Supporting Information

Characterization of changes in the electronic structure of platinum sub-nanoclusters supported on graphene induced by oxygen adsorption

Hinoki Hirase[a], Kenji Iida*[,a], and Jun-ya Hasegawa*[,a,b]

[a.] Institute for Catalysis, Hokkaido University, N21 W10 Kita-ku, Sapporo, 001-0021 Hokkaido, Japan.

[b.] Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology, Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.

S1 Geometrical Structures

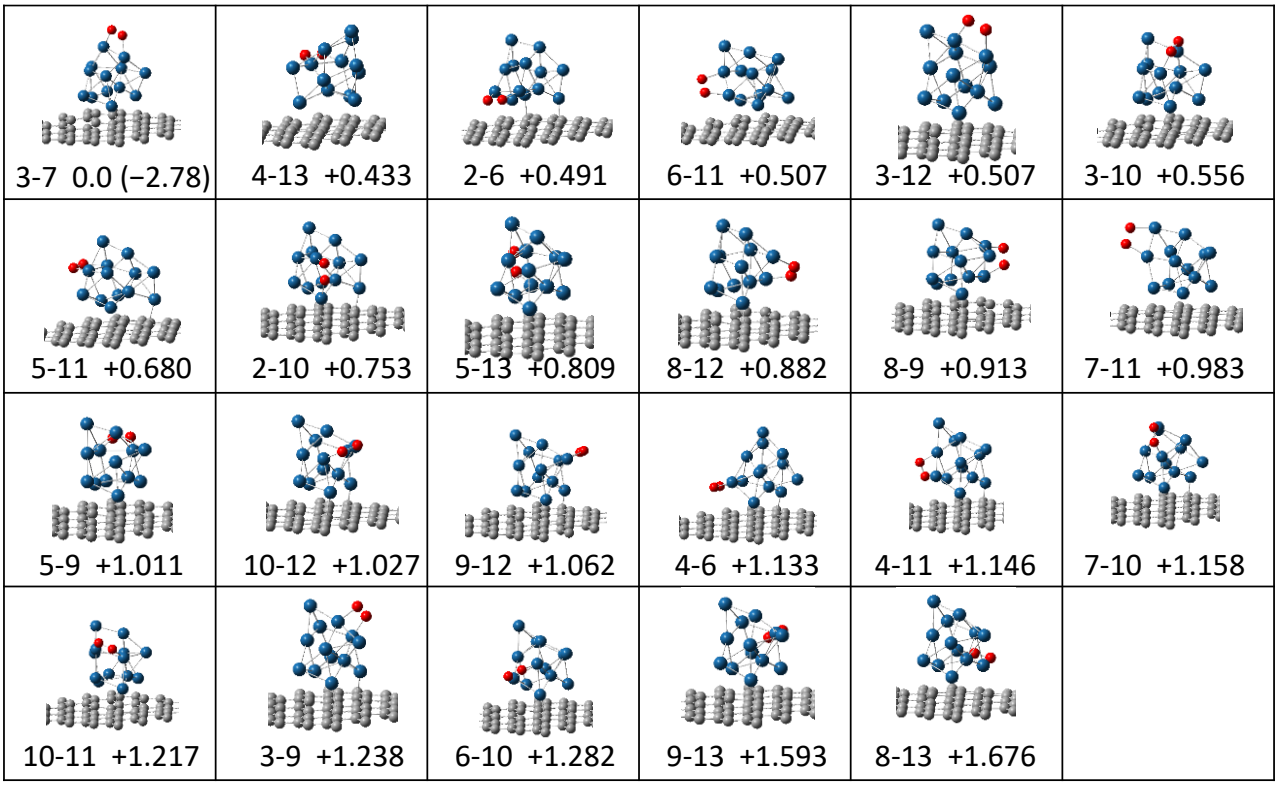

Figure S1. Side view of the heterostructures consisting of O_2, Pt_{13}, and a graphene monolayer. For example, the model labelled "3-7" means that two oxygen atoms are adsorbed on 3th and 7th Pt atoms, where the numbering of Pt atoms is shown in Figure 1 in the main manuscript. The number in parenthesis is the energy (eV) relative to that of the 3-7 model.

