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WU1R16 Summary Report: Controlling the Interaction between 2D Materials and Active Layers

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This report summarizes the accomplishments of the Materials and Chemistry 6.1 basic research performed under WU 6A61 titled "Controlling the Interaction between 2D Materials and Active Layers." The work was carried out FY20-FY23 with the objective to understand and manipulate the interaction between Liquid Crystal (LC) and 2D materials by characterizing the optical and electronic interactions between basic LC and 2D materials. We used experimental and computational methods to develop a framework for understanding interactions and employed computational methods to design system with optimized interactions. As this program seeks to combine 2-D Materials and soft matter, we will understand nanoscale interactions, use soft matter phases to improve the organic-inorganic heterojunction in terms of functionality and processing to develop new class of hybrid nanomaterials and potentially impart quasiparticle control.

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EXECUTIVE SUMMARY

This report summarizes the accomplishments of the Materials and Chemistry 6.1 basic research performed under WU 6A61 titled “Controlling the Interaction between 2D Materials and Active Layers.” The work was carried out FY20-FY23 with the objective to understand and manipulate the interaction between Liquid Crystal (LC) and 2D materials by characterizing the optical and electronic interactions between basic LC and 2D materials. We used experimental and computational methods to develop a framework for understanding interactions and employed computational methods to design system with optimized interactions. As this program seeks to combine 2-D Materials and soft matter, we will understand nanoscale interactions, use soft matter phases to improve the organic-inorganic heterojunction in terms of functionality and processing to develop new class of hybrid nanomaterials and potentially impart quasiparticle control.

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INTRODUCTION

The final year of this program culminated in work that touched on four main points that aligned with the research objectives: 1) liquid crystal (LC) alignment on two-dimensional (2D) materials, 2) demonstrating fully tunable photoanisotropy, 3) covalent and non-covalent functionalization of 2D materials, and 4) dynamic functionalization. Throughout the duration of the program, the work resulted in several publications and patent applications, with additional ones that are either in process or recently completed. A summary of the scientific progress is documented below and associated with peer-reviewed journal articles and intellectual property submissions.

LIQUID CRYSTAL ALIGNMENT USING 2D MATERIALS

The program focused on the alignment of nematic LC on graphene. We showed that certain molecules will align onto graphene but there is minimal change in the electronic coupling behavior, thus indicating weak interaction between the two materials. Using density functional theory (DFT) we showed a particular molecule well-known to self-assemble and form a nematic LC phase, 5CB, aligns on graphene in three preferred configurations: an armchair (AC), intermediate, and zig-zag alignment (ref 12). The energy difference between the three configurations is minimal and is affected by the 2D lattice, substrate composition, morphology (such as lattice step-edges within graphene), and how the LC material is applied to the 2D material, i.e. its flow properties.

An in-depth analysis of LC alignment on graphene was undertaken using DFT to map the energy barrier as a function of angle. The lowest energy state corresponded to the armchair configuration of 5CB on graphene. The energy barriers for the different AC orientations are relatively large compared to thermal fluctuations, but can be overcome by flow or symmetry breaking at the surface. The calculated AC orientations are consistent with previous surface tunneling microscopy (STM) observations of cyano biphenyl molecules on highly ordered pyrolytic graphite (HOPG) – a graphene surrogate. The landscape of the energy barrier suggests that once a molecule such as 5CB is adsorbed onto the surface, it is essentially locked into place until a thermal stimulus well above the nematic to isotropic phase transition is applied.

Instead of only considering LC alignment on a pristine graphene surface, we also tried to account for topological features present on epitaxially grown graphene, namely step edges that arise during the graphene growth process along the slightly offset Si face of 6H-SiC (silicon carbide). Treating the steps as groove-like features of the substrate, an anchoring energy can be approximated. However, this anchoring energy is weak compared to the strong anchoring arising

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from the graphene honeycomb lattice. When considering these two factors and comparing them to the observed LC orientation and alignment on epitaxial graphene (EG), the two do not match well and indicate that either a combination of factors or other anchoring influences are driving the alignment of LC on EG. Despite this challenge, we present the first model of LC molecular alignment (ref 15).

Another feature related to LC on graphene is the effect on carrier mobility and the Fermi energy. On EG, we observed about a 25% increase in the carrier mobility of 5CB on EG compared to EG alone. Further, there was a concomitant decrease in the Fermi energy by about 25% with the LC-graphene surface compared to EG alone.

