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Cite this: *RSC Adv.*, 2017, 7, 9628

## N<sub>2</sub>O-emission-free exhaust remediation by Rh-NbO<sub>x</sub> nanocomposites developed from Rh<sub>3</sub>Nb alloy precursor†

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Received 22nd November 2016

Accepted 13th January 2017

DOI: 10.1039/c6ra27168e

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Metal-oxide nanocomposites comprising rhodium (Rh) nanoparticles (<50 nm) and oxygen-deficient niobium oxides (NbO<sub>x</sub>;  $x < 5/2$ ) were developed from Rh<sub>3</sub>Nb alloy precursors. The Rh-NbO<sub>x</sub> nanocomposite exhibited enhanced activity toward the catalytic remediation of nitrogen oxide (NO) in the presence of carbon monoxide (CO) without emissions of nitrous oxide (N<sub>2</sub>O) due to the promoted dissociation of NO admolecules at the Rh/NbO<sub>x</sub> interface.

Green-house gases, such as carbon dioxide (CO<sub>2</sub>), are becoming a serious hazard for the world's environment.<sup>1</sup> In particular, nitrous oxide (N<sub>2</sub>O) is a universal issue because of its ability to absorb infrared light and is contributes 200 fold more than CO<sub>2</sub> to global warming.<sup>2</sup> Currently, 1.5% of atmospheric N<sub>2</sub>O is released as part of nitrogen oxides (NO<sub>x</sub>: N<sub>2</sub>O, NO, N<sub>2</sub>O<sub>5</sub> and NO<sub>2</sub>) contained in automobile exhaust.<sup>3</sup> The NO<sub>x</sub> are remediated to environmentally benign nitrogen (N<sub>2</sub>) through redox reactions with carbon monoxide (CO) that is produced by the incomplete combustion of fuels (NO<sub>x</sub> remediation).<sup>4</sup> Nanoparticles of precious-group metals (PGM), particularly rhodium (Rh), are widely used as the catalyst for the NO<sub>x</sub> remediation.<sup>5</sup> However, the current Rh catalysts preferentially promote the partial reduction of NO to N<sub>2</sub>O (*i.e.*,  $\text{NO} + 1/2\text{CO} = 1/2\text{N}_2\text{O} + 1/2\text{CO}_2$ ) instead of the desired NO<sub>x</sub> remediation, when applied to the low-temperature exhaust (<350 °C) from hybrid engines or two-stroke engines of motorcycles.<sup>6</sup> In order to meet the demands for hybrid cars and motorcycles in the advanced and emerging countries, respectively, it is of growing importance to develop high-performance NO<sub>x</sub> remediation catalysts for the low-temperature exhaust without N<sub>2</sub>O emissions.<sup>7</sup>

It is acknowledged that Rh nanoparticles exhibit enhanced performance for either the catalytic decomposition of N<sub>2</sub>O (*i.e.*,  $\text{N}_2\text{O} = \text{N}_2 + 1/2\text{O}_2$ ) or the low-temperature NO<sub>x</sub> remediation, when

finely dispersed and immobilized on oxide-based supporting materials (supported Rh catalysts).<sup>8</sup> Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub> (Mullite)-supported Rh nanoparticles efficiently decomposed N<sub>2</sub>O at 350 °C or higher temperatures.<sup>9</sup> Supporting materials comprising cerium-doped Al<sub>2</sub>O<sub>3</sub> realized the N<sub>2</sub>O decomposition even at 250 °C.<sup>10</sup> It was also demonstrated that the Rh nanoparticles supported on cerium-zirconium oxides ((Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>y</sub>;  $y < 2$ ) remediated the NO<sub>x</sub> at 250 °C or higher temperatures. Rh nanoparticles supported on aluminium phosphate (AlPO<sub>4</sub>) showed an improved low-temperature activity toward the NO<sub>x</sub> remediation.<sup>10</sup> However, none of these Rh catalysts has achieved the desired low-temperature NO<sub>x</sub> remediation without N<sub>2</sub>O emission.

