AFRL-AFOSR-UK-TR-2021-0004

Multiscale modelling of 2D Inorganic-Organic Hybrid Materials for Nonlinear Optics

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03/18/2021
Final Technical Report

Air Force Research Laboratory
Air Force Office of Scientific Research
European Office of Aerospace Research and Development
Unit 4515 Box 14, APO AE 09421

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
18-03-2021	Final	01 Nov 2017 - 30 Apr 2020

4. TITLE AND SUBTITLE
Multiscale modelling of 2D Inorganic-Organic Hybrid Materials for Nonlinear Optics

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-18-1-0032

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Hans Agren

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
KUNGLIGA TEKNISKA HOGSKOLAN
230 W 41ST STREET FL 7
NEW YORK, NY 10044
US

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
EOARD
UNIT 4515
APO AE 09421-4515

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/AFOSR IOE

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-AFOSR-UK-TR-2021-0004

12. DISTRIBUTION/AVAILABILITY STATEMENT
A Distribution Unlimited: PB Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The researchers report state-of-the-art simulation on various low-dimensional hybrid materials for optical and energy applications. Based on first principle calculations they revealed stability and proposed new structure of fluorinated phosphorene which prevents oxidation and subsequent degradation. Electronic and optical properties of low-dimensional PdSe2, AuI and CrI3 NTs were studied in this project using high-level theory that resulted in promising semiconducting and optical applications, while complex defects in single-layer PdSe2 can be a source of magnetism. In order to enable spintronic applications, they developed CrI3 ferromagnetic nanotubes and studied their structural and electronic properties and unique triple VTe2/Graphene/VTe2 heterostructures were proposed to be perspective magnetic tunnel junctions. The achievements and progress on MXene materials and their synthesis, opto-electro-magnetic properties and corresponding applications were systematically explored. The group explored the mechanism for the extremely efficient sensitization of Yb3+ luminescence in CsPbCl3 perovskite nanocrystals. The researchers believe their results will have wide ramification in this rewarding field of 2D Inorganic-Organic Hybrid Materials

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			JASON FOLEY
U	U	U	SAR	10	**19b. TELEPHONE NUMBER** *(Include area code)* 555-555-5555

Report on EOARD Collaboration Project

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Final Report for EOARD Grant FA9550-18-1-0032

Multiscale modelling of 2D Inorganic-Organic Hybrid Materials for Nonlinear Optics

Date 2020-03-14

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Period of Performance: 11/01/2017 - 04/30/2020

Abstract

We report state-of-the-art simulations on various low-dimensional hybrid materials for optical and energy applications. We analyzed nonlinear optical properties in organic–inorganic hybrid quasi-2D perovskites and could provide a design strategy for efficient IR photoactive organic materials to be used in such systems. Based on first principle calculations we revealed stability and proposed new structure of fluorinated phosphorene which prevents oxidation and subsequent degradation. Elctronic and optical properties of low-dimensional $PdSe_2$, AuI and CrI_3 NTs studied in this project using high-level theory propose promising semiconducting and optical applications, while complex defects in single-layer $PdSe_2$ can be a source of magnetism. For viable for spintronic applications, we developed CrI_3 ferromagnetic nanotubes and studied their structural and electronic properties and unique triple VTe_2/Graphene/VTe_2 heterostructures were proposed to be perspective magnetic tunnel junctions. The achievements and progress on MXene materials and their synthesis, opto-electro-magnetic properties and corresponding applications were systematically explored. Owe could uncover the mechanism for the extremely efficient sensitization of Yb3+ luminescence in CsPbCl3 perovskite nanocrystals. We believe our results will have wide ramification in this rewarding field of 2D Inorganic-Organic Hybrid Materials