S2 Atomic Charge

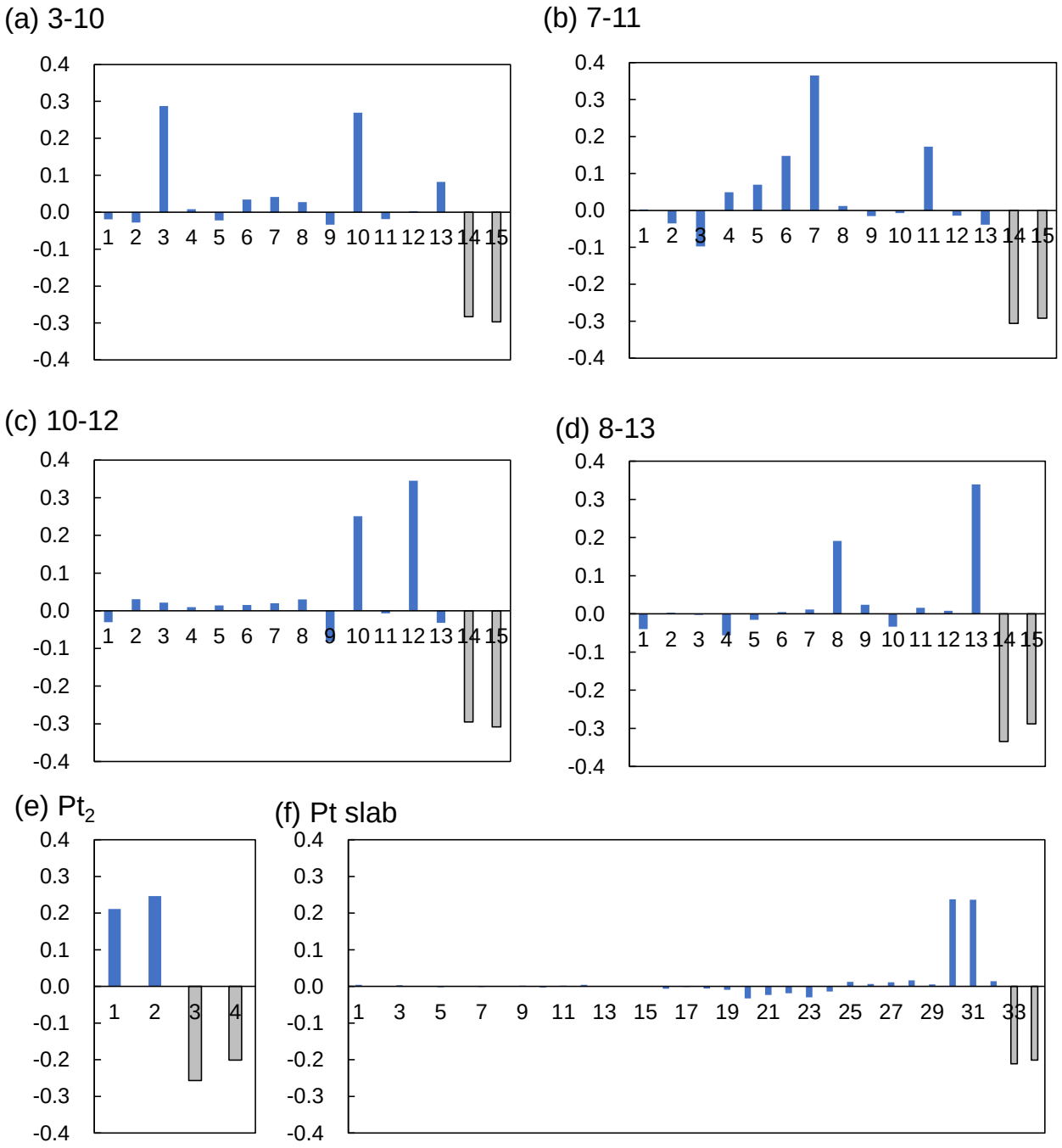

Figure S2. Change in Bader charge by O_2 adsorption onto the adsorption sites of (a) 3-12, (b) 7-11, (c) 10-12, and (d) 8-13 models, respectively. The results of Pt_2 and Pt slab are also shown in (e) and (f). The last two gray bars (14th and 15th for (a)-(d), 3rd and 4th for (d), and 33rd and 34th for (f)) are the results of the two O atoms. The numbering of Pt atoms in (a)-(e) is shown in Figure 1 in the main manuscript.

