PHYSICAL REVIEW A **83**, 013820 (2011)

High-order harmonic generation in carbon-nanotube-containing plasma plumes

R. A. Ganeev,[1,2,*] P. A. Naik,[1] H. Singhal,[1] J. A. Chakera,[1] M. Kumar,[1] M. P. Joshi,[1] A. K. Srivastava,[1] and P. D. Gupta[1]
[1]*Raja Ramanna Centre for Advanced Technology, Indore 425013, India*
[2]*Institute of Electronics, 33, Dormon Yoli Street, Tashkent 100125, Uzbekistan*
(Received 20 August 2010; published 24 January 2011)

High-order harmonic generation (HHG) in carbon-nanotube (CNT)-containing plasma plumes has been demonstrated. Various targets were ablated to produce the plasma plumes containing nanotubes for the HHG in these media. Harmonics up to the 29th order were generated. Odd and even harmonics were generated using a two-color pump. The integrity of CNTs within the plasma plume, indicating nanotubes as the source of high-order harmonics, was confirmed by structural studies of plasma debris.

DOI: 10.1103/PhysRevA.83.013820 PACS number(s): 42.65.Ky, 61.46.Fg, 78.67.Ch

I. INTRODUCTION

Carbon nanotubes (CNTs) have remarkable electronic and optical properties due to their particular structure combining one-dimensional solid-state characteristics with molecular dimensions. While their structure has extensively been studied by means of transmission electron and scanning tunneling microscopy, only few experimental studies have been reported on their nonlinear optical properties. Single-walled CNTs have a synthetic structure and from a structural point of view, they are graphene sheets rolled up into rather long cylindrical tubes [1]. The resulting low dimensionality determines most of the electronic properties relevant for the nonlinear optical response of single-walled CNTs. The quantum confinement of the delocalized p electrons in single-walled CNTs along the axis of symmetry of the cylinder, with the consequent minimization of the p-s electron mixing effects, is expected to enhance the third-order nonlinear optical response of single-walled CNTs with respect to other carbon-based structures such as fullerenes [2].

Past studies on the nonlinearity of CNTs have shown that CNTs possess much larger nonlinearity than other nonlinear materials [3–8]. The strong nonlinearity of single-walled CNTs prompted researchers to study their generation of high-order harmonics, motivated by the development of coherent extreme ultraviolet or soft x-ray pulsed sources [9], and to want to understand the electron dynamics of single-walled NTs in the intense laser field as well. Thus, the motivation for our studies of the high-order harmonic generation (HHG) in CNTs is based on the interest in the application of this medium to obtain the enhanced harmonic yield, as well as on the demand to understand the conditions when this enhancement occurs.

There are a few other reasons that can be given as to why the HHG by CNTs is of interest. The pronounced electron nonlinearity in CNTs with the two-dimensional confined electron distribution on the surface shows some potential for the generation of high-order harmonics and could thus represent a useful mechanism for the generation of coherent ultrashort light pulses at very short wavelengths. Next, the method considered here allows the generation of radiation with very short wavelengths in a device confined to a very small region. Finally, the spectra of the harmonics are expected to provide useful information on the dynamics of electron motion in CNTs [10].

More specifically, in Ref. [11], they have shown that CNTs should demonstrate some odd harmonics at some specific orders (19th, 21st, 39th, 41st, etc.) with *circularly* polarized light. Since such a thing is not predicted for any other target, it is interesting to analyze such an option. Hence, experimental verification of this prediction has been also one of the motivations of our study.

One has to note that most of theoretical predictions are still mostly unexplored experimentally. The main reason is that single-walled CNTs easily form bundles (or "ropes"), consisting of different tube types, due to their strong van der Waals forces. This results in significant broadening, smearing out any chirality-dependent features [12].

The nonlinear optical studies of CNTs have been limited so far to second and third harmonic generation of laser radiation [13–15] and measurements of third-order susceptibility [16]. In particular, in Ref. [15], third harmonic generation from solid samples of CNTs has been studied experimentally, using ultrashort pulses generated by a Cr:forsterite laser, at a wavelength of 1250 nm. Their results show an unusual nonperturbative behavior of the third harmonic yield, for relatively low-input laser fields at intensity $\sim 10^{10}$ W cm^{-2}. Second and third harmonic generation in single-walled CNT films, using the fundamental 1064-nm radiation from a Q-switched Nd:yttrium aluminum garnet laser, has also been investigated [17]. The reported measurements were performed both on commercially available CNTs and on samples of CNTs grown with a catalyst-free method. Third harmonic generation was observed in both samples, while second harmonic generation was observed only on the sample grown by catalyst-free method. Evidence for second-order nonlinear optical activity in CNTs has also been demonstrated in a second-harmonic-generation experiment performed at a femtosecond time scale [18].

