

Supporting Information.

Room temperature water splitting at the basal plane of graphene grown on nickel

Monica Pozzo,^{1,2,3,*} Paolo Lacovig,⁴ Marco Bianchi,⁴ Monika Schied,⁴ Luca Bignardi,⁵ Francesca Zarotti,⁶ Roberto Felici,⁷ Dario Alfè,^{3,8,9} Silvano Lizzit,⁴ and Rosanna Larciprete^{6,†}

¹*Faculty of Technological & Innovation Sciences,*

Universitas Mercatorum, Piazza Mattei 10, 00186 Rome, Italy

²*Institute for Materials Discovery, UCL East, Marshgate Building,
7 Sidings Street, Stratford, London, E20 2AE, UK*

³*Department of Earth Sciences, Thomas Young Center,
University College London 5 Gower Place London WC1E 6BS UK*

⁴*Elettra-Sincrotrone Trieste, S.S. 14 Km 163.5 in
AREA Science Park, 34149 Basovizza, Trieste, Italy*

⁵*Department of Physics, University of Trieste,
Via Alfonso Valerio 2, 34127 Trieste, Italy*

⁶*CNR-Institute for Complex Systems, Via dei Taurini 19, 00185 Roma, Italy[‡]*

⁷*CNR-ISM, via del Fosso del Cavaliere 100, 00133 Roma, Italy*

⁸*London Centre for Nanotechnology, Thomas Young Centre,
University College London 17-19 Gordon Street London WC1H 0AH UK*

⁹*Department of Physics "Ettore Pancini",
Università Federico II, Via Cinthia 21, 80126 Napoli, Italy*

* m.pozzo@ucl.ac.uk

† rosanna.larciprete@isc.cnr.it

‡ Current address: ENEA, Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Via Enrico Fermi, 45, 00044 Frascati, Rome, Italy

1. Gr/Ni(111) exposed to high water doses

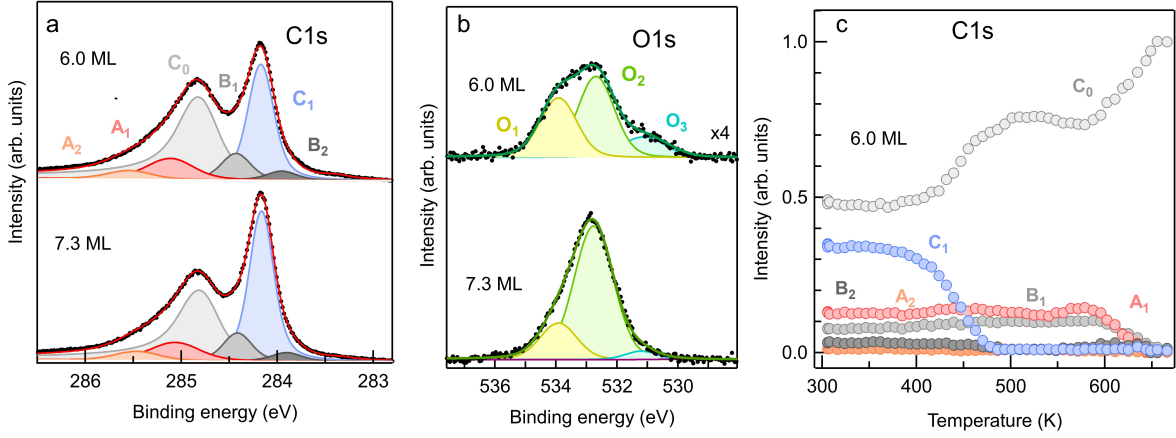


Fig.S 1. (a) C1s and (b) O1s spectra measured on Gr/Ni(111) exposed to 6.0 and 7.3 ML of water at RT. As reported in the main text, the component C₁ of the C1s spectrum represents the C atoms detached from the Ni substrate after the intercalation of water molecules or their fragments below graphene. In the O1s spectra, the O₁ and O₂ components represent H₂O molecules in different adsorption configurations, whereas O₃ is due to OH fragments [1, 2]; (c) Integrated areas of the C1s components measured while heating the Gr/Ni(111) sample dosed with 6.0 ML of water. Hydrogen atoms localized below Gr recombine and desorb as they do in the case of Gr/Ni(111) heavily hydrogenated with H atoms, when H intercalation occurs [3]. Hydrogen atoms chemisorbed on Gr desorb around 600 K as it happens for sample dosed with much lower water dose (see Fig.2 of the main text).

