Ultra-broadband light trapping using nanotextured decoupled graphene multilayers

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The ability to engineer a thin two-dimensional surface for light trapping across an ultra-broad spectral range is central for an increasing number of applications including energy, optoelectronics, and spectroscopy. Although broadband light trapping has been obtained in tall structures of carbon nanotubes with millimeter-tall dimensions, obtaining such broadband light-trapping behavior from nanometer-scale absorbers remains elusive. We report a method for trapping the optical field coincident with few-layer decoupled graphene using field localization within a disordered distribution of subwavelength-sized nanotexturing metal particles. We show that the combination of the broadband light-coupling effect from the disordered nanotexture combined with the natural thinness and remarkably high and wavelength-independent absorption of graphene results in an ultrathin (15 nm thin) yet ultra-broadband blackbody absorber, featuring 99% absorption spanning from the mid-infrared to the ultraviolet. We demonstrate the utility of our approach to produce the blackbody absorber on delicate opto-microelectromechanical systems, where the thin film comprises the key photoactive (2D) thin film for broadband light trapping is of particular technological interest (5, 6). This ability is central to applications in energy harvesting, sensing, imaging, optoelectronics, telecommunications, and spectroscopy, where the thin film comprises the key photoactive component of the devices (5–11). From Kirchhoff’s law, such 2D light-trapping film is also nontransmitting and antireflecting and is therefore a blackbody (12). This optical performance over broadband has been pursued technologically in a number of ways. For thickness dimensions significantly greater than the wavelength (3D), structures such as tall carbon nanotube forests or silicon nanowires provide a highly effective technique for light trapping (12–15). These structures enable index matching to air, followed by multiple scattering events, and are able to achieve record values of absorption when the tube heights are in the millimeter range (12). At smaller, few-micrometer dimensions, surface texturing (ordered and disordered) complemented by reflectors are used to randomize the angular scattering and enhance the effective path length for absorption (16, 17). Also, ordered arrays have been used to provide adiabatic coupling of the index of refraction to the substrate bulk through an effective medium to minimize reflection (18, 19). For nanometer-thin films of subwavelength dimensions, methods based on photonic crystals, plasmonic nanostructures, and nanocavity resonators are used to provide enhanced coupling of light (20–26). Photonic crystals have been designed to couple light from free space, into light trapping modes in the medium (20–22). Plasmonic arrays work either by scattering light into in-plane modes or by increasing the optical fields around metal nanostructures (23–26). However, this enhancement is based on resonance effects and thereby occurs over a selected but narrow-band spectral range (20–26). Until now, broadband light trapping from nanometer layers of subwavelength dimensions remains an elusive technological challenge.

Graphene, a single atomic layer of graphite, features a gapless band structure (27, 28). It also exhibits remarkably high absorption for a single layer of atoms (α = 2.3%), which is also wavelength-independent throughout the linear region of the band structure (~1 eV) (28–31). Beyond this energy [visible and ultraviolet (UV)], some deviation from this linearity is observed, although it remains almost wavelength-independent, to within a fraction of a percent (29). Despite this, the absolute absorption and quantum efficiency remain low, and avenues to enhance the optical coupling are required before viable optical device implementations. Enhanced optical interactions in resonant plasmonic clusters coupled to graphene layers (30, 31) have yielded increased absorption as well as electronic tunability, leading to the demonstration of graphene-based photodetectors with quantum efficiencies of up to 20% over a spectral range from 600 to 1000 nm. Very recently, emitters with plasmonic resonators formed from single-layer graphene nanostructures were demonstrated (32). Using an electrostatic gate to control the charge density in the graphene, modulation of the emissivity by up to 0.03 could be achieved within a narrow spectral range in the mid-infrared (IR); this is promising for applications that require tunability or fast switching. However, the ability to permanently modify a surface to emit blackbody radiation across ultra-broadband spectral ranges (UV to the mid-IR) has remained elusive until now.

Other coupling methods based on guided modes and nanocavity resonators (32–39) have shown significant improvements, but only at the specific design wavelength. Gan et al. (39) reported optical absorption of up to 45% from a single flake of graphene when coupled to a photonic crystal nanocavity designed to operate at wavelength of 1479 nm. Coupling using plasmonic resonances results in a broader wavelength range of operation. More recently, finite-difference time-domain models have shown that disordered (amorphous) nanostructuring of the 2D films has the ability to improve the absorption over broadband and wide angles as a result of the excitation of multiple in-plane
electromagnetic modes that become trapped in the random media (40, 41).

