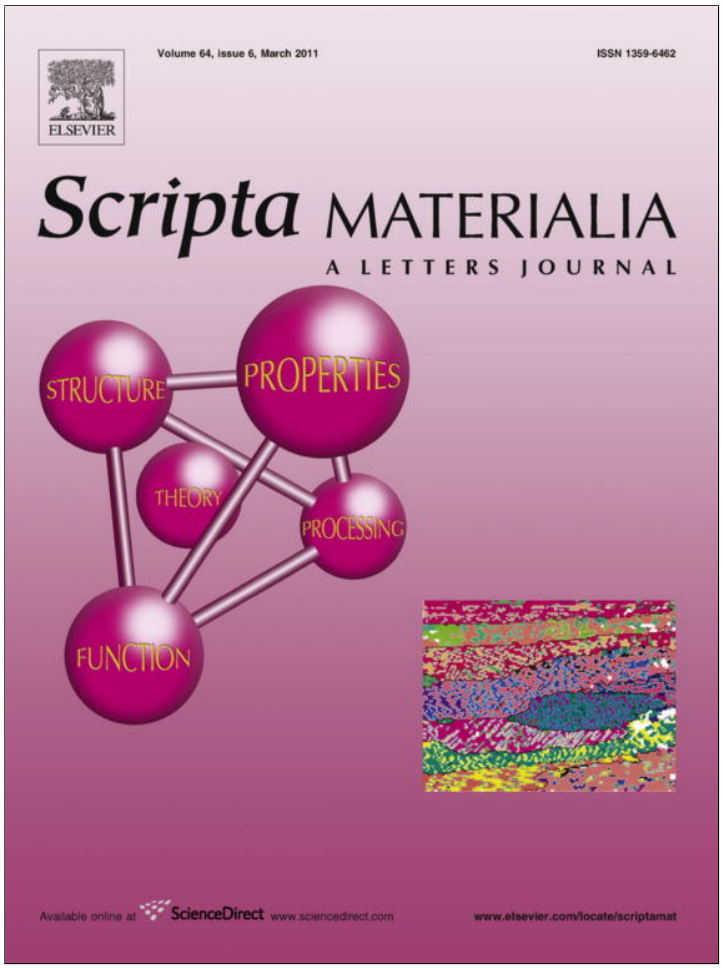

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Electrically driven incandescence of carbon nanotubes in controlled gaseous environments

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Carbon nanotube buckypaper was electrically driven to incandescence in controlled environments of air composition vacuum, argon and helium. The optical spectrum of the blackbody radiation was analyzed to characterize the emission at different pressures in the various environments. The incandescence intensity and temperature were found to be lower at higher pressures, with the observations attributed to increased heat loss by conduction and convection to the ambient. A modified thermal conduction equation is suggested to explain the experimental results.

Keywords: Carbon nanotubes; Incandescence; Heat equation; Gas sensing

Light emission and propagation in nanomaterials is an intriguing new field deeply driven by quantum effects, and promises a broad range of applications ranging from quantum communications to integrated nanophotonic circuits [1–3]. Electrically induced light emission from carbon nanotubes (CNT) was first observed in field emission experiments [4]. The mechanism was attributed to blackbody radiation of Joule-heated CNT [5,6] and directly proved so with demonstrations of current-induced incandescence from CNT bundles and filaments [7,8]. The intensity of incandescence from a single nanotube was found to be accurately described by the heat equation and Planck's law, thus providing a remarkable example of a nano-thermodynamical system where at least one length scale of the system lies deep in the quantum realm well outside the thermodynamic limits. Recent developments saw a single CNT field effect transistor integrated within a planar $\lambda/2$ microcavity and a superaligned CNT film used as large-scale incandescent display with response superior to that of liquid crystal displays [9,10]. This study investigates current-driven incandescence in a CNT network in various controlled gaseous environments. The role of the ambient gas molecules influencing the temperature and intensity of the incandescent CNT was analyzed and modeled with a modified heat equation. The varied responses to different gaseous environments also suggest potential application as gas sensors.

