Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Potential-Dependent Hydration Structures at Aqueous Solution/Graphite Interfaces by Electrochemical Frequency Modulation Atomic Force Microscopy

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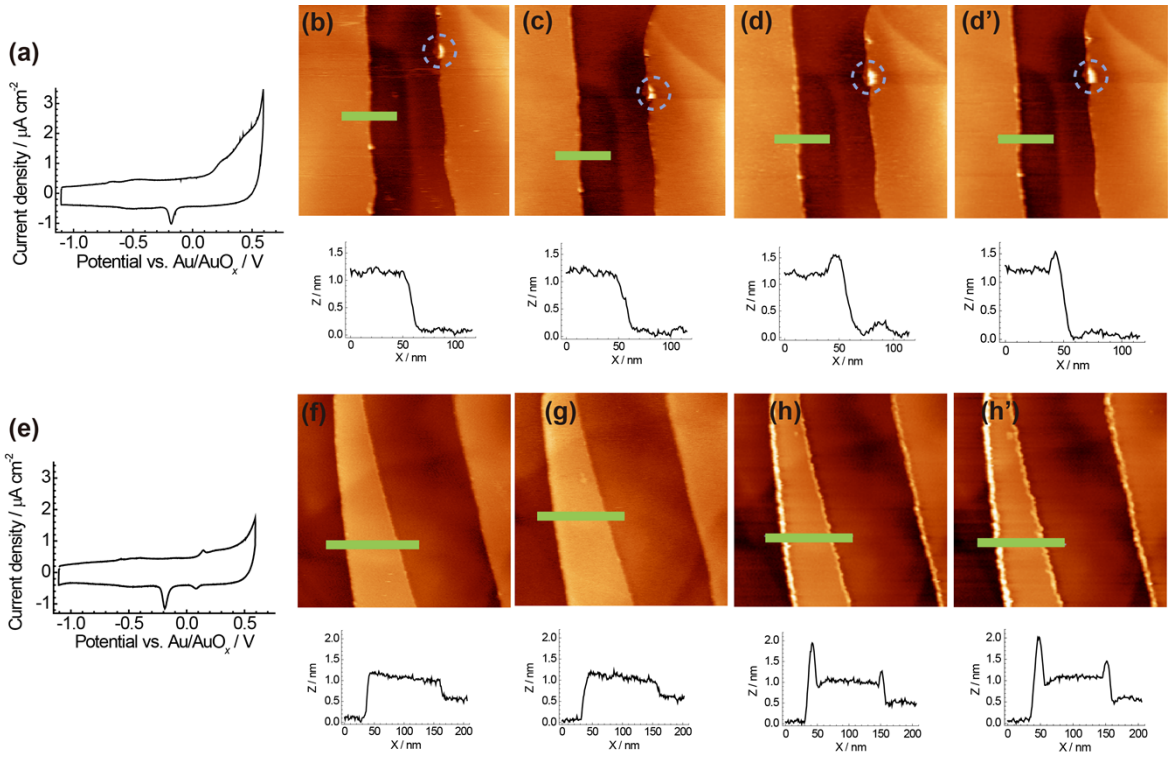

Figure S1. Cyclic voltammograms (scan rate 50 mV/s) of an HOPG basal plane in 0.1 M $HClO_4$ (a) and in 0.1 M H_2SO_4 (e) below the potential of oxygen evolution. (b)-(d') EC-□ FM-AFM images (500 × 500 nm^2, E_t = –0.9 V, $A_{p\text{-}p}$ = 0.58 nm) of an HOPG basal plane and the line profiles in 0.1 M $HClO_4$ at (b) E_s = –0.9 V, Δf = +292 Hz, (c) E_s = 0 V, Δf = +278 Hz, (d), (d') E_s = 0.4 V, Δf = +266 Hz. Blue broken line circles represent a reference position for all images. The image (d') was obtained about 4 min later of the image (d). (f)-(h') EC-FM-AFM images (500 × 500 nm^2, E_t = –0.9 V, $A_{p\text{-}p}$ = 0.49 nm) of HOPG basal plane and the line profiles in 0.1 M H_2SO_4 at (f) E_s = –0.9 V, Δf = +274 Hz, (g) E_s = 0 V, Δf = +258 Hz, (h), (h') E_s = 0.6 V, Δf = +280 Hz. The image (h') was obtained about 4 min later of the image (h).

