ANIONIC ORGANIC SPECIES DETECTION USING SILVER NANOPARTICLES?

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Abstract

Silver nanoparticles for spectroscopic applications, namely for surface-enhanced (resonance) Raman scattering (SE(R)RS), are usually prepared by a chemical reduction in aqueous solutions. The as-prepared nanoparticles mostly reveal negative zeta potential values among other important characteristic features. Therefore, it is really questionable if anionic organic species and/or pollutants dissolved in aqueous solutions can be directly and immediately detected by SE(R)RS using the as-prepared silver nanoparticles. In this contribution, we are going to show our results concerning SERRS detection of two anionic (4,4′,4″,4‴-(21H,23H-porphine-5,10,15,20-tetrayl)tetrais(benzenesulfonic acid, TSPP)), (4,4′,4″,4‴-(21H,23H-porphine-5,10,15,20-tetrayl)tetrais(benzoic acid), TCPP) and, for a direct comparison, of cationic (5,10,15,20-tetrakis(4-Trimethyl-ammoniophenyl)porphyrin tetra(p-toluenesulfonate), TTMAPP) porphyrins serving as model compounds. Several different types of silver nanoparticles prepared by diverse chemical reduction processes are tested in this study. Based on our data, SERRS spectral detection of selected water-soluble porphyrins strongly depends on their charge in aqueous solutions and on the type of silver nanoparticles being exploited for SERRS measurements. Furthermore, it can be claimed that the cationic porphyrin enables its immediate detection at low concentrations, while the anionic ones need an additional time in order to be detected.

Keywords: Ag nanoparticles, Ag colloid, porphyrins, surface-enhanced resonance Raman spectroscopy

1. INTRODUCTION

Exploitation of silver nanoparticles and/or electrodes for enhancement of Raman scattering of molecules being in a close vicinity of silver surface is known for many decades [1-3]. Silver nanoparticles can be prepared by several different ways: two most extensively used procedures include chemical reduction and/or laser ablation. Chemical reduction in aqueous solution of silver salt can be driven by e.g. sodium borohydride, sodium citrate, glucose (in alkaline pH values) etc. [2, 4, 5, 6]. The as-prepared nanoparticles differ in surface chemistry as it has been demonstrated in [7, 8] already. Generally, the as-prepared nanoparticles possess negative zeta potential values [7]. It can be thus presumed that the detection of anionic and cationic compounds will significantly differ.

Porphyrins serving in our study as model adsorbates are widely used in several different areas of research: for instance, in dye sensitized solar cells [9-11], for the detection of singlet oxygen [12], in conjunction with quantum dots as sensors of metal ions [13], as stabilizers of generated noble metal nanoparticles [14], for clinical diagnostics of early stages of cancer [15] etc.

Here, we focus our attention on the detection of two anionic (4,4′,4″,4‴-(21H,23H-porphine-5,10,15,20-tetrayl)tetrais(benzenesulfonic acid, TSPP)), (4,4′,4″,4‴-(21H,23H-porphine-5,10,15,20-tetrayl)tetrais(benzoic acid), TCPP) and one cationic (5,10,15,20-tetrakis(4-Trimethyl-ammoniophenyl)porphyrin tetra(p-toluenesulfonate), TTMAPP) porphyrins at the final concentrations of 1x10⁻⁶ M by means of SERRS (surface-enhanced resonance Raman scattering) spectroscopy. The final concentration has been chosen on the basis of previous studies made by us as well as by other research groups [2, 16].
2. EXPERIMENTAL

2.1 Materials

Analytical grade chemicals and distilled deionized water were used for all samples preparations. AgNO₃, NaBH₄, sodium citrate, aqueous solution of NH₃, NaOH, D-glucose, 4,4',4",4"′-(21H,23H-porphine-5,10,15,20-tetrayl)tetrakis(benzenesulfonic acid), TSPP, 4,4',4",4"′-(21H,23H-porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid), TCPP, and (5,10,15,20-tetakis(4-trimethyl-ammoniophenyl)porphyrin tetra(p-toluenesulfonate), TTMAPP) were used as received without any further purification. The glassware was cleaned by diluted nitric acid (1:1), extensively rinsed with distilled water and subsequently with deionized water. Alternatively, the mixture of sulphuric acid and hydrogen peroxide (1:1) was used, particularly when the glassware was polluted with porphyrin molecules.

