



This is a repository copy of *Theoretical and experimental studies of molecular interactions between engineered graphene and phosphate ions for graphene-based phosphate sensing*.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/206912/>

Version: Supplemental Material

Article:

Yong, X., Nagaraja, T., Krishnamoorthy, R. et al. (3 more authors) (2024) Theoretical and experimental studies of molecular interactions between engineered graphene and phosphate ions for graphene-based phosphate sensing. *ACS Applied Nano Materials*, 7 (16). pp. 18386-18397. ISSN 2574-0970

<https://doi.org/10.1021/acsanm.3c04147>

Reuse

This article is distributed under the terms of the Creative Commons Attribution (CC BY) licence. This licence allows you to distribute, remix, tweak, and build upon the work, even commercially, as long as you credit the authors for the original work. More information and the full terms of the licence here:

<https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

Theoretical and Experimental Studies of Molecular Interactions Between Engineered Graphene and Phosphate Ions for Graphene-Based Phosphate Sensing

Xue Yong,^a Thiba Nagaraja,^b Rajavel Krishnamoorthy,^b Ana Guanes,^b Suprem R. Das^{b,c} and Natalia Martsinovich^{a*}

^a Department of Chemistry, University of Sheffield, Sheffield S3 7HF, United Kingdom

^b Department of Industrial and Manufacturing Systems Engineering, Kansas State University, Manhattan, Kansas, 66506, United States

^c Department of Electrical and Computer Engineering, Kansas State University, Manhattan, Kansas, 66506, United States

*Corresponding author: n.martsinovich@sheffield.ac.uk

Figure S1. The most stable adsorption configuration for HPO_4^{2-} on pristine graphene (G), hydroxyl- (GOH) and epoxide-containing (GO-epo) graphene, curved graphene (arm-GC and zig-GC), graphene with vacancy (GV) and with oxygen-filled vacancy (GV-O). Top views are shown for all systems, except for arm-GC and zig-GC where side views are shown. In all figures, carbon atoms are shown in brown, oxygen atoms in red, phosphorus atoms in light purple, and hydrogen atoms in white.

Figure S2. The most stable adsorption configuration for H_2PO_4^- on pristine graphene (G), hydroxyl- (GOH) and epoxide-containing (GO-epo) graphene, curved graphene (arm-GC and zig-GC), graphene with vacancy (GV) and with oxygen-filled vacancy (GV-O). Top views are shown for all systems, except for arm-GC and zig-GC where side views are shown.

Figure S3. The most stable adsorption configuration for H_3PO_4 on pristine graphene (G), hydroxyl- (GOH) and epoxide-containing (GO-epo) graphene, curved graphene (arm-GC and zig-GC), graphene with vacancy (GV) and with oxygen-filled vacancy (GV-O). Top views are shown for all systems, except for arm-GC and zig-GC where side views are shown. In all figures, carbon atoms are shown in brown, oxygen atoms in red, phosphorus atoms in light purple, and hydrogen atoms in white.

Table S1. Adsorption energies of phosphate species on graphene-based materials in vacuum.

Table S2. Adsorption energies of phosphate species on graphene-based materials in implicit water solvent.

Figure S4. Band structures for pure graphene and modified graphenes without adsorbate. The band structure for GOH-ortho-2 is not shown in this figure and the following figures, because it is very similar to GOH-ortho.

Figure S5. Band structures for pure graphene and modified graphenes with H_3PO_4 adsorbate.

Figure S6. Band structures for pure graphene and modified graphenes with H_2PO_4^- adsorbate.

Figure S7. Band structures for pure graphene and modified graphenes with HPO_4^{2-} adsorbate.

Figure S8. Band structures for pure graphene and modified graphenes with PO_4^{3-} adsorbate.

