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PHYSICS

Amplification of a Raman Scattering Signal by Carbon Nanotubes

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Abstract—The effect of Raman scattering (RLS) signal amplification by carbon nanotubes (CNTs) was studied. Single-layered nanotubes were synthesized by the chemical vapor deposition (CVD) method using methane as a carbon-containing gas. The object of study used was water, the Raman spectrum of which is rather well known. Amplification of the Raman scattering signal by several hundred percent was attained in our work. The maximum amplification of a Raman scattering signal was shown to be achieved at an optimal density of nanotubes on a substrate. This effect was due to the scattering and screening of plasmons excited in CNTs by neighboring nanotubes. The amplification mechanism and the possibilities of optimization for this effect were discussed on the basis of the theory of plasmon resonance in carbon nanotubes.

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INTRODUCTION

The Raman scattering signal amplification effect produced by the interaction of light with rough or extensive conductive surfaces is widely used for the analysis of small molecular contaminants in materials and compounds, the diagnostics of diseases, and the detection of explosive and poisoning agents in safety systems, etc. [1–4]. The object used to amplify the Raman scattering signal is usually nanostructured surfaces or wires of noble metals. In this case, the amplification of a Raman scattering signal on certain molecules under optimal conditions may attain the level of 10^8–10^{11}, thus opening up a principal opportunity for the detection of ultrasmall substance amounts and even individual molecules. Despite the yearlong efforts of researchers, there is no sufficiently complete predictive theory for this effect until now. The dependence of the amplification magnitude on the structure of molecules generating a Raman scattering signal remains unclarified. This is caused by difficulties in the theoretical description of the simultaneous interaction between molecules, the electromagnetic field, and conductive substrates of different structure. In such a situation, the main source of information about the specific features of the surface enhanced Raman scattering (SERS) effect is experiments.

The interpretation of the SERS phenomenon results in an analogy with the effect of constant electrical field amplification near sharpened conductors. This effect has been studied rather well due to the development of studies aimed at the creation of CNT-based cold field emitters [5–9]. Using such an analogy, it is possible to conclude that the most efficient amplification of a Raman scattering signal should be expected when carbon nanotubes with an aspect ratio at the level of 10^2–10^3 are applied. The objective of our work is to perform the experimental detection and discussion of the Raman scattering signal amplification effect in the presence of carbon nanotubes.

EXPERIMENTAL

Carbon nanotubes were grown on a silicon substrate by the chemical vapor deposition (CVD)

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Table 1. Typical CNT synthesis parameters

Stage	T, °C	t, min	Ar, sccm*	H_2, sccm	CH_4, sccm	Total pressure, Torr
1	0	10	250	100	200	0
2	1000	60	200	0	0	0
3	1000	20	200	0	0	0
4	1000	10	0	100	0	10
5	1000	20	0	100	200	10
6	1000	20	200	0	0	0
7	200		200	0	0	0

*sccm is one standard cubic centimeter per minute (in terms of atmospheric pressure).

method. The growth catalyst was mixture of $Fe(No_3)_3$ and MoO_2 particles, which were deposited onto the substrate using an aqueous suspension with different contents of particles (0.15 mg/mL for catalyst A and 0.015 mg/mL for catalyst B). A suspension drop was deposited onto the substrate, which was placed into a centrifuge. Centrifugation resulted in a uniform suspension coating on the substrate. As a result of drying, the substrate was covered with a uniform array of mixture of $Fe(No_3)_3$ and MoO_2 particles, the size and density of arrangement of which depended on the suspension concentration. The synthesis of carbon nanotubes was performed on a Planar Tech setup in a quartz glass tube placed into a furnace. The typical CNT synthesis parameters are given in Table 1.

The typical microphotos of CNT arrays grown with the use of catalysts A and B are shown in Fig. 1. These microphotos were taken with the use of a JEOL scanning electron microscope. Unordered aggregates of CNTs of 10–30 nm in diameter can be seen in the photos, where the density of tubes synthesized with the use of catalyst A appreciably exceeds the value for catalyst B.

Raman spectra were measured on a WITec alpha 300 Raman spectrometer based on a confocal microscope. Distilled water drops with a volume of 20 μL were deposited onto the surface of samples. A Raman scattering signal was excited with the use of laser radiation with a wavelength of 532 nm (the second laser radiation harmonic on neodymium glass) and a power of 3 mW. The exposure time was 3 s, and the number of averagings was 5. Measurements were performed with the use of a 10×/0.25 objective lens. Raman spectra were recorded using an Andor spectrograph with a charge-coupled device (CCD) matrix cooled to –60°C.

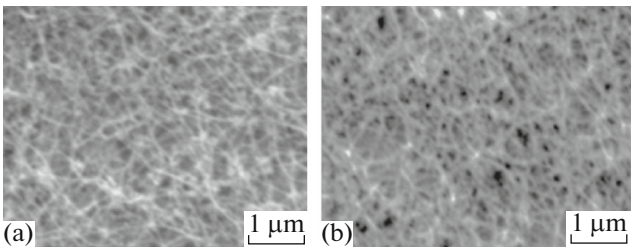

Fig. 1. Microphotos of the arrays of CNTs synthesized with the use of catalysts (a) A and (b) B.