Herein, we report that the N<sub>2</sub>O emission-free, low-temperature NO<sub>x</sub> remediation can be realized by a nanocomposite of Rh metal and niobium oxide (*i.e.* Rh@NbO<sub>x</sub>) that was developed from a Rh-Nb alloy precursor (*i.e.* Rh<sub>3</sub>Nb) through controlled annealing in a gas mixture comprising NO and CO. Powder X-ray diffraction (pXRD), hard X-ray photo-emission spectroscopy (HAXPES) and transmission-electron microscopy (TEM) have demonstrated that Rh@NbO<sub>x</sub> consisted of interconnected Rh nanoparticles (particle size < 50 nm) that were further incorporated in a matrix of oxygen-deficient niobium oxide (NbO<sub>x</sub>;  $x < 2.5$ ). *In situ* X-ray photo-emission spectroscopy (*in situ* XPS) has shown that the NbO<sub>x</sub> matrix can dissociate NO<sub>ad</sub> at room temperature through the formation of N-Nb bonds at the Rh/NbO<sub>x</sub> interface. As a result of the promoted NO<sub>ad</sub> dissociation, the Rh@NbO<sub>x</sub> efficiently catalysed the remediation of NO to N<sub>2</sub> ( $\text{NO} + \text{CO} = 1/2 \text{N}_2 + \text{CO}_2$ ) without N<sub>2</sub>O emission at low temperatures.

Pure-phased Rh<sub>3</sub>Nb ingots were first synthesized using arc-melting elemental metals in pure Ar atmosphere. The Rh<sub>3</sub>Nb ingot was then powdered to an average particle size of 50 μm. The obtained Rh<sub>3</sub>Nb powder was exposed to a He-balanced stream of NO/CO gas mixture at elevated temperatures up to

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra27168e



600 °C (NO : CO : He = 1 : 1 : 98 in volume) to convert the Rh<sub>3</sub>Nb precursor to the desired Rh@NbO<sub>x</sub> nanocomposite (see ESI for details†).

Fig. 1 shows the powder X-ray diffraction (pXRD) profiles for the Rh<sub>3</sub>Nb precursor and the Rh@NbO<sub>x</sub> nanocomposite. The pXRD peaks for the Rh<sub>3</sub>Nb precursor were located at 40.43, 47.02, 68.74, 82.86 and 87.44 degrees, which corresponded to the 111-, 200-, 220-, 311- and 322 reflections of the cubic Au<sub>3</sub>Cu structure (*Pm*3̄*m*, *a* = 0.3865 nm), respectively.<sup>11</sup> After the exposure to the NO/CO gas mixture, the pXRD peaks shifted toward higher diffraction angles as a result of phase separation of the uniform alloy into the nanocomposite consisting of Rh and NbO<sub>x</sub>. The major reflections from the Rh@NbO<sub>x</sub> were observed at 40.92, 47.62, 69.98, 84.19 and 88.93 degrees, corresponding to the 111-, 200-, 220-, 311- and 322 reflections of the face-center cubic (FCC) structure of Rh metal (*Fm*3̄*m*, *a* = 0.3804 nm).<sup>12</sup> In addition to the intense reflections from the Rh phase, there were recognized weak and broad reflections from a NbO<sub>x</sub> phase with the crystal structure identical to that of niobium pentoxide, Nb<sub>2</sub>O<sub>5</sub>.<sup>13</sup>

To investigate the chemical state of the Rh@NbO<sub>x</sub> nanocomposite, we conducted hard X-ray photoemission spectroscopy (HAXPES; photon energy = 5.9534 keV). Fig. 2a shows the HAXPES spectra for the Rh<sub>3</sub>Nb precursor and the Rh@NbO<sub>x</sub> in the Nb 3d region. The Nb 3d<sub>5/2</sub>- and 3d<sub>3/2</sub> photoemission peaks for the Rh<sub>3</sub>Nb were located at the binding energy of 203.0 and 205.9 eV, respectively.<sup>14</sup> The corresponding peaks for the Rh@NbO<sub>x</sub> were located at the peak positions of 206.9 and 209.7 eV, showing that the Nb cations had a valence close to +5.<sup>15</sup>

The HAXPES spectra in the Rh 3d region are presented in Fig. 2b. The Rh 3d<sub>5/2</sub> peaks for the Rh<sub>3</sub>Nb precursor and pure Rh metal were observed at different binding energies, 306.5 and 307.0 eV, respectively. The Rh@NbO<sub>x</sub> showed a Rh 3d<sub>5/2</sub> peak at 306.7 eV, in between those for the Rh<sub>3</sub>Nb alloy precursor and pristine Rh, indicating the metallic nature of the Rh phase included in the Rh@NbO<sub>x</sub>. The intense photoemission at 307.9 eV was assigned to a thin oxide layer (Rh<sup>3+</sup>O<sub>y</sub>) over the Rh surface because the emission was prominent when probed with surface-sensitive XPS (photon energy = 1.4866 keV; see Fig. S1†).

