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Tuning Coupled Dynamics of Electrons and Phonons in MoS₂ with Strain, Substrate and Electrodes.

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“Tuning Coupled Dynamics of Electrons and Phonons in MoS₂”

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Abstract

In this project, we have addressed fundamental aspects of (a) ferroelectricity originating from electron-phonon coupling in the 1T phase of MoS₂ and related transition metal chalcogenides, and (b) stabilization and tunability of their 1T phase itself with strain. We also analyzed properties and potential of 2-D materials for applications in photo-catalysis of water splitting reactions, in catalysis of oxygen reduction reactions and in Mg-batteries. Motivated by tuning of their properties, we have come up with prediction of two novel 2-D materials: (i) h-NbN, which has been shown to be suitable for use in photo-voltaic cell as well as in photo-catalysis of water splitting; and (ii) monolayer of V-porphyrin, which has been shown to be a 2-D half-metallic ferromagnet suitable for spintronic applications. We have shown how the catalytic properties of 2-D materials can be tuned with substitutional alloying (e.g. BCN, GaS) and through covalent functionalization. We collaborated with engineers and have developed a computational method to determine mechanisms of thermal transport in terms of phonons. Our work led to fruitful collaborations with researchers in Temple University, Purdue University and with experimentalists at JNCASR and at the Indian Institute of Science, Bangalore. The funding for this project supported one UG student, 2 visiting PhD students and two post-doctoral fellows over a period of 3 years. It has resulted in publication of a book, two chapters in a book, 7 research papers and 3 preprints on the ongoing work.

1. Work completed and published

1.1 Strain, Electron-phonon coupling and Ferroelectric Semiconducting properties in MX₂:

Among the 1H and 1T structures exhibited by monolayers of transition metal dichalcogenides, the group VI compounds MX₂ (M=Mo,W and X=S,Se) largely occur in the 1H form. Recently, transformation of the 1H form to the 1T form with metallic electronic structure at high temperatures was demonstrated in MoS₂ with Re substitution and electron irradiation by Lin et al (2014 Nat. Nanotechnology 9391). We used first-principles calculations to determine the energy landscape associated with the 1H to 1T phase transition, predict novel 1T structures and relate the observed by Lin et al (2014 Nat. Nanotechnology 9391) intermediate structures to structural instabilities of the 1T structure of MX₂ compounds. We show that the metallic centrosymmetric 1T(c1T) structure of these compounds is unstable with respect to dimerization or trimerization of metal atoms, leading to a competing metallic Root(3)x1 1T form and ferroelectric semiconducting Root(3)xRoot(3) 1T form respectively. While the former is a more stable 1T form of MoSe₂, WS₂ and WSe₂, the latter is a more stable 1T form of MoS₂ exhibiting rich ferroelectric dipolar domain structure. In the vicinity of metal semiconductor transitions, their semiconducting forms are shown to exhibit an anomalous response to electric fields. To facilitate the experimental verification of these subtle features of the 1T forms of MX₂ monolayers, we present comparative analysis of the IR vibrational properties, and identify their Raman and infra-red spectroscopic signatures [Ref. 1]. This has led to collaboration with an

experimental group trying to stabilizing 1T form of MoS₂ using strain at the interface in a hetero-structure [Ref. P1].

1.2 Prediction of a new 2D material, h-NbN, whose electronic structure is similar to MoS₂:

Using first-principles calculations, we predicted that monolayered honeycomb and rectangular two-dimensional (2D) lattice forms of NbN are metastable and naturally derivable from different orientations of its rocksalt structure. While the rectangular form is shown to retain the metallic and superconducting (SC) properties of the bulk, spectacularly contrasting properties emerge in the honeycomb form of NbN: it exhibits (a) semiconducting electronic structure suitable for valleytronics and photocatalysis of water splitting, (b) piezoelectricity with a spontaneous polarization originating from a rare sd²-sp² type hybridization, and (c) a wide gap in its phonon spectrum making it suitable for use in hot carrier solar cells. Our work demonstrates how low coordination numbers and associated strong bonding stabilize 2D nanoforms of covalently bonded solids and introduce novel functionalities of technological importance [Ref. 2].

1.3 Prediction of a 2D half-metallic ferromagnet: We predicted a 2D ferromagnetic half-metal based on vanadium porphyrin (V-PP) using first-principles density functional theoretical analysis. We establish the dynamical stability of its planar structure and magnetic ground state through determination of energetics and phonon dispersion. We find that the exchange interaction between spins of nearest neighbour V atoms is mediated by delocalized states of porphyrin, and determine its strength from the relative energies of states with ferromagnetic and antiferromagnetic ordering. Using it in an Ising model, our estimate of its Curie temperature (T_c) is 197 K, which is higher than that of 2D manganese phthalocyanine (Mn-Pc) and 2D Cr-PP. With estimated work function of 4.9 eV, moderate in-plane stiffness, and a branch of very low energy flexural modes evident in its phonon dispersion, we find that 2D V-PP is quite suitable for use in flexible spintronic devices [Ref. 3].