2. XPS characterization of Gr/Ni(111) exposed to water molecules and to H atoms

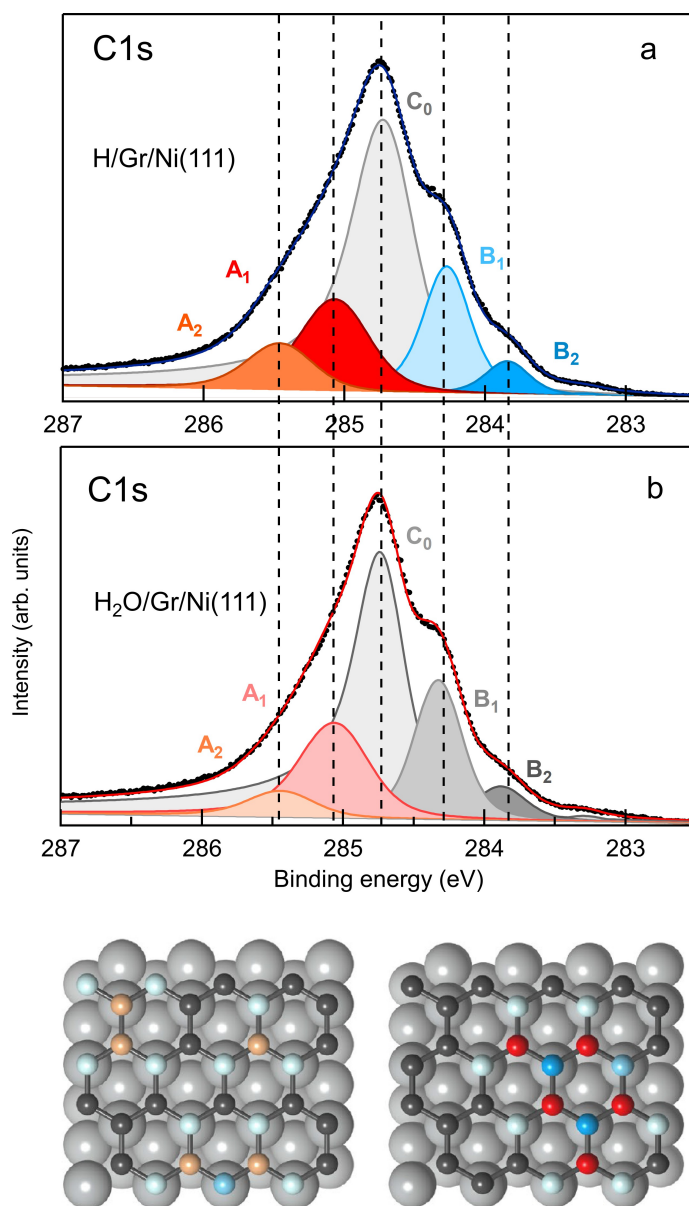


Fig.S 2. Comparison between the C1s spectra measured for the Gr/Ni(111) surface exposed (a) to a low dose of H atoms and (b) to 0.02 ML of water. In the first case the spectral components were assigned on the basis of DFT calculations [3] (see schemes at the bottom) to non-hydrogenated C atoms (C₀ 284.71 eV; dark grey atoms), C–H bonds in H monomers/dimers (A₂ 285.43 eV; orange atoms) and trimers/larger clusters (A₁ 285.05 eV; red atoms), and to C atoms, which are first neighbors of one/two (B₁ 284.32 eV; light cyan atoms) or three (B₂ 283.88 eV, dark cyan atoms) C–H bonds.