By adding a field to the fundamental one, the harmonic spectrum exhibits many new features. For example, with the combination of a fundamental field and its second-order harmonic, both even and odd harmonics can be generated by sum and difference frequency mixing [19,20]. Some harmonics, which cannot be observed in the monochromatic case, can be produced in a bichromatic field. The enhancement

---

[*] rashid_ganeev@mail.ru

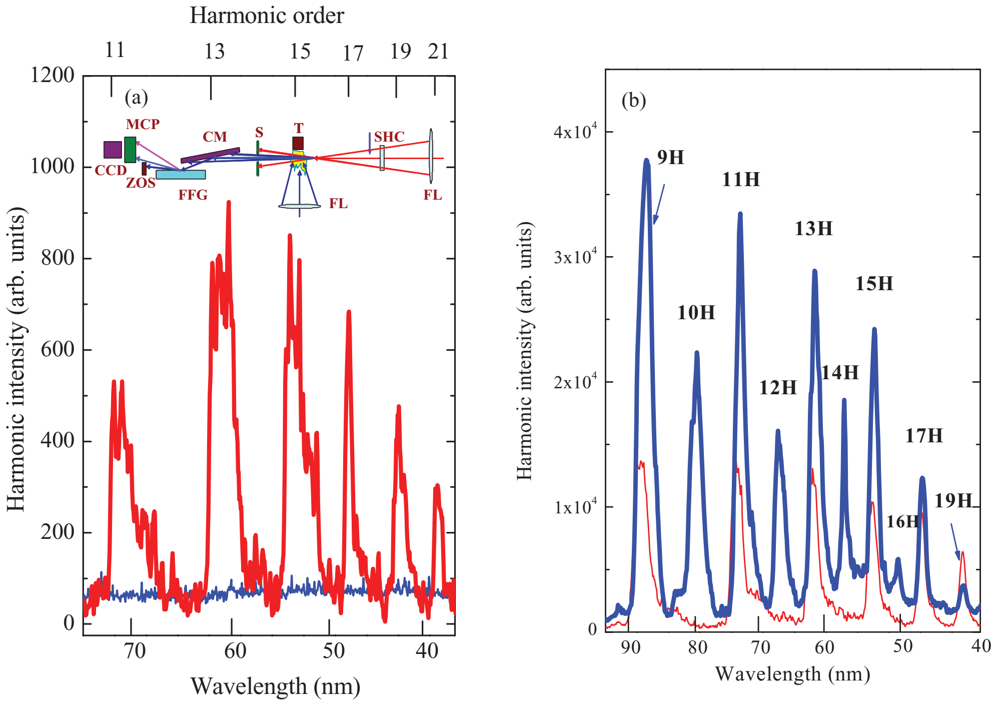

FIG. 1. (Color online) (a) Harmonic generation in CNT plasma in the case of linear polarization (thick curve) and circular polarization (thin curve) of the laser. (Inset) Experimental scheme. FL, focusing lenses; SHC, second harmonic crystal; T, target; S, slit; CM, cylindrical mirror; FFG, flat field grating; ZOS, zero-order beam stop; MCP, microchannel plate; CCD, charge-coupled device. (b) Comparison of the harmonics generation from carbon nanotube plasma plume, in the cases of single-color-pump (thin curves) and two-color-pump (thick curves) schemes.

of the HHG has been experimentally observed for both parallel and perpendicularly linearly polarized two-color fields. Two orders of magnitude intensity enhancement has been predicted theoretically in this HHG configuration. This has been recently demonstrated for atom- and ion-containing plasmas, where very intense odd and even harmonics were generated from various plasma plumes [21].

When intense laser fields are applied to the physical objects such as atomic systems and solid-state systems such as metallic clusters, and in particular CNTs, traditional perturbation theory is no longer suitable [22–24], and many phenomena, including HHG, cannot be understood by perturbative methods [25]. The theory papers on high harmonic generation in nanotubes, for example, Refs. [22] and [23], do not seem to rely on the "Corkum recollision model." There the specific "electronic structure" of the nanotubes seems to matter [22].

So far, only theoretical studies on the HHG in CNTs have been reported. The generation of high-order harmonics from a single-walled CNT interacting with a bichromatic laser field (fundamental and its second harmonic) has been investigated [26], where the nonlinear motion of electrons in metallic CNTs driven by intense laser fields has been studied and the induced current spectrum has been analyzed. The effect of variation of the intensity of the applied laser fields on electron current density and HHG has been investigated. Numerical calculations have shown that, with the application of the bichromatic laser field, both odd and even harmonics can be generated [26].

The HHG spectra of infinitely extended single-walled CNTs have also been theoretically studied [11,22,23,27,28]. Reference [23] shows that the high efficiency of HHG comes from the high density of states of conduction electrons in CNTs. In Ref. [11], it has been predicted that, in the case of CNTs, one should get harmonic emission at particular harmonics (19th, 21st, 39th, 41st, etc.) using circularly polarized laser light. HHG in open-ended and capped single-walled CNTs has been also studied theoretically [29]. It has been emphasized that single-walled CNTs can be ideal candidates to create coherent x-ray-pulsed sources because of the high efficiency of HHG. Our experiments confirm some of the theoretical expectations of the HHG in CNTs.