S3 Total Density of States

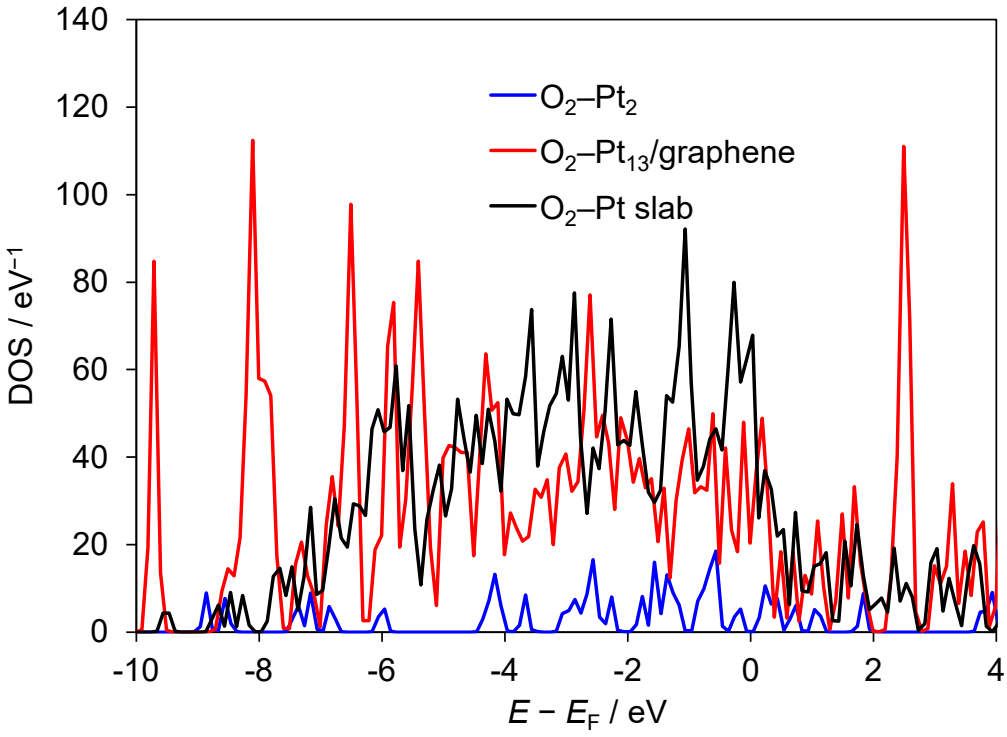

Figure S3. Total density of state for Pt_2, Pt_{13} and Pt slab models before O_2 adsorption.

