Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

N_2O-emission-free Exhaust Remediation by Rh-NbO_x Nanocomposites Developed from Rh_3Nb Alloy Precursor

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Experimental Details

Experimental Section

Sample Preparation. Pure-phased Rh_3Nb ingots were synthesized by arc-melting elemental metals in pure Ar atmosphere (99.9999 %). The Rh_3Nb ingots were powdered in an agate mortar and filtered to obtain powder samples with an average particle size of 50 μm. The prepared Rh_3Nb powder was then subjected to a stream of a gas mixture containing equimolecular NO and CO at elevated temperatures up to 400 ^{o}C. A single crystal of pristine Rh was purchased from Crystal Base, Inc. (cut and polished along with the (111) face, mirror finish) and used without further pretreatments.

Sample Characterization. The crystal structure of the synthesized material was characterized by powder X-ray diffraction (*p*XRD, X'Pert PRO, PANalytical) with Cu $K\alpha$ radiation. An obliquely finished Si crystal was used as a sample holder to minimize the background. Hard X-ray photoemission spectroscopy (HAXPES) was performed using X-ray with a photon energy of 5.9534 keV at the undulator beamline BL15XU of SPring-8, Japan. The HAXPES measurements were conducted at room temperature under UHV using a hemispherical electron energy analyser (VG SCIENTA R4000). The total energy resolution was set to 220 meV. The binding energy was referenced to the Fermi edge of a

Au thin film. A transmission electron microscope (TEM and/or STEM, JEM-2100F, JEOL) equipped with an X-ray energy-dispersive spectrometer was used for compositional analyses. TEM and STEM observation was conducted at an accelerating voltage of 200 kV. The sample for TEM and STEM observation was prepared by thinly slicing one of the Rh@NbO$_x$ powders with an Ar-ion mill (Model 691, GATAN) operated at the temperature of liquid nitrogen to minimize damage during the milling.

Catalytic Tests. The NO remediation performance of different catalysts was evaluated with a fixed-bed flow reactor (feeding rate = 10 ml min^{-1}; space velocity = 30000 h^{-1}). Reactant gases consisting of NO, CO and He (NO:CO:He=1:1:98) was used for the catalytic test in a fixed-bed configuration. The chemical composition of the effluent gas was analysed with a Fourier transformation infrared spectrometer (FTIR, Shimadzu Prestige-21) equipped with a gas cell. Rh powder was purchased from Furuya Kinzoku Co., sieved to adjust the particles size to 50 μm, and used as the control catalyst without further treatments.

Surface-chemistry characterization. *In situ* X-ray photoemission spectroscopy (XPS) was performed with an XPS spectrometer (UlVAC PHI, ESCA 1600) that was built in to an ultra-high vacuum (UHV) chamber with a NO gas feedthrough. Monochromatized Al *Ka* radiation (photon energy = 1.4866 keV) was used as the light. In prior to the XPS measurements, the samples were cleaned in UHV with Ar ion bombardment, followed by an annealing at 850 °C. The cleaned sample surface was subjected to one monolayer adsorption of NO gas at room temperature.

