FUNCTIONALIZATION OF NANOMATERIALS DRIVEN BY AB INITIO CALCULATIONS

The 23rd Sde Boker Symposium on Solar Electricity Production

September 5-7, 2022

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Si NWs in collaboration with: Prof. Muhammad Y. Bashouti and Dr. Awad Shalabny (Ben-Gurion University of the Negev)

ENEAGRID/CRESCO Clusters

www.cresco.enea.it
Computational RESsearch Centre on COmplex systems

CRESCO6 (1400 Tflops, 20832 cores)
• 434 nodes 2x24 cores Intel Xeon Platinum 8160 @2.1 GHz;
192 GB RAM, 500GB SATA II disk, Intel Omni-Path 100 GB/s.

CRESCO4 (40 Tflops, 2048 cores)
• 128 nodes 2x8 cores Intel E5-2670 @2.6 GHz;
64 GB RAM, 500GB SATA II disk, IB QDR 40 GB/s.

CRESCO4SM (60 cores)
• 5 nodes 2x6 cores Intel E5-2643 v2 @3.5 GHz;
768 GB RAM, 1TB SATA II disk, IB QDR 40 GB/s.

CRESCO4F (20 Tflops, 1024 cores)
• 64 nodes 2x8 cores Intel E5-2670 @2.6 GHz;
64 GB RAM, 500GB SATA II disk, IB QDR 40 GB/s.

CRESCO4C (10 Tflops, 512 cores)
• 32 nodes 2x8 cores Intel E5-2670 @2.6 GHz;
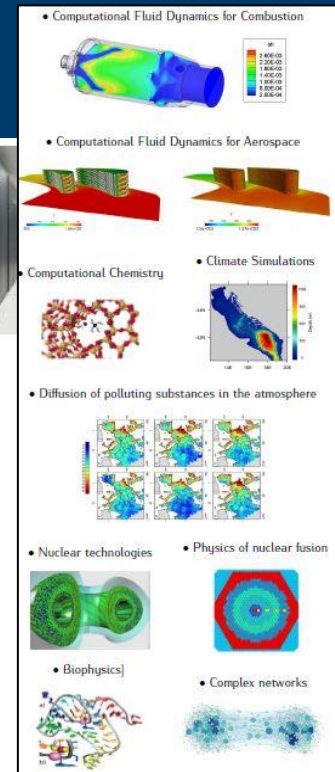64 GB RAM, 500GB SATA II disk, IB QDR 40 GB/s.

NEW FORTHCOMING CRESCO CLUSTERS IN 2022

CRESCO7 (1400Tflops)
• 100 nodes dual socket Sapphire 54 + 10 nodes single socket Sapphire 54, 2 GPU NVIDIA A100;

CRESCO7F
• 8 nodes dual socket AMD, 1 GPU NVIDIA A100 + 8 nodes dual socket IBM PPC 8, 4 GPU NVIDIA P100;

- CRESCO infrastructure for:
  o **EoCoE**: European Energy oriented Center of Excellence for computing applications
  o **Mission Innovation initiative**: The Italian Energy Materials Acceleration Platform (IEMAP)
  o **EUROfusion**: European organization for the fusion development
  o **VIPERLAB**: fully connected virtual and physical perovskite photovoltaics lab
  o ...

Outline

- Density functional theory fundamentals
- Ab initio approaches to
    - Silicon Nanowires (Si NWs) functionalization
    - Graphane Hydroxylation
- Conclusions

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Many body Schrödinger's for N atoms and n electrons system

Many body Schrödinger's Hamiltonian:

$$H = -\frac{\hbar^2}{2m}\sum_j \nabla_j^2 - \sum_{jl}\frac{Z_l e^2}{|r_j - R_l|} + \frac{1}{2}\sum_{j \neq j'}\frac{e^2}{|r_j - r_{j'}|}$$
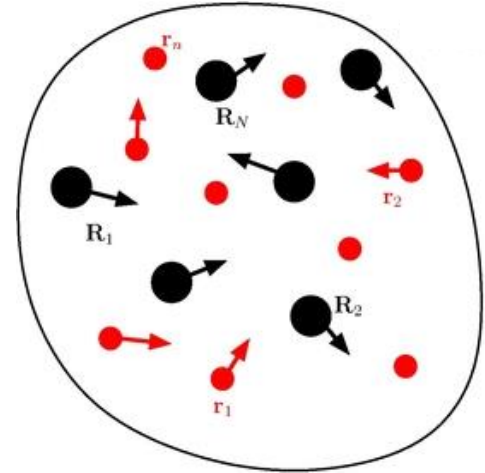
Many body Schrödinger's equation:

$$i\hbar\frac{\partial}{\partial t}\Psi(r_1, r_2, ..., r_n) = H\Psi(r_1, r_2, ..., r_n)$$

Solutions by the variational approach is a big issue!
M = number of parameters required, n = number of electrons,
p = number of parameters per variable ($3 \leq p \leq 10$): $M = p^{3n}$.

Set $n=100$ we get $M= 3^{300} \cong 10^{150}$ parameters!!!

W. Kohn's Nobel Lecture, Reviews of Modern Physics, Vol. 71 (1999)

⬤ nuclei

● electrons

$$P_{jj'}\Psi = -\Psi$$

Density functional theory

DFT is valid for *ground-state properties only* and transforms the quantum many-body problem into an equivalent problem of (fictious) non-interacting electrons, the Kohn-Sham Hamiltonian, giving a set of independent particle Schrödinger equations that can be solved numerically, which are called Kohn-Sham equations; eigenfunctions obtain the system electron density:

fictitious single-particle orbitals optimized in density

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) + V_{\text{eff}}(\mathbf{r})\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

Lagrange coefficients (merely auxiliary quantities or not?)

$$V_{\text{eff}}(\mathbf{r}) = V_e(\mathbf{r}) + \int d\mathbf{r}'V(\mathbf{r},\mathbf{r}')n(\mathbf{r}') + \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

E_{XC} is the exchange correlation energy.
The total energy is minimized as functional of the charge density:

Electrons charge density:

$$E_g = \sum_i \varepsilon_i - \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'V(\mathbf{r},\mathbf{r}')n_0(\mathbf{r})n_0(\mathbf{r}')$$
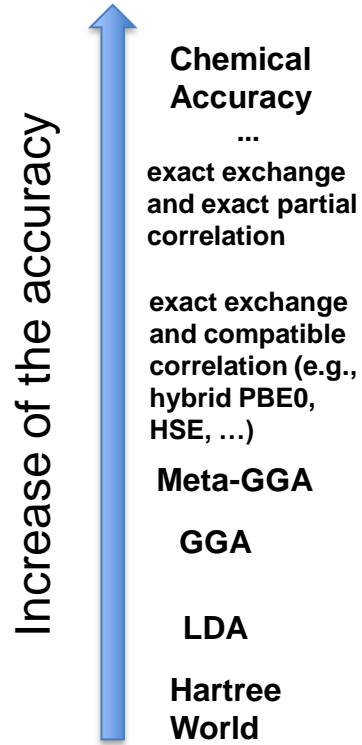$$+ E_{xc}[n_0(\mathbf{r})] - \int V_{xc}(\mathbf{r})n_0(\mathbf{r})d\mathbf{r}.$$

$$n_0(\mathbf{r}) = \sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2$$

sum extended to all the occupied fictitious states

We do not know the exact form of XC!
We solve choosing approximation of different accuracy.
More the accuracy and more the computation cost is.

