Supporting Information

XPS Study of Nanostructured Rhodium Oxide Film Comprising Rh^{4+} Species

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To confirm the formation of Rh nanoparticles under the RF-discharge in O_2 the particles were sputtered on a carbon film fixed on standard copper grids and analyzed by transmission electron microscopy. The resulted TEM data are presented in Figure S1.

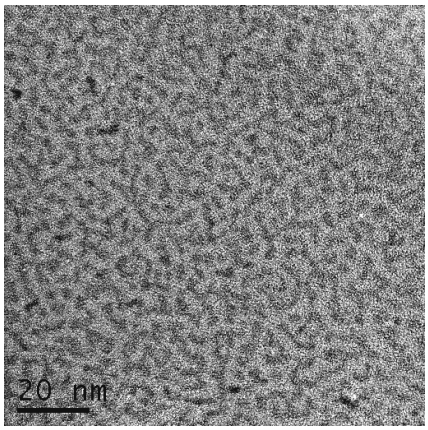

Figure S1. TEM data for Rh nanoparticles prepared by RF-discharge sputtering of rhodium wire in O_2 for 3 min.

The dendrite-like particles with average width about 2.5 nm were formed under 3-minutes RF-sputtering.

The Rh 3d and O 1s spectra of the oxidized rhodium nanoparticles deposited on the TaO_x foil by 9 min RF-discharge in O_2 are shown in Figure S2.

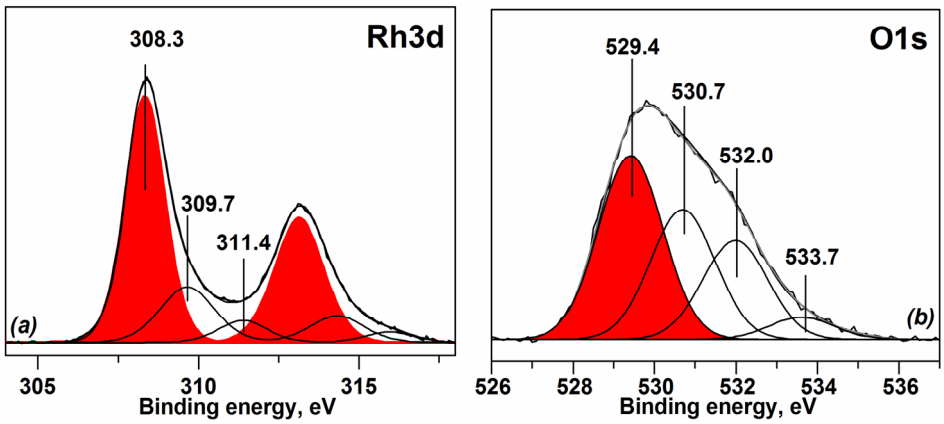

Figure S2. (a) Rh 3d and (b) O 1s spectra fitted with individual components of oxidized Rh nanoparticles RF-sputtered on oxidized tantalum foil. (O 1s spectrum is given after subtraction of TaO_x oxygen signal).

Fourier patterns of HRTEM images of oxidized rhodium nanoparticles prepared by RF-sputtering for 3 min are shown in Figure S3 and S4.

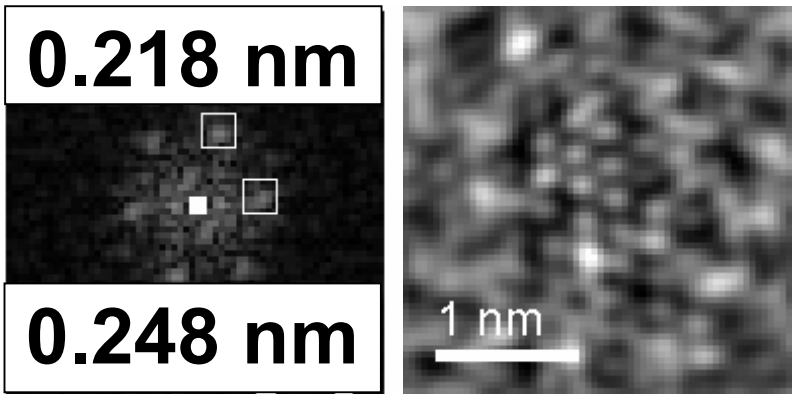

Figure S3. Fourier pattern of HRTEM image of oxidized rhodium nanoparticles prepared by RF-sputtering for 3 min.

The hexagonal metallic structures with widened interplanar spacing d=2.48 Å can be observed.

