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Protection of Molecular Microcrystals by Encapsulation under Single-Layer Graphene

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ABSTRACT: Microcrystals composed of the conjugated organic molecule perylene can be encapsulated beneath single-layer graphene using mild conditions. Scanning electron and atomic force microscopy images show that the graphene exists as a conformal coating on top of the crystal. Raman spectroscopy indicates that the graphene is only slightly perturbed by the underlying crystal, probably due to strain. The graphene layer provides complete protection from a variety of solvents and prevents sublimation of the crystal at elevated temperatures. Time-resolved photoluminescence measurements do not detect any quenching of the perylene emission by the graphene layer, although nonradiative energy transfer within a few nanometers of the crystal–graphene interface cannot be ruled out. The ability to encapsulate samples on a substrate under a graphene monolayer may provide a new way to access and interact with the organic crystal under ambient conditions.

INTRODUCTION

Two-dimensional (2D) materials have attracted the attention of researchers due to their novel physical properties, such as ultrahigh carrier mobilities, thermal conductivity, and mechanical toughness.1,2 As a prototypical 2D material, graphene has been the subject of extensive study. This atomically thin membrane allows photons, electrons, and even protons to pass through but is impermeable to other chemical species, even those as small as atomic helium.3–6 This impermeability has raised interest in the application of graphene as a protective coating, e.g., to prevent corrosion of an underlying metal.7 Typically, these coatings consist of many overlapping flakes of graphene such that there is not complete encapsulation, but rather a slowing of the diffusion as the reactive species navigate around the sheets.

Reports of complete encapsulation of objects using graphene are relatively rare. Several groups have used graphene to encapsulate liquid samples for electron microscopy experiments,8–10 but these methods are challenging to implement, since they rely on using a pair of sheets to sandwich a liquid droplet. Ideally, one would develop a method whereby individual microscale objects on a solid support can be “shrink-wrapped” by an atomically thin sheet of graphene, making them impervious to chemical attack while still allowing optical and/or electrical access. The encapsulation of metal nanowires between graphene and plastic using hot lamination suggests that such an approach is feasible.11 However, a more general encapsulation method using milder conditions on an inorganic surface would be desirable for organics. Ideally, graphene would make an atomically tight seal with an inert substrate such as glass.

Crystals composed of conjugated organic molecules make a good test system for graphene encapsulation. These crystals possess interesting electronic and photophysical properties,12 with those based on polycyclic aromatic hydrocarbons being of special interest.13,14 They tend to be sensitive to the presence of impurities like O2 or organic contaminants, which can degrade their electronic properties. Organic crystals also dissolve when exposed to organic solvents and sublime when exposed to high vacuum or elevated temperatures. Current protection strategies include isolating them under vacuum or an inert atmosphere and encapsulating them between glass plates sealed with epoxy. In both cases, the crystal becomes inaccessible to electrical or optical probes that require close sample contact like scanning probe microscopies.

This study describes a method to encapsulate single microcrystals composed of the prototypical conjugated organic molecule perylene (PER) beneath monolayer graphene. While graphene has been used previously as a substrate for organic crystal growth,15,16 its use as an encapsulation layer is relatively unexplored. We used PER as a test crystal because its α-polymorph tends to grow in a signature square shape and produces a strong visible photoluminescence (PL) signal. These characteristics allow us to optically detect the presence

Supporting Information

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of these crystals underneath graphene sheet and assess how they respond to solvent exposure and elevated temperatures. The effect of graphene layer on the PER excimer dynamics can be measured by the photoluminescence (PL) decay. Our results demonstrate that a 2D monolayer can completely encapsulate a molecular crystal and turn it into a sample that is robust with respect to air and solvent exposure as well as high temperatures. This new capability to protect fragile crystals should open the door to routine characterization of these fragile semiconductors using microscopy techniques with nanometer resolution, as well as new ways to interface them with other materials.