Jacob's ladder (the different approximations for XC from the Perdew's point of view)

Increase of the accuracy →

- **Chemical Accuracy**
  ...
- **exact exchange and exact partial correlation**

- **exact exchange and compatible correlation (e.g., hybrid PBE0, HSE, …)**

- **Meta-GGA**

- **GGA**

- **LDA**

- **Hartree World**

Jacob's Ladder, Villa Farnese (Caprarola, Rome)

Genesis 28:10-12
Jacob's Dream at Bethel
[10] Jacob left Beersheba and set out for Harran. **[11]** When he reached a certain place, he stopped for the night because the sun had set. Taking one of the stones there, he put it under his head and lay down to sleep. **[12]** He had a dream in which he saw a stairway resting on the earth, with its top reaching to heaven, and the angels of God were ascending and descending on it.

John P. Perdew, AIP Conf. Proc. 577, 1 (2001)

Example: Atomization Energies (in eV)

Molecule	LSDA	GGA	Exact
H_2	4.9	4.6	4.7
CH_4	20.0	18.2	18.2
NH_3	14.6	13.1	12.9
H_2O	11.6	10.1	10.1
CO	13.0	11.7	11.2
O_2	7.6	6.2	5.2

1 eV = 23.1 kcal/mol

GGA total energy calculations provide good approximation to the exact AE

The fundamental band gap problem in the Kohn-Sham theory

A Photoemission

E_{kin}, E_{vac}, hv, Φ, E_F, IP_s, ϵ_s

N-1 electrons

B Inverse Photoemission

hv, E_{kin}, ϵ_s, E_{vac}, $-EA_s$, Φ, E_F

N+1 electrons

D. Golze, et al. Front. Chem. (2019)
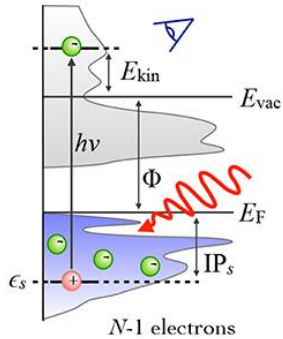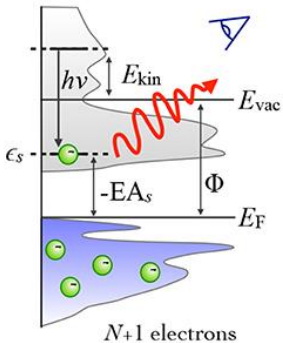
E(N) = DFT total energy of N electrons system

Photoemission IP = E(N) − E(N − 1) electron removal

Inverse Photoemission EA = E(N+1) − E(N) electron addition

Fundamental Band gap E_{gap} = IP − EA = E(N − 1) − 2E(N) + E(N+1)

The Khon-Sham gap is different from the fundamental band gap!

Indeed IP − EA $\neq$ ε_{LUMO} − ε_{HOMO}

Rather E_{gap} = ε_{LUMO} − ε_{HOMO} + ε_{XC}

$\varepsilon_{XC,GGA}$ = 0

Definitions from single-particle states (lacking XC energy in LDA/GGA)

E_{vacuum}, EA, ε_{LUMO}, IP, E_{gap}, ε_{HOMO}

K. Capelle, Brazilian Journal of Physics, vol. 36 (2006)
See also: Ab initio calculations of electron affinity and ionization potential of carbon nanotubes - F Buonocore, et al. Nanotechnology 19, 25711 (2008)

Electronic states meaning in Kohn-Sham equations

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) + V_{\text{eff}}(\mathbf{r})\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

fictitious single-particle orbitals optimized in density

Lagrange coefficients

In the formal Kohn-Sham theory the eigenvalues ε_i are merely auxiliary coefficients and the eigenvectors are fictitious single-particle orbitals.
But they are more than just that!
Indeed, for exact/accurate charge density:

- ε_i are well-defined zeroth-order excitation energies
- IP = - $\varepsilon_{\text{HOMO}}$ (exact equation)

and single-particle orbitals are used to define orbital functionals (hybrid, Meta-GGA, SIC, …)

K. Capelle, Brazilian Journal of Physics, vol. 36 (2006)

Examples of WF prediction for metals

Workfunction: $W = E_{vacuum} - E_F$

🟡 **1st layer atom**
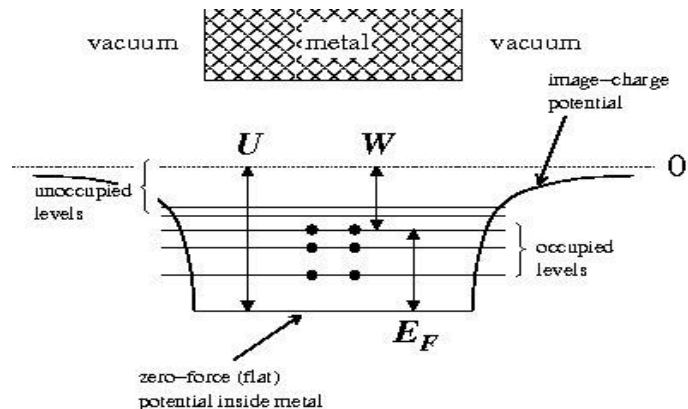
🟠 **2nd layer atom**

Metal	WF(exp) eV	WF(GGA) eV	a(exp) bulk Å	a(GGA) bulk Å
Au(111)	5.25	5.23	4.08	4.15
Pt(111)	5.69	5.70	3.92	3.99

fcc lattice

GGA = DFT General Gradient Approximation
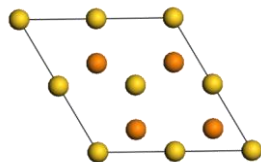
The metal substrate are all cleaved in the (111) direction, the most used in experiments.

