Thermal and optical properties of freestanding flat and stacked single-layer graphene in aqueous media

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Graphene, a two-dimensional atomic layer of carbon atoms, represents a class of nanostructures whose physical properties are strongly dependent on their morphology as well as the environment in which they exist. Aqueous media is one of the most common environments that play an important role in influencing the performance of these materials. Here, we investigate the thermal and optical properties of suspended flat and stacked graphene ribbons that are typical structures in aqueous media. We demonstrate that stacked graphene structures thermalize much more rapidly than flat graphene and display unequilibrated electron and phonon temperatures upon laser excitation. The interface thermal conductivity between graphene and water of \( (7.2 + 1.4/5.5) \times 10^5 \text{ W m}^{-2} \text{ K}^{-1} \) is also obtained. We also show that graphene hot electron luminescence not only depends on Fermi energy, but also exhibit dramatic differences between flat and stacked regions. This indicates the morphology of a graphene structure may affect its optical and thermal properties. © 2014 AIP Publishing LLC.

The exceptional properties and possibility of mass production have prepared graphene for potential applications in numerous fields. Although most research on the fundamentals of graphene is carried out in a dry condition, graphene is often immerged in aqueous media during the process of its applications, ranging from graphene paints and coating, composite materials, energy generation and storage devices, drug-delivery, to biosensors.1–5 Graphene has also become one of the most promising materials in photothermal therapy.7 In order to understand the mechanisms behind these encouraging applications, it is important to investigate the optical and thermal properties of graphene with different morphologies in water. Such investigations not only provide insight into the excited-state properties and phonon interactions in graphene but also offer new design rules for graphene-based devices to improve their performance, such as better power dissipation, higher optical sensitivity, efficient photothermal therapy, and wider operating temperature range in aqueous media.

In this study, we investigate the optical and thermal properties of both flat and stacked single-layer graphene suspended in aqueous media. Suspended graphene structures allow water molecules to cover both sides of the graphene surface, eliminating the interaction with the substrate. We demonstrate that the NIR emission from stacked single-layer graphene is much stronger than that from flat graphene ribbon, both in water and in air. At high laser powers, thermal radiation mainly contributes to the strong emission. The phonon temperature obtained from Raman spectroscopy is lower than the electron temperature extracted from the simultaneous NIR emission measurements, indicating that the electrons are not in full equilibrium with the phonons under laser excitation. Moreover, interface thermal conductivity between graphene and water of \( (7.2 + 1.4/5.5) \times 10^5 \text{ W m}^{-2} \text{ K}^{-1} \) is obtained. In addition, we show that graphene hot electron luminescence intensity not only depend on Fermi energy as previously reported8 but also displays great differences between single-layer flat and stacked graphene regions, suggesting that the morphology of a graphene structure plays an essential role in its physical properties.

Stacked graphene samples were prepared as described in our previous reports9,10 and the supplementary material.11 After annealing, although occasional suspended flat graphene ribbons still exist, most of the graphene above trench area folded and stacked into a structure as shown in Figure 1(a) (top view). While the edges of the freestanding graphene structure above the trench maintained their flat single-layer construction, the middle of the structure folded into a few stacking layers. Figures 1(b) and 1(c) show the corresponding NIR emission mapping of stacked graphene structure in air and in water, respectively. A suspended flat monolayer graphene ribbon (Fig. 1(d)) was also prepared, and its mapping in air is shown in Figure 1(e). When a single-layer graphene ribbon is stacked, it displays very distinctive emission characteristics in the NIR region from flat monolayer graphene. Under a high excitation laser power in air, the emission from stacked graphene is very strong, especially in the middle suspended region where more graphene layers are expected. In contrast, the NIR emission from the edges of the structure, corresponding to the suspended flat monolayer part, is much weaker. This is similar to the emission intensity from flat graphene ribbon in air where very weak emission signal can be observed. On the other hand, although the same excitation laser power is applied, the emission mapping of stacked graphene structure in water
becomes much weaker as a result of the higher interface thermal conductivity between graphene and water, which will be discussed later.

