



Tuning the electronic, magnetic and optical properties of 2D materials: *Ab initio* insights

Cecil NM Ouma (PhD), (Pr. Phys.)

Introduction



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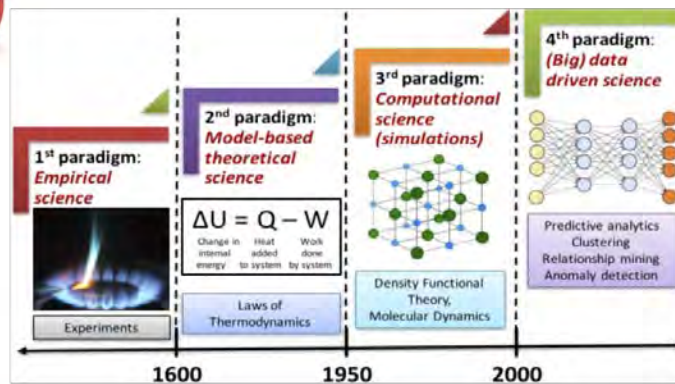
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There are several competing **RESEARCH PARADIGMS** when it comes to investigating properties of novel materials

The main drive behind these different paradigms is fuelled by the desire to design the *next generation* of materials/systems with *novel properties* needed for *novel applications* through;



- **Tuning** a material specific property to yield a desirable effect
- **Tuning** a material specific property to yield an effect observed another material but at lesser cost or improved efficiency



A. Agrawal, A. Choudhary, APL Mater. 4 (2016) 53208.

R. Seshadri, T.D. Sparks, APL Mater. 4 (2016) 53206.

Hypothesis testing



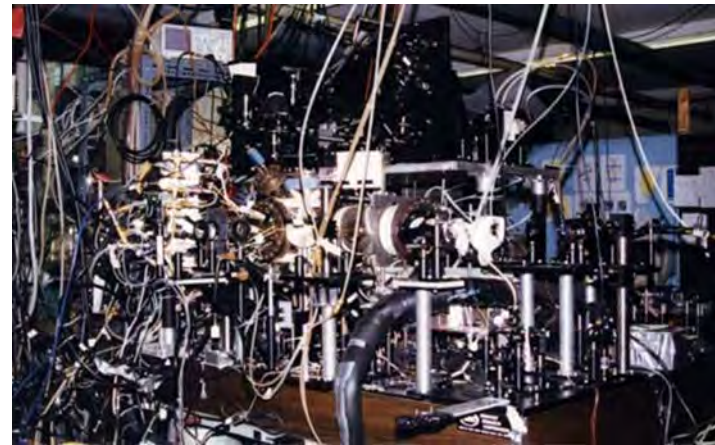
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According to the experimentalist/empiricist ...



How is a hypothesis tested



Hypothesis testing ...



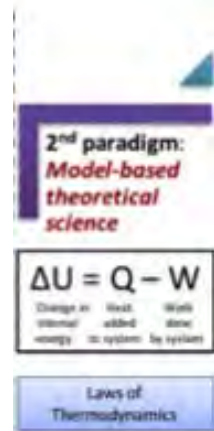
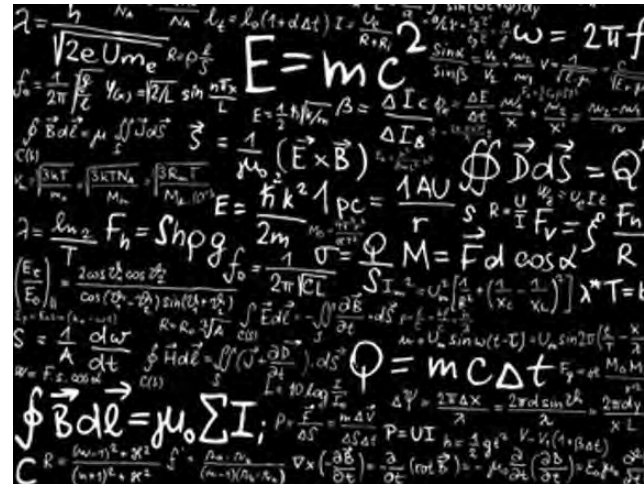
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According to the theorists ...