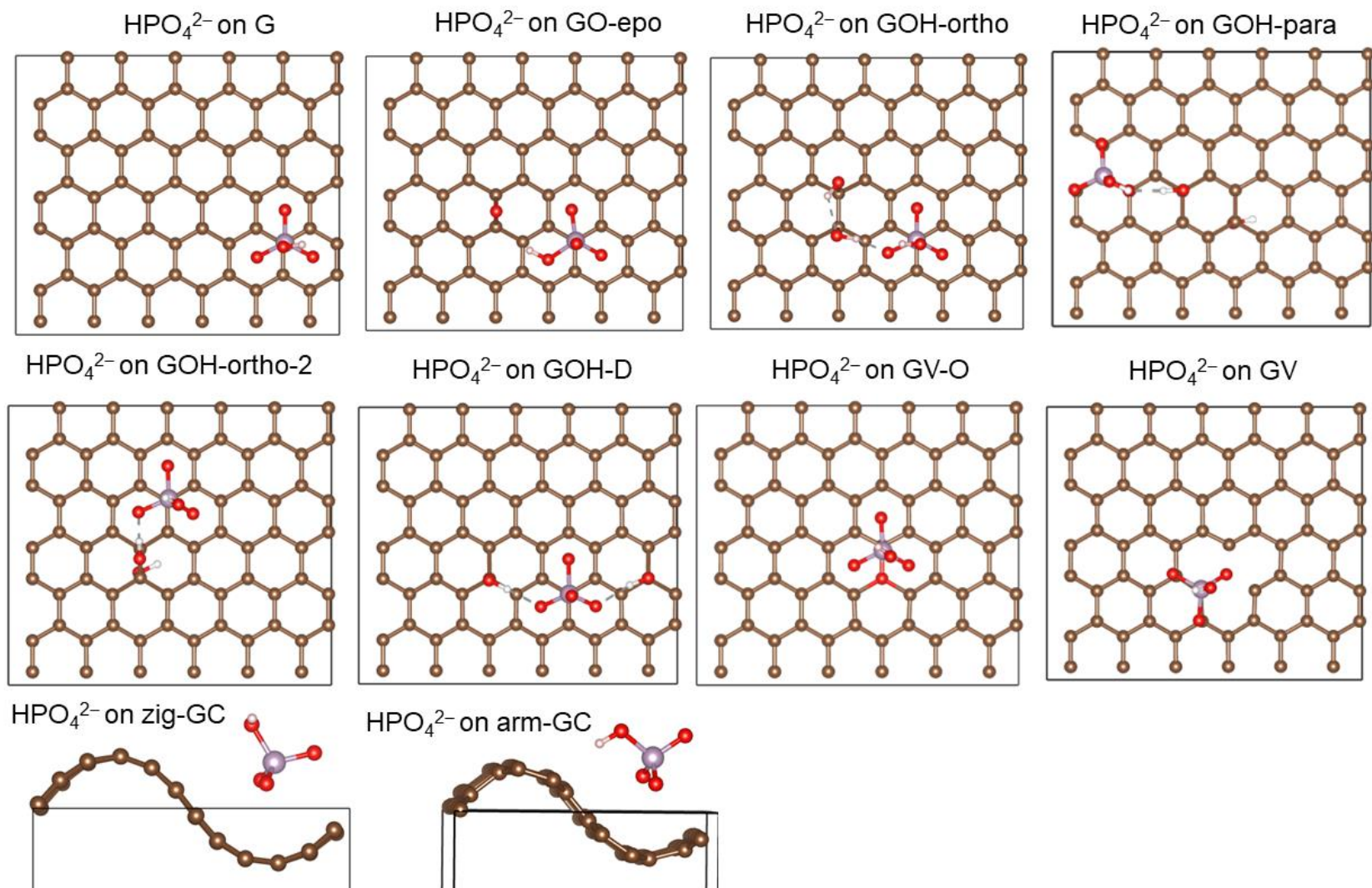


Figure S1. The most stable adsorption configuration for HPO_4^{2-} on pristine graphene (G), hydroxyl- (GOH) and epoxide-containing (GO-epo) graphene, curved graphene (arm-GC and zig-GC), graphene with vacancy (GV) and with oxygen-filled vacancy (GV-O). Top views are shown for all systems, except for arm-GC and zig-GC where side views are shown. In all figures, carbon atoms are shown in brown, oxygen atoms in red, phosphorus atoms in light purple, and hydrogen atoms in white.