We look into the NIR emission spectrum from stacked single-layer graphene structure. Previous reports suggest that the majority of the locally generated power is dissipated into the metallic contacts and the substrate.12 Although the thermal conductivity of graphene at room temperature is high, Umklapp scattering reduces the amount of heat carried into the metallic contacts at elevated temperatures.13,14 Moreover, freestanding graphene structures eliminate direct energy transfer into the substrate. Therefore, thermal radiation into the free space, which can be detected spectrally resolved in the NIR region, becomes an important pathway for energy dissipation. Figure 2(a) shows the NIR spectra of the stacked graphene structure. The thermal radiation spectra can be fitted to Planck’s law for grey body to extract the temperature

$$u(\nu, T) = \varepsilon \frac{8\pi}{h^2c^3} \frac{(h\nu)^3}{\exp(h\nu/k_BT) - 1}.$$  

(1)

In this equation, $u$ is the spectrum energy density, $h$ is Plank’s constant, $c$ is the speed of light in vacuum, and $T$ is the temperature. Assuming that the emissivity of graphene $\varepsilon$ is a constant over the studied energy range, the corresponding temperatures are calculated as shown in Figure 2(c) (blue squares). A temperature as high as $\sim 800$ K is achieved before the graphene structure breaks down. This calculation is based on the energy distribution of charge carriers. In other words, the temperature we obtained here from thermal emission is the electron temperature.

Raman spectroscopy was also applied to extract the local temperature of freestanding stacked graphene since Raman 2D-mode of flat single-layer graphene shows a temperature dependence as reported in previous literature.15 In our experiment, a stacked graphene ribbon was placed in a microscopy cryostat (Janis), and a 785 nm diffraction-limited laser spot
(<500 nm) was then fixed on the stacked region that displayed the highest thermal emission intensity. When the temperature of the whole sample was increased by a heating stage in the microscope chamber, the Raman 2D-mode of stacked graphene showed a linear downshift with the temperature-scaling coefficient of $-0.066 \text{ cm}^{-1} \text{ K}^{-1}$ (Fig. 2(c), inset). Here, the temperature dependence is related to the temperature of phonons to which 2D mode anharmonically couples.\textsuperscript{16} We also investigated Raman 2D peaks at the same region of the stacked graphene structure with different excitation laser powers as shown in Figure 2(b). Based on the Raman-temperature scaling coefficient, the phonon temperatures of stacked graphene under various laser excitation powers were obtained (Fig. 2(c) red triangles). We noticed that the electron temperature from thermal emission is higher than the phonon temperature, which is different from results obtained for electrically heated flat single-layer graphene.\textsuperscript{16,17}

To further explore how aqueous media influence the properties of graphene, we compare Raman spectra of graphene in air with those in water. Figure 3(a) shows that the downshift of Raman 2D peaks of suspended single-layer graphene in air is significantly larger than that in water, indicating more thermal energy was transferred from graphene to water than to air. In other words, the interface thermal conductivity between graphene and water is larger than that between graphene and air. In order to estimate this important parameter, we need to find the temperature dependence of Raman 2D peak shift of single-layer graphene ribbon. As described in the previous section, similar experiments were performed for a suspended flat graphene ribbon placed in a microscopy cryostat. The Raman 2D peak downshift with temperature at a rate of $-0.067 \text{ cm}^{-1} \text{ K}^{-1}$ is shown in the inset of Figure 3(a). This result is close to the reported value for monolayer graphene suspended above porous membrane,\textsuperscript{18} but higher than the values obtained from supported graphene,\textsuperscript{15,19} probably due to the elimination of substrate interaction. The temperature dependence of freestanding graphene ribbon on excitation laser powers is then acquired. By fitting the data linearly, we obtain the scaling factors between graphene temperature and the excitation laser power, 11.8 K/mW in air and 4.8 K/mW in water (Fig. 3(b)). These coefficients are an order of magnitude smaller than that of the stacked graphene (over 150 K/mW in air, Fig. 2(c)), which is much easier to thermalize than its flat graphene counterpart. The center of the stacked graphene can be considered as a few layers of graphene superposed together, where the optical absorption of graphene is proportional to the number of layers.\textsuperscript{20} For stacked graphene, a much higher percentage of excitation laser power is absorbed, leading to a more efficient thermalization. However, the enhanced absorption may not be the only factor affecting the thermal emission of stacked graphene since less than 10 layers of graphene is stacked in these structures as shown in Fig. 1(a) and our previous study.\textsuperscript{9,10} This indicates that the morphology change in the stacked region also affects the thermalization coefficient of graphene.

