

Electronic Supplementary Information

**Impact of surface arrangement and composition on ethylene
adsorption over Pd-Ag surface alloys: a computational study**

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S1 Electronic analysis for the top adsorption configuration

S1.1 (111) surface

Fig. S1 displays a series of the LDOS and the differential electron density as a function of Ag atom content, describing the electron state when the ethylene molecule adsorbed on the most stable top geometry for different surface alloys of (111) facet. The LDOS curves present the C-p of the ethylene molecule and the d of the surface Pd atom, which interacts directly with the ethylene molecule. The projection on the p orbital shows that this state remains close to the eigenvectors for the gaseous ethylene molecule, because they have still intense peaks in the bonding (-4.0 eV to -6.0 eV) and in the antibonding (+1.0 eV to +3.0 eV) regions, respectively.

When an ethylene molecule adsorbs on Pd(111) surface, the p orbital of the C atom is located at approximately -11.0 eV, -8.0 eV, and -7.0 eV, which are the localized states interacted with Pd atom. The delocalized states of the C atom are sit at -5.3 eV, -4.9 eV, and -4.1 eV. These three delocalized states don't hybrid with d orbitals of the Pd atom very well. The electronic states of the d orbital of the Pd atom are distributed from the Fermi energy to -5.8 eV and shifted to a more stable state compared with the bare surface. The interactions between the adsorbed ethylene molecule and surface which occurred at the area between the Fermi energy to -5.8 eV are not very good, illustrating the instability of ethylene adsorbed on the surface. The p orbital of C atom in ethylene also interacts with an out-of-phase combination of the d orbitals of the Pd atoms at +2.6 eV. These interactions lead to the deformation between the surface Pd atoms and the ethylene molecule. This deformation can also be shown as the differential electron density, which is presented on the insert figures of Fig. S1.

In the figure of the differential electron density, the yellow region shows the decrease of the electron density. Around the ethylene molecule, the loss of electron concerns clearly the p orbital, and the Pd in direct interaction with the ethylene molecule loses electrons in d_{z^2} -like orbitals. In the blue area, an increase of the electron density is observed on the ethylene, with a π^* -like distribution, and in d_{yz} and d_{xy} combinations on the Pd atoms. From the figure, the small size of the yellow area is observed in the ethylene molecule, but the blue area is much bigger than the yellow one. The increase of the electron density in the π^* orbital demonstrates a significant back-donation from a Pd atom to an acetylene molecule, which also can be proved by the value of the net charge of acetylene ($Q(C_2H_4)$).

When the Ag atomic concentration increases, the DOS projected on the C p orbitals of the ethylene only undergoes a small shift backward the Fermi level and the shape of the major peaks is not changed much. The peak in -4.2 eV of C p orbitals shift backward the Fermi level quickly to -4.7 eV and fuse with its previous peak. The states of the d orbitals in the Pd atom also shift, together with the p orbitals, and generate a more localized state around -2.5 eV after the adsorption. And the d states interact well with p states of C atom around -4.8 eV when the Ag concentration increases, indicating a stable bond between ethylene and surface. The changes of the electron density spatial distribution are very small for ethylene molecule that only traces of reduction can be found in the yellow region. However, the blue region of Pd d orbital is decreases as the Ag concentration increases especially when Ag concentration is larger than 50 %, representing that the ability of obtaining the electron is reduced. When the surface silver content reaches 50%, a significant decrease can be discovered for both the blue area of d_{yz} and d_{xy} combinations on the Pd

atoms and the yellow area of the ethylene molecule, indicating that the donation from ethylene to the surface becomes weak under the influence of the Ag atoms. This reduction is also due to the diminish of Pd-Pd bond on the surface that there is hardly electron transferred between Pd and Ag atoms according to the differential electron density.

