Synthesis of silver nanoparticles with polyols under reflux and microwave irradiation conditions

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Four polyols were used as stabilisers to synthesise silver nanospheres under reflux and microwave irradiation conditions. The nanoparticles were covered with a protective up to 10 nm silicon dioxide shell. The shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) technique was used to analyse the self-assembled monolayer of 4-mercaptobenzoic acid (4-MBA) by applying the produced silver core-silica shell nanoparticles. The article provides a detailed description of the synthesis, analysis and application of the nanoparticles based on UV/Vis, HR-TEM and SHINERS data.

Keywords: silver nanoparticles, polyols, ethylene glycol, 4-mercaptobenzoic acid, shell-isolated nanoparticle-enhanced Raman spectroscopy

INTRODUCTION

Metal nanoparticles have drawn a great deal of attention during the last few decades. The rapid development of nanotechnologies has expanded their application in microelectronics, industry, environmental protection, medicine, material and analytical sciences [1–3]. Due to their size and physicochemical properties silver nanoparticles are also used as highly effective antipathogenic agents in medical and household products [4–6].

Silver's plasmonic properties make it suitable for surface-enhanced Raman spectroscopy (SERS) based detection of different analytes. The majority of Raman observations take place in the 400–1000 nm wavelength range, and silver exhibits localised surface plasmon resonances that fall within this range [7, 8]. Silver nanoparticles scattered on the analysed surface act like small amplifiers and allow the recording of highly informative spectra of a low analyte concentration. However, the antimicrobial activity of silver nanoparticles often causes the degradation of bioanalytes and further biocompatibility problems [9]. Shell-isolated nanoparticles help to resolve the problems because an inert shell (SiO_2, MnO_2, TiO_2, SnO_2, etc.) protects from interaction with the environment and analyte increasing the stability and the reliability of the experiments. Consequently, the SERS technique that employs the nanoparticles called shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) is widely used for the detection and analysis of

different ions, molecules and more complex systems [10–12].

The nanoparticles are synthesised by physical, chemical or biological methods using top-down (laser ablation, lithography, mechanical process, etc.) and bottom-up (pyrolysis, spinning, sol-gel process, etc.) approaches [13, 14]. The used synthesis strategy and materials have an impact on the composition, morphology, and size distribution of particles. It was experimentally determined that larger and angled nanostructures allow obtaining greater Raman signal amplification [15, 16]. The three major groups of chemical reduction methods are reported for size- and shape-controlled synthesis of silver nanoparticles: citrate-based synthesis, borohydride-based synthesis and polyol-based synthesis. Additional surface stabilisers or capping agents such as oleylamine, polyethylene glycol, cetrimonium bromide (CTAB) and polyvinylpyrrolidone (PVP) are often used in such synthesis [17, 18]. The choice of precursor, solvent, reducer and stabiliser determines not only the nature of the particles but also their further suitability for SHINERS research. The residues of unreacted materials often complicate further spectral analysis. Therefore, synthesis methods are modified to find the most optimal conditions to produce larger nanoparticles with minimal reagents. Microwave (MW) irradiation is welcome for this purpose in comparison to the reflux approach; it is an appealing and quick method with a uniform size distribution of the resulting nanoproducts, high yields and good stability [19, 20]. In addition, this rapid method is convenient for optimising the synthesis conditions.

In this research, silver nanoparticles were synthesised by chemical citrate-based reduction using aqueous solutions of simple reagents. A minimal amount of polyols was adapted for the surface stabilisation of nanoparticles. The MW method was used for re-synthesis optimising new conditions, and the reflux method was used to compare results. Successfully modified polyol synthesis helped to prevent the contamination of nanoparticles. To achieve the best surface enhancement and minimise the interaction of the analyte with the plasmonic cores, such particles must be bigger than 50 nm in diameter and coated with a thin 2–10 nm dielectric shell [21, 22]. Therefore, produced silver nanoparticles were covered

with a thin (up to 10 nm) silica shell increasing the adaptability for SHINERS experiments. Next, the silver core-silica shell nanoparticles were employed for 4-mercaptobenzoic acid (4-MBA) self-assembled monolayer analysis by the SHINERS method.