Under the same laser power, the graphene temperature in water is much lower than the graphene temperature in air because the interface heat conductance between graphene and water is much higher than that between graphene and air. Therefore, considerable amount of heat is transferred into water when graphene is surrounded by aqueous media, while the majority of the heat propagates along the graphene ribbon in air. We estimate the interface thermal conductance per unit area, $g$, for suspended graphene in water. The temperature ($T$) distribution of diffusive phonons in graphene, with both sides exposed to water, is obtained in the cylindrical coordinate from the heat diffusion equation\textsuperscript{18,21}

$$
\frac{1}{r} \frac{d}{dr} \left( r \frac{dT}{dr} \right) - \frac{2g}{k} \Delta T + \frac{q}{k} = 0,
$$

where $r$ is the radial position, $q = \frac{p}{\text{NA}} \exp(-r^2/r_0^2)$ is the volumetric optical heating, $k$ is the thermal conductivity of graphene (see supplementary material\textsuperscript{11}), $r_0 = \frac{\text{NA}}{p}$ is the radius of the Gaussian laser beam, $\text{NA}$ is the numerical aperture, and $q_0$ is the peak absorbed laser power per unit area at the center of the laser beam. The total absorbed laser power $P = q_0 \pi r_0^2$. The boundary conditions are $\frac{dT}{dr}|_{r=0} = 0$ and $\Delta T|_{r=\infty} = 0$. For given $P$, $g$, and $k$ values, the temperature distribution of diffusive phonons in graphene can be obtained by simplifying Eq. (2) to a nonhomogeneous Bessel’s equation.\textsuperscript{21} Here, with $P$ and $k$ values already obtained, we adjust the $g$ value so that the measured temperature in the experiment matches the temperature rise in the model

$$
\Delta T = \frac{\int_0^\infty T(r) \exp\left(\frac{-r^2}{r_0^2}\right) r dr}{\int_0^\infty \exp\left(\frac{-r^2}{r_0^2}\right) r dr}.
$$

The resulting graphene interface thermal conductivity values are $g_{\text{graphene-water}} = (7.2 + 1.4/(-5.5)) \times 10^5 \text{ W m}^{-2} \text{ K}^{-1}$, which is an order of magnitude higher than the interface thermal conductivity...
conductivity in air reported by Chen et al. ($\kappa_{\text{graphene-air}} = (2.9 + 5.1/2.9) \times 10^7$ W m$^{-2}$ K$^{-1}$). As we expected, the amount of heat loss in air is negligible compared to the amount of heat lost in water when the graphene is in aqueous media. The obtained $\kappa_{\text{graphene-water}}$, however, is about an order of magnitude smaller than the reported interfacial thermal conductivity between graphene and SiO$_2$ measured by pump-probe method, indicating that SiO$_2$ is a much better heat dissipater for graphene.