1.4 Development of a computational method to determine phonon-by-phonon contribution to heat transport:

While the atomistic Green's function (AGF) method has the potential to compute spectrally resolved phonon transport across interfaces, most prior formulations of the AGF method provide only the total phonon transmission function that includes contributions from all phonon branches or channels. In this work, we present a formulation of the conventional AGF technique in terms of phonon eigenspectra that provides a natural decomposition of the total transmission function into contributions from various phonon modes. The method involves the use of Dyson and Lippmann-Schwinger equations to determine surface Green's functions from the phonon eigenspectrum of the bulk, and establishes a direct connection between the transmission function and the bulk phonon spectra of the materials forming the interface. We elucidate our formulation of the AGF technique through its application to a microscopic picture of phonon mode conversion at Si-Ge interfaces with atomic intermixing. Intermixing of atoms near the interface is shown to increase the phase space available for phonon mode conversion and to enhance thermal interface conductance at moderate levels of atomic mixing. The eigenspectrum-based AGF method should be useful in determination of microscopic mechanisms of phonon scattering and identification of the specific modes that dominate thermal transport across an interface [Ref. 4].

1.5 Analysis of 2D GaS for photo-catalysis of water splitting (collaboration with experiment): Using first-principles local and hybrid density functional theoretical calculations, a thickness-dependent electronic structure of layered GaS is determined, and it is shown that 2D GaS has an electronic structure with valence and conduction bands that straddle the redox potentials of hydrogen evolution reaction and oxygen evolution reaction up to a critical thickness (<5.5 nm). Here, simulations of adsorption of H₂O on nanoscale GaS reveal that localized electronic states at its edges appear in the gap and strengthen the interaction with H₂O, further activating the surface atomic sites. It is thus predicted that GaS synthesized with a controlled thickness and preferred edges may be an efficient catalyst for photocatalytic splitting of water. Experiments that verify some of the predictions in this study are presented, and it is shown that GaS is effective in absorption of light and evolution of H₂ (887 $\mu\text{mol h}^{-1} \text{g}^{-1}$) in the presence of aqueous solution of hydrazine (1% v/v). This study should open up the use of nanoscale GaS in conversion of solar energy into environment-friendly chemical energy in the form of hydrogen [Ref. 5].

1.6 Structural and electronic descriptors of the catalytic activity of 2-D BCN: Characteristic features of the d-band in electronic structure of transition metals are quite effective as descriptors of their catalytic activity toward oxygen reduction reaction (ORR). With the promise of graphene-based materials to replace precious metal catalysts, descriptors of their chemical activity are much needed. Here, a site-specific electronic descriptor is proposed based on the pz (π) orbital occupancy and its contribution to electronic states at the Fermi level. Simple structural descriptors are identified, and a linear predictive model is developed to precisely estimate adsorption free energies of OH (ΔG_{OH}) at various sites of doped graphene, and it is demonstrated through prediction of the most optimal site for catalysis of ORR. These structural descriptors, essentially the number of ortho, meta, and para sites of N/B-doped graphene sheet, can be extended to other doped sp² hybridized systems, and greatly reduce the computational effort in estimating ΔG_{OH} and site-specific catalytic activity [Ref. 6].

1.7 Covalent functionalization of 1T and 2H mono-layers of MoS₂ and MoSe₂ with benzene and derivatives (collaboration with experimentalists): By using first-principles density functional calculations, we show that the bonding of the functional groups with the 1T phase is stronger than with the 2H phase. This is reflected in notable changes in the electronic structure of the former upon functionalization; a gap opens up in the electronic spectrum of the 1T phase. Functionalization with para-substituted benzenes leads to a change in the work function [Ref. 7].

2. Work still continuing

2.1 MoS₂-MXene hetero-structure for Mg-batteries: Technological advances in energy storage are essential to efficient and large-scale use of the renewable energy sources. With Lithium-ion batteries reaching their theoretical limits of energy density, divalent Magnesium ion batteries (MgIBs) have attracted attention. However, low working voltages generated at cathodes and sluggish diffusion of Magnesium ions into intercalation cathodes are two scientific challenges to be met in improving the performance of MgIBs. Among the layered twodimensional materials with promise for efficient MgIB cathodes, MoS₂ offers faster surface-diffusion of Mg and Ti₂CO₂ offers high Mg adsorption energy and gravimetric capacity. Here, we