EXPERIMENTAL

Materials
The synthesis of silver nanoparticles and other experiments were carried out with Milli-Q water (18.2 MΩ·cm) and reagents from Sigma-Aldrich/Merck: silver nitrate ($AgNO_3$, 99%), trisodium citrate dihydrate (Na_3Cit, $HOC(COONa)(CH_2COONa)_2 \cdot 2H_2O$, 99%), diethylene glycol (diEG, $H(OCH_2CH_2)_2OH$, 99%), tetraethylene glycol (tetraEG, $H(OCH_2CH_2)_4OH$, 99%), pentaethylene glycol (pentaEG, $H(OCH_2CH_2)_5OH$, 99%), polyethylene glycol 200 (polyEG200, $H(OCH_2CH_2)_{200}OH$), (3-aminopropyl)triethoxysilane (APTES, $H_2N(CH_2)_3Si(OC_2H_5)_3$, 99%), and sodium silicate solution (10% NaOH, 27% SiO_2). 4-Mercaptobenzoic acid (4-MBA, 99%) and ethyl alcohol (EtOH, 99%) also purchased from Sigma-Aldrich/Merck were used to form the self-assembled monolayer. A stainless steel substrate (Tienta SpectRIM from Sigma-Aldrich/Merck) was employed for Raman measurements.

General equipment
Silver nanoparticles were synthesised by the MW method using a CEM Discover SP microwave synthesizer, and under reflux using an IKA RCT Basic magnetic stirrer. An Eppendorf Centrifuge 5420 was exploited to concentrate the nanoparticles. UV/Vis spectra (200–1300 nm) were recorded on a Peak instruments C-7200S UV/Vis spectrophotometer. An FEI Tecnai G2 F20 X-TWIN microscope was employed to gather high-resolution transmission electron microscopy (HR-TEM) data. Raman and SHINERS spectra were obtained on a PerkinElmer RamanFlex 400 Echelle spectrometer (settings: 785 nm excitation wavelength, 30 mW laser power and 10 × 10 s integration time).

Microwave synthesis of silver nanoparticles
Freshly prepared 5 mL of 10 mM $AgNO_3$ was mixed with X mL (0.5 mL, 1 mL, 2 mL or 5 mL) of polyol (diEG, tetraEG, pentaEG or polyEG200)

and 5 mL of 10 mM Na_3Cit. Next, it was placed in a microwave synthesiser and heated at the power of 150 W for two steps: firstly, it was heated to 60°C in 1 min with 2 min holding, and, secondly, to 95°C in 1 min with 5 min holding. Then, the mixture was cooled to 50°C in the microwave synthesiser (over 3 min), secondly, in a cold water bath without stirring (30 min), and finally, in a refrigerator (8–10°C, 30 min). A greenish-yellow suspension of silver nanoparticles (Ag NPs) was obtained. Next, 0.1 mL of 1 mM APTES was added to 7.5 mL of Ag NPs suspension and stirred for 20 min at room temperature. Then 0.8 mL of 0.54% sodium silicate was added and stirred for another 2 min at room temperature. Next, the reaction mixture was placed in the microwave synthesiser and heated at the power of 100 W for two steps: firstly, it was heated to 60°C in 0.5 min with 1 min holding, and, secondly, to 95°C in 1 min with 5 min holding. Then, the mixture was cooled to 50°C in the microwave synthesiser (over 3 min), secondly, in a cold water bath without stirring (30 min), and finally, left overnight in a refrigerator (8–10°C). The greenish silver nanoparticles covered with silicon dioxide (Ag@SiO$_2$ NPs) were obtained. The Ag@SiO$_2$ NPs were stored in the refrigerator (8–10°C) and centrifuged (10 min, 3500 rpm) before use in Raman and SHINERS measurements.

Reflux synthesis of silver nanoparticles

Freshly prepared 50 mL of 1 mM $AgNO_3$ was rapidly boiled (10 min) in a silicon oil bath. Then 2.5 mL of polyol (diEG, tetraEG, pentaEG or polyEG200) and 1 mL of 1% Na_3Cit were added and refluxed with stirring for 40 min. The mixture was cooled by stirring at room temperature (30 min), secondly, in a cold water bath without stirring (30 min), and finally, in a refrigerator (8–10°C, 30 min). A greenish-yellow suspension of silver nanoparticles (Ag NPs) was obtained. Next, 0.4 mL of 1 mM APTES was added to 30 mL of Ag NPs suspension and stirred for 20 min at room temperature. Then 6.4 mL of 0.54% sodium silicate was added and stirred for another 2 min at room temperature. The mixture was heated with stirring in a silicone oil bath for 40 min at 90–95°C temperature. Then the mixture was cooled by stirring at room temperature (30 min), secondly, in a cold water bath without stirring (30 min), and

finally, left overnight in the refrigerator (8–10°C). The greenish silver nanoparticles covered with silicon dioxide (Ag@SiO$_2$ NPs) were obtained. The Ag@SiO$_2$ NPs were stored in the refrigerator (8–10°C) and centrifuged (10 min, 3500 rpm) before use in Raman and SHINERS measurements.