Background

Low-dimensional materials and heterostructures have become the main part of modern material science since the discovery and isolation of graphene in 2004 and following synthesis of many other inorganic two-dimensional (2D) materials. We report the state-of-the-art simulation and experimental efforts on the various low-dimensional hybrid materials for energy applications. The stability of 2D materials is a key topic because some structures like phosphorene tend to degrade at ambient conditions. In this case, surface modification can help to protect sensitive materials without significant change in their electronic properties. Using first-principles methods, we reconsidered the previously reported structure of fluorinated phosphorene proposing its stable architecture which prevents oxidation and subsequent degradation of phosphorene. The second important thing is defects in 2D materials that are normally formed during their production and almost unavoidable. Often they bring additional interesting properties unreachable in defect-free layers. Moreover, the controlled introduction of defects in TMDs allows one to tailor the electromagnetic and optical properties of the

materials. We have investigated the defect-induced properties in single-layer $PdSe_2$ and demonstrated the emergence of ferromagnetism. Since ferromagnetism is a highly developed field of modern nanoscience, novel low-dimensional materials and heterostructures are viable for future spintronic applications. Based on recently exfoliated 2D CrI_3, we developed CrI_3 ferromagnetic nanotubes and studied their structural and electronic properties. The unique triple VTe_2/Graphene/VTe_2 heterostructures were proposed to be perspective magnetic tunnel junctions. The achievements and progress on MXene materials and their synthesis, opto-electro-magnetic properties and corresponding applications were systematically reviewed.

We prepared several pieces of research to develop efficient catalysts for electrochemical ambient ammonia synthesis to replace traditional high-energy consumption and environmentally polluted Haber-Bosch process. Previous studies have demonstrated that Au has a good performance in promoting ENRR, while there is a competition between ammonia yield and Faraday efficiency, and it is difficult to achieve satisfactory ammonia yield and Faraday efficiency at the same time. We prepared the unique Au-CNT nanocomposite exhibiting both high ammonia yield and Faraday efficiency simultaneously where nano-gold is anchored on carbon nanotubes via boron clusters. To further promote efficiency a simple and unique strategy was proposed to produce in-situ anchoring of nano Au on CB[7]-K2[B12H12]. This approach allowed us to increase the Faraday efficiency by 2.5 times compared to Au-CNT reaching the DOE utility indexes of ambient ammonia production. We studied the conversion pathway of N_2 on Au nanoparticles in detail by DFT methods and explained the effect of K^+ doping. The excellent stability and simple preparation of the studied Au based hybrid materials make its practical value as ENRR catalyst for industrial applications. Although it was believed that 3*d* metals are poor catalysts due to predomination of competing for hydrogen evolution reaction, we proposed a noble-metal-free catalyst for electrocatalytic NRR utilizing nickel nanoparticles implemented in the BCN matrix that outperforms most 3*d* metals and has good yield and efficiency. The mechanism of N_2 to NH_3 conversion and synergetic effect of the heterointerface were explained based on density functional theory simulations.

1 Sensitized Linear and Nonlinear Photoluminescence of Quasi-2D Hybrid Perovskites Using Organic Cation Layers

We studied the linear and nonlinear optical properties of the series of π-conjugated organic cations, and their neutral precursors which show π-stacking to exhibit aggregation-enhanced optical properties. These organic cations show promise as photoactive layers in hybrid quasi-2D perovskites for applications in optoelectronics, particularly in the short wavelength infrared region. A concept of interlayer-sensitized photoluminescence (PL) of quasi-2D hybrid perovskite (PVK) with π-conjugated optically interacting organic cation layer was introduced and demonstrated. A rod-shaped aggregation-induced enhanced emission (AIEE) organic cation (BPCSA+), well fitted into the lattice size of 2D PVK layers, was designed and synthesized to prolong the exciton lifetime in a condensed layer assembly in the PVK. The BPCSA+ promotes the PL of this hybrid PVK up to 10-folds from that of a non-π-conjugated organic cation (OA) 2D PVK. Notably, different from PL of OA 2D PVK, the increased PL intensity of BPCSA 2D PVKs with an increase of the BPCSA ratio in the PVK indicates a critical photon-harvesting contribution of BPCSA. The films of BPCSA 2D PVKs are incredibly stable in ambient environments for more than 4 months and even upon direct contact with water. Additionally, due to the strong two-photon absorption property of BPCSA, the BPCSA 2D PVK displays superior emission properties upon two-photon excitation with a short wavelength IR laser. Thus, the AIEE sensitization system for quasi-2D PVK hybrid system can make a drastic improvement in performance as well as in the stability of the PVK emitter and PVK based nonlinear optical devices.