These works reveal the nonlinear optical properties of nanotubes. However, no harmonics generation above third order in CNT medium has been reported so far. Therefore, it is of interest to study the higher-order harmonics in CNTs under monochromatic intense laser fields. The plasma plume method is perhaps the only way by which one can study the HHG from CNTs. In this paper, we demonstrate experimental evidence of strong HHG in CNT-rich plasma medium created by laser ablation of CNT-containing targets. The main focus of this paper is the interaction of intense laser fields with the nanotubes in a specially prepared laser plasma, which gives efficient harmonic generation in the extreme ultraviolet (XUV) range under optimal experimental conditions.

II. EXPERIMENTAL

For laser ablation, a pump pulse (pulse duration, $\tau = 210$ ps; pulse energy, 20 mJ; wavelength, $\lambda = 800$ nm; pulse repetition rate, 10 Hz), which was split from the uncompressed Ti:sapphire laser pulse, was focused on a target placed in a vacuum chamber by using a plano-convex lens (focal length, $f = 500$ mm). The intensity of the pump pulse (I_{pp}) on the target surface was varied between 1×10^9 and 3×10^{10} W cm^{-2}. After 25–57 ns, the compressed main pulse (pulse energy, 40 mJ; $\tau = 48$ fs; $\lambda = 800$ nm) was focused on the plasma from an orthogonal direction (see inset in Fig. 1) using a plano-convex lens (focal length, $f = 500$ mm). The experiment was performed with femtosecond pulse intensity (I_{fp}) up to 7×10^{14} W cm^{-2}, above which the HHG efficiency decreased due to impeding processes in the laser plasma. The harmonics were spectrally dispersed by an XUV spectrometer with a cylindrical mirror and a flat-field grating (1200 lines/mm, Hitachi). The XUV spectrum was then detected by a combination of a microchannel plate and a phosphor screen. The images were recorded using a CCD camera.

The experiments were performed using the femtosecond pulse and its second harmonic. For second harmonic (SH) generation, a β barium borate (BBO) crystal (1 mm thick, type I phase matched) was placed between the focusing lens and plasma plume, so that, after propagation through the crystal, the laser field consisted of both the SH ($\lambda = 400$ nm) and the fundamental ($\lambda = 800$ nm) laser radiation. The intensity of the fundamental radiation inside the SH crystal was maintained at such a level that no phase modulation, significant chirp, or white-light generation were introduced in the laser radiation. The SH conversion efficiency at these conditions was 8%. The polarizations of SH and fundamental fields were orthogonal due to type I phase matching. These conditions were used in most experiments with CNT-rich plasmas. The confocal parameters of the two beams were the same, as the SH conversion was after the focusing lens. At these conditions, the two pulses had spatial and temporal overlap.

In the present study, single-walled CNT powder and two types of single-walled CNT-rich polymer composites were used as targets for laser ablation. Laser ablation technique was used to produce a plasma plume containing CNTs. Most experiments were carried out using CNT powder glued on glass substrates using fast-drying glue (superglue). The following procedure was used to fabricate CNT-doped polymethyl methacrylate (PMMA) composites. In the first case, CNTs were doped in PMMA directly, while in the second case, the CNTs were first dispersed in MMA solution (the monomer of PMMA) and then the resultant mixture was polymerized *in situ* using a suitable initiator. The reference sample (PMMA without CNTs) was also prepared by the same polymerization technique. Bulk carbon targets and C_{60} powder targets were also used for comparison of the HHG in the plasma plume containing CNTs, C, or C_{60}. The analysis of the morphology of the CNT powder and the deposited CNT debris was carried out using a transmission electron microscope (TEM).

III. RESULTS

In the case of CNT targets, an extended cutoff with harmonics up to the 29th order was observed. This is an experimental observation of the high-order harmonics generated in the CNTs. CNTs showed that they are stable against fragmentation in intense laser fields. This is probably due to very fast distribution of the excitation energy among the large number of carbon atoms present in the CNT.

To understand the origin of the harmonic emission in the CNTs, its dependence on the polarization of the driving pulse was investigated. This also enables one to differentiate between the plasma emission and the HHG process. HHG is highly sensitive to laser polarization (linear or circular), since the trajectories of the recolliding electrons are altered significantly by the polarization, thereby inhibiting the recombination process, leading to a decrease in HHG. The harmonic signal was observed to disappear with change of polarization from linear to circular. For circular polarization, as expected, the harmonic emission disappears and the resulting background spectrum corresponds only to the plasma emission. Figure 1(a) shows the harmonic spectra obtained from CNT-containing plasma plume, using linear and circular polarization. One can see that, for circular polarization of the laser radiation, no harmonics were generated, while, for linear polarization, the high-order harmonics were observed. So the experimental observation of total absence of any harmonics for circularly polarized light does not support the theoretical prediction in Ref. [11] that one should get harmonic emission at particular harmonics using circularly polarized laser light.

No systematic investigation of the dependence of the harmonics on the ellipticity of the laser beam was done during these studies. Probably it might have given more insight into the physical mechanism behind the harmonic generation in the plasma plume that contains CNTs. We present only two spectra, for linear and circular polarization. One has to note that this is not sufficient pro or contra the "Corkum model" for harmonic generation in nanotubes or the other theoretical approaches to describe harmonic generation in nanotubes.