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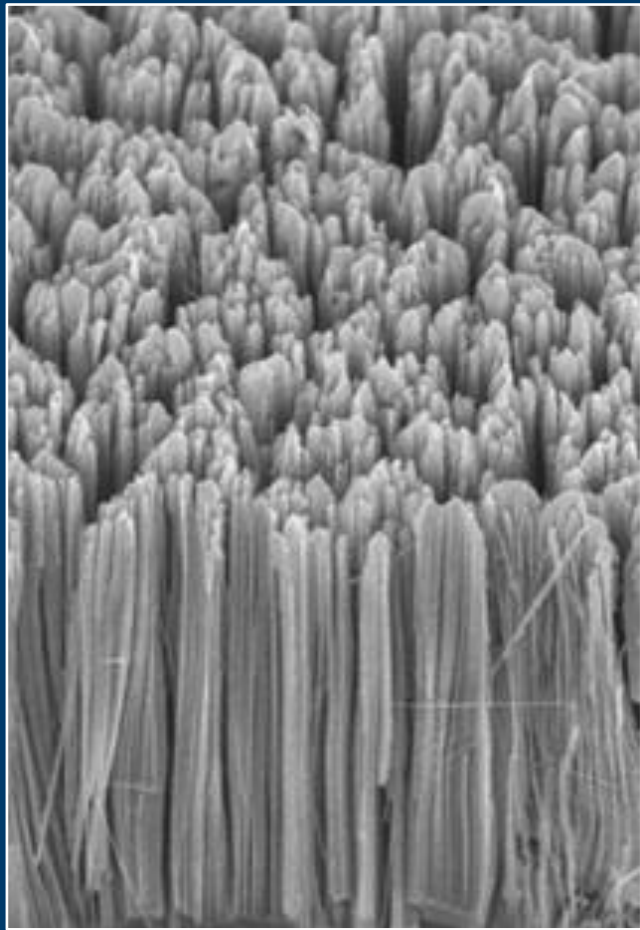
Silicon NanoWires (SiNWs)

The controllable growth of nanowires allows to uncover the growth mechanisms and tailor building blocks to construct functional devices.

SiNWs applications could make electronic devices neat, cheap, efficient, and powerful.

Benefits are seen from the implementation of SiNWs in solar energy conversion and storage devices.

Understanding the energetic of surfaces is the key to control the behavior of the devices and to suggest the chemical modification required to increase the device performances.

Electronic properties on VLS grown Silicon nanowires by surface charge transfer
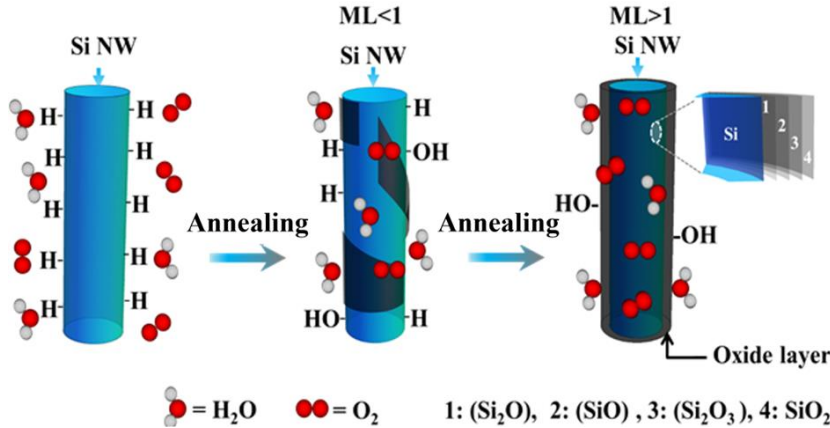
- Oxide thin layer growth by annealing pulses on the Silicon NWs.
- The Si_x-H_y-O_n interface replaces the starting hydrogen-silicon bonds (Si-H) at the Si NW surface.
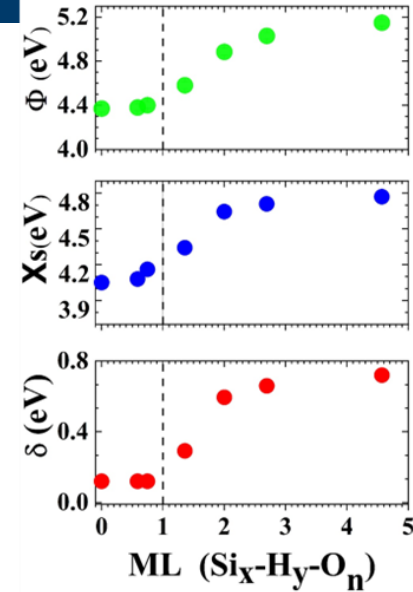
The experimental surface electronic parameters (work function Φ, electron affinity χ and surface dipole δ) vs. the number of monolayers. Quite flat for ML < 1.

Awad Shalabny, Francesco Buonocore, Massimo Celino, Lu Zhang, Kasra Sardashti, Michael Harth, Dirk W. Schubert, Muhammad Y. Bashouti. Applied Surface Science 599 (2022) 153957

We considered different configurations of the adsorption of dissociated oxygen and hydroxyl groups on the hydrogenated Si surface and calculated the variation of the work function Φ to be compared to the experimental $\Delta\Phi$.

All H desorbed and 100% O coverage gives $\Delta\Phi$ = 1.2 eV (too much high).
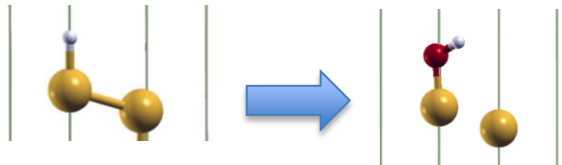
All H substitution with –OH gives $\Delta\Phi$ = -0.25 eV (opposite change)
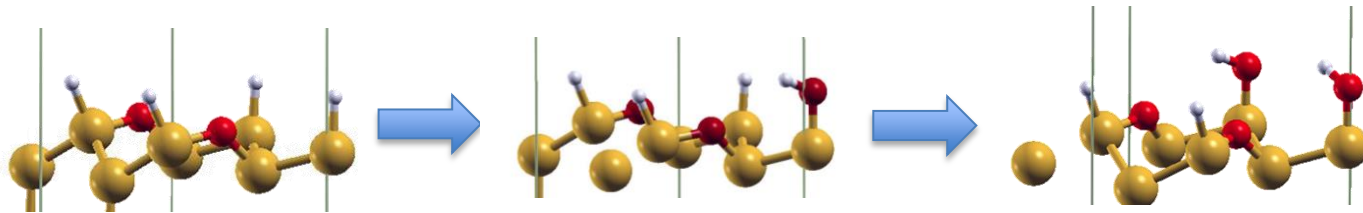
The H substitution with –OH in the low barrier early stage dissociated oxygen adsorption on hydrogenated Si surface gives $\Delta\Phi$ = 0.3 eV (closer to experiments).

More complex adsorption Si-OH and Si-O-Si patterns are possible. However, the simultaneous presence of both has been proved to give rise to low formation energy configurations. The intrinsic dipole carried by the hydroxyl group has the effect of mitigating the increase in the work function due to the atomic oxygen adsorption and the related electron charge transfer.