S4 Coordination Number

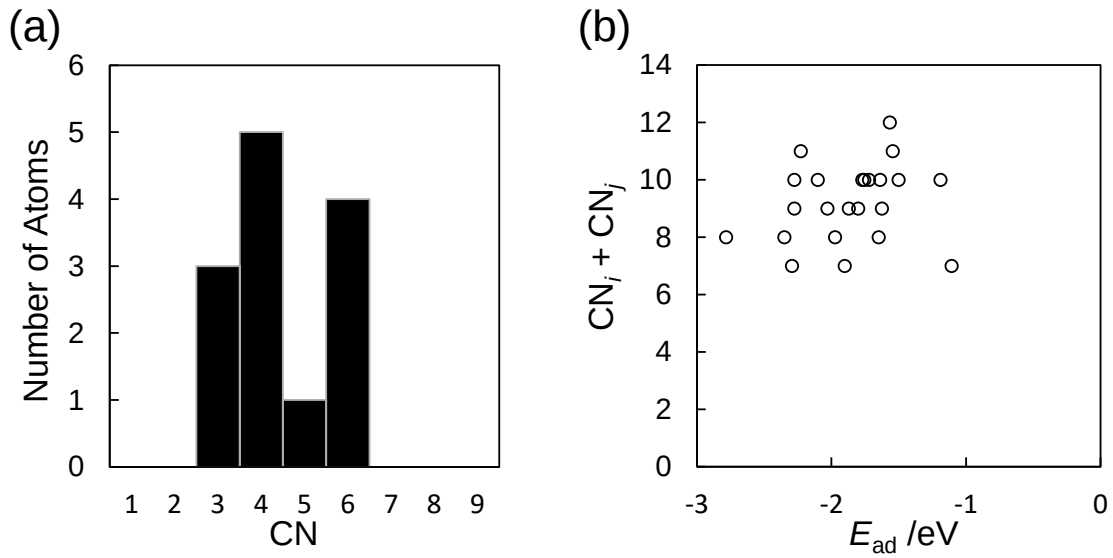

Figure S4. (a) Distribution of the coordination number (CN) before O_2 adsorption and (b) relationship between E_{ad} and the sum of CNs for Pt atoms at adsorption sites *i* and *j*.

S5 Relationship of Geometric and Electronic Structure Changes

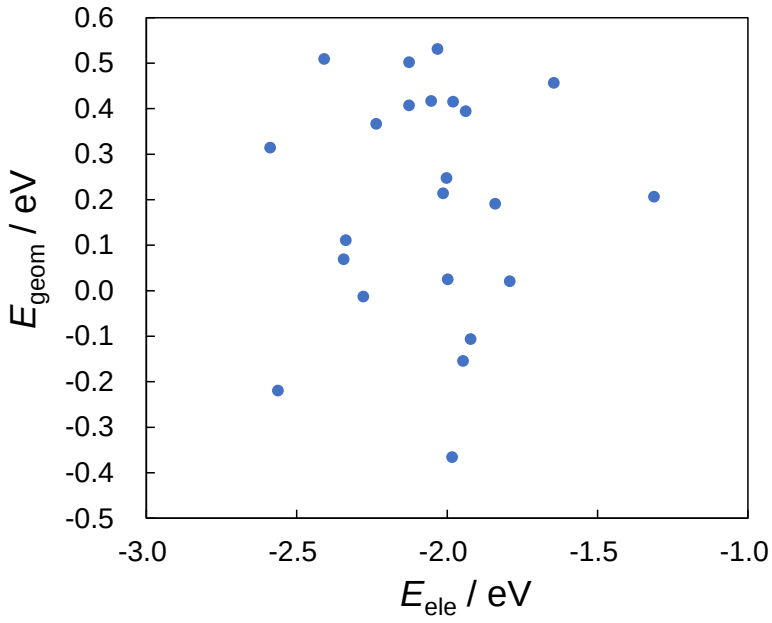

Figure S5. Relationship between the contribution of changes in geometric and electronic structures to the adsorption energy.

