Perfect blackbody radiation from a graphene nanostructure with application to high-temperature spectral emissivity measurements

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Abstract: We report the successful fabrication of a novel type of blackbody material based on a graphene nanostructure. We demonstrate that the graphene nanostructure not only shows a low reflectance comparable to that of a carbon nanotube array but also shows an extremely high heat resistance at temperatures greater than 2500 K. The graphene nanostructure, which has an emissivity higher than 0.99 over a wide range of wavelengths, behaves as a standard blackbody material; therefore, the radiation spectrum and the temperature can be precisely measured in a simple manner. Here, the spectral emissivities of tungsten and tantalum are experimentally obtained using this ideal blackbody material and are compared to previously reported spectra. We clearly demonstrate the existence of a temperature-independent fixed point of emissivity at a certain wavelength. Both the spectral emissivity as a function of temperature and the cross-over point in the emissivity spectrum are well described by the complex dielectric function based on the Lorentz-Drude model with the phonon-scattering effect.

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1. Introduction

An ideal blackbody absorbs all wavelengths of radiation. In a thermal equilibrium state, in accordance with the second law of thermodynamics, every part of the blackbody’s surface emits precisely the same amount of energy as it absorbs at every wavelength and in all directions. This flat response of the absorption and radiation spectra over a wide range of wavelengths and directions makes the blackbody valuable both from a fundamental point of view, such as in standards for absorption and emission spectra, and from an application point of view, such as in solar energy collectors [1,2] and heat-dissipation materials [3].

To obtain such an ideal blackbody, the refractive index must be reduced to almost unity to eliminate reflection; thus, the fabrication of highly porous layers or nanostructures, such as nanoarrays, on the surfaces of metals or semiconductors using chemical methods has been pursued [4–6]. However, a wide range of spectral blackness, a wide angle range of low reflection, and high temperature resistance cannot be achieved for such materials because the commonly used materials of this type are composed of only a few atomic elements, which leads them to exhibit certain characteristic absorption bands. Therefore, an ideal blackbody has not yet been achieved.

Carbon is a good absorber because of the π-band’s optical transitions, and a nearly flat reflection response has been reported for this material [7]; therefore, it is used in many conventional black materials, such as carbon black and graphite, with flat optical response characteristics. However, its minimum value of reflectance is limited to 0.05-0.1 because of moderate reflection at the air-dielectric interface. To reduce reflection while maintaining a flat optical response, the fabrication of carbon nanostructures seems to be promising in the search for an ideal blackbody material candidate. Recent theoretical calculations suggest that an extremely low index of refraction on the order of 1.1 can be obtained using a low-density nanotube array structure [8,9], and this prediction has been experimentally confirmed by Ajayan et al. [10,11], who demonstrated an extremely low reflectance of 0.045%, which is lower than the previously lowest reported reflectance values by a factor of three [4,12]. These results indicate that low-density carbon nanostructures are a candidate for achieving an ideal blackbody [10,13].

Here, we report a novel type of carbon nanostructure consisting of a graphene nanostructure array [14–17] fabricated via simple etching of a carbon substrate. We demonstrate that the graphene nanostructure exhibits not only a degree of low reflectance comparable to that of a carbon nanotube array but also heat resistance at temperatures above 2500 K, which is difficult to obtain using a nanotube array. (The results regarding the heat resistance of these carbon nanostructures are shown in section 4.) We demonstrate that an almost perfect blackbody radiation spectrum in the high-temperature region from 1000 K to 2500 K was obtained from the graphene nanostructure.

Using this blackbody material, we also review the spectral emissivities of refractory metals such as tungsten and tantalum. The thermal radiation properties of refractory metals have been studied over the past 100 years [18–24]; however, we consider that an ideal blackbody sample such as that obtained here offers a precise method for measuring the emissivity, temperature, and radiation spectrum. Therefore, this newly developed blackbody provides an excellent opportunity to confirm previously determined thermal radiation properties. Thus, this graphene nanostructure material paves the way toward the precise determination of spectral emissivity in a convenient manner.
Fig. 1. (a) Scanning electron microscopy image of a vertically aligned carbon nanotube sample. (b) Scanning electron microscopy image of a graphene nanoneedle array sample. The inset shows photographic images of the carbon substrate before etching (left side) and after etching (right side). (c) Transmission electron microscopy image of a single graphene nanoneedle. (d) High-resolution transmission electron microscopy image of a single graphene nanoneedle. (e) Selected-area electron diffraction pattern. Based on the spacing of the c-axis diffraction pattern, the structure of the needle was determined to be a two-dimensional graphene sheet with an interplanar spacing of 0.36 nm. Using the spacing of the a-axis diffraction pattern, the (010) plane spacing based on a six-member ring was determined to be 0.21 nm.

