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2D Magnetic Heterostructures and Application of TOMBO Code to Hyperfine Structures

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14. ABSTRACT
This 3-year effort focused on 2D materials, and resulted in 21 published papers related to this subject. When the project started in 2018, a survey of the present research on 2D magnets was published in one review paper in 2019. After that penta-graphene related 2D materials were investigated resulting in another paper that has been cited over 500 times. Electronic/magnetic properties, thermal conduction, application to nano-transistor, and the effect of doping in penta-graphene has been investigated. Penta-graphene structure attracted architects and one paper was published. 2D metal-organic structure was studied with Viet Nam Institute INOMAR. Pentagonal shaped new
materials have been studied theoretically. Thermal conductivity was estimated to be low for carbon nanotube(No.9). Stabilities, physical and chemical properties in MXenes and other 2D materials were studied.

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Final Report on The Project Research of
"*2D Magnetic Heterostructures and Application of TOMBO Code to Hyperfine Structures*"

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Accomplishments

Research Objectives

Lightweight materials are crucial for applications in air vehicles and satellites. New low-density and multifunctional materials are needed to realize unprecedented performance, low cost, and low energy consumption. One game-changing idea is to develop integrated two-dimensional (2D) magnets into selected matrices as smart hybrids with tailored functionalities. Such lightweight materials will have transformative applications in electromagnetic interference shielding, electrochromic devices, low-energy data storage, and ultralow-power switching. The 2017 breakthroughs in discovery of 2D magnetism in monolayer crystals and observation of layer-dependent magnetic phases open up new paradigms in fundamental science and device technologies. Monolayer semiconductors with intrinsic ferromagnetism (e.g., CrI_3 and $MnSe_2$) were discovered in 2017. These materials have enormous potential for magneto-electronics, as well as combining logic and memory for high-performance computing. Their atomically thin nature will enable unprecedented manipulation of magnetic properties (such as Curie and Néel temperatures and magnetic phases) by external control, including electric field, carrier density, and strain. It also enables incorporation of these materials into lightweight, flexible packages. The van der Waals nature of these magnets enables arbitrary design of heterojunctions, without lattice-matching constraints, formed either between different magnets or between magnets and, e.g., spin-orbit-coupled 2D materials. An atomically sharp interface, such as these material possess, is crucial for engineering emerging interfacial physical phenomena and functionalities. For example, in heterostructures between the monolayer valley semiconductor WSe_2 and a 2D ferromagnet, the interface enables ferromagnetic control of spin and valley dynamics in WSe_2 via large magnetic proximity effect, and the demonstration of an optical analog of the giant magneto-resistance effect. Thus, the discovery of 2D magnets combined with interfacial engineering capabilities breaks new ground in the fundamentals of magnetism, with unprecedented control and new functionality, and physical forms in data storage, sensing, and high-speed electronics

Experimentally the 2D materials should be on a proper substrate and/or layered structures are formed. Our program TOMBO is the first successful *ab initio* code to compute van der Waals force without any experimental support. This fundamentally new feature will help studying the layered structures of the 2D magnets. It is a kind of striking difference in the other *ab initio* simulation programs which modifies the exchange-correlation functionals to fit to the experimental values of van der Waals force. However, van der Waals force arises from the dipole-dipole interaction excited between two objects, and nothing related to exchange-correlation functionals. Therefore, we have a

very good advantage to estimate the layered hetero-structures in 2D magnets interacting via van der Waals force. The Curie and Néel temperatures of 2D magnets, which are currently below room temperature, should be increased to be useful in real industrial applications. These temperatures can be computed theoretically by Monte Carlo simulation technique. By adding the ternary component to the existing 2D magnets may help increasing these specific temperatures. Both magneto-anisotropy and exchange interactions are studied based on our experience to compute theoretically the necessary values without any experimental parameters. These results contribute to quantum engineering of magnetic ground states and developing THz-speed control in applications of the 2D magnets.

TOMBO (TOhoku Mixed-Basis Orbitals *ab initio* program package) is a full-potential all-electron code, which can estimate accurately core related physical/chemical properties, such as hyperfine structure, NMR chemical shift and so on. Since TOMBO has no muffin tins and we can relax the atomic structures completely. Pseudo-potential based *ab initio* simulation codes cannot compute these properties accurately. FLAPW code can treat core electron related properties, but it is computationally costly and atomic structures are not completely relaxed. In this project research, we apply TOMBO and other commercialized software such as VASP depending on the subjects to estimate both isotropic and anisotropic hyperfine parameters in 2D magnet heterostructures, and also in defect structures in cubic GaN/SiC. Since the physical/chemical properties in these first monolayer magnetic insulators had not been studied in details, our theoretical approach mentioned above contributed to explain deeply and accurately them, and more over to be able to predict new materials not yet studied experimentally which have more favorable properties in wide range of industrial applications in 2D magnetic heterostructures.

Our recent works proved that the magnetic theories, such as Hubbard model believed in these 95 years started from the Slater's perturbation theory are completely incorrect. The reason is simply they assume the degeneracies in kinetic and potential energy parts of the total system Hamiltonian, and accordingly assumes the same space wave functions in the electronic levels (magnetic ground state and excited non-magnetic state). However, we have proved that the main energy contribution to realize the magnetic ground state comes from the kinetic and potential energies, and not from the exchange energy (even exchange energy is reversed when total Hamiltonian is correctly computed with structure optimizations for each level). Therefore, in the course of studying theoretically this new 2D magnetic heterostructure, it could not be explained by such incorrect theoretical models, and *ab initio* computer simulation should be applied to explain existing experimental data and to predict new materials having better physical/chemical properties. Moreover, accurate calculations of magnetic ordering and structural stability of 2D magnets is not easy computationally, since the energy difference is very small. Especially theoretical estimation of magnetic anisotropy, which needs very accurate computational work, is a challenge in *ab initio* calculation.

We have developed our own *ab initio* simulation package TOMBO, which adopts all-electron full potential formulation and can estimate absolute energy levels for clusters and crystals. Especially, it can compute core related physical and chemical properties in high accuracy with small computational effort. Concerning the materials, we have already studied magnetic materials composed of various elements. Concerning 2D magnets we have studied mainly graphene related materials, and we have extended our experience to the presently interested materials stated above. We performed systematic *ab initio* simulations on XI_2 (X=Sr, Y, Zr, Nb, Mo, Tc, …) crystals, which are expected to be applicable for optical materials; some of them e. g. YI_2, show large band gaps, and are insulators. We have also tried to dope rare earth elements to tune the physical/chemical properties in these new materials. This experience is also useful for the study on the 2D magnet of similar component elements.

In this 3 year project, our research objectives have been to predict useful physical/chemical properties in new 2D nano-structured materials and the accurate calculation of hyperfine structure constants by *ab initio* simulation programs.