Formation of self-assembled monolayer

A self-assembled monolayer was formed using an evaporated gold layer on a cleaned glass substrate. The substrate was incubated in a 4-MBA (5×10^{-3} M) EtOH solution for 1 h. Then it was washed with alcohol and dried at room temperature.

Raman and SHINERS measurements

The synthesised silver nanoparticles (3 μL) were dropped onto a steel substrate and dried under a steam of N_2 at room temperature. The Raman spectrum of the nanoparticles was recorded. Next, the nanoparticles (3 μL) were dropped onto a formed self-assembled monolayer of 4-MBA and dried under a steam of N_2 at room temperature. The SHINERS spectrum of the 4-MBA self-assembled monolayer was obtained.

RESULTS AND DISCUSSION

Polyol synthesis is one of the most used reduction methods to produce nanoparticles. The liquid-phase reduction is performed in glycerol (GLY), ethylene glycol (EG), polyethylene glycol (poly-EG), propanediol (PDO), and other polyols. Polyols have many advantages: they mix with water and dissolve the metal-salt precursors; they have reducing properties and high-boiling temperatures; they functionalise the surface of nanoparticles and stabilise them [23]. The wide range of polyol structures allows them to be adapted to different synthesis conditions. Additional surface stabilisers, such as polyvinylpyrrolidone (PVP), are often used with polyols to avoid the aggregation of nanoparticles and control the shape [24]. Previous experiments conducted by our research group [25] have shown that unreacted PVP residues are difficult to wash away after nanoparticle production. Sometimes more than one centrifugation is necessary. If the particles are unstable, they degrade during a long centrifugation procedure. Therefore, we aimed to simplify the polyol process

and used polyols without additional stabilisers, like PVP. Since the nanoparticles were planned to be employed in SHINERS aqueous experiments, water was chosen as the main solvent. Due to this decision, the synthesis temperature was restricted up to 100°C. The reducing power of polyols reaches its limit at higher temperatures (>230°C) [23]. Thus, in our case, high-boiling polyols were used more due to their coordinating properties for surface functionalisation of nanoparticles and stabilisation of colloidal suspension. We set the goal of creating such a synthesis method, during which it would be possible to obtain the largest silver nanoparticles with the least amount of polyols. We chose three short-chain ethylene glycol derivatives (diEG, tetraEG and pentaEG) since they are quickly removed by water and will not hinder spectrum analyses in the future. A long-chain polyethylene glycol (polyEG200) was also used to compare results.

Earlier our experience in the microwave synthesis of silver nanoparticles [26] allowed using this effective method for re-synthesis optimising new conditions. A simple silver nitrate precursor and sodium citrate reducer were used by MW protocol in the optimal molar ratio (1:1). The selected 150 W power of the microwave synthesiser and the polyols allowed rising the temperature evenly up to boiling in two stages: firstly, the reaction mixture was heated to 60°C in 1 min with 2 min holding,

and, secondly, to 95°C in 1 min with 5 min holding (Fig. 1, Ag NPs). The optimal raising and holding time was determined experimentally according to the technical capabilities of the microwave synthesiser to raise the temperature uniformly at a power of 150 W. Four polyols (diEG, tetraEG, pentaEG and polyEG) at three volume ratios (1:20, 1:10 and 1:5) were tested in this manner (Table 1).

