Abstract:

Covalent organic frameworks (COFs), in which molecular building blocks form robust microporous networks, are usually synthesized as insoluble and unprocessable powders. We have grown two-dimensional (2D) COF films on single-layer graphene (SLG) under operationally simple solvothermal conditions. The layered films stack normal to the SLG surface and show improved crystallinity compared with COF powders. We used SLG surfaces supported on copper, silicon carbide, and transparent fused silica (SiO$_2$) substrates, enabling optical spectroscopy of COFs in transmission mode. Three chemically distinct COF films grown on SLG exhibit similar vertical alignment and long-range order. Two of these are of interest for organic electronic devices for which thin-film formation is a prerequisite for characterizing their optoelectronic properties.

Summary of Research:

Two dimensional (2D) layered COFs incorporate functional π-electron systems into ordered structures ideally suited for optoelectronic devices. However, the frameworks are inherently cross-linked and insoluble, and are produced as either microcrystalline powders from solvothermal reactions [1] or submonolayers by sublimation of starting materials on crystalline metal surfaces [2]. The limited utility of these forms precludes many applications for COFs.

The solvothermal condensation of 1,4-phenylenebis(boron-ic acid) (PBBA) and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) in a mixture of mesitylene:dioxane (1:1 v/v) at 90°C in the presence of single-layer graphene on copper (SLG/Cu) forms a framework known as COF-5 as both insoluble powder and continuous film on the graphene surface (Figure 1). The COF-5 powders and films on SLG were compared using synchrotron x-ray diffraction. X-ray diffraction of a COF-5 powder (Figure 2) shows Bragg peaks with no preferred orientation, observable as rings centered about the origin. Grazing incidence x-ray diffraction (GID) of a COF-5 film on SLG/Cu reveals diffraction peaks with their intensities localized about $Q_\perp = 0$, indicating that the c-axis of the grains is oriented around the surface normal (Figure 3). Projections of these data around $Q_\parallel = 0$ match the pattern predicted for COF-5.

Though our initial studies were performed on SLG supported by its copper growth substrate, the method is general for SLG transferred to other substrates, including transparent fused SiO$_2$ (SLG/SiO$_2$). This flexibility facilitates studying...
the role of the underlying substrate on COF film growth and provides a direct route for incorporating COFs into a wide range of devices. For example, films grown on SLG/Cu are consistently thicker than those grown on SLG/SiO₂, suggesting that the Cu surface (including its defect sites) plays a role in COF nucleation. Because the graphene on each substrate is derived from the same CVD process, we conclude that the thickness and uniformity of the film is strongly affected by the quality of the underlying substrate.

COF films also form on SLG derived from the thermal decomposition of SiC from its Si-terminated basal plane (SLG/SiC). SLG/SiC exhibits reduced surface roughness and larger graphene domains compared with SLG/Cu. In addition, the epitaxial relation between SLG and the single-crystal SiC substrate allowed us to determine that the COF-5 film does not grow epitaxially with respect to the graphene, as rotation of the sample during the GID experiment did not reflect the sixfold symmetry of the COF lattice. This finding suggests that matching the COF lattice size and symmetry to the underlying graphene is not necessary to obtain crystalline films.

The crystallinity and alignment of COF films on transparent SLG/SiO₂ substrates provides a means to organize functional π-electron system within optoelectronic devices. Accordingly, films of two of the first COF semiconductors were grown on SLG/SiO₂. One of these frameworks, known as triphenylene-pyrene (TP)-COF [3] arises from incorporating a pyrene-2,7-diboronic acid linker in place of PBBA into the hexagonal COF-5 lattice (Figure 4, Top). We obtained TP-COF in both thin-film and powder form using similar conditions to those described above. The transparent SLG/SiO₂ substrate enabled ultraviolet/visible/near infrared spectroscopy of a COF film in transmission mode for the first time. Finally, we confirmed that COFs lacking hexagonal symmetry may also be crystallized on SLG by preparing a Ni phthalocyanine (NiPc)-PBBA COF on SLG/SiO₂ (Figure 4, Bottom). The translucent film absorbs strongly over the visible range of the spectrum and is non-emissive, as is expected for H-aggregated phthalocyanines. These vertically aligned, porous phthalocyanine COFs are intriguing precursors of ordered heterojunction films long thought to be ideal for organic photovoltaic performance.

References:


Figure 3: GID data of a COF-5 film on SLG/Cu; (inset) schematic of oriented COF-5 grains in the film.

Figure 4: Top; The TP-COF chemical structure. Bottom; The NiPc-PBBA COF chemical structure.