, and palladium) are of interest in the few years due to those structures. More complicated synthetic method of anisotropic nanomaterials has been remarkable than isotropic nanomaterials. Seed-mediated method, polyol method, photochemical method, electrochemical method, galvanic replacement reaction method was generated anisotropic nanomaterials.

2.1.2.1 Seed-mediated method

The seed-mediated growth process is a widely use anisotropic nanostructures. This method including two steps, 1st step: seed fabrication process by conventional reduction reaction was created. Sodium borohydride is a simple reducing agent for generation nanoparticle. 2nd step: seed grew into the anisotropic structures then metal morphology using grows solution. Surfactant and mild reducing agent are mainly active species in the growth solution for controlling the growing of metal structures. Fig 2.3 shows gold nanorods preparing by growth solution with various aspect ratios. On the other hand, anisotropic structures could be dictated by varying parameter e.g., amount of concentration of seed, additive agent.

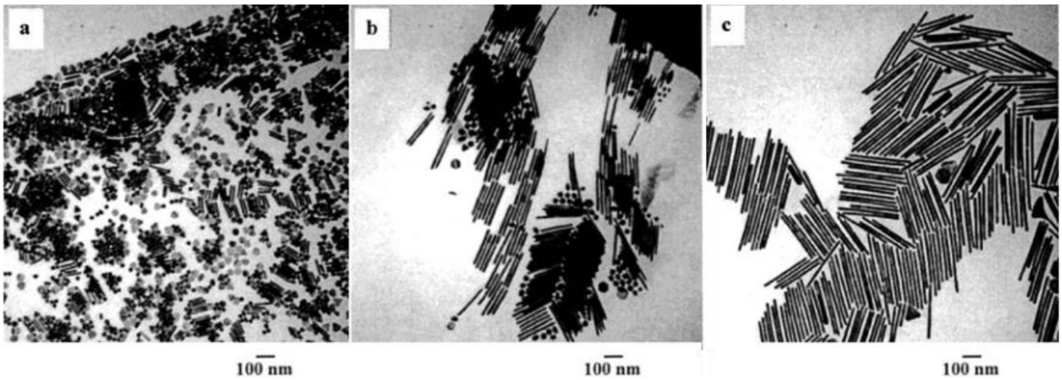


Figure 2.3 (a) TEM images of gold nanorods prepare by growth solution with various aspect ratios [32].

Preparation of gold nanorods with aspect ratios of 4.6±1.2, 13± 2, and 18± 2.5 nm by seeding growth approach is controlled by varying the ratio of seed to metal salt [32]. The gold nanorods were demonstrated with three steps of seed-mediated growth method using different surfactants, alkyltrimethylammonium bromides (CTAB) and cetylpyridinium chloride (CPC). The longer chain lengths of the surfactant tail are producing longer gold nanorods. “Zipping” mechanism was proposed which surfactant bilayer stabilized on the gold surface by Van der Waals. In general, the length of the surfactant chain increased which induced the increasing of aspect ratio of gold nanoparticles [33]. The seed-mediated deposition of Au nanorods directly on glass surfaces using CTAB was reported. The concentration of The $AuCl_4^-$ is the key factor of the experiment that average length and aspect ratio of the nanorods increases with increasing $AuCl_4^-$ concentration [34]. However, seed-mediated synthesis method could be changed the gold structures from cubic to trisoctahedral, and rhombic dodecahedral structures using cetyltrimethylammonium chloride (CTAC), surfactant, NaBr, and aromatic additives [35, 36]. Seed-mediated co-reduction shows new idea for synthesis gold palladium shape-controlled alloy nanostructures [37].