2. Graphene nanostructure fabrication

Graphene nanostructure blackbody materials were fabricated via anisotropic hydrogen plasma etching of a carbon substrate in a microwave (frequency: 2.45 GHz) plasma-assisted chemical-vapor-deposition apparatus. The typical etching conditions were as follows: a microwave power of 800 W, a gas pressure of 1.3 kPa, an H$_2$ gas flow rate of 80 sccm, a
substrate temperature of 600 °C, and an etching time of 30 min [25,26]. We also applied a negative bias of \(-200\) V to the substrate to fabricate a nanoneedle array on the substrate. Blackbody materials of a similar nanostructure were also fabricated using a conventional radio-frequency magnetron sputtering apparatus. In this case, a carbon substrate was positioned on the cathode electrode, and the substrate was sputtered in ambient H\(_2\) or Ar gas at a pressure of 30 Pa and a power of 600 W for a sputtering time of 30 min [27].

Figure 1(b) shows a cross-sectional image obtained via scanning electron microscopy (SEM) of the surface of the carbon substrate after etching, with a 1-\(\mu\)m scale bar. The etching created a nanoneedle array structure on the surface, with an aspect ratio on the order of 100. Furthermore, these nanoneedles are straight and vertically aligned with a low density; therefore, this surface structure leads to a low refractive index.

The magnified image of the spearhead region obtained using transmission electron microscopy (TEM) shown in Fig. 1(c) reveals a single graphene nanoneedle structure. The radius of curvature in the top region of the needle is less than 5 nm, which is promising for low light scattering. This nanometer-sized radius in the top region in combination with the high aspect ratio presents a suitable topology for light absorption because almost perfect impedance matching between the surface and the air is possible.

A high-resolution TEM image of the nanoneedle is shown in Fig. 1(d), where a lattice fringe pattern is shown to extend from the bottom to the top of the needle. Based on the lattice fringe and diffraction patterns (c axis) shown in Fig. 1(e), the top region of the nanoneedle consists of single or multilayers of two-dimensional graphene sheets with an interplanar spacing of 0.36 nm. This spacing is larger than that of the hexagonal graphite structure (0.34 nm), which indicates that the c-axis lattice is relaxed. The electronic structure of the nanoneedle array was also characterized via Raman microspectral analysis. An intense 2D band signal (2680 cm\(^{-1}\)) compared with G band (1580 cm\(^{-1}\)) provides further confirmation that the top region of the nanoneedle consists of single or bilayer graphene sheets [28].

Another diffraction pattern (a axis), whose direction is orthogonal to the interplanar direction, is also observed. Based on the separation distance of the a-axis diffraction pattern, we can determine the atomic level of spacing to be 0.21 nm. This value corresponds to the (010) plane spacing of the six-member ring in the graphene sheets. Because of this \(\pi\) band structure and the perfectly impedance-matched surface structure, the graphene nanoneedle structure is suitable for strong light absorption.

### 3. Reflectance measurements

We now demonstrate the significant reduction of light reflection achieved by the graphene nanoneedles, and we show that we can achieve low reflection of less than 1\% for a wide range of wavelengths, from 400 nm to 2 \(\mu\)m.

The inset of Fig. 1(b) shows photographic images of the carbon substrate before (left side) and after (right side) etching. The photographs were taken with a flash illumination; therefore, the carbon substrate before etching appears to be a brighter gray color compared to the original substrate viewed under normal illumination. In contrast, the fabricated carbon nanostructure remains black in color under flash illumination. This result indicates that the graphene nanostructure is the same type of super-black material as the well-known carbon nanotube forest shown in Fig. 1(a) in the visible wavelength region.

The total hemispherical (specular + diffuse) reflectance in the violet (400 nm) to near-infrared (IR) region (2 \(\mu\)m) was measured using a spectrometer with an integrating sphere whose inside surface was coated with barium sulfate (U4100, Hitachi Corporation), and in the near-IR (1.5 \(\mu\)m) to mid-IR range (10 \(\mu\)m), the reflectance was measured using a Fourier transform IR (FTIR) spectrometer with an integrating sphere whose inside surface was coated with an electrochemically plated, diffuse, gold-metallic coating (IFS 66v/S, Bruker Corporation). For both measurements, standard normalization procedures using NIST-certified samples were followed to obtain an accurate reflectance spectrum.