present first-principles theoretical exploration of two-dimensional heterostructure of MoS_2 and Ti_2CO_2 as a possible high performance cathode in MgIBs. From a detailed energy landscape of interaction of Mg with MoS_2 and Ti_2CO_2 , we estimate diffusivity of Mg within phenomenological models. We find a high intercalation energy of Mg (3.52 eV per Mg atom for 11% occupation of preferred intercalation sites) in $MoS_2:Ti_2CO_2$, and show that reduction in the energy barriers associated with Mg diffusion can be achieved by engineering the interlayer distance of the heterostructure. This permits much faster magnesianation of the $Ti_2CO_2:MoS_2$ cathode while maintaining a high electrochemical voltage. Our results augur well for use of $Ti_2CO_2:MoS_2$ heterostructure as a cathode in MgIB and should stimulate experimental work to validate our work [Ref. P1].

2.2 Stabilization of 1T phase using interfacial strain in the BN-MoS₂ hetero-structures (a collaboration with experimental group): we have provided a possible explanation for stabilization of 1T phase of MoS_2 when it is placed on top of h-BN in the form of a heterostructure. The mechanism is analogous to dislocations that are present at the interfaces or grain boundaries in 3-dimensions [Ref. P2], and the work here was stimulated by our earlier work described in section 1.1 above.

2.2 Phonons and thermal conducting properties of borocarbonitride (BCN) nanosheets: using classical force-fields and molecular dynamics, we are determining T-dependent phonons and thermal conductivity of B and N substituted graphene mono-layers [Ref. P3].

3. List of Publications

Books and chapters

B: CNR Rao and U V Waghmare, “2D Inorganic Materials beyond Graphene”, World Scientific (2017).

C1: Anjali Singh and U V Waghmare, “Point Defects, Grain Boundaries and Planar Faults in 2D h-BN and TMX_2 : Theory and Simulations”, Chapter 10, in a book “2D Inorganic Materials beyond Graphene”, by CNR Rao and U V Waghmare, World Scientific (2017).

C2: Arpita Paul and UV Waghmare, “Phosphorene”, Chapter 4, in a book “2D Inorganic Materials beyond Graphene”, by CNR Rao and U V Waghmare, World Scientific (2017).

Research Papers

1. Anjali Singh, Sharmila Shirodkar N, Waghmare UV (2015), “1H and 1T polymorphs, structural transitions and anomalous properties of $(Mo,W)(S,Se)_2$ monolayers: first-principles analysis”, 2D Materials, 2, 3, 035013.

2. Anand, Shashwat, Thekkepat, Krishnamohan Waghmare, UV, (2016), “Two-Dimensional Rectangular and Honeycomb Lattices of NbN: Emergence of Piezoelectric and Photocatalytic Properties at Nanoscale”, Nano Letters, 16, 1, 126-131.

3. Singh Harish, Pawan Kumar, Waghmare UV (2015), “Theoretical Prediction of a Stable 2D Crystal of Vanadium Porphyrin: A Half-Metallic Ferromagnet”, *Journal of Physical Chemistry C* , 119, 45, 25657-25662.
4. Sridhar Sadasivam, Umesh V Waghmare, Timothy S Fisher (2017), “Phonon-eigenspectrum-based formulation of the atomistic Green's function method”, *Physical Review B*, 96, 174302.
5. Kouser, Summayya, Thannikoth Anagha, Gupta Uttam, Waghmare UV, Rao CNR, (2015), “2D-GaS as a Photocatalyst for Water Splitting to Produce H₂”, *Small*, 11, 36, 4723-4730.
6. S Sinthika, U V Waghmare, Ranjit Thapa (2017), “Structural and Electronic Descriptors of Catalytic Activity of Graphene-Based Materials: First-Principles Theoretical Analysis”, *Small*, DOI: 10.1002/sml.201703609.
7. P Vishnoi, A Sampath, UV Waghmare, CNR Rao (2017), “Covalent functionalization of nanosheets of MoS₂ and MoSe₂ by substituted benzenes and other organic molecules”, *Chemistry-A European Journal* 23 (4), 886-895.

Preprints

- P1. Aseem Kshirsagar and UV Waghmare (2018), “Two Dimensional Ti₂CO₂:MoS₂ heterostructure for high-performance cathode in Magnesium-ion battery: first-principles theoretical analysis”, a preprint.
- P2. Tanweer Ahmed, Mit H. Naik, Simran Kumari, Sudipta Dutta, Umesh V Waghmare, Manish Jain, and Arindam Ghosh, (2018) “Thermodynamically stable octahedral MoS₂ in van der Waals dimers”, a preprint.
- P3. Himanshu Chakraborty, Santosh Mogurampelly, Vivek K. Yadava, Umesh V. Waghmare and Michael L. Klein, (2018) “Phonons and thermal conducting properties of borocarbonitride (BCN) nanosheets”, a preprint.