A. Shalabny, et al. Applied Surface Science 599 (2022) 153957

SiNWs functionalization

Purpose: to prevent extensive oxidation of the SINWs through chemical methods while preserving the low surface recombination velocity.

Bashouti et al. have shown that through a chlorination/alkylation process for functionalizating SiNWs with C_1-C_6 alkyl chains, provides surface stability that depends on the chain length and molecular coverage (J. Phys. Chem. 2008, 112, 19168–19172).
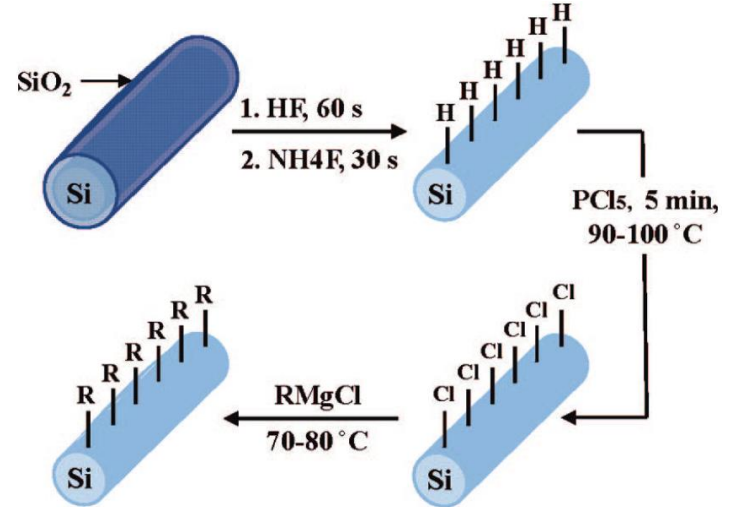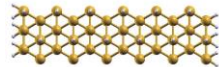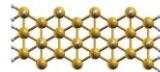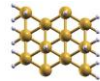
Si NWs: optimized atomic structures

<112> H-SiNWs

<112> Cl-SiNWs

cross-section

Top-view (110) surf.

Top-view (111) surf.
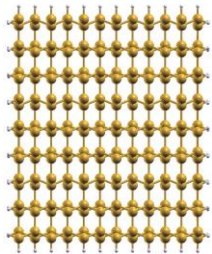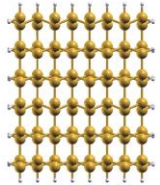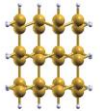
cross-section
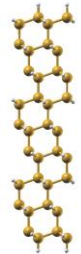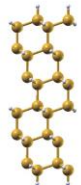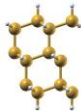
Top-view (110) surf.

Top-view (111) surf.

24 atoms
D = 0.7 nm

96 atoms
D = 1.7 nm

216 atoms
D = 2.6 nm
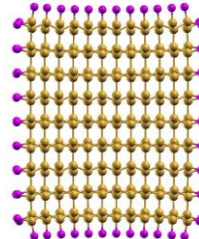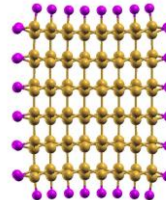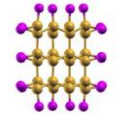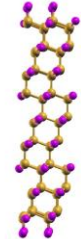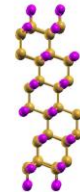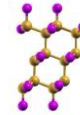
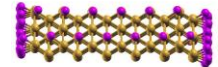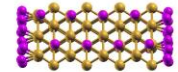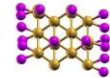# Electronic properties of Cl- and H-SiNWs

H/Cl- SiNWs	E_{FORM} (eV/at)
$Si_{24}H_{20}$	-0.0025
$Si_{96}H_{40}$	-0.035
$Si_{216}H_{60}$	-0.068
$Si_{24}Cl_{20}$	-0.73
$Si_{96}Cl_{40}$	-0.51
$Si_{216}Cl_{60}$	-0.41

The formation energy per atom (E_{FORM}) shows that Cl atoms improve the structural stability of the wire better than H atoms.

Ferrucci, B.; Buonocore, F.; Giusepponi, S.; Shalabny, A.; Bashouti, M.Y.; Celino, M. Ab Initio Study of Octane Moiety Adsorption on H- and Cl-Functionalized Silicon Nanowires. Nanomaterials **2022**, 12, 1590. https://doi.org/10.3390/nano12091590

The band-gap energy of the three H-SiNWs is larger than that of the respective Cl-SiNWs. The difference of the gaps decrease vs the diameter.
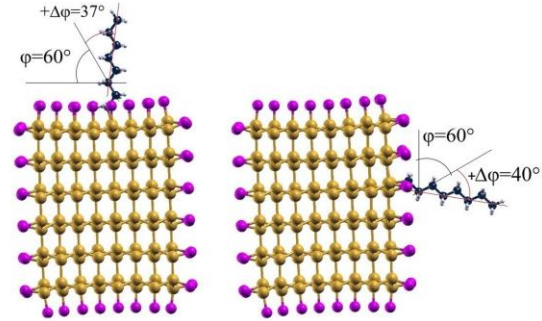

GGA   GGA   GGA
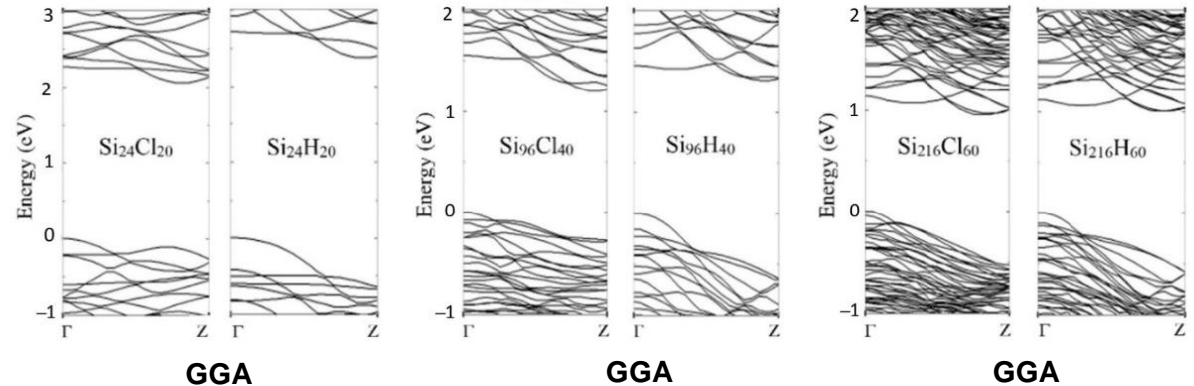
Octane moiety adsorbed on the (111) and (110) surfaces of H- and Cl- SiNWs