RESULTS AND DISCUSSION

The typical Raman spectra of water molecules in the absence and presence of CNTs are shown in Fig. 2 (curves *1* and *2*, *3*, respectively). It can be seen that appreciable amplification of the Raman scattering signal is observed for CNTs synthesized with the use of catalyst B. In this case, the amplification coefficient (the ratio between the signal intensities in the presence and absence of CNTs) attains several hundred percent. Such an amplification, which is not so great from the SERS viewpoint, can be explained by the fact that the fraction of water molecules that are located in the neighborhood of nanotube tips and subjected to amplification, is very small in comparison with the total mass of water, which is a Raman scattering signal source. Indeed, as follows from the experiments [10], the Raman scattering signal amplification effect is implemented at a distance from the amplifying object of no more than 40 nm. Thereby the water volume subjected to the amplification effect is nearly $V_a \sim 10^{-16}$ cm^3, being approximately 10^{-14} of the total volume of a water drop ($V_w \approx 0.02$ cm^3). We suppose that the major Raman scattering signal amplification mechanism is associated with the electrical field amplification effect on extensive conducting wires, which are carbon nanotubes. The maximally possible amplification is attained in "metallic" CNTs, if the effective plasma frequency is much greater than the frequency of exciting radiation, and the length of CNTs is less than the electron free path. The maximally possible electrical field amplification coefficient in the neighborhood of a CNT tip is almost equal to the aspect ratio of the nanotube, i.e., $\alpha \approx L/D$ (length-to-diameter ratio) [5–9]. The SERS signal amplification coefficient is proportional to α^4 [1–4], the order of magnitude of which is 10^{12}. However, this result should be multiplied by the ratio of volumes $V_a/V_w \sim 10^{-14}$ and the number N_{CNT} of nanotubes, which make a contribution to the amplification effect.

Measurements show that the Raman scattering signal amplification effect increases with a decrease in the density of nanotubes on the substrate. This unexpected result may be associated with the screening of an electrical field [5–9] and the scattering of plasmons excited in CNTs by incident radiation.

We presume that the Raman scattering signal amplification effect considered is caused by the appearance of plasmon resonance in nanotubes with metallic conductivity. Let us remember that the frac-

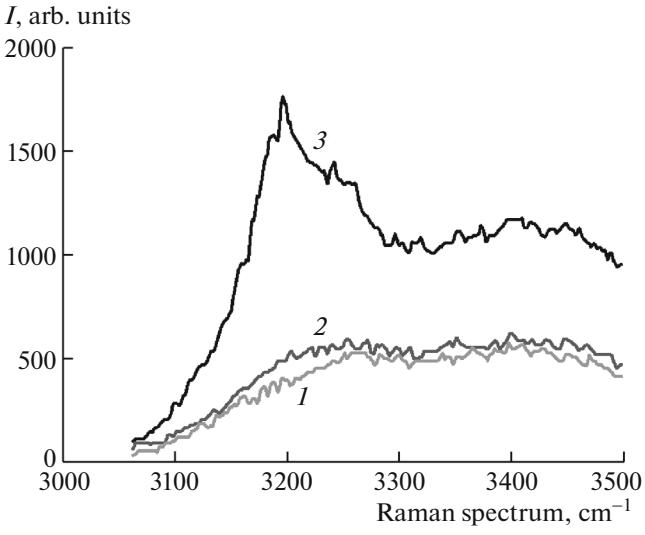

Fig. 2. Raman spectrum of water (*1*) without CNTs and with CNTs synthesized with the use of catalysts (*2*) A and (*3*) B.

tion of such nanotubes is nearly 1/3 of the total amount of CNTs, when the standard approaches to their synthesis are used. Plasmon resonance can be efficiently excited in tubes for which the length is less than the electron free path [11–14]. The value of this parameter depends on the concentration of structural defects in CNTs and usually lies within the range of 0.5–1 μm [15]. The presence of tubes with a great length may efficiently decrease the Raman scattering signal. Electrons "move" over the surface of the tube, and the function ψ goes outside the boundary of CNTs up to a distance of several sizes of a unit cell, i.e., $H \cong 0.25$ nm. When two CNTs intersect each other, the electrons of one tube "cling" to the other tube and the free path length decreases. The probability p_2 for the intersection of CNT with a length $2a$ with other tubes can be found from the elementary probability theory as $p_2 = 1 - \exp(-2pa/\pi b)$, where a is the length of a nanotube, b is its diameter, and p is the surface density of tubes. The average number of intersections $w(a) = p_2/(1 - p_2)^2$ depends exponentially on the tube length. If $w(a) \sim \exp(4pa/\pi b) \gg 1$, plasmon resonance is damped and CNTs of such a length do not participate in the amplification of the field. Hence, the summary field and Raman scattering signal amplification begin to decrease, when the critical concentration $p = p_c \sim b/a \ll 1$ is exceeded. Let us note that the obtained estimate for the critical concentration $p_c \sim b/a$ coincides with the percolation threshold in a two-dimensional system of elongated aciculae [11]. Electrons cannot only be reflected at the point of intersection between two CNTs, but also skip between tubes. The kinetic theory for the motion of electrons in a system of intersecting CNTs is a problem for further studies. However, the estimates presented here show that the greatest amplification should be expected in nematic structures, in which tubes do not intersect each other at all.

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