2.2 Preparation of colloids

Ag colloids were prepared by different methods. Agbh were prepared by reduction of AgNO₃ by NaBH₄ [2]: 3.5 mg of NaBH₄ in 75 mL of distilled deionized water was cooled to 4°C. To this solution, 7.5 mL of 2.2 x 10⁻³ M aqueous solution of AgNO₃ (precooled) was added dropwise with constant stirring (100 rpm). Stirring was continued without interruption for 45 min. The resulting silver colloid was bright yellow with maximum wavelength of surface plasmon absorption at 395 nm. This colloid has average zeta potential -41 ± 9 mV and size of nanoparticles by DLS was 13 ± 2 nm.

Second colloid (AgCit) was prepared by dissolving 45 mg AgNO₃ in 250 mL distilled deionized water and brought to boiling. A solution of 1% sodium citrate (10 mL) was added. The solution was kept on boiling for ca. 1 h [4]. The resulting colloid was still centrifuged at 4000 rpm. AgCit has maximum wavelength of surface plasmon absorption at 410 nm. This average zeta potential was -37 ± 15 mV and size of nanoparticles by DLS was 52 ± 10 nm.

Next silver colloid AgG was prepared by the modified Tollens method [5]: 20 mL of 5 x 10⁻³ M aqueous solution of AgNO₃, 20 mL of 0.025 M aqueous solution of NH₃, 4 mL of 0.24 M aqueous solution of NaOH and 36 mL water was mixed. Under stirring was added 20 mL of 0.05 M aqueous solution of glucose. After 10 minutes stirring the gray colloid done. AgG has maximum wavelength of surface plasmon absorption at 415 nm. This average zeta potential was -32 ± 19 mV and size of nanoparticles by DLS was 75 ± 15 nm.

2.3 Preparation of SERRS-active systems

Were prepared stock solutions of the porphyrin concentration of 10⁻⁴ M that were used to prepare the SERRS active systems. To 1.5 mL Ag colloid was added 15 μL porphyrin. For TCPP were prepared systems with Agbh, AgCit and AgG. The same systems were prepared for TSPP and TTMAPP.

2.4 Instrumentation

DXR Raman microscope (Thermo Scientific, Nicolet CZ) equipped with a macro-sampling holder and thermoelectrically cooled CCD detector (-50 °C) was used for all SERRS spectra acquisition. The excitation wavelength of 532 nm of a diode-pumped solid state laser was used and set to the power of 10 mW at the sample. The samples were placed in a 1 cm quartz cuvette. Raman scattered light was collected in a 180° geometry, with the exposition time of 5 s, repeated 16 times.

UV-visible spectra were measured using Specord S600 (Analytic Jena). DLS and zeta potential were recorded on Zetasizer Nano Series (Malvern Instruments).

3. RESULTS AND DISCUSSION

According to the literature [1,2], two SERRS spectral forms of TCPP can be detected on silver surfaces: metallated (i.e. Ag atom incorporated in the center of porphine macrocycle) and/or non-metallated (free
base). The former can be clearly distinguished in SERRS spectrum by the appearance of characteristic bands (so called metallation markers) located at ~380 (390), 1340, and 1540 cm\(^{-1}\). Our SERRS spectra of TCPP introduced into the Ag colloids, prepared by three different procedures, and recorded in given time intervals are shown in Figs 1A-C. While in the case of borohydride-reduced (Agbh) colloid (Fig. 1A), the metallation markers tend to appear in the 19\(^{th}\) minute; there are no such bands detected in the cases of citrate-reduced (AgCit) and glucose-reduced (AgG) colloids in the same time interval elapsed from the SERRS-active systems preparation, Figs 1B and 1C, respectively. Moreover, no SERRS signal is seen on AgCit colloid in the 19\(^{th}\) minute (Fig. 1B) and only Raman signal of free base TCPP is distinguished on AgG colloid in the 19\(^{th}\) minute (Fig. 1C). It can be thus concluded that surfaces of Ag nanoparticles differ in their abilities to detect TCPP in one of its SERRS spectral forms. This behavior can stem form the fact that Agbh is stabilized by an electrostatic bilayer created by inorganic ions (borrates), whereas the two others are surrounded by organic molecules (carboxylic and polycarboxylic anions).

