

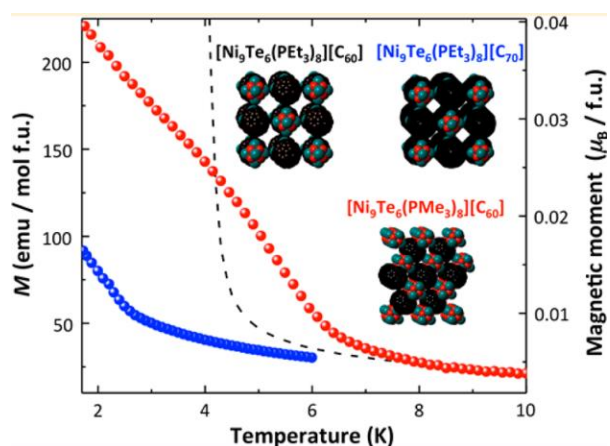
## Research Proposal

### Ultrafast Excitation Kinetic Study of Nanostructured Materials for Photonic Applications

Nanostructured materials have shown great potential in various modern light-electricity transformation and quantum processing applications such as solar cells, photodetectors, transistors, ultrafast data storage, and quantum information processing. Besides their compact size, low cost, and large surface-to-volume-ratio, materials at the nanoscale size and low dimension also show enhancement of quantum light-matter coupling, quantum confinement of charge and spin wave, and tunable physical properties. The performance of the devices is intimately related to the flow of energy, charges, and spins in their respective materials and across the interfaces. Understanding these processes is of importance for controlling and improving the efficiency of those devices. My research interest is to explore new nanostructured materials for semiconducting and magnetic applications. I will employ state-of-the-art ultrafast spectroscopic techniques to understand the excited state and charge/spin-wave dynamics; to characterize carrier/energy transport in nanostructured materials/devices and transfer through interfaces. The techniques include, but are not limited to, femtosecond pump-probe, time-resolved THz detection, time-resolved optical Kerr effect, and magneto-optical Kerr effect.

#### 1. Programmable Nanostructured Functional Materials

In quest of rationally functional materials, self-assembling of nanoscale building blocks into superlattices and superatomic crystals has recently emerged as a promising approach to expand materials to meet new challenges for photonic and electronic applications.<sup>1-3</sup> By this approach, desired physical properties can be achieved by programming constituent building blocks and controlling crystal structure via coupling between them. Several reports have shown that nanocrystal superlattices exhibit remarkable tunability and functionalities.<sup>1</sup> However, designing and controlling the structures/properties of these materials are rather difficult due to intrinsically lack of atomic precision, polydispersity, and complex surface chemistry of the nanocrystals. Unlike nanocrystals, molecular clusters are particularly attractive due to their atomic precision and well-defined surface chemistry with a rich library of molecular clusters.<sup>4-6</sup> These molecular clusters can be self-assembled into a rich family of hierarchical materials. The use of charge transfer between a pair of an electron deficient (acceptor) and relatively electron-rich (donor) molecular clusters results in a binary solid-state compound. In this method, ionic solids are formed by electrostatic interaction. Because of their resemblance to the roles of atoms/ions in the solid state, these molecular clusters are named superatoms. In general, a molecular cluster consists of an inorganic core containing a finite number of atoms and passivated by ligands. The later provides stability and solution processability. The most common electron donor clusters are made of metal chalcogenide cores, i.e.,  $M_6E_8L_6$ ,  $M_9E_6L_8$ ,  $M_{20}E_{18}L_{12}, \dots$  where M is a metal such as V, Co, Cr, Ni, ...; E is a chalcogen: S, Se, and Te; and L is a two-electron donor ligand such as PEt (ethyl-



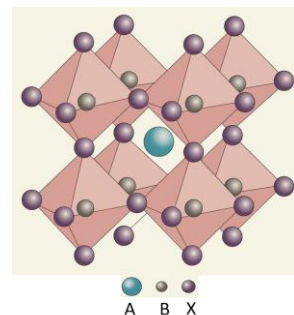
**Fig. 1.** Field-cooled magnetizations of three superatomic solids using the same core cluster of  $Ni_9Te_6$  for two different ligands and combined with  $C_{60}$  and  $C_{70}$ . The applied field is 100 Oe.<sup>7</sup>