2.1.2.2 Polyol synthesis method

Polyol reduction is one of the methods to synthesize anisotropic structures with controllable shapes and optical properties as shown in Fig. 2.4. In a typical synthesis, ethylene glycol acts as reductant generating metal atoms from a salt precursor at an elevated temperature (100-160 °C) [38-40]. The formation of nanostructures with controlled shapes is facilitated by adding capping agent e.g., poly (vinyl pyrrolidone) (PVP). Uniform shape of the quasi-spherical gold particles prepared using polyol reduction between $AuCl_4^-$ in a PVP-ethylene glycol solution. The solution was heated up to the desirous reaction temperature (100°C to the boiling point of ethylene glycol). The 0.1 to 0.4 µm showed the ranges size of the powder [40]. Large quantities of silver nanocubes with edge length of 175 nm and nanowires with diameters of 30-40 nm, and lengths up to 50 µm was synthesized by ethylene glycol in the presence of PVP as capping reagent. The silver cubes use as sacrificial templates for single-crystalline nanoboxes and hollow polyhedra of gold synthesis by galvanic replacement reaction [38, 39]. Different seeds (single-crystal, cuboctahedrons, and cubes seeds) can be grown to nanostructures with different shapes by controlling growth rates as shown in Fig. 2.5. For example, a single-crystal seed can grow into an octahedron or cube, single-crystal cuboctahedrons and cubes grow to nanorods with octagonal cross sections and nanobars with rectangular cross sections, multiply twinned seeds with a decahedral shape can be directed to grow into rods or nanowires with a pentagonal cross section, and plate-liked seeds grow into hexagonal and then eventually triangular plates [41].

2.1.2.3 Photochemical synthesis method

Photochemical synthesis gold nanoparticles as well as general photochemistry are similar to the previous method with chemical reductant. Generally, the method using a soft templates, macromolecular polymers, dendrimers or surfactants to form micelles or reverse micelles, control size and structures of gold nanostructures. Under UV irradiation conditions, intramolecular photoreduction generated reducing agent and also were protective action of polymer or coordination compound for the reduction process of Au (III) ions as shown in Fig.2.6 [42].

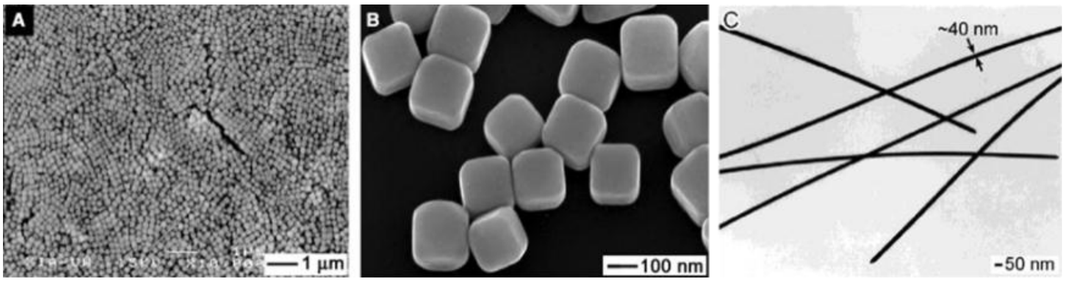


Figure 2.4 (A) Low- and (B) high-magnification SEM micrographs of slightly truncated silver nanocubes synthesized with the polyol process. (C) TEM images of a purified sample of silver nanowires [38, 39].

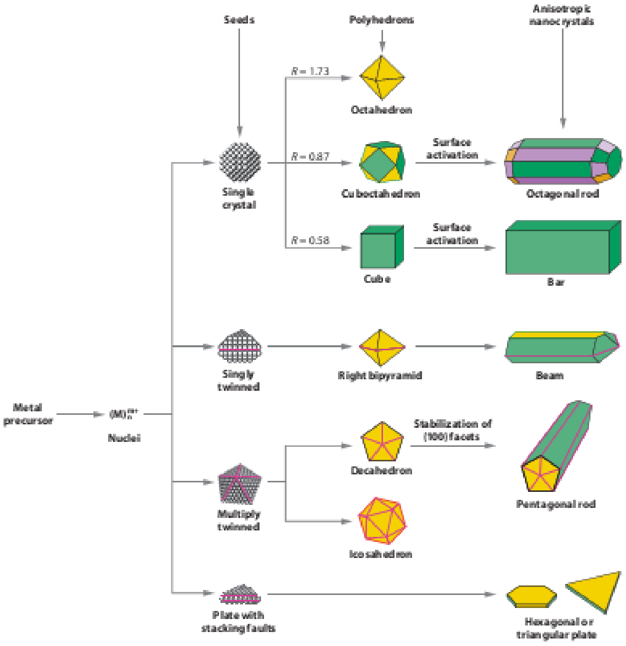


Figure 2.5 A schematic illustrating the reaction pathways that leads to noble-metal nanoparticles having different shapes. [41].