We also reported report pure theoretical analysis of the one- and two-photon absorption transition strengths of several excited states in the considered systems at the coupled-cluster level theory employing the CC2 model. Furthermore, a microscopic insight into their two-photon activity was obtained using the generalized few-state model (GFSM). Based on our GFSM results, we pinpoint the origin of the desired nonlinear optical properties and provide a design strategy for efficient IR photoactive organic materials with potential application in organic–inorganic hybrid quasi-2D perovskites.

Two-photon active organic molecules for infrared responsive materials†

2. Spontaneous Decomposition of Fluorinated Phosphorene and Its Stable Structure

Single- and few-layer black phosphorus demonstrates intriguing properties appropriate for various optoelectronic, photovoltaic, gas sensing applications owing to its high carrier mobility, electrical and thermal anisotropy, layer-dependent flexibly variable direct band gap. However, phosphorene rapidly degrades in environments that hinder its real sector application. To solve this issue, various approaches have been explored to passivate the phosphorene surface. Likely the most popular of them suggest chemical modification of the phosphorene surface by small functional groups including fluorination. Several structures of fluorinated phosphorene have thus recently been reported to demonstrate this approach. However, those the proposed structures have signs of structural instability. Utilizing state-of-art a combination of first-principles electronic structure calculations and ab initio molecular dynamics we reconsidered the structure of fluorinated phosphorene marking previously reported configurations as thermodynamically unstable with a tendency to decompose spontaneously. The instability of the PF_2 monolayer is induced by a Berry pseudorotation, while single-layer PF decomposes to chains due to the tendency to form a more stable triple-coordinated phase. The step-by-step, energy convex hull and random cluster approach allowed us to reveal the most probable structural arrangement of partially fluorinated phosphorene which is adsorption of two fluorine atoms to the same phosphorus position. It was shown that such configuration can effectively prevent oxidation of phosphorene due to the induced negative electrostatic surface potential. The thermodynamic stability of the proposed structure is confirmed by AIMD simulations at ambient conditions (298 K) and 350 K demonstrating the possibility to utilize it in real devices. The partially fluorinated structure demonstrates almost the same band gap compared to bare phosphorene, making it possible to utilize them in nano-optoelectronic applications.

3. Triple VTe2/Graphene/VTe2 Heterostructures as Perspective Magnetic Tunnel Junctions

There is a great deal of interest in the design of new magnetic tunnel junctions (MTJs) based on tunnel magnetic resistance (TMR) as perspective elements of a number of future spintronic nanodevices, including MRAM, radio-frequency sensors, microwave generators and artificial neural networks. The most frequently used materials for MTJs fabrication are ferromagnetic metals and alloys like Fe and CoFeB, various Heusler alloys and dielectrics such as AlO_x and MgO. Over the last

