# Barium-functionalized multiwalled carbon nanotube yarns as low-work-function thermionic cathodes

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Barium-functionalized multiwalled carbon nanotube yarns were fabricated by drawing and twisting multiwalled carbon nanotube forests through a solution containing barium nitrate. After heat activation under vacuum, the functionalized yarns were enriched in barium oxide due to the high surface-to-volume ratio of the nanotubes. The cathodes exhibited good thermionic properties, with a work function as low as 1.73–2.06 eV and thermionic current density that exceeded 185 mA/cm$^2$ in a field of 850 V/5 mm at 1317 K. The barium-functionalized yarns had high tensile strength of up to 420 MPa and retained strength of ~250 MPa after a 2 h activation process. © 2008 American Institute of Physics. [DOI: 10.1063/1.2909593]

Carbon nanotubes (CNTs) have great potential for use as field and thermionic emitters due to their excellent electrical and mechanical characteristics. Effective thermionic emission was obtained from micrometer-long defective CNTs, highlighting the possibility of using CNTs as miniature electron sources for e-beam and x-ray instruments and display applications.[1] CNT yarns have recently attracted great interest due to their high electrical conduction, flexibility, and favorable mechanical properties.[2–4] As electron sources, they have been demonstrated to exhibit large current-carrying capacity as field emitters[5] with current density exceeding 100 A/cm$^2$ and thermionic emitters with large effective surface area and work function of 4.54–4.64 eV.[6] We report here an effective method to produce barium-functionalized multiwalled CNT (Ba-MWCNT) yarns as low-work-function thermionic cathodes. The work function measured by the Richardson method was 1.73–2.06 eV and the thermionic emission current density exceeded 185 mA/cm$^2$ for a field of 850 V/5 mm at 1317 K. The tensile strengths of the Ba-MWCNT yarn were ~420 and 250 MPa before and after vacuum heating activation, respectively. These low-work-function MWCNT yarns are suitable as thermal electron sources in devices such as vacuum fluorescent displays (VFDs), x-ray tubes, and electron guns.

MWCNT yarns were drawn from MWCNT forests synthesized by low-pressure chemical vapor deposition.[4] The yarns then were drawn through droplets of solution containing a barium salt and simultaneously twisted. The solution was prepared by dissolving 9.2 g of barium nitrate, 7.4 g of strontium nitrate, and 0.3 g of calcium nitrate in 100 ml of equal volumes of de-ionized water and ethanol. After evaporating the solvent at 100 °C in air, the Ba-MWCNT yarn was heated at 1100–1200 K for several minutes in vacuum by using a dc to decompose the nitrates to oxides. Scanning electron microscopy (SEM) images of an as-prepared yarn are shown in Figs. 1(a) and 1(b). The energy-dispersive x-ray spectrum (EDS) in Fig. 1(c) reveals the presence of barium

and strontium, but the calcium content was too low to be detected. The detection of oxygen but no nitrogen suggests that the nitrates had fully decomposed on the as-heated yarns.

The mass ratio of nitrates in the Ba-MWCNT yarns was determined (STA-499C thermal analyzer, Netzsch) before vacuum decomposition. Thermal gravimetric analysis was performed by increasing the temperature from 50 to 1200 °C at 10 °C/min in oxygen. The mass percentage of nitrates was as high as 72% in the functionalized
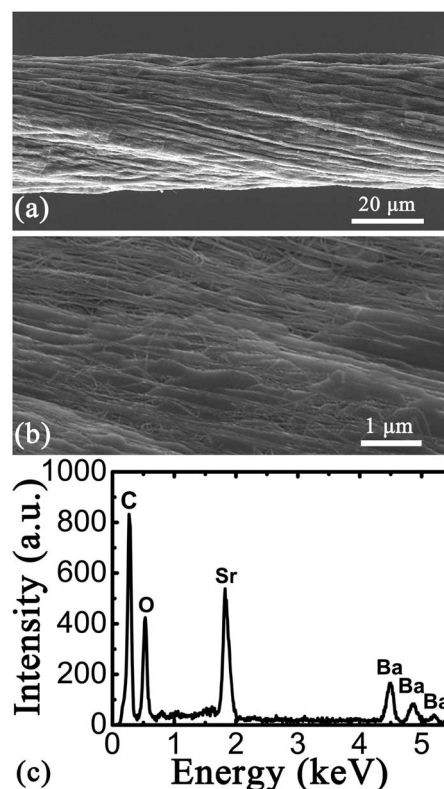


FIG. 1. SEM and EDS images of Ba-MWCNT yarn after heat treatment at 1127 K for 5 min in vacuum. [(a) and (b)] SEM images of the yarn at different magnifications. (c) EDS image of the yarn.

