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Low density carbon nanotube forest as an index-matched and near perfect absorption coating

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We demonstrate broadband, near perfect absorption with a conformal coating of a multi-walled carbon nanotube (CNT) forest on an arbitrarily shaped surface. The complex refractive index of such a CNT forest is retrieved from the measured transmission and reflection spectra using Kramers-Kronig constrained variational analysis, which gives a typical value of $n_{\text{eff}} = 1.04 + 0.01i$ at visible wavelengths. Therefore, when used as a conformal coating on an object, a thick layer of the CNT forest can provide an excellent impedance match to air and near perfect absorption, preventing any detectable light reflection and scattering from the object. © *2011 American Institute of Physics*. [doi:10.1063/1.3663873]

Perfect optical absorption has attracted increasing research interest in recent years due to the potential applications in anti-reflection coatings and photo-detectors.[1–3] Using resonant plasmonic structures, nearly perfect absorption can be obtained within a limited bandwidth.[4,5] On the other hand, non-resonant structures such as vertically aligned carbon nanotube (CNT) forests can give considerable broadband absorption[6,7] due to the low volume ratio of the CNTs and the consequent low effective refractive index.[8,9] So far, the real part of the effective refractive index has been experimentally determined from the reflection spectrum of the CNT forest and proved to be close to 1, but the imaginary part has not been experimentally available.[10] Due to its significance in absorption performance of the CNT forest, we designed an experiment to determine the imaginary part of the refractive index, which also confirmed the real index as close to 1. Moreover, we demonstrated near perfect absorption by conformal coating of a CNT forest on an arbitrarily shaped surface. The non-reflecting and non-scattering characteristics of the CNT coating make the arbitrary shaped object appear as a flat sheet and indistinguishable from the background.

Generally, both the real and imaginary parts of the refractive index are equally important in the impedance matching to get ultra-low reflection and considerable high absorption. According to Fresnel equations, the specular reflectivity from an air/material interface can be calculated by

$$R_{TE} = \left| \frac{k_{1z} - k_{2z}}{k_{1z} + k_{2z}} \right|^2; \quad R_{TM} = \left| \frac{\varepsilon_2 k_{1z} - \varepsilon_1 k_{2z}}{\varepsilon_2 k_{1z} + \varepsilon_1 k_{2z}} \right|^2, \qquad (1)$$

for TE and TM polarizations, respectively, where $k_{iz} = (k_i^2 - k_x^2)^{1/2}$, $k_i = \sqrt{\varepsilon_i} 2\pi/\lambda$ $k_x = (2\pi/\lambda)\sin\theta$, and permittivity ε_i is the square of the complex refractive index n_i. Fig. 1(a) shows the calculated reflectivity from the air/material interface as a function of the complex refractive index $n = n' + in''$. The calculation is for normal incident light and therefore the reflectivity for TE and TM waves are identical. The result indicates that the smaller the real and imaginary part of refractive index, the lower the reflection at the interface due to better impedance matching to air. Ideally, a near unity refractive index of $n = 1 + i\delta$, with $\delta \ll 1$, can provide both impedance matching to air to obtain minimum reflection and total absorption with sufficient material thickness. For example, the specular reflectivity on a flat material surface with $n = 1.02 + i0.04$ can be as low as 0.049% at normal incidence. The angle dependent reflection can also be calculated from Eq. (1), and the results shown in Fig. 1(b) indicate that such a low refractive index material has a reflectivity smaller than 0.6% for large incident angles up to 60 degree for both TE and TM polarized light. In contrast, Fig. 1(b) also presents the reflectivity from an air/silicon interface at a wavelength of 632.6 nm, and the values are 1000 times larger than that of the low refractive index material. Considering the low refractive index property of CNT forests, most of the previous works theoretically calculated it from effective media theory.[8,9] Although the real part of the effective index can be fit from the measured reflection spectrum, the imaginary part of the refractive index still remains unavailable using such a method.[10]

By measuring both the transmission and reflection spectra and using Kramers-Kronig constrained variational analysis,[11,12] we experimentally retrieved the complex refractive index of the CNT forest and unambiguously obtained its imaginary part. Figs. 2(a) and 2(b) show the scanning electron microscope (SEM) images of the multi-walled CNT forest on a flat surface grown by plasma-enhanced chemical vapor deposition (PECVD) processing.[13] Fig. 2(c) shows the measured reflection and transmission spectra of the CNT forest with different thicknesses. For thick CNT forests with a 70 μm thickness, the magnitudes of the reflection and transmission spectra are too low, around 0.1%, to be detected by our OceanOptics spectrometer because the signal is at the same level as the stray light. For thin CNT forests with a thickness of 6.5 μm, the transmission is considerably large due to insufficient absorption, while the reflection value is less than 1.2% over the entire visible spectrum (most of reflection is from the CNT/SiO_2 interface