The optical properties of silver nanoparticles depend on the size, shape, and surface capping. The growth of spherical nanoparticles causes a red shift in the UV/Vis spectrum [24, 27]. We did not intend to synthesise angular particles, so we did not use any additional stabilisers or capping agents, except polyols. Expected to produce silver nanospheres, the UV/Vis was used as an initial method for size analysis of the synthesised nanoparticles. Due to UV/Vis data represented in Table 1, the largest silver nanoparticles were produced in all MW syntheses with bulky polyEG200. Compared to the others used, it is the largest polyol with the most polar groups (Table 2). In addition, it maintains high temperatures well, which is especially important during MW irradiation. Comparing the volume optimisation conditions (1:20, 1:10 and 1:5), the best results were obtained using a 1:20 volume ratio of polyols to the MW reaction mixture. The maximum peak wavelength (λ_{max}) was observed at 451 nm for the silver nanoparticles
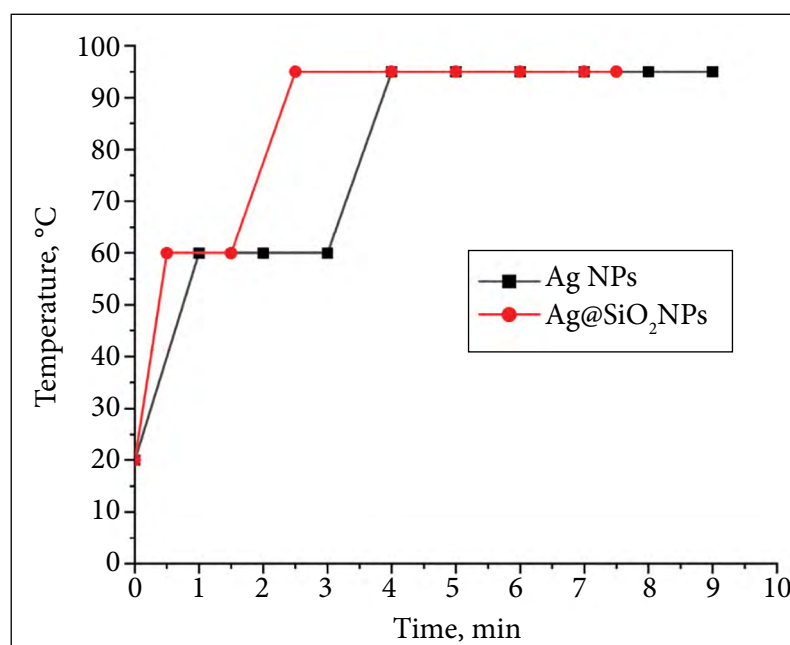

Fig. 1. MW heating conditions of Ag NPs and Ag@SiO$_2$ NPs synthesis

Table 1. **MW synthesis optimisation and UV/Vis data**

Volume ratio (polyol: MW reaction mixture)	Polyol	λ_{max} of nanoparticles
1:20	diEG	451 nm
	tetraEG	446 nm
	pentaEG	449 nm
	polyEG200	454 nm
1:10	diEG	443 nm
	tetraEG	436 nm
	pentaEG	441 nm
	polyEG200	444 nm
1:5	diEG	431 nm
	tetraEG	428 nm
	pentaEG	430 nm
	polyEG200	441 nm

synthesised with diEG, and 454 nm for the silver nanoparticles synthesised with polyEG200. Those were the two best MW synthesis results.

Next, silver nanoparticle synthesis was repeated by the modified reflux method of Lee and Meisel [28] adding polyols. Analogically, four polyols (diEG, tetraEG, pentaEG and polyEG200) were used at the optimal volume ratio (1:20) determined earlier by the MW method. The absorption peaks (Fig. 2b–d) were observed for the silver nanoparticles synthesised with pentaEG (423 nm), tetraEG (412 nm) and diEG (438 nm). The maximum peak wavelength was difficult to observe at the UV/Vis spectrum of nanoparticles synthesised with polyEG200 (Fig. 2a).

The trend of the results obtained with three short ethylene glycol derivatives (diEG, tetraEG and pentaEG) was replicated under MW and reflux conditions. Due to the UV/Vis data (Table 1, Fig. 2), the largest nanoparticles were produced with diEG, smaller with pentaEG and the smallest ones with tetraEG. The chemical reduction was slower under
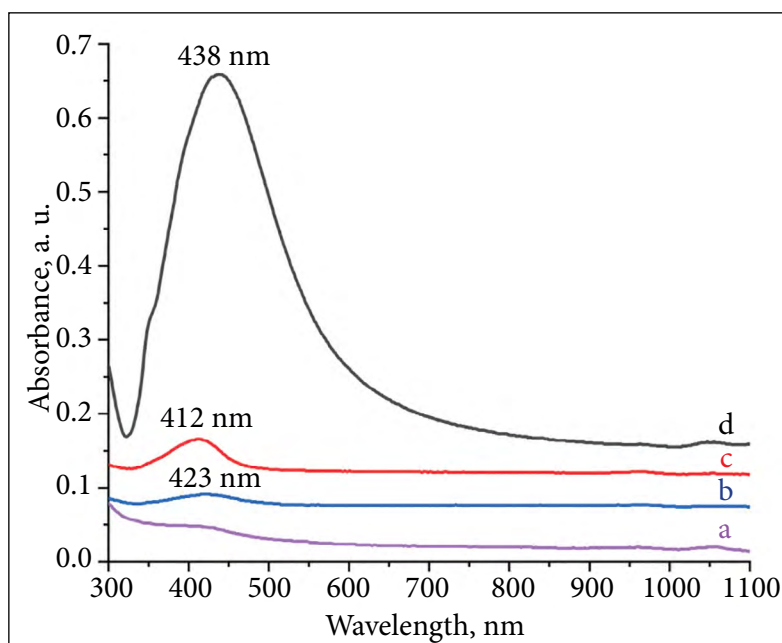
Fig. 2. UV/Vis spectra of Ag NPs synthesised with polyols: polyEG (a), pentaEG (b), tetraEG (c) and diEG (d)