S1.2 (100) surface

In order to explain the effect of the site differences, the LDOS and the differential electron density of the T45 adsorption, of which the circumstances is more sensible, on Pd(100) surface is presented in Fig. S2 together with the two kinds of sites on Pd₃Ag/Pd(100) surface, which are the site T45/Pd₃Ag and site T'45/Pd₃Ag in Fig. 3 of main manuscript that is presented in Fig. S2(b) and S2(c) respectively. When an ethylene molecule adsorbs on Pd(100) surface, the p orbital of the C atom is located at approximately -10.8 eV, -8 eV, and -7 eV, which are the localized states interacted with Pd atom. The delocalized states of the C atom are mainly around -4.0 eV ~ -6.0 eV, in which a peak of -4.2 eV is hybridized with Pd atom. The electronic states of the d orbital of the Pd atom are shifted to a more stable state compared with the bare surface and distributed from +1.0 eV above the Fermi energy to -5.8 eV. The p orbital of C atom in ethylene also interacts with an out-of-phase combination of the d orbitals of the Pd atoms at +2.1 eV. These interactions lead to the deformation between the surface Pd atoms and the ethylene molecule. This deformation can also be shown as the differential electron density, which is also presented on the insert figure of Fig. S2(a). From the figure of the differential electron density, the yellow areas in ethylene molecule is even smaller than the blue one, indicating an electronic transference from Pd atom to ethylene.

When the Ag atom added on the NN site, as shown in Fig. S2(b), all the states of C p orbital shift forward to the Fermi level about 0.4 eV. The movement is the same as the N site sitting the Ag atom, as presented in Fig. S2(c), except the peak around -4 eV that the NN site Ag atom will provide more localized states than the N site and even than the adsorption on Pd(100) surface, just indicating that the adsorption on site T45/Pd₃Ag is much stronger than site T'45/Pd₃Ag and site T45/Pd. The d sates of Pd atom generate different peaks which is localized with p states of C atom. Localized state around -3.8 eV is generated after the adsorption for the sites 4 that have the NN site Ag atom, while the state around -4.2 eV is generated for the sites that have the N site Ag atom.

The changes of the electron density spatial distribution are very small for ethylene molecule that only traces of reduction can be found in the yellow region, which is the same as the (111) surface, indicating that the donation from ethylene to the surface becomes weak under the influence of the Ag atoms. The data of the charges showed that, when the ethylene adsorption on the top site, the Ag atom in both N and NN sites have no influence on the ethylene. The charge of ethylene for this three adsorption mode is -0.18. But the charge in Pd is different though the change of it is the same. The Ag atom in N site will provide more electrons to Pd atom. But the large number of electronic of Pd atom is not conducive to the stability of adsorption because of the elimination between Pd and π electrons in ethylene molecule.

S1.3 (110) surface

Both the LDOS and the differential electron density are displayed in Fig. S3 that the T90 adsorption mode is chosen to figure out the differences of Ag atom site and discuss the relationships between

the distance of Pd-Ag and the weight of the ligand and ensemble effects. When ethylene adsorbed on Pd(110) surface, the interaction of p orbitals of C atom is maximum with d orbitals of Pd atom at -10.7 eV, -7.7 eV, -6.7 eV, -4.9 eV, and -3.8 eV. When the Ag atom add in the N site, which is nearest to the top Pd atom, the states in -3.8 eV of p orbital of C atom shift backward the Fermi level to -4.2 eV, and the d states of Pd atom in this area is also shifted and become localized around -3.6 eV ~ -5.2 eV, as shown in Fig S3(b). If the Ag atom sit more further, to the NN site and NNN site, the influence is insignificant for the change of LDOS. For the differential electron density, however, the change is evident for the Pd atom. The d_{xz} and d_{xy} combinations gains more electronics for the Ag atom in N site than the pure Pd(110) surface. The ability to obtain electrons is followed the order of N site > NNN site > NN site, on which the Ag atom is for the top Pd atom on the Pd₃Ag/Pd(110) surface. This order is fully consistent with the change of Hirshfeld charge on Pd atom according to the Table 3 in main manuscript. The electronic obtaining for the d_{xz} and d_{xy} combinations can reflex the extent of the backdonation from ethylene to surface molecule. The Ag atom for the N site can let the top Pd atom gained much electrons from adsorbed ethylene molecule, which let the charge of ethylene down to -0.14 from -0.20 for the pure Pd(110) surface as discussed before. These results indicate that the Ag atom can influence the nearest Pd atom to decrease the adsorption ability.