S6 Local Density of States

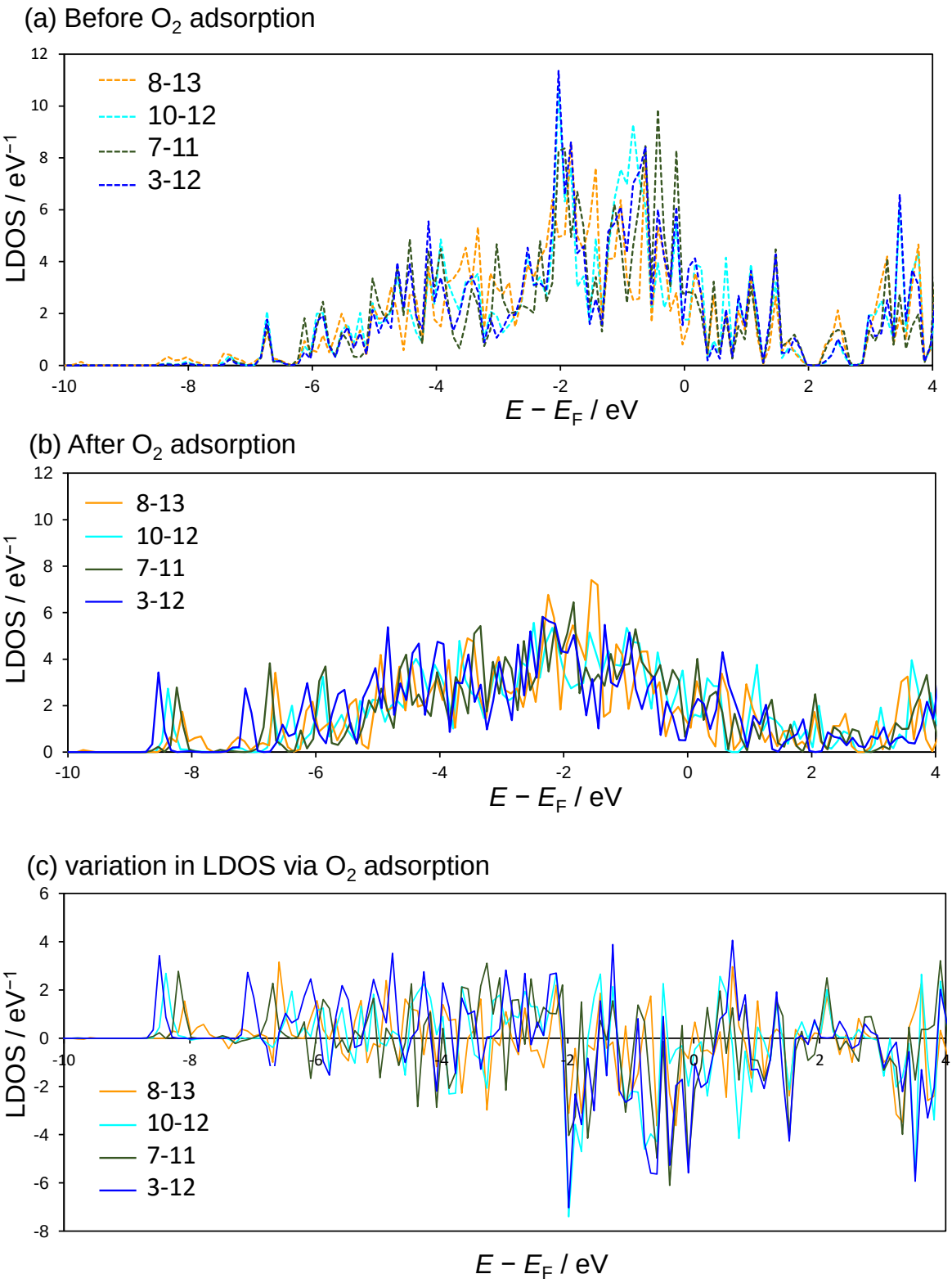

Figure S6. Local density of states (a) before and (b) after O_2 adsorption, and (c) the difference between (a) and (b). The labeling of Pt atoms is shown in Figure 1 in the main manuscript.