Insertion of a 1-mm-thick SH crystal (BBO) in the beam path after the focusing lens led to the generation of enhanced harmonic yield and the appearance of even and odd harmonics with approximately equal intensities in the case of lowest observed harmonics. An enhancement of HHG efficiency was observed in the two-color case compared to the single-color 800-nm pump [Fig. 1(b)]. Even harmonics of the fundamental radiation up to the 16th order were obtained in these studies. The variation of laser chirp led to a change of harmonic generation efficiency of the odd and even harmonics. This was accompanied by tuning of the harmonic wavelengths, as well as increase in the harmonic efficiency for negatively chirped laser pulses.

Varying the temporal delay between the heating pulse and main pulse (from 25 to 57 ns) did not change the harmonic yield from CNT plasma considerably. By calibrating our detection system using a technique applied to harmonics from C_{60} plasma reported in Ref. [30], we estimated the efficiency of the harmonics in the range of 70–30 nm on the order of 8×10^{-6}.

Most of our studies were carried out at pump pulse intensities below 7×10^{14} W cm^{-2}. It may be noted that the harmonics were observed at higher pump pulse intensities as well. However, in that case, the harmonic spectra were different compared to those at moderate excitation of CNT-containing targets. This indicates that, at high excitation of a CNT target, the harmonic generation takes place in a mixture of neutral and ionized nanotubes, as well as fragmented CNT clusters, carbon atoms, and ions. It is difficult to define the relative output of harmonics from these plasma components in the absence of the analysis of the plasma by the time-of-flight technique. It is found experimentally that the intensity of the harmonics from CNT-rich plumes was stronger than those generated from plasma-rich plumes in single particles, created on the surface of bulk metal targets under the same experimental conditions.

The femtosecond pulse intensity is another important parameter, which can drastically affect the HHG in CNT. Figure 2 shows the harmonic spectra during single-color pump in the cases of focusing (a) in front, (b) inside, and (c) after the plasma plume. Focusing inside the CNT-containing plasma led to the appearance of strong plasma lines [Fig. 2(b)], which were identified with ionic transitions of carbon. Note that the intensity of the laser radiation in the plasma plume in that case was in the range of 10^{16} W cm^{-2}. Defocusing the femtosecond pulse before or after plasma plume led to creation of optimal conditions for harmonic generation, when most of impeding processes (such as disintegration of CNT, self-phase modulation, and phase mismatch due to growth of the free electron concentration) became diminished, the "clear" harmonic spectra were registered [Figs. 2(a) and 2(c)].

An interesting feature of the CNT harmonic spectrum is that the spectral width is about 3–5 times broader than harmonics generating in atom- and ion-rich plasmas. For example, full width at half maximum for medium-order harmonics was 1.5 nm in the case of CNTs versus 0.4 nm for different metal plasmas. Broader width of the harmonics can be explained by self-phase modulation (SPM) and chirping of the fundamental radiation propagating through the CNT plasma. Broadening of the main pulse bandwidth causes the broadening of the harmonic bandwidth.

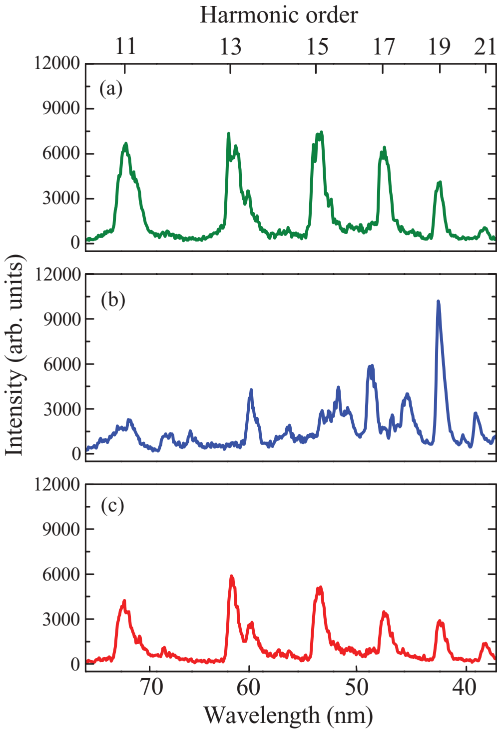

FIG. 2. (Color online) Harmonic and plasma spectra obtained from the CNT plasma during focusing of femtosecond pulse: (a) before the plasma plume, (b) inside the plasma plume, and (c) after the plasma plume.

In the case of SPM in laser plasma, one can expect a considerable variation of the harmonic spectrum compared to the case of moderate intensities of laser radiation, when no change in spectrum of the fundamental or harmonic radiation is expected. Such a variation of the harmonic spectrum was mostly governed by the modulation of the fundamental spectrum. A strong extension of the harmonic spectral distribution toward the blue side was observed, which shows that, in the case of CNT plasma, one can expect a considerable SPM and corresponding modulation of the harmonic spectrum. It may be noted that such lobes on the blue side of the harmonics were observed in the case of harmonics from graphite plasmas as well. Probably, the plasma conditions for these media were sufficient for achieving the SPM of the driving laser pulses. Note that, at overexcitation of targets, the harmonic spectrum was accompanied by the ionic transitions of highly ionized carbon atoms at 54, 46, and 38 nm.