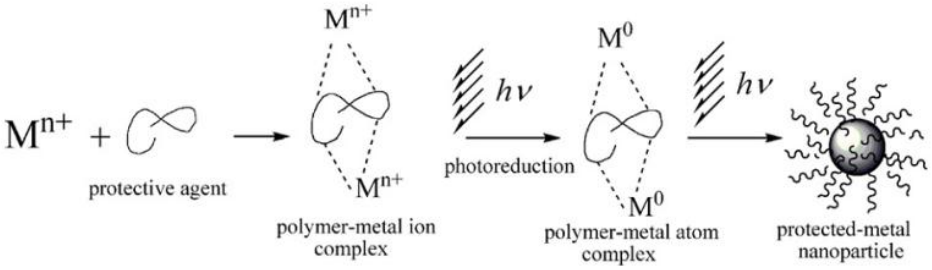


Figure 2.6 Schematic illustration of the reduction process of metal salts in the presence of a polymer or coordination compound [42].

Rod-liked gold colloidal was prepared by UV irradiation (253.7 nm light) in the presence of hexadecyltrimethylammonium chloride (HTAC) as a template. At the concentration of HTAC 30 wt % containing with 5-40 mmol dm^{-3} of $AuCl_4^-$ will be formed to rods while prolong the irradiation time. The results of reaction shown the length of rod liked gold particles were increased depending on irradiation time [43]. Synthesis of polygonal gold nanoparticles, the method does not use either surfactants or polymers. Gold nanoparticles with particle size of 25-200 nm was reduced by odium oxalate under illumination of a mercury lamp [44].

2.1.2.4 Sonochemical method

Chemical and physical effects of ultrasonic irradiation are known to prepare metal particles (Ag, Pd, Au, Pt and Rh) with nanometer size. There are three pathways of different reduction under sonication [45-47].

(i) Reduction by H atoms.

$H_2O \rightarrow \cdot OH + \cdot H$ (1)

(ii) Reduction by secondary reducing radicals.

$RH + \cdot OH(\cdot H) \rightarrow R\cdot + H_2O(H_2)$ (2)

(iii) Reduction by radicals from pyrolysis of the additives.

$RH \rightarrow$ reducing radicals $+ \cdot(CH)_3$ etc,. (3)

$\cdot(CH)_3$etc.$+RH \rightarrow (CH)_4$etc.+reducing radicals (4)

* RH: stabilizer such as a surfactant or polymer

However, the surfactant and reducer free of gold nanoparticles were synthesized using a high-frequency (950 kHz) ultrasound (in the absence of any stabilizing, capping and reducing agents). Addition of NaCl, HCl and increasing $AuCl_4^-$ concentration could be enhanced plates formation that caused by the specific adsorption on crystal facets e.g. (1 1 1) facets of Cl^- [48]. Ultrasound could be assisted fusion of gold nanoparticles (average diameter 25±7 nm) to dumbbell-liked, worm-liked, and ring-liked gold nanostructures [49]. The ultrasonic method created of extremely high pressures (∼108 Pa) and temperatures (∼5000 K). Ultrasonic cavitation is known to provide very rapid heating/cooling rates (e.g., greater than 2109Ks^{-1} and may be as large as 1013Ks^{-1}) leading to dramatic changes of material crystalline structures [50]. However, the physical effect of ultrasound is the most effective mean for cleaning technologies e.g. ultrafiltration membranes [51]. The effect of a cleaning process parameters within an ultrasonic bath results of cleaning process controlled hydrodynamic cavitation in the shear layer using ultrasonic [52].

2.1.2.5 Galvanic replacement reaction method

The galvanic replacement reaction was simple method for creating complex structures by consuming the more sacrifice metal component. Spontaneous redox reaction occurred if standard reduction potential of total reaction was positive. In the case of Ag metal and $AuCl_4^-$, the standard reduction potential of $AuCl_4^-$/Au pair (0.99 V vs standard hydrogen electrode, SHE) is higher than that of the Ag^+/Ag pair (0.80 V vs SHE), According to previous report when a silver metal was galvanized by gold (III) ion, the following reactions occurred [53, 54].

