Load Characteristics of a Suspended Carbon Nanotube Film Heater and the Fabrication of a Fast-Response Thermochromic Display Prototype

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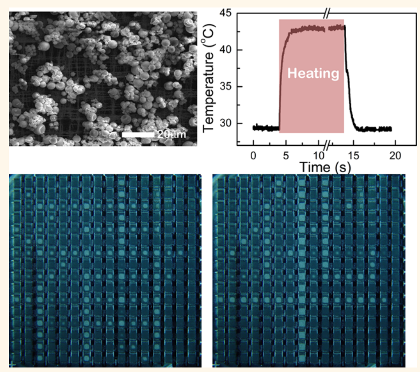
ABSTRACT The influence of heating load on the thermal response of a CNT film heater has been studied. Two kinds of heat dissipation modes, thermal radiation in a vacuum and convection in the atmosphere, are investigated, respectively. It is found that the thermal response slows down with the load quantities in the both cases. We have further studied the thermal response of a CNT film loaded with thermochromic pigment, which is a kind of phase change material. In addition to the thermal response slowing down with the load quantity, it is also found that the phase change of the thermochromic pigments can also slow down the thermal response. With a suspended CNT film heater structure, we have fabricated a thermochromic display prototype, which can switch from room temperature to 50 °C in about 1 s with a brightness contrast of 4.8 under normal indoor illumination. A 16 × 16 pixel thermochromic display prototype can dynamically display Chinese characters driven by a homemade circuit.



KEYWORDS: carbon nanotube · microheater · thermochromic · display

Carbon nanotube (CNTs) films show very fast thermal response due to their ultrasmall heat capacity per unit area (HCPUA).[1,2] Loud speakers,[1] incandescence displays,[2] and thermochromic displays[3] made with CNT films have been demonstrated. It is hoped that CNT film may be used as a potential fast response and addressable microheater in a broader field.[4−8] However, except for applications such as loud speakers[1] or incandescence displays,[2] the heaters usually need to heat other parts or materials to fulfill certain functions such as in refs 4, 5, 9, and 10. These parts or materials play the role of heating load and should be usually viewed as a whole with the heater in applications. It is necessary to consider the influence of the heating load on the thermal response for the applications of heaters.

However, the difference in the surroundings, temperature range, and heating dissipation modes will induce the different thermal behavior. At the same time, a different load type will also show different thermal behavior. We investigated the load characteristics of a CNT film heater from the above aspects in this paper. First, by using graphite powder as the heating load, we have studied the load characteristics at high temperature in a vacuum and the load characteristics at room temperature in the atmosphere. The differences in circumstance and temperature induced different heat dissipation modes, which will influence the load behavior differently. To study the influence of load difference, we have studied a kind of load that will undergo a phase change in the working temperature range. A thermochromic pigment is used as the heating load, which has been widely used as a temperature indicator and also been demonstrated to be potentially used in information display. The color transition with temperature is triggered by the phase change of the working materials.

The results show that the thermal response will be lengthened with load quantity in the different cases. Radiation and convection show different temperature relations

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with load quantities. The thermal response difference between the CNT film and the CNT film with a load in the convection case is smaller than that in the radiation case. The phase changes can be clearly observed in the thermal response curves and will also induce an obvious elongation of the thermal response whatever the on and off delays. However, both the on and off delay of a thermochromic pigment on a suspended CNT film can be as short as less than 1 s. Therefore, we have further demonstrated a dynamic thermochromic display with the CNT film heater array. It can display Chinese characters frequently with a homemade drive circuit.

RESULTS AND DISCUSSION

As is well known, the thermal response of the heater system can be analyzed with the thermal transport partial differential equation,[3,11]

$$c\rho_{\mathrm{m}}\frac{\partial T}{\partial t} = k(T_{xx}+T_{yy})+i^2\rho_{\mathrm{E}} - 2h(T - T_0) - 2\varepsilon\sigma(T^4 - T_0{}^4)$$

It is the thermal transport equation in two-dimensional form. Here c, ρ_{m}, T, and t are specific heat, mass density, temperature, and time, respectively. k is the thermal conductivity. i and ρ_{E} are the current density and electrical resistivity, respectively. T_0 is the environment temperature. h is the convection coefficient. σ and ε are the Stefan–Boltzmann constant and the radiation coefficient, respectively. The mass density, heat conductivity, and electrical resistivity here are all the definitions under two dimensions. From the thermal transport equation, we can see that the specific heat, mass density, and the ratio of convection and thermal radiation terms can all influence the temperature evolution. Their influence should be analyzed for the purpose of application.

