Synthesis and comparison of gold nanoparticles coated with silicon, manganese and titanium dioxides

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The synthesized gold nanoparticles (50–60 nm) were coated with thin (1.5–8 nm) layers of silicon, manganese and titanium dioxides. The obtained three species of nanospheres were applied for the analysis of self-assembled monolayer of thiophenol by shell-isolated nanoparticle-enhanced Raman spectroscopy method. Detailed synthesis and comparison of the particle properties are provided in this report.

Keywords: gold core–shell nanoparticles, shell-isolated nanoparticle-enhanced Raman spectroscopy, thiophenol

INTRODUCTION

Metal and oxide-based nanoparticles are widely used in electronics, medicine, food, and environment protection [1–3]. Gold and silver nanoparticles covered by a thin layer of dielectric are the most popular for plasmonic sensing by shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) analysis method [4, 5].

Gold nanoparticles (Au NPs) are relatively easy to prepare. The reduction by citrates is the most used chemical method [6, 7]. The modification by inert silica shell has been proposed to expand the application of nanoparticles [8] because such coating prevents the gold core from interactions with the analysed object and environment. Consequently, stable gold core–silica shell nanoparticles became the most popular for SHINERS experiments [9]. Various metal and nonmetal coatings (graphene, polymers, SiO_2, MnO_2, TiO_2, Al_2O_3, ZnO, SnO_2, ZrO_2, etc.) have been tested for successful analysis of different bioconjugates (proteins,

DNA, bacteria, etc.) [4]. Due to their catalytic activity, chemical stability, nontoxicity, and low-cost gold combinations with semiconductor oxides they are also used for catalytic applications [10], solar energy utilization [11], radiotherapy in the treatment of tumors [12], etc.

In this research, gold nanoparticles were covered by silicon, manganese and titanium dioxides. All synthesized core-shell nanoparticles were successfully employed for SHINERS measurements with thiophenol as a model compound. In this way, it was shown that three types of nanoparticles – gold core–silicon dioxide shell ($Au@SiO_2$), gold core–manganese dioxide shell ($Au@MnO_2$) and gold core–titanium dioxide shell ($Au@TiO_2$) – could complement each other in SHINERS experiments.

EXPERIMENTAL

Materials

Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, 99%), trisodium citrate dihydrate ($HOC(COONa)(CH_2COONa)_2 \cdot 2H_2O$, 99%), (3-aminopropyl)trimethoxysilane ($H_2N(CH_2)_3Si(OCH_3)_3$, APTMS, 97%),

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sodium silicate solution in water (NaOH, 10%; SiO_2, 27%), potassium permanganate ($KMnO_4$, 99%), potassium hydroxide (KOH, 85%), potassium oxalate ($K_2C_2O_4 \cdot H_2O$, 99%), titanium (IV) (triethanolaminato)isopropoxide solution in isopropanol (TTEAIP, 80%), ammonia solution in water (NH_4OH, 25%), isopropanol (99%), ethanol (99%) and thiophenol (98%) were purchased from Merck and used without additional treatment. Purified in the Millipore system Mili-Q water (18.2 MΩ·cm) was used in all experiments. The Tienta SpectRIM steel substrate from Merck was employed for Raman experiments.

General equipment

A Lambda 25 spectrophotometer was used for recording UV/Vis spectra (300–1100 nm) of the synthesized nanoparticles.

High-resolution transmission electron microscopy (HR-TEM) analyses of the nanoparticles were carried out using a FEI Tecnai G2 F20 X-TWIN microscope; specimens for the measurements were prepared by a FEI Helios Nanolab 650 dual beam microscope.

SHINERS spectra were taken using a Perkin-Elmer RamanFlex 400 Echelle type spectrometer with a 785 nm beam diode laser and a thermoelectrically cooled (–50°C) CCD detector. The spectra were recorded by the accumulation of 10 scans with an integration time of 10 s; the laser power was 50 mW.