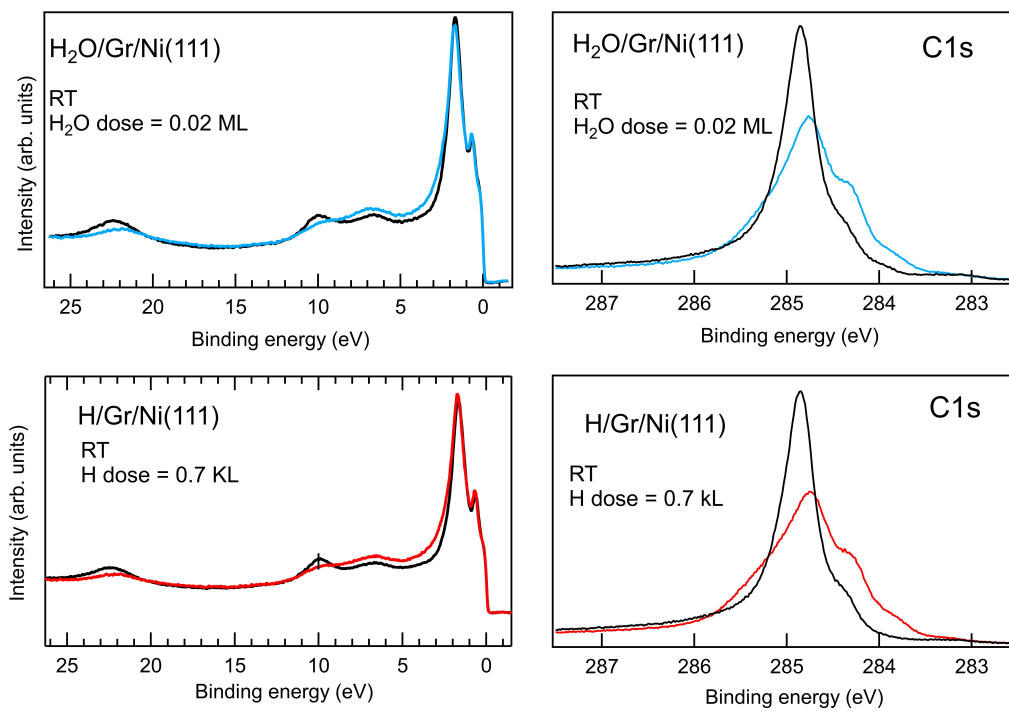


Fig.S 3. *left* Valence band and *right* C1s spectra measured for the Gr/Ni(111) surface exposed to *top* 0.02 ML of water and *bottom* 0.7 kL of H atoms.[3] In each case the black (colored) curves were acquired on the clean (dosed) surface.

3. C-H bonds in hydrogenated Gr/Ni(111)

After the exposure to water, the formation of C-H bonds shifts out of the Gr plane the C atoms directly involved in the bonding, which assume the sp^3 geometry, whereas the surrounding C-Ni bonds get reinforced and the Gr-Ni distance is somewhat reduced.

Figure S4 shows the Gr/Ni(111) surface bonded to 0.25 ML_{Gr} of H atoms, which is the coverage estimated by XPS for the sample exposed to 0.2 ML of water. In the graphene layer, the C atoms directly bonded to H (white color) and those first neighbors of two (C_2 , yellow color), one (C_1 , green color) and zero (C_0 , grey color) C-H bonds are differently displaced from their original positions. In comparison to the C-Ni distance of 2.13 \AA calculated for the clean Gr/Ni(111) interface, in the presence of chemisorbed H atoms the C-Ni distance becomes of 2.46 \AA for the C atoms bonded to H, and of 1.96 , 2.05 and 2.01 \AA for C_2 , C_1 and C_0 , respectively. Therefore, the average Gr-Ni distance, which is the value measured by x-ray surface diffraction, is 2.12 \AA , i.e. similar to that of the clean interface.

