MICROWAVE-ASSISTED SYNTHESIS OF GOLD-SILVER BIMETALLIC NANOPARTICLES

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Introduction

Nanoparticles (NPs) of noble metals (silver, gold, platinum, etc.) have received considerable attention in recent years due to their unique physicochemical, optoelectronic properties and application in various fields such as public health and medicine, environmental protection, biotechnology, material sciences, etc. [1].

Bimetallic nanoparticles, composed of two different metals, has higher catalytic, electronic, optical, and other properties than the corresponding monometallic particles [2].

Bimetallic gold-silver nanoparticles (Au-Ag NPs) extend the surface plasmon resonance range (defined by UV-Vis absorption band) compared with single metal nanoparticles. Such an effect allows to probe molecules in wider Raman excitation range. [2]. Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) is a non-destructive and sensitive method which can be applied to detect low concentrations of different analytes. For this application in order to improve stability and biocompatibility of the nanoparticles various coatings (SiO_2, MnO_2,TiO_2, etc.) are widely used [3].

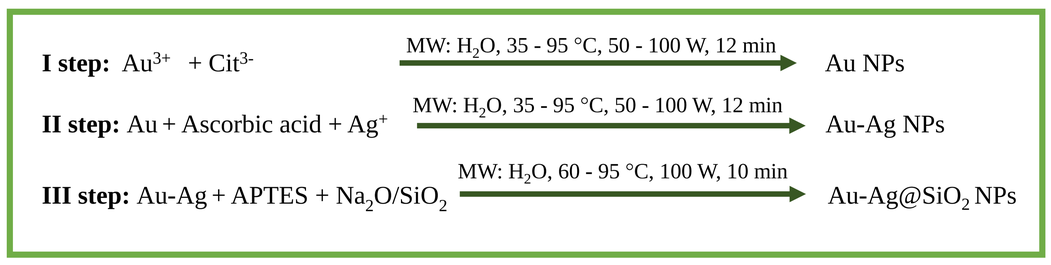
Synthesis of nanoparticles

Chemical reduction is one of the most commonly used methods for the synthesis of bimetallic nanoparticles. It allows flexibly modify composition, size, and shape of particles [2].

Compared with other synthesis conditions, microwave-assisted synthesis is becoming increasingly popular. It helps to reduce reaction time, energy consumption, and size distribution of the nanoparticles [4].

Typically, to get Au-Ag NPs with uniform size and shape different reducing (citrates, ascorbic acid, $NaBH_4$, etc.) and stabilizing (ammonium salts, polymers, etc.) agents are used. In this work, we successfully combined microwave synthesis and chemical reduction to synthesize Au-Ag NPs using eco-friendly reductors (sodium citrate, ascorbic acid) without taking any stabilizers except (3-aminopropyl)triethoxysilane (APTES).

Synthesis procedure of three steps (Scheme 1) was performed under microwave irradiation (MW). In first step Au NPs were prepared using chloroauric acid and sodium citrate. In second step ascorbic acid and silver nitrate were added. In last step silica shell was formed using APTES and sodium silicate. This more convenient, efficient, fast method allows to prepare 30±5 nm gold-silver-silica shell (Au-Ag@SiO_2) nanoparticles with 1-4 nm of SiO_2 (Fig. 1). The UV-Vis absorption spectra were recorded after each step (Fig. 2). To demonstrate the bimetallic nature of the nanoparticles HR-TEM elemental analysis was used (Fig. 3).



Scheme 1. Synthesis of Au-Ag@SiO_2 nanoparticles.

Purified by centrifugation Au-Ag@SiO_2 nanoparticles began to degrade after 2 weeks storage them in the refrigerator (5-7 ºC). The initiated process of particle adhesion was assessed visually – a gray precipitate appeared in the yellow-green suspension of the particles. A shift towards longer waves was also observed in the UV-VIS spectrum (Fig. 4).