Synthesis of Au NPs

To boiling 100 mL of 0.01% $HAuCl_4$ solution, 0.7 mL of 0.9% sodium citrate was added. The reaction mixture was refluxed for 30 min and self-cooled to room temperature within 1 h.

Synthesis of Au@SiO₂ nanoparticles

To 30 mL of Au NPs solution, 0.4 mL of 1 mM APTMS was added and stirred at 20°C for 15 min. Then 3.2 mL of 0.54% sodium silicate solution was added and stirred for another 3 min. After stirring at 90°C for 45 min, it was cooled in an ice bath for 30 min. The Au@SiO₂ nanoparticles were centrifuged at 3000 rpm for 20 min and washed twice with water.

Synthesis of Au@MnO₂ nanoparticles

All reagents were cooled to 10°C before use. 30 mL of Au NPs solution was alkalized to pH = 9.8 by the addition of 0.2 mL 0.1 M KOH with stirring. Then, to the cooled mixture 0.3 mL of 10 mM $KMnO_4$ and 1.5 mL of 10 mM $K_2C_2O_4$ were added. Next, it was kept at 20°C for 5 min and at 60°C for 1 h without stirring. The reaction mixture was cooled at room temperature for 15 min and in an ice bath for 15 min. The Au@MnO₂ nanoparticles were centrifuged at 3000 rpm for 20 min and washed twice with water.

Synthesis of Au@TiO₂ nanoparticles

18 mL of Au NPs were centrifuged at 3000 rpm for 20 min. Concentrated Au NPs were diluted in 1 mL of water and 3 mL of isopropanol was added. Next, 100 µl of 1.1 mM APTMS was added and stirred at 20°C for 10 min; 100 µl of 2.5 mM TTEAIP was added and stirred at 20°C for 30 min; 20 µl of 25% NH_4OH was added (mixture pH = 11.2) and stirred at 20°C for 1 h. The Au@TiO₂ nanoparticles were centrifuged at 3000 rpm for 20 min and washed one time with isopropanol and one time with water.

Raman and SHINERS measurements

Synthesized Au@SiO₂, Au@MnO₂ and Au@TiO₂ nanoparticles were dropped onto the Tienta steel substrate and dried at room temperature. Then the Raman spectra of the nanoparticles were recorded. Next, an evaporated gold layer on a cleaned glass substrate was incubated in 10^{-3} M thiophenol solution in ethanol for 1 h, washed with ethanol and dried. Then, 3 µL of synthesized nanoparticles were spread on the plate with the formed self-assembled monolayer, dried at room temperature, and the SHINERS spectra of thiophenol were obtained.

RESULTS AND DISCUSSION

Gold core–silica shell [13, 14], gold core–manganese shell [15, 16] and gold core–titanium shell [17, 18] nanoparticles were synthesized earlier. However, the search for new more effective, low-cost and environment-friendly methods continues. Anyway, the synthesis of nanoparticles must ensure the main properties of core–shell structures, which determine their further application. In our case, the core should be 50–100 nm in diameter, which is suitable for SHINERS measurements. Also, a chemically and electrically inert shell should be compact and thin enough (about 2–10 nm) avoiding decreasing signal intensity [13]. The pin holes were experimentally obtained in shells with the thickness under

2 nm of SiO_2 [13], 1.2 nm of MnO_2 [15] and 3 nm of TiO_2 [18]. Besides, each coating has its specific properties. The silica shell can dissolve in strong alkaline media, but manganese dioxide is stable under such conditions [15]; titanium dioxide is thermally stable and has a high laser damage threshold [19]. Based on these observations, it was set to create three different types of 50–60 nm gold nanoparticles with 3–5 nm SiO_2, MnO_2 and TiO_2 coatings suitable for SHINERS. The HR-TEM method was used to identify the thickness of the shell, the form and size of the nanoparticles. Other properties of the synthesized nanoparticles were observed visually during synthesis, and employing spectroscopic UV/Vis and Raman techniques (Table).