The nanostructure of the Rh@NbO<sub>x</sub> was investigated with a scanning transmission electron microscope (STEM) equipped

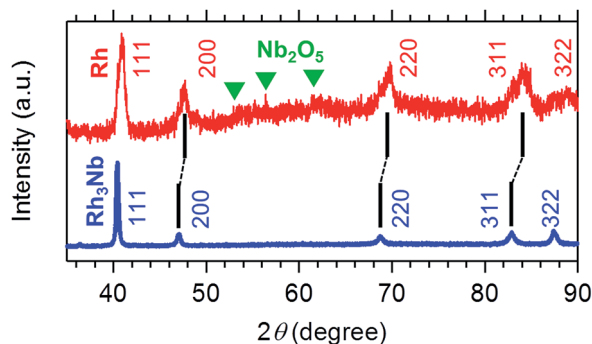


Fig. 1 Powder X-ray diffraction (pXRD) profiles for the Rh<sub>3</sub>Nb precursor (blue) and the developed Rh@NbO<sub>x</sub> nanocomposite (red). The green triangles correspond to the reflections from Nb<sub>2</sub>O<sub>5</sub>.

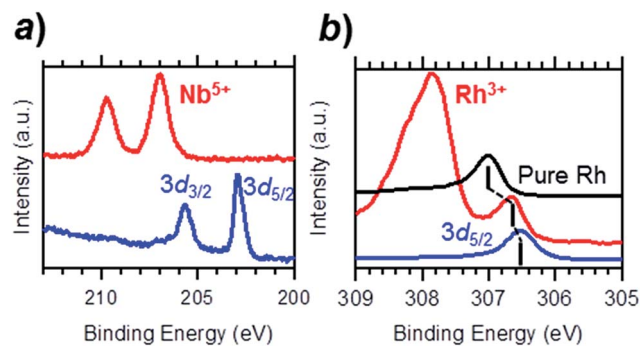


Fig. 2 Hard X-ray photoemission spectroscopy (HAXPES) profiles for the Rh<sub>3</sub>Nb precursor (blue) and the Rh@NbO<sub>x</sub> (red) in the (a) Nb 3d- and (b) Rh 3d regions.

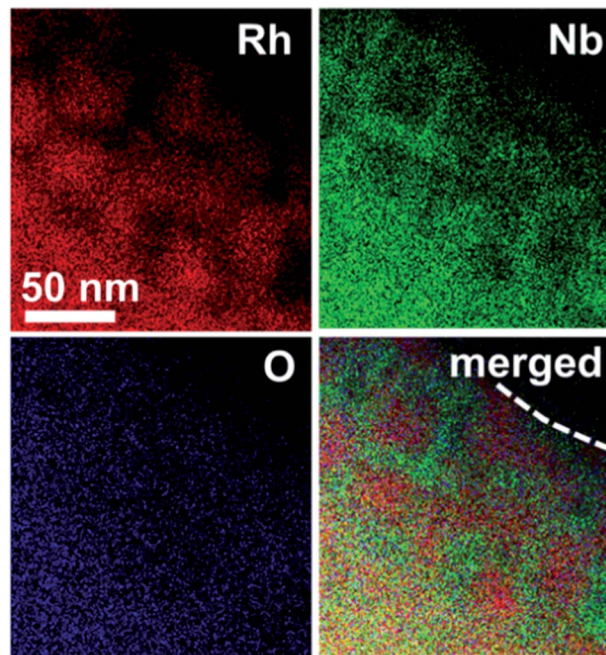


Fig. 3 Compositional mapping images of the Rh@NbO<sub>x</sub> acquired with a scanning transmission microscope (STEM) equipped with an energy-dispersive spectrometer (EDS). The broken curve in the merged image corresponds to the interface between the materials surface and the atmosphere.

with an energy-dispersion spectrometer (EDS) (Fig. 3, see also Fig. S2–S4† for STEM/TEM images). It was demonstrated that Rh was distributed in the bulk and/or over the surface of the Rh@NbO<sub>x</sub> as nanoparticles with an average size of 50 nm. Importantly, the Rh nanoparticles were connected to each other to form a network structure. The distributions of Nb and O were exclusive to that of Rh, showing that Nb and O formed a NbO<sub>x</sub> phase. Most of the Rh network was incorporated in the NbO<sub>x</sub> matrix and partly exposed to the atmosphere (see Fig. S5† for the scanning-electron microscope (SEM) images of the Rh@NbO<sub>x</sub>). The Rh exposure was surrounded by the NbO<sub>x</sub> matrix over the catalyst surface, forming a metal/oxide interface around its perimeter.