Under a low laser power, graphene temperature is also lower. Planck’s law predicts that the majority of thermal radiation redshifts beyond the spectrum range we study. We investigate the NIR emission from flat and stacked single-layer graphene at different Fermi energies at a low laser power by looking into the accumulated infrared emission from the suspended graphene structure. Figure 4(a) displays the electrical resistance curve of the graphene, which shows a Dirac point at 1.55 V. We mainly investigate the graphene at the hole-doping region. The SEM image of the suspended graphene is shown in Figure 4(b), with the edge of the trench marked by thick dashed lines. A 785 nm (1.58 eV) excitation laser was focused and scanned along the suspended graphene structure (Fig. 4(b) thin dashed line from upper left to lower right). The emission signal (900–1600 nm) from each point on this dashed line was collected at different gate voltages as shown in Figure 4(c). At the same gate voltage, the stacked graphene region displays a stronger emission compared to the flat region owing to higher absorbance and interlayer interactions. When the Fermi energy rises to $\sim 0.67$ eV ($|V_g - V_{\text{Dirac}}| \sim 3$ V), the NIR emission becomes much stronger, and this bright emission diminishes when the Fermi energy further increases to $\sim 0.8$ eV ($|V_g - V_{\text{Dirac}}| \sim 4.1$ V).

Four spots on the scanned line are picked, and their emission intensities are plotted against the gate voltage (Fig. 4(d)). $S_1$ is supported graphene on fused silica substrate. $S_2$–$S_4$ are suspended regions of the graphene structure, where $S_2$ is flat single-layer graphene and both $S_3$ and $S_4$ are stacked graphene of different layers. The enhanced NIR emission at high Fermi energies in $S_1$ is similar to the recent report by Chen et al. for supported single-layer graphene. In that study, photoluminescence over a wide spectral range in the NIR region was observed due to the excited-state relaxation channels (an empty valence band state) that are only available when the graphene was heavily doped. Here, similar results are observed for both flat and stacked graphene. The non-zero emission in the lightly doped region mainly results from the thermal emission, which does not depend on the graphene doping level significantly. The emission in the suspended single-layer region ($S_3$) is stronger than that in the supported single-layer region ($S_1$), possibly because the free-standing graphene region has more wrinkles that can absorb more incident laser energy. Figure 4(e) shows the emission intensities of the four points normalized by that from the single-layer suspended region ($S_2$) as a function of gate voltage. At supported single-layer region ($S_1$), this emission intensity ratio remains roughly a constant. If the high emission in the stacked regions ($S_3$ and $S_4$) is attributed to the enhanced absorption in the multi-layer stacked region, we...
expect to observe a constant ratio. Interestingly, the intensity ratio of stacked graphene (S3 and S4) to monolayer graphene (S2) is gate-dependent, with a higher ratio observed at a higher Fermi energy. This gate-modulated emission ratio change may result from the increase of hot carriers in the stacked region. This indicates that the local morphology change influences the electronic band structure of graphene.

In conclusion, we synthesized freestanding flat and stacked single-layer graphene structures and investigated their optical and thermal properties in aqueous media. Stacked graphene structure is much easier to thermalize than flat graphene structure. Moreover, the photon temperature obtained from Raman spectroscopy is lower than the electron temperature extracted from simultaneous NIR emission measurements of stacked graphene structures exposed to NIR radiation. The interface thermal conductivity between graphene and water are calculated. The optical properties of the graphene structures are further studied at elevated Fermi energies, where hot electron luminescence and Raman G- and 2D-mode peak shift are observed. These studies shed light on the knowledge on the photothermal properties of graphene in aqueous media and the mechanisms behind the promising applications of graphene in various fields, such as graphene-based ultracapacitors,23 efficient photosensitizers for photothermal therapy,24,25 phosphene in various fields, such as graphene-based ultracapacitors,23 efficient photosensitizers for photothermal therapy,24,25 phene in various fields, such as graphene-based ultracapacitors,23 efficient photosensitizers for photothermal therapy,24,25 image-guided drug delivery,26 nanoelectronic circuits,27 and thermal interface materials.28,29

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11See supplementary material at http://dx.doi.org/10.1063/1.4881136 for fabrication of the stacked graphene structure, experimental setup, estimation of graphene thermal conductivity, electrolyte gating of graphene, and Fermi level calculation.