

Electron confinement due to the two-dimensional (2D) nature of layered materials accounts for their fascinating electronic properties and for their applications in new-generation electronic devices. Moreover, the large specific surface area of 2D materials also enables their use in surface-related applications, such as catalysis and adsorption. In addition, these 2D materials are promising photocatalysts thanks to the shorter migration distance of photogenerated electrons and of electron holes. The research reported in this thesis aimed to provide atomistic insight into 2D layered materials, particularly into their structures, electronic properties and potential applications in the field of catalysis, photocatalysis and alkali metal ion batteries. Our findings are not only theoretically relevant but also open new research avenues for our experimental collaborators to improve specific properties and activities of their materials. The main results from this thesis, for five different classes of 2D materials, are summarized below.

2D covalent organic frameworks (COFs). CTF-type COFs with similar topology but different nitrogen-to-carbon ratios were investigated for their potential in photocatalytic water splitting. More specifically, torsion and bending effects on structure stability were investigated in detail. In addition, structural effects on band gap and band edge positions were discussed herein considering the conditions required for photocatalytic water splitting. Our results showed that these COFs are potential photocatalysts for water splitting, whose performance can be tuned by adjusting the nitrogen-to-carbon ratio and by layer arrangements, depending on the synthesis strategy. Importantly, both factors can be experimentally tuned; therefore, our results help to guide the preparation of CTF-type COFs with optimal photocatalytic performance. Accordingly, in collaboration with experimental groups, we explored several applications of COFs. For sulphur- and nitrogen-containing COFs, we calculated their structures and band structures, which were in good agreement with the corresponding experimental data. For triazine-based graphdiyne polymers, we calculated their structures and compared simulated and experimental SAED patterns. For polyimide COF, we obtained structures in good agreement with experimental data and calculated its specific capacity as a sodium-ion battery electrode, which were also in satisfactory agreement with experiments.

Silicene. High-quality silicene, which was synthesized by our experimental collaborators via CaSi_2 oxidation and exfoliation in the liquid phase, forms a monolayer or few-layer-thick sheets with high crystallinity. Silicene has been experimentally explored as a new anode for lithium ion batteries (LIBs) with impressive cycling stability. To evaluate its performance as an

LIB electrode, from an atomistic point of view, silicene was modelled as both monolayer and bilayer. Considering different adsorption sites, the formation energy profile was assessed based on the most stable configurations. Subsequently, the specific capacity for each model was calculated with respect to their fully lithiated structures. The results from the bilayer model were in excellent agreement with the experimental data on the specific capacity of the silicene anode.

Transition metal dichalcogenides (TMDs). An interlayer-expanded MoS₂ material previously prepared by oxygen incorporation has been shown to have superior performance as an LIB electrode material by our experimental collaborators. Thus, first-principle calculations were performed to gain atomistic insight into its interlayer structures and performance as an LIB electrode. Our results show that the interlayer-expanded MoS₂ has higher specific capacity than pristine MoS₂, in qualitative agreement with experimental findings. A quantitative agreement with the experimental data was also assessed when considering the presence of molybdenum oxide species (resulting from oxygen incorporation) in the interlayer space. PtSe₂ monolayers, another type of TMDs, embedded with 3*d* transition metal atoms in Se vacancies, were investigated for their potential as CO oxidation catalysts under mild conditions. The results showed that the Fe-PtSe₂ system was the best candidate, and reaction mechanisms for this catalyst were investigated in detail. Our kinetic analysis showed that both Langmuir-Hinshelwood and Eley-Rideal mechanisms have comparable reaction rate constants under mild conditions.

Transition metal carbides (MXenes) and transition metal trihalides (TMTs). Two-dimensional materials often show interesting magnetic properties. For practical applications in spintronics, these two-dimensional materials must maintain their magnetic properties near room temperature. However, only a limited number of 2D materials intrinsically meet such requirement. Therefore, we investigated suitable candidates for spintronics, in particular 2D Cr- and Mn-based MXenes as well as V- and Ni-based TMTs. These two-dimensional materials showed various intrinsic magnetic properties, such as antiferromagnetism with spin-polarized semiconductivity (Cr-based MXene), ferromagnetism with half-metallicity (Mn-based MXene), ferromagnetism with Dirac half-metallicity (V_I3 and VCl₃) and ferromagnetism with Dirac spin-gapless semiconductivity (NiCl₃). In addition, Monte-Carlo simulations indicated high Curie/Néel temperatures for these materials, thus suggesting their high potential for practical applications in spintronics.

Layered double hydroxides (LDHs). LDHs have already been extensively studied for various applications. Hence, understanding their structures will enable us to advance research on these materials. However, the structure of mössbauerite, belonging to the special fougèrite group (having the same divalent and trivalent ions – Fe), remains poorly understood. Thus, mössbauerite was computationally investigated, in addition to fougèrite. Both theoretical and experimental results showed that the mössbauerite structure consists of both carbonate-grafted and non-grafted layers, whereas no carbonate grafting was found for fougèrite. The mechanism of grafting and fougèrite oxidation to mössbauerite was also computationally explored, showing that the driving force of the formation of carbonate-grafted structures in mössbauerite is a strongly exothermic reaction between fougèrite and hydrogen peroxide.

Keywords: Two-dimensional Material; Covalent Organic Framework; Silicene; Transition metal Dichalcogenide; MXene; Transition Metal Trihalide; Layered Double Hydroxide; Density Functional Theory; Modeling; Monte Carlo Simulations; Photocatalysis; Catalysis; Reaction Mechanisms; Alkali-ion Battery