How is a hypothesis tested



Hypothesis testing ...



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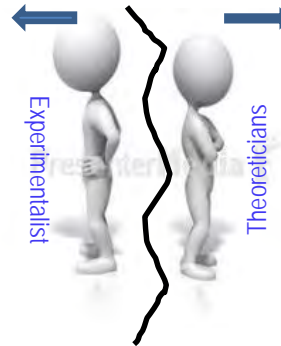
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And then ...



I have OBSERVED ...

Experimental meetings



I have PROVEN...

Theoretical meetings

Competing interests!!!



**NOT ALL EXPERIMENTALLY OBSERVED
PROPERTIES CAN BE MODELLED AND ALSO
NOT ALL MODELLED PROPERTIES CAN BE
MEASURED EXPERIMENTALLY**

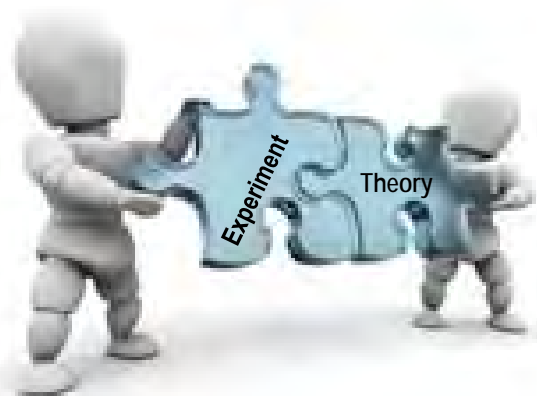
Hypothesis testing ...



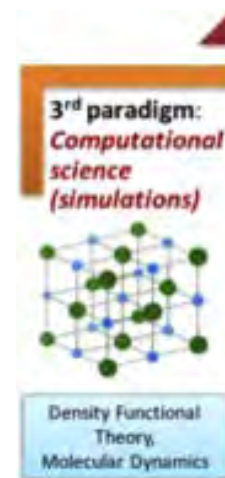
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The birth of computational modelling



Supercomputing



Objective was to;



- carry out **complementary investigations** (theory + experiments)
- test developed theories (**limits and boundaries/Applicability domains**)
- provide **fundamental explanations** to experimentally observed phenomena
- design novel experiments

Why computational ...