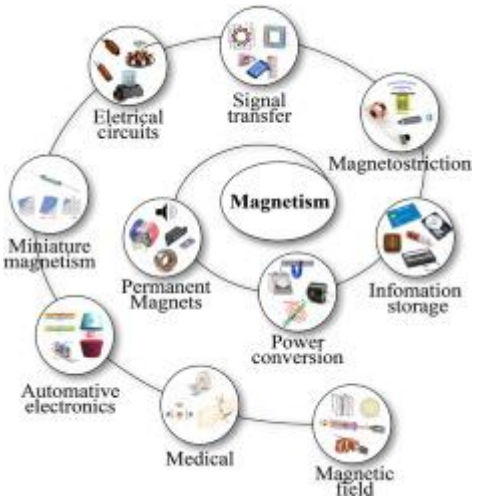
Details of Accomplishments during this Reporting Period

We have finalized a paper entitled "Effects of nitrogen on the density of states at 4H-SiC MOSFET interfaces", which is the direct output from this collaborative work, based on experimental work by the members from National Institute of Standards and Technology, The Pennsylvania State University, Air Force Research Laboratory, and Sandia National Laboratories. In this team we have contributed by performing *ab initio* simulation to estimate hyperfine structure constants. All necessary research works have been completed and the paper was written. We have submitted this paper to an international journal and was not accepted. We modified the manuscript and now try to submit it to another journal for publication. In the publication list this one is indicated as No. 22.

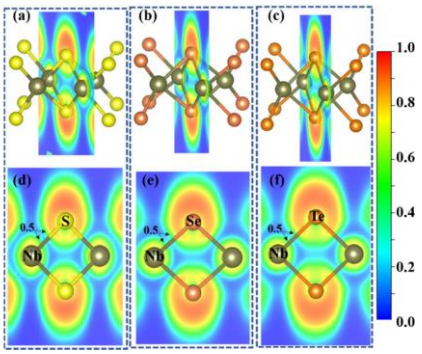
In these 3 years we have worked on 2D materials in general according to this project research, and published 21 papers related to this subject. When we started this project in 2018, we surveyed the present research on 2D magnet and published one review paper in 2019(No.1 in the publication list). After that we worked on penta-graphene related 2D materials, which is our original and the first paper has been cited over 500 times. In these 3 years we have studied electronic/magnetic properties, thermal conduction, application to nano-transistor, and effect of doping in penta-graphene(No. 2, 3, 5, 10, 15, 17). Penta-graphene structure attracted architects and one paper was published (No. 4). 2D metal-organic structure was studied with Viet Nam Institute INOMAR(No.6). Pentagonal shaped new materials have been studied theoretically (No. 7,8). Thermal conductivity was estimated to be low for carbon nanotube(No.9). Stabilities, physical and chemical properties in MXenes and other 2D materials were studied (No. 11-14, 16, 18-19, 20-21).

According to the works completed, which are listed at the end of this report, we now clearly know that the functions realized by new 2D materials depend strongly on atomic structures and atom species used. Therefore there should be more possible candidates and we are keep on working in this great subject in the near future.

Publication 1, "Magnetism in two-dimensional materials beyond graphene", is a review paper collecting information on magnetic materials which enjoy an envious position in the area of data storage, electronics, and even in biomedical field. This review provides an overview of low-dimensional magnetism in graphene, h-BN, and carbon nitrides, which originates from defects like vacancy, adatom, doping, and dangling bonds. In transition metal dichalcogenides, a tunable magnetism comes from doping, strain, and vacancy/defects, and these materials offer spintronics, as well as photoelectronic potentials, since they have an additional degree of freedom called valley state (e.g. MoS_2). Strain- and layer-dependent magnetic ordering has been observed in layered compounds like $CrXTe_3$, CrI_3, and trisulfides. The magnetism in 2D oxides like MoO_3, $Ni(OH)_2$, and perovskites are also interesting as they are potential candidates for next-generation devices having faster processing and large data storage capacity. Quasi 2D magnetism in MXene and in atomically thin materials supported on 3D materials will also be discussed. Finally, some of the challenges related to the control of defects and imperfections in 2D lattice, promising approaches to overcome them will be covered.

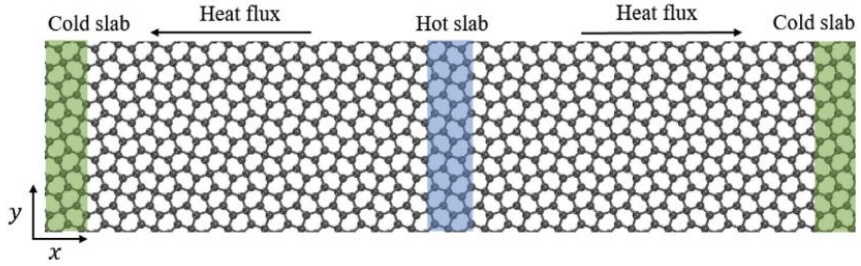


Publication 2, "Design of pentagonal NbX monolayers for electronics and electrocatalysis", indicates that two-dimensional (2D) materials with versatile properties are promising for diverse applications. In this work, anew family of 2D pentagonal NbX (penta-NbX, X = S, Se or Te) monolayers are designed to achieve the ob-jectives. We demonstrate that these new materials are stable against mechanical strains, lattice dynamics andthermalfluctuations, because of the co-existence of ionic and covalent bonding between the Nb and X elementsin these materials. Wefind that penta-NbX changes from metal to semiconductor as X changes from S/Se to Te.We show that penta-NbTe is a direct band-gap semiconductor with ultra-high carrier mobility (in the order of~104cm2V−1s−1), which is higher than or comparable to that of most 2D semiconductors and promising forultra-fast electronics. We further show that metallic penta-NbS are catalytically active for hydrogen evolutionreaction because of its low overpotential over a wide range of hydrogen coverages. We expect that the penta-NbXmonolayers mayfind applications in electronics and electrocatalysis.

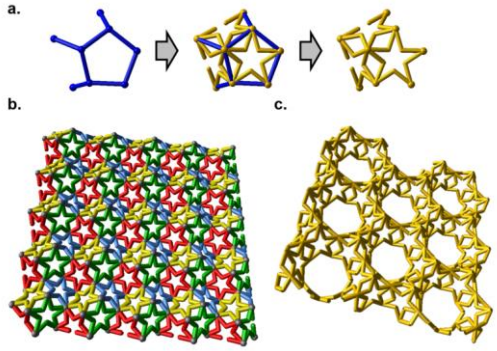


Publication 3 "Thermal transport properties of penta-graphene with grain boundaries", showing that Penta-graphene (PG), composed of carbon pentagons, has attracted considerable attention because of its unique atomic configuration and novel properties. Here, for the first time, we study the effect of grain boundaries (GBs) on the thermal transport properties of PG by using non-equilibrium molecular dy- namics simulations. Compared with pristine PG, the thermal conductivity of grains in polycrystalline penta-graphenes (PPGs) decreases by about 20%. The boundary conductance of PPGs with different GBs is in a small range of 0.43 1010 to 0.57 1010 W/mK, which differs from the situation of polycrystalline graphene where the boundary conductance decreases dramatically with the increase of grain orientation angles. The critical size of the grains is found to be about 25 nm, below which the contribution from GBs to the thermal conductivity is comparable to that from the grains.

This critical size is much smaller than that of polycrystalline graphene (100 nm). A detailed analysis of the phonon group velocity and vibra- tional density of states reveals that the geometric anisotropy and the phonon scattering induced by the GBs in PPG are the main reasons for the reduction of thermal conductivity. Our study sheds lights on tuning thermal conductivity via GB engineering in 2D materials.