Samples used in this work are single-walled CNT (P3-SWNT, Carbon Solution Inc.). CNT buckypaper (BP) was prepared by vacuum filtering a single-walled CNT suspension (0.2 mg ml^{-1} in deionized water) through a filter membrance (Whatman, 20 nm pore size, 47 mm diameter). The CNT were trapped on the surface of the filter, forming a free-standing interconnected network. After drying, the CNT film was peeled off from the filter membrane [11,12]. Figure 1a shows the scanning electron microscopy (SEM) image of the as-prepared CNT BP. The typical thickness of the BP was 20 μm. The BP was cut into a rectangular strip 12 × 1 mm, and copper wires were attached to the far ends of the BP with silver paint to complete the two-terminal resistor device. The device was then secured and suspended above a clean microscope glass slide with Si/SiO_2 wafers as spacers. Figure 1b shows the schematic of the experiment setup. The device assembly was placed in a transparent quartz vacuum chamber

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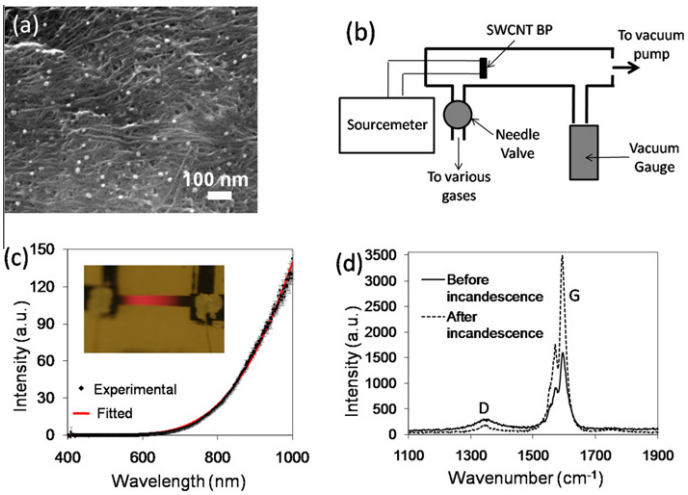

Figure 1. (a) Schematic of experiment setup. (b) SEM image of as-prepared SWCNT BP. (c) Intensity spectrum of a typical incandescence fitted with a rescaled Planck blackbody distribution. Inset shows a photograph of the incandescent device. (d) Raman spectroscopy of the CNT before and after incandescence. A drop in I_D/I_G from 0.19 to 0.056 was observed.

connected to various gas cylinders and a micrometer screw gauge needle valve to control the pressure in the chamber. The two-terminal device was connected via an electrical feedthrough to a sourcemeter (Yokogawa GS610) outside the chamber. A typical bias of 3.6 V applied across the terminals passed a current of 145 mA and resulted in a bright and sustained incandescence visible to the naked eye through the transparent quartz chamber, as shown in the inset of Figure 1c. Sustainability of the incandescence up to 24 h was achieved.

To study the optical characteristics of the current-driven incandescence, an optical fiber, which was part of an optical spectrometer system (Ocean Optics USB4000), was brought close to the sample. Calibration of the as-collected data was required owing to the wavelength-dependent detection efficiency of the spectrometer. A calibrated tungsten halogen light source (Ocean Optics LS-1-CAL) was used for this purpose. Figure 1c shows the intensity spectrum of a typical incandescence emission at 10^{-4} mbar vacuum. The spectrum followed a close fit to the (rescaled) Planck blackbody radiation equation

$$I(\lambda, T) = S\frac{2\pi hc^2}{\lambda^5(e^{hc/\lambda k_B T} - 1)} \tag{1}$$

where S is the scaling factor to account for the geometrical factor for the experimental setup. The best-fit curve obtained with temperature $T = 1295$ K falls within the error bars of the experiment, indicating a good fit to the experimental data. Raman spectroscopy characterizations of the CNT before and after incandescence were carried out, and the results are shown in Figure 1d. Two distinct groups of peaks, the disorder-induced D-band centered at 1344 cm^{-1} and the tangential G-band modes which peak at 1594 cm^{-1} were clearly seen. It is observed that, after incandescence, the D-band peak becomes lower and sharper, and the ratio of the peak intensities of the bands I_D/I_G reduce from 0.19 to 0.056, suggesting a significant reduction of defects in the post-incandescence CNT. This is attributed to the removal of carbonaceous impurities and residual charge-transfer intercalants [13] from the Joule-heated CNT in vacuum.