Application for SHINERS

In order to apply the obtained nanoparticles, a self-assembled monolayer of 4-mercaptobenzoic acid (4-MBA) was formed onto a gold plate and Au-Ag@SiO_2 nanoparticles were spread on it to amplify the Raman signals. The clear enhanced SHINERS spectrum of 4-MBA on a smooth gold plate was obtained (Fig. 5; Table 1).

Table 1. Assigned Raman peaks for different molecular groups of 4-MBA onto a smooth Au surface [5].

Wavenumber/cm^{-1}	Band assignment
1787	C=O symmetric stretching
1587	C-C stretching
1481	Ring bending
1384	COO^- symmetric stretching
1185	C-H bending
1141	C-H bending
1077	CH in-plane bending
1012	Ring breathing
845	COO^- bending
525	Ring out-of-plane bending
232	Au-S

References

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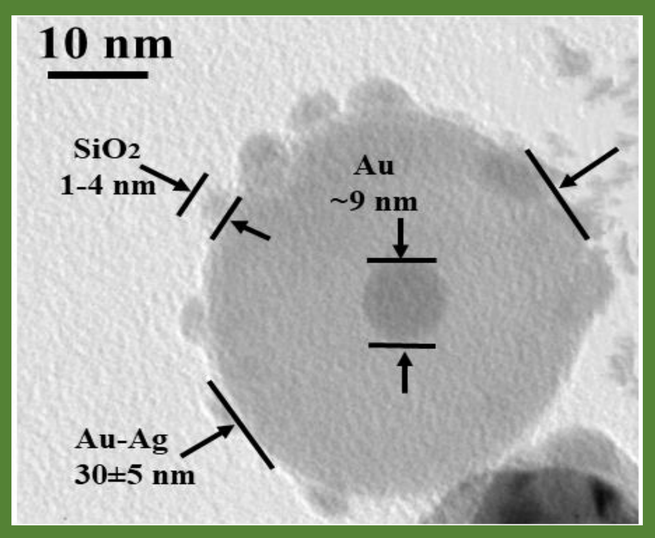

Fig. 1. HR-TEM images of 30±5 nm Au-Ag@SiO_2 nanoparticles with 1-4 nm of silica shell.

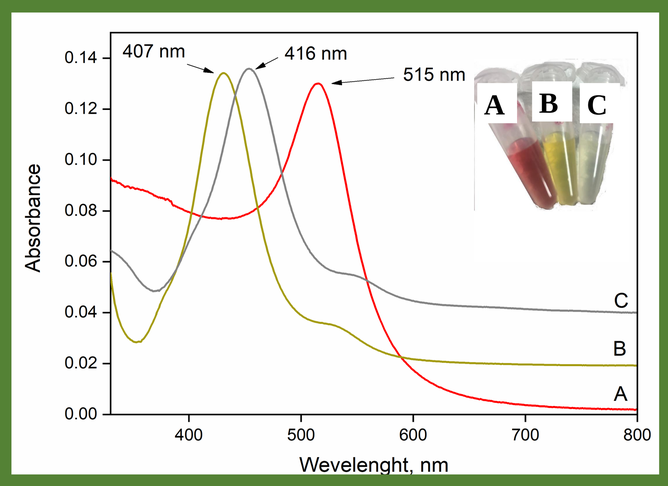

Fig. 2. UV/Vis spectra of Au (A), Au-Ag (B), Au-Ag@SiO_2 (C) nanoparticles.