We have used a two-layered cross-stacked CNT film due to its better mechanical properties.[12−16] The CNT film is first placed on a metal frame as shown in Figure 1a. Graphite powder is used as the heating load due to its stability and similar properties to those of CNTs. To sustain the free-standing state of the CNT film, the graphite powder is dispersed into ethanol by supersonication and sprayed on the CNT film with an airbrush, as shown in Figure 1b.[17] Four different samples with mass loads of 255, 453, 704, and 884 μg/cm^2 are prepared to study the influence of different mass density. Figure 1c−f shows the scanning electron microscope (SEM) images.

We have first investigated the thermal response of different load quantities at high temperature in a vacuum, where the heat dissipation mode is thermal radiation. The sample is adhered on two metal rods as electrodes. The images of the samples heated to incandescence are shown in the Supporting Information. The temperature is calculated based on the simulation of the incandescence spectrum with that of blackbody radiation.[18,19] The incandescence spectra are collected with a spectrometer. The thermal response is measured based on the incandescence signals recorded with a photodiode. The results are shown in Figure 1g. The on delay is defined as the period from the time when the heating pulse is applied to when 90% of maximum photodiode signal is reached. The off delay is defined as the period from the time when the heating signal is stopped to when 1.5 times the standard deviation of the minimum photodiode signal is reached. As a comparison, the thermal response of a two-layered CNT film is also plotted in Figure 1g labeled with 0. We can see that the thermal response of the two-layered CNT film is about 2−4 ms and below 1 ms for on and off delays, respectively. The on delays of the samples with a graphite powder load are all about 0.1−0.3 s and decrease with temperature. The off delays of the samples with a load are all about 20−50 ms, increase obviously with temperature at the lower temperature, and enter a plateau at the higher temperature. The possible reason for the plateau is analyzed in the Supporting Information. The temperature relations of on and off delay change for the sample with a load are similar to those of a CNT film.[2] At the different heating powers, the larger power will induce a higher temperature and shorter on delay. For the off delay, the higher temperature will show a larger value due to the longer cooling time. However, it can be found that both on and off delays increase with load quantity, which is easy to understand according to the thermal transport equation.

The thermal response of the samples at lower temperature in the atmosphere is also studied. Convection will be the main heat dissipation mode in the temperature range and circumstance. The result is shown in Figure 1h. Here the temperature is recorded with an infrared imager with a 120 Hz frame rate. The infrared images are also shown in the Supporting Information. The on delay is defined as the period from the time of 32 °C to 90% of the highest temperature, and the off delay is defined as the period from the time of 90% of the highest temperature to 32 °C. The on and off delays are roughly about 50 ms to 0.4 s. We can see that the on delay decreases with temperature and the off delay increases with temperature. This originates from the same reason as in the high-temperature behavior in a vacuum. Both the on and off delays also increase with load following the thermal transport equation. Here, the on and off delays of the CNT film are also included in the figure and are about 50 ms, and those of the CNT film with load are all about 0.1−0.5 s. The difference between the CNT film and the samples with load is not as large as that in the case of high temperature in a vacuum. This should be attributed to the difference between the thermal radiation in a vacuum and convection in the atmosphere.