We combine the broadband absorption properties of a graphene absorber (a few-layer graphene stack) with disordered nanotexturing, using subwavelength-sized metal nanostructures. This combination exhibits a marked enhancement of the broadband absorption, wherein we report absorption enhancement from that of a bare metal surface (15%) to that of a near-perfect absorber (99%) throughout the entire mid-IR to UV spectral range, despite using only a nanometric-scale (15 nm) absorber layer. The optical enhancement takes place uniformly across this broad range, elucidating true blackbody behavior from such a thin film. This improvement shows the arrangement acting as an efficient means to obtain broadband light trapping from free space, across this wide spectral range. We have used a stack of individual graphene layers grown by the solid-state carbon source method (42–44) as the optical absorber layer. This stack of individual graphene layers [turbostratic graphene (45)] is differentiated from ultrathin graphite because each layer is electronically decoupled from its adjacent layers by a random twist angle of the planes (44–46). This decoupling is evidenced by the observation of a single Lorentzian fit to the 2D peak of the Raman signal, which is known from this method of graphene growth (47, 48). It is further manifested by an increase in the $d$ spacing between the planes from 0.335 nm in nominal graphite to 0.344 nm reported in turbostratic graphene (44–46). Here, we report a $d$ spacing of 0.356 nm, concurrent with the Raman observations, which elucidates plane decoupling. The formation of multiple decoupled graphene layers by the solid-state growth method is well understood (44–48).

We demonstrate the practicality of our approach in the production of absorber layers on top of the pixels in a thermal picture synthesizing (TPS) device (Fig. 1; see Materials and Methods). For this particular application, we use the absorber as an optical emitter of blackbody radiation by thermally heating up the layer to a set temperature. From Kirchhoff’s law, the efficiency of the blackbody emission from a surface at a particular wavelength (compared to a perfect blackbody) known as the emissivity, $e(\lambda)$, is equal to the absorptivity of the surface, $\epsilon(\lambda) = \alpha(\lambda)$. A light-trapping surface is also an equally good emitter of thermal radiation ( emissivity), and both measurements can be used interchangeably. The top surface of the pixels operates at a maximum temperature of 800°C (Fig. 1A, inset) and is where the optical absorber (and emitter of blackbody radiation) is produced during the final stages of the production (Fig. 1, B and C). This surface exhibits ultra-broadband antireflection from UV to mid-IR (Fig. 1D) and zero transmission. This demonstrates high values for $e(\lambda) = \alpha(\lambda) \sim 99\%$ across this spectral range in the figure. Emissivity values were also confirmed using IR imaging (see Materials and Methods). The figure inset shows the

![Fig. 1. TPS pixel with nanostructured ultrathin emissivity coating on top surface. (A) TPS design with raised surface. Inset: Model of pixel in operation [hot scale, 20°C (blue); 800°C (red)]. (B) Top surface of TPS showing nanostructured ultrathin absorber. Area shown is denoted in red in (A). Inset: Comparison to a real “moth-eye” from the nymphalid Bicyclus anynana (50). Scale bar, 500 nm. (C) High-resolution scanning transmission electron microscopy (HR-STEM) from top of nanostructures, showing the graphene planes of the optical absorber layer. (D) Reflectance for the decoupled multilayer (DM) graphene absorber (black curve), uncoated nanostructures (pink), nanostructures coated with amorphous carbon (a-C) (red), and a-C on a plain silicon substrate. The DM graphene absorber (black curve) shows broadband antireflection. For all cases, the transmittance is zero; therefore, the absorbance is 1 − reflectance. Inset: Transitions in the linear band structure of the DM graphene absorber involved in the broadband absorptivity and emissivity.](http://advances.sciencemag.org/)

electron transitions in the band structure of graphene that give rise to the broadband optical behavior. An ultrathin absorber layer is required to minimize the heat capacity of the pixel and thereby to rapidly raise the temperature at the surface, which is necessary for dynamic imaging.

RESULTS AND DISCUSSION

The disordered ensemble of Ti nanostructures was produced on the top surface of the pixels using a sputter-etch process that preferentially etches the grain boundaries to produce the nanoscale island particles (see Materials and Methods). The diameters exhibit a Gaussian distribution with a mean diameter of 135 nm and an SD of 20 nm (Fig. 1B). These nanostructures are of subwavelength dimensions compared to the blackbody emission at 800°C, which peak in intensity for wavelengths in the 3- to 5-μm spectral range, where the device is designed to operate. The nanostructures feature similar dimensions and profiles to those found in moth-eye structures (Fig. 1B, inset) (49, 50).