S7 Atomic-Scale Analysis of the Electronic Structure of Pt

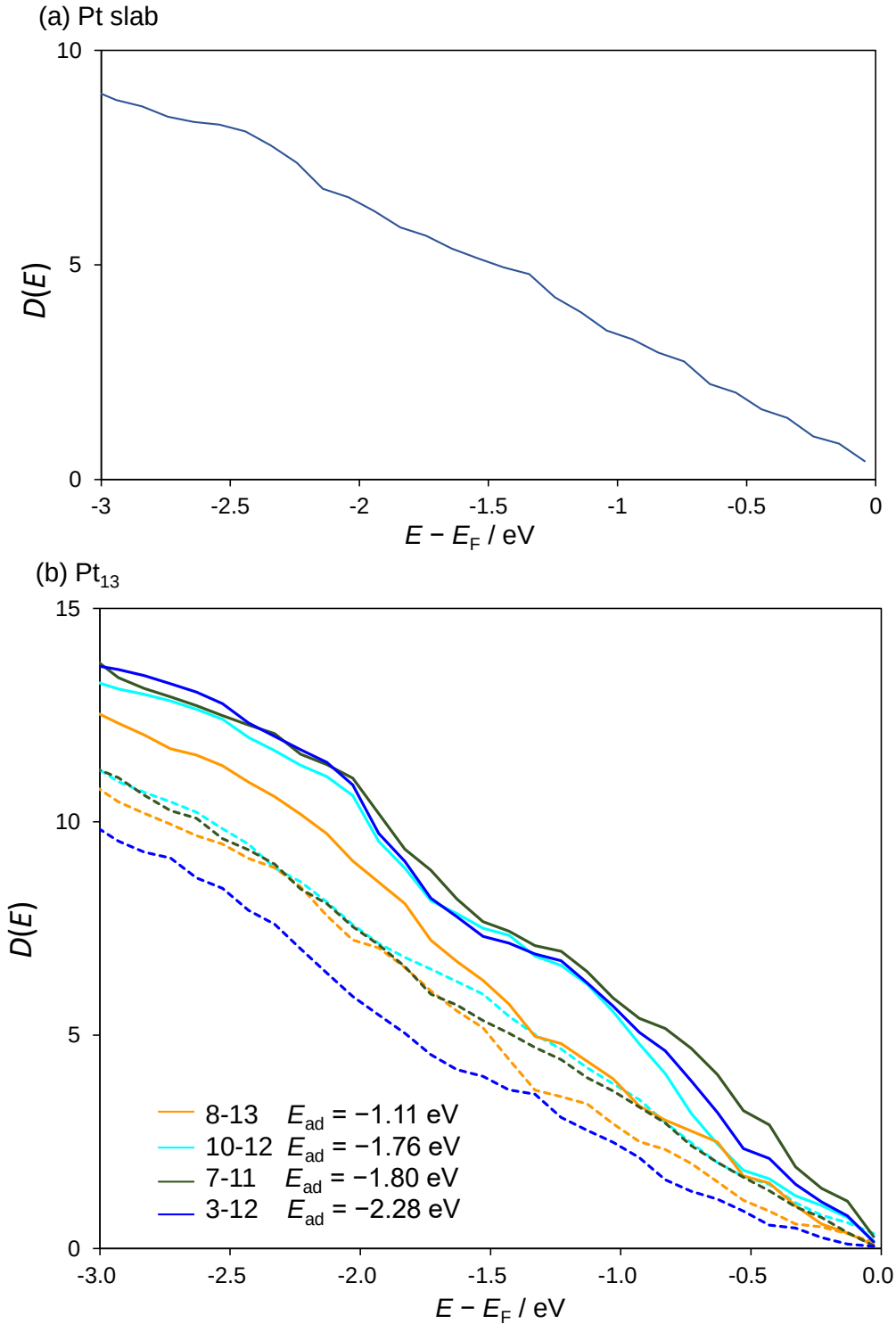

Figure S7. Integrated local density of states, $D(E)$, of the Pt moiety in the (a) Pt slab, and (b) Pt_{13}–graphene heterostructure before (solid) and after (dashed) O_2 adsorption. The numbering of Pt atoms is shown in Figure 1 in the main manuscript.