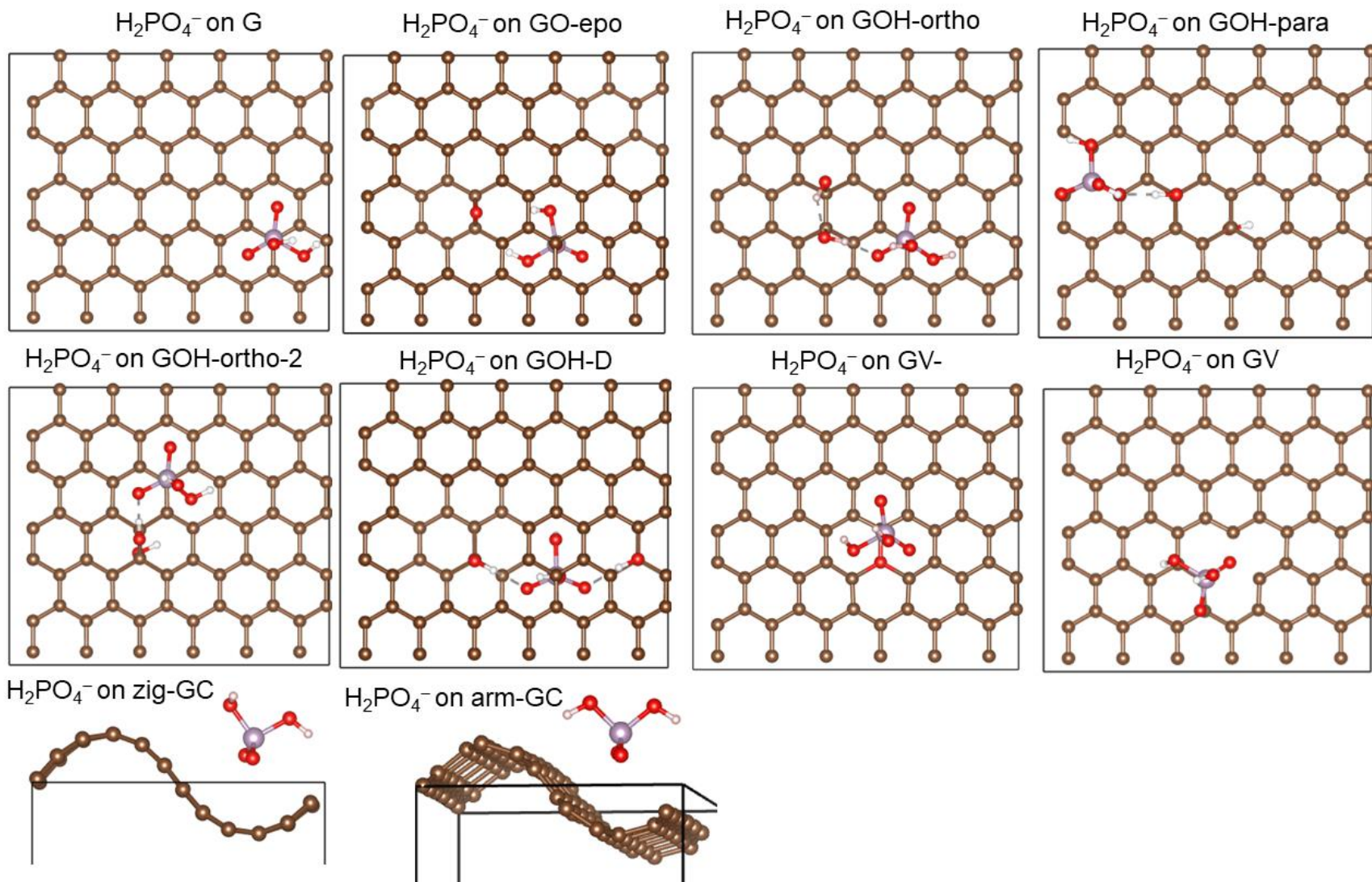


Figure S2. The most stable adsorption configuration for H_2PO_4^- on pristine graphene (G), hydroxyl- (GOH) and epoxide-containing (GO-epo) graphene, curved graphene (arm-GC and zig-GC), graphene with vacancy (GV) and with oxygen-filled vacancy (GV-O). Top views are shown for all systems, except for arm-GC and zig-GC where side views are shown.

