Surface enhanced Raman spectroscopy of fullerene C\textsubscript{60} drop-deposited on the silvered porous silicon

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Abstract. Surface enhanced Raman spectroscopy (SERS) of fullerene C\textsubscript{60} drop-deposited from the 1.4 \times 10^{-4} \text{M} aqueous solutions on the silvered porous silicon (Ag/PS) is reported for the first time. The used concentration is found to be not detected by the ordinary Raman spectroscopy. It is shown that SERS-spectrum of the fullerene deposited from the air-aged solution are characterized by less intensity than that of the fullerene solution kept out of the air. This indicates degradation of the fullerene solution due to oxidation. The results are prospective for the fast qualitative and quantitative analysis of the fullerene-based materials.

Introduction

Closed cage structures of carbon atoms such as C\textsubscript{60}, C\textsubscript{70}, C\textsubscript{76}, C\textsubscript{84} molecules are called fullerenes. In these molecules, atoms of carbon are located at the vertices of regular hexagons or pentagons that cover the surface of sphere or spheroid. C\textsubscript{60} occupies special position among all the fullerenes. This molecule demonstrates the highest symmetry and, as a consequence, the greatest stability. Fullerenes are characterized by a number of unique properties including high sorption capacity, photoconductivity, mechanical strength, low surface energy, biocompatibility, etc. Thorough study of these features can lead to the breakthrough in the areas of materials’ strengthening, energy storage, catalytic systems, micro- and nanoelectronics and biomedicine [1]. Accurate qualitative and quantitative analysis of the fullerenes is an urgent task to realize their successful application. Considering biomedicine, this problem has to be overcome at very low concentrations to control fullerene transfer through biological membranes, accumulation in proteins or cells and interaction with other submicron bioorganic objects. Scanning tunneling microscopy, nuclear magnetic resonance spectroscopy, different methods of vibrational spectroscopy have been used to study the fullerenes [2]. Since the beginning of fullerene discovery its Raman frequencies have been calculated [3] and measured [2]. Theoretical analysis [4] showed that 46 fundamental modes can be distinguished from the 174 possible types of C\textsubscript{60} molecular vibrations. Two of these modes are characterized by Ag symmetry, one – A\textsubscript{1g}, three – T\textsubscript{1g}, four – T\textsubscript{1u}, five – T\textsubscript{2u}, six – G\textsubscript{s}, six – G\textsubscript{u}, eight – H\textsubscript{g} and seven – H\textsubscript{u}. Vibrational modes of the T\textsubscript{1g} symmetry are active during registration of the optical absorption spectra, those of the H\textsubscript{g}, A\textsubscript{g} symmetries are active in Raman spectroscopy, while the other types of oscillations can’t be detected by optical methods. Remarkable advantage of Raman spectroscopy comparing to other techniques is in possibility to realize SERS effect. This means enormous enhancement of the Raman intensity by study of analyte adsorbed on the nanostructured metallic surfaces that are usually called SERS substrates. SERS spectroscopy allows to detect and investigate trace amounts of substances and thus is very attractive for the study of fullerenes. Several approaches of registration of C\textsubscript{60} SERS spectrum in nonaqueous Ag and Au colloidal systems have been already developed [5, 6]. These methods provide good sensitivity,
however, the solvent media contributes to the resulting Raman spectrum. That is why it requires to make additional manipulations to see only the Raman spectra of fullerenes. In this work, we propose to solve such a problem by using SERS substrate based on porous silicon (PS). PS covered with metallic nanostructures can be used as an effective SERS substrate [7]. In this work, we were able to register intensified Raman scattering of the C_{60} fullerene thanks to the SERS substrate composed of silver nanoparticles on PS (Ag/PS). According to our knowledge, such results have not been previously published.