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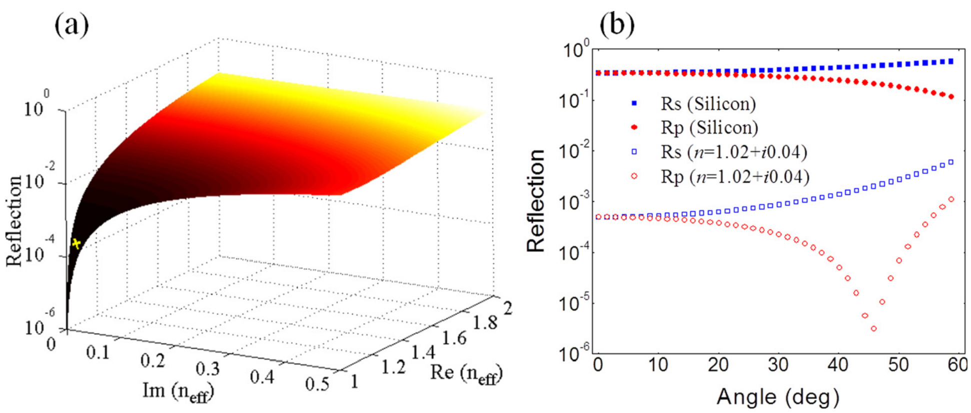

FIG. 1. (Color online) (a) Calculated specular reflectivity at air/material interface as a function of complex refractive index. The mark corresponds to refractive index of $n = 1.02 + i0.04$. (b) Calculated angle dependent reflectivity at material interface with $n = 1.02 + i0.04$ for TE and TM polarizations, the wavelength is 632.8 nm and the reflectivity of an air/silicon interface is also shown for comparison.

because of insufficient absorption by the short CNTs. The complex refractive index is retrieved using a multi-oscillator model to fit both the experimental reflection and transmission data simultaneously, where the Kramers-Kronig constrained variational analysis is used to ensure the consistency of the retrieved refractive index.[12] The obtained complex refractive index is shown in Fig. 2(d), which shows a highly uniform refractive index value over the entire visible spectrum. This unambiguously demonstrates its extremely low effective refractive index for both real and imaginary parts to match with that of air.

Considering the subwavelength, random roughness of the surface of the CNT forest and the resultant diffused reflection, any reflected light is redistributed to all directions and the observer only receives a small portion of the reflection. This will be several orders of magnitude lower than specular reflection, making it almost undetectable. Meanwhile, the absorption inside the CNT forest is considerably effective. Therefore, we point out an interesting application by exploiting the perfect absorption characteristics of the low density CNT forest. By making a conformal coating of such a perfect black material on an arbitrarily shaped object, the 3D object will optically appear as a 2D black sheet, and all the geometric information disappears. In this case, the CNT forest acts as a perfect magic black cloth that can completely conceal the 3D structure of the object.

As a proof-of-concept, an arbitrarily shaped object was fabricated on a 500 μm thick silicon substrate by focused ion beam (FIB) milling. In this case, a "tank" pattern of $65 \times 22.5\,\mu$m in size (SEM image in Fig. 3(a)) was made, and its reflected image was taken under an optical microscope illuminated by unpolarized white light (Fig. 3(d)). To conformally cover the object with the perfect absorption coating, a 60 μm-thick CNT forest was grown on top of the whole silicon sample and therefore follows the profile of the original "tank" object (Fig. 3(b)). To fabricate the CNT forest, first, a 300 nm-thick SiO_2 layer is deposited on the silicon sample by PECVD, and then a 1 nm-thick Fe catalyst layer is deposited by electron beam evaporation. The sample is loaded in a single-zone tube furnace, which is heated to 775 °C under the gas mixture of $C_2H_4/H_2/He$. An optical