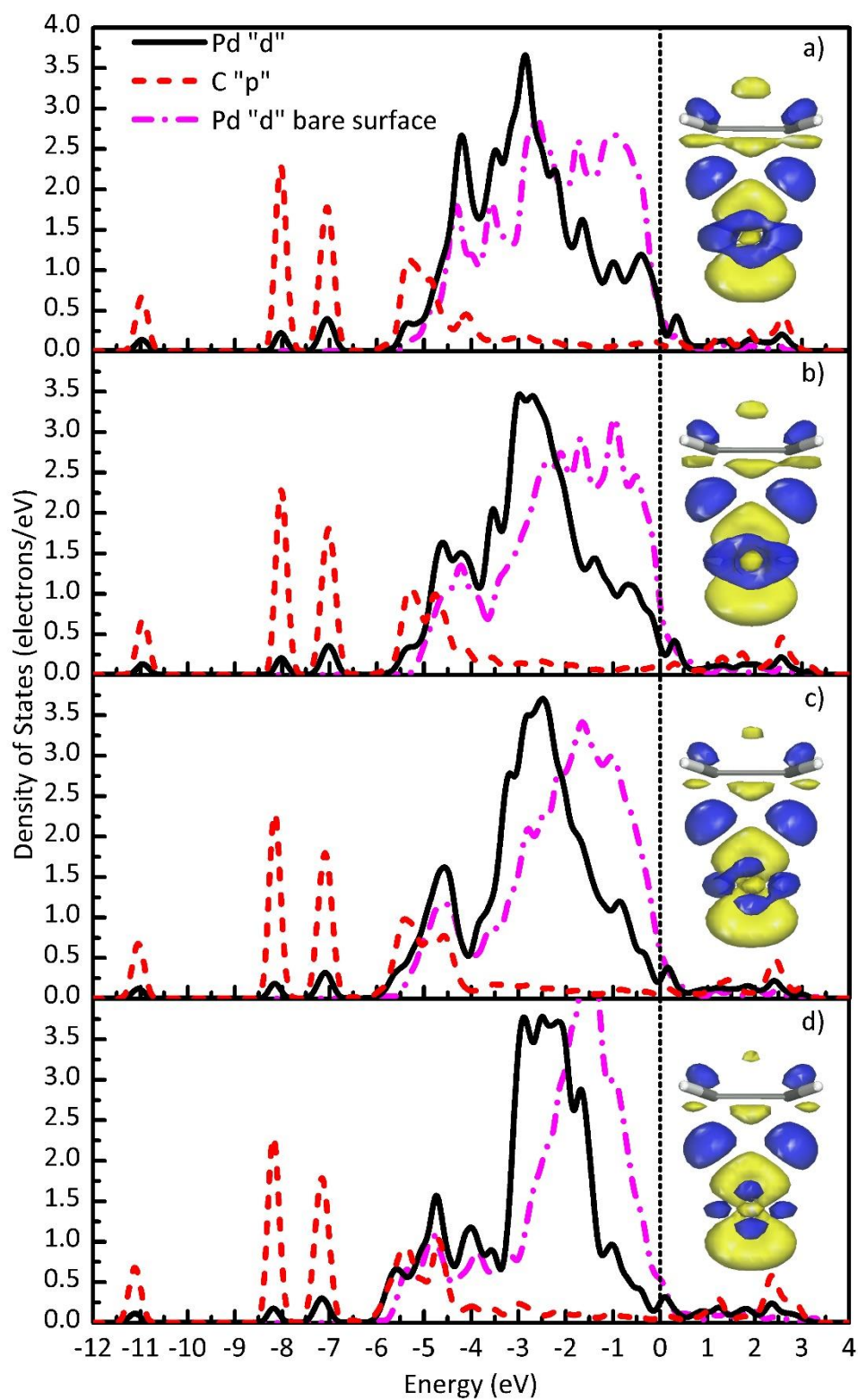


Fig. S1. Local densities of state and the differential electron density in the case of top adsorption mode on Pd(111) (a), Pd₃Ag/Pd(111) (b), PdAg/Pd(111) (c), and PdAg₃/Pd(111) (d) surfaces.