Fig. 4 shows the exhaust-remediation performance of the Rh@NbO<sub>x</sub> and the control Rh catalyst (see ESI for the experimental details†). The Rh- and Rh@NbO<sub>x</sub> catalysts were subjected to a steady stream of simulated exhaust (NO : CO : He = 1 : 1 : 98 in volume%; space velocity = 30 000 h<sup>-1</sup>; flow rates of NO and CO = 5 μmol min<sup>-1</sup>) at different temperatures from 200 to 400 °C (see Fig. S6† for the FTIR spectra for the effluent gas).

The Rh catalyst converted NO to N<sub>2</sub> and/or N<sub>2</sub>O at 250 °C and higher temperatures (Fig. 4a). The flow rate of N<sub>2</sub>O in the effluent gas was 1.1 μmol min<sup>-1</sup> at 250 °C, showing that 44% of the incoming NO was converted to N<sub>2</sub>O (see bar charts in the inset). The conversion rate from NO to N<sub>2</sub>O still remained 13% at 300 °C (inset). The residual N<sub>2</sub>O disappeared from the effluent gas when the temperature exceeded 350 °C. By clear contrast to the trend observed for the Rh catalyst, the Rh@NbO<sub>x</sub> remediated NO with much lowered N<sub>2</sub>O emission (Fig. 4b). The N<sub>2</sub>O concentration in the effluent gas was less than 2% at 250 °C or higher temperatures (see insets). Moreover, the Rh@NbO<sub>x</sub> fully converted NO to N<sub>2</sub> at 300 °C or higher temperatures. Considering the experimental data and the reported lower performance of the palladium-based catalysts than that of Rh-based catalysts, we concluded that the Rh@NbO<sub>x</sub> was superior to the state-of-the-art PGM catalysts for the N<sub>2</sub>O emission-free NO remediation at low temperatures.<sup>16</sup>

Finally, *in situ* X-ray photoemission spectroscopy (*in situ* XPS) was conducted to reveal the mechanism behind the N<sub>2</sub>O emission-free NO remediation over the Rh@NbO<sub>x</sub> catalyst. A polycrystalline Rh<sub>3</sub>Nb sample was polished to a mirror finish prior to use in the experiments. Single-crystalline Rh was sliced and mirror-polished to develop the (111) surface (see ESI for details†). The samples were introduced into an ultra-high vacuum (UHV) chamber, cleaned by Ar<sup>+</sup> bombardment and exposed to NO gas up to one-monolayer adsorption (1.0 L) at room temperature. The NO-adsorbed sample surfaces were then observed using an XPS spectrometer (monochromatized ALKα; photon energy = 1.4866 keV) in the N 1s- and O 1s regions at elevated temperatures from room temperature to 800 °C.

Fig. 5a shows a contour plot of the N 1s photoemission intensity for the Rh(111) surface as a function of temperature

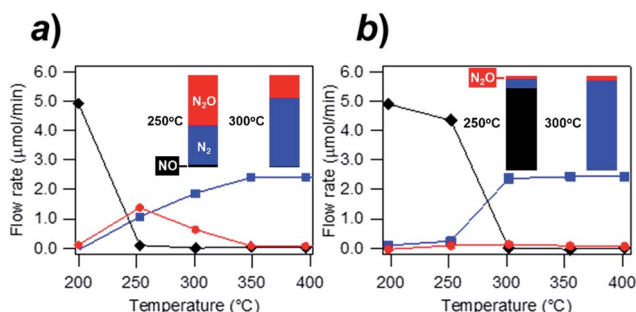


Fig. 4 Remediation of simulated exhaust (NO : CO : He = 1 : 1 : 98 vol%) at different temperatures using the (a) Rh catalyst and (b) Rh@NbO<sub>x</sub> catalyst. The black, blue and red curves respectively correspond to the flow rates of NO, N<sub>2</sub> and N<sub>2</sub>O in the effluent gas. Bar charts in the insets show the nitrogen concentration (%) in the flows of NO, N<sub>2</sub> or N<sub>2</sub>O at 250 and 300 °C.