A final piece related to LC alignment on graphene was the discovery of graphene's ability to ask as both an electrode and alignment layer for LC-related electro-optic (E-O) applications. In a traditional LC E-O transmissive device, there is an organic layer of material on the order of ~100nm that provides uniform alignment of the LC over the active region. Past the alignment layer is another conductive material that serves as the electrode layer (~10s to 100s of nm thick) for voltage-driven E-O switching. Our discovery was that atomically thin graphene may serve as both an alignment layer and electrode. The advantages being a single material for an E-O device as opposed to a multi-layered stack, a reduction in the distance between electrodes, the elimination of organic absorption peaks (especially relevant for infrared E-O applications), an increased order at the electrode interface, and an increase in the anchoring strength resulting in faster E-O response times. The concept was demonstrated for a basic E-O device – a transmissive LC device consisting of a cell composed of two pieces of graphene on quartz separated with micron-sized spacers and filled with nematic LC. We showed the device had a uniform alignment as indicated when viewed between crossed polarizers under a microscope. Further, when a voltage was applied across the graphene electrodes, the orientation of the LC was uniformly switched from a planar orientation (parallel to the substrate) to a near-homeotropic orientation (perpendicular to the substrate). Thus, using only a graphene layer on a transparent substrate, we demonstrated the graphene layer acted as both an alignment layer and electrode (refs 5,8,11).

TUNABLE PHOTOANISOTROPY

The research program invested time into understanding the interaction of various molecules with 2D materials such as graphene. One class of molecules was photoactive dyes, specifically the azobenzene dye Brilliant Yellow (BY). A more detailed use of this material and its interaction with graphene is detailed in section 4 below. The molecule BY is known for several applications, one of which is as an LC alignment material following a photoexposure step. It is known to produce highly uniform planar alignment along any user-defined orientation parallel to the substrate surface. In terms of coordinates, BY provides excellent control of the azimuthal orientation of LC, i.e. the in-plane orientation. This material also provides strong surface anchoring, thus providing a superior electro-optic response that maximizes the stroke of the LC as the refractive index is modulated and aids in fast LC response times to the application or removal of an applied voltage. However, one limitation of BY (and other azo-based photoalignment materials) was the limited range of the pre-tilt angle, i.e. the polar angle at which BY can be oriented out of the plane of the substrate. This pre-tilt angle is critical in providing a

uniform response of the LC to an applied voltage (as opposed to a degenerate response with different LC domains tilting in different directions). The ideal photoalignment material would be able to provide a re-writeable and user-defined azimuthal and polar orientation to LC.

Under this program, we developed a two-step light exposure method to enable a full range of azimuthal and polar LC alignment. The basic procedure is to first write the azimuthal LC alignment by exposure of a thin film of BY (deposited by simple spin-casting) to polarized light (435 nm at ~25 mW/cm^2). Following this exposure an LC cell is assembled and either left empty or filled with the LC of interest. To then induce a polar pretilt angle, the cell is then exposed a second time to unpolarized light (415 nm at ~100 mW/cm^2). Several additional conditions affect the resulting alignment conditions including the angle at which the light exposure is performed, the dose (intensity) of the light, the type of substrate (transparency, thickness, refractive index, etc.), the type of LC and its refractive index, the amount of counter-ions present, and the thickness of the BY films. We have considered all these factors and shown that we have complete control of the azimuthal (0-180 degrees) and polar pretilt (0 – 90 degrees) angles. Access of the full range of the polar pre-tilt was realized by utilizing the range of refractive indices produced in the absence or presence of the LC, specifically performing the second unpolarized exposure either in the absence or presence of LC. In so doing, we demonstrated a polar pretilt of ~ 0-40 degrees or ~40-90, respectively. These values were unprecedented and captured in both publications and intellectual property. Because the method is photoalignment, we also demonstrated that the LC alignment can be re-written be exposing the LC cell under different conditions. The results have far-reaching implications for LC E-O applications covering interference coatings, optical filters, and phase correction coatings (refs 6,7,10).

FUNCTIONALIZATION OF 2-D MATERIALS

A third area of research covered under this program was understanding the potential for molecular interactions with graphene. It is expected that molecules strongly adsorbed onto graphene will result in a change in the electronic properties of graphene such as a shift in the Fermi energy (i.e. band gap) or charge transfer.

