Carbon nanotube composite optoacoustic transmitters for strong and high frequency ultrasound generation

Hyoung Won Baac,[1] Jong G. Ok,[2] Hui Joon Park,[3] Tao Ling,[1] Sung-Liang Chen,[1] A. John Hart,[2] and L. Jay Guo[1,a)]
[1]*Department of Electrical Engineering and Computer Science, The University of Michigan, Ann Arbor, Michigan 48109, USA*
[2]*Department of Mechanical Engineering, The University of Michigan, Ann Arbor, Michigan 48109, USA*
[3]*Macromolecular Science and Engineering, The University of Michigan, Ann Arbor, Michigan 48109, USA*

(Received 22 August 2010; accepted 9 November 2010; published online 8 December 2010)

We demonstrate carbon nanotube (CNT) composite-based optoacoustic transmitters that generate strong and high frequency ultrasound. The composite consists of CNTs grown on a substrate, which are embedded in elastomeric polymer used as an acoustic transfer medium. Under pulsed laser excitation, the composite generates very strong optoacoustic pressure: 18 times stronger than a Cr film reference and five times stronger than a gold nanoparticle composite with the same polymer. This enhancement persists over a broadband frequency range of up to 120 MHz and is confirmed by calculation. We suggest the CNT-polymer composites as highly efficient optoacoustic transmitters for high resolution ultrasound imaging. © *2010 American Institute of Physics*. [doi:10.1063/1.3522833]

Laser-induced ultrasound generation is an effective way to make high frequency ultrasound transmitters by exploiting the high frequency spectra of laser pulses to achieve broad acoustic bandwidths. Typically, such transmitters are made of light-absorbing thin films containing specific structures designed to have high optical absorption that are capable of efficient optoacoustic conversion, for example, thin metal,[1] dye-doped polymer composites,[2,3] and two–dimensional (2D) gold nanoparticle (AuNP) arrays.[4] They are often integrated with optical interferometric detectors (e.g., Fabry–Pérot etalon)[5] to make all-optical ultrasound transducers working over broadband and high frequency in 2D array platforms. In these arrays, the size of each element was determined by the spot size of the focused laser beam that is of the order of several microns.

Thin metallic coatings on solid substrates are suitable as a common reference material for qualifying the performance of optoacoustic transmitters.[1,2] While these thin films (<1 μm) can be used as high frequency ultrasound sources their optoacoustic conversion efficiency is poor mainly because of the low thermal expansion. Also, a significant percentage of light is reflected back from the film surface.

As large thermal expansion is desirable for strong pressure generation, an elastomeric polymer, polydimethylsiloxane (PDMS), has been used as an acoustic transfer medium to interface with light-absorbers.[2–5] A composite film of PDMS with carbon black as a light-absorber has shown nearly 20 dB improvement in optoacoustic signal strength as compared to a reference Cr film alone.[2] However, high frequency response was severely limited due to the composite film thickness (~ 25 μm) due to the acoustic attenuation. This is a serious issue because high frequency performance is vital for optoacoustic transmitters. Moreover, it is challenging to obtain uniform mixing and dispersion of carbon black particles in the PDMS matrix. Agglomeration of carbon black can cause uneven light absorption within the same film. Significant progress has been recently made using a planar array of AuNPs with an overlying PDMS layer of several microns.[4] High frequency output was improved by ~ 5 dB over 70–100 MHz as compared with those carbon black-PDMS composites. However, the overall pressure strength was compromised because the optical absorption in the AuNP is usually lower than that in the carbon black-PDMS composite. In addition, the AuNP has a lower damage threshold ($\sim 1/6$) than the carbon black-PDMS composite, which limits the ultimate attainable pressure.[3,5]

Carbon nanotubes (CNTs) are known to efficiently transform absorbed light into thermal energy,[6] which is attractive for optoacoustic generation. For example, CNTs conjugated with peptides have been used as high contrast optoacoustic agents for tumor imaging in living mice.[7] However, CNTs have not been exploited as optoacoustic transmitters for ultrasound imaging.