The interaction between a plane wave (4-μm wavelength) and the disordered array (Fig. 2) shows that the electric field of the wave experiences strong localization to the spaces between and around the nanostructures (Fig. 2A). In Fig. 2, the electric field oscillates in the y axis, and the wave travels from left to right along the x axis. The model shows that localization is strongest at the regions between the particle nodules that are more closely spaced, giving rise to the strongest field enhancements. The model shows that localization takes place in spite of the lack of long-range order. In addition, the interaction of the wave induces displacement currents on the metallic structures, producing Joule-heating effects (Fig. 2B). The location of these displacement currents shows that the wave interacts strongly with the surfaces around the nanostructures. The displacement currents induced around the nanostructures (Fig. 2B, inset) generate additional magnetic fields in the z direction (perpendicular to the page in Fig. 2C) of opposite sign for adjacent nanostructures. This leads to the excitation of additional modes that are in-plane with the nanostructured surface (22, 39–41).

We additionally report that treating the nanostructure in Fig. 1 as a disordered photonic crystal yields similar conclusions. It is known that an ordered photonic crystal exhibits strong optical absorption for wavelengths (λ) such that a/λ < 0.2, where a is the lattice constant. This occurs for wave energies well below the gap (51, 52). In this regime, there is a strong interaction between the mode and the material that the crystal is made from, resulting in wave attenuation (51, 52). An active optical absorber (graphene layers) located at this surface is the ideal location to enhance optical absorption. For an amorphous arrangement of nanostructures, the lattice constant a = L/√N, where N is the number of nanostructures in a cell of side L (51). This “strongly interacting” condition is met in our case, where a/λ ≈ 10−2 for wavelengths within the 3- to 5-μm spectral range.

The decoupled multilayer graphene absorber was deposited around the surface of the nanostructures by the solid-state method, by sputter-depositing 20-nm catalytic Fe film, followed by 40-nm a-C.

![Fig. 2. Interaction of 4-μm wavelength radiation with metal nanostructures (without graphene absorber layer).](http://advances.sciencemag.org/)
around the nanostructures, and by thermal annealing (see Materials and Methods). This method facilitates the growth of numerous turbostratic layers of decoupled graphene (20, 43, 44). It is favored here over standard chemical vapor deposition methods because these quickly become self-limited by even a small number of graphene layers, which separate the catalytic surface from the carbon feedstock in the vapor (44). The excess a-C provided in the feedstock (excess carbon not taking part in the catalytic formation of graphene) becomes oxidized into volatile components during the thermal process (20, 43, 44). A second reference sample was produced by depositing the a-C directly on the Ti, without involving a catalytic metal layer.

The catalytic crystallization of the a-C was monitored non-destructively by Raman spectroscopy (53) (Fig. 3). Before annealing, both samples feature broad D (~1350 cm\(^{-1}\)) and G (~1580 cm\(^{-1}\)) bands and no presence of the 2D second-order peak (~2700 cm\(^{-1}\)), revealing a true amorphous carbon structure for both types of substrates. After annealing, the Fe-coated structures reveal a spectrum with the characteristic fingerprints of graphene materials (53). This spectrum consists of a pronounced 2D peak of comparable intensity to the G peak and a pronounced reduction in the full width at half maximum (FWHM) of the D and G bands (Fig. 3, C and D). HR-STEM (Fig. 1C) reveals the presence of ~40 graphene planes at the surface of the nanostructures, with a mean separation between the planes of around 0.356 nm, which is around 6% greater than the \(d\) spacing in pure graphite (0.335 nm). This higher separation is associated with the decoupling of the graphitic planes into individual graphene layers (44, 47, 48). Additional evidence for electronic decoupling of the layers is the observation of a 2D peak that fits a single Lorentzian

![Graph showing Raman spectroscopy results](image)