Figure 2 shows the total-reflectance spectra of the carbon substrate (blue line) and the graphene nanostructure (red line) in the wavelength region from 400 nm to 10 \(\mu\)m.
carbon substrate exhibits total reflectance of the order of 0.1 at 4 μm, and the reflectance gradually increases with increasing wavelength. The total reflectance was significantly reduced to the order of 0.01-0.02 at 4 μm for the graphene nanostructure on the carbon substrate. Another characteristic of the total-reflectance spectrum of the graphene nanostructure is the flat spectral response of the reflectance over a wide range of wavelengths. The reflectance of the graphene sheets parallel to the incident light is not as clearly understood as that obtained in the perpendicular direction (0.1% for single layer and 2% for ten layers [29,30]). However, we examined both the large magnitude of the absorption coefficient (10^6 cm\(^{-1}\)) over a wide spectral range and the light-trapping topology; in particular, the random surface profile depicted in Fig. 1(b) provides the physical mechanism for the low interference, reflectance, and flat spectral response.

Fig. 2. Total-reflectance spectra of the carbon substrate (blue line) and the graphene nanostructure (red line) in the wavelength region from 400 nm to 10 μm. The inset shows the total-reflectance spectra of the vertically aligned carbon nanotube forest (green line) and the graphene nanostructure (red line) from 400 nm to 2 μm.

Here, we compare the total-reflectance spectrum of the graphene nanostructure with that of a vertically aligned carbon nanotube forest fabricated on a silicon substrate. We used a multi-walled nanotube sample for this comparison because the multi-walled nanotubes are superior to single-walled nanotubes because of their low and flat spectral responses for the reflectance [10,13]. The vertically aligned carbon nanotube forest was prepared via the thermal chemical vapor deposition (CVD) process using acetylene gas as the carbon source [31–33]. Its nanostructure, which is suitable for a low-reflectance material, was confirmed by SEM observation, as shown in Fig. 1(a). Our multi-walled nanotube sample exhibits a well-aligned structure with a tube diameter on the order of 10 nm and a thickness on the order of 25 μm. This structure represents the lowest reflectance material ever achieved [10,13]. The inset of Fig. 2 shows the total-reflectance spectra of the vertically aligned carbon nanotube forest (green line) and the graphene nanostructure (red line). In the visible wavelength region,
the nanotube forest exhibits a very low reflectance of less than 0.005. However, the graphene nanostructure exhibits a lower reflectance than the carbon nanotube forest in the IR region. We consider that the lower reflectance in the IR region originates from the angular independence of reflectance for the graphene nanoneedles because the aligned carbon nanotube forest exhibits anisotropic optical behaviors, such as birefringence [34] and iridescence [35], which lead to a higher reflectance. Both carbon nanostructures exhibit low reflectances of less than 0.01 between 400 nm and 2 \( \mu \)m, which suggests that the graphene nanostructure is also an ideal candidate for use as a super-black object with the advantage of a simple fabrication process compared to the CVD process used for the fabrication of the carbon nanotube array.

4. High-temperature blackbody radiation

The super-low-reflectance materials with no wavelength dependence consisting of the nanotube forest and the graphene nanostructure demonstrate absorptivities equal to 1, and these carbon nanostructures are therefore suitable for obtaining an ideal blackbody radiation spectrum because Kirchhoff’s law ensures that the absorptivity of a body is equal to its emissivity under the condition of thermal equilibrium.

Here, the sample was resistively heated in vacuum or in an argon gas atmosphere at a pressure of 100 Pa. A series of radiation-spectrum measurements was performed using an FTIR spectrometer (Frontier-NIR, PerkinElmer Corporation) with a detection range from 8 \( \mu \)m to 700 nm, whose spectral response was precisely calibrated using a blackbody calibration source (M390, MIKRON Corporation). The precise temperature of the heated blackbody samples was also determined using a spectroradiometer (SR3-AR, Topcon Technohouse Corporation) with a temperature accuracy within 0.5%, which was confirmed by the blackbody calibration source.

The inset of Fig. 3 shows the radiation spectrum of the graphene nanostructure at 1600 K (blue circles). The radiation spectrum can be perfectly fitted by the blackbody radiation spectrum (red line) obeying Planck’s law [36] with a high degree of accuracy, and the error between the fit to Planck’s law and the results is less than 1%. The blackness of the blackbody radiation of these carbon nanostructures (nanotubes and graphene nanostructure) is evident over a wide range of wavelengths, with a high emissivity of more than 0.99 for 700 nm to 8 \( \mu \)m.