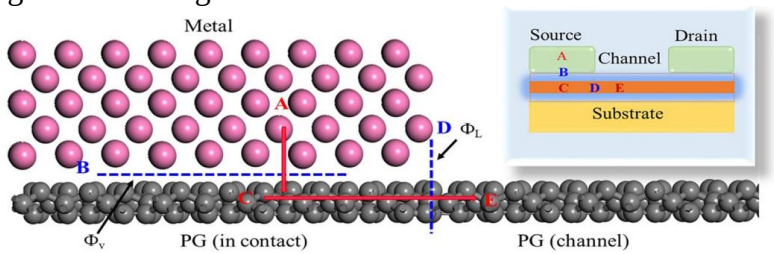


Publication 4 "Applications of aesthetic pentagon-shaped stereo tiling employing pentagraphene carbon-star walls and embossment design", gives a result on a three-dimensional pentagon-shaped stereo-tiling concept which has been realized through use of penta-graphene carbon structures, although mathematically, regular planar pentagon shapes cannot be used to completely tile the Euclidean plane. Two applications of the findings of this study have been considered from the mathematical and engineering viewpoints. First, the proposed discovery facilitates math-rule-based generation of beautiful designs comprising star shapes formed using regular pentagons. The underlying mathematical logic and hexagon- division rules have been deduced to obtain the proposed pentagonal stereo-tiling pattern comprising equal-length bonds, and two aesthetic designs have been derived using the deduced logic. A fence-like structure exclusively comprising pentagram stars has been designed and given the name "Star Walls." Emphasis has also been laid on application of the proposed stereo-tiling concept in industrial design operations, such as emboss manufacturing. To this end, finite element analysis of embossed steel sheets has been performed to verify the feasibility of the said industrial application.

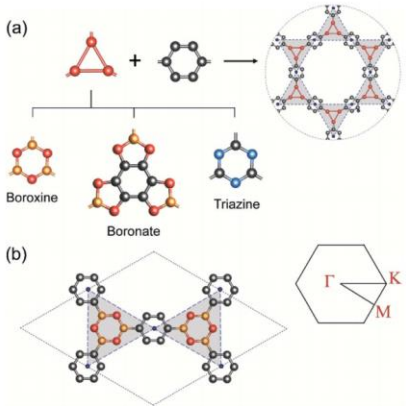


Publication 5, "Interfacial properties of penta-graphene-metal contacts", shows that novel properties of penta-graphene (PG) have stimulated great interest in exploring its potential for device applications. Here, we systematically study the interfacial properties of the heterojunctions constructed by stacking PG on several metal substrates (Ag, Al, Au, Cr, Cu, Pd, and Ti), which are commonly used in field-effect transistors. We consider PG as the channel material because of its semiconducting feature, while treating the metal surfaces as the electrodes. Based on first principles calculations, we show that PG preserves its pentagonal feature with some small distortions when deposited on the metal substrates but undergoes metallization due to the chemical bonding between PG and the metal surfaces. We evaluate the device potential of these PG-metal contacts by studying their tunneling barriers, orbital overlaps, and Schottky barriers. We find that PG forms an n-type Schottky barrier when in contact with Al, Cu,

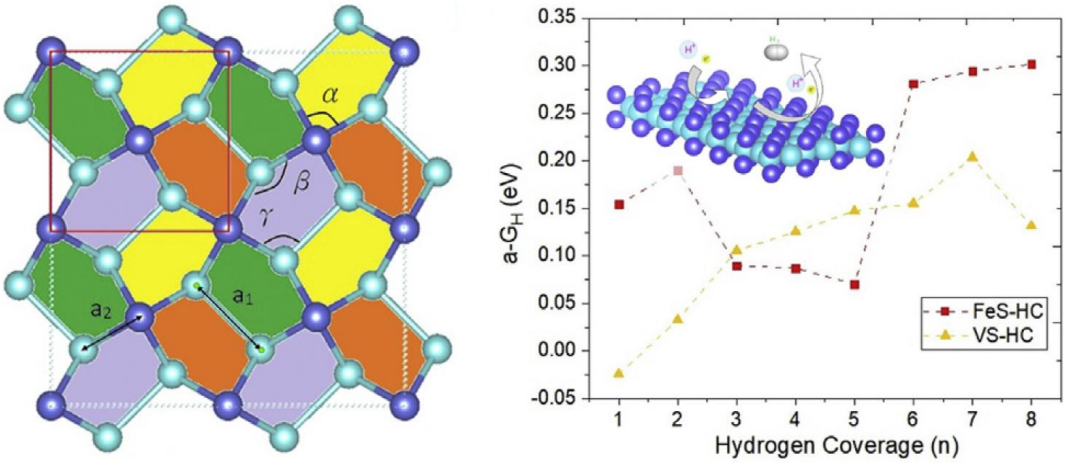
and Ti, but forms a p-type Schottky barrier when supported on Ag, Au, Cr, and Pd. Our study sheds light on the design and fabrication of PG-based electronic devices.



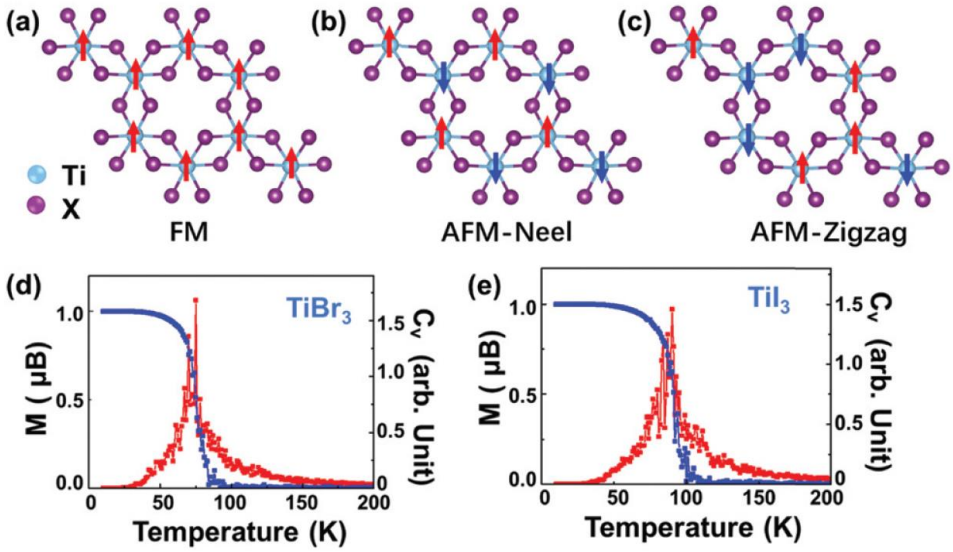
Publication 6, "Electron delocalization in single-layer phthalocyanine-based covalent organic frameworks: a first principle study", introduces that we first investigate the localized electronic states in the band structures of three single-layer COFs based on typical building units of COFs chemistry. Our results confirm that the polar nature of strong bonds in these building units is a hindrance to a fully delocalized structure and disfavors the band-like mechanism of transport. We then show that a rational design of the building units can lead to dispersive band states in the electronic structure and results in conducting single-layer COFs. We demonstrate this strategy by investigating the charge carrier transport in a series of single-layer Ni-phthalocyanine (NiPc) covalent organic frameworks (COFs), namely, NiPc-P, NiPc-2P, and NiPc-3P. Three proposed COFs exhibit semiconducting band gaps ranging from 0.55 to 0.91 eV. Their room-temperature intrinsic mobility is predicted to be in range of 200–600 cm2 V1 s1 and 20 000–60 000 cm2 V1 s1 for electrons and holes, respectively, which are comparable to those of phosphorene and higher than those of the trigonal prismatic molybdenum disulfide. NiPc are dynamically and mechanically stable and can be synthesized via the co-evaporation between Ni and corresponding tetracyano linkers. Importantly, we demonstrate that the properties of the single-layer COFs can be tuned by engineering the organic building blocks. Our theoretical study not only provides insight into the design principles for semiconducting single-layer COFs but also highlights the significance of reticular chemistry in the development of a new generation of two-dimensional materials for optoelectronic applications.