■ RESULTS AND DISCUSSION

The procedure for coating PER microcrystals with graphene is outlined in Figure 1 and described in detail in the Supporting Information. Briefly, large-area single-layer graphene sheets grown on a Cu foil substrate by chemical vapor deposition are purchased from a commercial vendor. A cellulose acetate polymer layer with a thickness of several microns is spin-cast on top of the graphene and then the Cu is dissolved in a solution of HCl/H2O2. After the Cu layer is completely etched away, the solution is replaced with clean water and the graphene–polymer layer is floated on the water surface. A glass substrate, on top of which random PER microcrystals have been grown by solvent evaporation, is then dipped into the water and positioned underneath the supported graphene. It is then lifted up with the graphene layer on top. The end result is a sample consisting of the glass substrate with PER crystals underneath a blanket of graphene with the polymer support layer on top. The final step involves dissolving the polymer-supporting layer by rinsing with acetone. The presence of graphene can be readily discerned by its modified reflectivity, and it is easy to see breaks and holes in the coating.

Figure 1. Schematic illustration of the graphene encapsulation process for molecular microcrystals.

Figure 2. (a,b) SEM images of graphene covered PER crystals on glass with low and high magnification. Note that the continuation of the graphene wrinkles from the substrate surface across the PER crystal in (b) provides visual evidence the encapsulation. (c) AFM image of graphene covered perylene crystals with (d) cross section analysis. The typical diameter of the covered crystals is around 2 μm and the thickness is around 150 nm.
Most of the original PER microcrystals are dissolved by the acetone rinse, but in regions containing intact graphene sheets, the underlying PER crystals can be readily imaged using optical, electron, and atomic force microscopy (AFM) methods.

Figure 2a,b shows scanning electron microscopy (SEM) images of PER crystals under single-layer graphene. We note that this imaging was done without a metal coating, since graphene's high conductivity prevents charging of the low-conductivity organic crystal and enables electron microscopy to be performed under vacuum without further treatment. In Figure 2b, one can see a wrinkle in the graphene sheet that continues from the substrate across the edge and onto the crystal surface. This wrinkling was an exception; in almost all other cases, close adhesion of the graphene sheet to the crystal and glass surfaces led to a conformal coating. There is no sign of "tenting," in which the graphene sheet detaches from the surface and is free floating between the crystal and the surface. Tenting was observed for taller or more irregularly shaped objects such as inorganic dust particles adhered to the substrate surface (Supporting Information, Figure S1). The conformal nature of the encapsulation was confirmed by atomic force microscopy (AFM). Figure 2c shows an AFM image of a pair of encapsulated crystals, while Figure 2d shows the height profile of the crystals taken along the axis shown in Figure 2c. The profile image in Figure 2d illustrates the size variation in the PER crystal plates, whose thickness typically ranged from 100 to 200 nm. The images also show how the graphene conforms to the crystal, following the sharp crystal edge down to the substrate surface.

Raman spectroscopy is a standard method to evaluate the quality of graphene layers.19 Figure 3 compares the Raman spectra of graphene on top of both the SiO2 substrate and a PER crystal. Both Raman spectra show the signature G peak in the range of 1580–1590 cm⁻¹ and the 2D peak at around 2600 cm⁻¹. The G/2D peak intensity ratio (I_G/I_2D < 1) indicates monolayer coverage. The small amplitude of the D peak at 1300 cm⁻¹ for the graphene layer on SiO2 shows that it is largely free of defects.19 The Raman spectrum on the PER does not appear to have an enhanced D peak intensity, suggesting that it has the same low defect level, but two additional peaks at 1297 and 1369 cm⁻¹ also appear on top of this feature. These peaks are also prominent in the Raman spectrum of PER microcrystals (Supporting Information, Figures S3 and S4) and originate from the PER double-bond stretches.20,21 It is interesting that the PER and graphene Raman signals are of comparable strength. The 780 nm excitation wavelength is far from the PER absorption at 500 nm but still resonant with the semimetallic graphene. The very strong Raman signal of the delocalized electrons in graphene more than compensates for its lower mass fraction in this sample.

The exact positions of the G and 2D peaks can provide information about the state of the graphene. In pristine graphene, the G peak is located at 1580 cm⁻¹. The G peak of our graphene on glass is located at 1589 cm⁻¹, consistent with doping by exposure to ambient O2 after preparation in air.22,23 The Raman spectrum of graphene on top of PER exhibits a slight downshift in both the G (~8 cm⁻¹) and 2D (~18 cm⁻¹) peaks relative to those of graphene on SiO2. Larger PER crystals resulted in larger downshifts of the Raman peaks, with the largest crystal shifting the G peak all the way to 1570 cm⁻¹ (Supporting Information, Figure S5). These larger G peak shifts were accompanied by larger 2D peak shifts up to 25 cm⁻¹. These shifts were robust with respect to background subtraction and data reduction methods.