The chlorinated systems present a higher bond dissociation energy (BDE) of octane moiety with respect to the hydrogenated systems.
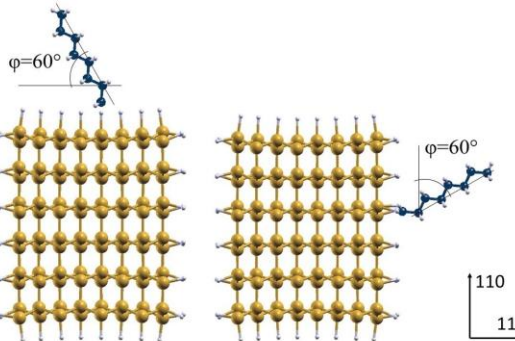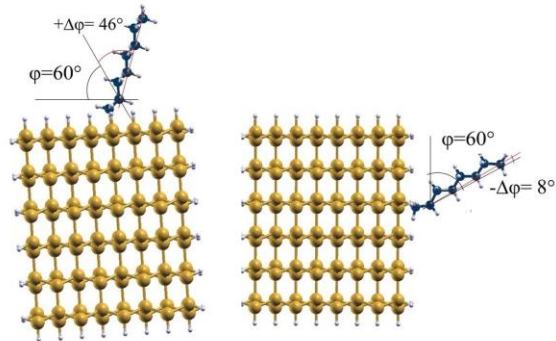

Cl-SiNW initial geometry
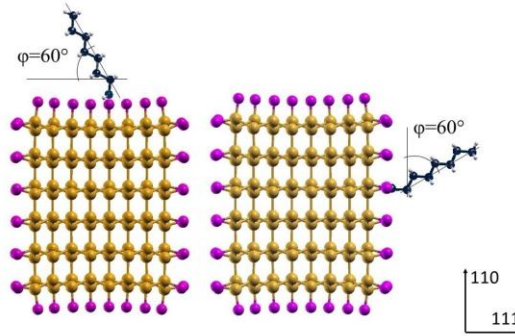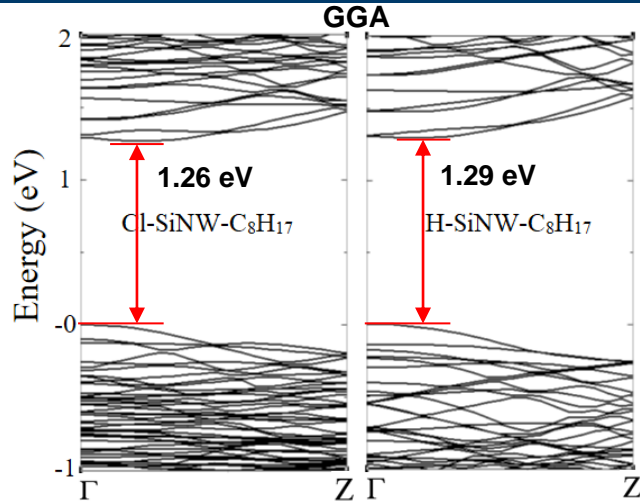
Cl-SiNW optimized geometry

H-SiNW initial geometry

H-SiNW optimized geometry

NW Structure	BDE (kJ/Mol)	E_{FORM} (eV/atom)
Cl-Si-C_8H_{17}(111)	733.85	-0.48
Cl-Si-C_8H_{17}(110)	716.47	
H-Si-C_8H_{17}(111)	637.30	-0.053
H-Si-C_8H_{17}(110)	632.67	

B. Ferrucci, et al. Nanomaterials 2022, 12, 1590

GGA

1.26 eV

Cl-SiNW-C$_8$H$_{17}$

1.29 eV

H-SiNW-C$_8$H$_{17}$

Eg(H-SiNW-C8H17) < Eg(H-SiNW)

ΔE_{gap} = 0.01 eV

Eg(Cl-SiNW-C8H17) > Eg(Cl-SiNW)

ΔE_{gap} = 0.07 eV

B. Ferrucci, et al. Nanomaterials 2022, 12, 1590

The octane moiety adsorption does not give rise to any energy level inside the energy band gap, differently from the case of alkene molecule adsorption.

intragap energy level
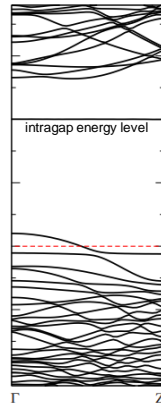
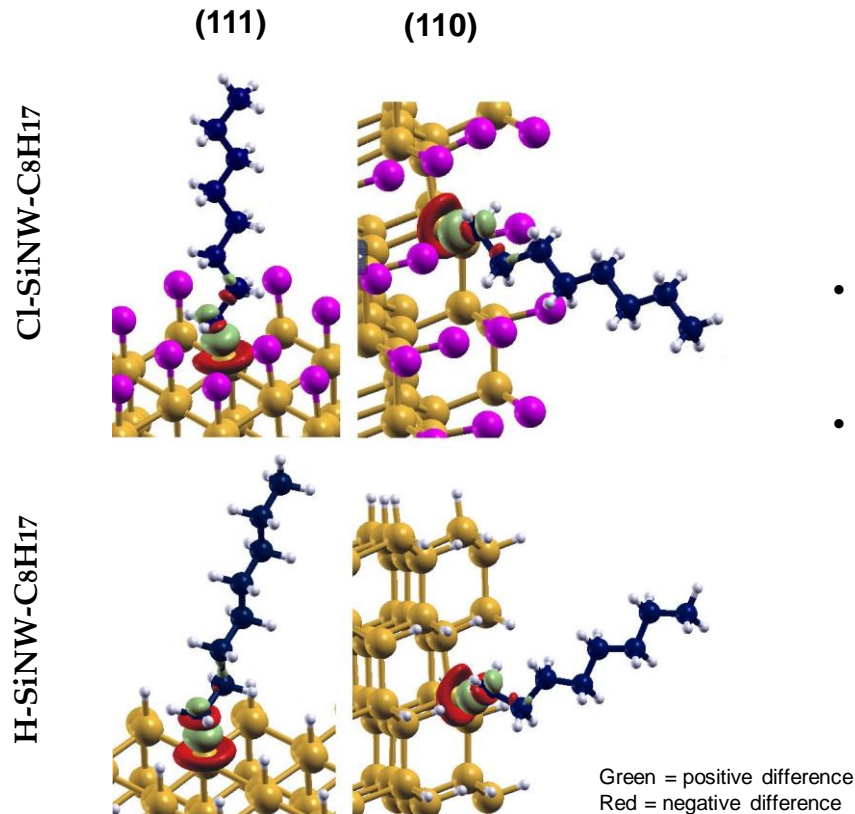Band structure and intragap energy level of <112> SiNW with the adsorption of alkenyl chain (H. Xu, et al. Appl. Phys. Lett. 2011, 98, 073115)
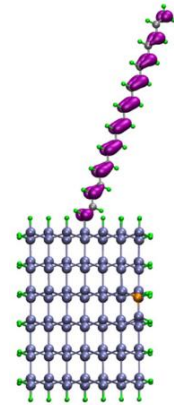
Differential charge density of Cl/H-SiNW-C₈H₁₇ (111)/(110)

(111) **(110)**

Cl-SiNW-C₈H₁₇

H-SiNW-C₈H₁₇

Green = positive difference
Red = negative difference

- Charge transfer does not dependend on Cl- or H-functionalization;

- charge transfer of 0.2 e from the Si NW to the octane moiety (partial charge of 48.3 e for the isolated C_8H_{17}).