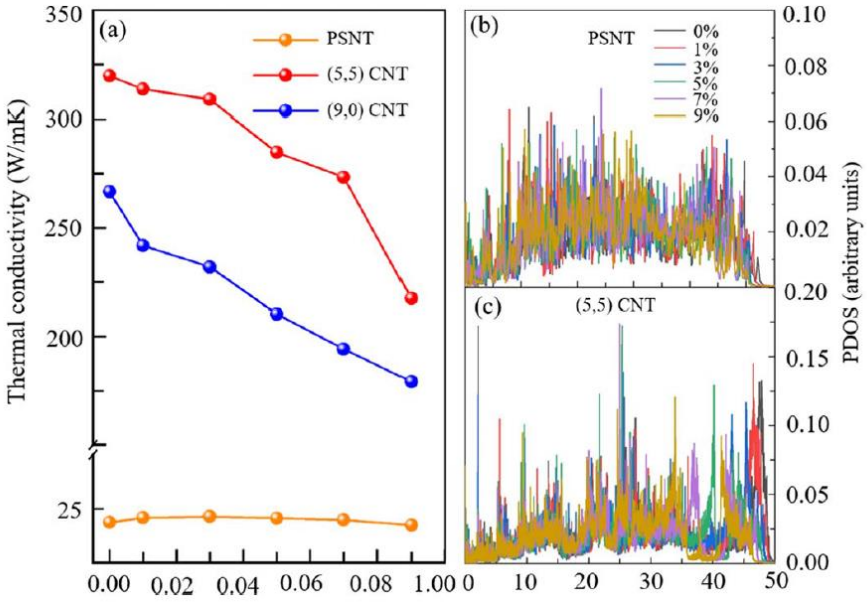
Publication 7, "Design of novel pentagonal 2D transitional-metal sulphide monolayers for hydrogen evolution reaction" , introduced a new functional materials without expensive noble metals for hydrogen evolution reaction, which is expected to be realized industrially. Left figure shows the atomic structure of penta-metal sulphide monolayer, where the cyan and blue spheres denote the M(M=Fe, Mn, V) and S atoms, respectively (red square is the unit cell). Right figure shows the calculated differential Gibbs free energies of FeS and VS monolayers as a function of H coverage.



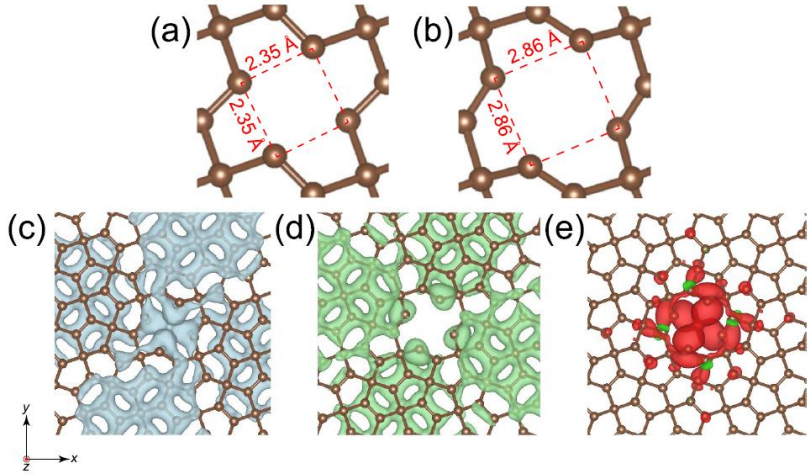
Publication 8, "Magnetic and electronic properties of 2D TiX_3 (X = F, Cl, Br and I)", shows special magnetic properties expected to occur in these new 2D materials, which are useful in applications in space, since they are light weight materials with tunable magnetic properties. Schematic illustrations of (a) ferromagnetic (FM), (b) Nee´l antiferromagnetic (AFM-N) and (c) zig–zag antiferromagnetic (AFM-z) couplings in the TiX_3 (X = F, Cl, Br, and I) monolayers. The Ti and halogen atoms are marked in blue and purple, respectively. The magnetic moment and the heat capacity (Cv) as a function of temperature for (d) $TiBr_3$ and (e) TiI_3.



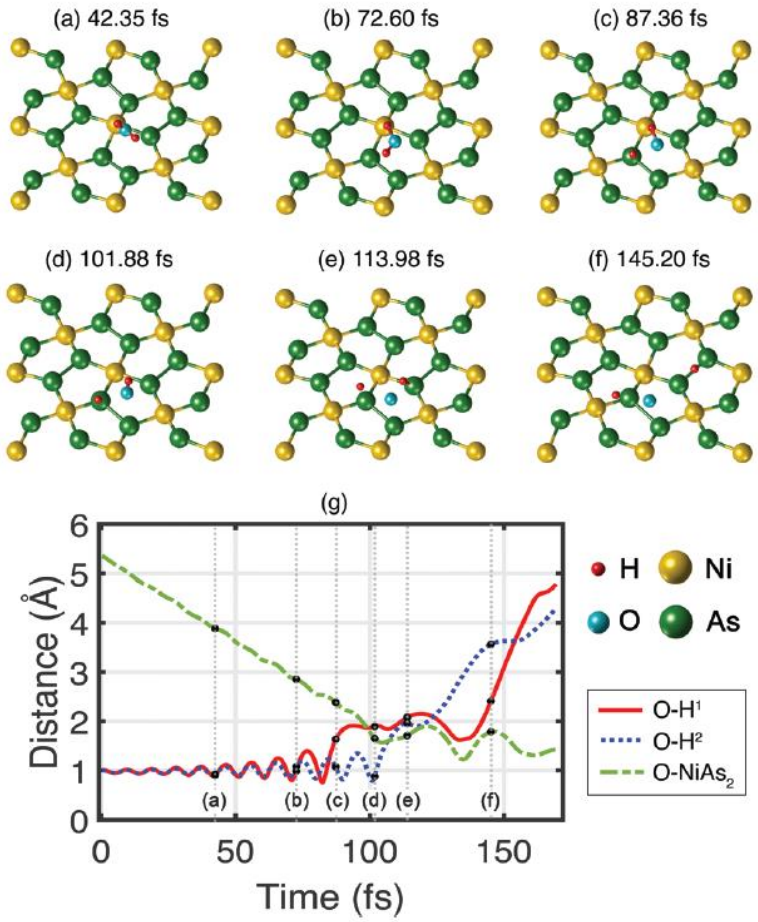
Publication 9, "Low thermal conductivity of peanut-shaped carbon nanotube and its insensitive response to uniaxial strain", successfully indicates tunable thermal conductivity under strain, which is useful for new devices in thermal transport control. Thermal conductivity of (a) the PSNT, (5, 5) and (9, 0) CNT with the length of 50 nm versus strain. PDOS of (b) the PSNT and (c)(5, 5) CNT versus the frequency under different strains.