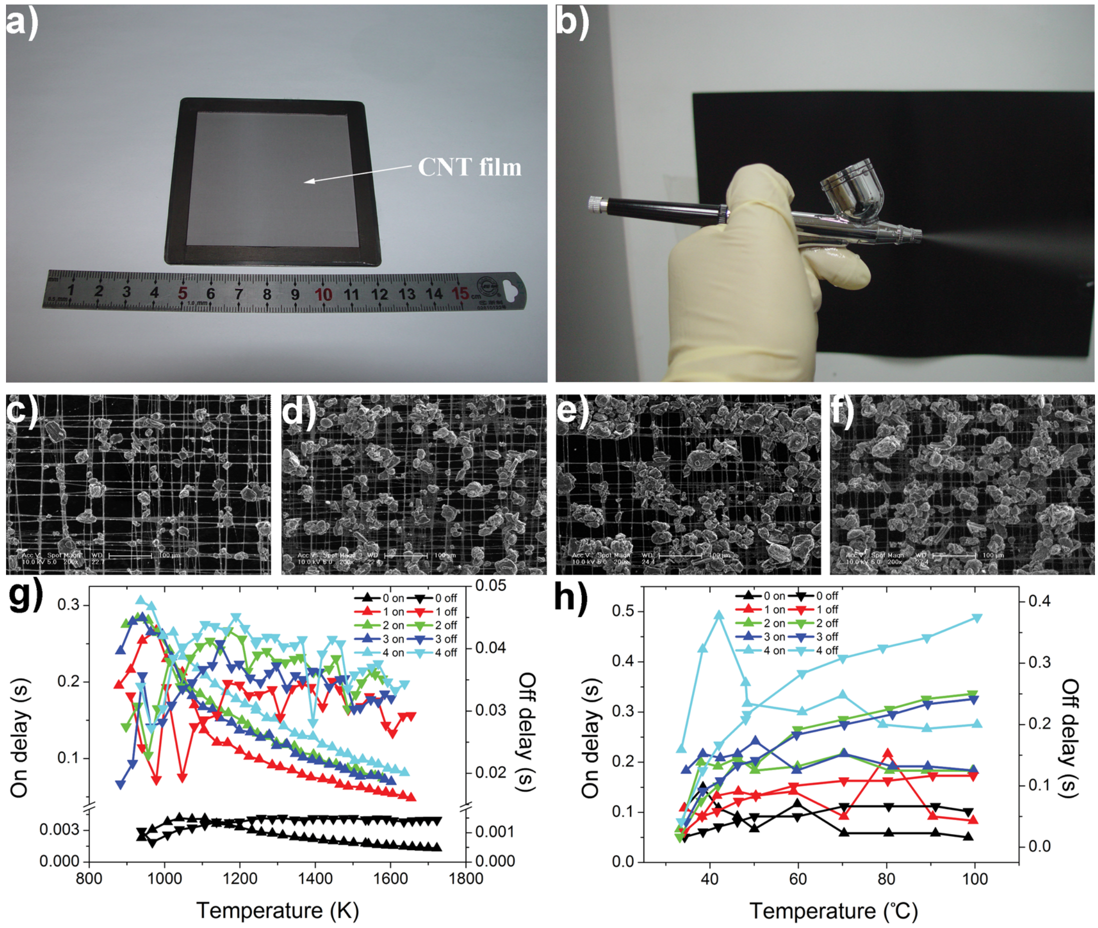

Figure 1. (a) CNT film on the metal frame; (b) airbrush to deposit the graphite powder on the CNT film; (c–f) SEM images of the graphite powder on the CNT film; 1–4 are the samples with mass loads of 255, 453, 704, and 884 μg/cm^2, respectively; (g) high-temperature thermal response of the CNT film with different loads under the thermal radiation dissipation mode in a vacuum; (h) the low-temperature thermal response of the CNT film with different loads under the convection heat dissipation mode in the atmosphere.

The air around the sample is also heated in the convection mode, which can induce a thermal response time elongation by lowering the convection. The thermal response of the CNT film is slowed down as a result.

The thermal response of the CNT film integrated with phase change loads is further studied. Their thermal physical parameters will not continuously change with temperature. The influence on thermal response will be obviously different from the loads without a phase change. One requirement for the phase change load is that it should not react with the CNT film heater. An encapsulated thermochromic pigment is a suitable choice due to its outer protective capsule, which can prevent reactions with other materials. We have used a spherical-shaped thermochromic pigment of diameter about several micrometers. The color change components are a mixture of two kinds of materials. It will become colorless when the temperature is above the transition temperature. The detailed mechanism of the thermochromic phenomena can be found in refs 20 and 21. The color change process accompanies the phase change at the transition temperature. Four different samples with mass loads of 204, 310, 365, and 816 μg/cm^2 are also prepared. Figure 2a–d show the SEM images of the thermochromic pigments on the CNT film support. Figure 2e and f show the temperature curves and the on and off delays for different loads. The on and off delays are about 0.2–2 s for samples 1–4, and both increase with the load. Compared with the result of the graphite powder in the atmosphere, we can notice that the result of the thermochromic pigment is obviously different. First, although the mass load is almost the same as that of the graphite powder, the on and off delays of the thermochromic pigment are obviously larger than those of the graphite powder. This originates from the larger specific heat of the organic thermochromic pigment. The specific heat of graphite powder is about 710 J/(kg·K), while the specific heat of the organic materials is about 1000–3000 J/(kg·K).[22,23] Second, the temperature curves and on and off delay show an obvious difference when the temperature is above about 40 °C. The on and off delays are both larger