The process of Joule heating the CNT film to incandescence was described by the thermal conduction equation [9,14]

$$c_p\rho_m\frac{\partial T}{\partial t} = k_{CNT}A\frac{\partial^2 T}{\partial x^2} + I^2\frac{\rho_c}{A} + \varepsilon A\frac{2\sigma}{h}\left(T_0^4 - T^4\right) \tag{2}$$

where c_p, ρ_m, k, ε, I, A, ρ_c and h are the volume specific heat, mass density, thermal conductivity, emissivity, heating current, cross-sectional area, resistivity and thickness of the CNT film, respectively. As the current-heated CNT reach thermal equilibrium within a millisecond, which is faster than the response of the optical spectrometer, the case of thermal equilibrium or $\partial T/\partial t = 0$ is considered [14]. Solving the differential equation numerically for the case of full vacuum (10^{-4} mbar) gives $k_{CNT} = 32.6$ W m^{-1} K^{-1}, which falls in the range of thermal conductivity values for single CNT and CNT BP found in the literature [15–19]. While the above equation provides a good model for current-heated CNT in moderate to high vacuum, it is insufficient to account for interactions with the ambient gas molecules, which are likely to be significant in lower vacuum levels. Quantifying such heat dissipation from the CNT is therefore important for practical situations. This work sought to investigate the behavior of CNT incandescence in various gaseous environments. Figure 2 shows the intensity spectrum of the incandescence in various pressures of (a) air-composition vacuum, (b) argon and (c) helium environments. Each spectrum was fitted to the blackbody radiation equation to obtain the temperature of incandescence as labeled in the figures. It is observed that, in all the tested environments, the incandescence intensity and temperature scale inversely with the chamber pressure. This is attributed to the additional heat loss from CNT by conduction and convection to the gaseous molecules in the environmental chamber. It is noted that, unlike laser-induced

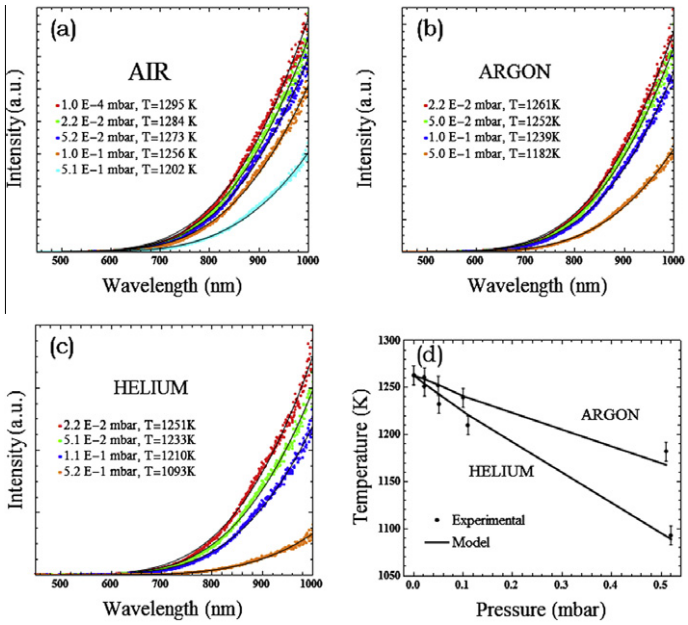

Figure 2. (a–c) Intensity spectra and blackbody fittings of incandescent emissions in various pressures in air, argon and helium environments. (d) Temperature of incandescence against pressure in argon and helium environments compared with the model described in Eq. (3).