reflux conditions. The synthesis under reflux was successfully performed in 40 min and under MW irradiation in 9 min. Under reflux conditions, the reaction vessel collects the heat from the oil bath system and exchanges the thermal energy with the reaction mixture. The generation of thermal gradients complicates the transformation of reactants into products [19, 20]. In our synthesis, the slow reduction under reflux appears to be further complicated by the long-chain polyol, which could partially block the access of citrate to silver ions (Fig. 3). On the other hand, MW irradiation allows a rapid and even heat transfer through the uniform heating and mixing of reactants [19, 20]. Bulky polyEG200 is welcome in this case because it withstands the sudden heating of the microwave synthesiser and stabilises the surface of nanoproducts. Altogether, this explains why polyEG200 was not enough effective for the synthesis of silver nanoparticles under reflux, and on the contrary, it allowed to synthesise the largest particles under MW conditions.

Based on the obtained synthesis results, diEG was selected as more suitable for further research. By the way, it is a short-chain ethylene glycol miscible in water (Table 2). So, its residues will be easily removed from an aqueous suspension by centrifugation after nanoparticle production. The risk of nanoparticle contamination will be reduced and extraneous signals in the Raman spectra will be avoided. Consequently, silver nanoparticles were re-synthesised with diEG under MW and reflux conditions. An inert SiO_2 shell increases the stability of the nanoparticles and compatibility with SHINERS experiments [10]. Therefore, both Ag NPs (synthesised under MW and reflux) were coated with silicon dioxide. A silica shell was formed over the nanoparticles in the presence of reactants (silver nitrate, sodium citrate and diEG) residues. The Daublyte et al. procedure [26] was used to cover nanoparticles with SiO_2 under MW irradiation. Briefly, the mixture of Ag NPs, APTES and sodium silicate was heated at the power of 100 W for 7.5 min (Fig. 1, Ag@SiO_2 NPs). The silver
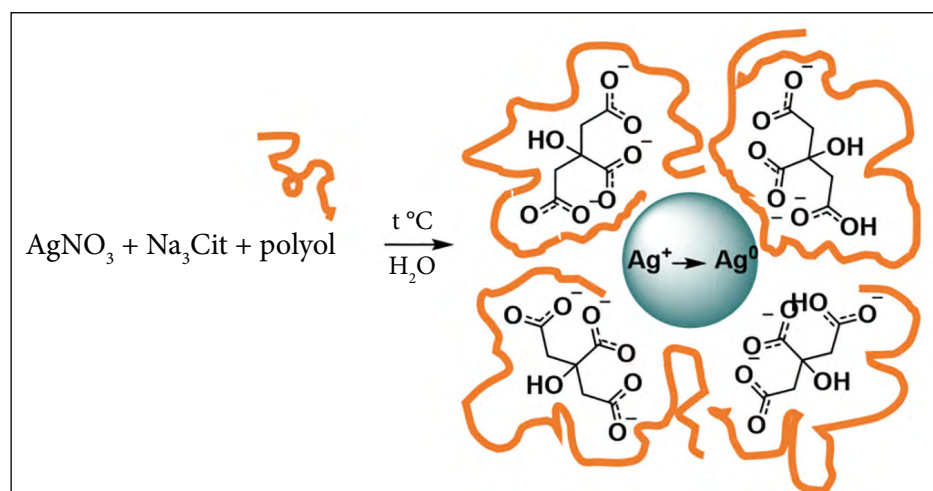

Fig. 3. Scheme of Ag NPs chemical reduction with polyol

**Table 2. Main properties of used polyols (according to Sigma-Aldrich/Merck safety data sheets)**

Polyol	Structure	Mr	H₂0 solubility	Density	Boiling point	Melting point
diEG	$H(OCH_2CH_2)_2OH$	106.12	1.000 g/l at 20°C (miscible)	1.118 g/mL at 25°C	245–246°C	−10°C
tetraEG	$H(OCH_2CH_2)_4OH$	194.23	1.000 g/l at 25°C (soluble)	1.125 g/mL at 25°C	313–314°C	−5°C
pentaEG	$H(OCH_2CH_2)_5OH$	238.28	no data available (miscible)	1.126 g/mL at 25°C	338–340°C	187°C
polyEG	$H(OCH_2CH_2)_{200}OH$	>3200	256.084 g/l at 25°C (soluble)	1.127 g/mL at 25°C	>200°C at 1013 hPa	< −14.08°C at 973. hPa