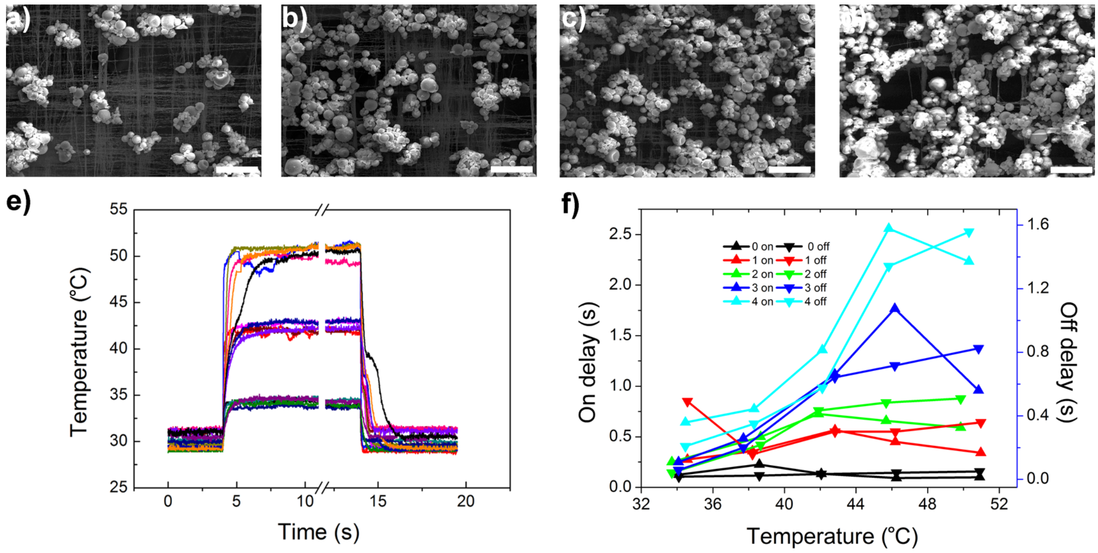

Figure 2. Thermal response of the CNT film with thermochromic pigment load. (a−d) SEM images of the samples with loads of 204, 310, 365, and 816 μg/cm^2, respectively. The scale bars are all 20 μm. (e) Temperature curves of the samples. The labels 0, 1, 2, 3, and 4 are the pure CNT film and CNT films with a mass load of 204, 310, 365, and 816 μg/cm^2, respectively. (f) Corresponding on and off delays of the thermochromic samples 0, 1, 2, 3, and 4.

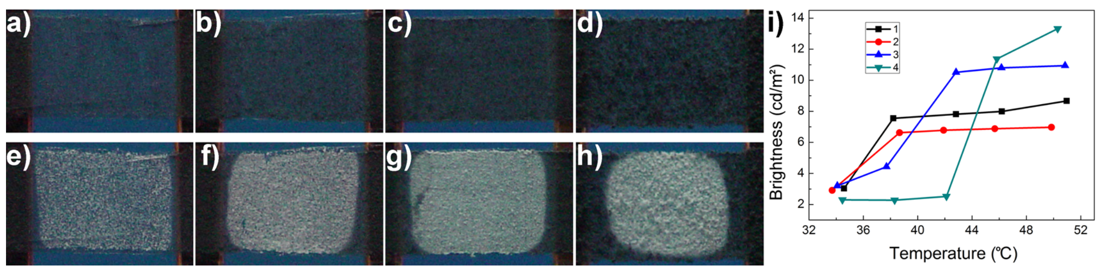

Figure 3. Color transition images of the different thermochromic pigment loads on a CNT film. (a−h) Photos of the thermochromic samples 1, 2, 3, and 4, respectively. (i) Brightness changes with temperature for samples of different loads.

compared with those below 40 °C. The color change temperature of the thermochromic pigments is about 42 °C; the difference should be caused by the phase change of the thermochromic pigment. As is well known, the phase change will adsorb latent heat to trigger the color transition during the heating process and will release latent heat during the cooling process. The latent heat in both processes will induce the delay elongation. The on and off delays increase sharply above 42 °C, as shown in Figure 2f, while for the graphite powder without a phase change in this temperature range, its sensible heat will not induce abrupt changes in the thermal response.