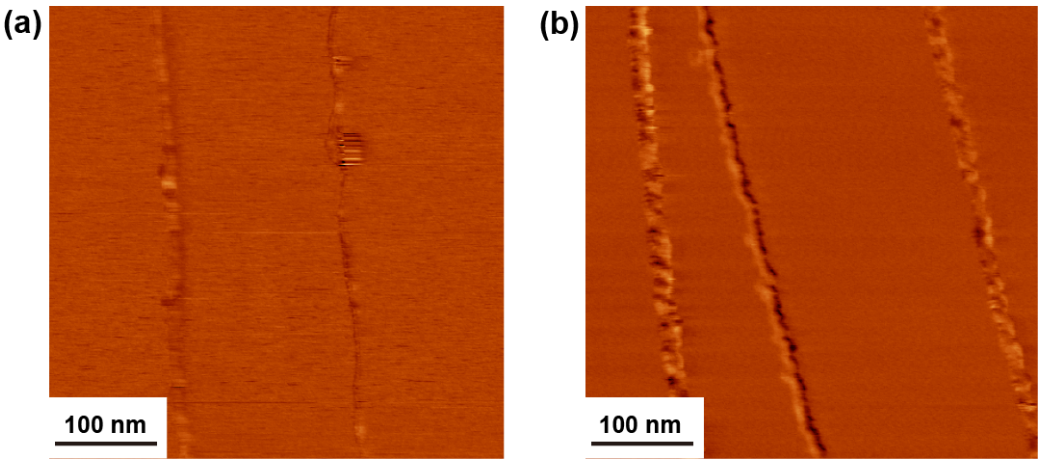

Figure S2. The results of image subtraction (z-scale: 3.5 nm) for the corresponding area of Figs. S1(d),(d') and Figs.S1(h), (h'), respectively, to clarify the time evolution of the structure at the anodic potential: (a) Fig. S1(d') – Fig. S1(d) (E_s = 0.4 V in 0.1 M $HClO_4$), (b) Fig. S1(h') – Fig. S1(h) (E_s = 0.6 V in 0.1 M H_2SO_4). These images clearly show that the structural changes during the anodic conditions are limited only near the step edges (5% and 10% at the maximum estimation for the changed area in (a) and (b), respectively) and probably did not affect the force curve measurements performed on the basal plane. A brighter line along the step indicates that the height of the edge protrusion slightly increased and its area slightly expanded to the inner part with time. The darker line along the brighter line maybe suggests that the step edge moved to the inner-plane direction by crimping of the top graphene layer along the formation of the protrusion.