Figures

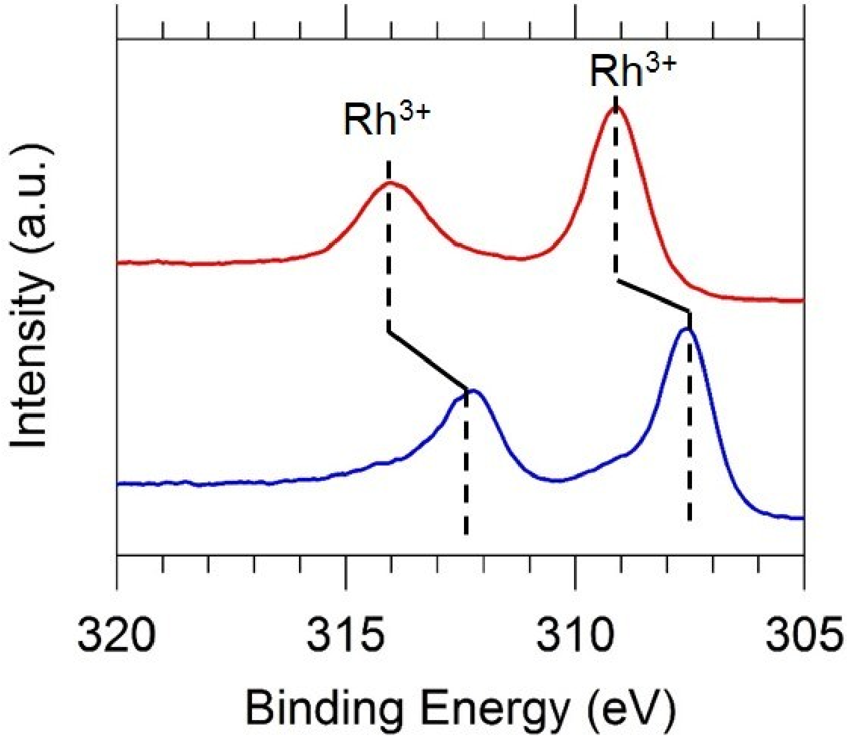


Figure S1. X-ray photoemission spectra (Al $K\alpha$ radiation) in the Rh 3*d* region for the Rh_3Nb precursor (blue) and the Rh@NbO_x. The intense peaks at 307.5 and 312.2 eV for the Rh_3Nb sample and the peaks at 309.2 and 314.1 eV correspond to the Rh $3d_{5/2}$ and Rh $3d_{3/2}$ emissions for the Rh@NbO_x, respectively.

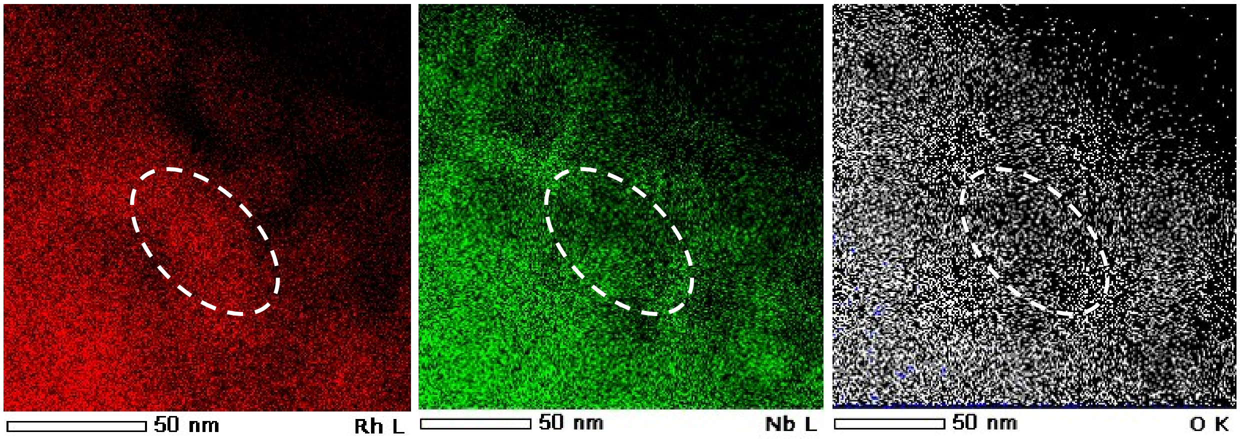


Figure S2. Compositional mapping images of a section of the Rh@NbO$_x$. Note that both of Rh and O are depleted from the area surrounded by broken ellipsoids.