Periodic Table of the Elements

Element symbol represents state at room temperature: Solid, Liquid or Gas

Atomic Number, Atomic Mass, Symbol Name, Electron Shells, Electron Configuration

1 IA 1A H Hydrogen 1.008	2 IIA 2A He Helium 4.003																
3 IA Li Lithium 6.941	4 IIA Be Beryllium 9.012											5 IIIA 3A B Boron 10.811	6 IVA 4A C Carbon 12.011	7 VA 5A N Nitrogen 14.007	8 VIA 6A O Oxygen 15.999	9 VIIA 7A F Fluorine 18.998	10 VIIIA 8A Ne Neon 19.998
11 IA Na Sodium 22.990	12 IIA Mg Magnesium 24.305											13 IIIA Al Aluminum 26.982	14 IVA Si Silicon 28.086	15 VA P Phosphorus 30.974	16 VIA S Sulfur 32.06	17 VIIA Cl Chlorine 35.45	18 VIIIA Ar Argon 39.948
19 IA K Potassium 39.098	20 IIA Ca Calcium 40.078	21 Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 IIIA Ga Gallium 69.723	32 IVA Ge Germanium 72.61	33 VA As Arsenic 74.922	34 VIA Se Selenium 78.971	35 VIIA Br Bromine 79.904	36 VIIIA Kr Krypton 84.958
37 IA Rb Rubidium 85.468	38 IIA Sr Strontium 87.62	39 Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.906	44 Ru Ruthenium 101.07	45 Rh Rhodium 101.07	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 IIIA In Indium 114.818	50 IVA Sn Tin 118.710	51 VA Sb Antimony 121.760	52 VIA Te Tellurium 127.6	53 VIIA I Iodine 126.905	54 VIIIA Xe Xenon 131.29
55 IA Cs Cesium 132.905	56 IIA Ba Barium 137.328	57-71 Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.21	77 Ir Iridium 192.227	78 Pt Platinum 195.084	79 Au Gold 196.967	80 Hg Mercury 200.592	81 IIIA Tl Thallium 204.384	82 IVA Pb Lead 207.2	83 VA Bi Bismuth 208.980	84 VIA Po Polonium 209	85 VIIA At Astatine 209	86 VIIIA Rn Radon 222.018
87 IA Fr Francium 223.018	88 IIA Ra Radium 226.025	89-103 Actinide Series	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 266	107 Bh Bohrium 264	108 Hs Hassium 269	109 Mt Meitnerium 268	110 Ds Darmstadtium 269	111 Rg Roentgenium 272	112 Cn Copernicium 277	113 Nh Nihonium 278	114 Fl Flerovium 289	115 Uup Ununpentium 288	116 Lv Livermorium 293	117 Uus Ununseptium 289	118 Uuo Ununoctium 289
<p>Alkali Metal Alkaline Earth Transition Metal Basic Metal Metalloid Nonmetal Halogen Noble Gas Lanthanide Actinide</p>																	

Too many elements to be considered ...

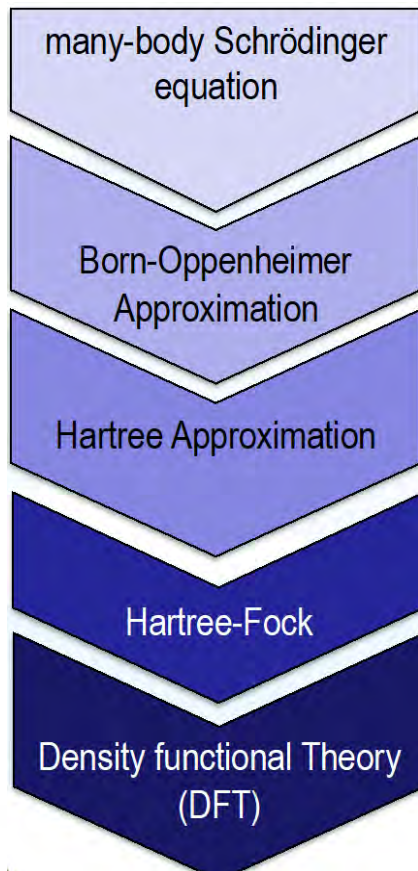
- *Intrinsic* material **properties** are governed by the *intrinsic characteristics* of the elements forming the material
- Doping has been *successful* to some extent in *improving* the materials' properties
- **NOT** all materials can be **supper** materials

3rd paradigm: Computational science (simulations)

Density Functional Theory, Molecular Dynamics

Computational methodology...

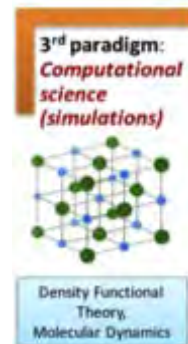
- *Ab initio* formalism



- If the ground-state charge density of a system is known, all the properties of the system can be determined
- The energy associated with the ground state of system is the ground-state energy