More importantly, CNTs have not been demonstrated as high frequency ultrasound sources. The CNTs are very attractive for high frequency ultrasound generation due to the following advantages. Their nanoscale dimension inherently allows fast heat transition to the surrounding medium. This heat transfer can occur of the order of nanoseconds to the surrounding water as thermal diffusion time decreases approximately with $d^2/16\chi$, considering a CNT to be a solid cylinder having diameter d surrounded by a medium with thermal diffusivity χ.[8] This becomes a crucial motivation of efficient generation of high frequency ultrasound. While this dimensional feature is shared with other metallic nanoparticles,[9] the CNTs have extraordinary thermal conductivity (20–30 times larger than that of typical metal) facilitating heat conduction within the structure.[10]

We demonstrate the use of CNTs as optoacoustic transmitters for strong and high frequency ultrasound generation. A CNT-PDMS composite was made by growing multiwalled CNTs on a fused silica substrate, followed by the spin-coating of PDMS. The output pressure of the CNT-PDMS

a)Author to whom correspondence should be addressed. Electronic mail: guo@umich.edu.

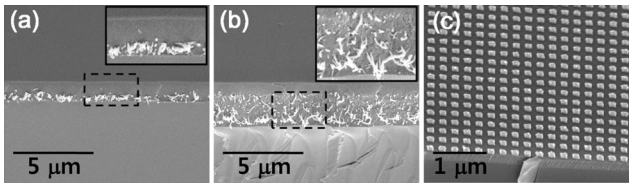

FIG. 1. SEM photographs of the CNT-PDMS composite films where the CNT growth time was 1 min in (a) and 3 min in (b) and the AuNP array before PDMS coating in (c). Fused silica substrates were used for all cases. The final film thickness of 1.2 μm in (a) and 2.6 μm in (b) under the same spin-coating condition of PDMS.

composite was compared to a bare Cr film and a planar AuNP array. We obtained >25 dB stronger pressure in the composite film than in the Cr reference. A frequency-domain analysis shows that the CNT-PDMS composite exhibits excellent optoacoustic conversion that closely follows the spectrum of the laser pulse used for excitation. We note that the CNT density is uniform on the growth substrate, which gives uniform density in the composite.

A 6 ns pulsed laser beam with 532 nm wavelength (Surelite I-20, Continuum, Santa Clara, CA) was used for optoacoustic generation. We used an optical microring ultrasound detector to characterize broadband and high frequency optoacoustic signal.[11] The pulsed laser beam was directly irradiated onto the transparent substrate with 3 mW/cm^2 intensity.[12,13] This beam size is 200 times larger than the diameter of the microring detector and 14 times larger than the distance between the sample and detector (~1.4 mm). Therefore, the acoustic wave incidence onto the microring detector satisfies a plane wave configuration. This arrangement minimizes diffraction-induced errors, and the temporal waveforms of the acoustic pulse replicate the laser pulse shape.[14]

Figure 1 shows scanning electron microscopy (SEM) pictures for the fabricated samples of the CNT-PDMS composite and the AuNP array before PDMS coating. A 100 nm thick Cr film was used as a reference. The multiwalled CNTs were grown on a fused silica substrate coated with a catalyst layer of Fe (≈1 nm thickness).[15] Then, the as-prepared CNTs were spin-coated with PDMS which has a modified composition to enhance the elastic modulus.[16] The cross-sectional view confirms that the CNT strands are dense near the substrate. The planar AuNP array in Fig. 1(c) was fabricated by using a metal transfer method onto the fused silica substrate.[17] The dimension of a single AuNP is about 110 nm×110 nm×30 nm. The AuNP array was spin-coated with an 800 nm thick PDMS layer.