First, gold nanoparticles were synthesized by Tian's protocol, and the silica shell was coated over the core by the modified procedure [13, 20]. The standard reagents – gold (III) chloride and sodium citrate, were used for the synthesis of Au NPs. In the boiling $HAuCl_4$ solution the citrate ions reduce $AuCl_4^-$ to Au^+. Then an electrostatically stable complex of citrate and Au^+ ions forms microdomains and the self-catalyzed disproportionation of Au^+ to Au^0 occurs. Citrate oxidizes to byproducts, which stabilize initial nuclei in agglomerates; finally, they grow into gold nanospheres (Fig. 1). Next, the silica shell is formed over the Au NPs, using APTMS coupling agent and sodium silicate [21]. The 50 ± 5 nm $Au@SiO_2$ nanospheres with 2–3.5 nm of SiO_2 were synthesized in this way (Fig. 2a).

The exchange in colour (from yellow to wine red) during the synthesis and the data from the UV/Vis spectrum suggest the formation of Au NPs. The UV/Vis absorption peak of Au NPs is 538 nm, and 539 nm that of silica covered gold nanoparticles. After one month keeping at 8–10°C, we notice the exchange in colour (from wine red to grey) and a red-shifted broadened peak (about 750 nm) in the UV/Vis spectrum of aggregated gold core–shell nanoparticles (Fig. 3).

Lin's reported synthesis was modified for the $Au@MnO_2$ nanoparticles [15]. In neutral, weak acid and weak alkaline media permanganate ions are reduced by oxalates to form manganese dioxide. The high concentration of hydrogen ions leads to the loss of the shell [15]. Seeing that, pH plays an important role in the formation of MnO_2 defects, some conditions of media (pH = 9–14) were tested. The pH = 9.8 was observed as perfectly suitable for the synthesis of 55 ± 5 nm $Au@MnO_2$ with 2–4.5 nm MnO_2 shell (Fig. 2b, Fig. 3). Consequently, the conditions were successfully optimized and the reaction time decreased twice. The $Au@MnO_2$ nanospheres were stable up to 3 weeks keeping cold (8–10°C). Then the purple colour exchanges to grey and a broadened peak above 750 nm occurs in the UV/Vis spectrum.