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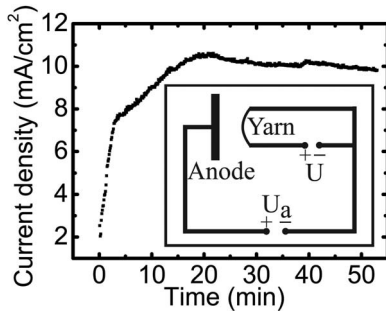c)Electronic mail: jiangkl@tsinghua.edu.cn.

FIG. 2. Activation process for Ba-MWCNT yarn at ~1150 K and $10^{-5}$ Pa. Inset: Schematic diagram of the electric circuit used for thermionic emission tests.



FIG. 3. (Color online) (a) $J_a$-$U_a$ curves for Ba-MWCNT yarn at different temperatures. (b) Experimental data (solid squares) and fitted line for a plot of $\log(J_0/T^2)$ vs $1/T$ for Ba-MWCNT yarn.

yarns; SEM images revealed that most of them filled the spaces between nanotubes in the yarn. This high Ba loading means that Ba-MWCNT yarns are good storage thermionic cathodes.

The thermionic emission of Ba-MWCNT yarns was measured under vacuum ($10^{-5}$ Pa) by using the electric circuit shown in Fig. 2 (inset). A 2-cm-long Ba-MWCNT yarn with a diameter of 42 $\mu$m used as the cathode (resistance ~167 $\Omega$) was heated by a dc power supply. The anode was a stainless steel plate placed 5 mm from the yarn. A Keithley 237 source meter was used to apply potential $U_a$ to the anode and test the emission current $I_a$ simultaneously. The current density $J_a$ was calculated as the emission current divided by the yarn's geometric area (0.0264 $cm^2$). The temperature was derived by fitting the candescent light spectrum (Konica-Minolta CS-1000A spectroradiometer) of the yarn to that of black body radiation.

After nitrates on the MWCNT yarn decomposed to oxides, further heat treatment was carried out to produce a constant high emission current. This activation was necessary to produce an adequate level of Ba and to remove residual gases from the cathode.[7] Figure 2 shows the current density for thermionic emission as a function of time at ~1150 K. The emission current rapidly increased during activation and reached a relatively steady state after 20 min. The work function of the Ba-MWCNT yarn was tested after complete activation. Figure 3(a) shows the emission current density as a function of the anode voltage at different temperatures. A current density of 187 mA/$cm^2$ (total current 4.94 mA, heating power 0.0602 W) was obtained in an electric field of 850 V/5 mm at 1317 K. Attributed to the high barium oxide coverage on MWCNT yarn and the large surface area of CNTs, the current density could be further increased according to recent works.[8,9]

We recently used the Richardson method to determine the thermionic emission constant and work function of MWCNT yarns and sheets.[6,10] For a thermionic emission cathode, the emission current density versus external electric field in the accelerating field region can be described by the Richardson–Dushman equation[11]

$$J_a = J_0 e^{e\sqrt{eE/4\pi\epsilon_0}/k_B T}, \qquad (1)$$

where $J_0 = AT^2 e^{-\phi/k_B T}$ is the zero-field current density, $e$ is the electron charge, $\epsilon_0$ is the permittivity of free space, $E$ is the external electric field, $T$ is the absolute temperature, $k_B$ is the Boltzmann constant, $A$ is Richardson's emission constant, and $\phi$ is the work function of the cathode at absolute zero temperature.
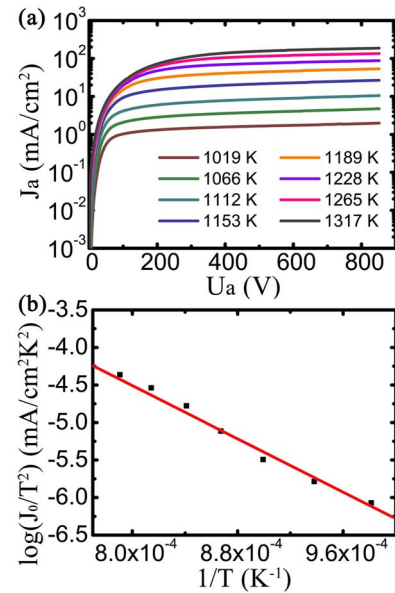
Taking logarithms on both sides and replacing the external field $E$ by $\alpha U_a$, we obtain