incandescence in air-composition vacuum, where thermal runaway was readily observed in moderate to low vacuum [20], the current-driven incandescence remains stable even at a low vacuum of 5×10^{-1} mbar. The stability is attributed to the lower incandescence temperature (1200–1300 K) in this work compared with that of laser-induced incandescence at >2400 K [20]. Nevertheless, incandescence in air-composition vacuum may induce exothermic reactions between the CNT and oxygen molecules, resulting in higher temperatures than in an inert environment such as argon or helium. It is also observed that the temperature and intensity of the incandescence is much lower in helium compared with argon, suggesting a significant role played by the thermal conductivity of the ambient gas. A modified thermal conduction equation with an additional term which scales linearly with pressure is proposed:

$$c_p \rho_m \frac{\partial T}{\partial t} = k_{CNT} A \frac{\partial^2 T}{\partial x^2} + I^2 \frac{\rho_c}{A} + \varepsilon A \frac{2\sigma}{h}\left(T_0^4 - T^4\right) + k_g M_g \alpha P (T_0 - T) \quad (3)$$

where k_g, M_g are the thermal conductivity and molar mass of the ambient gas, respectively, P is the pressure in the environmental chamber, and α is a constant. The suggested model was tested for the various pressures of argon and helium by solving Eq. (3) with the corresponding values of k_g and M_g for each gas. A satisfactory match of the experimental results and the theoretical model was obtained, as shown in Figure 2d.

Note that Eq. (3) may be further modified to include fluid dynamics parameters such as flow speed to account for heat dissipation by convection in the compressible fluid. In the present experiments, however, the flow rate to achieve the maximum pressure of 5.0×10^{-1} mbar does not exceed 20 sccm. This translates to an average flow velocity approximately seven orders of magnitude lower than the velocity of the gas molecules, owing to random thermal motion at the incandescence region. Heat loss by conduction to the gaseous molecules in the moderate vacuum environment therefore towers over the contribution due to convectional losses within the experimental conditions, justifying the simple form of the additional term in Eq. (3).

The gas-dependent emission characteristics of the current-induced incandescence of CNT suggest gas-sensing capabilities of the system. As an example of the application, the incandescent CNT is subjected to periodic exposure of pure argon and argon (95%)/hydrogen (5%) environments. As shown in Figure 3, the incandescent intensity in the latter mix is lower than that in pure argon. This may be due to a higher effective thermal conductivity of the Ar/H_2 mixture, resulting in greater heat loss to the environment, or an increase in resistance of the device due to adsorption of H_2 molecules onto the surface of the CNT [21,22].

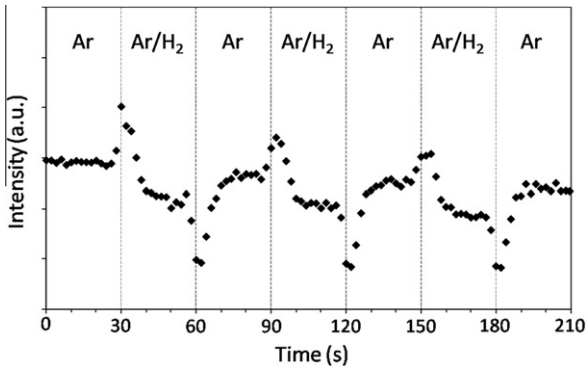

Figure 3. Variation in incandescence intensity under periodic cycling of argon and argon/hydrogen (5%) environments.

In conclusion, current-driven incandescence from Joule-heated CNT in various controlled gaseous environments was studied. A modified heat equation with an additional term proportional to the chamber pressure was proposed to quantify the heat dissipation from the hot CNT to the gas molecules in the environment. The results of this study are likely to be useful for practical applications of CNT incandescence. Finally, a potential gas-sensing device of incandescent CNT is demonstrated.

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