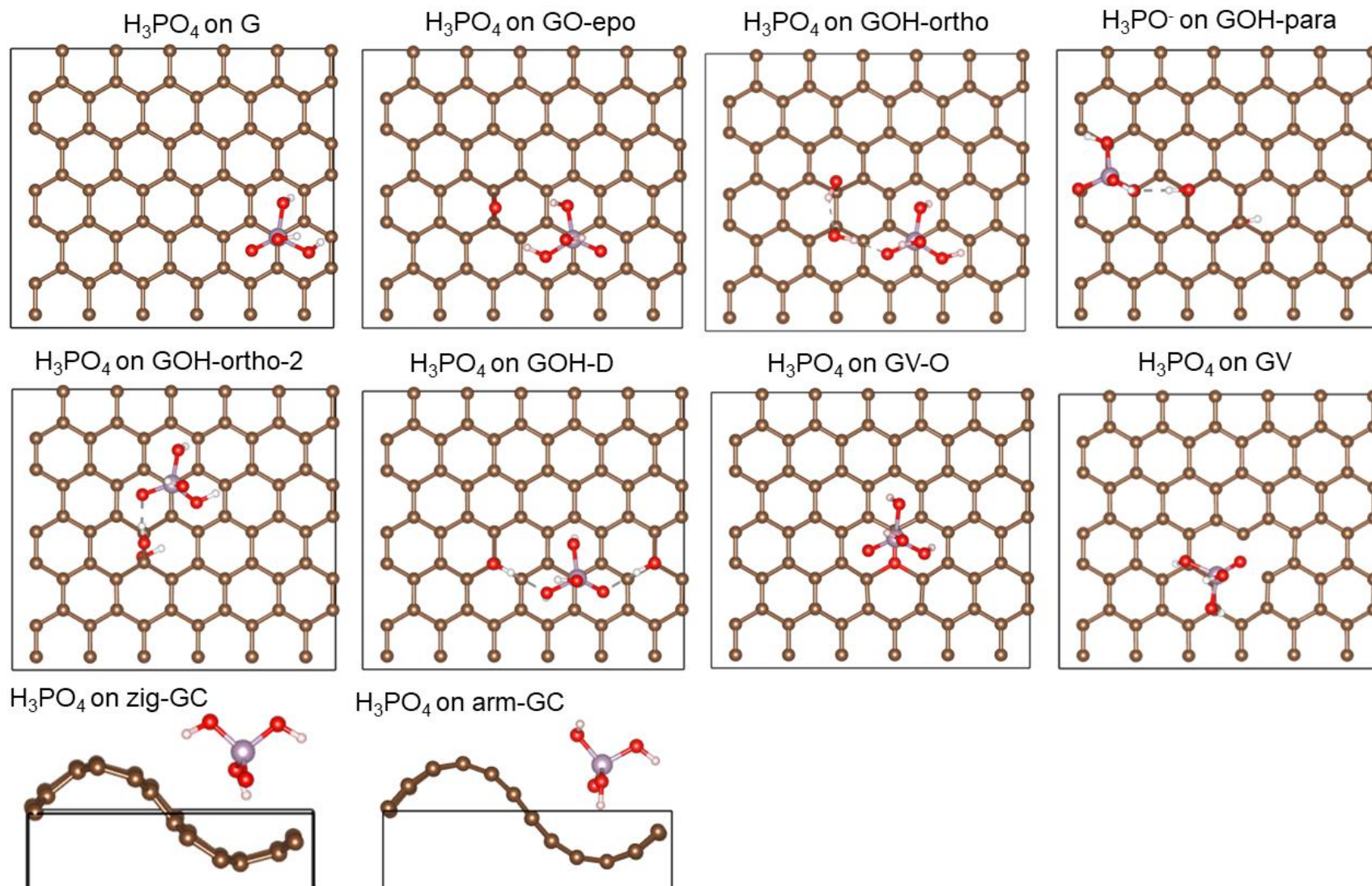


Figure S3. The most stable adsorption configuration for H_3PO_4 on pristine graphene (G), hydroxyl- (GOH) and epoxide-containing (GO-epo) graphene, curved graphene (arm-GC and zig-GC), graphene with vacancy (GV) and with oxygen-filled vacancy (GV-O). Top views are shown for all systems, except for arm-GC and zig-GC where side views are shown.

Table S1. Adsorption energies of phosphate species on graphene-based materials in vacuum.

Graphene materials	Adsorbates			
	PO_4^{3-}	HPO_4^{2-}	H_2PO_4^-	H_3PO_4
G	-2.28	-2.14	-1.63	-0.18
GO-epo	-2.25	-1.95	-1.40	-0.54
GOH-ortho	-2.85	-2.73	-2.41	-0.87
GOH-ortho-2	-2.72	-2.50	-2.15	-0.53
GOH-para	-2.69	-2.50	-2.20	-0.63
GOH-D	-3.23	-2.57	-2.54	-0.66
zig-GC	-3.04	-2.74	-2.26	-0.60
arm-GC	-2.86	-2.61	-2.13	-0.52
GV-O	-3.19	-2.97	-2.25	-0.37
GV	-2.77	-2.42	-1.91	-0.50

Table S2. Adsorption energies of phosphate species on graphene-based materials in implicit water solvent.

Graphene materials	Adsorbates			
	PO_4^{3-}	HPO_4^{2-}	H_2PO_4^-	H_3PO_4
G	-3.11	-2.61	-1.73	0.15
GO-epo	-2.95	-2.28	-1.37	-0.15
GOH-ortho	-3.44	-2.99	-2.31	-0.43
GOH-para	-3.49	-2.79	-2.10	-0.21
zig-GC	-3.86	-3.04	-2.11	-0.07
arm-GC	-3.66	-2.95	-1.98	0.12
GV-O	-4.20	-3.56	-2.29	0.06
GV	-3.66	-2.97	-1.99	-0.11