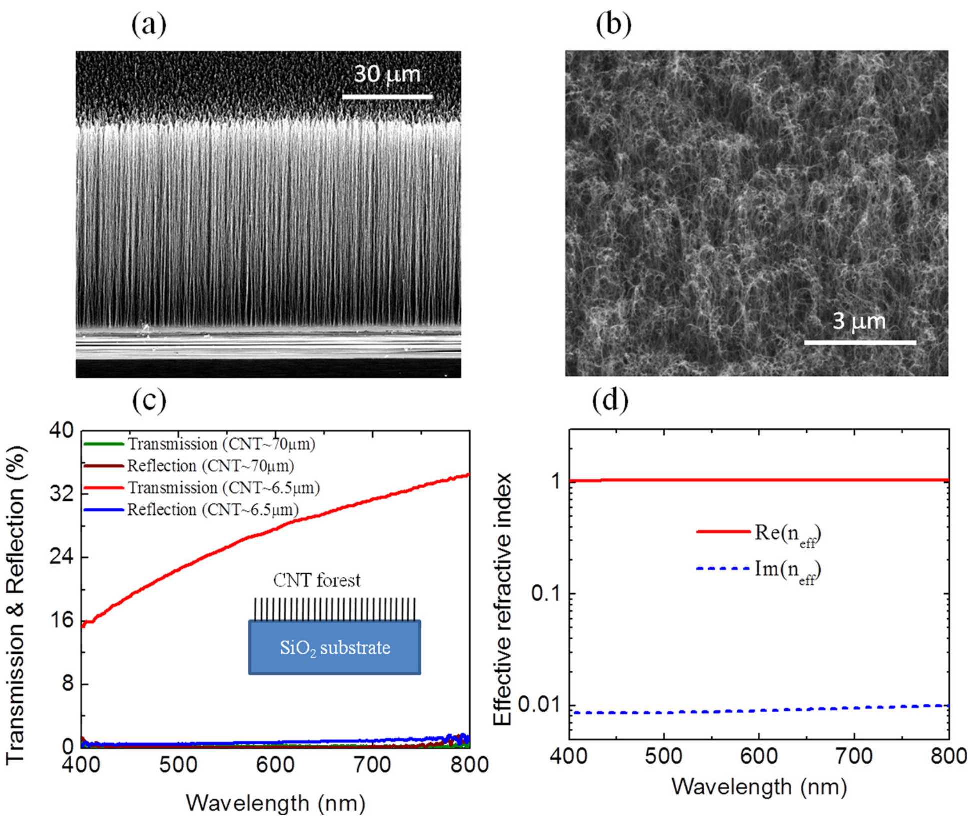

FIG. 2. (Color online) CNT forest and its refractive index retrieved from measured transmission and reflection spectra. (a) Cross section SEM image of vertically aligned multi-walled CNT forest. (b) Top view of the CNT forest with rough surface. (c) Measured transmission and reflection spectra for CNT forest with thickness of 70 μm and 6.5 μm grown on a 500 μm SiO_2 substrate. (d) Retrieved complex effective index of CNT forest over visible spectrum. The retrieval method is discussed in Ref. 11 in detail. We used three Drude-Lorentz oscillators to fit the experimental spectra, and the spectra data are from thinner CNT forest to get high signal noise ratio.