B. Ferrucci, et al. Nanomaterials 2022, 12, 1590
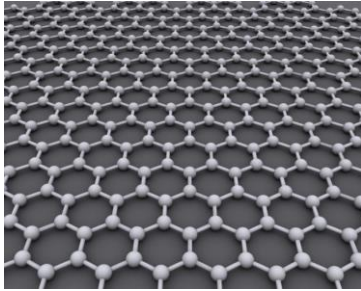
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Graphene and its derivatives

In the fully sp^2 hybridized 2D lattice, some carbons can be altered into the sp^3 hybridization while bonds pop out to become available out of the plane
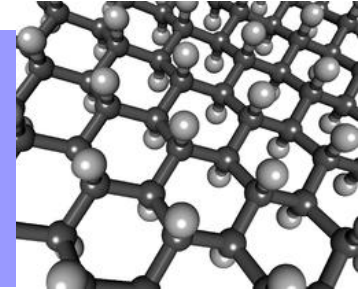
Graphene
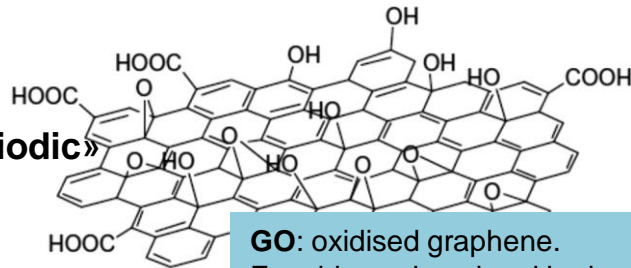

periodic Graphene Based Derivatives

Graphane: all carbons are sp^3 and bonded to hydrogen

Fluorographene: the same structure with fluorine

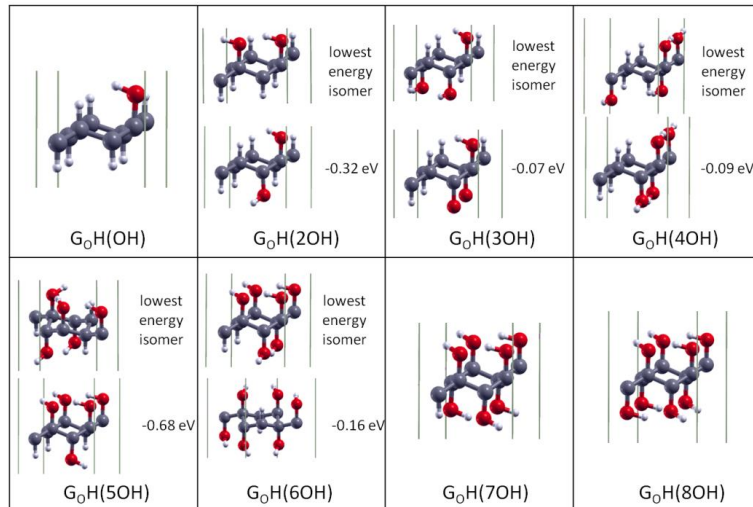**Graphone**: hydrogen only on the top

irregular and «aperiodic»

GO: oxidised graphene. Epoxide, carboxyl and hydroxyl

Also fully sp^3 GOH structures are possible: hydrogenated, epoxide, hydroxyl mix are predicted to be stable (Buonocore et al., The Journal of Chemical Physics vol. 147, 104705 (2017)).
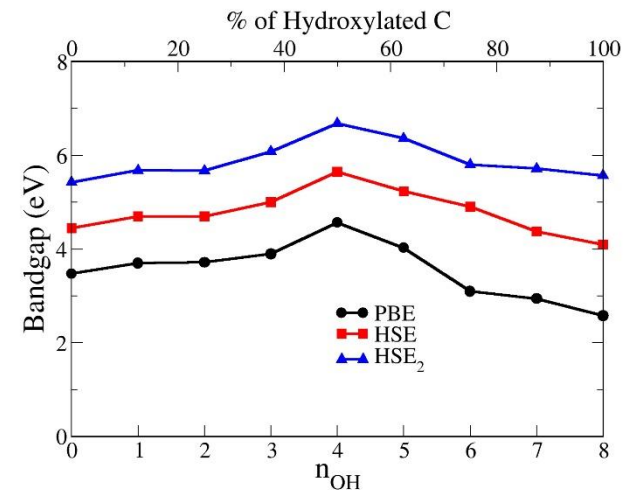
Example of ab initio energy gap: the hydroxylated graphane case

$E_{gap} = \varepsilon_{LUMO} - \varepsilon_{HOMO}$ **with (HSE and HSE$_2$) and w/o (PBE GGA) exact exchange fraction**

The lowest and second lowest energy hydroxylated graphane isomers.

Ab initio thermodynamic stability investigated in Buonocore et al., The Journal of Chemical Physics vol. 147, 104705 (2017)
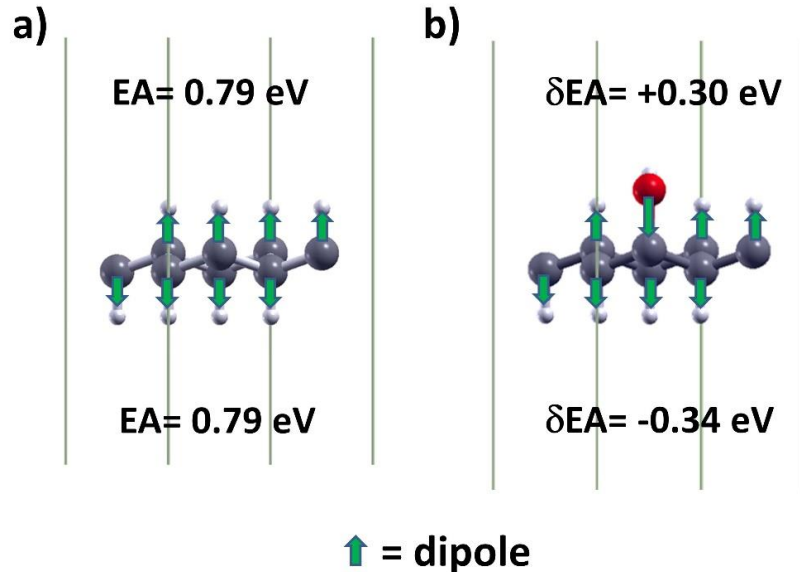
Energy gap of the lowest energy isomers.