There are several factors that can lead to shifting Raman peaks in graphene. Both n- and p-doping typically lead to an upshift of the G-band Raman frequencies,24 but this is the opposite of what we observe. Given that the graphene sheet is already p-doped due to oxygen exposure, one possibility is that the organic crystal removes charge carriers or O2 from the graphene sheets. Such an undoping process would be expected to shift the G peak back to 1580 cm⁻¹, but not below. The fact that we observe shifts of both G and 2D peaks to positions well below those of pristine graphene suggests that the more likely culprit is strain as the graphene stretches to accommodate the underlying crystal. The shifts in both G and 2D peaks are consistent with a strain of approximately 0.5% on a crystal with thickness of about 150 nm, based on previous measurements on stretched sheets of graphene.25,26 This stretching would explain the conformal nature of the coating deduced from the images in Figure 2 and is consistent with the "shrink-wrap" concept. The Raman shifts provide evidence that the interaction of graphene with the underlying crystal induces a slight stretching but no dramatic changes in the electronic structure or defect density. It is possible, however, that the graphene sheet experiences higher localized strain at the crystal edges, which could lead to larger effects on its electronic properties.27

PER is a highly soluble small molecule that sublimes easily, but the graphene–glass encapsulation stabilizes the microcrystals under a variety of conditions. The samples can be left on the benchtop, under room light, for days without any change in PL brightness. The encapsulated crystals survive immersion in a variety of organic solvents (acetone, tetrahydrofuran (THF), toluene, methanol, and methylene chloride) for more than 1 day without change. Unprotected crystals dissolved within 1 min under the same conditions. When heated to 100 °C in air, unprotected crystals sublimed within 40 min, but encapsulated crystals resisted sublimation up to 250 °C, close to PER’s melting point of 278 °C. At
higher temperatures, the PER melted and then rapidly disappeared. Comparisons of graphene-protected and unprotected PER crystals after exposure to solvent and elevated temperatures are shown in Figure 4. The fact that the graphene sheet provides protection from solvent dissolution and sublimation is evidence that the graphene makes an atomically tight seal with the glass substrate that completely prevents penetration by solvent molecules as well as escape of the PER molecules at elevated temperatures. The encapsulation only failed when the PER itself could diffuse (after melting) or if the graphene did not remain intact. Objects with large height variations tended to rupture the graphene (Supporting Information, Figure S1), allowing solvent penetration and dissolution.

Graphene is not a completely inert coating, since it is a semimetal that may be expected to affect the electronic properties of the crystal. For example, it is likely to quench molecular excitons due to either energy transfer or electron transfer.31,32 Although the precise distance dependence and mechanism of the PL quenching remain a subject of active investigation, the characteristic distance has been estimated to extend up to 60 nm.33 To investigate the possibility of PL quenching, the excimer lifetime of the PER microcrystals was measured by time-resolved PL experiments. The PL spectra

Figure 4. Transmitted and fluorescence microscopy images showing the effect of monolayer graphene encapsulation on the stability of PER microcrystals. The substrates are standard microscope slides with gold alignment marks. (a) Before and after washing with THF: 30 s washing resulted in 100% dissolution of unprotected crystals, while 20 min THF washing had no effect on protected crystals. (b) Before and after heating at 100 °C for 40 min: the unprotected crystals sublime completely, but the protected crystals remain intact. The scale bar is 50 μm.