Without adsorbate

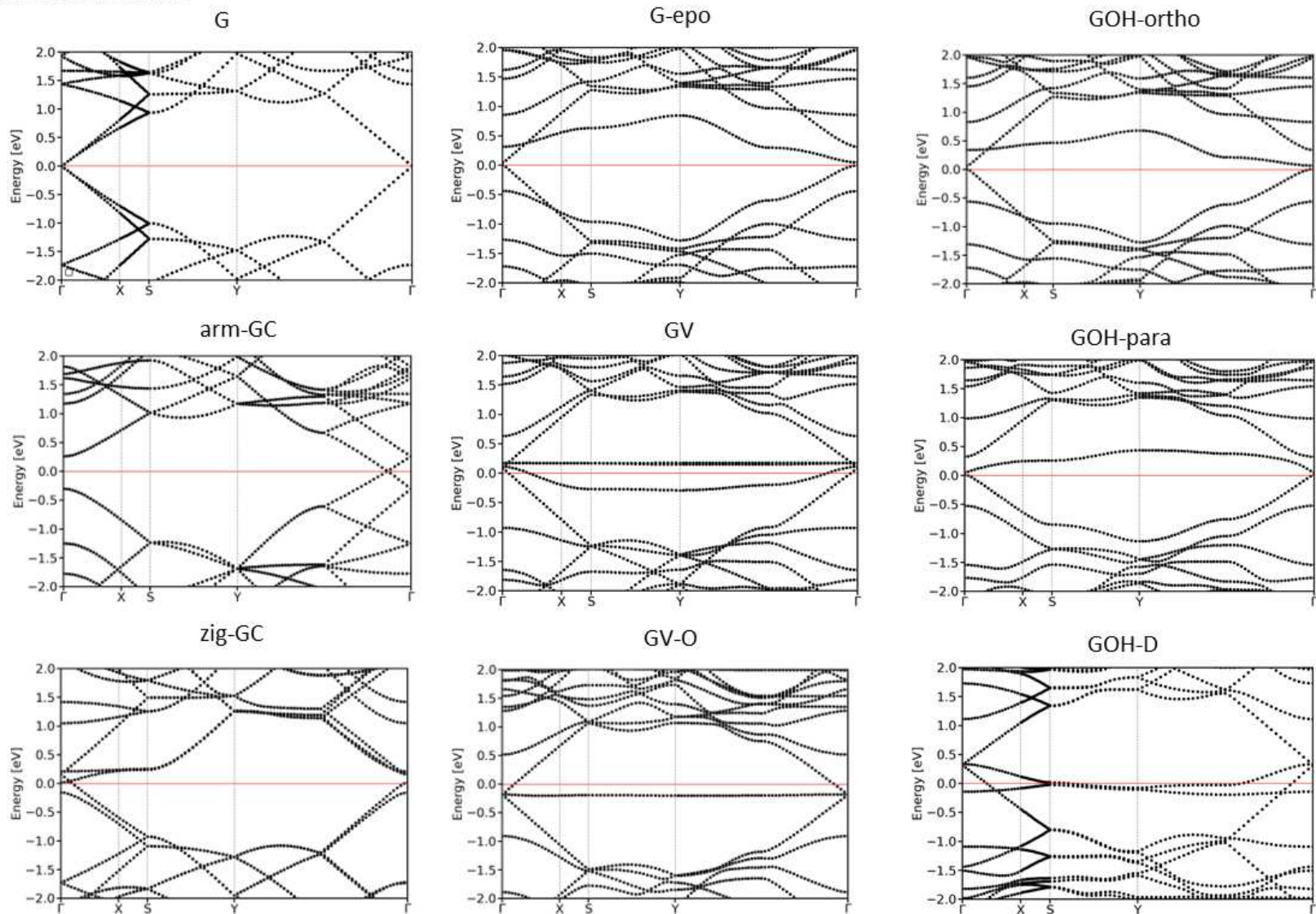


Figure S4. Band structures for pure graphene and modified graphenes without adsorbate. The band structure for GOH-ortho-2 is not shown in this figure and the following figures, because it is very similar to GOH-ortho.