Both the nanotubes and the graphene nanostructure exhibit the same radiation spectrum; however, emissivity degradation and evaporation of the nanotubes occur at temperatures above 1600 K. (The degradation of single-walled nanotubes occurs at much low temperature [37].) This temperature range coincides with previously reported values for heating experiments of carbon nanotubes [37–39]. Our SEM observations concerning the degradation of the nanotube samples demonstrate that vertically aligned, long nanotubes will bend and come into contact with each other at temperatures higher than 1600 K, which leads to the formation of a micrometer-sized bulky carbon structure. In contrast, the graphene nanostructure exhibits high temperature resistance above 2500 K. The upper inset of Fig. 3 shows the graphene nanostructure before (upper photograph) and after (lower photograph) heating to 2600 K. Our SEM observations illustrate that the graphene nanostructure fabricated on the surface of a carbon substrate maintains its nanostructure when heated to 2600 K, and we did not observe any degradation such as thinning or a reduced density of the graphene nanoneedle layer. The nanostructure degradation was also confirmed via Raman microspectral analysis. We did not observe any change in the Raman spectrum before and after heating, which indicates that the graphene nanostructure is highly heat resistant.

Figure 3 shows the blackbody radiation spectrum of the graphene nanostructure at a temperature of 2480 K (blue circles). An almost perfect blackbody radiation spectrum with an emissivity of 0.99 was obtained (the dip at 4.2 \( \mu \)m can be attributed to CO\(_2\) absorption.). This result strongly suggests that the graphene nanostructure fabricated via simple etching may serve as a convenient standard calibration source for measurements of thermal radiation and temperature, eliminating the need for a massive blackbody calibration source.

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5. High-temperature spectral emissivity measurements

The normal spectral emissivity of a heated planar surface is obtained by defining the ratio of the energy radiated normal to the surface in a narrow wavelength range to that radiated by an ideal blackbody radiator. However, until now, no ideal blackbody radiator has been available, and the spectral emissivities of various refractory materials have traditionally been determined by creating a small radial hole on the surface of the refractory material and then comparing the emission from the surface of the sample to that from the radial hole [18–24]. A more recent approach to obtaining the spectral emissivity is the use of a blackbody furnace as a standard radiation source; the emission from the surface of a sample is compared to that from the blackbody furnace at the same temperature with the same optical arrangement [40]. The small-hole method has a number of limitations, such as the low intensity of the thermal radiation signal because of the small area of radiation, stray radiation from the edge of the hole, the possibility of different surface conditions inside the hole, and temperature inhomogeneities inside the hole; these problems are discussed in [21] by De Vos. However, the blackbody furnace method has other difficulties, such as the necessity of a massive and expensive furnace, especially for high-temperature emissivity measurements. Furthermore, to obtain the same heating conditions, the sample is placed in the same type of oven; however, it is difficult to properly measure radiation from the sample surface because the oven itself emits thermal radiation, and the reflection of this component will overlap the emissivity of the sample [40].

In this section, we demonstrate the ability to determine the emissivity of a tungsten metal surface using an ideal graphene blackbody. The emissivity and other thermal radiation
properties of refractory metals such as tungsten have been studied over the past 100 years [18–24]; however, we consider that the ideal blackbody sample obtained here offers a precise method for measuring the spectral emissivity, radiation spectrum, and radiation temperature and thus presents an opportunity to review previous results.

Fig. 4. Normal spectral emissivity of tungsten for temperatures of 1690 K (blue line), 2140 K (green line), and 2670 K (red line) obtained by dividing the emission spectrum of tungsten by that of the graphene nanoneedle blackbody. The inset shows the theoretically derived spectral emissivity curve of tungsten metal based on the Lorentz-Drude model with the phonon-scattering effect for temperatures from 1500 K to 3000 K (1500 K, blue line; 2500 K, green line; and 3000 K, red line).

To accurately measure the radiation spectrum and the spectral emissivity of tungsten, a tungsten sample of the same size as the graphene nanoneedle blackbody material, e.g., a sheet with dimensions of 5 mm × 100 mm × 0.1 mm, was prepared. The tungsten metal sheet was resistively heated by applying a DC bias voltage under a high vacuum of 10^{-5} Pa or in an inert gas atmosphere (Ar) at a pressure of 100 Pa. The same optical setup as described above for the graphene nanoneedle radiation-spectrum measurements (section 4) was also used to precisely measure the radiation spectrum of the tungsten. The temperature of the tungsten surface was determined from the color temperature obtained using a spectroradiometer (SR3-AR, Topcon Technohouse Corporation), and the accuracy was ensured by constructing a calibration curve between the color temperature and the real temperature, which describes the correlation between the color temperature of the tungsten surface and the furnace temperature. Our temperature calibration curve coincides with the results obtained by Forsythe and Worthing 90 years ago [18].