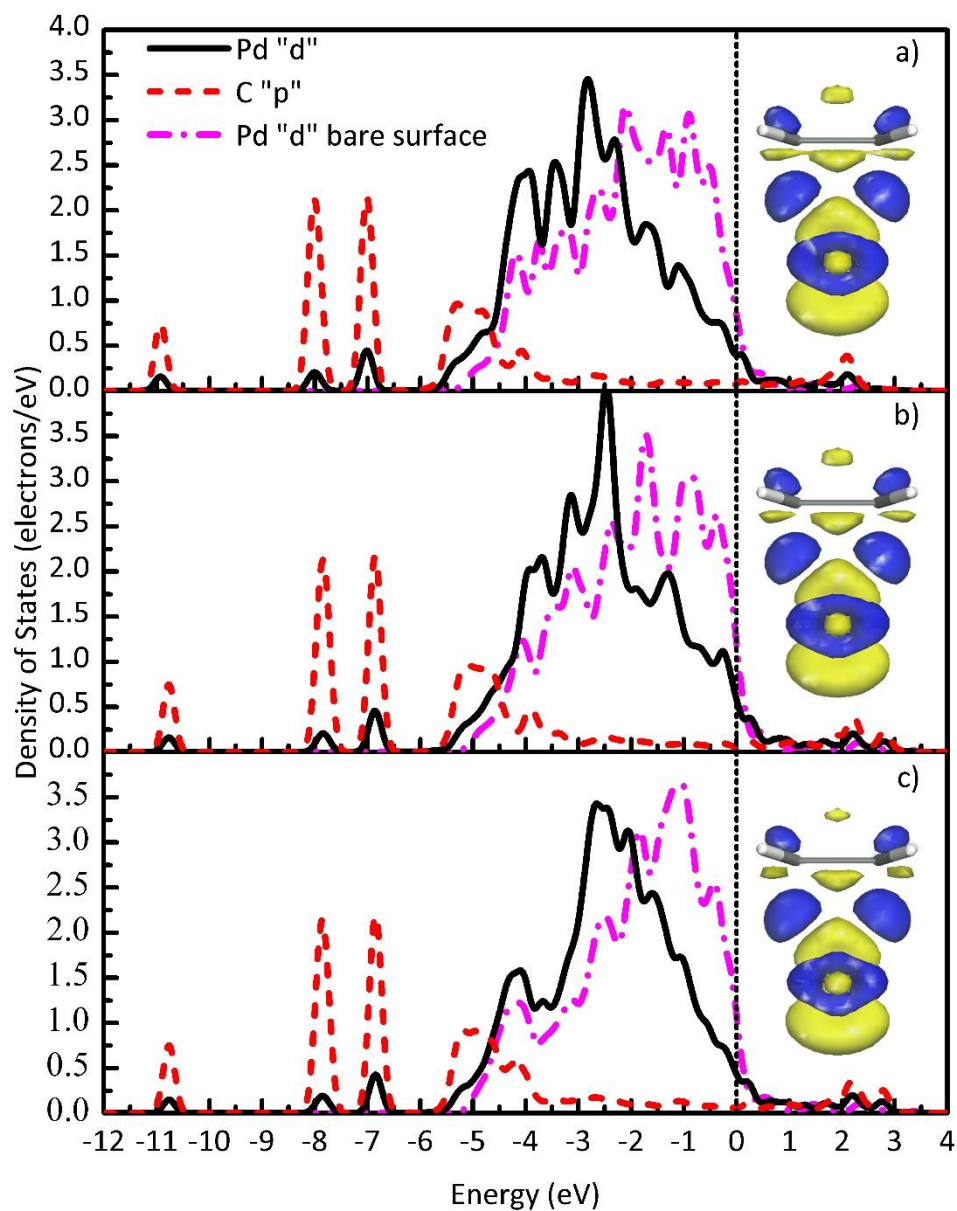


Fig. S2. Local densities of state and the differential electron density in the case of T45 adsorption mode on Pd(100) (a) and Pd₃Ag/Pd(100) surface where the Ag atom is on the NN site (b) and the N site (c) respectively.