The highest harmonic order achieved in the case of the CNT powder (glued to the glass substrates) was the 29th harmonic [Fig. 3(a)]. A comparative study of the harmonic generation from the plasma plumes produced on the targets containing (a) CNT powder, (b) CNT in PMMA, and (c) CNT in MMA showed that highest cutoff was in the case of CNT powder. The maximum intensity of harmonics in the plateau range was also achieved from the CNT-powder target, probably due to higher concentration of the nanotubes in the plasma plume compared with CNT in PMMA or CNT in MMA targets. At the same time, in the case of CNTs dispersed in PMMA, better shot-to-shot stability of harmonics was observed. In the case of CNT powder glued on the glass substrates, the harmonic yield considerably decreased after a few tens of laser shots on the same spot, due to depletion of CNT concentration, unless the target was moved to a fresh spot.

The difference in the intensities of harmonics presented on Figs. 1–3 is mostly related to different experimental conditions of collection of the XUV radiation by our registration system. As for the comparison of three types of CNT targets (powder, mixture of powder in PMMA, and mixture of powder in MMA), we have presented the relative intensities of harmonics in these three cases [Fig. 3(a)].

There is a drawback in the application of CNTs for HHG. On the basis of the work by Lenzner *et al.* [31], one can assume the appropriate ionization threshold intensity for CNTs as $I = 10^{14}$ W cm^{-2}. The ionization is expected to take place above this threshold. Besides causing irreversible damage to the nanotube sample, the breakdown would be accompanied by the free electron generation having a negative effect on the propagation of the emitted harmonics. The limitation in applied laser intensity can restrict the available harmonic yield from this CNT-containing plasma.

One need not worry about the survival of CNTs during the interaction with femtosecond pulse. The HHG occurs during very short period equal to round-trip movement of ejected electron, which is much shorter than disintegration time for the CNTs. It means that nanotubes may disintegrate, but only after emitting the harmonics. The next laser shot produces new plasma with fresh nanotubes, which can be used for further harmonic generation.

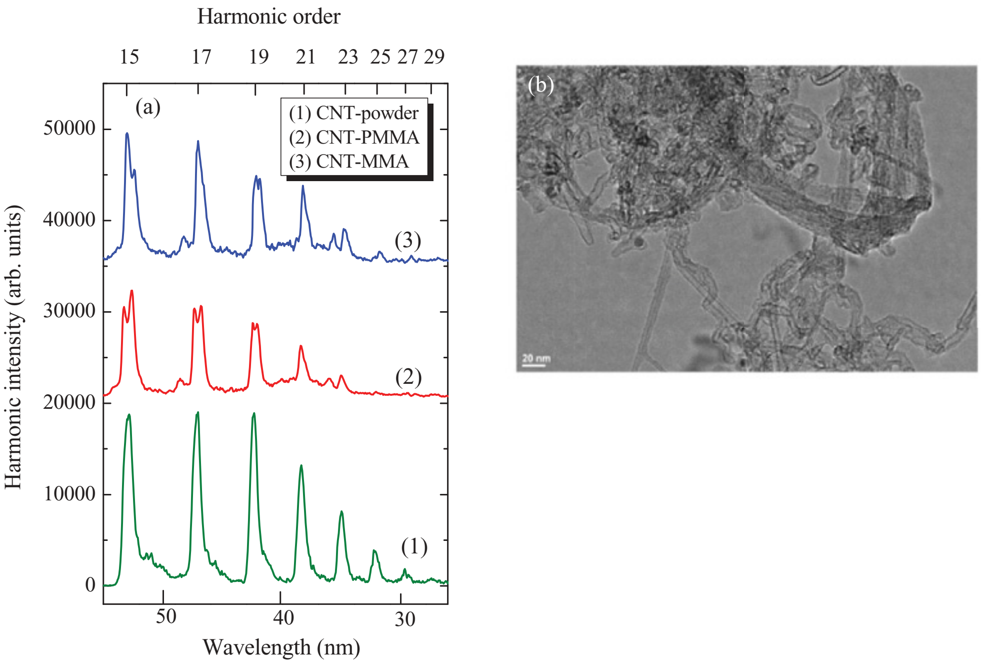

FIG. 3. (Color online) (a) Harmonic spectra observed from (1) CNT powder, (2) CNT in PMMA, and (3) CNT in MMA targets. The curves are shifted with regard to each other for better visibility. (b) TEM image of the deposited CNTs. The length of the marked line is 20 nm.