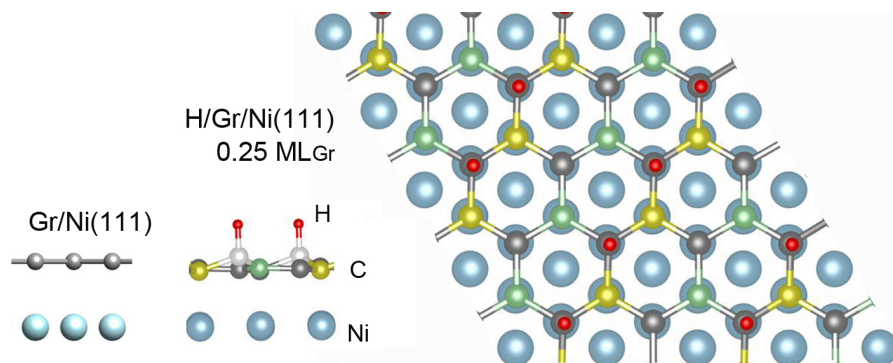


Fig.S 4. H atoms chemisorbed on Gr/Ni(111) at a coverage of 0.25 ML_{Gr} . The Ni and H atoms are represented with light blue and red colors, respectively. The C atoms involved in the C-H bonds are plotted in white, whereas the C atoms first neighbors of zero, one or two C-H bonds are indicated by grey, green and yellow colors, respectively.

4. STM characterization of the Gr/Ni(111) surface exposed to water.

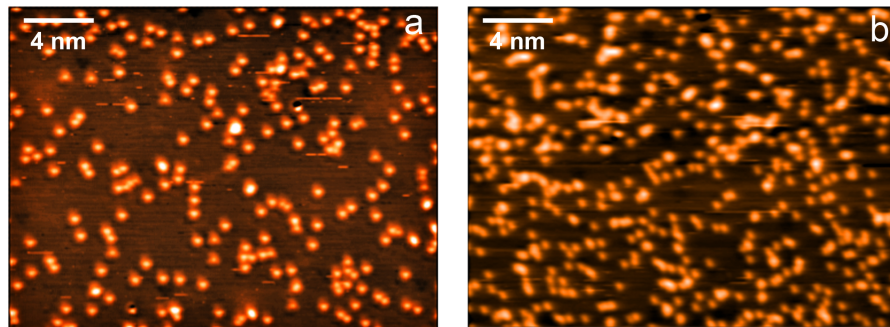


Fig.S 5. STM characterization of the Gr/Ni(111) surface exposed to (a) $w_d = 4.5 \times 10^{-3}$ and (b) $w_d = 9.0 \times 10^{-3}$ ML of water [(a) 0.68 V, 0.28 nA; (b) 2.15 V, 0.09 nA]. The graphene layer is evenly covered by H atoms. The H coverage is directly proportional to the water dose which doubles from (a) to (b).

5. Water dissociation on an incomplete Gr layer on Ni(111)

In order to verify the role of Gr defects in the dissociation of water, we have exposed to increasing water doses an incomplete Gr monolayer, obtained by stopping the growth on Ni(111) slightly before the saturation of the C1s signal intensity, and, therefore having a small percentage of C vacancies (see Fig.S6).

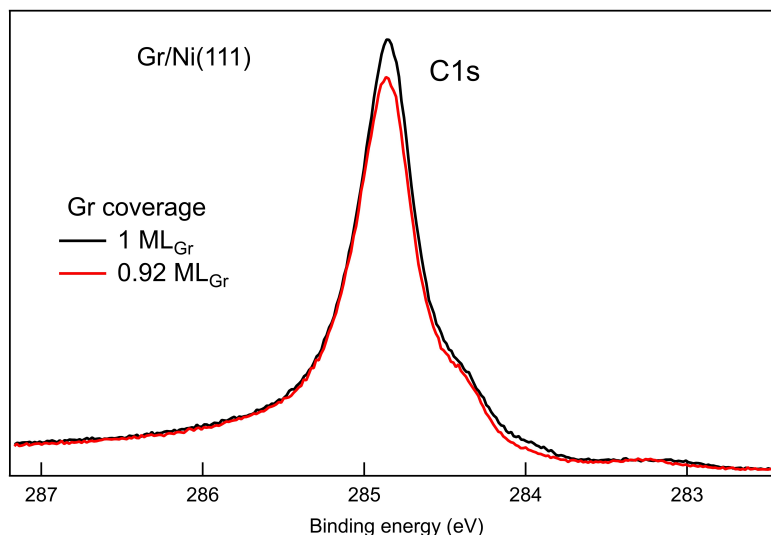


Fig.S 6. C1s spectra measured after the growth of an incomplete (red curve; coverage 0.92 ML_{Gr}) and complete (black curve; coverage 1 ML_{Gr}) Gr layer on Ni(111)