nanoparticles were coated with SiO_2 under reflux by a modified Li et al. protocol [22]. The same reagents (APTES and sodium silicate) successfully formed a SiO_2 shell in 40 min. Silica shell formation was proved by UV/Vis and HR-TEM techniques. An absorption maximum shifted slightly to a longer wavelength: from 451 to 454 nm for the nanoparticles synthesised under MW irradiation (Fig. 4a, b), and from 438 to 440 nm for the nanoparticles synthesised under reflux (Fig. 4c, d). The HR-TEM analysis allowed observing the dominated spherical form of nanoparticles and a thin SiO_2 layer: 6–10 nm for the nanoparticles synthesised under MW (Fig. 5a) and 4–8 nm for the nanoparticles synthesised under reflux (Fig. 5b). It was also found that the MW method was more efficient as the resulting nanoparticles were larger and had a narrower size distribution.

Produced Ag@SiO_2 nanoparticles were stored at low temperatures (8–10°C) and centrifuged once (10 min, 3500 rpm) before being used in SHINERS measurements. The nanoparticles were stable and successfully used for up to 3 months without any changes in their UV/Vis spectra.

It is widely known that getting more intense Raman spectra of analyte requires bigger than 50 nm nanospheres with a thin 2–10 nm inert shell [21, 22]. Silver nanospheres produced by the MW method were 95 ± 5 nm in diameter with a 6–10 nm SiO_2 coating, and the nanoparticles synthesised under reflux conditions were 80 ± 5 nm in diameter with 4–8 nm SiO_2. Both silver core-silica shell nanoparticles were used for