years, MTJs have been the subject of intense development in the targeting of a high TMR ratio. However, further, improvement has progressively unveiled issues relating to the downscaling, the thermal stability, the control of the oxide barriers at the interfaces, the annealing tolerance, and the robustness of the lifetime of the device. Two-dimensional materials may offer promising routes towards solving some of these issues. Its applications add some advantages for novel electronic devices like flexibility, extremely high scaling, layer-by-layer control of the thickness, the possibility of new functionalities and so on. New nanoscale bilayer and trilayer vertical heterostructures based on graphene and vanadium ditelluride monolayers were proposed and their atomic and electronic structure and magnetic properties were studied using the state-of-the-art DFT approach. The results show that graphene has a significant influence on VTe_2 monolayers, resulting in the electron density redistribution in the vicinity of the Fermi level accompanied by significant changes of structural parameters and magnetic moments. In contrast to freestanding monolayer *T*-VTe_2, *T*-VTe_2/graphene is half-metal with the indirect spin-up band gap of ~0.3 eV that something reflects promises for spintronic applications. The formation of *H*-VTe_2/graphene leads to an increase of band gap of *H*-VTe_2 electronic subsystem while keeps its original semiconductor nature. In both heterostructures, graphene is slightly hole-doped due to the electron charge transfer to VTe_2 fragment with the lifting of the Dirac point up to ~0.2 eV above the Fermi level. The electronic subsystems of graphene and VTe_2 monolayers are insensitive to the stacking ways. The *T*-VTe_2 MAE has the magnetic easy axis along with the layer (in-plane) with the energy two orders of magnitude larger than those of Fe and Ni bulks. The spin-polarization in the triple sandwich heterostructure equal to 76 and 69% for top and bottom VTe2 layers, respectively, and the TMR ratio estimated within the Julliere model is equal to 220%. Unique electronic and magnetic properties of proposed bi- and trilayered sandwiched vertical heterostructures open a promising possibility to use the materials as magnetic tunnel junctions for novel spintronic devices.

4. Two-Dimensional MXenes: From Morphological to Optical, Electric, and Magnetic Properties and Applications

The family of two-dimensional transition metal carbides, nitrides and carbonitrides, called MXenes, has started to expand since the discovery of Ti_3C_2 in 2011. MXenes are defined by the general formula $M_{n+1}X_nT_x$ (n = 1-3), where M represents an early transition metal, X is carbon and/or nitrogen and T stands for the surface terminations such as OH, F and O. Owning to their intriguing mechanical and electronic properties, together with the richness of elemental composition and

chemical decoration, MXenes are extensively studied both experimentally and theoretically providing a new 2D nanoplatform for various applications. The number of experimentally observed MXenes rise every year and has already passed 30 and many more have been theoretically proposed. Their properties are well-defined and can be tuned by surface functional groups, allowing to induce such properties as half-metallicity, nearly free electron states and non-trivial topological order edge states. The multiple options for MXene synthesis enrich the variability of material surface terminations and mesoscopic engineering of morphology. Thanks to low optical attenuation and high electrical conductivity, pristine MXenes have been used for prototype demonstrations of transparent conductive electrodes, efficient EMI shielding and absorption, THz absorption, plasmonics manipulation, SERS, electronic-based sensors, *etc.* We have systematically reviewed the state-of-the-art achievements and progress on MXene materials and their synthesis, opto-electro-magnetic properties and corresponding applications.

5. CrI3 Magnetic Nanotubes: A Comparative DFT and DFT+U study, and strain effect

The recent synthesis of 2D CrI_3 – the first ferromagnetic two-dimensional material, opened a new chapter in the physics of low-dimensional materials. The integration of magnetic order into two-dimensional heterostructures exhibits vast possibilities for the development of new devices. Like some other 2D materials such as graphene and transition metal dichalcogenides, the CrI_3 monolayer could be folded into a nanotube preserving of its magnetic order and generating novel one-dimensional ferromagnetic materials for valuable fundamental and nanoelectronic applications. We studied structural and electronic properties of CrI_3 magnetic nanotubes (NTs) are studied using density functional theory. Both armchair and zigzag CrI_3 nanotubes demonstrate a high correlation in strain energy between each other independently on accounting the Hubbard correction. Both PBE and PBE+U approaches demonstrate quantitatively similar dependency of the tube diameter on strain energy. The strain energies decrease with expansion of the tube diameter making the tubes' synthesis with a diameter larger than 45 Å to be energetically possible. Similarly, to the experimentally synthesized CrI_3 monolayer, nanotubes possess semiconducting ferromagnetic properties and suppressed band gaps with reducing their diameter due to the deformation of octahedral Cr-I crystal field and as a result changes in the bond lengths. The applied external strain can be utilized to flexibly tune the electronic properties of CrI_3 nanotubes with the desired spin-up/spin-down band gap ratio providing a platform for realization of spin field-effect transistors and other spintronics elements based on this material. Strong distortion of the octahedral Cr-I crystal field under compression results in