**Fig. 3. Evolution of absorber with annealing.** (A and B) Raman spectroscopy of carbon films on Fe-coated (A) and bare Ti (B) nanostructures as a function of annealing, using a 514-nm laser. (C and D) Evolution of the D/G and the 2D/G peak height ratio (C) and FWHM of the D and G peaks, showing the formation of graphene structures for the Fe-coated nanostructures (D). (E and F) Optical absorption with annealing for films from (A) and (B), respectively. The increase in the broadband absorption is evident in the Fe-coated nanostructures in (E) and corroborated by emissivity measurements.
curve (with an FWHM of 65 cm$^{-1}$) (Fig. 4A, inset), evidencing electronic decoupling of the layers (47, 48). Fully coupled layers (as for the case of graphite) give rise to multiple bands in the 2D peak structure, whereas individual sheets of graphene show a single Lorentzian 2D peak (47, 48). This known decoupling effect by the solid-state growth method originates from the individual formation of each graphene sheet at different times during the growth as a result of the temperature-dependent solubility of carbon in the catalyst (44). This results in the formation of each layer independently of the previous layer and consequently with a different orientation, resulting in a twist angle (44–46). This step-growth mechanism leads to the formation of a stack of independent graphene planes. The Raman spectra show a weak D-band remnant even after annealing at 950°C, which is further indicative of turbostratic graphene sheets (48). A strong and broadband enhancement of the optical absorption corroborates the formation of these graphene planes on the nanostructures (Fig. 3E). This is also corroborated by a strong increase in the thermal emissivity measurements (Fig. 4A). The details of the spectral characteristics observed in the absorption spectrum may not be characteristic of the density of states of pristine graphene (or graphene stacks) because the nanostructured surface also influences the absorption measurement.

In contrast, annealing the a-C on the Ti only (without the catalytic activity of Fe) reveals roughly equal intensities of D and G bands and weak second-order bands in the Raman spectrum even after annealing at higher temperatures, indicating a disordered form of carbon (Fig. 3, C and D). The absorption spectrum reveals an absorption edge that red-shifts with each progressive anneal, suggesting a reduction in the band gap of the a-C due to an increase in the amount of sp$^2$-hybridized amorphous carbon in the bulk (Fig. 3F). However, a clear absorption edge remains even after annealing at higher temperatures, which indicates the presence of a finite band gap, as is characteristic of sp$^2$-rich amorphous carbon featuring a parabolic band structure (Fig. 3F, left). Despite this, a significant increase in the absorption in the IR with each progressive anneal is also observed for the a-C samples, which is also corroborated by emissivity measurements (Fig. 4B, inset), which reflect direct optical transitions within local sp$^2$ clusters.

The interaction between the decoupled graphene absorber with the nanostructure and the resultant effect on the emissivity is depicted in Table 1. This shows that the nanostructures alone (without carbon) provide only a minor enhancement of the emissivity because of the lack of an active absorber. The table also shows that the absorber layer deposited on a flat surface also provides a low emissivity enhancement due to the absence of the coupling effect that the nanotexturing provides. The table shows

![Fig. 4. Emissivity measurements in the 3- to 5-μm spectral range obtained by IR imaging. (A) Improvement of the emissivity with the formation of the multilayer graphene absorber around the Fe-coated nanostructures. Inset: Single Lorentzian peak in Raman spectrum indicating decoupled graphene layers. (B) Emissivity improvement from reference sample using a-C as the absorber (deposited directly on nanostructures without Fe catalyst). Inset: Increase in peak absorption intensity with reduction in the band gap of a-C films.](http://advances.sciencemag.org/)

![Table 1. Evolution of the thermal emissivity (3- to 5-μm wavelengths) for samples with different layer structures, before and after annealing at 800°C for 10 min. The table shows strong enhancement and necessity to have both the nanostructured titanium and carbon active absorber combined to enhance the emissivity.](http://advances.sciencemag.org/)

<table>
<thead>
<tr>
<th>Sample structure</th>
<th>Emissivity before annealing (%)</th>
<th>Emissivity after annealing (%)</th>
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<tbody>
<tr>
<td>Si</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>a-C/Si</td>
<td>10–20</td>
<td>10</td>
</tr>
<tr>
<td>Ti-nano/Si</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>a-C/Ti-nano/Si</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>a-C/Fe catalyst/Ti-nano/Si</td>
<td>20</td>
<td>99</td>
</tr>
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that the optical enhancement is observed only for the combined structure, whereas the effect of the absorber is amplified by the nanostructure. The spectral characteristics of these are shown in Fig. 1D.