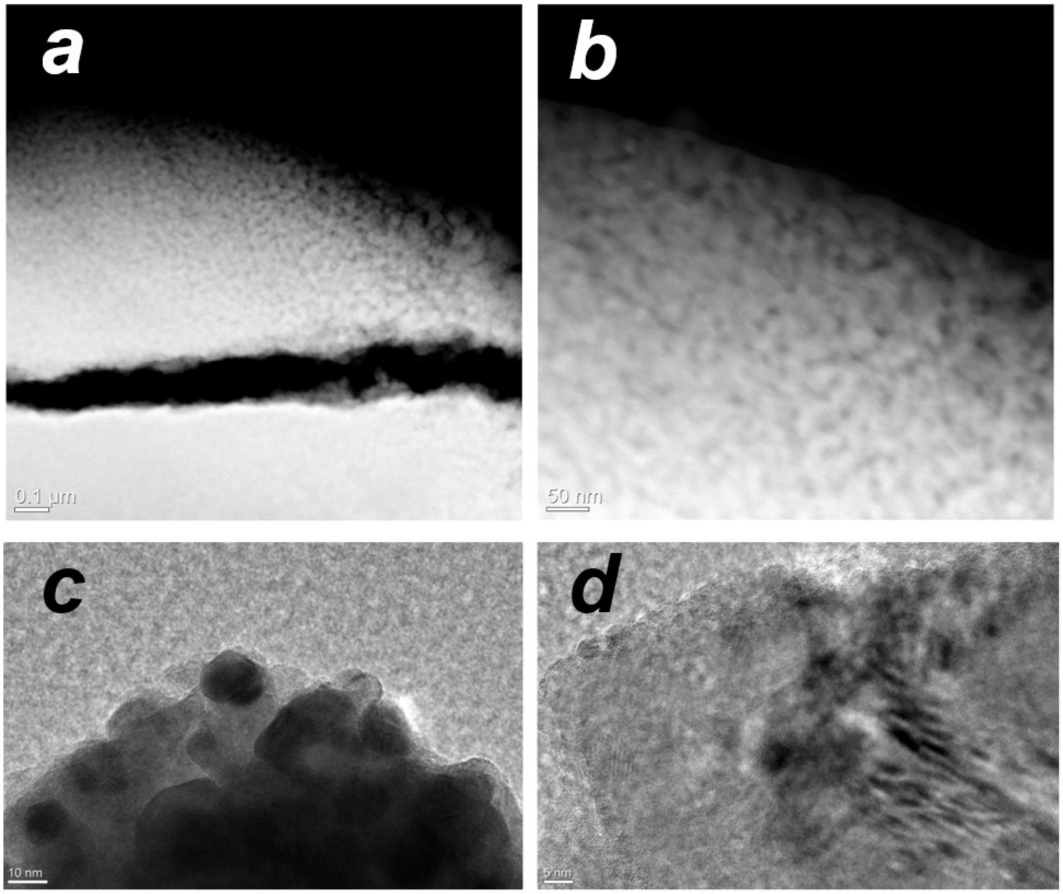


Figure S3. Scanning transmission electron microscope (STEM; *a* and *b*)- and transmission microscope (TEM; *c* and *d*) images of the Rh@NbO$_x$ material.