Thermochromic phenomena have been widely used as temperature indicators in many different applications.[20,24] It has also been demonstrated that the thermochromic phenomena can be used as reflective-type information displays.[9] Various thermochromic pigments of different colors indicate that a full-color thermochromic display may also be possible.[21] However, as a real display device, fast response is very important. We can see that the on and off delay of the CNT film with thermochromic pigments can be as fast as 1 s. Furthermore, the on delay can also be shortened by the design of the heating signal waveform, and the off delay can also be shortened by some extra cooling settings. A thermochromic display with fast response might be realized.[3,9] To study the performance of the suspended CNT film with thermochromic pigment for display applications, we have further compared the brightness contrast of the samples with different loads. The result is shown in Figure 3. Figure 3a−h show the images of the thermochromic pigment on a CNT film at room temperature and 50 °C. Figure 3i shows the brightness data of different temperatures under indoor illumination. It can be clearly seen that the contrast increases with the load. Considering the trade-off with thermal response, the sample of medium load such as 365 μg/cm^2 may be suitable for use in real applications.

A thermochromic display with the suspended CNT film sample has been fabricated as a prototype. The CNT film incorporating with a thermochromic pigment is integrated on the glass substrate. To realize the suspended CNT film structure, the substrate is treated with sandblasting to form a precise concave pattern as shown in Figure 4a.[25] The concave pattern is about

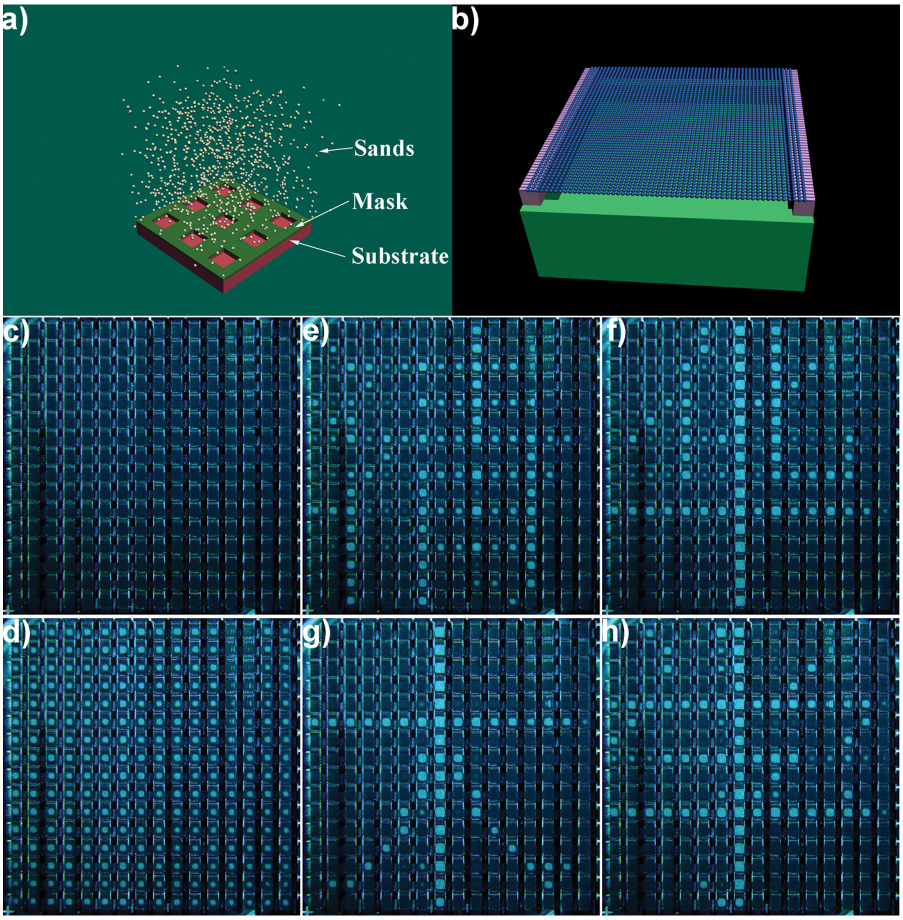

Figure 4. (a) Sandblasting to form the holes on the glass substrate; (b) schematic of the suspended CNT film thermochromic displa;, (c and d) all-off and all-on state, respectively; (e−h) Chinese characters for "Tsinghua University".

200 μm deep. Screen printing is adopted to form the electrodes. The CNT film with the thermochromic pigment is placed on the screen-printed electrodes and cut into the desired pattern with a laser. Figure 4b shows the schematic model of a single pixel of the CNT film thermochromic display on the substrate.

A 16 × 16 pixel thermochromic display prototype drived by a homemade circuit is demonstrated. Figure 4c−h show photos of the thermochromic display. The whole power consumption at the all-on state is about 6 W. A dynamic display movie can be found in the Supporting Information. Although we still have not adopted extra methods to improve the thermal response in the present samples, we can find the speed is fast enough to display the dynamic characters.