SHINERS experiments. Therefore, a model self-assembled monolayer of 4-MBA onto a smooth gold (Au/4-MBA) plate was formed. The Ag@SiO_2 nanoparticles were spread over the Au/4-MBA plate, dried at room temperature, and then SHINERS spectra were recorded. The Raman spectra of Ag@SiO_2 nanoparticles on the Tienta steel substrate were also performed. The obtained data showed that the nanoparticles amplified pollutants from the environment and therefore had their specific spectra (Fig. 6a, c). However, the intensity of the spectra was quite modest and did not interfere with the further spectral analysis of the analyte. The enhanced SHINERS spectra of 4-MBA (Fig. 6b, d) were successfully recorded with both silver core-silica shell nanoparticles. All 4-MBA bands were identified and assigned according to our reported previous results [25, 26]. As suspected, a more intense spectrum (Fig. 6b) was obtained with larger nanoparticles synthesised by the MW method. It is noticeable that contaminants in the immediate surroundings were enhanced extremely well (Fig. 6a) by the Ag@SiO_2 nanoparticles synthesised under MW irradiation. But their SHINERS spectrum (Fig. 6b) was more
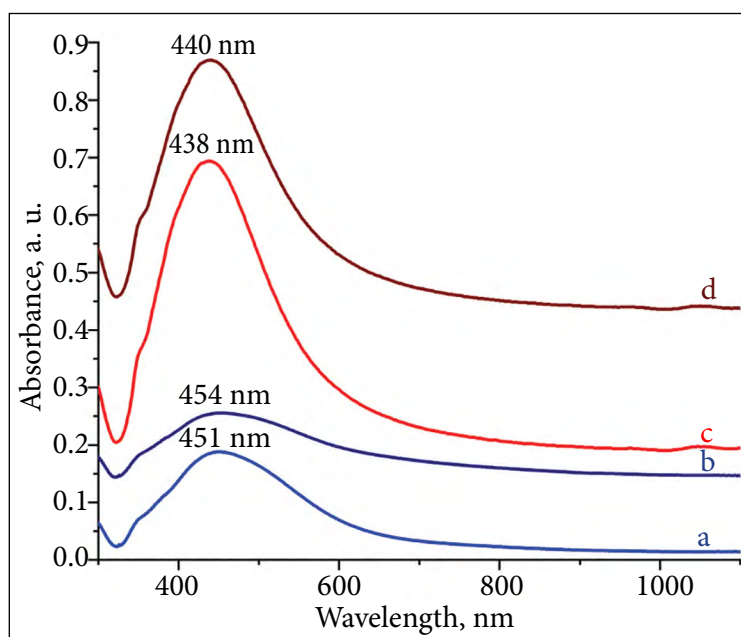
Fig. 4. UV/Vis spectra of Ag NPs (a) and Ag@SiO_2 NPs (b) synthesised under MW irradiation; Ag NPs (c) and Ag@SiO_2 NPs (d) synthesised under reflux
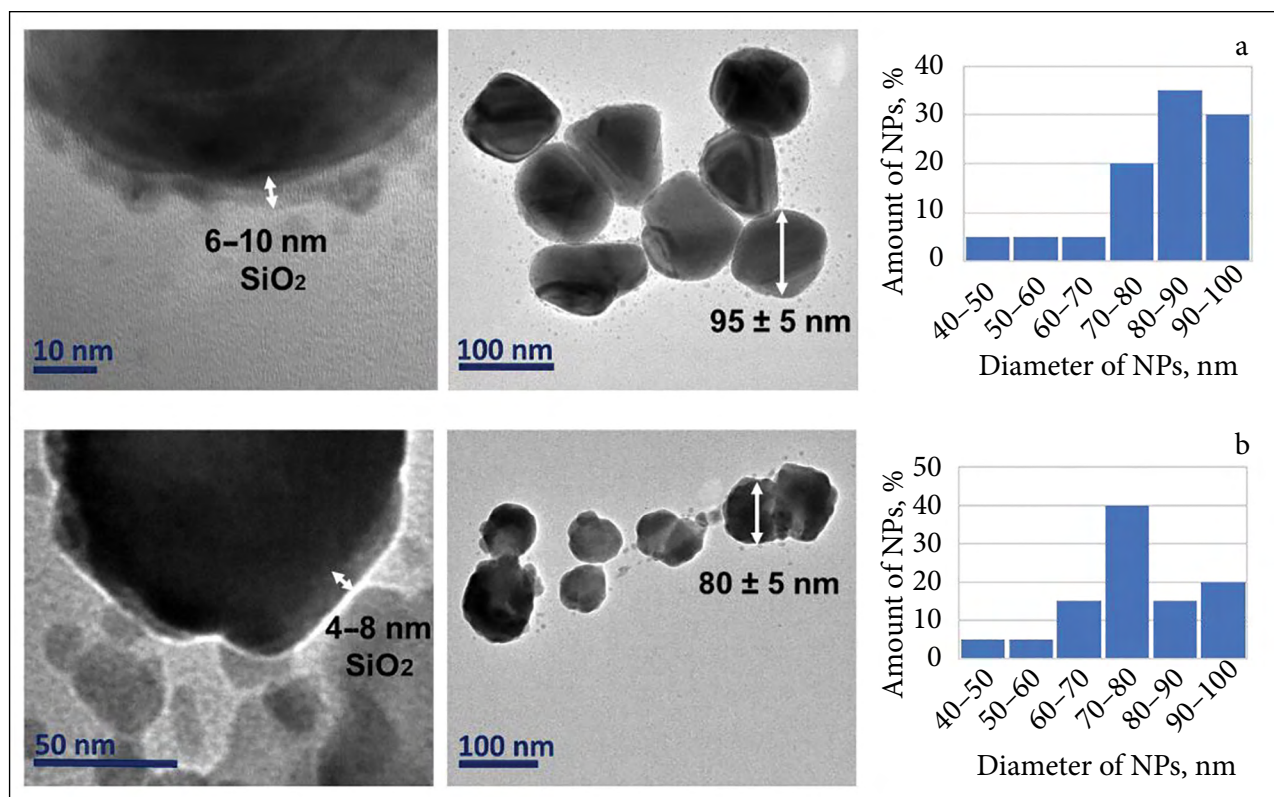
Fig. 5. HR-TEM data of AgSiO$_2$ NPs: synthesised by the MW method (a) and under reflux (b)
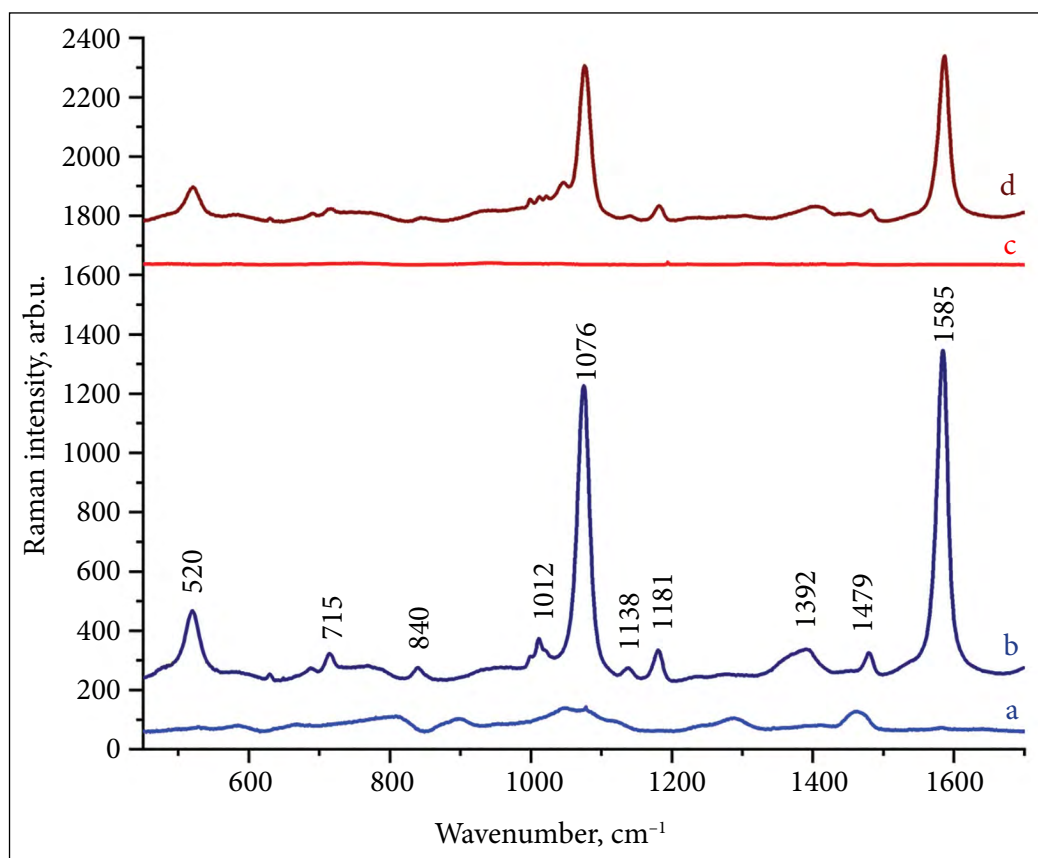