Experimental

Fabrication of SERS substrates based on PS consists of two major steps: formation of porous template and deposition of metallic nanostructures on its surface. PS was fabricated by an electrochemical anodization of n-type silicon wafer in electrolyte of HF, deionized H_2O and C_3H_7OH mixed in the volume ratio 1:3:1. Prior to anodization process silicon wafer was cleaned in a solution NH_4OH, H_2O_2 and H_2O mixed in a volume ratio of 1:1:4. To remove native oxide from silicon wafer 4.5 % HF aqueous solution was used. Thickness of the PS layers is 5 µm and an average pore diameter is 60 nm. Silver nanostructures were formed on PS by a chemical deposition from aqueous solution of AgNO_3. Deposition process was carry out at room temperature. Before applying of analyte SERS-substrates were rinsed in HCl aqueous solution to remove contaminants which adsorbed on the surface of the substrates from environment. Fullerenes C_{60} were drop-deposited on the Ag/PS substrate from the air-aged and kept out of the air aqueous solutions and then dried at 21°C. Concentration of the fullerene solutions was 1.4·10^{-4} M. SERS-spectra of fullerene were recorded with the 3D scanning confocal microscope Confotec NR500 using 633 nm laser and signal accumulation time 1 s. The laser spot varied in the 500 nm range while power of laser beam coming from the microscope objective was about 0.68 mW.

Results and discussion

Combinations of PS morphologies and regimes of metal deposition give rise to create the metallic nanostructures with fascinating SERS characteristics. In this work we used regimes of Ag/PS samples formation favourable for the most effective SERS according to [7]. SERS substrates presented silver nanostructures on the external surface of PS with an average size of silver nanoparticles in the range varying from 50 to 300 nm. Figure 1 shows SEM images of the virgin Ag/PS samples and those after drop deposition of the fullerene C_{60} at different magnifications. It is well-seen that the analyte is non-uniformly distributed on the Ag/PS surface (Fig. 1, b). Figure 1, f presents enlarged top view of the fullerene-coated Ag/PS. Following this image fullerene molecules formed the fullerite crystals with dimensions of 150 – 360 nm that are coalesced in aggregates of sizes varied in the range from 50 to 100 µm. Figure 2 shows the results of the SERS measurements of fullerene C_{60} drop-deposited on the SERS substrates. Measurements of the ordinary Raman spectra of fullerene deposited on the glass plate, samples of the silicon wafer and Ag-free PS were impossible due to low concentration of the carbon nanostructures. Both spectra in Figure 2 have three prominent bands of fullerene C_{60} such as H_g(1), A_g(1) and A_g(2) [8]. The last one has the highest intensity and corresponds to the “pentagonal pinch” mode. It is known that the shift of this mode is caused by the symmetry breaking of the fullerene molecule. For instance, this can be observed at the molecule polymerization. Linear polymerization is accompanied by the A_g(2) shift from 1470 to 1459 cm\(^{-1}\) [9]. The peak position at 1464 cm\(^{-1}\) is usually connected with formation of C_{60} dimer or C_{60}O_2 [10]. The A_g(2) band of the kept of air fullerene is most intensive near the 1466 cm\(^{-1}\) while the maximum of the same band of the air-aged sample is shifted to the 1464 cm\(^{-1}\) position indicating the stronger oxidation of the last one. Both samples have a left shoulder in the A_g(2) band extending to 1459–1460 cm\(^{-1}\) which shows a presence of a small amount of the polymerized fullerene molecules. This occurs due to C_{60} photopolymerization at the natural light. The bands H_g(1) and A_g(1) of the air-aged sample are slightly red-shifted. The kept out of the air sample is also characterized by weak bands H_g(2) – H_g(8) typical for fullerene C_{60} [8]. The marked bands in the SERS spectra correspond to ten vibrational modes of fullerene C_{60} (A_{2v}, H_{g}) which are
Raman-active [4]. SERS intensity of the air-aged sample is about four orders of magnitude lower than that of the other sample. These results are caused by the changes in the fullerene structure due to oxidation of the air-aged sample and its destruction.

**Figure 1.** SEM images of the Ag/PS substrates (a, c, e) before and (b, d, f) after C$_{60}$ deposition.
Figure 2. SERS-spectra of fullerene C_{60} deposited on Ag/PS from (a) kept out of air and (b) air-aged solutions.

Conclusion

We showed that Ag/PS can be used as effective SERS substrates for the detection and study of the structure of the submolar concentration of the fullerene C_{60} aqueous solutions. Structural changes of the air-aged fullerenes in comparison with the kept out of the air samples were revealed. The both fullerene samples were photopolymerized. At the same time, the air-aged sample was much more oxidized in comparison with the kept of the air fullerene solution. The obtained results open new opportunities for the precise control of the fullerene properties in different materials.

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