With H_3PO_4

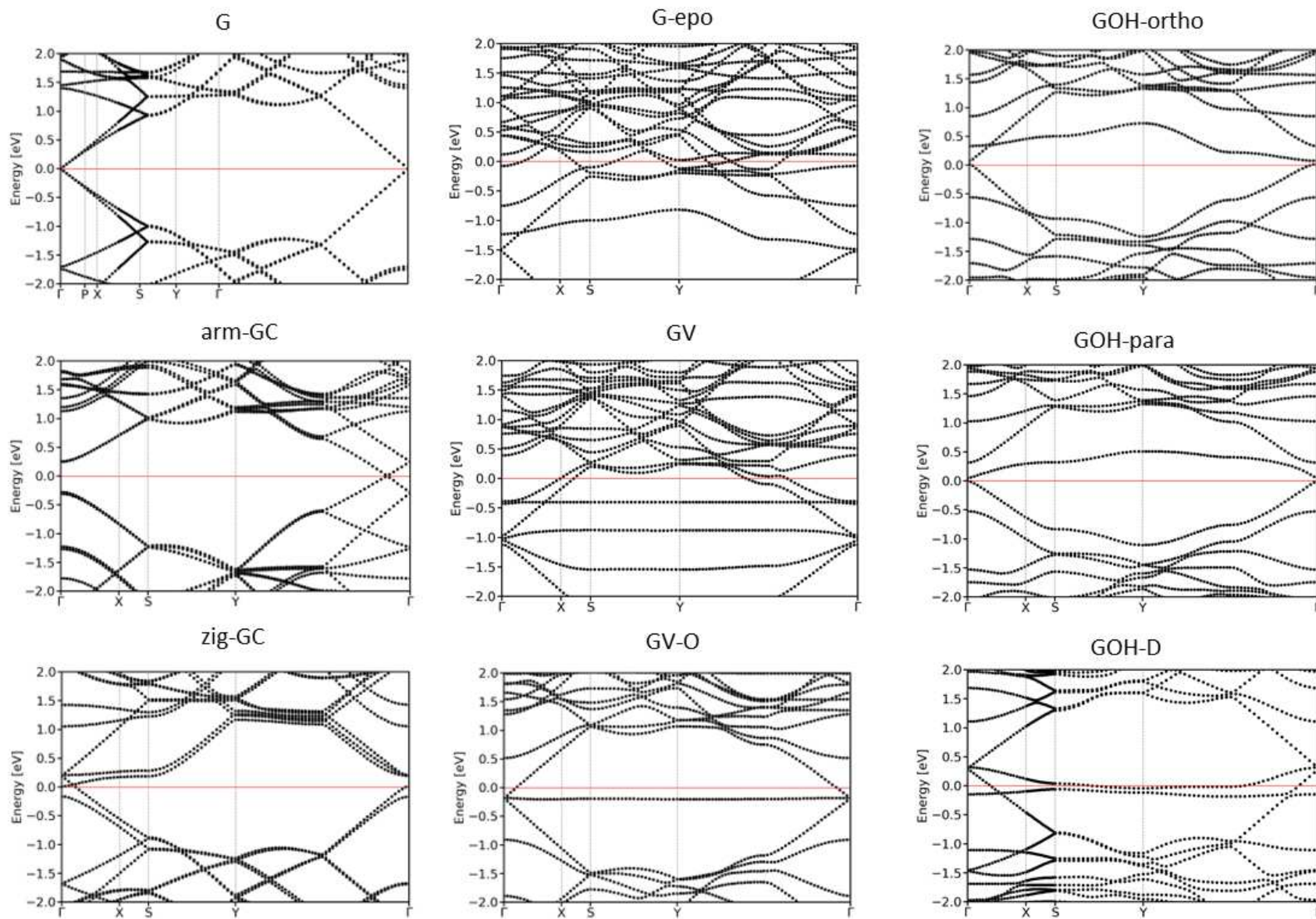


Figure S5. Band structures for pure graphene and modified graphenes with H_3PO_4 adsorbate.