Furthermore, the SERRS-active systems containing TCPP were measured in one week elapsed from their preparation and revealed all three metallation markers in Agbh (Fig. 1A) and AgG (Fig. 1C) colloids. On the contrary, only the 378 cm\(^{-1}\) band was detected in AgCit (Fig. 1B). This trend is maintained even after several weeks (Figs 1A-C). It could be explained by a slightly different orientation of TCPP on AgCit which is most probably induced by the organic anions (citrates) being present on AgCit nanoparticles. Citrates can serve as an orientation matrix for TCPP molecules similarly as it has been observed for porphyrins tested on nanoparticles prepared by laser ablation in the presence of citrate and citric acid in ref. [17].

In a very similar way, we investigated the possibilities of TSPP detection on the three types of Ag nanoparticles used in our study. This porphyrin can be again detected in two SERRS spectral forms as known from the literature [1]: metallated (manifesting itself by 355, 422, 1341 and 1541 cm\(^{-1}\)) and free base. Agbh (Fig. 2A) and AgCit (Fig. 2B) colloids revealed no signal of TSPP in the spectra recorded 19 minutes from the systems preparation. Just a few SERRS spectral peaks of TSPP were observed due to nanoparticles of AgG colloid (Fig. 2C). The situation dramatically changed after one week: TSPP on Agbh nanoparticles was fully metallated and several bands of free base TSPP form appeared on AgCit and AgG nanoparticles. However, the observation of all metallation markers of TSPP was never achieved in AgCit and/or AgG colloids measured during several weeks (Figs 2B,C). This is most probably caused by the presence of organic anions serving as an orientation matrix as it has been mentioned above already.
Fig. 1 SERRS spectra of TCPP (532 nm excitation) in (A) Agbh, (B) AgCit, (C) AgG colloids. Spectra of AgG and AgCit after 1 and 2 weeks were divided by 5 for the sake of clarity.

Fig. 2 SERRS spectra of TSPP (532 nm excitation) in (A) Agbh, (B) AgCit, (C) AgG colloids. Spectra of AgG and AgCit after 1 and 2 weeks were divided by 5 for the sake of clarity.

Last, but not least, SERRS spectra of TTMAPP on nanoparticles of Agbh, AgCit and AgG colloids were recorded (Figs 3A-C). Since in this case a cationic porphyrin is measured, it is not surprising that SERRS spectra are observed from the first minute after the systems preparation. Indeed, metallation markers of TTMAPP (382, 1343, 1540 cm\(^{-1}\)) were obvious in the SERRS spectrum of Agbh-TTMAPP system from the very beginning (Fig. 3A). The ratio of mettallation vs. free base form in Agbh-TTMAPP increased during the time as it can be seen from the relative intensities of the bands located for instance at ~380 and 320 cm\(^{-1}\), respectively (Fig. 3A). In the two other colloids (AgCit and AgG), no metallation markers appeared during the whole 43 min period elapsed from the SERRS-active systems preparation (Figs 3B,C). It should be noted that due to a rather fast aggregation of the systems containing TTMAPP, they could not be measured after one and/or several weeks.

Taking into account the data from the literature [8, 16] concerning the extent and kinetics of metallation of another cationic porphyrin, TMPyP (5,10,15,20-tetrakis(1-methyl-4-pyridyl)21H,23H-porphine), it can be generalized that Ag nanoparticles being surrounded by a shell of loosely bounded anions (e.g. borrates) are easily accessible to cationic porphyrins which are immediately metallated. On the other hand, Ag nanoparticles with organic molecules on their surfaces hinder the immediate metallation of cationic porphyrins and thus only free base forms are detected in short times after the SERRS-active systems preparation. The metallation can be enabled in longer times elapsed from the systems preparation [8] if lower concentrations of porphyrins used (otherwise the system collapses).
Fig. 3 SERRS spectra of TTMAPP (532 nm excitation) in (A) Agbh, (B) AgCit, (C) AgG colloids.

4. CONCLUSIONS

Two anionic and one cationic porphyrins were tested on silver nanoparticles prepared by chemical reduction driven by sodium borohydride, sodium citrate and glucose (in alkaline medium). Based on our data, SERRS spectral detection of the selected water-soluble porphyrins strongly depends on their charge in aqueous solutions and on the type of silver nanoparticles being exploited for SERRS measurements. While the SERRS signal of the cationic porphyrin can be immediately observed at low concentrations, the two anionic porphyrins in our study need an additional time in order to be detected. Moreover, their SERRS spectral forms differ on Ag nanoparticles prepared by the three employed procedures due to the presence of significantly different ions which stabilize these Ag nanoparticles in aqueous solutions.

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LITERATURE