(i) Oxidation reaction.(anode site)

$$Ag(s) \rightarrow Ag^+ + e^- \qquad (5)$$

(ii) Reduction reaction (cathode site)

$$AuCl_4^-(aq) + 3e^- \rightarrow Au(s) + 4Cl^-(aq) \qquad (6)$$

(iii) Redox reaction

$$3Ag(s) + AuCl_4^-(aq) \rightarrow Au(s) + 3AgCl(s) + Cl^-(s) \qquad (7)$$

Different Ag nanostructures were transformed metal nanostructures with hollow interiors with different morphologies including cubic nanoboxes, cubic nanocages, nanorings, nano-boxes, single-walled nanotubes, and multiple-walled nanoshells or nanotubes [53-55]. The galvanic replacement reaction mechanism generated nanobox and nanocages as shown in Figure 2.7. However, the galvanic replacement reaction could be generated complex gold nanostructures as film on metal substrate. Ge and Si mostly use as metal substrate under HF and Au (III) ions solution. HF play importance role induce oxidation reaction of galvanic replacement, Au (III) ions were reduced to gold atom growing to complex gold nanostructures on metal substrate as shown in Table 1.

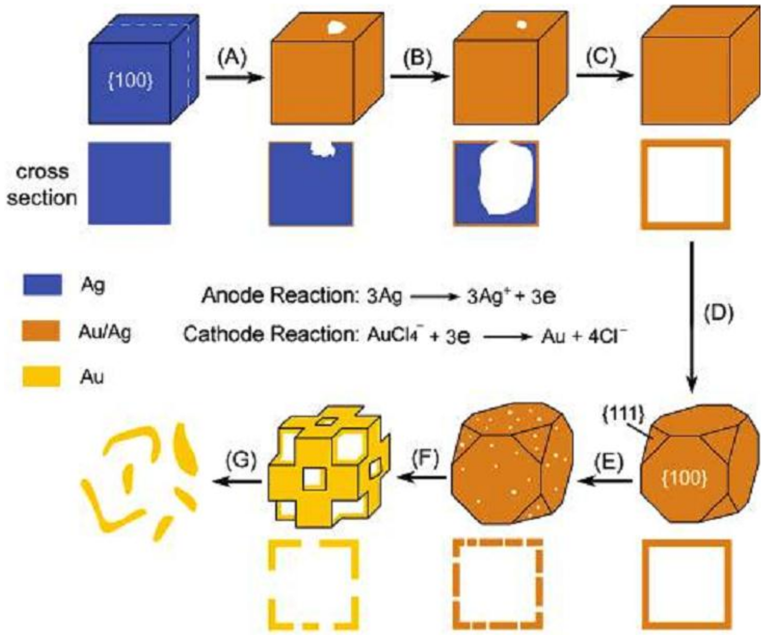
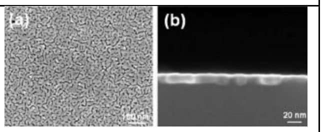
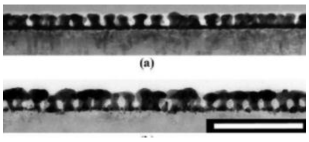
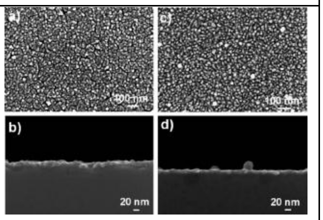
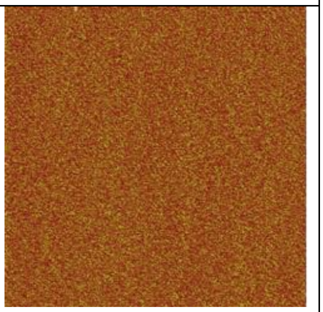
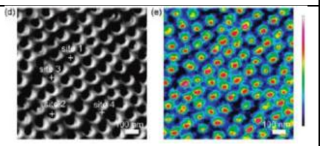


Figure 2.7 Schematic diagrams summarizing all steps of structural evolutions involved the galvanic replacement reaction of a silver nanocube and an aqueous $AuCl^-_4$ solution. (A) The galvanic replacement reaction start to dissolve at the site that with high surface energies as oxidation reaction. The electron from the reaction was migrated to surface then reduce $AuCl^-_4$ to Au atom. Incomplete layer of gold film epitaxial deposited on the face of a cube (B) continues galvanic replacement reaction between Ag and $AuCl^-_4$ formed a partially hollow nanostructure. (C) Formation of nanoboxes with a uniform and homogeneous wall. In the step A, B, and C the alloying occur underlying silver surface (D) initiation of dealloying and morphological reconstruction of the Au-Ag nanobox; (E, F) continuation of dealloying, together with the formation of pores in the wall; and (G) fragmentation of the porous Au nanobox. The cross-sectional views correspond to the plane along dashed lines [53].