We used the CNT powder, which was glued on the substrates, to ablate and produce the plasma plume. An analogous technique was established earlier in the experiments with fullerene powder. In those studies [32,33], the C_{60} powder was also glued using superglue on the substrate and then ablated to create the fullerene-containing plasma. Exact measurement or calculation of fullerene or CNT concentration in the ablation plume is difficult. In the bulk targets, simulation techniques based on the hydrodynamic code HYADES can accurately predict the atomic concentration [34]. However, when extended to nanoparticle-rich targets they provide only a rough estimate of the density due to a lack of information on the absorbance of these materials. For C_{60}, the fullerene density was estimated to be no less than 5×10^{16} cm^{-3}. Experimentally, under identical conditions, the concentration of the ablated material from CNT and fullerene powders is assumed to be the same, suggesting nearly identical densities.

The morphological characteristics of the targets prior to laser ablation were analyzed and compared with the ablated material debris deposited on a copper grid and carbon film. The diameter of the CNTs glued on the substrates was 3–6 nm, with length varying from 0.3 to 10 μm. The debris of the plasma plumes was studied at various pump pulse intensities. At a pump pulse intensity in the range of 3×10^{9}–2×10^{10} W cm^{-2}, CNTs were observed to be deposited. Figure 3(b) shows the TEM image of the deposited CNTs ($I_{\text{pp}} = 7\times10^{9}$ W cm^{-2}). No harmonics were observed during ablation of pure PMMA, superglue, or the glass substrate alone, without CNTs. The above-described morphology and HHG results indicate the ability of CNT to survive a strong excitation and also that the HHG originates from unfragmented nanotubes. From the above observations, one can conclude that CNTs are responsible for HHG.

IV. DISCUSSION

According to the semiclassical and quantum-mechanical theories, high harmonics are produced in the strong-field regime due to electron tunneling to the continuum and their return to the parent particle under the action of the oscillating field. The recollision of the electrons with the nucleus results in the emission of coherent, high-order odd harmonics of the laser irradiation in forward direction. The harmonic spectrum has a very characteristic shape: It falls off for the first few harmonics, then exhibits a plateau when all the harmonics have approximately the same intensity, and ends with a sharp cutoff. This mechanism is the same for both harmonics from gas particles and harmonics from plasma particles. In the case of CNT plasma harmonics, the fast drop of lowest-order harmonics, plateaulike distribution of higher harmonics, and abrupt cutoff were observed.

The coherence of plasma harmonics was confirmed by the focusing properties of converted radiation. The harmonics could be focused down to few tens of micrometers, while the incoherent radiation from the plasma plume was focused at analogous conditions down to few millimeters.

In our studies, we confirmed the expectations about this medium as the promising one for efficient conversion of IR radiation toward the extreme ultraviolet range. The physical reasons of the observed enhanced harmonic generation from CNT-containing plasma plumes could be as follows.

(1) One can assume that, in the case of clusters, the ejected electron, after returning back to the parent particle, can recombine with any of the atoms in the cluster (in our case, CNT), leading to enhanced cross section of the recombination with the parent particle compared with a single atom, which considerably increases the probability of harmonic emission in the former case. Thus, the enhanced

cross section of the recombination of accelerated electron with the parent particle compared with a single atom can be a reason for the observed enhancement of the HHG yield from the nanotube-containing plume compared with atom- and ion-containing plasma. Our experiments have confirmed this enhancement.

(2) The original electronic structure of the nanotubes mainly originates from the sp^2 hybridization of the carbon atoms, resulting in a greatly delocalized π-electron cloud along the tube axis. Theoretical studies show that this configuration leads to a strong enhancement of the nonlinear optical susceptibilities with a fast response time since these nonlinearities mainly result from electronic contributions [23,35,36]. Since CNTs also show striking stability under high light flux, they are expected to be a very promising material for new nonlinear optical devices.

(3) The quantum confinement of the delocalized π electrons in single-walled CNTs is expected to enhance the nonlinear optical response of CNTs. In addition, the quasi-one-dimensional structure of single-walled CNT gives rise to spikes in the spectrum of the electronic density of states which can strongly enhance the nonlinear optical response of single-walled CNTs once the excitation wavelength matches the energy difference between two such resonances [37].

(4) The material directly surrounding the nanotubes is a polymer (epoxy glue), which has a considerably lower ablation threshold than the metallic materials. Therefore, the CNT-carrying polymer begins to ablate at relatively low intensities, resulting in the lower laser intensity required for the preparation of the appropriate nonlinear medium for the HHG. This feature allowed for easier creation of the optimum plasma conditions, which resulted in a better HHG conversion efficiency from the CNT-containing plume compared to the plume from the bulk target.

(5) Throughout the description of our studies we assumed that there are no decomposition processes in the plume or nucleation on the substrates at optimal excitation of the CNT-containing targets. Arguments supporting these assumptions are based on our analysis of the deposited debris of nanoparticles. The structural studies of deposited CNTs confirmed the presence of the clusters of same morphology as initial nanotubes in the plasmas. This means that femtosecond pulses interact with CNTs during propagation through the plasma plumes.