The $Au@TiO_2$ nanoparticles were prepared using TTEAIP and APTMS. Optimization of the ratio of the reagents allowed a significant shortening of the Hartman's protocol (from 12 to 1 h) [18]. Also,
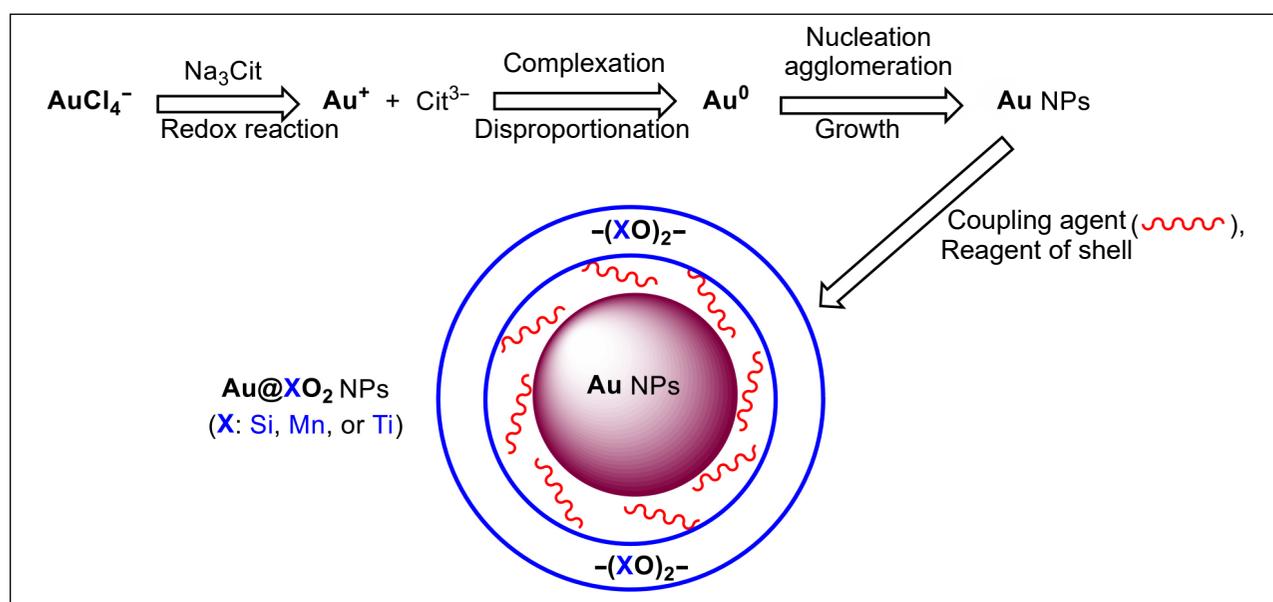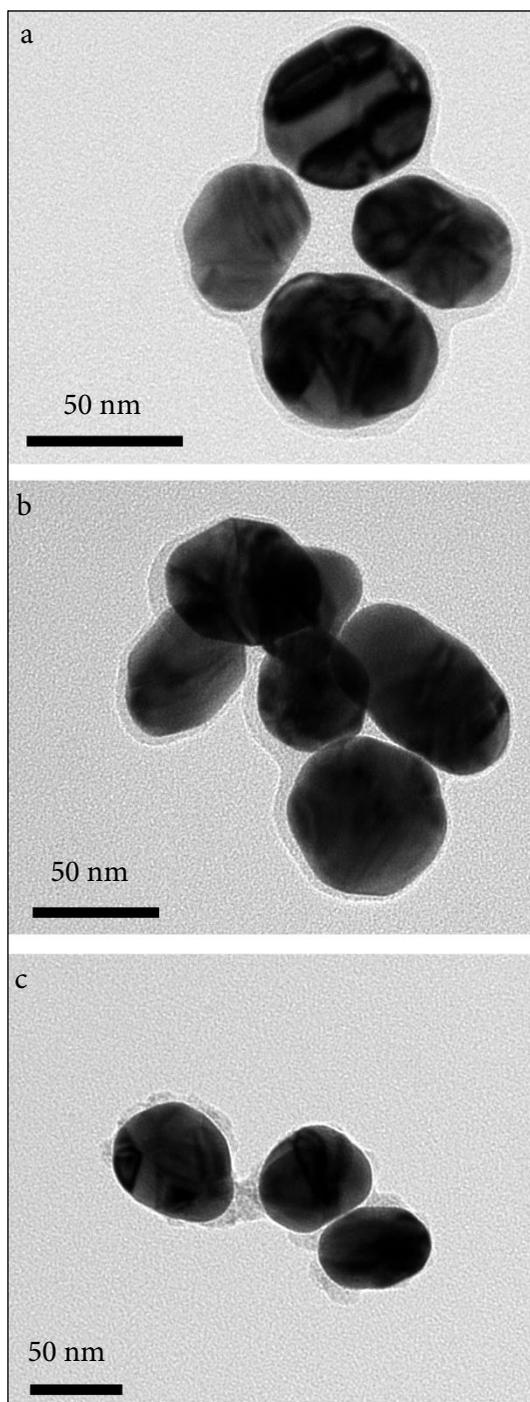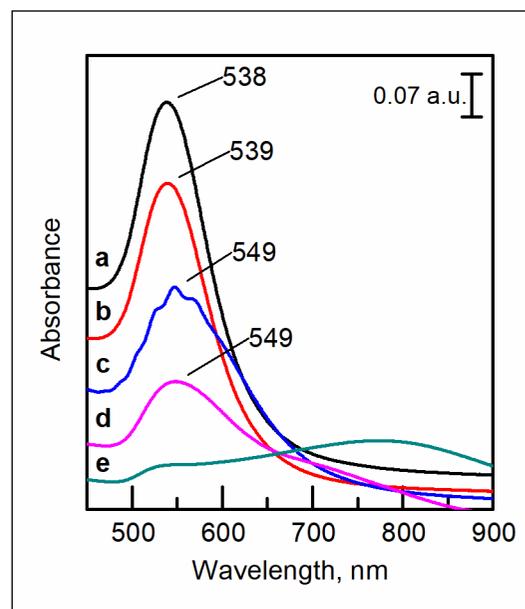