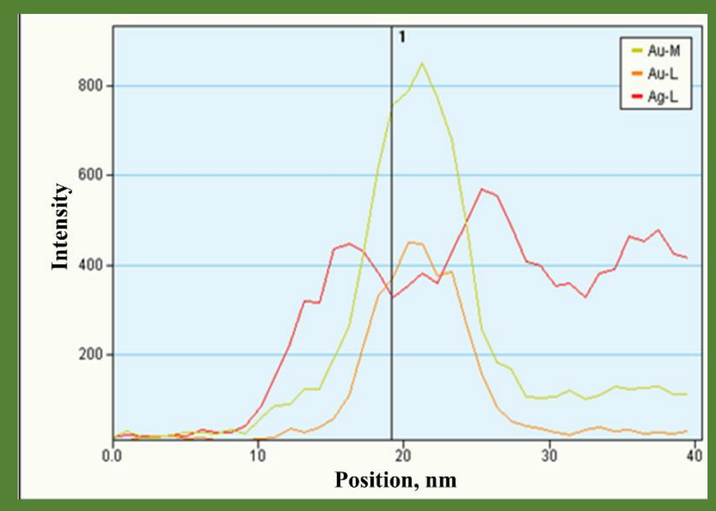

Fig. 3. HR-TEM elemental analysis of Au-Ag@SiO2 nanoparticles (M , L - metal electronic layers).

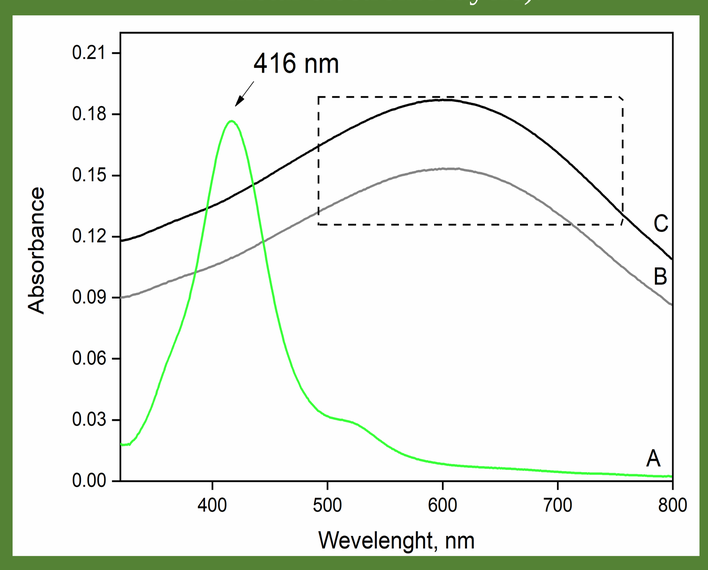

Fig. 4. Au-Ag@SiO2 UV-VIS absorption spectra (A - 0 days from the beginning of the synthesis; B - 14 days from the beginning of the synthesis; C - 28 days from the beginning of the synthesis).

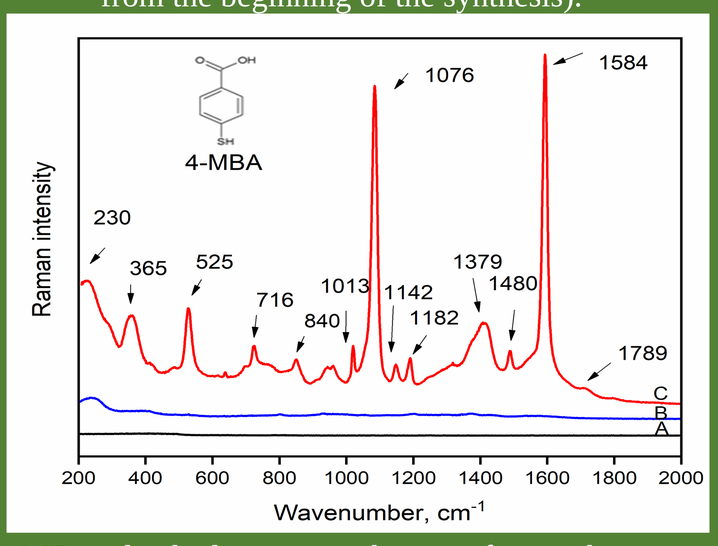

Fig. 5. Raman spectrum of 4-MBA adsorbed on a smooth Au surface without nanoparticles (A), Raman spectrum of Au-Ag@SiO_2 nanoparticles (B) and SHINERS spectrum of 4-MBA with Au-Ag@SiO_2 nanoparticles (C).