CHAPTER III

EXPERIMENTAL SECTION

3.1 Chemicals and materials

Sodium chloride (NaCl, ≥ 99.99%), nitric acid (HNO_3, 65%), ammonia (NH_3, 25%) and hydrochloric acid (HCl, 37% w/v) were purchased from Merck® (All chemicals were analytical grade and were used as received without an additional purification). De-ionized water was used as the solvent. Silver globules (≥ 99.99%) and gold globules (≥ 99.99%) with a diameter of 2-3 mm were purchased from a local precious metal retailer (UmniCore (Thailand)). A solution of gold (III) chloride (100,000 ppm/0.5 M Au^{3+}), $AuCl_4^-$, was prepared by dissolving 10 g of gold globules in aqua regia under a mild agitation and heating (80-100 °C). When all gold globules were completely dissolved after heating for at least 10 hours, the solution was further heated until almost dry. De-ionized water was added into the solution and adjusted volume to 100 mL. The gold (III) ion concentration was employed as a source of gold (III) ion for further investigation. {Caution: aqua regia, a mixture of HCl and HNO_3 with a volume ratio of 3:1, is very toxic chemicals and should be handled with care}. Prior to use, all glasswares were thoroughly cleaned with detergent, rinsed with de-ionized water, rinsed with aqua reqia, and thoroughly rinsed with copious amounts of de-ionized water. Silver globules were ultrasonic cleaned before galvanic replacement.

3.2 Synthesis of coral-liked gold nanostructures

The corals-liked gold nanostructures on the surface of silver globules were prepared by galvanic replacement of silver metal (Ag^0) by gold (III) ion (Au^{3+}). Briefly, a few silver globules were immersed into a gold (III) ion solution under a continuous stirring. The 5,000 ppm (0.025 M) Au^{3+} solution was prepared by diluting 0.5 mL gold stock solution with 10 mL de-ionized water, After a 30 min immersion, the silver globules were removed from the solution and were cleaned with a copious amount of de-ionized water. The cleaned silver globule was further analyzed. The effect of gold (III) ion concentration on the corals-liked gold nanostructures was

examined by performing the galvanic replacement reaction in 50, 100, 500, 1,000, 5,000 ppm gold (III) ion solutions (10 mL). The effect of pH gold solution was investigated by adjustable pH of gold (III) ion, pH 0 (without NaOH), pH 7, and 14, with NaOH (1 M) solution. The gold nanostructures development on the silver surface globules were examined after a 30min immersion. The time-dependent structural evolution of the corals-liked gold nanostructures was performed on a 5,000 ppm gold (III) ion solution (10 mL). The gold nanostructures developments on the silver surface were examined after 1, 5, 10, 20, 30, and 60 min immersion.

3.3 Synthesis of needle-liked gold nanostructures

The needle-liked gold nanostructures on the silver surface were prepared by galvanic replacement reaction between silver metal (Ag^0) and gold (III) ion under high concentration of chloride ion (Cl^-), in a typical experiment, silver globules were immersed into Au^{3+} (10 mL, 5,000 ppm) with 2 M NaCl. After 30 min immersion with a continuous stirring, the silver globules were removed and thoroughly cleaned under a flow of de-ionized water. The cleaned silver globule was further analyzed. The influences of the concentration of Cl^- on the NLGNs formation were examined by performing the reaction in a 5,000 ppm Au^{3+} solution with 0.1, 0.3, 0.5, 1.0, 2.0, and 3.0 M NaCl. The silver globules were immersed in the Au^{3+} solution with extra Cl^- for 30 min. The time dependent structural evolution of the NLGNs was performed on a system after 5, 10, 20, 30, and 60 min immersion time.

3.4 Ultrasonic assisted fabrication of coral-liked gold nanoporous

Free standing nanoporous gold was fabricated by galvanic replacement of a silver plate with Au^{3+} under an ultrasonic radiation. The ultrasonic radiation source was performed with ultrasonic cleaning bath. The 5,000 ppm of Au^{3+} (10 mL) solution was under an ultrasonic radiation, then silver plate with 0.5×0.5 mm diameter and 500 μm thicknesses were dropped into the solution. Silver plate was consumed and generated Au/AgCl composites within 10 min reaction time. Au/AgCl composites were removed from the solution and cleaned with a copious amount of de-ionized

water. The standing CLGPs were generated by dissolution of AgCl from gold structures using ammonia treatment method.

3.5 Dissolution of AgCl by ammonia treatment

The white AgCl salt, concomitantly developed along with the galvanized Au/AgCl composites, could be removed from the gold covered silver plate by immersion into ammonia solution (NH_3, 10 mL, 10 % w/v) for 15 min. The residual ammonia was removed by rinsing with copious amount of water.

3.6 Characterizations

3.6.1 Scanning electron microscopy (SEM)

A galvanized silver globule was attached to a stainless steel stub through a carbon tape. Scanning electron microscopy micrographs were recorded with a JELO 6500A (analytical electron microscope) operated at 10-30 kV under high vacuum mode using a secondary electron imaging (SEI) and back scattering electron image (BSI). Elemental analysis was carried out using energy dispersive spectrometer (EDS) attached to the SEM.

3.6.2 X-ray diffraction (XRD)

Cleansed coral-liked and needle-liked gold film were performed using a Rigaku D/MAX-2200 instrument (Cu Kα1 radiation) operated at 50 kV and 250 mA over range of 30 -90 by step scanning with a step size of 0.02.

3.6.3 Surface enhanced Raman scattering (SERS) measurement

The standing CLGPs were employed as SERS substrates while crystal violet (CV) and rhodamine 6G (R6G) used as a probe molecules. The silver globules after ammonia treatment was immersion into the solution with 0.01, 0.001, 0.0001 mM of probe molecule for 15 min. They were then immediately cleaned with copious amount of de-ionized water. The SERS acquisitions were performed on a room-temperature dried silver globules. A Raman microscope (DXR Raman, Thermo Scientific) was employed to record the SERS spectra. He-Ne laser at 532 nm was used as the excitation laser. A 10X long objective lens with a numerical aperture of

0.75 focused the excitation beam onto diameter of approximately 1 μm. The scattered light was collected using the same objective lens.

3.6.4 UV-visible spectroscope (UV-vis)

5,000 ppm of $AuCl_4^-$ solution diluted to 10 ppm with de-ionized water was used as a UV-visible simple. The quartz cuvette was cleaned by de-ionized water before collecting the spectrum. The sample was collected using a reference as pure distilled de-ionized water. USB 2000 spectrophotometer was a detector and light source using as Deuterium lamp (Bandwidth 200-850 nm).