HSE and HSE$_2$ are hybrid functionals with 25% and 50% of the exact exchange energy, respectively. (F. Buonocore, et al. J. Physical Chemistry C vol. 125 (2021))

Effect of hydroxylation on EA of graphane

a)

EA= 0.79 eV

EA= 0.79 eV

b)

δEA= +0.30 eV

δEA= -0.34 eV

⬆ = dipole

- Hydrogen less electronegative with respect to C → outward-pointing surface dipoles → decrease of the EA
- Oxygen more electronegative than C → inward-pointing surface dipole → increase of the EA
- The different EA on the two sides give rise to an electric dipole μ_z = 0.219 D (ΔEA = 0.64 eV).
- Two different faces → Janus structure
- EA = E_{vacuum} − ε_{LUMO} with exact exchange energy fraction (HSE$_2$)

δEA is the electronic affinity (EA) variation due to the first hydroxylation.

Electric dipoles in Janus 2D structures

Electronic affinity and induced microscopic electric dipoles
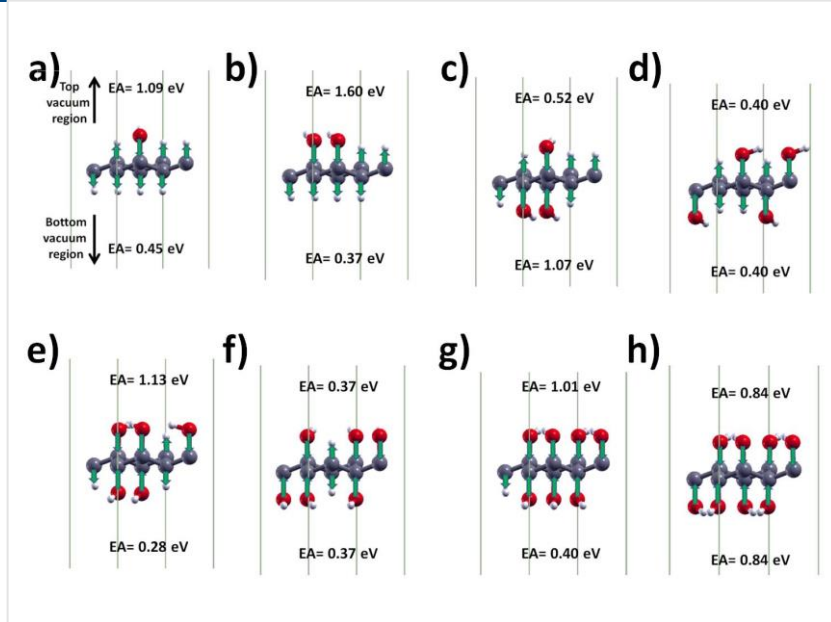
Difference in EA and total intrinsic dipole moment μ_z for the HyGH structures (HSE$_2$).

	Δn_{OH}	$\|\Delta EA\ (eV)\|$	$\|\mu_z(D)\|$
GH(1OH)	1	0.64	0.219
GH(2OH)	2	1.23	0.423
GH(3OH)	1	0.55	0.189
GH(5OH)	1	0.85	0.297
GH(6OH)	2	1.03	0.364
GH(7OH)	1	0.61	0.218

Buonocore et al., J. Phys. Chem. C 2021, 125, 29, 16316−16323
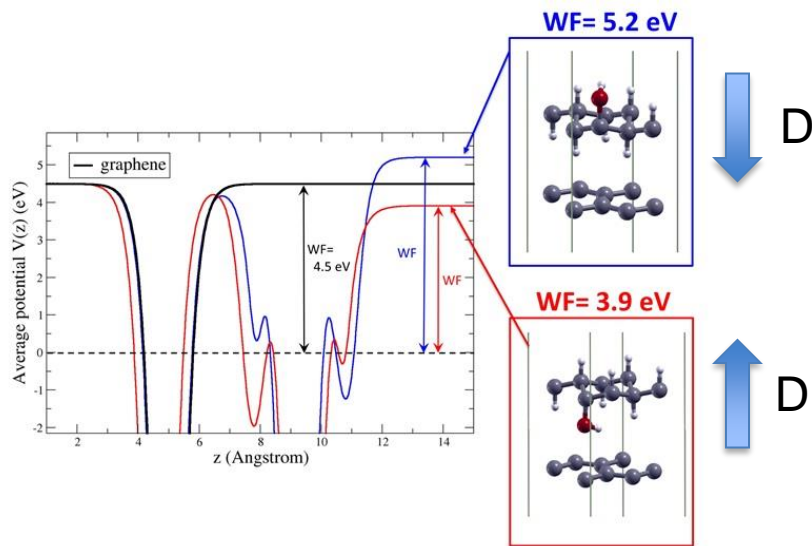
Having a commensurate lattice structure to graphene and affording the WF tunability of different isomers, HyGH family materials could be ideal interlayers in graphene-based devices and 2D heterostructures.
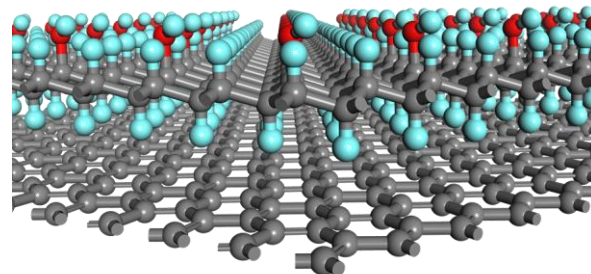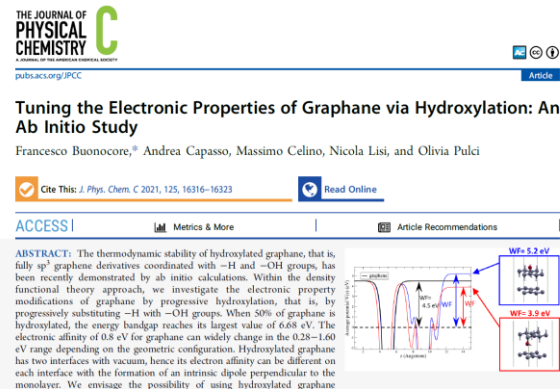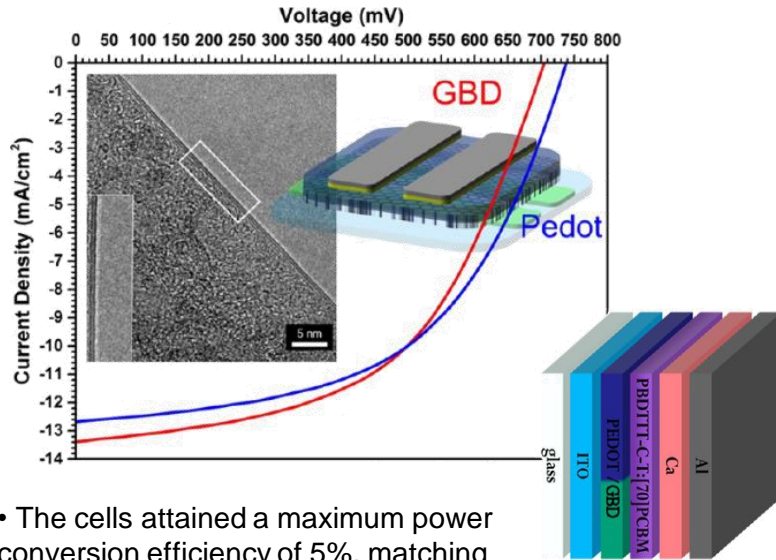
Buonocore et al., J. Phys. Chem. C 2021, 125, 29, 16316−16323