Figure S7a shows that even in the presence of lattice defects the C1s line shape evolves with the water dose as it does for complete Gr (Fig.1a of the main text). In particular, the spectrum measured on the sample dosed with 0.2 ML of water indicates H chemisorption on Gr, as it was found for the complete Gr layer after comparable water doses. However, for incomplete Gr, even after such a moderate water dose, the O1s region does not appear flat, as it does when the Gr layer is complete, but shows the presence of four spectral components, namely O₁ (533.92 eV) and O₂ (532.70 eV), attributed to water molecules adsorbed in different interface configurations and sites, and O₃ (531.14 eV) and O₄ (530.1 eV) assigned to OH and O fragments, respectively [1, 2, 4]. Accordingly, the C1s spectrum shows some extra-intensity around 284 eV, that hints at anticipated intercalation in comparison to what happens at the complete Gr layer, where intercalation occurs after much higher water doses.

The higher intercalation yield favored by the incomplete Gr coverage is confirmed by the faster growth rate of the C₁ intensity with increasing water dose in comparison with

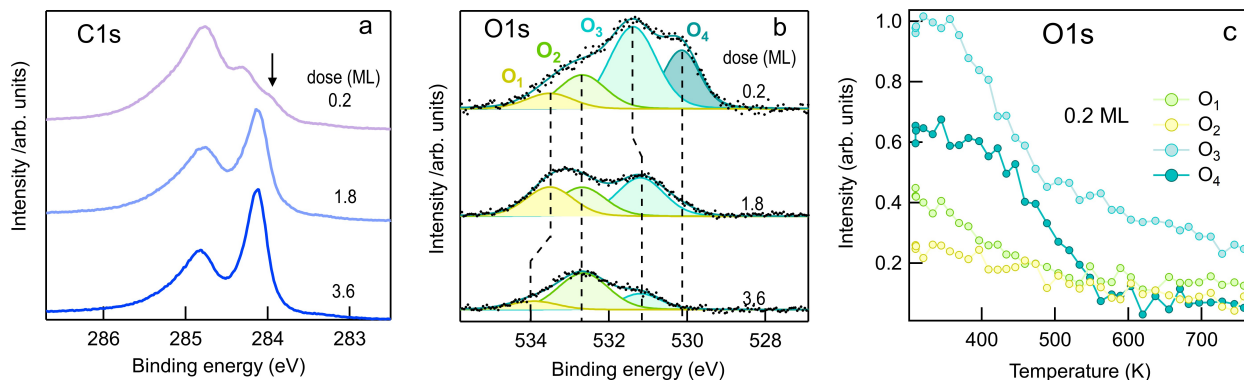


Fig.S 7. (a) C1s and (b) O1s spectra measured for incomplete Gr/Ni(111) (Gr coverage 0.92 ML_{GR}) exposed to increasing water doses. The O1s components O₁ (533.5-534.0 eV) and O₂ (532.67 eV) are assigned to water in different configurations at the interface whereas O₃ (531.16-531.30 eV) and O₄ (531.12 eV) are attributed to OH and O adsorbates, respectively. The arrow in (a) indicates the appearance of the C₁ component (see Figure 1 of the main text). (c) Integrated intensities of the O1s components measured while heating the sample dosed with 0.2 ML of water. It is evident that water molecules are the least stable adsorbates, whereas OH and O adsorbates start to desorb around 350 K and 400 K, respectively.