Figure 4 shows the normal spectral emissivity of tungsten for temperatures of 1690 K (blue line), 2140 K (green line), and 2670 K (red line), where the spectral emissivity was obtained by dividing the tungsten emission spectrum by the graphene nanoneedle blackbody emission spectrum at the same temperature. It is interesting to note that there exists a wavelength (1.37 μm) for which the emissivity is not dependent on temperature but exhibits a constant value of 0.26 over a wide range of temperatures; the emissivity tends to increase...
with increasing temperature above this cross-over wavelength, while the temperature dependence is reversed for shorter wavelengths. We also observed similar behavior in the normal spectral emissivity of tantalum metals, for which the cross point exists at a wavelength of 0.82 μm and an emissivity value of 0.29.

6. Discussion and conclusion

Many studies have been conducted to determine the spectral emissivity and cross-over points of various refractory metals [18–24]. When these reported spectra are compared to our spectral emissivity measurements, the reported values of the cross-point wavelength coincide with our observations; however, the magnitude of the spectral emissivity over the entire wavelength region observed here is smaller compared to previously reported values. The magnitude of the emissivity is influenced by sample characteristics such as purity and surface roughness, and the discrepancy in the spectral emissivity may originate from these extrinsic properties. However, because we obtained a smaller value of spectral emissivity but the same wavelength at the cross point, we believe that our ideal blackbody has a superior quality of blackness, in addition to an emissivity of more than 0.99 and a flat spectral response from 700 nm to 8 μm.

Here, we briefly discuss the cross-over point by analyzing the optical dielectric function based on the Lorentz-Drude model. Initially, the emissivity cross-over points for refractory metals were analyzed based on the same model; however, many parameters were adopted to allow the spectral emissivity curve to be a function of temperature [41–43]. Here, we consider the phonon-scattering process during the lifetime of the model instead of using many fitting parameters, and we show that the Lorentz-Drude model with the phonon-scattering effect clearly reproduces the spectral emissivity and cross-over point for various refractory metals.

For the complex dielectric function, the intraband part (free-electron term) and the interband part are combined and are described by the Lorentz-Drude model as follows:

\[
\varepsilon(\omega) = \varepsilon_0 + \sum_{j=0}^{k} \frac{f_j \omega_p^2}{(\omega^2 - \omega_j^2) + i \gamma_j},
\]

where \(\varepsilon_0\) is the dielectric constant of vacuum, \(\omega_p\) is the plasma frequency, \(k\) is the number of oscillators with frequency \(\omega_j\) \((\omega_0 = 0)\), \(f_j\) is the oscillator strength, and \(\gamma_j\) is the damping constant \((1/\gamma_j\) is the lifetime). We replaced \(\gamma_0\) in the Drude term with the phonon-scattering term as \(\gamma_0 = \alpha kT\), where \(\alpha\) is a unique fitting parameter that can be straightforwardly derived from the linearized Boltzmann transport equation [44]. We used a single Drude term and four Lorentz terms, and we applied the parameter values given by Rakic et al. [45] to reproduce the reflectivity of tungsten metal at room temperature.

The inset of Fig. 4 shows the spectral emissivity curves of tungsten metal that were theoretically derived using a fitting parameter of \(\alpha = 2\); the analysis was performed for a wide range of temperatures from 1500 K to 3000 K (1500 K, blue line; 2500 K, green line; 3000 K, red line). The theoretically derived spectral emissivity curve for each temperature well describes the temperature dependence of the spectral emissivity behavior; in particular, the wavelength of the cross-over point is clearly reproduced at 1.36 μm for tungsten metals and at 0.8 μm for tantalum metals. We note that when a smaller value is chosen for the fitting parameter \(\alpha\), the spectral emissivity takes on a lower value across the whole wavelength region, and the wavelength of the cross-over point shifts to a longer wavelength. However, the character of the cross-over point is preserved as this parameter is changed. The physical origin of the cross-over point of the spectral emissivity is not clearly understood; however, we find that the introduction of the phonon-scattering effect into the Lorentz-Drude model well explains the temperature dependence of the spectral emissivity behavior of not only refractory metals such as tungsten and tantalum but also other noble metals, such as silver and gold, and the theoretically estimated wavelengths of the cross-over point presented here well agree with previously reported values [23].
In summary, we have demonstrated the successful fabrication of an ideal blackbody sample using graphene nanoneedles. Using this blackbody material, we succeeded in determining the spectral emissivity of various refractory metals with an error of less than 1% at temperatures above 2500 K. The graphene nanostructure obtained here will provide a novel method for precisely measuring thermal radiation spectra in a simple manner.

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