

## Chemical modification of graphene with Cl

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Chemical functionalization of graphene is an attractive and versatile means to modify its electronic properties to suit the intended applications. For example, a band gap can be induced through introduction of hydrogen [1], or fluorine [2] atoms onto the carbon network. Both for hydrogen and fluorine, theoretical calculations [3,4] agree well with the experimental results, although one-sided attachment of hydrogen on free-standing graphene should not be energetically stable. In the case of the next halogen species, chlorine, theoretical approaches [5], however, predict no covalent binding between the chlorine atoms and pristine graphene, whereas a recent experiments report signals associated with covalent C-Cl bonds [6,7]. Our density-functional theory calculations do not show covalent C-Cl bonding between chlorine and graphene, not even in the case where the van der Waals interaction and the presence of a silicon dioxide substrate are taken into account. Of the four considered surface terminations, there is a weakly stable chlorinated graphene structure only on the hydroxyl-terminated surface. This is similar to the case of graphene hydrogenation on SiO<sub>2</sub> [8].

We are able to provide an alternative explanation to the experiments. Using an ab initio thermodynamics approach, we show that the experimental observations may be explained by the formation of graphene segments with chlorine-containing edges [9]. We calculate the energetic stability of a large number of edge terminations with different degree of chlorination, both in terms of edge formation energy and chlorine binding energy. We also consider both reaction conditions with atomic chlorine, and ambient conditions with molecular chlorine as the reference state. The low-energy structures are compatible with the lowest-energy hydrogenated edge structures [10]. Chlorine-containing armchair edges are, in general, more stable than their zigzag-based counterparts, and most importantly, even in ambient conditions, some of them are more stable than chlorine atoms adsorbed onto the basal plane of graphene.

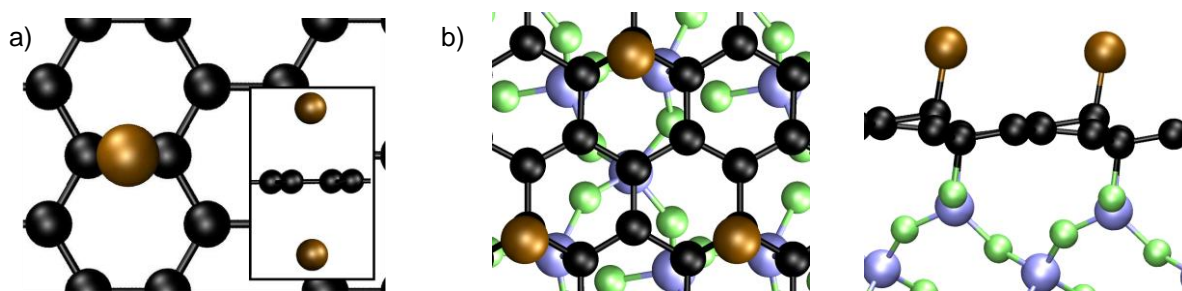


Figure 1: (a) Chlorine on freestanding graphene (b) chlorinated graphene on the O-terminated  $\alpha$ -quartz surface.

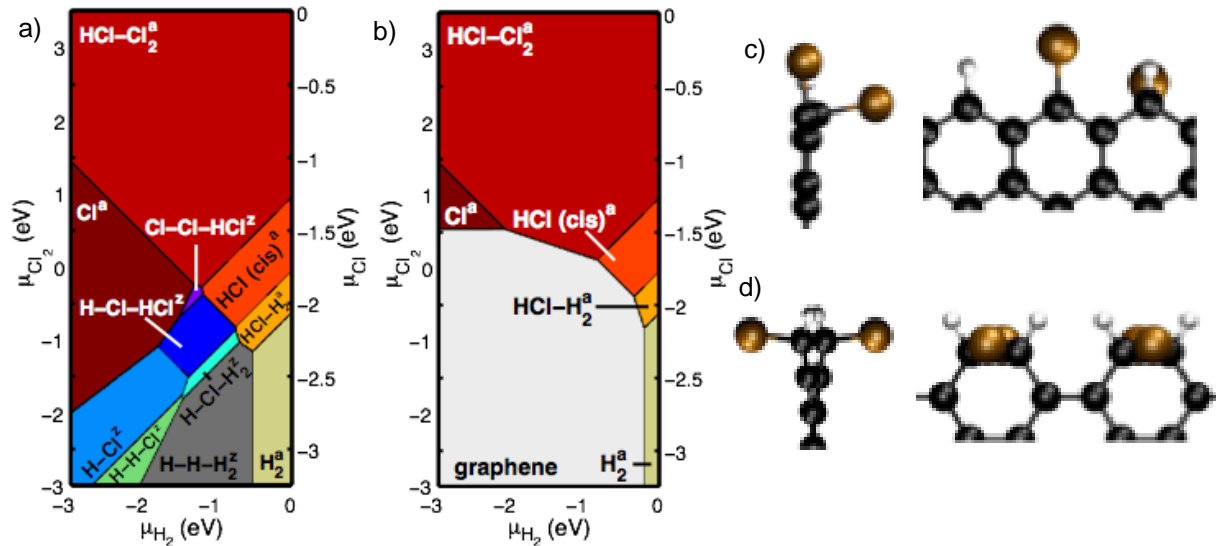


Figure 2: The stability of different chlorine-containing graphene edges. a) pristine graphene not taken into account b) pristine graphene region included. The superscripts a and z refer to armchair- and zigzag- type edges. c) The lowest-energy chlorinated zigzag edge [H-Cl-HCl] and d) the lowest-energy chlorinated armchair edge [HCl (cis)] in vacuum conditions.

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