# ADVANCED ENERGY MATERIALS

## Supporting Information

# Role of Transition Metal in Fast Oxidation Reaction on the Pt₃TM (111) (TM = Ni, Co) Surfaces

*Yong Su Kim, Sang Ho Jeon, Aaron Bostwick, Eli Rotenberg, Philip N. Ross, Vojislav R. Stamenkovic, Nenad M. Markovic, Tae Won Noh, Seungwu Han,\* and Bongjin Simon Mun\**

# Supporting Information

**Role of Transition Metal in Fast Oxidation Reaction on the Pt$_3$TM (111) (TM = Ni, Co) surfaces**

*Yong Su Kim, Sang Ho Jeon, Aaron Bostwick, Eli Rotenberg, Philip N. Ross, Vojislav R. Stamenkovic, Nenad M. Markovic, Tae Won Noh, Seungwu Han,\* Bongjin Simon Mun\**

Prof. Y. S. Kim[+], Dr. A. Bostwick, Dr. E. Rotenberg
Advanced Light Source
Lawrence Berkeley National Laboratory, Berkeley, California 94720 (USA)
[*]     Dr. S. H. Jeon[+], Prof. S. Han
Department of Materials Science & Engineering
Seoul National University, Seoul 151-744 (Korea)
E-mail: hansw@snu.ac.kr
       Dr. Philip N. Ross
Material & Molecular Research Division
Lawrence Berkeley National Laboratory, Berkeley, California 94720 (USA)
       Dr. V. R. Stamenkovic, Dr. N. M. Markovic
Material Science Division
Argonne National Laboratory, Argonne, Illinois 60439 (USA)
       Prof. Y. S. Kim, Prof. T. W. Noh
CFI-CES, IBS and Department of Physics & Astronomy
Seoul National University, Seoul 151-747 (Korea)
[*]     Prof. B. S. Mun
Department of Physics and Photon Science
Ertl Center for Electrochemistry and Catalyst
Gwangju Institute of Science and Technology, Gwangju 500-712 (Korea)
E-mail: bsmun@gist.ac.kr
       [+] Y.S.K. and S.H.J contributed equally to this work

**Methods**

Since the properties of oxygen adsorption on the metal surfaces and surface band structures of metals are highly sensitive to surface properties, such as surface structure and impurities adsorbed on the surface, Pt(111) and $Pt_3TM(111)$ (TM=Ni, Co) surfaces were carefully prepared by repeated sputtering and annealing cycle, and its well-ordered surfaces were checked with LEED as shown in Figure S1. High-resolution core-level XPS and APRES measurements were carried out at beamline 7.0.1 of the Advanced Light Source at the Lawrence Berkeley National Laboratory. The hemispherical electron analyzer, Sicenta R4000, was used for core-level XPS and APRES measurements and the total energy resolution of XPS spectra and ARPES scans were set to below 0.1 eV and to 25 meV, respectively.
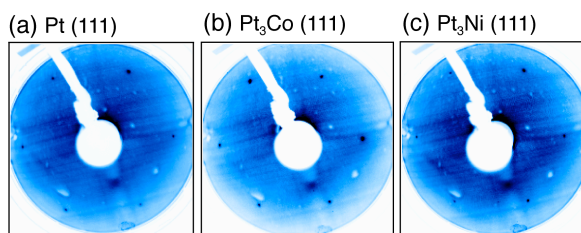
(a) Pt (111)   (b) $Pt_3Co$ (111)   (c) $Pt_3Ni$ (111)

**Figure S1.** a,b) LEED pattern of clean Pt, $Pt_3Co$, and $Pt_3Ni$(111). The well-ordered (1×1) surface structures were obtained by repeated sputtering and annealing.

**Core level spectroscopy measurements of $Pt_3TM$ and $O/Pt_3TM$(111) surfaces**

The Ni $2p$ and Co $2p$ core level spectra of $Pt_3TM$(111) (TM = Ni, Co) were measured at photon energy of 1 keV. What is noteworthy is that while the core level spectra of Pt $4f$ show significant variations due to chemical boding with atomic oxygen, those of Ni and Co do not display any changes after atomic oxygen is adsorbed on the surfaces (Figure S2). Recent studies on the $Pt_3TM$(111) single crystals show that there is a surface reconstruction due to the alloying of transition metals; the surface segregation of Pt to top-most surface layer with the

16          16

enrichment of transition metal at surface layer, a so-called Pt skin structure.[1,2] The results of Figure S2 are consistent with one can expect from the Pt skin structure, showing only Pt is exposed to atomic oxygen. Our findings also suggest that the *d*-electrons of transition metal in the sub-surface layer and deeper layer do not directly participate in chemical bonding interaction with atomic oxygen on the surface.
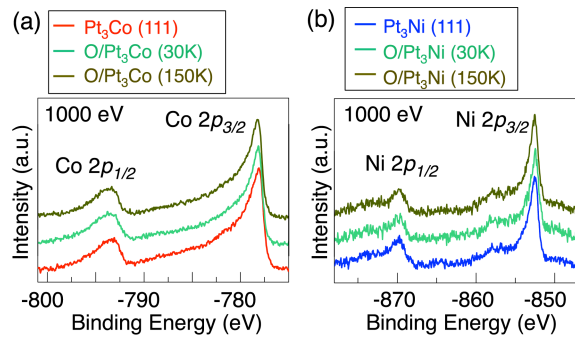


**Figure S2.** Core level spectra of Co 2*p* and Ni 2*p* at 1000 eV of photon energy. Both of the spectra show no changes after dosing with oxygen, indicating *d*-electrons of transition metals in the subsurface layer are completely separated from the direct chemical bonding with the 2*p* orbital of oxygen atom.