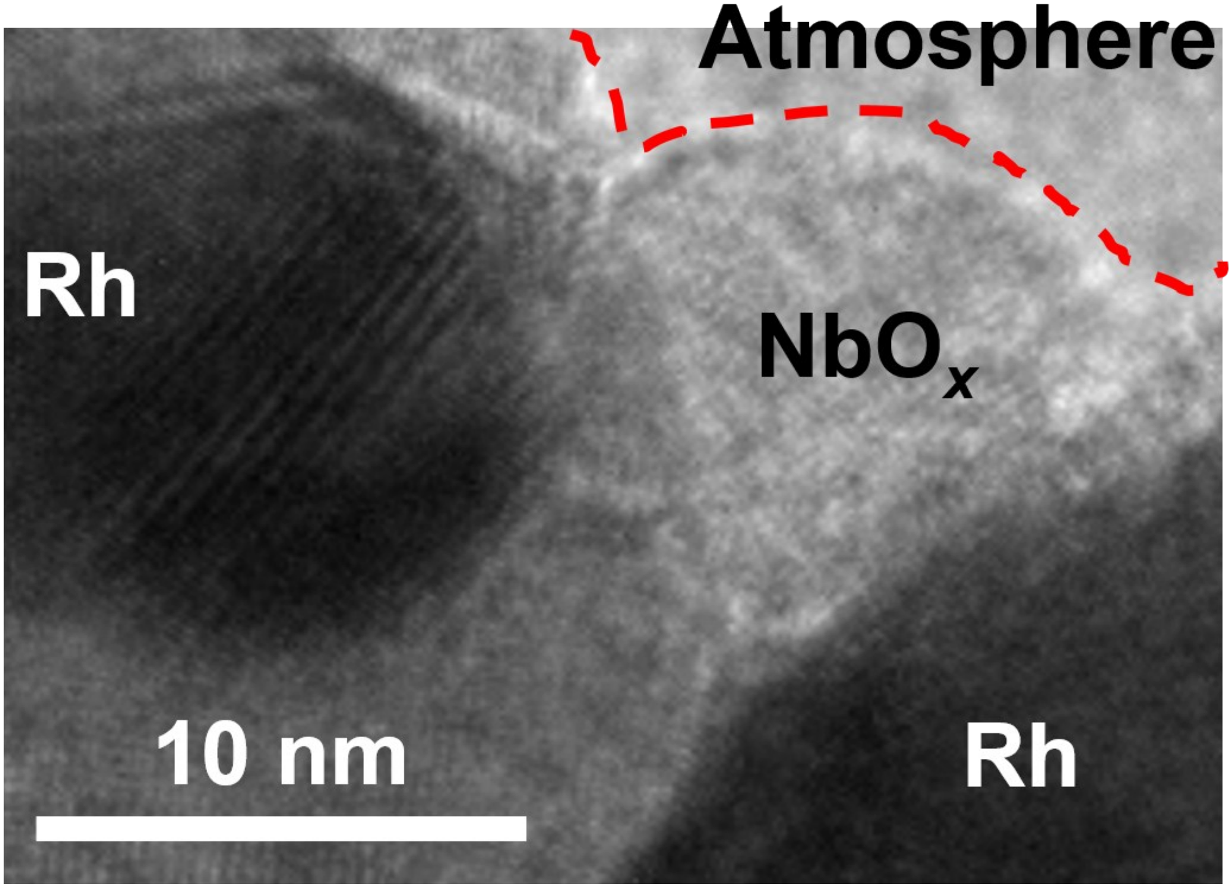