Fig. 1. The formation process of gold core–shell nanoparticles (coloured online)

Fig. 2. HR-TEM images of 50 ± 5 nm Au@SiO$_2$ nanospheres with 2–3.5 nm of SiO$_2$ (a), 55 ± 5 nm Au@MnO$_2$ nanospheres with 2–4.5 nm MnO$_2$ (b) and 55 ± 5 nm Au@TiO$_2$ nanospheres with 1.5–8 nm TiO$_2$ (c)

Fig. 3. UV/Vis spectra of Au NPs (a), Au@SiO$_2$ (b), Au@MnO$_2$ (c), Au@TiO$_2$ (d), and aggregated gold core–shell nanoparticles (e) (coloured online)

the centrifugation was clarified. Our modified procedure allows obtaining 55 ± 5 nm Au@TiO$_2$ with 1.5–8 nm TiO$_2$ shell (Fig. 2c, Fig. 3). Unfortunately, the conditions for the formation of an even TiO$_2$ shell were not optimized. Probably of this, the Au@TiO$_2$ nanospheres were stable only for 1–2 weeks. It was not possible to observe the colour change visually because the particles were dark grey from the beginning. However, the aggregation of the nanoparticles was confirmed by a red-shifted broadened peak (>750 nm) in the UV/Vis spectrum.

For SHINERS experiments a self-assembled monolayer of thiophenol onto smooth gold was formed. Three species of the synthesized nanoparticles amplify Raman signals of thiophenol. All assignments of spectra were based on reported earlier data [21]. The vibrational mode at 419 cm^{-1} is related to C–S out-of-plane bending vibrations. Other vibrational modes can be attributed with benzene ring: 693 cm^{-1}, 999 cm^{-1} suitable with ring out-of-plane deformation, and C–H out-of-plane bending. The band at 1073 cm^{-1} is assigned to the ring in-plane deformation and C–C symmetric stretching. The most intensive and strong feature near 1574 cm^{-1} is associated with C–C symmetric stretching vibrations. No matter which nanoparticles (Au@SiO$_2$, Au@MnO$_2$ or Au@TiO$_2$) were used to amplify Raman signals, the most important modes and their relative intensities of thiophenol coincide (Fig. 4). However, the most intensive and clear features of thiophenol were obtained with Au@SiO$_2$ nanoparticles.

For comparison, the spectra of each type of the nanoparticles were recorded onto the Tienta steel substrate. This allowed obtaining vibrational regions of the nanoparticles in the SHINERS
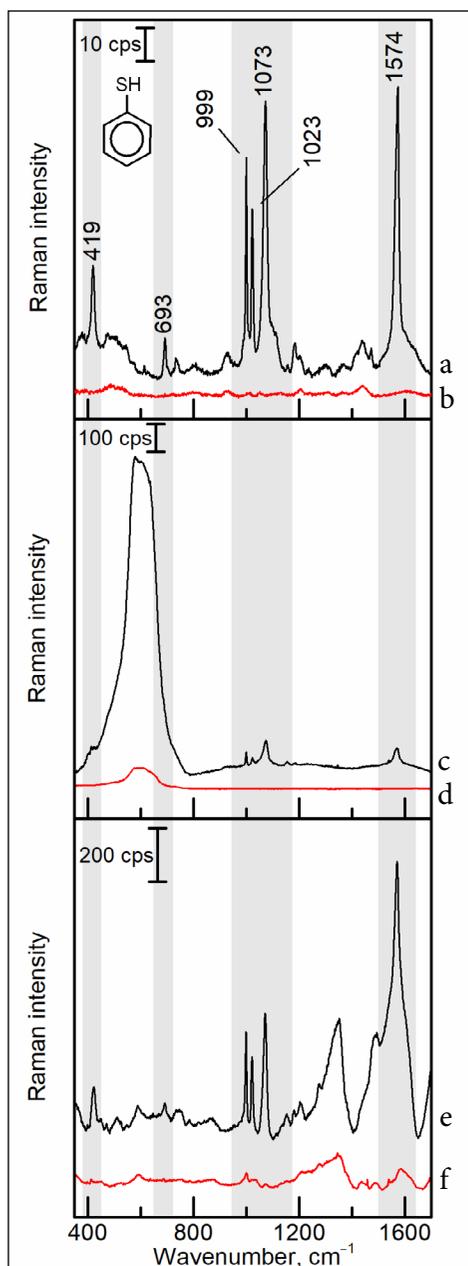
Fig. 4. SHINERS spectra of thiophenol with Au@SiO$_2$ (a), Au@MnO$_2$ (c) and Au@TiO$_2$ (e) – black lines. Raman spectra of Au@SiO$_2$ (b), Au@MnO$_2$ (d) and Au@TiO$_2$ (f) – red (online) lines. The SHINERS spectra are background corrected