(6) Nanotubes are members of the fullerene structural family. The fullerene medium has previously demonstrated both direct and delayed ionization and fragmentation processes during further interaction with femtosecond pulses. The ionization and fragmentation of fullerene plasma in moderate laser fields occur predominantly via multiphoton excitation of the 20-eV plasmon resonance of C_{60}. The experimentally observed survival of fullerenes at rather intense laser fields can be ascribed to the very large number of internal degrees of freedom of the fullerene molecule, which leads to the fast dissipation of the excitation energy followed by inefficient redistribution into ionizing and fragmenting modes. The same can be said about the ablation and maintenance of CNTs in plasma plumes. Our studies have confirmed the maintenance of CNTs in the plasma plumes at appropriate ablation of targets. These peculiarities of CNTs can be effectively used for the creation of the plasma medium containing a considerable amount of nanotubes for their further studies in laser-matter interaction.

(7) The stability of CNT molecules to ionization and fragmentation is of particular interest, especially for their application as a medium for HHG. The structural integrity of the nanotubes ablated off the surface should be intact until the driving pulse arrives. Therefore, the heating pulse intensity is a very sensitive parameter. At lower intensities the concentration of clusters in the plume would be low, while at higher intensities one can expect fragmentation. The CNT powder directly glued on the glass surface could survive for a longer time during interaction with pump pulse radiation. Our analysis of harmonic spectra at these conditions showed that harmonics could be observed over 100 shots on the same spot. The appearance of crater on the CNT-containing targets also induced the change of optimal conditions for the HHG in laser plasma. Hence, we implemented different types of CNT-containing targets and found that, in the case of CNTs dispersed in PMMA, the stability of harmonics increases due to less depletion of nanotubes.

(8) It has been underlined in literature that, from a practical point of view, the nanotube targets lack a number of serious drawbacks, which are characteristic of the molecular ones [22]. Unlike the molecules, the nanotubes can be oriented in space just like solid targets. Arrays of nanotubes parallel to each other can be achieved by present-day methods [38]. The chemical bonding between carbon atoms in nanotubes is rather strong, which means that their deformation and dissociation in intense fields take place on longer time scales than that of aromatic molecules. The lack of light hydrogen atoms in nanotubes contributes to the stability effect. Moreover, the potential significance for the generation of the coherent, almost monochromatic, high-frequency radiation, the HHG by CNTs can be used for the structural analysis of the nanotube samples. The relative strengths of the harmonics allowed for different nanotubes can provide information about the relative abundances of the various symmetry species in a nanotube sample.

The above assumptions support our phenomenological observations of high conversion efficiency of laser radiation in the plasma plumes containing CNTs.

V. CONCLUSIONS

In conclusion, the main message of this paper is the observation of HHG in nanotubes. The method employed to observe HHG in nanotubes is not new (see the Refs. [21] and [30] where the HHG was observed in fullerene-containing plumes). In our present work, we applied this method for plasma formation on the surfaces containing CNTs and successfully generated harmonics (up to the 29th order) in plasma plumes. The morphology of ablated CNTs before and after laser-induced deposition on substrates has been analyzed. It is observed that, at moderate laser intensity ($\leqslant 8\times10^9$ W cm^{-2}) of the 210-ps pump pulses on the surface of CNT-rich materials, the deposited material remains approximately the same as the initial nanotubes, while, at higher pump pulse intensity, the disintegration of CNTs takes place. The presence of CNTs in laser plumes allowed investigation of their high-order nonlinear optical properties. The HHG during two-color pump of CNT plasma, when enhanced even and odd harmonics were generated, has been demonstrated. The comparative studies of harmonic spectra from CNTs and fullerenes have shown better HHG efficiency in the latter case. One important negative result is the total absence of any harmonics observed for circularly polarized light, contradictory to the theoretical prediction in Ref. [11] that one should get the emission at particular harmonics using circularly polarized laser light in the CNTs.

ACKNOWLEDGMENTS

One of the authors (R. A. Ganeev) gratefully acknowledges the support from the TWAS-UNESCO Associateship Scheme. He also thanks Raja Ramanna Centre for Advanced Technology for financial support and the invitation to carry out this work.