With H_2PO_4^-

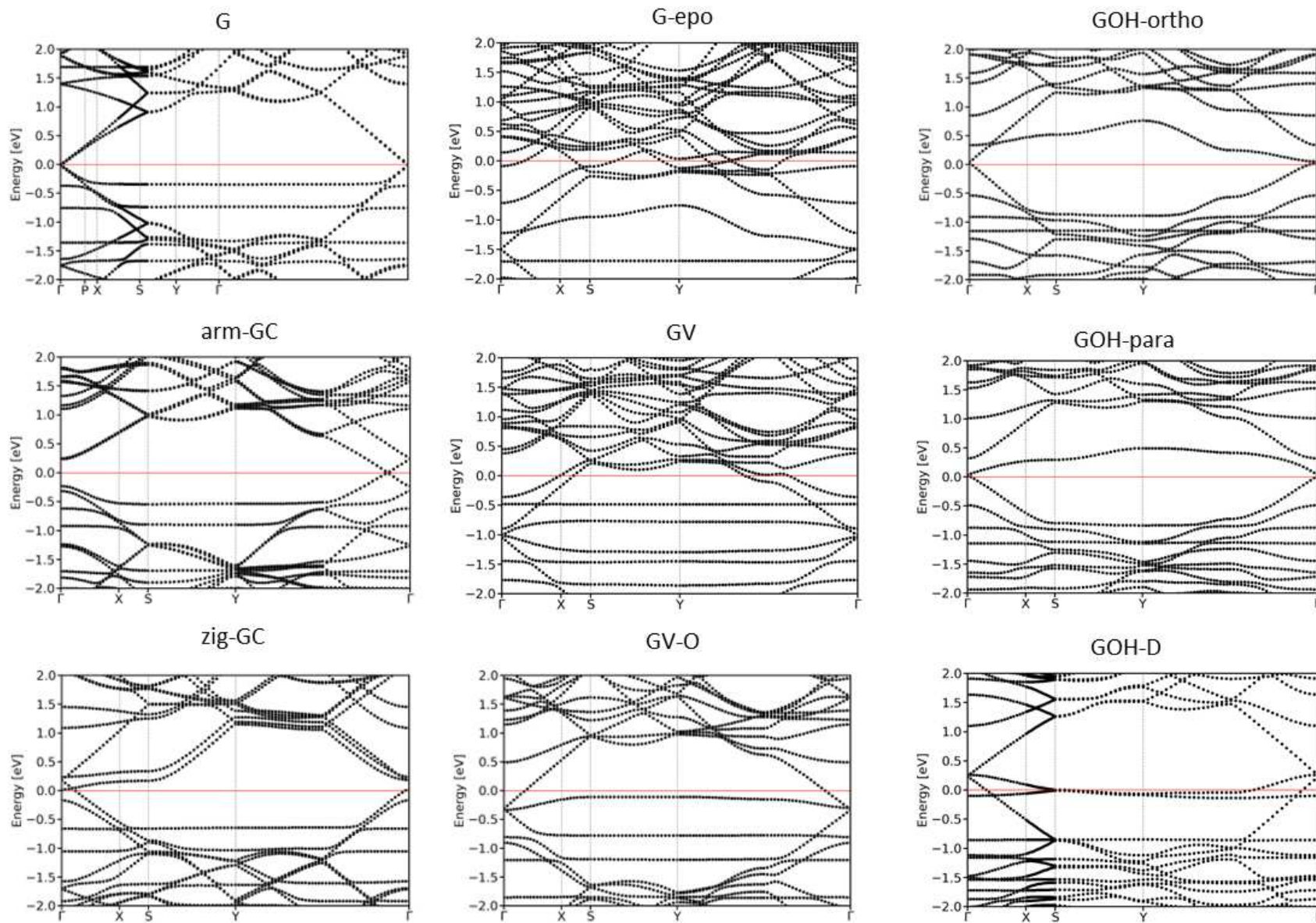


Figure S6. Band structures for pure graphene and modified graphenes with H_2PO_4^- adsorbate.