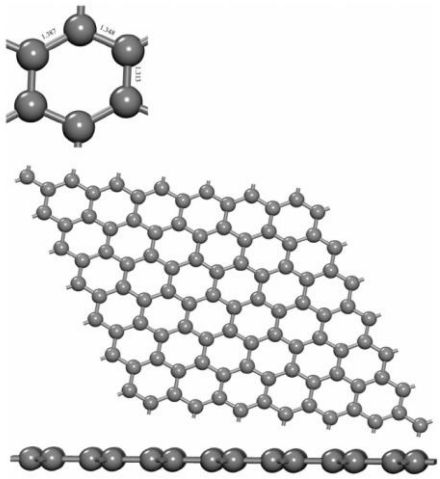
Publication 10, "Tuning the electronic and magnetic properties of pentagraphene through the C1 vacancy", predicts special electronic and magnetic properties originated by vacancies in penta-graphene. This study is important, since experimenally realized material should have defects. In the figure below, (a) initial and (b) final configurations of atoms in the C1 vacancy (VC1) structure. (c) Charge depletion (muddy-blue) and (d) accumulation (light-green) plots of VC1 in the neutral charge state. The isosurface is set to 0.016 e $Å^{-3}$. (e) Spin polarization density plot of VC1 in the neutral charge state (q = 0). The red and green isosurfaces denote α and β spins, respectively. The isosurface level is set to 0.003 e $Å^{-3}$.



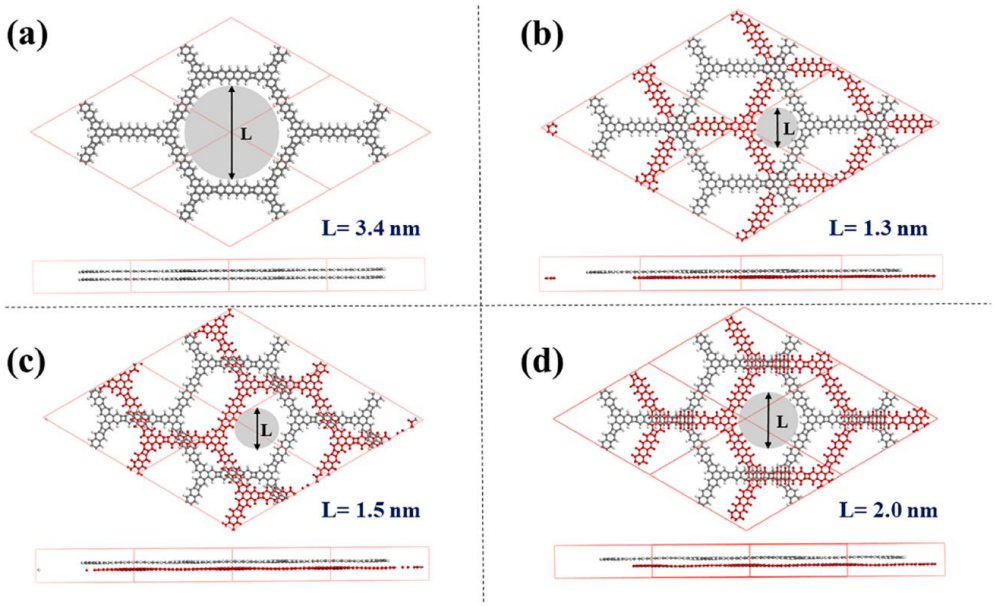
Publication 11, "Reaction probability and kinetics of water splitting on the penta-$NiAs_2$ monolayer from an *ab initio* molecular dynamics investigation", worked out water splitting kinematics, which is useful to generate hydrogen in low cost. In the figure below, (a)–(f) snapshots of H_2O dissociation stages on the $NiAs_2$ surface, (g) two O–H distances (red solid and blue dotted lines) and the projected distance between O and the $NiAs_2$ surface (green dashed line) with respect to time. The black dots and vertical lines indicate the selected configurations shown in (a)–(f).



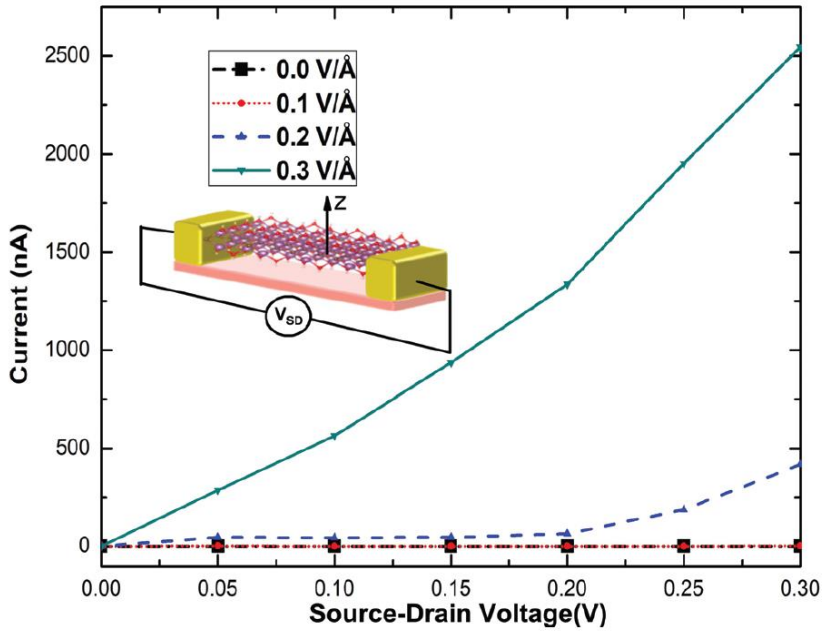
Publication 12, "Non-regular hexagonal 2D carbon, an allotrope of graphene: a first-principles computational study", predicts new atomic structures which are different from well known graphene, and have useful chemical/physical properties not realized by graphene. Relaxed structure of 2(1.387)-2(1.348)-2(1.313) non-regular hexagonal graphene is shown in the figure below. Band gap is tunable by changing the anles, without extra modification atoms.