Fig. 6. Raman spectra (on steel) of AgSiO$_2$ NPs synthesised by the MW method (a) and under reflux (c); SHINERS spectra (on Au/4-MBA plate) with AgSiO$_2$ NPs synthesised by the MW method (b) and under reflux (d)

intense and cleaner compared to the SHINERS spectrum (Fig. 6d), recorded with the Ag@SiO$_2$ nanoparticles synthesised under reflux. The bigger size of the nanoparticles and their greater amplification could have influenced the result.

CONCLUSIONS

Three short ethylene glycol derivatives and one polyethylene glycol were used as stabilisers to synthesise silver nanoparticles. Two methods of chemical reduction (under MW and reflux) with a minimal amount of polyols were optimised. Silver core-silica shell nanoparticles were successfully synthesised in two steps without additional purification. The nanospheres produced by the MW method were 95 ± 5 nm in diameter with a 6–10 nm SiO$_2$ shell, and the nanospheres synthesised under reflux were 80 ± 5 nm in diameter with 4–8 nm SiO$_2$. Both produced nanoparticles were stable for up to 3 months and had low traces of contaminants. The nanoparticles were successfully applied for the analysis of the 4-MBA self-assembled monolayer by the SHINERS method.

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SIDABRO NANODALELIŲ SINTEZĖ SU POLIOLIAIS VIRINANT IR MIKROBANGŲ POVEIKIO SĄLYGOMIS

Santrauka

Sidabro nanosferos susintetintos panaudojant tris trumpus etilenglikolius ir vieną polietilenglikolį kaip paviršiaus stabilizatorius. Cheminė redukcija sėkmingai optimizuota virinant ir mikrobangų poveikio sąlygomis. Gautos nanodalelės buvo padengtos apsauginiu plonu (iki 10 nm) silicio dioksido sluoksniu be tarpinio gryninimo. Mikrobangoms veikiant pagamintos nanosferos buvo 95 ± 5 nm skersmens su 6–10 nm SiO_2, o susintetintos virinant – 80 ± 5 nm skersmens su 4–8 nm SiO_2. Abiem būdais pagamintos nanodalelės buvo stabilios tris mėnesius ir turėjo mažai priemaišų. Nanodalelės buvo sėkmingai pritaikytos 4-merkaptobenzoinės rūgšties monosluoksnio analizei panaudojant nanodalelių, padengtų apsauginiu sluoksniu, sustiprintos Ramano spektroskopijos (angl. *Shell-isolated nanoparticle-enhanced Raman spectroscopy – SHINERS*) metodą. Straipsnyje pateikiamas išsamus nanodalelių sintezės, analizės ir pritaikymo aprašymas, pagrįstas UV/Vis, HR-TEM ir SHINERS duomenimis.