Table 2.1 Summarized galvanic replacement reaction method for metal film creation

Author /Year	Chemical	Structures	Figure
S.Y. Sayed et.al [56] (2009)	Si, $KAuCl_4$ xH_2O, HF	Gold film on Si	
Y. Wang et.al [57] (2009)	Si, $NaAuCl_4$, HF,	mushroom-shaped gold nanopillars (50 nm)	
S. Y. Sayed et.al [58] (2010)	Ge (111), $KAuCl_4$ xH_2O, HF	Gold films on germanium	
A. Gutes et.al [59] (2011)	Si, HF, and $KAuCl_4$	Ultrasmooth Gold Thin Films	
X. Zhang et.al [60] (2011)	Si, HF, $HAuCl_4$	Pseudo hexagonal arrays	

2.2 Characterization techniques

2.2.2 Scanning electron microscope

Scanning electron microscope (SEM) was widely used for observation and characterization of the material on a nanometer to micrometer scale. The signal was generated from interaction of electron beam and simple include secondary electron and backscattered electron. Those signals were processed and displayed to imaging signal that obtained from specific emission volumes of simple. The image signals of the secondary and backscattered electron of great interest because these primarily show difference in the surface topography. Figure 2.8 show electron column component of SEM.

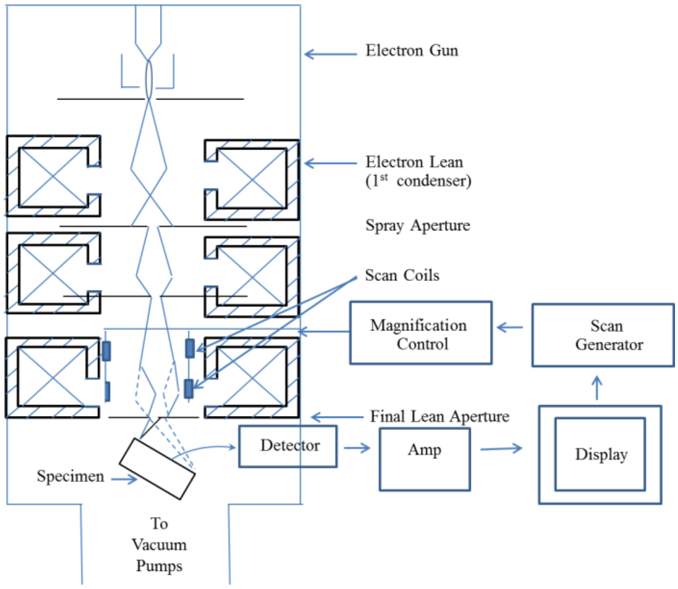


Figure 2.8 Schematic drawing SEM of the column showing electron gun, lenses the electron deflection, and electron detector.

2.2.3 Energy-dispersive X-ray spectrometer

Chemical analysis in the scanning electron microscope was performed by counting X-ray signal generated by electron beam interacting with matter. The principle of X-ray generations in the SEM specimen, the electron beam generated X-ray photon in the beam while interact with specimen surface. The EDS technique measures when X-rays as characteristic of the element was emitted from the sample during bombardment.

2.2.4 Raman spectroscopy

Raman spectroscopy is the characterization technique based on an inelastic scattering of a monochromatic excitation source. Raman is common vibrational spectroscopies similar with IR spectroscopy for assessing molecular motion and fingerprinting species. However, Raman spectroscopy was scattering technique that the scattering efficiency of detection depends on those molecules. In my work, Raman spectroscopy was used for observing the enhanced scattering efficiency of Au structures.

2.2.5 UV-visible spectroscopy

UV-visible spectroscopy is widely used for study of molecules and their electronic transitions of organic and inorganic material in solution phase. While light is traveling through the sample and transmitted light to detector, the characteristic of simple e.g., light absorption, is measured. The range UV-visible absorption directly affects the color of material. However, in case Ag and Au of metal nanomaterial show absorption and scattering in UV-visible range. In the UV-visible spectroscopy could be detected the optical property of metal nanomaterial by measuring absorbance spectrum which is the summation of absorption and scattering intensity of nanoparticles.