Figure 5 shows this absorption behavior, depicting the energy of the incident wave as it travels from free space (left to right in the figure) and through the nanotextured region (blue-highlighted region). The energy of the wave is shown for the case of interaction with the bare-metal nanostructures (black curve and left case in the figure inset) and for the absorber-coated nanostructures (red curve and right case in the figure inset). The green dashed lines marked in the figure inset depict the traces used to plot the energy density curves. The model shows that the energy density of the wave increases to values above 100% within the gap regions between the nanostructures as a result of wave confinement in these spaces. For the case of the uncoated nanostructures, the wave travels the full length of the nanostructured region and reaches the bulk metal surface after losing only ~15% of the incident energy. A zoomed-in portion of the nanostructure (lower portion of the left inset) shows that most of the waves’ energy can reach this surface. This results in a predominantly reflective surface. In contrast, for the case of the absorber-coated nanostructures (right case in figure inset and zoomed-in section below), the wave is strongly attenuated, losing more than 90% of its energy in this path. As a result, the wave energy close to the bulk metal surface is lower than in the uncoated case (bottom left in the inset). After this, the reflected wave experiences further attenuation in its return path, resulting in a highly absorbing surface.

The absorption obtained in our nanotextured graphene layers is remarkable given that the thickness dimension of the active absorber component, 15 nm thin, is significantly smaller than the 4 μm wavelength. The results presented here are the highest values reported from an absorber layer of subwavelength dimensions across a broad spectral range. Additional modeling shows that the absorption (and emissivity) drops only by 7% upon reducing the height of the metal nanostructures to 150 nm and by 40% upon reducing the height to 50 nm. The nanostructures result from partially etching the top surface of the Ti pixels and therefore do not contribute an additional component of the emissivity surface.

CONCLUSION

We have presented here a method for providing strong optical coupling between free space and an optical absorber to arrive at an ultrathin yet highly efficient optical absorbing surface that exhibits blackbody behavior across a broadband range spanning from the UV to the IR. The absorber exploits the remarkable optical properties of graphene as a result of its gapless semiconducting structure and amplifies the absorption using a combination of layer stacking and nanotexturing around metal nanostructures, causing the optical enhancement. We show that this combination of properties is required to achieve strong optical performance. To our knowledge, this is the thinnest absorber that spans this wavelength range in literature and is of subwavelength dimensions. This constitutes a significant advancement in the field of subwavelength optical active components. Our approach is fundamentally different from similar results obtained using 3D nanostructures (larger dimensions than the wavelength) that rely on multiple-scattering events. These may not be applicable to new systems requiring compactness, such as our TPS pixels. Also, our nanostructure represents a significant improvement over previous developments that rely on the optical properties of flat surfaces alone. The production processes developed are noncontact and highly suited for large-area applications, such as our TPS devices, and are compatible with applications requiring light absorption, such as absorbers for sensors, and design of light absorption components and structures within the active region of new photovoltaic devices.

MATERIALS AND METHODS

The TPS is a flat-panel pixelated display device fabricated on a 100-mm-diameter silicon wafer, which is used to generate dynamic thermal images in the IR. Each pixel (Fig. 1) is an opto-microelectromechanical device that consists of a mechanically elevated planar metal structure that includes an electrical resistor heating element (Fig. 1A). Ti metal coatings were sputtered on the top of the pixels from a Ti metal target using a system from CVC at 10 mtorr and 100 W radio frequency (rf) power at 13.54 MHz onto TPS pixel structures, which were obtained from BAE Systems. The nanostructures were produced by pretreating the Ti surface with an argon plasma run at 40 W of rf power, 20 mtorr, and 40 sccm (standard cubic centimeters per minute) of argon gas using a system from Nordiko and were formed as a result of grain boundary erosion. The Ti used for the nanostructures is part of the mechanical structure of the pixel and therefore does not contribute an additional component of the emissivity surface. Fe catalyst layers were deposited over the nanostructures from a pure Fe metal target using a system from JLS with 5 mtorr of argon at 20 sccm and 20 W of DC power. The a-C coating was sputter-deposited from a pure graphite target using 20 W of DC power and 20 mtorr of argon gas at 20 sccm. Computer modeling was done using the rf module of COMSOL Multiphysics. Emissivity measurements were obtained

![](https://example.com/image.png)
by viewing the thermally heated samples with a thermal imaging camera and comparing them against a control bulk blackbody source at the same temperature of 200°C. Emissivity measurements were verified using the camera’s emissivity function. Fourier transform infrared (FTIR) measurements were obtained using a diffused and specular reflectance attachment to a spectrometer from Nicolet. Raman measurements were made using a system from Renishaw with the 514-nm line of an argon ion laser.

REFERENCES AND NOTES


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