Fig.1a. Hence, the presence of Gr edges opens additional dissociation routes occurring at the dangling bonds terminating the graphene borders. It must be noted that in regions exposing the bare Ni(111) surface, RT dissociation is highly unlikely for water molecules which are not vibrationally excited [5] and therefore possible Gr-free regions are not expected to contribute to water splitting. Prolonged exposure to water tends to remove water fragments from the sample (Figure S7b). For doses of the order of 1.8 ML, O atoms disappear at first, and then also hydroxyl groups tend to vanish, leading to a O1s line shape where the component O₂ arising from adsorbed H₂O molecules prevails. The shifts of O₁ and O₃ by 0.5 and -0.3 eV, respectively, with water dose increasing from 0.22 L to 3.6 ML, are likely due to different adsorption sites and/or interaction with the surroundings. The evidence that O and OH fragments tend to be removed from the interface with increasing water dose hints at the predominant localization of -O and -OH species at the sample surface rather than below graphene, where the direct interaction with impinging water molecules would be shielded.

6. Adsorption energy and diffusion barrier of OH on Gr/Ni(111)

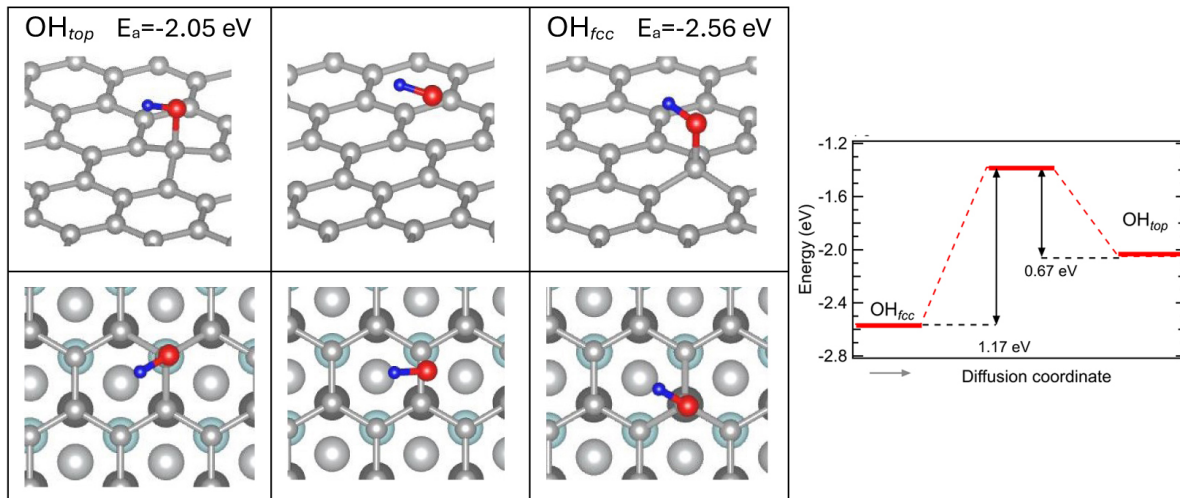


Fig.S 8. (left) The most stable configuration of OH adsorbed on Gr/Ni(111) is with the C-O bond nearly perpendicular to the Gr plane and the H atom pointing towards the center of the hexagon. The adsorption energies are -2.05 eV for OH_{top} and -2.56 eV for OH_{fcc} . The C atom bonded to OH_{fcc} (OH_{top}) is lifted up by 0.48 Å (0.37 Å) with respect to the Gr plane and the C-O bond length is 1.47 Å (1.54 Å). The top and bottom rows in the figure show in order the side and top view of the diffusion from the (OH_{top} to the (OH_{fcc} configurations. C, H and O atoms are represented with grey, blue and red colors, respectively. Ni atoms in the first, second and third crystal layer from the top appear in order light blue, light grey and dark grey. In order to allow a better visualization of the graphene buckling, the Ni crystal has been removed from the images in the top row. (right) OH diffusion barriers: the activation energy needed to move from the *top* to the *fcc* site is 0.67 eV and raises to 1.17 eV in the opposite direction.