S8 Atomic-Scale Analysis of the Electronic Structure of Pt

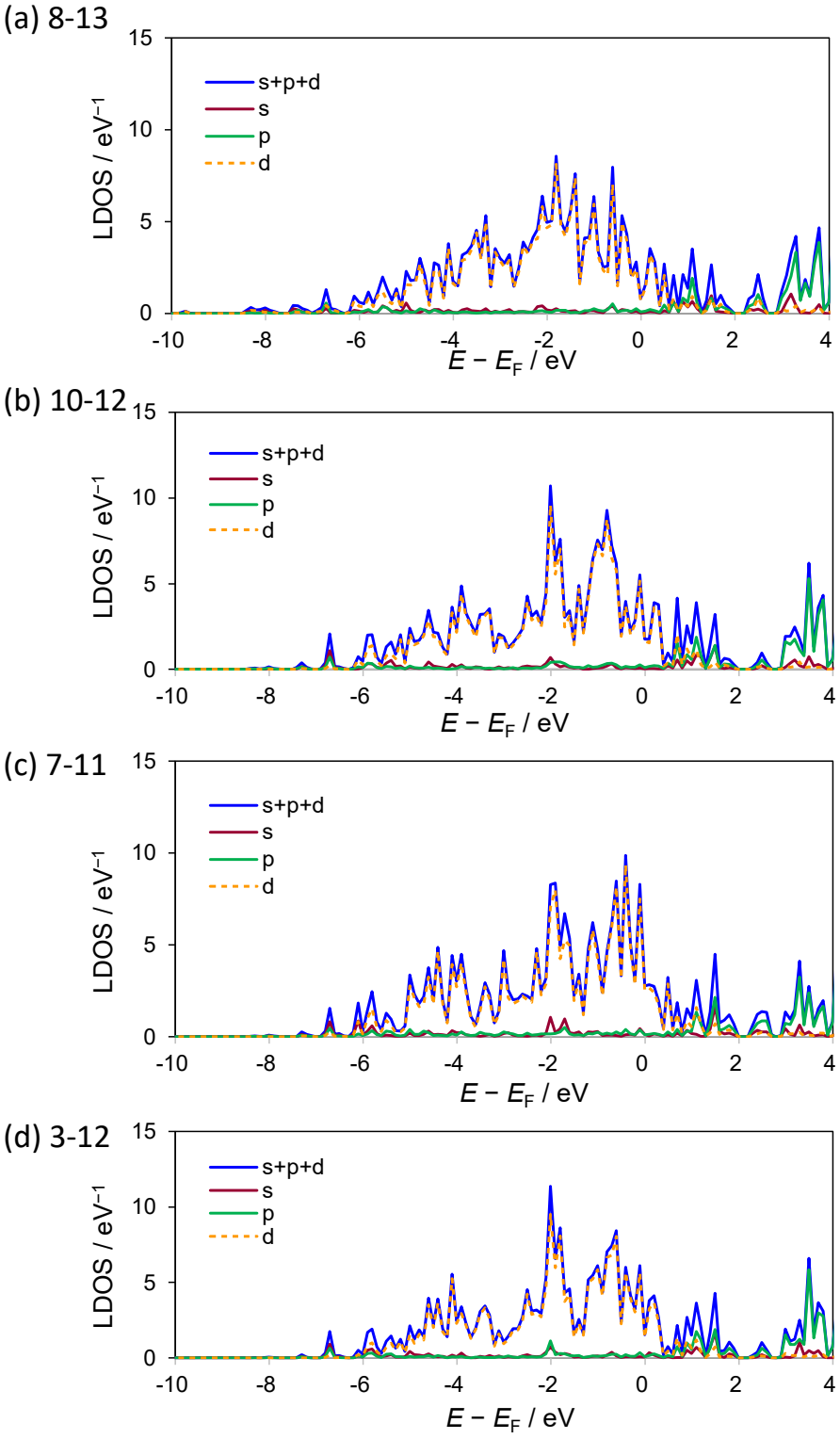

Figure S8. Local density of states of the four O_2 adsorption sites of the Pt_{13} model and their s, p, and d components before O_2 adsorption.