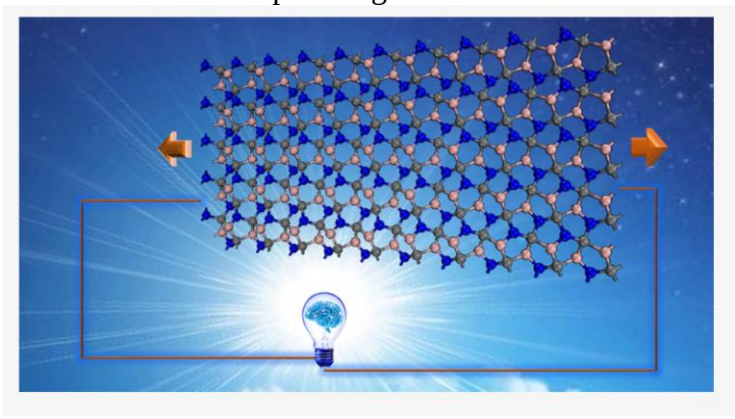
Publication 13, "Triphenylene and tetracene based porous sheet: Stability and electronic properties", is a theoretical study on new 2D materials composed of small molecules, which indicate useful properties in storage of molecules. Figure below, (a–d) Optimized structures of bilayers of TP-T in different stacking configurations.



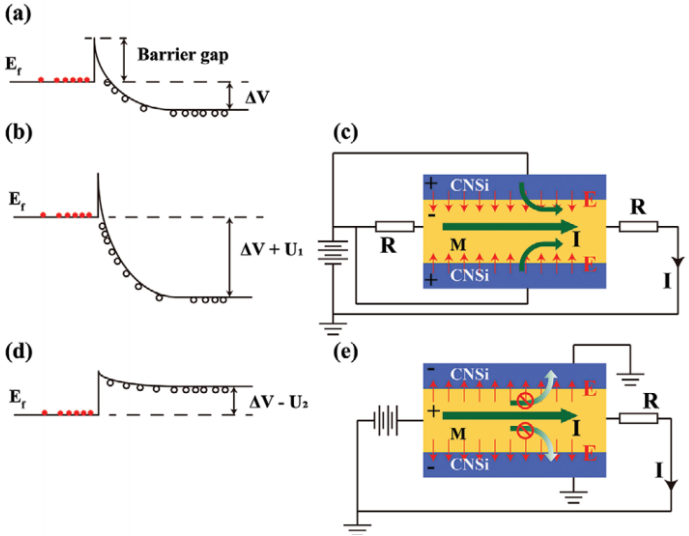
Publication 14, "Modulation of nearly free electron states in hydroxyl-functionalized MXenes: a first-principles study", introduced special properties in MXenes as functional 2D materials with hydroxyl, which idea of functionalized MXene is our invention. Figure below indicates the IV curves represent the current with respect to source–drain voltage. Different gate fields (0.0, 0.1, 0.2 and 0.3 V $Å^{-1}$, along the z axis) are applied.



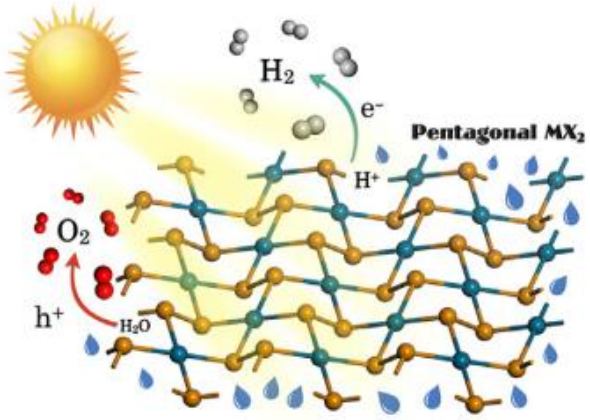
Publication 15, "Penta-BCN: A New Ternary Pentagonal Monolayer with Intrinsic Piezoelectricity", treates intrinsic piezoelectricity in 2D material. Since B, C, and N are rich in resources, light in mass, and benign to the environment, the intrinsic polarization and piezoelectricity make the penta-BCN monolayer promising for technological applications. This study expands the family of 2D pentagonal structures with new features. The figure below demonstrates elecricity generation by penta-BCN under vibrational shape change.



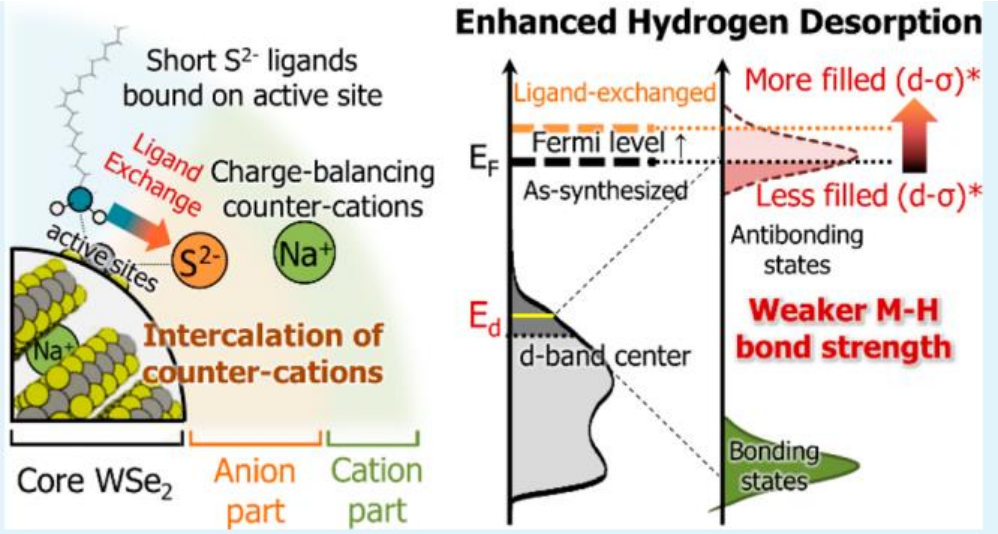
Publication 16, "CNSi/MXene/CNSi: Unique Structure with Specific Electronic Properties for Nanodevices", investigated 2D materials for applications into nanodevices due to their intriguing physical properties. In this work, four types of unique struc- tures are designed that are composed of MXenes and C/N-Si layers (CNSi), where MXene is sandwiched by the CNSi layers with different thicknesses, for their practical applications into integrated devices. The systematic calcula- tions on their elastic constants, phonon dispersions, and thermodynamic properties show that these structures are stable, depending on the compo- sition of MXene. It is found: 1) different from MXene or N-functionalized MXene (M2CN2), SiN2/M2X/SiN2 possess new electronic properties with free carriers only in the middle, leading to 2D free electron gas; 2) CNSi/MXene/ CNSi shows an intrinsic Ohmic semiconductor-metal-semiconductor (S-M-S) contact, which is potential for applications into nanodevices; and 3) O/M2C/ SiN2 and N/M2C/OSiN are also stable and show different electronic prop- erties, which can be semiconductor or metal as a whole depending on the interface. A method is further proposed to fabricate the 2D structures based on the industrial availability. The findings may provide a novel strategy to design and fabricate the 2D structures for their application into nanodevices and integrated circuits.