phosphine) or  $\text{PEt}_2\text{Ph}$  (Ph = phenanthrene). The electron acceptor could be chosen from metal oxide clusters such as  $\text{W}_6\text{X}_{14}$ ,  $\text{FeX}_4$ ,  $\text{Fe}_8\text{O}_4\text{pzX}_4$  (X = halogen; pz = pyrazolate) or commercially available fullerenes,  $\text{C}_{60}$  or  $\text{C}_{70}$ .<sup>6</sup> The desirable physical properties of the superatomic materials can be *achieved by encoding* into the building blocks and manipulate their coupling and hence the crystal structure via ligands and cluster ratio. The structural dimensions can be obtained ranging from 0- to 3- dimensions with the tunable properties varying from ferromagnetism, metal to semiconductors with the bandgap in mid-IR to visible region.<sup>7–10</sup> Figure 1 presents the temperature dependence of field-cooled magnetizations of three different superatomic crystals formed from  $\text{Ni}_9\text{Te}_6$  with PEt and PMe (methyl-phosphine) ligands combined with  $\text{C}_{60}$  or  $\text{C}_{70}$ . At a low temperature, these superatomic crystals exhibit ferromagnetism with long-range cooperative magnetic properties.<sup>7</sup> Clearly, the magnetic property strongly depends on the coupling between molecular clusters. As in its immature stage, many properties of superatomic solid have not been yet fully explored, such as the roles of coupling between molecular clusters or charge transfer in optical, electrical, and magnetic properties. No high Curie temperatures ( $T_c$ ) superatomic material has been found yet.

My research in this direction will focus on expanding the family of superatomic solid crystals by manipulating their inter-molecular cluster coupling and on their individual cluster compositions. A particular interest will be focused on magnetic materials. At Wayne State University, I would use the existing departmental facilities such as very high sensitive Helium cooled SQUID (MPMS) and PPMS to characterize magnetic properties of the superatomic solids. Collective properties such as ferromagnetism, ferroelectricity, and superconductivity emerge as a result of long-range exchange interactions between the constituents. In this aspect, I will employ the ultrafast spectroscopy such as transient absorption, time-resolved (TR) second harmonic generation, TR optical Kerr effect, and quantum Hall effect to investigate charge/spin-wave dynamics and long-range interactions in these new materials.

## 2. Ferroelectric Perovskite Solar Cells With Above-bandgap Generated Photovoltages

Ferroelectricity of a nonconducting material is a property that exhibits a spontaneous electric polarization. Ferroelectric (FE) effect has been reported in many perovskite materials including halide perovskites (Fig. 2). It has been proposed that the polarization in ferroelectric material drives charge separation and transport resulting in the above-bandgap generated photovoltages.<sup>11</sup> This effect potentially leads to the high power conversion efficiency (PCE) of a solar cell that exceeds the S-Q limit. However, the origin of the FE effect in halide perovskite is still unclear whether it is intrinsic to the perovskite crystals or due to the crystal grain boundaries. Most of the inorganic perovskites, e.g. perovskite oxides, display FE effect arising from the breaking of crystal centrosymmetry. However, the wide bandgap of perovskite oxides limits their applications in photovoltaics. Figure 3 illustrates the schematic of the charge separation in a conventional p-n junction and FE solar cells. While in the conventional solar cell, the charge separation takes place in the depletion region, FE materials separate charges from built-in electric field arising from electric polarization, this effect is named as bulk photovoltaic.



**Fig. 2.**  $\text{ABX}_3$  crystal structure of perovskite. A and B are cations, and X is an anion.

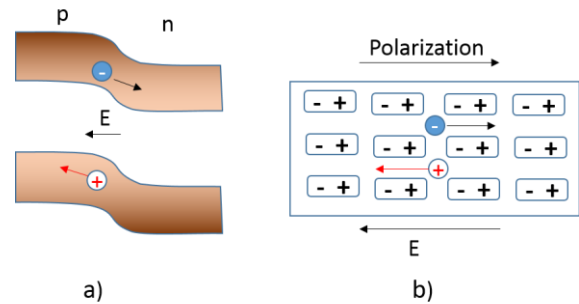
### 2.1. The Origin of the FE Effect in Halide Perovskites