Figure 2 shows the output pressure waveforms generated from the three samples under the same laser fluence. Each curve was obtained by averaging 200 waveforms. The signal amplitude from the CNT-PDMS composite film shown in

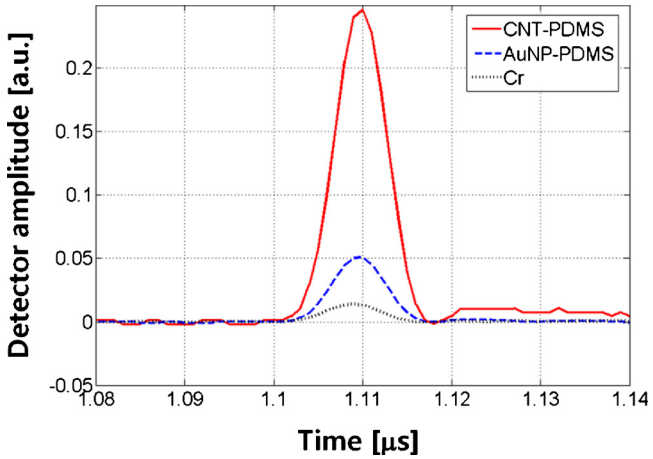

FIG. 2. (Color online) Optoacoustic signal waveforms from Cr, AuNP coated with PDMS, and CNT coated with PDMS.

Fig. 1(b) was 18 times (25 dB) stronger than that of the Cr and five times (14 dB) stronger than that of the PDMS-coated AuNP array. The CNT-PDMS film had 80% light extinction (mostly absorption+slight scattering). The strong pressure originates from the high optical absorption and consequent heating of the CNTs, and the large thermal expansion of the PDMS. The pressure strength could be further enhanced by growing denser CNTs to increase optical extinction, which can approach up to 100%. However, we found that the dense CNTs increase the film thickness (>5 μm), causing significant attenuation of high frequency ultrasound. We chose the composite film of 2.6 μm for measurement, which has sufficiently high optical absorption (~80%) for strong pressure generation and efficient high frequency performance. The AuNP array in this measurement had 33% light extinction. Even if the AuNPs can be designed to have an equal level of optical extinction to CNTs (e.g., nanorods[9]), the pressure will only be improved by 2.4 times assuming a linear relationship between light extinction and pressure strength.

Next, we investigate the frequency-domain performance of the CNT-PDMS composite optoacoustic transmitter over broadband frequency. Based on the measured waveforms in Fig. 2, we obtained the corresponding frequency spectra as shown in Fig. 3(a). The spectra of the three types of optoacoustic transmitters were normalized to the maximum value (low frequency asymptote, i.e., dc value) from the CNT-PDMS composite. It is shown that the magnitude of the frequency spectrum of the CNT-PDMS composite has a 25 dB enhancement relative to the Cr reference, and this enhancement persists up to 120 MHz.

The high frequency efficiency of each optoacoustic transmitter was also investigated by comparing the frequency

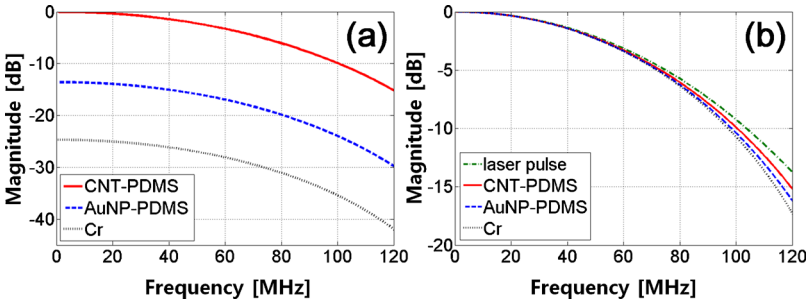

FIG. 3. (Color online) (a) Frequency spectra for the time-domain optoacoustic waveforms in Fig. 2. The amplitude enhancement is clear, up to 120 MHz. (b) The same frequency spectra shown after normalization to each maximum (dc value). They are compared with the ideal spectrum of laser pulse (top trace).