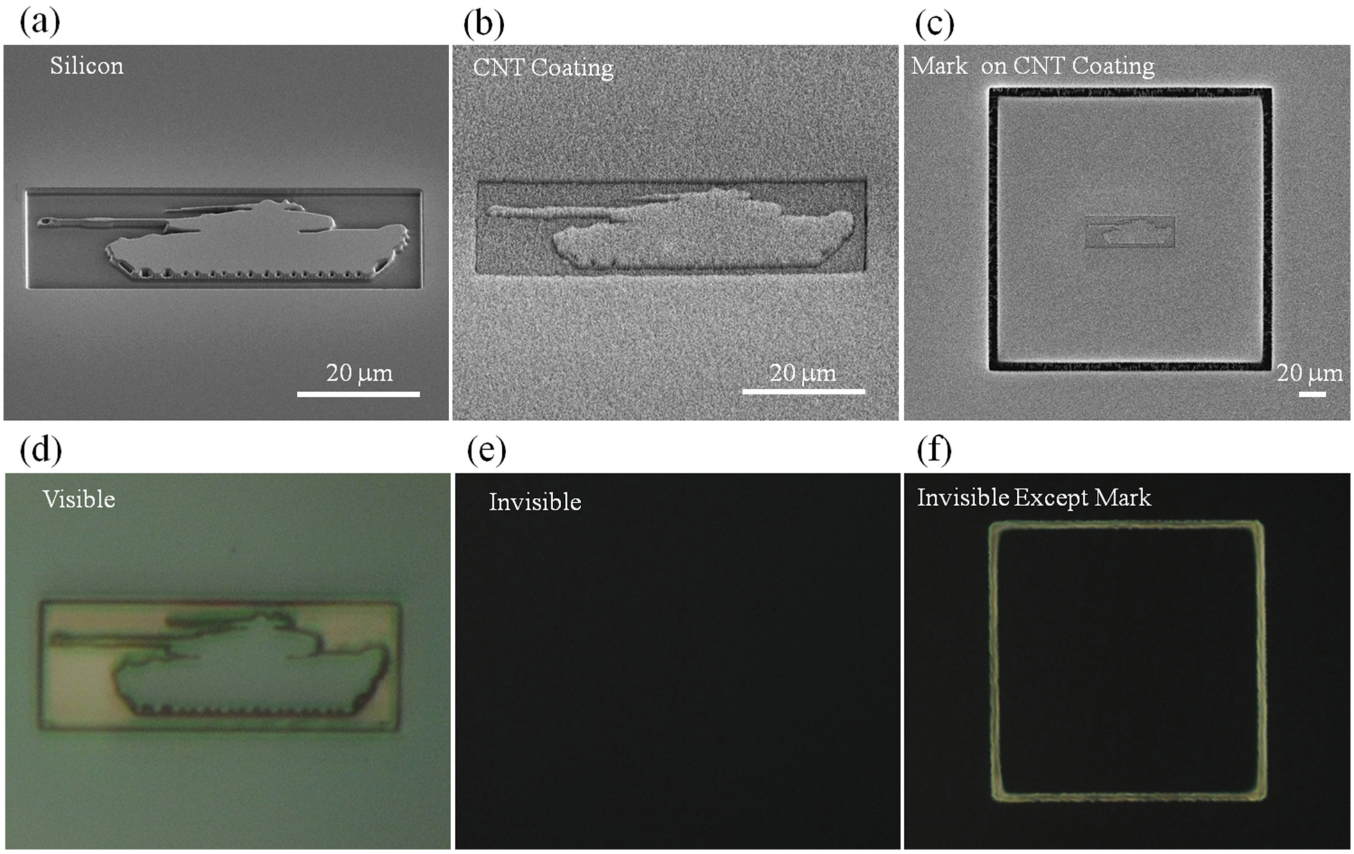

FIG. 3. (Color online) Perfect absorption from conformal CNT forest coating. SEM image of a $65 \times 22.5\,\mu$m "tank" pattern fabricated by FIB ((a) taken at a tilt angle of 45°); with the whole "tank" sample surface covered by a 60 μm thick CNT coating (b); and with a rectangular mark around the "tank" by removing the rectangular CNT layer using FIB (c). The corresponding optical reflection images taken under broadband visible illumination of the as fabricated "tank" object (d), CNT forest coated "tank" sample (e), and the rectangular mark surrounding the "tank" (f).

image of the object covered with the CNT coating was taken again. Fig. 3(e) shows that the tank completely disappears and the surface looks exactly the same as a flat CNT sheet. As a further proof, a control experiment was performed where a rectangle mark around the "tank" was made by FIB milling that removed the CNT (Fig. 3(c)). The optical image now clearly shows the rectangle mark, but the tank pattern inside the mark remains invisible (Fig. 3(f)). All the optical reflection images in Figs. 3(d)–3(f) were taken using a $10\times$ objective lens with a numerical aperture of 0.25. The optical images taken by $4\times$, $20\times$, and $40\times$ magnification objective lens with numerical apertures from 0.10 to 0.55 showed similar performance. One can also appreciate the scalability of this approach because increasing the object size will not increase the complexity of the homogeneous coating due to the impedance matching to air.

In conclusion, by measuring both transmission and reflection spectra and using Kramers-Kronig constrained variational analysis, we have retrieved the low effective refractive index of a CNT forest and unambiguously obtained its imaginary part. We also demonstrated broadband, near perfect absorption with a conformal coating of impedance matched CNT forest on arbitrarily shaped surface. Moreover, an object covered with this low density absorbing material will become totally invisible to our eye if the object is placed on a perfect absorption background. Such an approach is neither restricted to CNT forest nor to visible frequency, but can be applied to a broader frequency range from ultraviolet to THz for arbitrarily large objects. It is interesting to note that the deep space itself is a perfect background without reflecting any radiations; so it would only take a "magic veil" consisting of low density and broadband absorbing particles to render matters and objects totally invisible to our instruments based on the detection of electromagnetic waves.

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