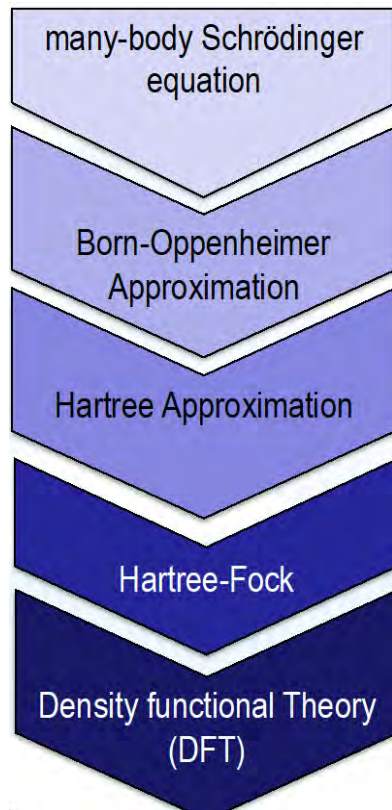


This is just one approach for computational modelling others do exist



Computational methodology...

- *Ab initio* formalism



- If the ground-state charge density of a system is known, *almost* all the properties of the system can be determined



Need to go beyond DFT



This study ...

Application of ab initio DFT modelling to

1. Defects in 2D materials (semiconductors)
 - Transition metal dichalcogenides (TMDC): MoS₂, TcS₂, ReX₂
 - Graphene and Holey doped graphene
 - g-III-IV compounds (AlN, GaN and InN)
2. van der Waals heterostructures

Computational packages/CODES used

Quantum ESPRESSO (PWSCF)

Properties investigated

1. Formation energies
2. Optical properties
3. *Binding energies*
4. *Migration energies*



Applications

CASE 1: (Collaborative project on lanthanide doped TMDCs (MoS₂))



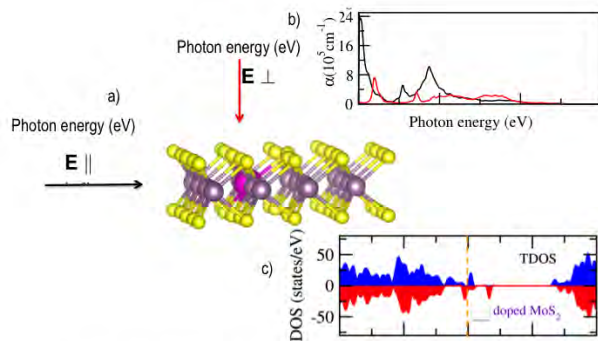
Journal Name

ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxxx

Controlling the magnetic and optical response of MoS₂ monolayer by lanthanide substitutional doping: a first-principles study

Cecil N. M. Ouma^{a*}, Sobhit Singh^{1,b}, Kingsley O. Obodo^c, George O. Amolo^d and Aldo H. Romero^{2,b}



Absorption spectrum and TDOS of lanthanide doped MoS₂ for E-filed parallel and perpendicular to xy-plane

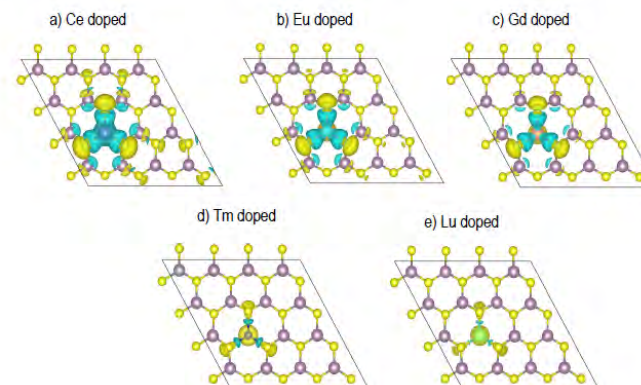
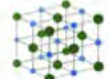


Fig. 3 Charge density difference plots for a) Ce-doped, b) Eu-doped, c) Gd-doped, d) Tm-doped, and e) Lu-doped MoS₂ monolayer.