S9 Local Density of States after O_2 adsorption

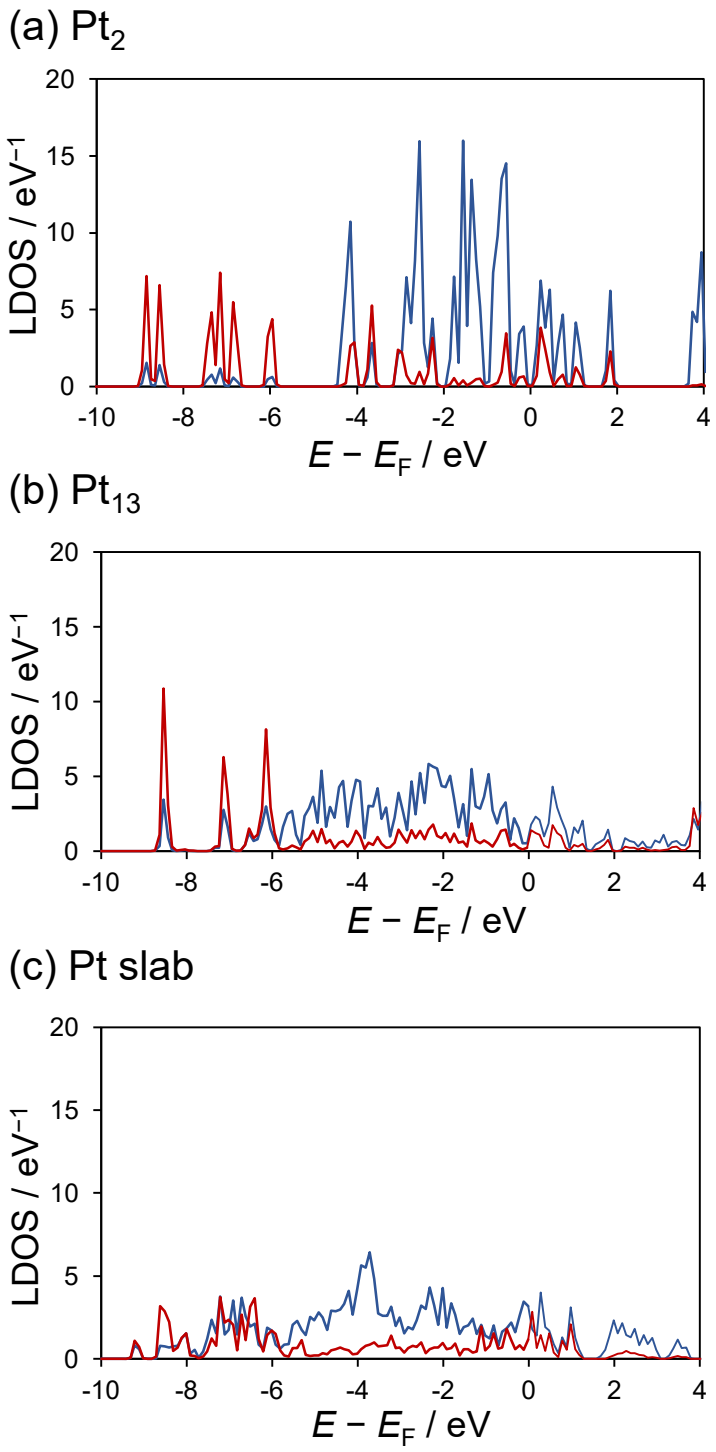

Fig. 9 Local density of states (LDOS) of the Pt (blue) and O_2 (red) moieties after O_2 adsorption for the (a) Pt_2, (b) Pt_{13}/graphene heterostructure, and (c) Pt slab. The band energy is given as the energy difference from the Fermi level energy, EF. The selected Pt atoms are labeled as 3 and 7 in Figure 1 in the main manuscript.

S10 Dependence of Charge on the Adsorption Energy

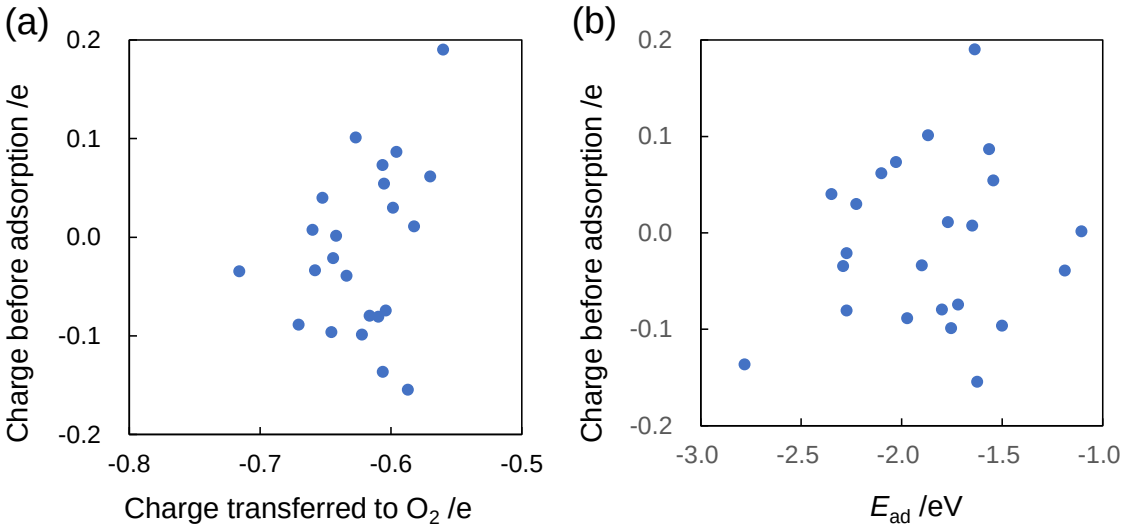

Figure S10. Electronic charge on the two Pt atoms involved in Pt–O bond formation depending on the (a) charge transferred to O_2 and (b) adsorption energy.