Graphene based derivative (GBD) as hole transport layer (HTL) for organic photovoltaics

- The cells attained a maximum power conversion efficiency of 5%, matching reference cells made with state-of-the-art PEDOT:PSS as the hole transport layer
- The advantage is that GBD do not corrode the ITO electrode.

A. Capasso, et al., ACS Appl. Mater. Interfaces, 2016, 8, pp 23844–23853
Low T GBD characterization: A. Capasso, et al., Advanced Functional Materials Volume 31 2005300 (2021)
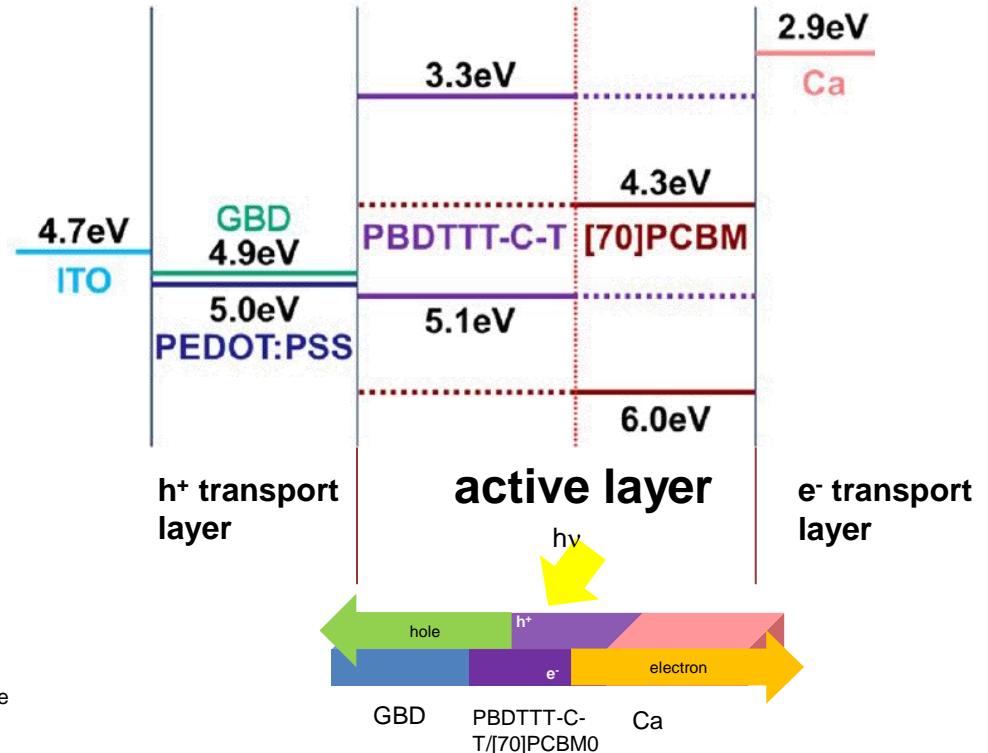
EERAdata: Towards a FAIR and open data ecosystem in the low carbon energy research community

European H2020 CSA – 3 years project started in March 2020
Building a Low-Carbon, Climate Resilient Future: Secure, Clean and Efficient Energy (LC-SC3-CC-3-2019)

EERAdata consortium
■ Consortium partner
■ Co-hosting institution
Created with mapchart.net

Vision:
- **Energy data** **exploitation with useful metadata and quality assurance to choose, monitor and implement sustainable transition pathways**
- **Industrial and research applications in** **4 use cases**: 1) *Materials for energy, 2) Power transmission and distribution, 3) Buildings efficiency, 4) Low carbon and energy efficiency policies*

Objectives:
- Low carbon **energy research databases** opening and **FAIR**ification (**F**indable, **A**ccessible, **I**nteroperable, **R**eusable)
- Develop a **community platform** for both providers and users of energy data
- Build **technical, operational and financial capacities** for the management of data in energy research communities: **The European Energy Research Alliance (EERA) , EOSC (European Open Science Cloud)**

website: www.eeradata.eu

Partners

TOWARDS A FAIR AND OPEN DATA ECOSYSTEM IN THE LOW-CARBON ENERGY RESEARCH COMMUNITY
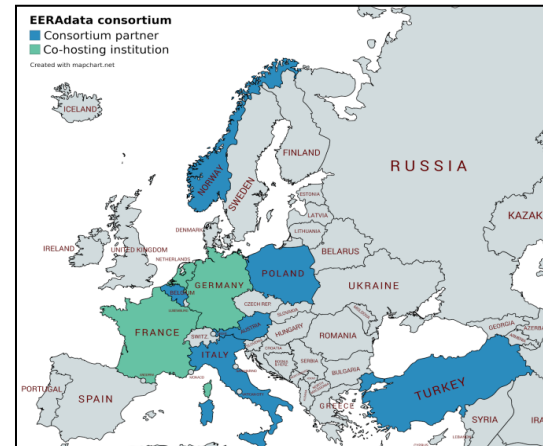
Conclusions

- Density functional theory is a powerful theoretical approach that must be used wisely.

- The functionalization of nanomaterials plays a critical role since it determines, to a large extent, the properties and performances of the devices in applications. The alkyl functionalization can enhance protection of the hydrogenated and chlorinated nanowire quantum surfaces against oxidation without substantial modification of the electronic properties of H- and Cl-functionalized Si NWs.

- Heterostructures fabricated with Janus monolayers (asymmetric bifacial functionalization) may play the role of charge transport layer in solar cells, depending on the polarity of the 2D crystal.

Thank you for your
kind attention

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