---

[1] S. Iijima, Nature (London) **354**, 56 (1991).
[2] S. R. Flom, R. G. S. Pong, F. J. Bartoli, and Z. H. Kafafi, Phys. Rev. B **46**, 15598 (1992).
[3] O. M. Yevtushenko, G. Y. Slepyan, S. A. Maksimenko, A. Lakhtakia, and D. A. Romanov, Phys. Rev. Lett. **79**, 1102 (1997).
[4] G. Ya. Slepyan, S. A. Maksimenko, A. Lakhtakia, O. M. Yevtushenko, and A. V. Gusakov, Phys. Rev. B **57**, 9485 (1998).
[5] J. Dong, J. Jiang, J. Yu, Z. D. Wang, and D. Y. Xing, Phys. Rev. B **52**, 9066 (1995).
[6] X. Wan, J. Dong, and D. Y. Xing, Phys. Rev. B **58**, 6756 (1998).
[7] Y.-Z. Ma, L. Valkunas, S. L. Dexheimer, S. M. Bachilo, and G. R. Fleming, Phys. Rev. Lett. **94**, 157402 (2005).
[8] K. Watanabe, T. Taniguchi, and H. Kanda, Nat. Mater. **3**, 404 (2004).
[9] Ch. Spielmann, N. H. Burnett, S. Sartania, R. Koppitsch, M. Schnörer, C. Kan, M. Lenzner, P. Wobrauschek, and F. Krausz, Science **278**, 661 (1997).
[10] M. S. Dresselhaus, G. Dresselhaus, and Ph. Avouris, *Carbon Nanotubes* (Springer, Berlin, 2001).
[11] O. E. Alon, V. Averbukh, and N. Moiseyev, Phys. Rev. Lett. **80**, 3743 (1998).
[12] J. Hwang, H. H. Gommans, A. Ugawa, H. Tashiro, R. Haggenmueller, K. I. Winey, J. E. Fischer, D. B. Tanner, and A. G. Rinzler, Phys. Rev. B **62**, R13310 (2000).
[13] X. Liu, J. Si, B. Chang, G. Xu, Q. Yang, Z. Pan, S. Xie, and P. Ye, Appl. Phys. Lett. **74**, 164 (1999).
[14] S. Wang, W. Huang, H. Yang, Q. Gong, Z. Shi, X. Zhou, D. Qiang, and Z. Gu, Chem. Phys. Lett. **320**, 411 (2000).
[15] C. Stanciu *et al.*, Appl. Phys. Lett. **81**, 4064 (2002).
[16] J-S. Lauret, C. Voisin, G. Cassabois, J. Tignon, C. Delalande, Ph. Roussignol, O. Jost, and L. Capes, Appl. Phys. Lett. **85**, 3572 (2004).
[17] L. De Dominicis, S. Botti, L. S. Asilyan, R. Ciardi, R. Fantoni, M. L. Terranova, A. Fiori, S. Orlanducci, and R. Appolloni, Appl. Phys. Lett. **85**, 1418 (2004).
[18] S. O. Konorov *et al.*, J. Raman Spectrosc. **34**, 1018 (2003).
[19] E. E. Aubanel and A. D. Bandrauk, Chem. Phys. Lett. **229**, 169 (1994).
[20] T. Zuo, A. D. Bandrauk, M. Ivanov, and P. B. Corkum, Phys. Rev. A **51**, 3991 (1995).
[21] R. A. Ganeev, H. Singhal, P. A. Naik, I. A. Kulagin, P. V. Redkin, J. A. Chakera, M. Tayyab, R. A. Khan, and P. D. Gupta, Phys. Rev. A **80**, 033845 (2009).
[22] O. E. Alon, V. Averbukh, and N. Moiseyev, Phys. Rev. Lett. **85**, 5218 (2000).
[23] G. Y. Slepyan, S. A. Maksimenko, V. P. Kalosha, J. Herrmann, E. E. B. Campbell, and I. V. Hertel, Phys. Rev. A **60**, R777 (1999).
[24] G. Y. Slepyan, S. A. Maksimenko, V. P. Kalosha, A. V. Gusakov, and J. Herrmann, Phys. Rev. A **63**, 053808 (2001).
[25] S.-I. Chu and D. A. Telnov, Phys. Rep. **390**, 1 (2004).
[26] A. Bahari, N. Daneshfar, and H. Khosravi, Carbon **47**, 457 (2009).
[27] H. Khosravi, A. Bahari, and N. Daneshfar, Phys. Scr. **77**, 055702 (2008).
[28] H. Hsu and L. E. Reichl, Phys. Rev. B **74**, 115406 (2006).
[29] J. Sun, Z. Guo, and W. Z. Liang, Phys. Rev. B **75**, 195438 (2007).
[30] R. A. Ganeev, L. B. Elouga Bom, J. Abdul-Hadi, M. C. H. Wong, J. P. Brichta, V. R. Bhardwaj, and T. Ozaki, Phys. Rev. Lett. **102**, 013903 (2009).
[31] M. Lenzner, J. Krüger, S. Sartania, Z. Cheng, Ch. Spielmann, G. Mourou, W. Kautek, and F. Krausz, Phys. Rev. Lett. **80**, 4076 (1998).
[32] R. A. Ganeev, L. B. Elouga Bom, M. C. H. Wong, J.-P. Brichta, V. R. Bhardwaj, P. V. Redkin, and T. Ozaki, Phys. Rev. A **80**, 043808 (2009).
[33] R. A. Ganeev, H. Singhal, P. A. Naik, J. A. Chakera, A. K. Srivastava, T. S. Dhami, M. P. Joshi, and P. D. Gupta, Appl. Phys. B **100**, 581 (2010).
[34] L. B. Elouga Bom, J.-C. Kieffer, R. A. Ganeev, M. Suzuki, H. Kuroda, and T. Ozaki, Phys. Rev. A **75**, 033804 (2007).
[35] V. Margulis and T. Sizikova, Physica B **245**, 173 (1998).
[36] R. H. Xie and J. Jiang, J. Appl. Phys. **83**, 3001 (1998).
[37] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).
[38] S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, and H. Dai, Science **283**, 512 (1999).