cecam Centre Européen de Calcul Atomique et Moléculaire	**Workshop Scientific Report** Please do not repeat the program (unless there were last-minute changes) or the initial description - we already have this material.
Title	**Chemical and topological functionalization of graphitic surfaces: Open challenges for computational modeling**
Organizers	Giorgio Benedek and Stefano Fabris

Scope of the workshop (one-two paragraphs)

A broad sector of present and future nanotechnologies is relaying on the very large variety of sp^2 carbon forms and on their flexibility towards chemical functionalization. The occurrence of stable 0-, 1-, 2- and 3-dimensional sp^2 structures belonging to the wide families of fullerenes, nanotubes, graphene and random schwarzites, respectively, provides the building blocks for assembling carbon-based architectures with tailored physical and/or chemical properties. The workshop focused on the chemical and topological functionalization of the graphitic surfaces exposed by these nanostructured materials, and had the scopus of identifying the main open challenges for accurate and reliable computational modeling of these materials.

The key topics of the workshop were: i) the use of atomic/molecular adsorbates to control the electronic, chemical, optical, and catalytic properties; ii) the controlled anchoring of semiconductor/metallic nanoparticles on 2D carbon supports, iii) the dynamics, stability, clustering, thermal evolution, as well as chemical reactivity of these atomic/molecular/metallic adsorbates at graphitic surfaces, iv) the epitaxial growth/support of high-purity graphene on metallic/insulating surfaces and the precise characterization of structural, electronic and (electro)-catalytic properties. The workshop allowed to establish the status of numerical modeling in clarifying this structure/property interplay, and to identify the fundamental shortcomings that limit the predictive power of both quantum and empirical approaches.

Main **outcomes** of key presentations (one page)

The main scientific discussions at the meeting addressed the recent advances in the functionalization of extended sp^2-carbon, notably graphene and C-nanotubes, and how they have widened and accelerated their applications in technological sectors such as nano-electronics, catalysis, sensorics and optoelectronics. The results presented at the meeting demonstrated how the structural, electronic, and catalytic properties of these C-based materials can be tuned and controlled by the formation of patterned defects and adsorbates on the surfaces (atoms/large molecules), of specific structural morphologies (junctions, ribbons, edges, etc.), by chemical functionalizations (oxidation/reduction, covalent, cycloadditions, etc.), or by supporting these graphitic systems on metallic/insulating surfaces (epitaxial graphene on transition metal surfaces, Moirè overlayers, etc). The lively discussion stimulated by the oral presentations focused on how research on C-based nanostructures provided important insight into their electronic and structural properties but stressed that many fundamental issues in the complex systems resulting from these chemical/structural functionalizations still remain unresolved or debated. Some examples include the assemblies and dynamics of atomic/molecular adsorbates on graphene, the formation and structure of point and extended lattice defects, edges and junctions, the products of surface reactions ranging from simple oxidation/reduction to complex cycloaddition functionalizations, and the electronic and chemical properties of the graphitic surfaces supported by metal/insulating surfaces. These issues constituted the main scientific content and discussion of the event.

The workshop was attended by more than 40 participants, it comprised of 7 tenatic sessions and 1 poster session. The thematic sessions were: Chemical functionalizations; Magnetism and transport; Graphene oxide; Supported graphene I; Supported graphene II; Dynamics; and Surface defects. These sessions consisted in one or more key-invited talks from experimentalists, which set the state-of-the art in the synthesis and characterization of the materials and of the control of their functions. Most of the oral presentations addressed the field from the point of view of numerical modelling. Contributed presentations from young researchers were introduced in the program together with the invited ones. The poster presentation was very lively and about 15 posters were discussed.

Report on selected discussions (one page)
eg. Were there interesting hints for new research? for new developments? for collaborations?

The event gathered together experimental and theoretical representatives of the solid-state physics, chemistry, and materials science communities to discuss the open and challenging issues descrive above. The presentations and lively discussions stimulated by the reported results allowed to identify future directions of the field. In particular, it was shown how the functionalization approaches allowed to achieve an unprecedented control of several properties of the graphitic surfaces, including the bandgap and electronic structure, the surface chemical stability, the hydrophobic/hydrophilic behavior, and the selectivity towards chemical reactions. DFT and empirical modeling played an important role into these issues but it was evident that these chemically/topologically functionalized graphitic surfaces presented severe challenges to numerical simulation. On the one hand there is the large variety of structures that can be formed by connecting C networks, often resulting in highly complex structures/topologies, which are difficult to predict without a close connection with the experiment. The main example of this, discussed at length in the meeting, was the prediction of the actual structure of graphene oxide. Novel computational methods based on metadynamics and advanced collective variables resulting from graph theory were shown to have a very high predictive power in predicting the structure of carbon-based nanomaterials. This is a very important direction identified at the meeting that aims at closing the crucial gap between theoretical predictions and real materials.

Other important future directions identified by the discussions were the delicate interplay between the chemical bonding of atoms/molecules/clusters at graphitic surfaces and the long-range electronic and elastic responses of the pi-conjugated C network were shown to require accurate electronic structure methods and large computational supercells. Addressing the one (ex: the adsorbate binding and mobility) without fully considering the others (ex: the lattice constrain by the surrounding C network on the adsorbates) often lead to important drawback. Moreover, most of the DFT simulations addressing functionalized graphene supported by transition metal surfaces neglect the effect of dispersion forces, which have instead been recently shown to be crucial for capturing the amplitude of the Moire` and the covalent contribution into the metal-C bonding. Finally, it was shown how surface chemical processes and reactions are often simulated by approximating the graphitic surface with small organic molecules and how this can led to important discrepancies with experiment. This issue certainly requires improvement.

One of the most critical issues and urgent needs of numerical modeling of functionalized graphitic surfaces concern the possibility of simulating explicitly large portions of graphitic surfaces in the presence of defects, adsorbates, boundaries or junctions. This calls for empirical and semiempirical modeling, but there is presently no satisfactory empirical potential capable to capture accurately complex surface structures, defects/adsorbate binding geometries, or defects/adsorbate relative energetics. Reactive force fields have been used to simulate complex chemical reactions at surfaces, such as the structural evolution during the reduction of chemically derived graphene oxide, but their accuracy, specifically on the energetics of the functional groups, still has to be established. Similar questions concern the application of REBO potentials on adsorbate binding/mobility/clustering on graphene and nanotubes. The availability of more reliable empirical/semiempirical models would allow to make important progress in the field. Advances into several fundamental questions with computational techniques require large scale simulations comprising thousands of atoms, which can only be performed with reliable empirical or semiempirical potentials, still to be developed or refined.

To what extent were the **objectives** of the workshop achieved (strong points, weak points)? (one paragraph at least)

The objectives of the workshop were mainly achieved thanks to the speakers who really prepared talks that stimulated discussion rather than simply presenting good results. The direct confrontation between experimental research and numerical modeling on very closely related subjects was in my opninion one of the strongest point of the workshop, which really allowed to establish the present status of the predictive power of computational techniques. Also the poster session turned out to be lively and gave the chance to younger scientists to interact with the most experienced researchers in an informal way. Maybe the weak point was the highly dense program, which could have reserved slightly more space to discussion.

Do you have suggestions for new workshops/tutorials/conferences on the topic?

This CECAM workshop on C-based materials is becoming a traditional meeting. The organizers received encouragement from the participants to repeat a smilar event in the future, maybe in two years from now.