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Highly efficient silver particle layers on glass substrate synthesized by the sonochemical method for surface enhanced Raman spectroscopy purposes

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ABSTRACT

A fast method for preparing of silver particle layers on glass substrates with high application potential for using in surface enhanced Raman spectroscopy (SERS) is introduced. Silver particle layers deposited on glass cover slips were generated in one-step process by reduction of silver nitrate using several reducing agents (ethylene glycol, glycerol, maltose, lactose and glucose) under ultrasonic irradiation. This technique allows the formation of homogeneous layers of silver particles with sizes from 80 nm up to several hundred nanometers depending on the nature of the used reducing agent. Additionally, the presented method is not susceptible to impurities on the substrate surface and it does not need any additives to capture or stabilize the silver particles on the glass surface. The characteristics of prepared silver layers on glass substrate by the above mentioned sonochemical approach was compared with chemically prepared ones. The prepared layers were tested as substrates for SERS using adenine as a model analyte. The factor of Raman signal enhancement reached up to $5 \cdot 10^5$. On the contrary, the chemically prepared silver layers does not exhibit almost any pronounced Raman signal enhancement. Presented sonochemical approach for preparation of silver particle layers is fast, simple, robust, and is better suited for reproducible fabrication functional SERS substrates than chemical one.

1. Introduction

Discovery of surface enhanced Raman scattering (SERS) on a silver electrode by Fleischmann in 1974, and especially its rediscovery on colloidal silver particles by Creighton in 1977 [1] initiated the extensive development of a new and very sensitive analytical method that allows the detection of molecules in the concentration range from pico to femtomoles [2]. The most widely used materials for SERS include silver or gold. Silver is preferable due to its cheaper price and better optical properties for utilization in SERS [3].

A high enhancement of SERS, reaching the values of up to 10^{15}, even allowed the detection of a single molecule adsorbed on an individual silver nanoparticle [4,5]. Some studies have shown that such a high value of the enhancement can be achieved only on particles of certain sizes which are referred as "hot particles". The particles' optimum size depends on the wavelength of the laser used for the excitation and ranges approximately from 70 to 200 nm for the excitation wavelengths in the range from 488 to 647 nm [6]. Based on the dependence of the "hot particles" size for a given laser wavelength, it can be expected, when using lasers with wavelengths 785 nm and 1064 nm, the maximum enhancement of the Raman signal should be obtained on silver particles of the size of around 400 nm [7–9]. Unfortunately, particles of these dimensions are unstable and settle within a short time. Silver nanoparticles with sizes equal to a few tens of nanometers are generally stable for several months or years, however, these small particles do not provide sufficient surface enhancement of the Raman signal themselves. For this purpose, they must be treated by addition of some inorganic ions. The inorganic ions added into the dispersion of silver nanoparticles induces their slow and often uncontrollable aggregation resulting in the irreproducibility of the Raman signal [2,4,10–13].

The disadvantages connected with aggregation or sedimentation of silver nanoparticles can be overcome through the formation of metal particle layers [14] on suitable substrate such as quartz or

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glass [15]. The chemical techniques for the formation of metal particle layers can be divided into deposition from gas phase and formation by growing up of layers from solution, which is represented by electrochemical deposition, chemical deposition from solution, Langmuir–Blodgett film technique, and self-assembling [16]. Deposition of particles on the glass substrate can also be performed by lithographic method based on formation of self-assembled layers of polystyrene particles serving as a lithographic mask. After deposition of metal nanoparticles (silver or gold in most cases), the polystyrene particles are removed by organic solvent [17–21]. Another possible technique of metal layers formation involves deposition of one or more layers using polyelectrolytes such as polydiallyldimethylammonium chloride (PDDA) or polyethylenimine (PEI) [22,23]. In this approach, the layers of particles are captured between layers of polyelectrolyte through electrostatic interactions. Other way to obtain silver particle layers involves exploitation of 3-aminopropyltriethoxysilane (APTES) [24], which is able to form covalent bond with the activated surface of glass or quartz substrate. When APTES is bonded on the surface, its amino groups can interact through free electron pair with silver nanoparticles [25].

Unfortunately, the described methods are usually time consuming, very sensitive to thorough cleaning of the surface, and also require activation of substrate surface prior to deposition of silver particles. Due to these disadvantages, it is desirable to find new techniques, which are more effective, time-saving and which do not require addition of other chemicals, which could affect the enhancement of Raman signal. One of the promising techniques is based on sonochemical preparation of silver layers. Through sonochemical approach, Perkas et al. prepared layers of silver particles stabilized by polyvinylpyrrolidone (PVP) on glass substrates [26] with substantial antibacterial activity. However, application of the reported method in preparation of the effective SERS substrate is questionable due to interfering of the Raman signal originated from the PVP polymer used as stabilizer with Raman signal of analyzed molecules adsorbed on this type of silver nanoparticle layer.