Lanthanide dopants
Ce, Eu, Gd, Tm and Lu

3rd paradigm:
Computational
science
(simulations)



Density Functional
Theory
Molecular Dynamics

Applications

CASE 1: (Collaborative project on transition metal doped TMDCs (ReS₂ and ReSe₂))

PCCP

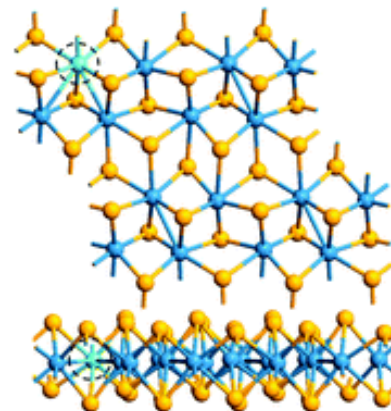
PAPER



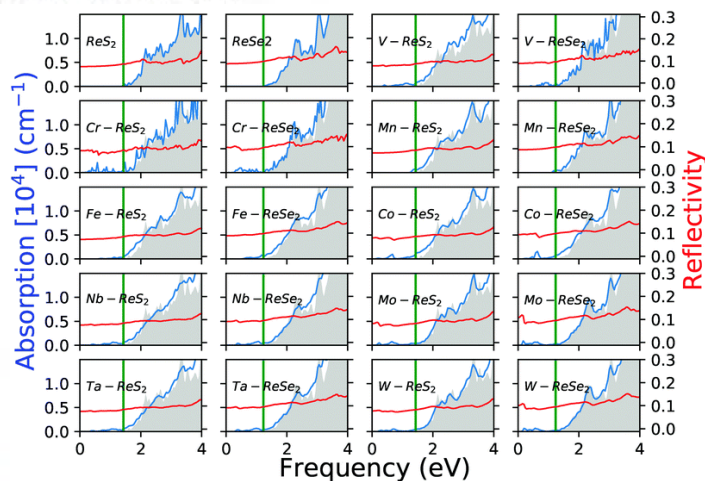
Cite this: *Phys. Chem. Chem. Phys.*, 2017, 19, 19050

Influence of transition metal doping on the electronic and optical properties of ReS₂ and ReSe₂ monolayers

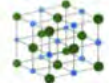
Kingsley Onyebuchi Obodo,^a Cecil Naphtaly Moro Ouma,^b Joshua Tobechukwu Obodo^c and Moritz Braun^d



Transition metal dopants
V, Cr, Fe, Nb, Ta, Mo and W



3rd paradigm:
Computational
science
(simulations)



Density Functional
Theory,
Molecular Dynamics

Applications

CASE 3: (Collaborative project on transition metal dopants and adatoms TMDs (TcS₂))



Journal Name

ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxxx

Effect of transition metal substitutional dopants and adatoms on mono layer TcS₂: *ab initio* insights †

Cecil N. M. Ouma,^{*a} Kingsley O. Obodo,^b Sobhit Singh^c, Moritz Braun^b and George O. Amolo^d

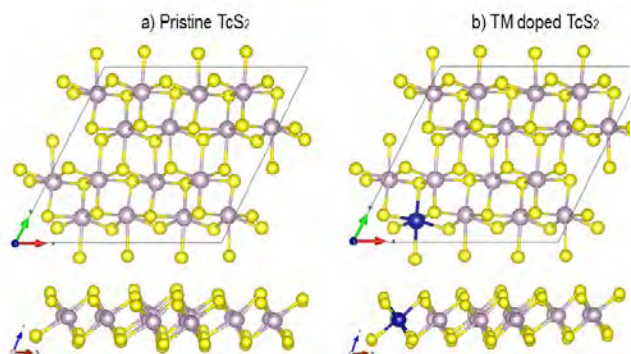


Fig. 1 Top and side view of the optimized crystal structures of pristine and transition metal (TM) doped TcS₂. (Blue ball represents the substitutional dopant on a Tc site)