**Angle resolved photoemission spectroscopy (ARPES) measurements: Fermi surfaces**

The ARPES measurements were performed at photon energy of 120 eV. The Fermi surfaces of clean $Pt_3Ni(111)$ (Figure 2) show a considerable difference compared to that of clean Pt(111),[3] indicating transition metal atoms, placed in the sub-surface and deeper layer, are responsible for the changes of the surface band structure. However the Fermi surface do not show significant change after dosing with oxygen.

**ARPES measurements: Surface states and resonances**

In order to identify bulk band and Surface-States (surface state and surface resonance) in the surface band structure of $Pt_3Ni(111)$ (Figure 2), we employed two experimental analysis methods. Surface-States are highly localized states in the real space surface layer. Therefore, these states are sensitive to the adsorbate-surface interaction and, in particular, they show little dispersion in the momentum plane, which is perpendicular to the surface plane. In our experiments, Surface-States were identified by observing the changes of band dispersion induced by adsorbed hydrogen (not shown here), and the ARPES band structure cut along the MKΓK direction of Brillouin zone were collected with different photon energy from 100 to 160 eV along momentum axis, $k_\perp$, perpendicular to the surface. Spectral function of $Pt_3Ni(111)$ along $k_\perp$ direction dose not seem to have much delocalized bands near the Fermi level compared to that of Pt(111) (Figure S3)
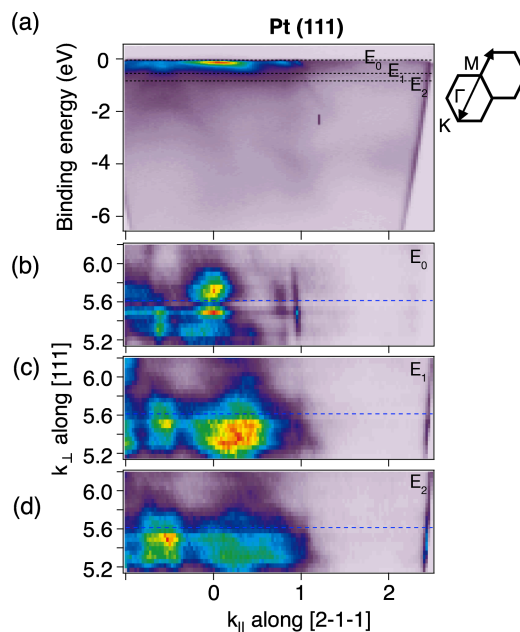


**Figure S3.** a-d) The energy-momentum dispersions relations along the perpendicular momentum, $k_\perp$, to the $Pt_3Ni(111)$ surface. The spectral function along the $k_\perp$ direction was measured by varying the photon energy. Constant-energy maps correspond to binding energy

of L1, L2, and L3. The blue dashed line indicates photon energy 120 eV, which was used for

band structure measurements in Figure 2.

### Density functional theory calculations

The interlayer spacing between $i$-th and $j$-th layers in Pt(111) and Pt-Ni(111) was

estimated by DFT calculation. The TM in the subsurface layer changes local charge

distribution resulting in variation of adjacent layer distacne due to alternating layer potential.

The interlayer spacing near the surface, i.e., $d_{12}$ and $d_{23}$, is reduced, while that of bulk-like

region, i.e., $d_{34}$ and $d_{45}$, is almost maintained.

|  | Pt | Pt-Ni ($\Delta$) |
|---|---|---|
| $d_{12}$ | 2.32 | 2.04 (-0.28) |
| $d_{23}$ | 2.29 | 2.02 (-0.27) |
| $d_{34}$ | 2.29 | 2.33 (+0.04) |
| $d_{45}$ | 2.3 | 2.31 (+0.01) |

Table I. Interlayer spacing (in Å) between slab-layers in Pt(111) and Pt-Ni(111). Here, $d_{ij}$

denotes layer distance between $i$-th and $j$-th layer. The interlayer spacing difference between

Pt and Pt-Ni slab-layer displays in parentheses, i.e., $\Delta= d_{ij}(Pt-Ni) - d_{ij}(Pt)$.

|  | Pt | Pt-Ni |
|---|---|---|
| Surface | +0.05 | +0.23 |
| Sub-surface | -0.04 | -0.42 |
| 3rd layer | -0.02 | +0.17 |
| 4th layer | +0.01 | +0.02 |

Table II. Bader change of each Pt and Pt-Ni slab-layers for relaxed ground state
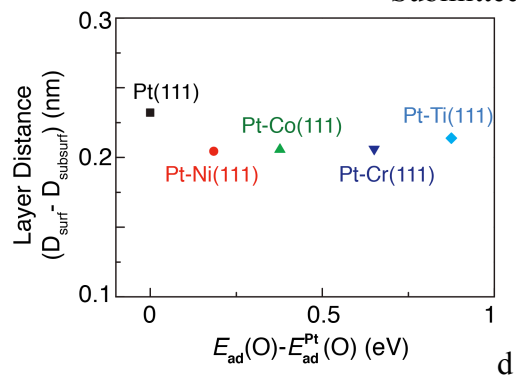
compared to unrelaxed Pt raw state.

**Figure S4** Layer distance between Pt-surface layer and TM-subsurface layer.

References

[1] V. R. Stamenkovic *et al*., Science **315**, 493 (2007).

[2] V. R. Stamenkovic *et al*., Nature Materials **6**, 342 (2007).

[3] Y. S. Kim et al. (to be published).