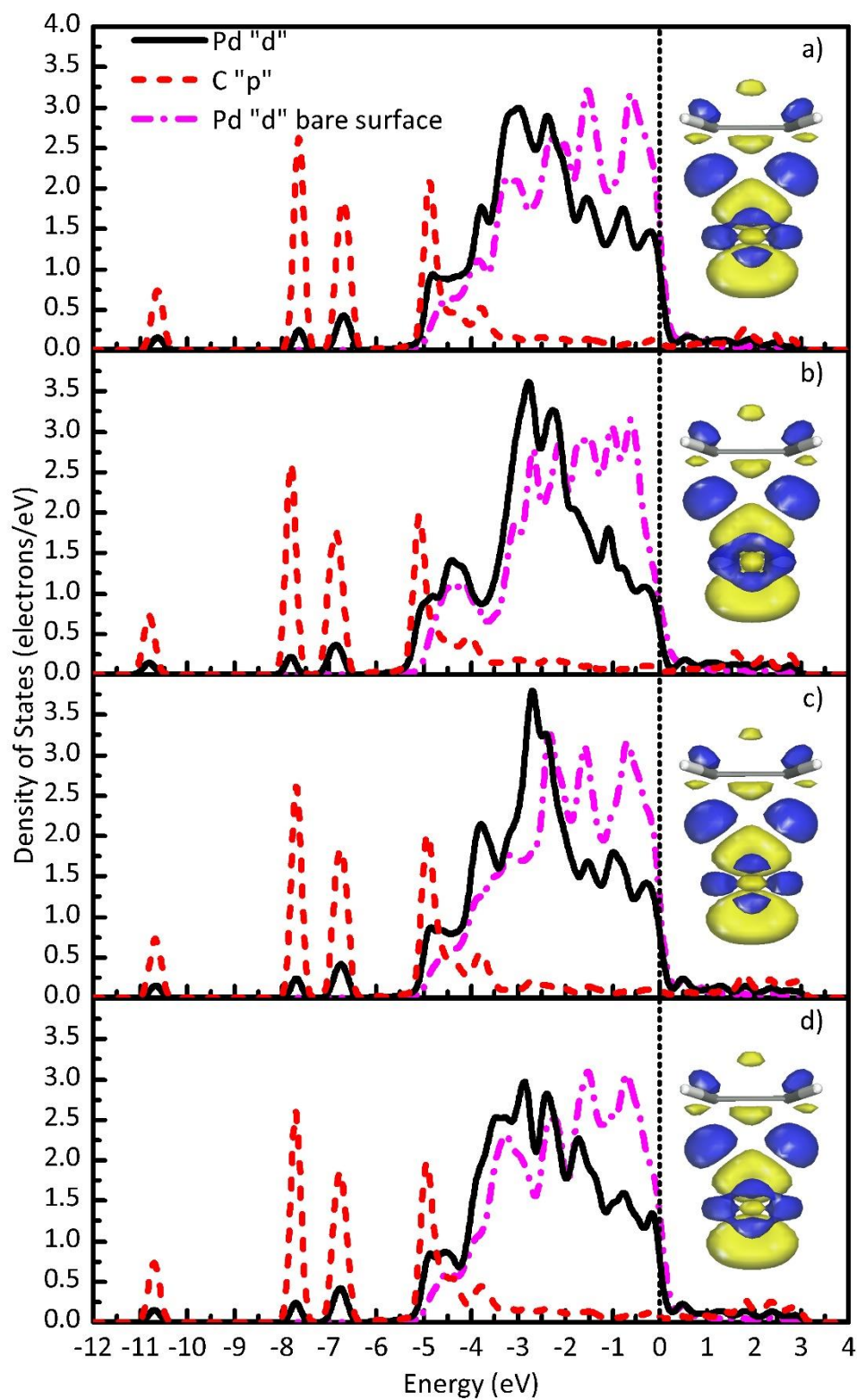


Fig. S3. Local densities of state and the differential electron density in the case of top90 adsorption mode on Pd(110) (a), and Pd₃Ag/Pd(110) surface where the Ag atom is on the N site (b), NN site (c) and NNN site (d)