nontrivial behavior in the spin-up band gap of (4, 4) tube. Stretching of tubes leads to the enhancement of the exchange energy that should result in higher Curie temperature, therefore providing a good platform for potential applications in spintronic nanodevices.

6. Point and complex defects in single-layer PdSe2: evolution of electronic structure and emergence of ferromagnetism.

Layered transition metal dichalcogenides (TMDs), an emerging class of materials, provide researchers a good platform to realize fundamental studies and to create promising optoelectronic devices. Defects are an almost unavoidable part of TMDs while they bring additional interesting properties absent in defect-free layers. Moreover, the controlled introduction of defects in TMDs allows one to tailor the electromagnetic properties of the materials. Here we investigate the defect-induced properties of single-layer $PdSe_2$ and demonstrate the emergence of ferromagnetism in nanoscale. Our first-principle calculations show Se vacancies create in-gap defect states, which should be responsible for carriers trapping. The complex square Pd+4Se vacancy induces spin-polarized states with the total local magnetic moment of 2 μ_B per defect. The defect formation energies are much lower compared to many other TMD materials that explain the presence of a large number of Se defects after mechanical separation of $PdSe_2$ layers, while central location Pd atoms preserve them from exfoliation-induced defect formation. The small diffusion barrier of V_{Se} in 2D $PdSe_2$ leads to its easy room-temperature migration, while V_{Pd} demonstrates a high diffusion barrier preventing its spontaneous migration. As a guide for experimentalists, we simulate and characterize STM images in valence and conduction states. Finally, we estimate no defects should be produced with electron beam energy smaller than 55 keV, while and in contrast to 2D MoS_2 a number of various defect patterns can be created at moderate conditions making $PdSe_2$ be an ideal platform to study defect-induced phenomena.

7. Two-dimensional gold halides with giant spin-orbit splitting

Recently noble-metal dichalcogenides (NMDCs) attracted special attention due to their more flexibly tunable properties and unusual atomic structures. While 2D noble metal dichalcogenides have been observed and their electronic structures have been much studied, 2D noble metal halides (such as AuBr, AuI) are surprisingly still in the shades, not observed experimentally, and not explained theoretically. Using density functional theory (DFT), we predicted stable and unexplored 2D gold halides (AuBr and AuI) nanosheets with a unique morphology. Besides, the electronic and optical properties of bulk AuHal are also explained. 2D AuHal are thermodynamically stable at ambient

conditions and demonstrate the possibility to be exfoliated from their bulk counterparts. Te found exfoliation energy is comparable to that of graphene. Both AuBr and AuI reveal semiconducting nature with direct (AuBr) and indirect (AuI) band gaps. The monolayer AuBr and AuI exhibit 2.19 and 1.94 eV band gaps respectively that is suitable for various optoelectronic applications, while the bulk phase demonstrates ~2.5 time smaller gaps therefore allowing to control band gaps by varying thickness of the materials. Notably, the giant SOC induced splitting (~1.1 eV) of VBM caused by presence of unpaired electrons was found in both materials. We also expect strong exciton binding energy normally observing in 2D materials will decrease fundamental band gaps that is highly desirable and should lead to ideal band gaps for photovoltaic applications. Due to the unique structures of AuHal, their conductivity should be anisotropic and mechanically induced perturbations are also of high interest.

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