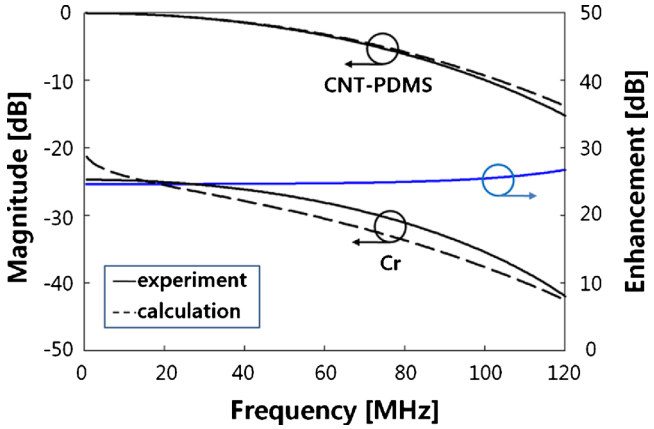

FIG. 4. (Color online) Experimental frequency spectra (solid) compared with the calculated results (dashed), which were obtained by using the 1D layered model, following the left axis. The difference in the experimental spectra is shown as pressure enhancement, following the right axis.

spectra to the laser pulse spectrum, as shown in Fig. 3(b). Each spectrum was normalized to its dc value. The laser pulse spectrum was directly measured by the photodetector. Ideally, the optoacoustically generated ultrasonic wave should replicate this frequency spectrum exactly. As shown in Fig. 3(b), the frequency spectrum of the CNT-PDMS composite closely follows that of the laser pulse. It is shown as even better than the Cr film, which is already a good high frequency source, as the duration of laser pulse (6 ns) is much longer than the acoustic transit time across the film ($\sim$0.02 ns). This efficient high frequency generation from the composite is due to the fast heat transfer from the nanoscale absorbers to the surrounding media.

Note that in these results, we compensated for the acoustic attenuation in water for all frequency spectra. However, we did not include (1) attenuation through the PDMS layer, (2) the frequency response of microring detector, and (3) the electronic bandwidth of the photodetector (3 dB roll off around 125 MHz). We confirmed that the acoustic attenuation in the current PDMS film without the CNTs is <0.1 dB/μm at 100 MHz, which is negligible for our evaluation. As the effect of the detector bandwidth is common to all spectra, the relative comparison among them is still valid. Also, the frequency bandwidths of the microring and photodetector are almost flat up to 100 MHz. If we compensate these effects of (1)–(3), the optoacoustic frequency spectra will be even closer to the laser pulse spectrum.

The strong optoacoustic generation in the CNT-PDMS was also confirmed by theoretical calculations. Based on a 1D layered model for optoacoustic generation,[12] we calculated the frequency spectra for the CNT-PDMS composite and the Cr film. For the thermophysical parameters of CNT-PDMS, we took the values of PDMS except for the optical absorption. This is based on the assumption that the acoustic property is dominated by the PDMS matrix. The assumption is reasonable because the CNT strands occupy less than a few percent in volume fraction in the CNT-PDMS composite. As shown in Fig. 4, the calculation results match well with the experimentally obtained frequency spectra. The optoacoustic pressure enhancement near 25 dB is quite consistent over broadband frequency, which is referred to as the right axis. This agreement between the experiment and the calculation suggests that the CNT-PDMS composite behaves essentially like the polymer but with high optical absorption due to the inclusion of the CNTs.