With HPO_4^{2-}

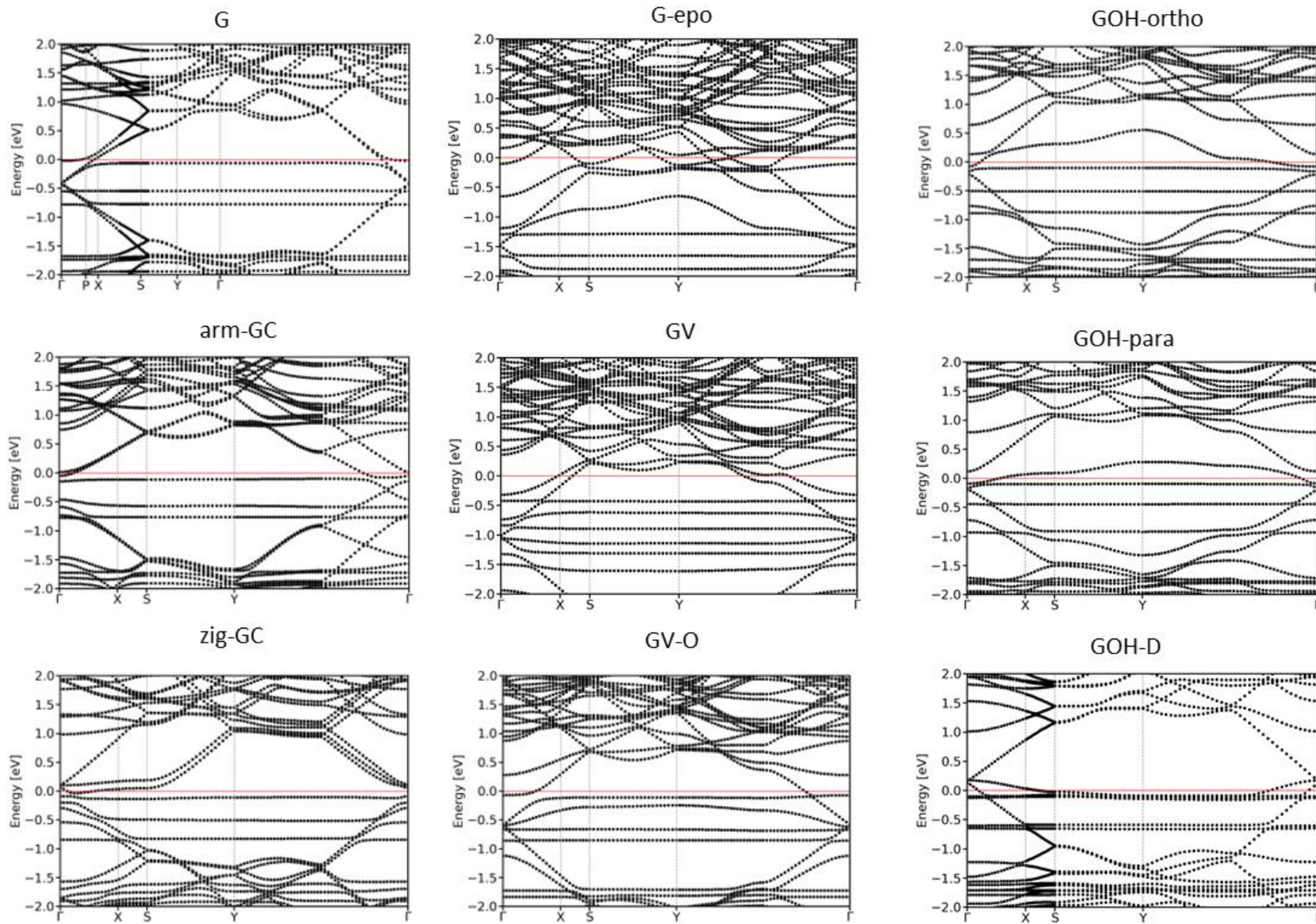


Figure S7. Band structures for pure graphene and modified graphenes with HPO_4^{2-} adsorbate.

With PO_4^{3-}

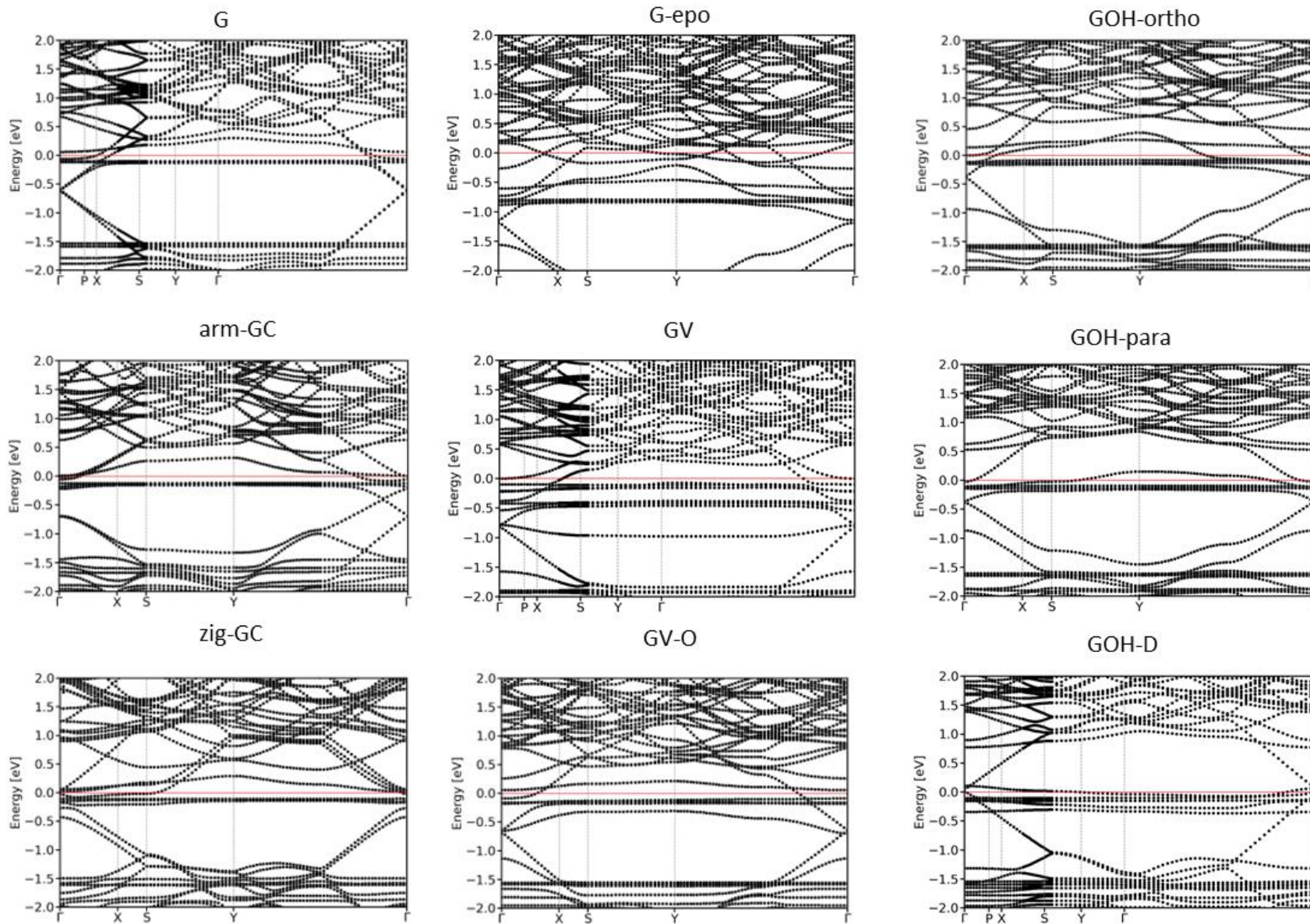


Figure S8. Band structures for pure graphene and modified graphenes with PO_4^{3-} adsorbate.