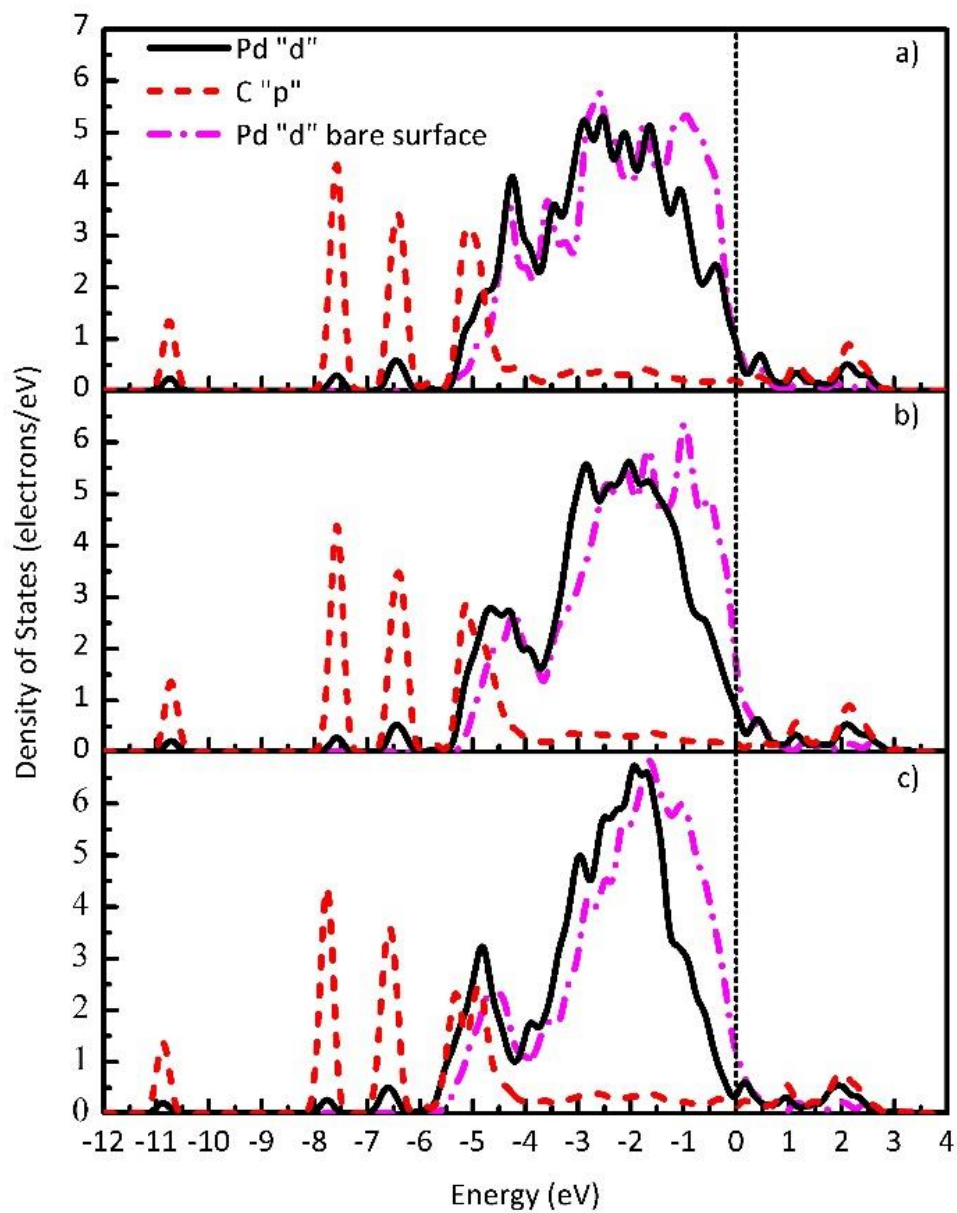


Fig. S4. Local densities of state in the case of bridge adsorption mode on Pd(111) (a), Pd₃Ag/Pd(111) (b), and PdAg/Pd(111) (c) surfaces.