7. Adsorption energies of dissociated water on Gr/Ni(111)

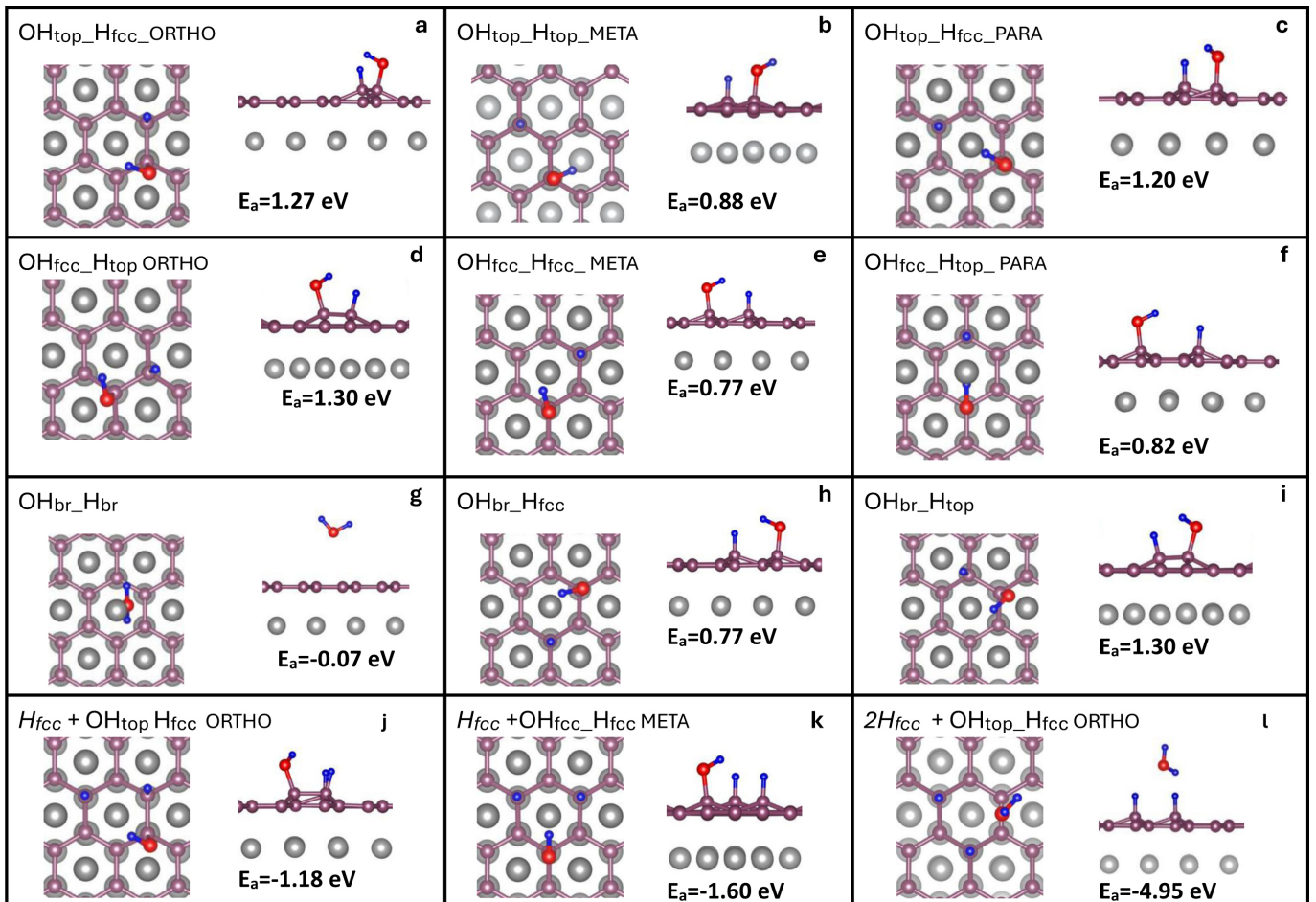


Fig.S 9. Adsorption configurations of a dissociated water molecule on the Gr/Ni(111) surface shown with the calculated adsorption energies. In each case the label at the top-left corner indicates the initial configuration before relaxation. The presence of an extra-H_{fcc} atom (bottom row) renders the water dissociation exothermic. By contrast, two pre-adsorbed H_{fcc} atoms in the same hexagon prevent the dissociation of the water molecule, which remains stably physisorbed in a configuration close to the *up* geometry (Figure S9l). This means that when the H coverage reaches the occupation of two atoms per hexagon, water dissociation gets inhibited.

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