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Preparation of silver particles and its application for surface enhanced Raman scattering with near-infrared excitation

Robert Prucek *, Václav Ranc, Olga Balzerová, Aleš Panáček, Radek Zbořil, Libor Kvítek

Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry, Faculty of Science, Palacky University, Slechtitelu 11, 78371 Olomouc, Czech Republic

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ABSTRACT

The preparation of silver nanoparticles through the reduction of silver ammonia complex by glucose is reported. The average of the as-prepared particle sizes varied from approx. 35 nm to 120 nm in a dependence of ammonia concentration. The mechanism of silver particle formation is dependent on the ammonia concentration. At low ammonia to silver ions ratios (1:1 and 2:1), the silver oxide particles are formed at first and subsequently are reduced by glucose. Higher ammonia concentrations are able to bind silver ions sufficiently without forming silver oxide as an intermediate and in these cases are silver particles generated through direct reduction of $[Ag(NH_3)_2]^+$ by glucose. The obtained silver particles were tested in surface enhanced Raman scattering experiments with infrared laser excitation (1064 nm). The adenine was used as a model analyt for evaluation of the surface enhancement efficiency. Before surface enhanced Raman measurements, sodium chloride of a resulting concentration equals to 0.1 mol L^{-1} was used for treatment of silver particles, leading to a partial etching and coalescence of silver particles. It was found out that the enhancement efficiency of Raman signal is considerably dependent on silver particle size. The highest enhancement factors after addition of concentrated sodium chloride solution were achieved using particles with sizes about 60 nm.

1. Introduction

There is a growing interest in the preparation and study of metal nanoparticles (NPs) inspired by their potential applications in the field of biosensors, chemical sensors, catalysis. Silver, thanks to its physicochemical properties, is one of the most widely used metals in modern nanotechnology (e.g. antimicrobial properties of silver NPs). Another important application is their usage as substrates for surface enhanced Raman scattering (SERS), which represents a new and very sensitive analytical method [1–5], enabling to detect molecules in the concentration ranges from pico- to femtomols [6]. High enhancements of Raman signal even allowed the detection of individual molecule adsorbed on a single silver particle [7–10].

It is well known that nanomaterial properties are determined by its size, shape, and interaction between nanoparticles. Some studies concerning surface enhanced Raman experiments have shown that the highest value of enhancement is achieved only on the silver particles of a certain size which are referred to as 'hot particles'. The optimal size of these hot particles depends on the wavelength of the laser used for excitation and ranges from approx. 70 nm to 200 nm for excitation wavelengths between 488 and 647 nm [11]. However, silver nanoparticles of smaller sizes can provide high enhancement of the Raman signal after their aggregation induced by the addition of some inorganic ions [5,12–15], particularly chlorides [16–19]. The final concentration of chloride ions varied usually from 0.1 mmol L^{-1} to 20 mmol L^{-1} [19–22] which leads to the slow aggregation of silver nanoparticles. On the contrary very high concentrations of chlorides (400 mmol L^{-1}) cause recrystallization of silver nanoparticles (~30 nm) to one-order larger crystallites which are efficient enhancers of Raman scattering both for visible (488 nm) and for near infrared (NIR) (1064 nm) excitation [23]. Utilization of NIR excitation can be advantageous for wide types of samples (e.g. biological or clinical) due to its ability to avoid most of the background fluorescence. For these purposes, the gold particles and their layers or arrays are usually used as substrates [24–27]. However, for NIR-SERS can be also exploited cheaper substrates based on silver particles or aggregates [28,29], which can possess comparable efficiency of Raman signal enhancement [23,30,31].

In this work, we report the method for synthesis of silver particles with sizes between approx. 35 nm and 120 nm prepared through a reduction of silver ammonia complex by glucose. The ammonia concentration in the reaction system was proved as

* Corresponding author. Tel.: +420 585634427; fax: +420 585634761.
E-mail address: robert.prucek@upol.cz (R. Prucek).

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the key parameter which influences the resulting size of silver particles. High enhancement efficiency of the as-prepared silver particles after their treatment using 0.1 mol L^{-1} NaCl in the surface enhanced Raman scattering with inrared excitation was proved.

2. Experimental

2.1. Preparation of the silver nanoparticles

The silver particles were prepared using a modified Tollens procedure by a reduction of $[Ag(NH_3)_2]^+$ cation. This complex was prepared by a mixing of silver nitrate ($c = 1 \times 10^{-3}$ mol L^{-1}) with a variable concentration of ammonia solution (from 1×10^{-3} to 6×10^{-3} mol L^{-1}). Sodium hydroxide solution (0.3 mol L^{-1}) was then added to the reaction system to adjust the value of pH at 10.5 ± 0.1 and the silver was afterwards reduced using glucose of concentration $c = 1 \times 10^{-2}$ mol L^{-1}. All the measurements were performed at the laboratory temperature.

For the purpose of SERS measurements, 0.2 mL of the stock solution of Ag NPs was diluted with 0.7 mL of deionised water. Then 0.1 mL of 1 mol L^{-1} NaCl was quickly added to the diluted dispersion of Ag NPs and the solution was shaken. Immediatelly after that, 10 microliters of 10^{-3} mol L^{-1} solution of adenine was added, and the solution was shaken again. The Raman spectrum was collected 5 min after addition of sodium chloride solution.