We looked into both covalent and non-covalent functionalization of graphene. In the first scenario, we used DFT to examine the likelihood and effect of covalent insertion of the LC mesogen 4-cyan-4′-pentylbiphenyl (5CB) into a graphene monovacancy. We found that if the molecule is able to approach the monovacancy homeotropically with the cyano head group in proximity to the monovacancy, 5CB undergoes a chemical reaction, releasing 4.5 eV in the process. This reaction follows a step-by-step process gradually adding bonds, inserting and covalently bonding cyano group into monovacancy. The reaction proceeds through several salient steps: 1) an initial bond with a monovacancy carbon pulls the 5CB toward the sheet; 2) the cyano-nitrogen forms a tetrahedral bond with the three carbanions in the monovacancy; 3) the resulting under-coordinated cyano-carbon is pulled further into the monovacancy; 4) one of the three monovacancy carbons unbinds the cyano-nitrogen and binds with the cyano-carbon. From a density of states (DOS) analysis, the process is mediated by the conjugated biphenyl core of the molecule. The resulting structure stabilizes the monovacancy by inserting both the cyano-carbon and cyano-nitrogen into the sheet, with the biphenyl core aligned normal to the surface.

This allows charge to flow between the sheet and the 5CB, shifting the Fermi energy of the graphene. We concluded that this irreversible insertion reaction is likely spontaneous, potentially providing a new avenue for controlling both LC behavior and graphene properties (ref 4).

For non-covalent functionalization, we also utilized DFT to understand the impact of nitrogen (N) and boron (B) atomic substitution into the core of a well-characterized discotic LC and the subsequent intermolecular interactions as well as the impact in the presence of graphene. The substitution of these p-block heteroatoms into polyaromatic hydrocarbons (PAH) offers the potential for introducing enhanced molecular properties and advancing material development for E-O applications. Using DFT, we characterized the substitution of boron and nitrogen atoms into a 2,3,6,7,10,11-hexakis(hexathiol)triphenylene (TTP) core, a precursor for a material with a discotic LC phase, to determine the strength of exciton dissociation and the influence doping has on the formation of a heterojunction with graphene. The substitution of N- and B- into the TTP motif enables tunability of both electron and hole coupling between hetero- and homo-dyads. The coupling is found to far exceed that of TTP and varied transport behavior with different combinations of doped cores of N-TTP and B-TTP is reported. Hetero-dyads of N-TTP with B-TTP appear to be ambipolar in electron/hole-coupling, whereas hetero-dyads of B- or N-TTP with TTP form strong electron coupling dyads and homo-dyads of N-TTP and B-TTP form strong hole coupling. In our analysis of the heterojunction of N- or B-TTP with monolayer graphene and observe Ohmic contacts with large hole-transport barriers. The presence of induced dipoles occurs at the interface in all heterojunctions suggesting the possibility of tuning the junction with external potentials and improving exciton dissociation.

The introduction of electropositive (B) and electronegative (N) atom pairs into the TTP motif has helped us understand the impact on the molecular unit, hetero- and homo-dyads, and interaction when the molecules are in proximity to MLG. Borylated triphenylene presents an interesting prospect for further synthesis as an electron acceptor compound with its low lowest unoccupied molecular orbital (LUMO) states. However, preparing borane PAHs is limited by the strong electrophilic behavior that attends to electropositive elements, like boron. Our results raise the prospect for a new class of active organic layers where the properties emerging from intermolecular interactions may be tuned for different applications. Coupling between cores could be tuned by changing the substitutional dopant stoichiometry or by the formation of hetero-dyads or homo-dyads. If monolayer graphene is used as an electrode with substituted TTP favorable Ohmic contact is observed, with the strongest adhesion obtained with B-TTP. The heterojunctions we examined raise the prospect of establishing efficient transport materials with graphene that possess a reduced barrier for electron transfer from the doped cores, yet larger barriers for hole transport. The presence of interface dipoles resulting in charge accumulation at the interface can be modulated with external potentials to drive carriers at the junction further leveraging the heterojunction for charge transport. In addition to this analysis, we have also examined the impact of azo-dyes in the presence of graphene and observe splitting of phonon modes. Thus, our analysis has provided a foundation for molecular manipulation to tune intermolecular interactions and the interaction with graphene (refs 1,2).

DYNAMIC FUNCTIONALIZATION

Another area of research examined the impact of light-responsive materials and molecules in contact with graphene. Early on, we observed that graphene in the presence of light resulting in tunable n-doping of the graphene. When the azo-dye BY was spun cast on graphene, static p-doping was observed. When that same surface was then exposed to light, we observed tunable p-doping. These basic observations led to a further examination of the influence of photo-responsive molecules on graphene. Within the class of azo-dyes, we discovered the ability to tune the photoconductivity of the graphene-dye hybrid material.