With the power conversion efficiency exceeding 22%,<sup>12</sup> organo-metal halide perovskites are promising materials for low-cost and highly efficient solar cells owing to the large optical absorption cross-section, long carrier lifetime and diffusion lengths, and high carrier mobilities.<sup>13</sup> Recently FE domains have been discovered in methylammonium (MA)  $\text{PbI}_3$  perovskite.<sup>14</sup> However, whether FE effect in  $\text{MAPbI}_3$

perovskite has a positive impact on the photovoltaic performance remains unclear. The ferroelectricity may also be the explanation for the hysteresis between forward and backward I-V scans in working solar cells.<sup>15</sup> The origin of the FE effect in halide perovskite is still unclear whether it is intrinsic to the perovskite crystals or due to the crystal grain boundaries. To answer this question a piezoresponse force microscopy (PFM) and second harmonic generation microscopy can be used to map FE domains in perovskite with different sample preparation methods. Perovskite poly- and single crystals can be prepared by a spin cast from a solution, thermal deposition, and single crystal grow in solution and epitaxially grow on PbSe[001] single crystal surface. The latter is believed to have a strong reduction of crystal symmetry thus enhance the ferroelectricity due to strain at the interface arising from lattice mismatch. In contrast, the single crystal perovskites should exhibit less ferroelectricity due to its perfect crystallinity. The electric polarization in halide perovskites can also be tuned through judicious choice of the organic cations<sup>16</sup> or in the low dimensional structures.

## 2.2. Low Bandgap Perovskite Oxides

Different from halide perovskites, perovskite oxides strongly display spontaneous electric polarization leading to strong bulk photovoltaic effects. Furthermore, perovskite oxides are non-lead compounds and water insensitive. However, most of the perovskite oxides are wide bandgap semiconductors (3-5 eV), which absorb very little of the solar spectrum resulting in very low photocurrent. Lowering the bandgap of such perovskites without affecting their FE properties is a promising conceptual route to utilize these materials for solar cells with high PCE. Rappe and coworkers<sup>17</sup> reported the first strongly visible light absorbing solution-based FE perovskite material  $(\text{KNbO}_3)_{1-x}(\text{BaNi}_{1/2}\text{Nb}_{1/2}\text{O}_{3-\delta})_x$  with the bandgaps in the range of 1.1-3.8 eV. This study paved the way for the use of FE perovskite oxides in practical photovoltaics. It has been shown that the PCE of FE solar cells can also be enhanced by engineering the FE domain architectures and reducing FE domain walls.<sup>11,18</sup> Recently the solar cells based on multiferroic oxides was reported with a PCE of 8.1%.<sup>19</sup> My research interest is to synthesize and characterize low bandgap perovskite oxides by substituting suitable ions and engineering device nanostructure and use these materials for solar devices. In addition, the tandem solar cells of the halide and perovskite oxides is also one of my research interests.



**Fig. 3.** Charge separation in a conventional p-n junction (a) and in a ferroelectric material (b). In FE material, the electric field (E) induced by the polarization and that field drives charge separation.

## 3. Ultrafast Femtosecond Pulse Manipulates Magnetism and Spin Wave in 2D Materials

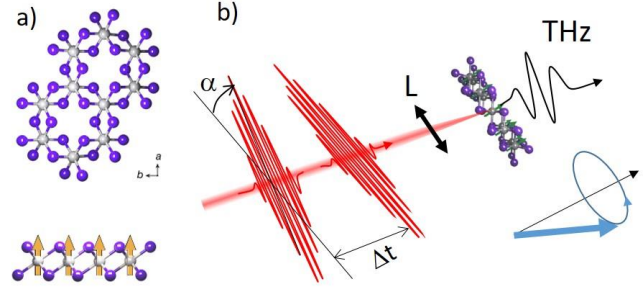
Atomically thin two-dimensional (2D) van der Waals (vdW) crystals are emerging as semiconductors at the true 2D limit for electronics and optoelectronics.<sup>20</sup> The best-known examples of these 2D semiconductors are transition metal dichalcogenides (TMDCs), such as  $\text{MoS}_2$  and  $\text{WSe}_2$ . The high charge-carrier mobility, strong optical absorption due to the direct bandgap in the monolayer, excitonic nature of electron/hole pairs, and coupling of light to spins make these 2D semiconductors exciting candidates for optoelectronic applications.<sup>21</sup> Very recently, 2D vdW materials have started a new surge of ultrathin magnetism. That is the discovery of intrinsic long-range ferromagnetic order in atomically thin monolayers, namely  $\text{CrI}_3$ ,<sup>13</sup>  $\text{Cr}_2\text{Ge}_2\text{Te}_6$ ,<sup>14</sup> and  $\text{VSe}_2$ .<sup>24</sup> These 2D magnetic materials exhibit high Curie temperatures ( $T_c$ ),

especially above-room-temperature  $T_c$  in case of VSe<sub>2</sub> monolayer. This new family member of 2D materials offers new interesting physical phenomena and potential for spintronic applications. Because of its infancy, magnetic properties in vdW materials have remained nearly unexplored. There remain many challenges and opportunities for these new materials.