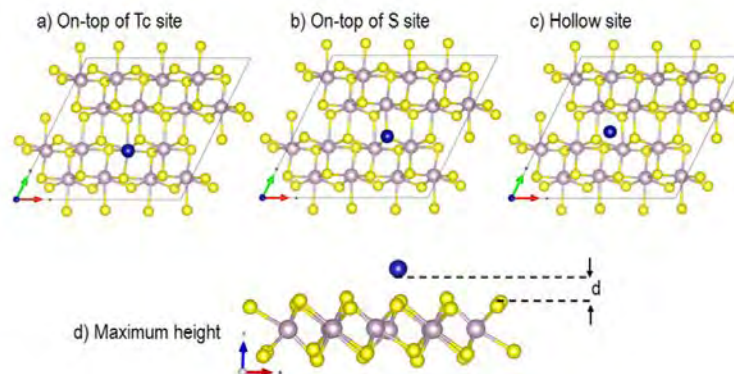
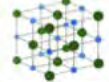


Fig. 2 Transition metal adsorption site considered namely on-top of Tc, (T_{Tc}) on-top of S (T_S) and the hollow position (H) (Blue ball represents the adatom and d is the distance between the adatom and the TcS₂ surface)

3rd paradigm:
Computational
science
(simulations)



Density Functional
Theory
Molecular Dynamics

Applications

CASE 4: (Collaborative project on graphene like AlN (g-AlN))

In progress

Journal Name



ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxxx

Graphene/g-AlN van der Waals nanocomposite for rechargeable Li ion battery (LIB) anode: *Ab initio* insights[†]

Cecil N. M. Ouma,^{*a}

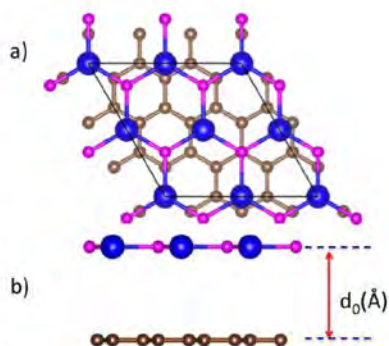


Fig. 1 Gr/g-AlN van der Waals nanocomposite. Blue, magenta and brown balls represents Al, N and C atoms respectively.

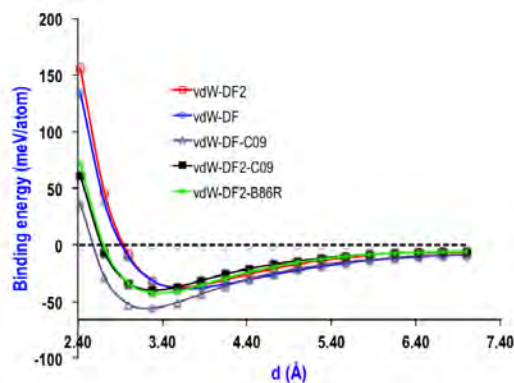
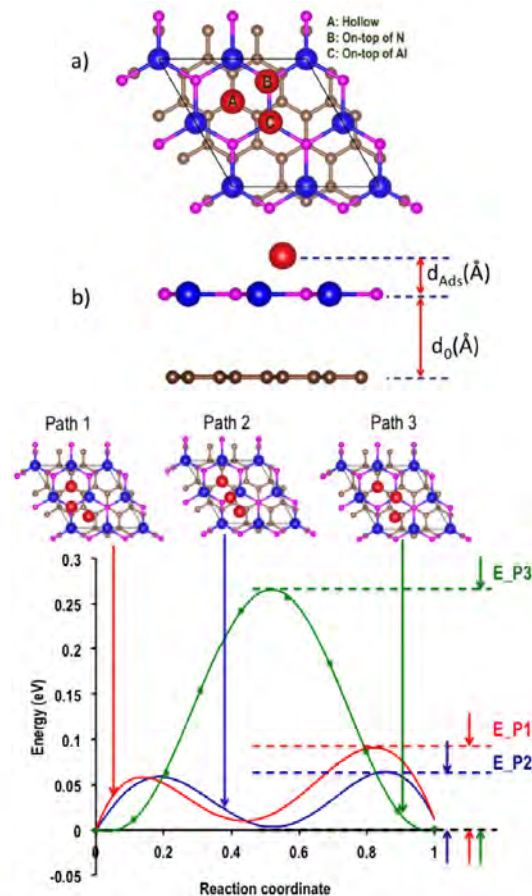
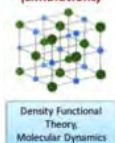


Fig. 2 Calculated binding energy if the Gr/g-AlN van der Waals nanocomposite as function of interlayer distance d for different vdW-D.