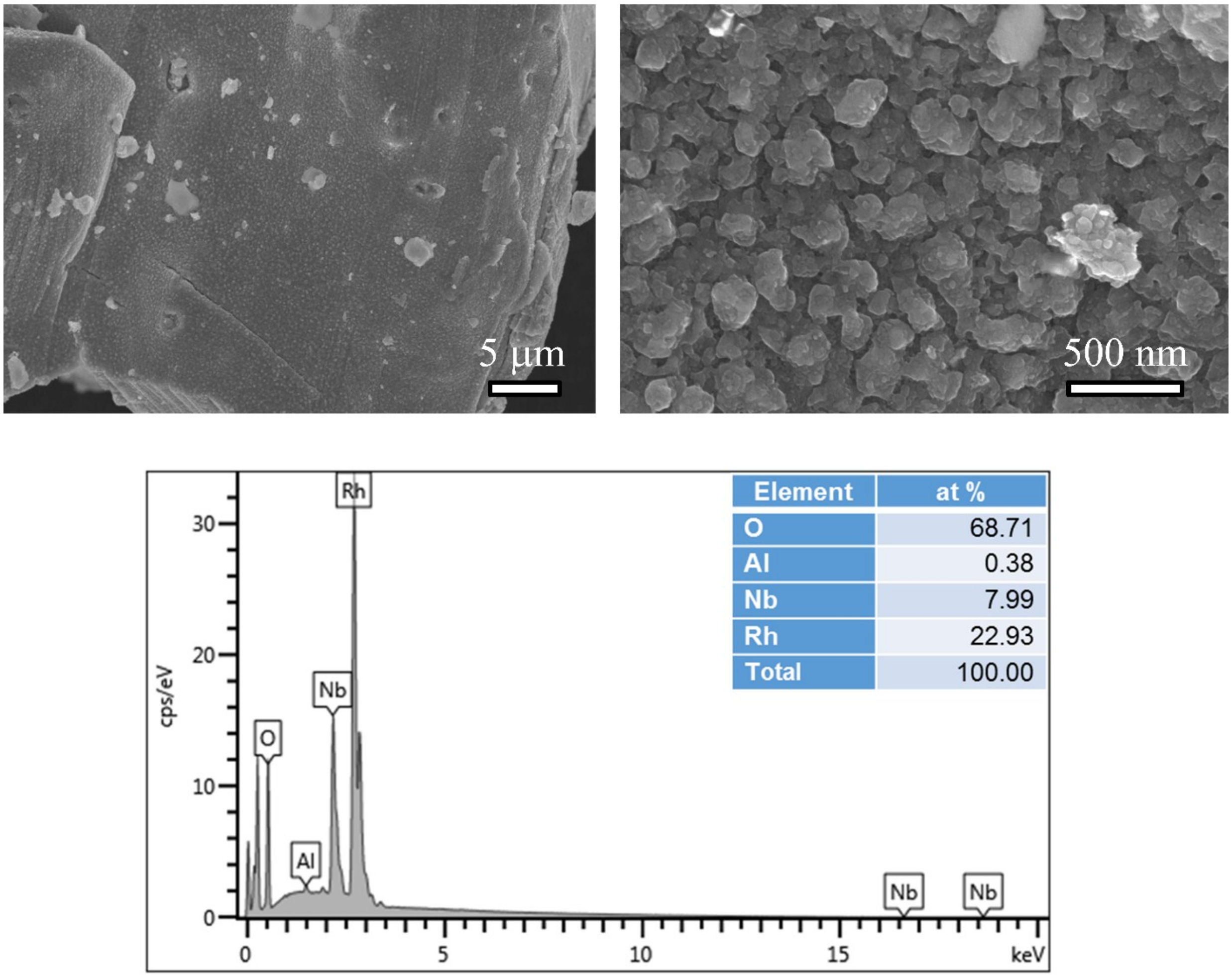