In the current study, we report the innovative preparation method of the silver particle layers usable as efficient SERS substrate based on the combination of sonochemistry and modified Tollens reaction. The influence of experimental parameters such as sonication parameters, concentration of silver salt, type of reducing sub-stance, absence or presence of PVP, and choice of beaker type (glass or polypropylene), used for preparation, on the characteristics of silver particle layers was investigated. The prepared silver particle layers deposited on glass slips were tested and evaluated as highly effective substrates for surface enhanced Raman spectroscopy purposes.

2. Materials and methods

2.1. Chemicals and instruments

Silver nitrate (Sigma–Aldrich, p.a.) was used as a precursor of silver particle layers. Ethylene glycol (Sigma–Aldrich, p.a.), glycerol (Sigma–Aldrich, p.a.), maltose (Sigma–Aldrich, p.a.), glucose (Sigma–Aldrich, p.a.) and lactose (Sigma–Aldrich, p.a.) were used as reducing agents. Polyvinylpyrrolidone (PVP, Sigma–Aldrich, M. W. 40,000) was used as a stabilizer. Ammonium hydroxide (Sigma–Aldrich, 28–30% aqueous solution) was used as a complexing agent. Adenine (Sigma–Aldrich, 99%) was used for the SERS experiments as a model analyte. All chemicals were used without additional purification. Deionized water (18 MΩ cm, Millipore) was used for preparation of all solutions.

Silver layers on glass slips were prepared by ultrasonic processor Q700 with standard titanium probe 4220 (QSonica LLC, USA). Glass slips covered by silver nanoparticles were characterized by using of scanning electron microscope Hitachi SU6600 (Hitachi, Japan) and UV–vis spectrometer Specord S600 (Analytic Jena AG, Germany). Silver concentrations were determined by the AAS technique with flame ionization using a ContrAA 300 (Analytik Jena AG, Germany) equipped with a high-resolution Echelle double monochromator (spectral bandwidth of 2 pm at 200 nm) and with a continuum radiation source (xenon lamp). The absorption line used for these analyses was 328.0683 nm. Surface enhanced Raman spectra were recorded using iRaman Plus with the 785 nm excitation laser (BWTEK Inc., USA), scan time 10 s, 6 accumulations were made. The laser light power was 100 mW. For the SERS measurement, 10 μl of 10^{-5} M adenine solution was used.

2.2. Preparation of silver particle layers deposited on glass substrate

The silver particle layers were deposited on glass microscope cover slips (Menzel-Gläser, 18 × 18 mm) by using of sonochemical approach. Before deposition, cover slips were thoroughly cleaned by detergent and washed by deionized water. After cleaning, cover slips were carefully inserted vertically using wire holders into beaker and then solutions of reaction precursors were added. Several modifications of the silver particle layers preparation process based on the reduction of silver ammonia complex related to changes of concentrations of the reactants were performed. Two polyols: ethylene glycol and glycerol, and three reducing saccharides: maltose, glucose and lactose, were used as reducing agents. Typically, 5 ml or 1 ml of 0.25 M silver nitrate solution was diluted by an appropriate amount of deionized water and 5 ml or 1 ml of reducing substance (ethylene glycol, glycerol or 0.25 M solution of reducing saccharide) was added. The final volume of reaction mixture was 25 ml. After mixing, the sonication tip was immersed into the reaction mixture. Parameter of sonication was adjusted to the amplitude value equal to 30% and the sonication begun. Few seconds after the start, 1.5 ml or 0.3 ml of ammonia solution was rapidly injected into the beaker. Also, the effect of presence of stabilizing polymer PVP on formation of silver nanoparticle layers was tested. In this case, 0.5 ml of 15 g/L PVP solution was added into the reaction system with ethylene glycol before sonication. Synthesis of silver particle layers on glass cover slips was terminated after 5.5 min of sonication. Glass slips were then pulled out of the holders, washed by deionized water and dried by air flow. For comparison to sonochemical approach of deposition of silver particle layers on glass susbtrate, the silver layers were also prepared using chemical method. As an example of such method, the Tollens process was chosen because this method exploits almost the same chemicals. In this case, cleaned glass slip was activated by tin dichloride, immersed into beaker and then silver layer was formed by mixing of silver nitrate (0.1 M) and ammonia (0.1 M) solution with solution of sodium hydroxide (1 M) and glucose (1.1 M) in the ratio equal to 1:1.

3. Results and discussion

3.1. Preparation of silver particle layers deposited on glass slips using ethylene glycol and glycerol

The main goal of the presented study was development of a simple and reproducible preparation of silver layers applicable as SERS substrates. The new synthetic route based on combination of two synthetic approaches, sonochemical method of silver nanoparticles deposition on glass [26] and modified Tollens process [27] was studied as an alternative methods. The procedure,