The tunability of magnetism in layered materials attracts enormous attention. One way to control magnetism in 2D magnetic materials is to manipulate the number of material layers. Indeed, the magnetic phase strongly depends on the coupling between layers; it can be tuned from ferromagnetism in the monolayer into antiferromagnetism in the bilayer of CrI<sub>3</sub>.<sup>22</sup> A giant tunneling magnetoresistance has also been achieved in a bilayer CrI<sub>3</sub> device.<sup>25</sup> For VSe<sub>2</sub>, its strong paramagnetic in bulk turns into strong ferromagnetism in a monolayer. The stacking of two different types but compatible monolayers of vdW materials into heterostructures could open up a new avenue for interlayer spintronics, magneto-electrics, and magneto-optics. In such way, we can combine the rich electronics and optics with magnetism. Calculations predicted that some ferromagnetic 2D materials possess fully spin polarization leading to very strong coupling between the magnetic state and other electronic properties. Therefore, heterostructure could provide various ways to control magnetism in layered materials. The dependency of magnetism on the heterostructure has not been explored yet. In the heterostructures, the inherent lack of inversion symmetry at interfaces leads to the formation of interfacial spin-orbit coupling (ISOC) leading to new exciting phenomenon in comparison to the bulk counterpart. Interestingly, this ISOC can be controlled by an external magnetic field.

One of the intriguing questions is *can we manipulate the magnetism in 2D magnetic materials by light?* If yes then the ultrafast controlling magnetism in atomically thin materials will have enormous applications. Examples include optical data storage, sensing technology, magnon (quantized spin wave) devices, quantum information processing, ultrafast optical switch technology, to name a few. It is known that femtosecond laser pulses can increase the effective spin temperature in dielectrics and even trigger magnetic phase transitions. In antiferromagnetic materials, magnons can be generated and emitted in the THz regime by a femtosecond laser pulse via second-order impulsive stimulated Raman-type process.<sup>26</sup> Very recently, it has been shown that magnetoelectricity in CuB<sub>2</sub>O<sub>4</sub> multiferroic material (not a layered material) can be activated using a femtosecond laser.<sup>27</sup> Femtosecond pulses can act as magnetic field pulses to instantly magnetize a medium. This exciting method could open up a new way to manipulate magnetism in 2D materials, control both charges and spins, by optical pulses.

In this research direction, I will expand 2D magnetic materials by both methods top-down, exfoliation from the prospective bulk counterparts, and bottom-up, chemical vapor deposition and molecular beam epitaxy growths. Besides the standard methods to characterize magnetic properties, I will use femtosecond laser pulse to trigger and manipulate magnetism in these materials. In this study, the dynamics of the



**Fig. 4.** a) Top and side views of CrI<sub>3</sub> crystal structure where grey and purple balls are Cr and I atoms, respectively. Six I ions formed a hexagonal honeycomb lattice.<sup>13</sup> b) Schematic illustrations of the double-pulse excitation. The polarization-twisted angle,  $\alpha$ , and the delay time,  $\Delta t$ , between two pulses are used to coherently control the vectorial angle (the blue arrow), phase and amplitude, of magnetic oscillation.<sup>28</sup> The black wave is the THz emission from magnetic oscillation.

quantized spin wave and magnetization are probed using THz detection method, using pump-induced rotation of probe polarization, and scanning magneto-optic Kerr microscopy. Example: to use femtosecond to activate and control magnetism in the even number of stacking layers of CrI<sub>3</sub>, which exhibit antiferromagnetic properties employing the method in reference.<sup>27</sup> In addition, I plan to use double-pulse excitation to coherently control both phase and amplitude of magnetic oscillation modes (Fig. 4).<sup>28</sup> This is of interest for quantum information processing.

**Current collaborators:** Prof. Colin Nuckolls, Prof. Xavier Roy, and Prof. Xiaoyang Zhu at Columbia University; Prof. Steve Cundiff, Prof. Jinsang Kim, Prof. Stephen Rand at the University of Michigan; Prof. Joshua Choi at the University of Virginia; And with the Center for Functional Nanomaterials, BNL.

**Funding Opportunities:** DOE Basic Energy Sciences, NSF Early Career Development (CAREER) Program, NASA Early Career Faculty (ECF), NSF grant in the Physics and Chemistry divisions, Beckman Foundation for Young Investigators, Sloan Research Fellowships, and funding from private sectors.

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