Figure S4. Atomic-resolution TEM image of the Rh@NbO$_x$, which corresponds to the TEM image presented as Figure S3 *c*.



Element	at %
O	68.71
Al	0.38
Nb	7.99
Rh	22.93
Total	100.00

Figure S5. Scanning electron microscope (SEM) characterization on the Rh@NbO$_x$ surface.

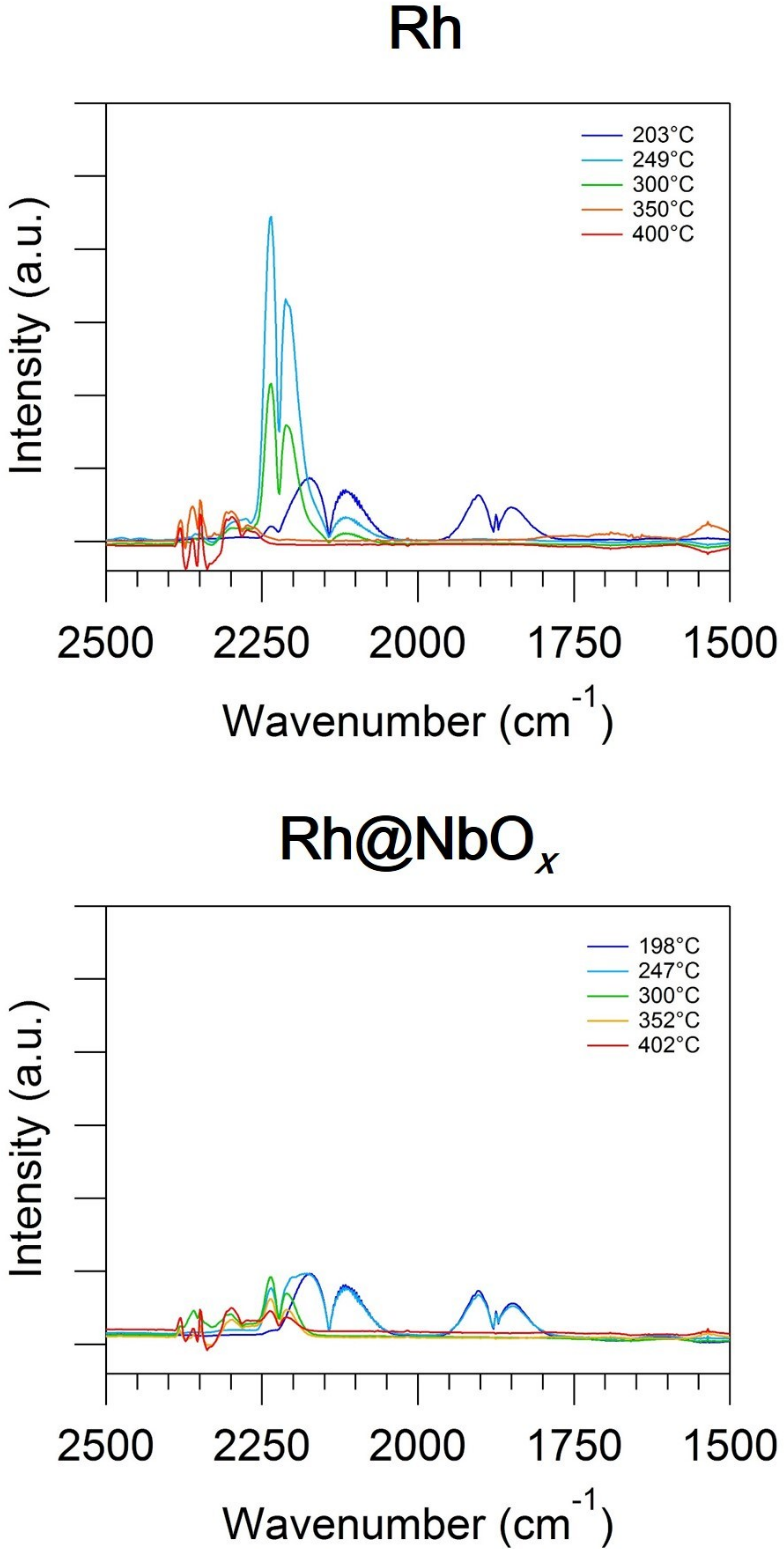


Figure S6. Fourier transform infrared spectra for the effluent gas of the NO remediation.

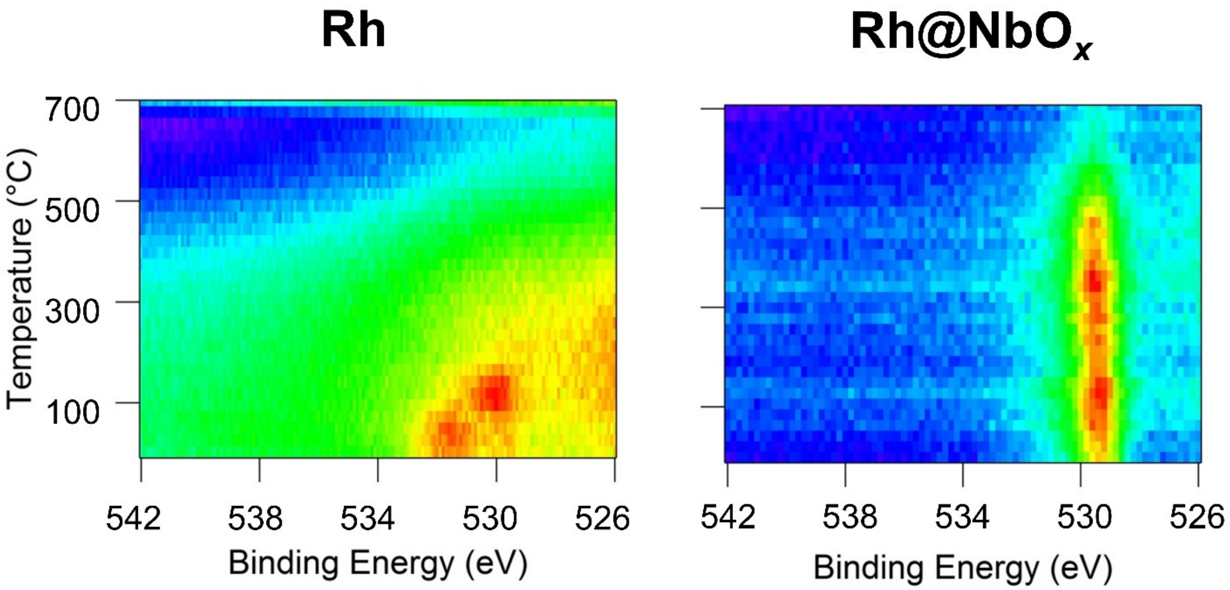


Figure S7. *In-situ* X-ray photoemission spectroscopy (*in-situ* XPS) spectra in the O 1*s* region for the NO-adsorbed catalyst surfaces.