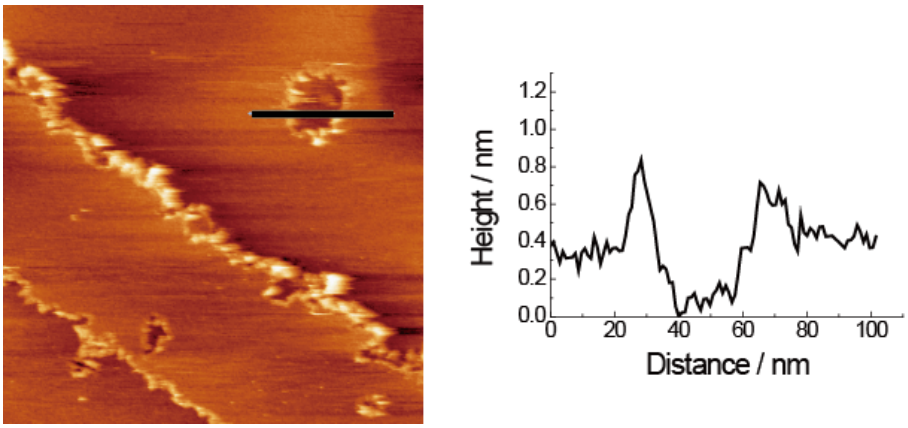

Figure S3. EC-FM-AFM image (300 × 300 nm^2, E_s = 0.6 V, E_t = –0.8 V, Δf = +360 Hz) of an HOPG basal plane in 0.1 M $HClO_4$ and a line profile showing a one-layer depth pit formed by applying +0.6 V to HOPG.

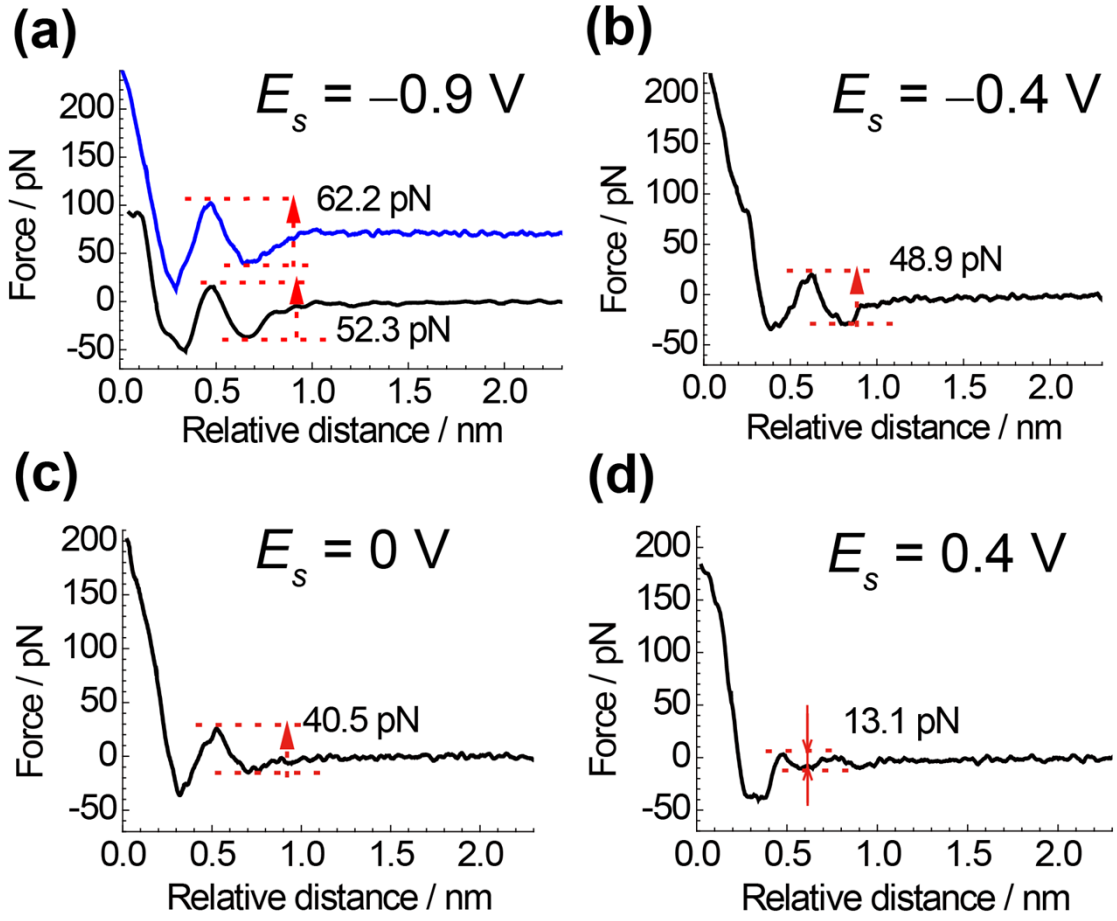

Figure S4. (a-d) Force versus distance calculated from Figures 1a-1d (data smoothed by a factor of 5). A blue curve in (a), which was calculated from the blue curve in Figure 1a, is shifted by 70 pN for illustration. The red arrows indicate the magnitude of the primary hydration peak adjacent to the surface.