$$\log J_a \approx \log J_0 + 1.906\frac{\sqrt{\alpha}}{T}\sqrt{U_a}, \qquad (2)$$

where $U_a$ is the anode voltage and $\alpha$ is a constant ($cm^{-1}$) determined by the electrode geometry. If $\log J_a$ is plotted against $\sqrt{U_a}$ and fitted by a straight line, the intercept on the $y$ axis should be $\log J_0$.

According to the expression for zero-field current density $J_0$, we have

$$\log\left(\frac{J_0}{T^2}\right) = \log A - 0.4343\frac{\phi}{k_B T}. \qquad (3)$$

A plot of $\log(J_0/T^2)$ against $1/T$ yields a straight line with slope $-0.4343\phi/k_B T$ and intercept $\log A$ [Fig. 3(b)]. The work function can thus be determined from the slope of this line. The work functions were determined to be 1.76, 2.06, and 1.73 eV for three different samples. This variation in work function might be attributed to different surface states for different samples during measurement.[12]

Flexible MWCNT yarns can have tensile strength as high as 460 MPa for a diameter of just several micrometers[3] and are thus good candidates for ultrathin but strong and tough thermionic cathodes used as miniature electron sources operating at a relatively low temperature. We measured the strength of Ba-MWCNT yarns by using an Instron 5848 microtester at a strain rate of 2% $min^{-1}$. The cross-sectional area was measured by SEM. Figure 4 shows tensile test results for MWCNT yarn after barium functionalization and further heat treatment. The tensile strength of Ba-MWCNT yarn was ~420 MPa, which is similar to that reported for two-ply yarns.[3] After further heating at 1200 K for 2 h under vacuum ($10^{-5}$ Pa), the tensile strength decreased to 250 MPa, which is comparable to that of pure copper.[13] As the D band of the Raman spectrum at 1348 $cm^{-1}$ increased after heat treatment (Fig. 4, inset), the decrease in tensile strength can be ascribed to an increase in defects in the yarn.
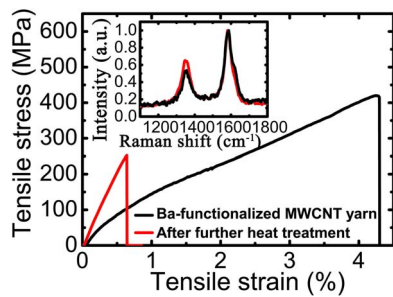
FIG. 4. (Color online) Stress-strain tests for MWCNT yarns after barium functionalization and further heat treatment. Inset: Corresponding Raman spectra.

Furthermore, since the tensile strength of pure CNT yarns decreased by <6% after heating at 2000 K,[4] the increase in defects can mainly be attributed to the oxidation-reduction reaction between oxides and carbon atoms of the yarn. This drawback could be avoided by using additional activators such as Mg and Si in the oxides, as commonly applied in commercial oxide cathode production.[14] The activators employed in CNT yarns should have greater activation capability than carbon to prevent CNT-oxide reaction. This should lead to higher tensile strength after heat treatment.

In summary, Ba-MWCNT yarns were easily fabricated by drawing and twisting MWCNT forests through a barium salt solution. The yarns had a work function as low as 1.73–2.06 eV and emission current density exceeding 185 mA/cm$^2$ in a field of 850 V/5 mm at 1317 K. The tensile strength was 420 MPa after barium functionalization and 250 MPa after high-temperature activation. As Ba-MWCNT yarns of micrometer diameter exhibit good thermionic and mechanical properties, they can be used as miniature thermionic electron sources in devices such as VFDs, x-ray tubes and electron guns.

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