Figure 5. (a) Time-resolved photoluminescence of PER (black) and graphene-coated PER crystals (red) excited at 400 nm. The lifetime of crystalline PER is unchanged when coated with graphene. (b) Calculated PL decays for different R0 values for the graphene quenching function described in the text for a 150 nm thick crystal. When R0 ≥ 20 nm, there is a notable deviation from the intrinsic PER decay.
with and without graphene encapsulation are similar, showing the Y (550 nm) and E (600 nm) peaks as observed in α-PER crystals (Supporting Information, Figure S6). The Y peak in our samples is more pronounced than for typical bulk crystals, as often observed for nanocrystalline samples with higher defect densities. The PL decays of the two samples are identical, as shown in Figure S5a, although the signal level of the encapsulated sample is considerably lower due to the scarcity of surviving crystals. We note that these PER crystals, grown from solution, have a more rapid PL decay than sublimation-grown crystals from zone-refined PER. It is likely that the PL decay is accelerated by the presence of defects in our solution-grown PER crystals. But the important point is that there is no detectable PL quenching by the graphene overlayer.

Even though there is no detectable change in the PL decay, it is likely that excitons near the top surface of the crystal, close to the graphene layer, are quenched. We can place an approximate upper bound on the quenching radius of the graphene using a simple model to analyze the PL decay. We assume an average crystal thickness of 150 nm and that the quenching rate of the 2D graphene sheet is given by $k_{\text{quench}} = \frac{A}{R_0^2}$, where $R_0$ is the critical distance for a dipole interacting with a 2D energy acceptor. The experimental PL decay is parameterized as a biexponential with amplitudes $A_1 = 0.925$ and $A_2 = 0.075$ and decay times $\tau_1 = 7.5$ ns and $\tau_2 = 17.4$ ns. The functional form of the PL decay is then the product of the intrinsic biexponential and the quenching term

$$\text{PL}(t) \approx [A_1 e^{-(t/\tau_1)} + A_2 e^{-(t/\tau_2)}] \times e^{-k_{\text{quench}}t}$$ (1)

In Figure S5b, we compare the PL decays calculated assuming different values of $R_0$ and summing up the contributions of eq 1 for all $R$ values in a 150 nm thick crystal. For $R_0 = 20$ nm, the deviation of the calculated decay from the intrinsic decay should be observable. Similar results are obtained for crystal thicknesses of 100 and 200 nm (Supporting Information, Figure S8). The fact that this deviation is not experimentally observed allows us to estimate a conservative upper bound of $R_0 \lesssim 20$ nm. This limit is consistent with a value of $R_0 \sim 10$ nm extracted from distance-dependent quenching of a rhodamine dye on top of graphene and suggests that only excitons in the top layer of the PER crystal are quenched by the graphene.

The ability to observe electronic perturbations due to graphene will depend on the nature of the organic sample. In PER, the effect of the graphene quenching may be more easily observed for thinner crystals that have a larger fraction of molecules close to the surface or for higher-quality crystals that can support longer exciton diffusion lengths. Different types of crystals may have significant electronic interactions with the graphene layer, for example, charge transfer. Surface-sensitive measurements of the electronic properties will likely be sensitive to the graphene–organic interaction. A second issue is that the method of preparation exposes the sample to water during the graphene lift up. While the graphene clearly prevents access by molecules outside the encapsulation layer, it can also trap impurities or water molecules inside the layer with the crystal. The stability of the graphene-encapsulated sample might be sensitive to the presence of such extrinsic chemical species.

**CONCLUSIONS**

In summary, we have demonstrated that it is possible to create robust molecular crystal samples that are fully encapsulated beneath a monolayer of graphene. The graphene layer provides complete protection from a variety of solvents and prevents sublimation of the crystal at elevated temperatures. Raman measurements show that the graphene layer is only slightly perturbed by the underlying crystal, while time-resolved PL measurements show no detectable quenching of the PER excimers by the graphene. The fact that graphene can make a tight seal with glass suggests that this method can be extended to other 2D encapsulating materials, for example, hexagonal boron nitride, whose large band gap would preclude any possibility of energy transfer. This technique may also make it possible to interface organic crystals with other materials that have incompatible processing conditions like metal electrodes created by focused ion beam deposition under high vacuum or polymers cast from solvents that would normally dissolve the crystal. The ability to keep organic solid crystals intact under such processing conditions raises the possibility of fabricating an organic–organic heterojunction to study energy transfer and/or charge transfer across a 2D membrane.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00872.

Experimental procedures, Raman data work-up, SEM images, PL spectra, and linear PL time trace of PER (PDF)

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Notes

The authors declare no competing financial interest.

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