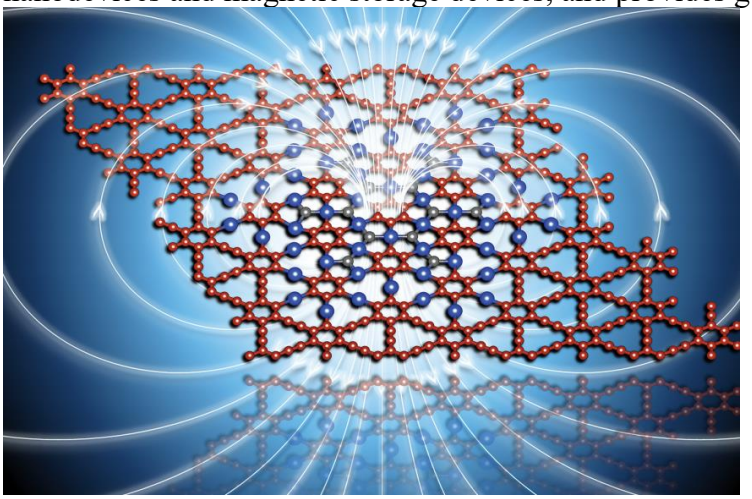
Publication 17, "Pentagonal transition-metal (group X) chalcogenide monolayers: Intrinsic semiconductors for photocatalysis", introduces two-dimensional (2D) materials, which attract enormous attention and show promising appli- cations in many fields of science and technologies (nanodevices, energy storage/harvest and catalytic processes, etc.). Pentagonal compounds emerge as a new family in 2D materials along with classic trigonal transition metal dichalcogenides and MXenes, which have been intensively investigated to date. Encouraged by the successful synthesis of pentagonal PdSe2 using CVD method, we explore nine pentagonal monolayers, MX2 (M ¼ Ni, Pd & Pt, and X ¼ S, Se & Te), based on the first-principles calculations. We find that all MX2 are dynamically and thermodynamically stable, and intrinsic semiconductors. Our results show that PdTe2 exhibits excellent potential application in solar water splitting due to optimal band gap and suitable band-edge positions matching with both the water reduction and oxidation potentials (0 and 1.23 V vs. NHE). We further find that the majority of MX2 monolayers (except NiTe2) are applicable in photocatalytic oxygen production. Our findings are expected to shed light on the possible synthesis of pentagonal MX2 and their application in photocatalytic water splitting.



Publication 18, "Uncovering the Role of Countercations in Ligand Exchange of WSe2: Tuning the d-Band Center toward Improved Hydrogen Desorption", indicates the role of countercations that do not bind to core nanocrystals (NCs) but rather ensure charge balance on ligand- exchanged NC surfaces, which has been rarely studied and even neglected. Such a scenario is unfortunate, as an understanding of surface chemistry has emerged as a key factor in overcoming colloidal NC limitations as catalysts. In this work, we report on the unprecedented role of countercations in ligand exchange for a colloidal transition metal dichalcogenide (TMD), WSe2, to tune the d-band center toward the Fermi level for enhanced hydrogen desorption. Conventional long-chain organic ligands, oleylamine, of WSe2 NCs are exchanged with short atomic S2− ligands having countercations to preserve the charge balance (WSe2/S2−/M+, M = Li, Na, K). Upon exchange with S2− ligands, the charge-balancing untercations are intercalated between WSe2 layers, thereby serving a unique function as an electrochemical hydrogen evolution reaction (HER) catalyst. The HER activity of ligand-exchanged colloidal WSe2 NCs shows a decrease in overpotential by down-shift of d-band center to induce more electron-filling in antibonding orbital and an increase in the electrochemical active surface area (ECSA). Exchanging surface functionalities with S2− anionic ligands enhances HER kinetics, while the existence of intercalated countercations improves charge transfer with the electrolyte. The obtained results suggest that both anionic ligands and countercationic species in ligand exchange must be considered to enhance the overall catalytic activity of colloidal TMDs.

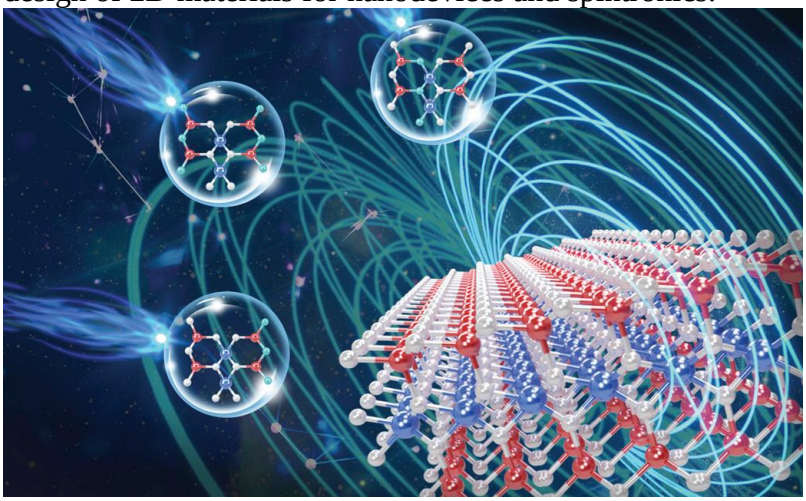


Publication 19, "*Ab initio* design of a new family of 2D materials: transition metal carbon nitrogen compounds (MCNs)", indicates that two-dimensional (2D) materials with unique structures and diverse applications have attracted extensive interest. Here, we survey a new series of two-dimensional materials, transition metal carbon nitrogen compounds (MCNs), and investigate their physical properties based on density-functional theory (DFT). We show that 2D MCN (M = Ti, Mn, Co, Cu and Zn) monolayers are dynamically, thermodynamically and mechanically stable as evidenced by the calculated phonon dispersion, molecular dynamics simulations, and elastic properties. We find that TiCN with an in-plane stiffness of 32.64 GPa nm shows nonmagnetic and semiconducting nature, and MnCN is anti-ferromagnetic in the ground state with an indirect bandgap. CoCN is ferromagnetic with half-metal characteristics. Different from the strong coupling between Co and nonmetal atoms in CoCN, the magnetic moments in antiferromagnetic CuCN and ferromagnetic ZnCN are mainly localized on the N atoms. Our study predicts a new family of 2D materials, which could be applied in nanodevices and magnetic storage devices, and provides guidance on the design of novel 2D materials

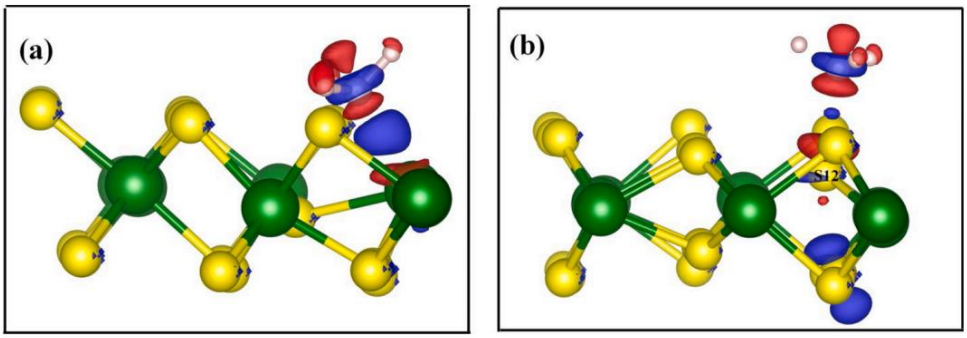


Publication 20, "Design of 2D materials – MSi 2CxN4−x (M = Cr, Mo, and W; x = 1 and 2) – with tunable electronic and magnetic properties", designed a new family of 2D materials, MSi 2CxN4-x, and investigated their physical properties based on DFT calculations. We found that tunable electronic property (semiconductor, half-metal and metal) and magnetic property (ferromagnetism,