CONCLUSION

In conclusion, we have studied the influence of a heating load on the thermal response of a CNT film heater under thermal radiation and convection heat dissipation modes. It is found that in both cases the thermal response slows down with the load. With a phase change thermochromic pigment load, we have found that the phase change will also slow down the thermal response. We have further fabricated a thermochromic display prototype of 16 × 16 pixels, which can be dynamically driven by a circuit. The all-on power consumption is about 6 W for the 25 cm^2 display area. It is hoped that the display can find applications in information displays such as advertisements, newspapers, or books.

EXPERIMENTAL SECTION

Assembly of the Graphite Powder and Thermochromic Pigment on the CNT Film. A 0.5 g amount of graphite powder is dispersed with 20 mL of ethanol. Uniform dispersion can be achieved after about 5 min of supersonication. To sustain the free-standing state of the CNT film, an airbrush purged by pressurized N_2 is used to deposit the graphite powder load. The pressure of N_2 is about 0.2 MPa. Because the CNT film is only hundreds of nanometers, to avoid the destruction to the CNT film, the distance between the airbrush and the CNT film is set at about 20 cm. Because the ethanol can be evaporated during the jet process, no other drying procedure is needed. The quantity of the thermal load is adjusted by the deposition time. For the deposition of thermochromic pigments, 0.3 g of thermochromic pigment is dispersed into 12.5 mL of ethanol by supersonication. The parameters for the jet are the same as those for the graphite powder.

Thermal Response Measurement at High Temperature in a Vacuum and at Low Temperature in the Atmosphere. The CNT film is cut into 3 mm × 4 mm by a yttrium aluminum garnet (YAG) laser and adhered on two nickel rod electrodes with silver paste. Then the sample is placed in a vacuum chamber of base pressure 5×10^{-5} Pa. The samples are first heated to incandescence by a dc power source. The voltage and current are monitored with two digital multimeters. The incandescence spectra are recorded with a spectra radiometer (Konica-Minolta CS1000). The temperature is calculated by the simulation of the incandescence spectrum with that of the radiation of the blackbody. Then the CNT film with a load is heated with a pulse source (Agilent 8114A). The heating voltage is kept at the same value as that during the temperature measurement and monitored with an oscilloscope (Agilent Infinium 54832B DSO). The thermal response is calculated according to the incandescence signal recorded with a photodiode signal (Thorlabs DET10A). The on and off delays are calculated following their definitions in the text.

The temperature curves at low temperature in the atmosphere are recorded with an infrared imager (Optris PI 160). The wavelength range of the infrared imager is 7.5−13 μm. The infrared imager works at a 120 Hz frame rate. Therefore, the response time of the infrared imager is about 8 ms. We have also studied the temperature curves of a CNT film heated with a pulse generator. The result is shown in the Supporting Information and shows that the response of the infrared imager is fast enough for our experiment. To avoid the influence of air fluctuations in the experiment, the sample is placed in a box with only one side exposed to record the infrared image. The on and off delays are calculated according to the temperature curves following their definitions in the text.

Fabrication of the Thermochromic Display Prototype. Sandblasting is used to form a concave pattern on the glass substrate. A metal mask with a designed pattern is used, which is formed with lithography on the steel foil. The mask is adhered on the glass substrate. Sandblasting can transfer the pattern of the mask onto the glass substrate at about 100 μm precision, which is enough for the application of a thermochromic display. Then silicon carbide sand of 80−100 mesh is sprayed with 0.4−0.8 MPa condensed air. The depth of the concave hole can reach about 200−300 μm in about 1 min. The aligning markers are formed on the glass substrate. Screen printing is adopted to form the electrodes. The printing pattern is aligned with the sandblast pattern. At first, silver paste is screen printed to form the column electrodes, and dielectric paste is printed to form the insulating layer; then the silver paste is printed again to form the row electrode. The substrate with screen-printed paste is then sintered at about 500 °C for 30 min. Then the CNT film with thermochromic pigment is placed on the substrate with the screen-printed electrodes. A further laser cutting is performed to remove the parts between the adjacent pixels. The device is driven with a specially designed current-type drive circuit.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: The following information is available for interested readers: incandescence images of the CNT film with different graphite powder loads, high temperature on and off delays with error bars, power−temperature relationship of the samples, infrared images and temperature curves of the samples in the atmosphere with different loads, response of the infrared imager to the pulse heating signal for the CNT film sample. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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