As confirmed by both experiment and calculation, the optoacoustic frequency spectrum of the CNT-PDMS composite is almost the same as the spectrum of the laser pulse. This implies that the optoacoustic conversion process is frequency independent. This is explained by a localized thermal volume of the optoacoustic sources.[12,13] Within the PDMS, the thermal penetration depth is less than 40 nm for the duration of the laser pulse. Then, a characteristic volume of thermoacoustic excitation is still close to that of the CNT itself. The PDMS thickness of $1-2$ μm does not allow thermal waves to reach to the water-composite interface. As the water is not directly heated, the output signal spectrum is purely contributed by thermoacoustic transients of the CNTs. The laser-induced heating process is essentially instantaneous in the CNTs due to their nanoscale volume and large thermal conductivity. As a result, the optoacoustic transient from the composite should follow that of the laser pulse without distortion caused by the heating of water.

In conclusion, we demonstrated a CNT composite-based optoacoustic transmitter capable of generating strong and high frequency ultrasound. This enhancement persisted from the dc frequency up to 120 MHz was verified by the analytical modeling. We expect that the CNT-PDMS composite can be integrated with optical ultrasound detectors to form all-optical transducers that transmit and receive the original spectrum of a laser pulse with strong amplitude.

This work was supported by the NIH under Grant No. EB007619.

[1]R. J. von Gutfeld and H. F. Budd, Appl. Phys. Lett. **34**, 617 (1979).
[2]T. Buma, M. Spisar, and M. O'Donnell, Appl. Phys. Lett. **79**, 548 (2001).
[3]Y. Hou, S. Ashkenazi, S.-W. Huang, and M. O'Donnell, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **54**, 682 (2007).
[4]Y. Hou, J.-S. Kim, S. Ashkenazi, M. O'Donnell, and L. J. Guo, Appl. Phys. Lett. **89**, 093901 (2006).
[5]Y. Hou, J.-S. Kim, S. Ashkenazi, S.-W. Huang, L. J. Guo, and M. O'Donnell, Appl. Phys. Lett. **91**, 073507 (2007).
[6]P. M. Ajayan, M. Terrones, A. de la Guardia, V. Huc, N. Grobert, B. Q. Wei, H. Lezec, G. Ramanath, and T. W. Ebbesen, Science **296**, 705 (2002).
[7]A. de la Zerda, C. Zavaleta, S. Keren, S. Vaithilingam, S. Bodapati, Z. Liu, J. Levi, B. R. Smith, T.-J. Ma, O. Oralkan, Z. Cheng, X. Chen, H. Dai, B. T. Khuri-Yakub, and S. S. Gambhir, Nat. Nanotechnol. **3**, 557 (2008).
[8]A. L. McKenzie, Phys. Med. Biol. **35**, 1175 (1990).
[9]A. A. Oraevsky, in *Photoacoustic Imaging and Spectroscopy*, edited by L. V. Wang (CRC, Boca Raton, FL, 2009), Chap. 30.
[10]S. Berber, Y.-K. Kwon, and D. Tomanek, Phys. Rev. Lett. **84**, 4613 (2000).
[11]S.-W. Huang, S.-L. Chen, T. Ling, A. Maxwell, M. O'Donnell, L. J. Guo, and S. Ashkenazi, Appl. Phys. Lett. **93**, 113501 (2008).
[12]D. S. Kopylova, I. M. Pelivanov, N. B. Podymova, and A. A. Karabutov, Acoust. Phys. **54**, 783 (2008).
[13]I. M. Pelivanov, D. S. Kopylova, N. B. Podymova, and A. A. Karabutov, J. Appl. Phys. **106**, 013507 (2009).
[14]G. J. Diebold, T. Sun, and M. I. Khan, Phys. Rev. Lett. **67**, 3384 (1991).
[15]J. G. Ok, S. H. Tawfick, K. A. Juggernauth, K. Sun, Y. Zhang, and A. J. Hart, Adv. Funct. Mater. **20**, 2470 (2010).
[16]C. Pina-Hernandez, J.-S. Kim, and L. J. Guo, Adv. Mater. (Weinheim, Ger.) **19**, 1222 (2007).
[17]M.-G. Kang and L. J. Guo, J. Vac. Sci. Technol. B **26**, 2421 (2008).