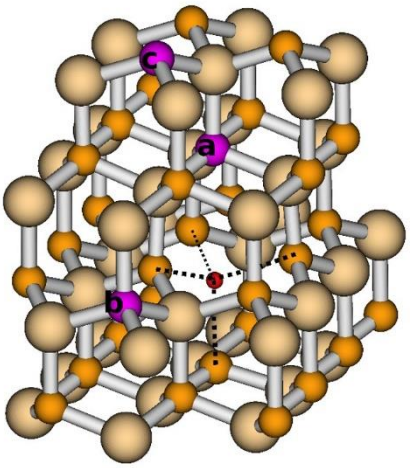
antiferromagnetism, and paramagnetism) can be achieved. The work may provide guidelines on the design of 2D materials for nanodevices and spintronics.



Publication 21, "Charge transfer driven interaction of CH4, CO2 and NH3 with TiS2 monolayer: Influence of vacancy defect", has investigated the dissociation of hydrogen rich CH4 and NH3 molecules along with CO2 on the surface of pristine and various defect induced TiS2 monolayer. The aim is to see whether the monolayer surfaces are able to produce H2 by decomposing the feedstock adsorbates and also to examine whether it can be a sorbent for CO2. We have tried to explore a monolayer surface which can simultaneously act as a catalyst to dissociate CH4, as well as to adsorb CO2 which is the only harmful by-product in steam reforming method for hydrogen production from CH4. The hydrogen generation has been predicted from the nature of gas adsorption, and the adsorption energies have been estimated to see whether it falls under chemisorption or physisorption range. Both S and Ti vacancy defects have been studied and the first-principles electronic structure calculation helps to envisage the charge redistribution of the three adsorbates on both pristine and defective TiS2 surfaces.



Publication 22, "Effects of nitrogen on the density of states at 4H-SiC MOSFET interfaces", utilized electrically detected magnetic resonance (EDMR) measurements, a technique with the ability to identify defects involved in charge trapping, and density functional theory (DFT) calculations to better understand the defects and the effects of NO anneals on their density of states at the interface of 4H-SiC MOSFETs. EDMR results show that N is very near a great majority of the dominating defect in our devices, a silicon vacancy. |We also show that nearby N significantly changes the silicon vacancy energy levels. DFT calculations show that N substitutes into nearby C sites and can shift the silicon vacancy energy levels up to 0.5 eV, enough to explain the EDMR results.



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Impacts

Development of the principal discipline of the project

The present results contributed to indicate that the reliable *ab initio* computer simulations can predict new nano-structured materials prior to experiments. Penta-graphene is the best example, which

theoretically and experimentally had never been considered before our prediction. In the textbooks there is an definition of "IPR=Isolated Pentagon Rule", and therefore people believed that such a 2D structure composed only by pentagons are not existing. To be able to predict new materials in atomic level, it is necessary to prove that the material is dynamically stable, which is based on the method of *ab initio* phonon calculation, our invention (First-Principles Determination of the Soft Mode in Cubic ZrO_2, Phys. Rev. Lett., 78[21] (1997) pp.4063-4066), K. Parlinski, Z. Q. Li and Y. Kawazoe)..

Other disciplines

PI contributed to a group of architects, who are interested in the penta-graphene shape, which has negative Poisson's ratio useful in construction of buildings (Publication 4).

Describe the impact in this reporting period on the development of human resources

…. PI visited many countries to deliver his talk on 2D materials prediction, and especially in Macau University, Professor Hui Pan was impressed and started to work with PI and published 6 papers in this time period (Publications 2, 7, 8, 16, 17, 19, 20). His students are also interested in this topic an are working hard.

Describe the impact on teaching and educational experiences

PI gave a series of lectures on 2D materials based on this project research to encourage students and researchers in SRM Institute of Science and Technology, India and in Sunararee University of Technology in Thailand, where he is invited as distinguished professor.

Impact on society beyond science and technology

PI is the leader of a Non-Profit Organization, Center for Collaborative Interdisciplinary Sciences, where he delivers his talk on 2D materials to citizens in the 3 year period.

Honors

"Honorable PhD Degree" from Suranaree University of Technology, Thailand, November, 2020. In the one-line ceremony, the Degree was given to Dr. Kawazoe directly from the Her Royal Highness Maha Chakri Sirindhorn, and Dr. Kawazoe delivered a short message to accept this honor.

Changes

Basically this project has been performed according to the plan made 4 years ago.

Changes in approach

As planned we have applied *ab initio* simulation software, our original program TOMBO and commercialized software VASP.

Problems or delays

No delays happened and we could have done a number of simulation works more than planned 4 years ago.

Expenditure Impacts
Only one change happened is that the COVID-19 situation prohibited PhD person expected to come to work in Sendai, Japan could not visit us. The planned amount of money for PhD person has been shifted to be used to support PI, since a large fraction of expected support from private companies were canceled because of the economical reason.

Significant changes in the use or care of human subjects, vertebrate animals and/or biohazards
No change in these aspects.

Changes to the primary place of performance from that originally proposed
We performed the task as planned 4 years ago.

Technical Updates

PI has worked out theoretical results on 2D materials which made a great impact in the research community, especially in Asian region. He is the founder and leader of ACCMS (Asian Consortium on Computational Materials Science) and in this community he has a number of collaborators and published totally 1280 papers, which is at present the number one in Tohoku University. To maintain PI's research activity this support from AFOSR as a 3 year program has contributed a most important part. He has led the development group of TOMBO, and the main developer has been Prof. Kaoru Ohno in these days, but he retired in March, 2021, and PI needs more person to contribute the development of TOMBO code now. If AFOSR supports this activity he is very thankful to contribute the research society, since TOMBO is the only one which can trace chemical reaction by TDDF (Time Dependent Density Functional Theory, time course tracing keeping the electronic states excited, which is essential for example in catalytic reactions), and more unique functions.

As an international collaborator of INOMAR (Center for Innovative Research on Materials and Architecture, Vietnamese Research Institute), PI has been working on MOF(Metal-Oxide Frameworks). He leads the theoretical group there to work together with experimentalists there to perform high levels works to produce new functional MOFs. PI expect support on this topic by AFOSR, already submitted a White Paper.

From this fiscal year a new project on "Rotating Detonation Engine" has started where the present PI acts as PI again and help experimental works. He applies TOMBO code to compute burning process which is too fast for experimentalists to observe, and he applies TDDFT to visualize the process. At the moment TOMBO is the only possible *ab initio* code which can simulate such chemical processes.

PI has a number of collaborators (mainly theorists some experimentalists) basically in Asian region, who need help from him such as computing resourses and paper publishing charge etc. They are good researchers and work collaboratively with PI according to the requirements (subjects) from AFOSR.

Thank you for all the help in these years.

Yoshiyuki Kawazoe