spectra (Table). It is noticeable that Au@MnO$_2$ and Au@TiO$_2$ NPs have specific spectra that overlap with the thiophenol spectrum in 400–700 cm^{-1} and 1200–1600 cm^{-1} regions, respectively. Au@SiO$_2$ NPs also have a specific spectrum, but the intensity of vibrational bands is extremely low compared to the SHINERS spectra of thiophenol; this can affect data minimally (Fig. 4).

The different properties of nanoparticles allow choosing each type of them for specific experimental conditions. However, there is no doubt that three synthesized types of nanoparticles (Au@SiO$_2$, Au@MnO$_2$ or Au@TiO$_2$) could perform a comprehensive research of complex structures, complementing each other in SHINERS experiments.

CONCLUSIONS

Three species of gold core–shell nanoparticles (Au@SiO$_2$, Au@MnO$_2$, Au@TiO$_2$) were successfully synthesized and used for the analysis of self-assembled monolayer of thiophenol by the SHINERS method. The produced gold core–silica shell nanoparticles were the smallest compared to the others. However, the SiO$_2$ coating was the most even and the thinnest. For this reason, the most stable Au@SiO$_2$ nanospheres mainly amplify thiophenol signals in the SHINERS spectrum.

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Table. Experimental data on the obtained properties of the synthesized nanoparticles

Obtained property	Au@SiO$_2$	Au@MnO$_2$	Au@TiO$_2$
Form	Nanospheres	Nanospheres	Nanospheres
Diameter	50 ± 5 nm	55 ± 5 nm	55 ± 5 nm
Formation of shell	45 min	1 h	1 h
Thickness of shell	2–3.5	2–4.5	1.5–8
UV/Vis absorption peak	539	549	549
Vibrational region of nanoparticles in SHINERS spectra	Low intensity	400–700 cm^{-1}	1200–1600 cm^{-1}
Stability keeping at 8–10°C	1 month	3 weeks	2 weeks

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DENGTŲ SILICIO, MANGANO IR TITANO DIOKSIDAIS AUKSO NANODALELIŲ SINTEZĖ IR PALYGINIMAS

S a n t r a u k a

Susintetintos aukso nanodalelės (50–60 nm) sėkmingai padengtos plonais (1,5–8 nm) silicio dioksido, mangano dioksido ir titano dioksido sluoksniais. Gautos trijų rūšių (Au@SiO$_2$, Au@MnO$_2$, Au@TiO$_2$) nanosferos pritaikytos tiofenolio monosluoksnio analizei panaudojant nanodalelių, padengtų apsauginiu sluoksniu, sustiprintos Ramano spektroskopijos metodą (angl. shell-isolated nanoparticle-enhanced Raman spectroscopy). Straipsnyje išsamiai aprašytos sintezių metodikos ir pateiktas dalelių palyginimas.