2.2. Materials and chemicals

Silver nitrate (99.9%, Sigma–Aldrich), ammonia (28% (w/w) aqueous solution, p.a., Sigma–Aldrich), sodium hydroxide (p.a., Lachema), sodium chloride (p.a., Sigma–Aldrich), D-glucose (p.a., Sigma–Aldrich), and adenine (p.a., Sigma–Aldrich) were used for the preparation of silver particles without any further purification.

2.3. Instrumentation

The size of the silver particles was determined by a dynamic light scattering method (DLS) using a Zeta Plus analyzer (Brookhaven, USA). TEM observations of the silver NPs were performed with a JEM 2010 (Jeol, Japan) electron microscope at 160 kV of the acceleration voltage. UV–vis absorption spectra of the silver NP dispersions were acquired using a Specord S 600 (Analytic Jena AG, Germany) spectrophotometer. Experiments concerning the usage of Raman spectrometry were performed using an FT-IR spectrometer (Nicolet FT-IR 6700, USA) with a Raman accessory (NXR FT-Nicolet module, USA) equipped with a liquid nitrogen-cooled germanium detector. The FT-Raman was equipped with a Nd:YAG laser with a wavelength of 1064 nm with 4 cm^{-1} resolution and 1 s scan time, laser power deposition onto a sample was 300 mW, 128 scans were obtained for each measurement and data were averaged. Spectra were measured in the range from 500 to 2000 cm^{-1}.

3. Results and discussion

The presented preparation method of silver particles is partially based on already well-established modified Tollens process. This procedure involved primary formation of a silver ammonia complex cation $[Ag(NH_3)_2]^+$, which is the reduced by a reducing sugar. The molar ratio of silver ions and ammonia ranged between 1:5 and 1:200 [32]. The present study is aimed at investigation of influence of low molar ratio of silver ions and ammonia (1:1–1:6) on preparation of silver particles.

The average size of the prepared silver particles varied from approx. 35 to 120 nm (determined by a DLS method) in a dependence on ammonia concentration (Fig. 1). The experiments

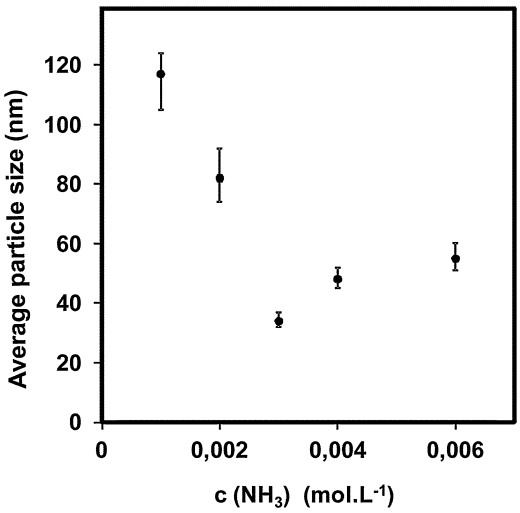

Fig. 1. The dependence of average size of silver particles on ammonia concentration prepared through a reduction of silver ammonia complex by glucose.

were repeated six times in order to verify reproducibility of the mentioned silver particle preparation procedure (see error bars, Fig. 1). When using the lowest ammonia concentration, the resulting average particle size was the highest (~120 nm). With the increased ammonia concentration the average size of silver particles at first decreased, reaching the minimum at ammonia concentration equal to 0.003 mol L^{-1} (34 nm), and after that the average particle size gradually increased. The silver particle sizes determined by DLS method corresponds to the positions of UV–visible absorption peaks. With increasing average size of silver particles, the absorption maximum shifted to the longer wavelengths (Fig. 2). The positions of absorption maxima of silver particles were 444 nm, 428 nm, 403 nm, 416 nm, and 424 nm for ammonia concentrations 0.001, 0.002, 0.003, 0.004, and 0.006 mol L^{-3}, respectively. The sizes of the silver particles were also confirmed by TEM images (Fig. 3) when the average sizes of silver particles were determined by the image analysis performed for several independent images containing at least 50 silver particles. The average particle sizes of silver particles determined from TEM images were 118 nm, 82 nm, 34 nm, 45 nm, and 58 nm for ammonia concentrations 0.001, 0.002, 0.003, 0.004, and 0.006 mol L^{-3}, respectively.

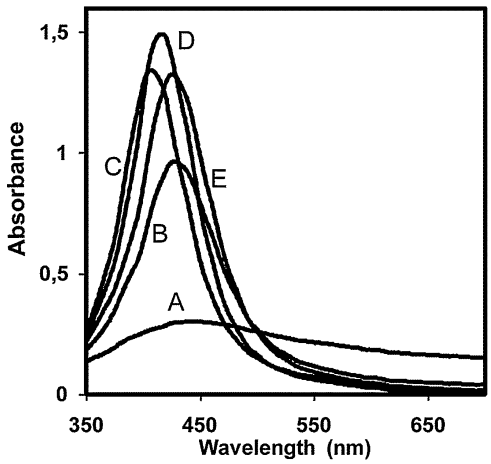

Fig. 2. UV–visible absorption spectra of silver nanoparticles prepared via reduction of silver ammonia complex by glucose at different ammonia concentrations: 0.001 (A), 0.002 (B), 0.003 (C), 0.004 (D), and 0.006 mol L^{-1} (E).