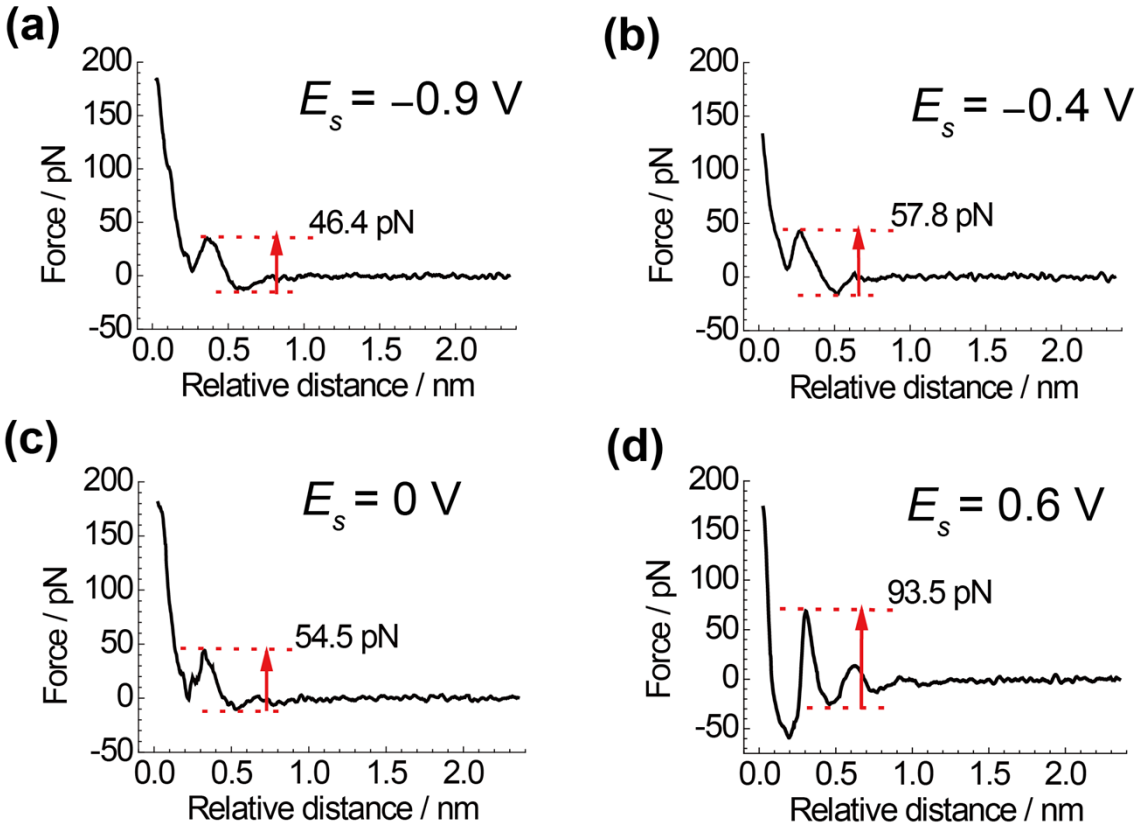

Figure S5. (a-d) Force versus distance calculated from Figures 2a-2d (data smoothed by a factor of 5). The red arrows indicate the magnitude of the primary hydration peak adjacent to the surface.