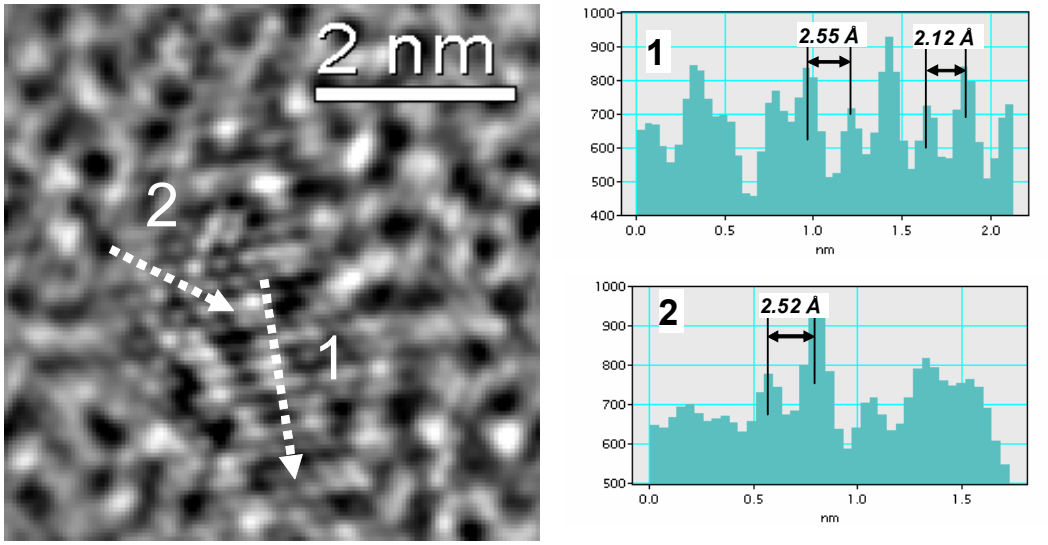

Figure S4. HRTEM image with analysis of interplanar spacing of defect particle.

HRTEM image shows several areas with interplanar spacings corresponding to metallic (d=2.12 Å) and oxidized (d~2.52-2.55 Å) rhodium species within one particle.

The Rh 3d and O 1s spectra for thermally oxidized Rh foil after CO exposure at 100^0C are shown in Figure S5.

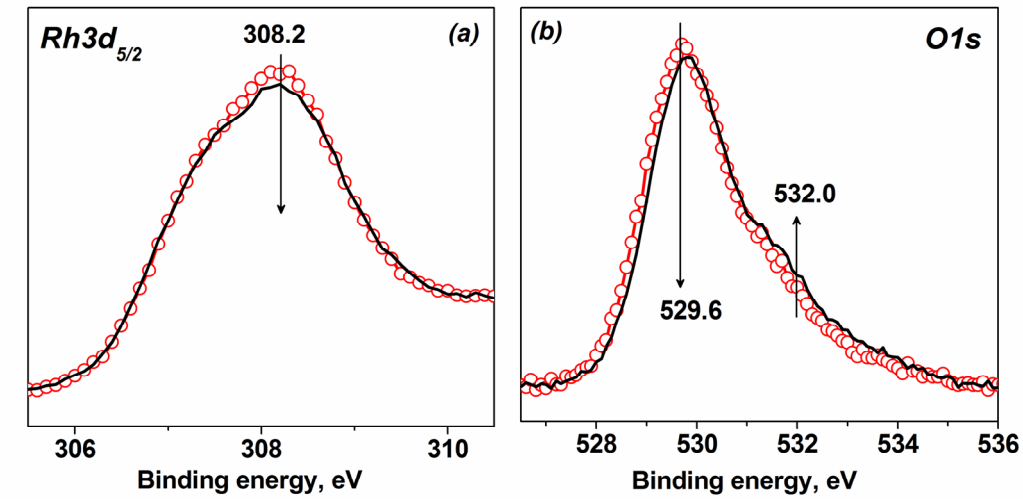

Figure S5. (a) Rh $3d_{5/2}$ and (b) O 1s spectra of Rh foil oxidized by molecular oxygen at 400^0C. Initial surface (symbol lines), after 10^9 L CO at 100^0C (solid line).

In good agreement with literature data[1–3] thermally prepared Rh_2O_3 oxide did not show noticeable reactivity towards CO oxidation at 100^0C. Slight changes in Rh 3d and O 1s spectra can be explained by CO adsorption on the surface.

References

(1) Flege, J.; Sutter, P. In Situ Structural Imaging of CO Oxidation Catalysis on Oxidized Rh(111). *Phys. Rev. B* **2008**, *78*, 153402.

(2) Gustafson, J.; Westerstrom, R.; Balmes, O.; Resta, A.; van Rijn, R.; Torrelles, X.; Herbschleb, C. T.; Frenken, J. W. M.; Lundgren, E. Catalytic Activity of the Rh Surface Oxide: CO Oxidation over Rh(111) under Realistic Conditions. *J. Phys. Chem. C* **2010**, *114*, 4580–4583.

(3) Gao, F.; Cai, Y.; Gath, K. K.; Wang, Y.; Chen, M. S.; Guo, Q. L.; Goodman, D. W. CO Oxidation on Pt-Group Metals from Ultrahigh Vacuum to Near Atmospheric Pressures. 1. Rhodium. *J. Phys. Chem. C* **2009**, *113*, 182–192.