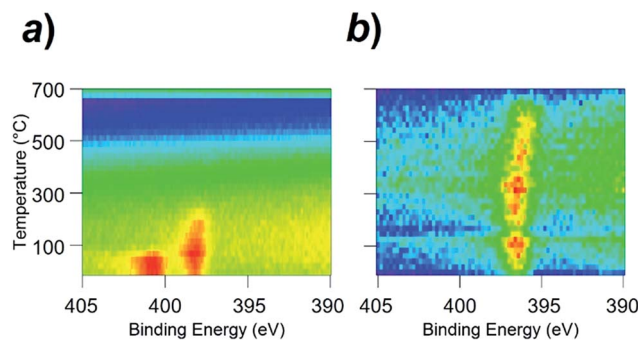


Fig. 5 *In situ* X-ray photoemission spectra (*in situ* XPS) for (a) the clean Rh surface and (b) Rh<sub>3</sub>Nb surface. In terms of colour, red indicates high intensity, blue indicates low intensity.

and binding energy. At room temperature, the N 1s emission peak was located at the binding energy of 400.6 eV. This value is assigned to the NO molecules adsorbed onto the Rh surface (NO<sub>ad</sub>).<sup>11</sup> With an increase in the surface temperature, the N 1s peak was 2.5 eV shifted at 100 °C toward the lower binding energy, as the result of the dissociation of NO<sub>ad</sub> into N<sub>ad</sub> and O<sub>ad</sub> (see Fig. S7† for the *in situ* XPS spectra in the O 1s region).<sup>11</sup> The N<sub>ad</sub> was thermally desorbed from the surface when the temperature reached 250 °C, diminishing the N 1s emission.

Unlike the Rh surface, as seen in Fig. 5b, the N 1s-emission peak from the NO-adsorbed Rh<sub>3</sub>Nb surface was located at 396.8 eV at room temperature, which corresponds to the atomic N<sub>ad</sub> instead of the molecular NO<sub>ad</sub>. This binding energy (396.8 eV) is close to the value for the N 1s emissions from niobium nitride (NbN) and/or niobium oxynitride (NbON), 396.2 eV.<sup>15</sup> The Rh<sub>3</sub>Nb precursor adopted dissociative adsorption of NO to develop the Rh@NbO<sub>x</sub> phase on the surface, and the nitrogen adatoms were adsorbed not on the Rh site but on the Nb site to form N–Nb bonds.

One of the major paths for the catalytic N<sub>2</sub>O generation is the combination of NO<sub>ad</sub> and N<sub>ad</sub> over the catalyst surface (NO<sub>ad</sub>–N<sub>ad</sub> reaction: NO<sub>ad</sub> + N<sub>ad</sub> = N<sub>2</sub>O).<sup>17</sup> The low performance of the traditional Rh catalysts for the N<sub>2</sub>O emission-free NO<sub>x</sub> remediation is ultimately due to the limited ability of the Rh surface dissociating the NO<sub>ad</sub> only at temperatures higher than 100 °C.<sup>18</sup> The Rh@NbO<sub>x</sub> catalyst can efficiently promote the NO<sub>ad</sub> dissociation because the NbO<sub>x</sub> matrix adopts the N<sub>ad</sub> from the Rh surface to form thermodynamically stable NbON at the Rh/NbO<sub>x</sub> interface.<sup>19</sup> Indeed, the Rh@NbO<sub>x</sub> catalyst containing larger Rh grains and fewer Rh/NbO<sub>x</sub> interfaces on the surface (Fig. S8†) did not realize the desired N<sub>2</sub>O-free NO remediation.

## Conclusion

In conclusion, we successfully materialized a catalytic nanocomposite comprising nanometer-thick Rh networks and oxygen-deficient NbO<sub>x</sub> matrices, namely Rh@NbO<sub>x</sub>, by annealing an Rh<sub>3</sub>Nb alloy precursor in the NO/CO atmosphere. The synthesized Rh@NbO<sub>x</sub> nanocomposite exhibited higher catalytic performance than that of pristine Rh catalysts toward the N<sub>2</sub>O emission-free NO remediation. The enhanced performance of the Rh@NbO<sub>x</sub> catalyst was attributed to the promoted NO





dissociation due to the formation of N–Nb bonds at the metal/oxide interface. The N<sub>2</sub>O emission-free NO remediation using the Rh@NbO<sub>x</sub> catalyst will prompt further research and development for high-performance nanocomposite catalysts, realizing reduced impacts to the global atmosphere.

## Acknowledgements

This study was preliminarily supported by Toyota Motor Corporation and the JST PRESTO program “New Materials Science and Element Strategy”. The HAXPES measurements were performed under the approval of the NIMS Synchrotron X-ray Station (Proposal No. 2015B4605). This study was also supported by NIMS microstructural characterization platform as a program of “Nanotechnology Platform” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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