To understand the photoconductive interaction between graphene and soft materials, various molecules were presented on graphene samples (with silicon as the substrate) and electronically probed upon exposure to light. The main objective was to probe the hybrid system to observe interactions and postulate a mechanism and a device structure in which increasing photoresistance observed in graphene layers on silicon-based substrates can be converted to increasing photoconductance by capping the graphene layer with a photoactive layer of organic dyes. This mechanism can be explained by the creation of charge traps in graphene due to photogenerated point defects in the substrate, followed by doping of these trap states with photo-excited charges created in the azo-dye photoactive layer.

The basic setup consists of a graphene layer sandwiched between an inorganic substrate (silicon) and a photoactive (azo-dye) capping layer to achieve properties not achievable with each component on its own. Photogenerated trap states in graphene resulting from the illuminated substrate are simultaneously filled by photoexcited charges originating from the organic photoactive layer. This results in a photoconductance (decrease in resistance upon photoexposure) with a long relaxation lifetime, i.e. many minutes, in graphene. The structure of the device differs from others in that while the photoactive material is an essential component of the structure, the gate effect is not utilized as in a phototransistor. Instead, the observed resistivity of graphene is similar to that of chemiresistive detector, rather than a transistor. The graphene we use is grown either directly from a substrate, e.g. epitaxially grown graphene on silicon carbide (SiC), or transferred to a substrate of choice using established techniques. A thin film of the organic photoactive layer is then cast on the graphene, typically using spin-casting. The device is then ready for subsequent photoexposure.

The simple system consists of 3 layers. The first is the substrate and we have tested silicon dioxide, silicon carbide and quartz to observe and reproduce the photoconductive effect. The graphene layer is in intimate contact with the substrate, and the upper organic layer is the photoactive material. We tested several types of molecules, including the two organic azo dyes Brilliant Yellow and Congo Red which possess photoisomerizable azobenzene moieties and sulfonate groups. We also tested the discotic liquid crystal hexapentyloxytriphenylene (HAT5) and a perylene derivative. The graphene monolayer is sandwiched between the top photoactive layer and the bottom substrate. Under illumination, we postulate that charged point defects are generated both in the bulk and the surface of the substrate, thus causing trap states to form in the graphene. This results in an increase in resistance in the device when photoexposed. Under illumination, excited charges generated in the photoactive layer are transferred into graphene and then subsequently trapped in graphene by the photogenerated trap states. This proposed mechanism results in a decrease in resistance, i.e. increase in photoconductivity, when the system is illuminated (ref 3).

In the absence of the photoactive layer and when exposed to illumination at four different wavelengths of light (532, 550, 565, and 600 nm), there is a continuous logarithmic increase in resistance the longer the device is exposed to light. This observation indicates the generation of traps, which lowers the mobility of the charges and increases the resistance of the device (observed as a negative photoconductivity). When the illumination is removed, an abrupt transition occurs where the defects in the substrate start to become passivated, decreasing the number of trap states in graphene and therefore the resistance.

In the presence of an organic photoactive layer such as BY, an exponential decrease in resistance or a positive photoconductivity is observed. This indicates the trap states created in graphene by the photogeneration of defects in the substrate are simultaneously filled by photoexcited charges created in the BY layer via charge transfer. The additional charges added to graphene contribute to the lowering of its conductivity. If our assumptions are accurate, we are basically observing a photo-doping process. When the photo-stimulus is removed, a steady increase in resistance of the graphene is observed, which is the opposite effect observed with no photoactive layer present. The increase in resistance can be attributed to the trap states disappearing with concomitant release of their trapped charges, corresponding to a de-doping effect. This combination of materials and observations are being submitted as a patent disclosure and a forthcoming publication. The relatively rapid increase in conductivity and slow decrease upon the removal of the stimulus appears to mimic the behavior of a photonic synapse, albeit as a much simpler system. The potential application fits within the development of neuromorphic systems (ref 13).

CONCLUSIONS

With the overall objective to understand and manipulate the interaction between Liquid Crystal (LC) and 2D materials, the effort sought to lay a foundation for creating novel electro-optic devices that can optimally utilize surface interactions to fully tune the interaction with light. Using experimental and computational methods, we developed a framework for understanding strong and weak interactions between 2D materials and anisotropic soft organic layers. We demonstrated that in the weak interaction case, 2D materials can be used as a method of liquid crystal alignment, which can greatly improve fabrication and SWaP. In the strong interaction case, we showed that charge transfer between soft matter and 2D materials can be used to general simple photonic synapses with applications in neuromorphic systems. Finally, we demonstrated the full polar and azimuthal control over the anisotropic properties of thin azo-dye films that can be used for improved liquid crystal alignment and various coating applications.

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