3rd paradigm:
Computational
science
(simulations)



Density Functional
Theory,
Molecular Dynamics

Applications

CASE 5: (Collaborative project on lanthanide embedded holey doped grapheme (g-C₂N))



Journal Name

In progress

ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxxx

Tunable electronic and magnetic properties of mono-layer g-C₂N through embedding of lanthanide ions †

Cecil N. M. Ouma,^{*a} and George O. Amolo^d

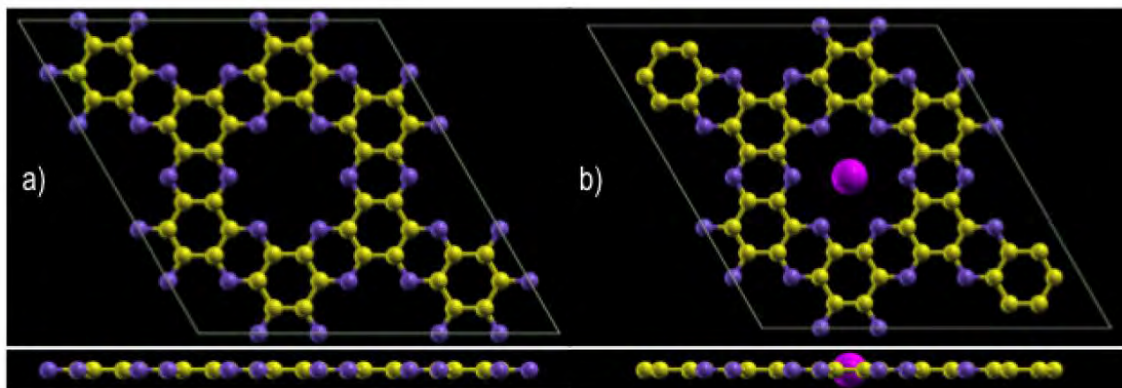


Fig. 1 : Top and side views of pristine and lanthanide emended g-C₂N. Gold, violet and magenta balls represents carbon, nitrogen and lanthanide atoms respectively.

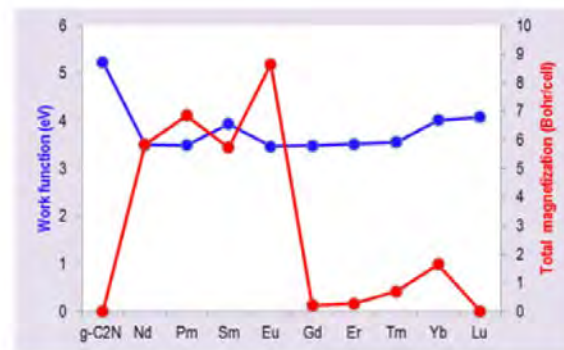
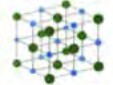


Fig. 6 Induced magnetization and calculated work function of lanthanide embedded g-C₂N.

3rd paradigm:
Computational
science
(simulations)



Density Functional
Theory
Molecular Dynamics

Conclusions



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- Both lanthanide and TM doping influenced the optical properties 2D materials
- Both lanthanide and TM doping induced magnetism in 2D materials in some instances
- Its possible to create van der Waals heterostructures of of graphene and winde band gap monolayers of g-AlN
- Its possible to embed lanthanide ions in g-C2N



Ahsanteni sana ...

Thank you for



Any