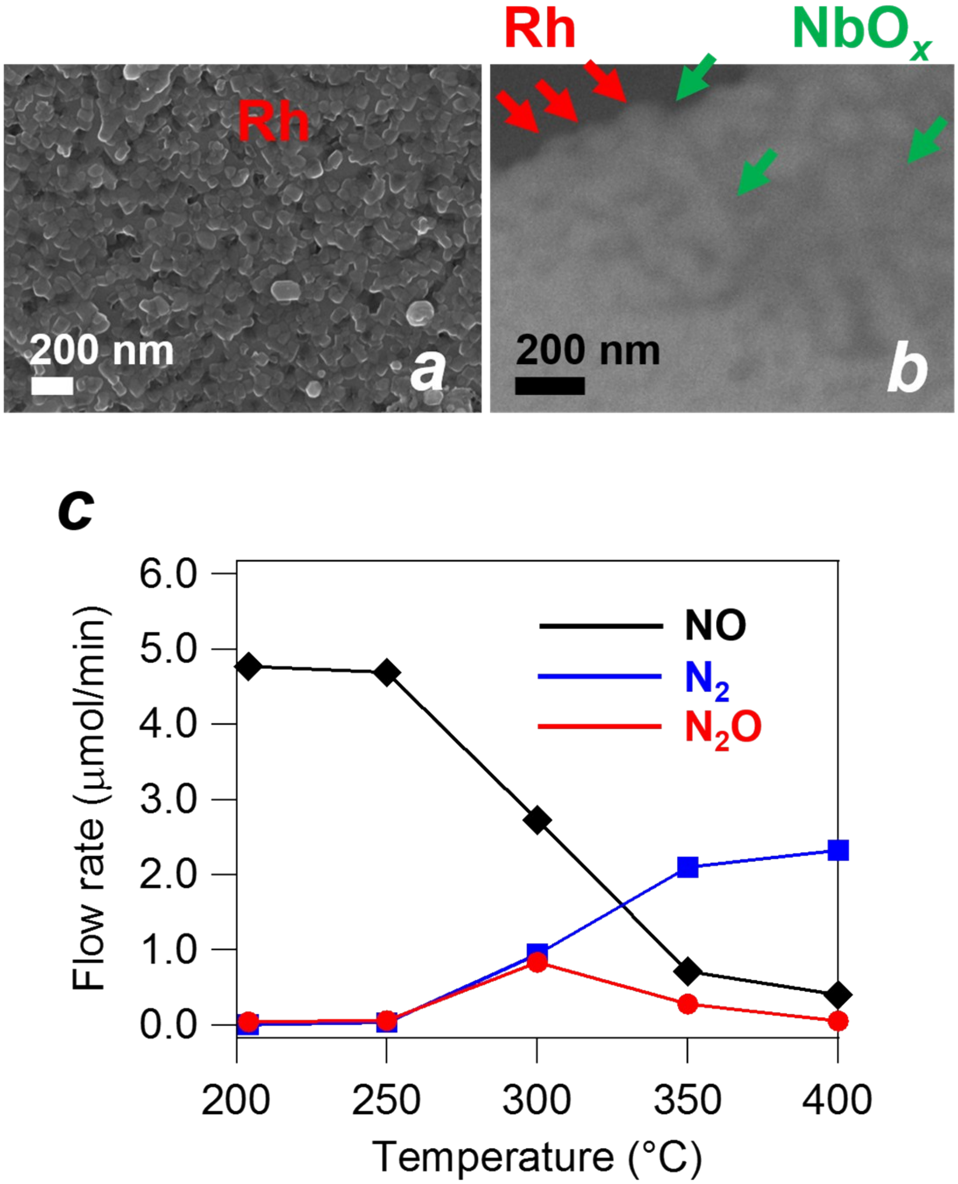


Figure S8. SEM image (*a*) and cross-section SEM image (*b*) of a Rh@NbO$_x$ material prepared at high temperatures (hereafter called H-Rh@NbO$_x$: prepared at 600 °C in NO:CO=1:1:98 atmosphere). The Rh phase in the H-Rh@NbO$_x$ was larger in grain size (~100 nm) than that in the material prepared at temperatures up to 400 °C (Figure 3; Figures S2-S5). The H-Rh@NbO$_x$ rarely exposed the NbO$_x$ phase (green allows in (*b*)) to the atmosphere, the surface of which was almost fully coated with Rh (red allows in (*b*), see also (*a*)). The NO remediation over the H-Rh@NbO$_x$ was followed by N$_2$O generation in the temperature range from 300 to 350 °C (*c*).