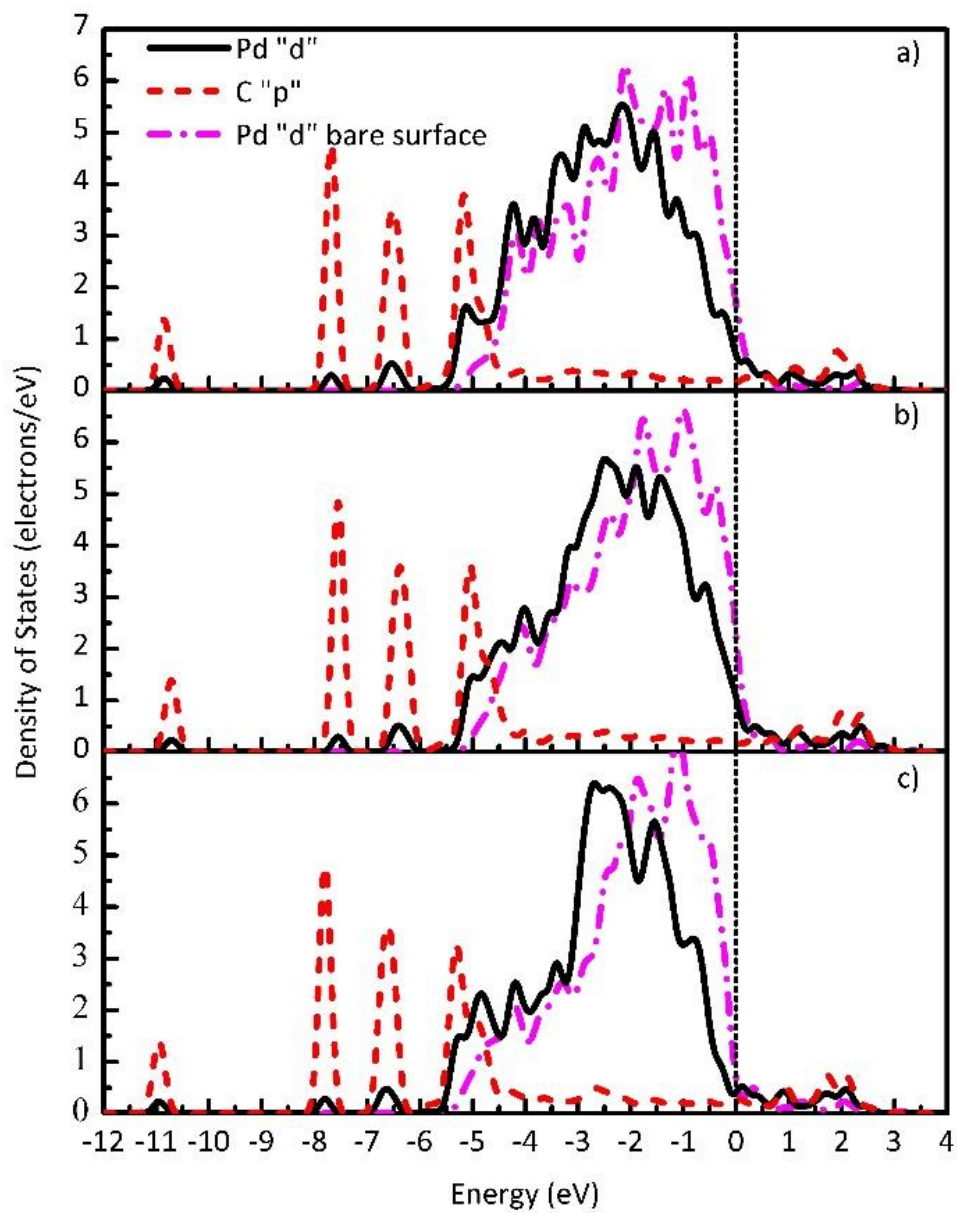


Fig. S5 Local densities of state in the case of bridge adsorption mode on Pd(100) (a), Pd₃Ag/Pd(100) (b), and PdAg/Pd(100)-2 (c) surfaces.