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Genie in the Egg: a nanophase-separated catalyst emerges out of  $\text{Ni}_3\text{Nb}$  alloy precursor to exhibit higher performance than the state-of-the-art Pt catalysts toward the remediation of automobile exhaust.

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# Nanophase-separated Ni<sub>3</sub>Nb as an automobile exhaust catalyst†

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Catalytic remediation of automobile exhaust has relied on precious metals (PMs) including platinum (Pt). Herein, we report that an intermetallic phase of Ni and niobium (Nb) (*i.e.*, Ni<sub>3</sub>Nb) exhibits a significantly higher activity than that of Pt for the remediation of the most toxic gas in exhaust (*i.e.*, nitrogen monoxide (NO)) in the presence of carbon monoxide (CO). When subjected to the exhaust-remediation atmosphere, Ni<sub>3</sub>Nb spontaneously evolves into a catalytically active nanophase-separated structure consisting of filamentous Ni networks (thickness < 10 nm) that are incorporated in a niobium oxide matrix (*i.e.*, NbO<sub>x</sub> ( $x < 5/2$ )). The exposure of the filamentous Ni promotes NO dissociation, CO oxidation and N<sub>2</sub> generation, and the NbO<sub>x</sub> matrix absorbs excessive nitrogen adatoms to retain the active Ni<sup>0</sup> sites at the metal/oxide interface. Furthermore, the NbO<sub>x</sub> matrix immobilizes the filamentous Ni at elevated temperatures to produce long-term and stable catalytic performance over hundreds of hours.

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## Introduction

The environmental impact of automobile exhaust is becoming a challenge not only for rising countries but also for the global community.<sup>1–3</sup> Remediation of automobile exhaust relies on catalytic converters consisting of precious metals (PMs) including platinum (Pt). The consumption of PMs is increasing to meet the demands of ground transportation in emerging countries and the tighter emissions limits in advanced countries.<sup>4</sup> Moreover, PM catalysts are required by different technologies, such as polymer-electrolyte membrane fuel cells.<sup>5</sup> The development of PM-free catalytic materials is highly desirable to reduce the use of PMs in the automobile industry due to possible depletion of PMs in the near future.<sup>6</sup>

Earth-abundant 3d metals including nickel (Ni) were once considered for use as automobile exhaust catalysts.<sup>7,8</sup> However,

none of these 3d metals were realistic alternatives to PMs primarily due to their inherent susceptibility to dissociative adsorption of nitrogen oxides (NO<sub>x</sub>) in the exhaust.<sup>9,10</sup> Indeed, the adsorption energies of oxygen and nitrogen atoms to the Ni surface are, 470 kJ mol<sup>−1</sup> (O<sub>ad</sub>-Ni(111))<sup>9</sup> and 470 kJ mol<sup>−1</sup> (N<sub>ad</sub>-Ni(111)),<sup>10</sup> respectively, which is 10–15% larger than the corresponding values for the Pt surface (*i.e.*, 405 kJ mol<sup>−1</sup> (O<sub>ad</sub>-Pt(111))<sup>9</sup> and 430 kJ mol<sup>−1</sup> (N<sub>ad</sub>-Pt(111))), respectively.<sup>10</sup> The 3d metals are readily deactivated when subjected to the exhaust atmosphere because the adatoms form stable blocking layers over the surface that inhibit further catalysis (*i.e.*, catalyst poisoning).<sup>11</sup> Another drawback of the 3d metals for exhaust remediation is their low stability to thermal cycles. Automobile exhaust catalysts are assembled into catalytic converters in the form of supported nanoparticles (particle size < 10 nm).<sup>12,13</sup> The 3d metal nanoparticles are prone to particle agglomeration *via* the Ostwald ripening process because their melting points are close to the operation temperatures of catalytic converters (<300 °C for four-stroke gasoline engines).<sup>14,15</sup>

Herein, we report that a nanophase-separated structure emerging from an intermetallic phase of Ni and niobium (Nb) (*i.e.*, nanophase-separated Ni<sub>3</sub>Nb) exhibits significantly higher catalytic performance than that of Pt catalysts for the remediation of one of the most toxic chemical species in exhaust (*i.e.*, nitrogen monoxide (NO)) in the presence of carbon monoxide (CO).<sup>16</sup> Microscopic investigations including *in situ* transmission electron microscopy have demonstrated that the catalytic performance of nanophase-separated Ni<sub>3</sub>Nb is ultimately attributed to filamentous Ni and a NbO<sub>x</sub> matrix, which spontaneously emerges on the intermetallic surface in the reaction atmosphere due to selective oxidation of Nb. The NbO<sub>x</sub> matrix

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absorbs nitrogen adatoms from the Ni surface to retain the active  $\text{Ni}^0$  sites for improved NO remediation activity. Moreover, the filamentous Ni forms an agglomeration-tolerant network inside and/or over the surface of the  $\text{NbO}_x$  matrix, which results in long-term stable NO remediation for more than 500 hours.

## Results and discussion

A  $\text{Ni}_3\text{Nb}$  intermetallic precursor (average particle size: 50  $\mu\text{m}$ ) was obtained by powdering  $\text{Ni}_3\text{Nb}$  ingots synthesized by arc-melting elemental metals in a pure argon atmosphere (see Fig. S1 and S2† for characterization data of the different intermetallics including  $\text{Ni}_3\text{Nb}$ : powder X-ray diffraction (pXRD)<sup>17</sup> and hard X-ray photoemission spectra (HAXPES)). The powder of the elemental metals, such as Ni, Pt, Nb and  $\text{Nb}_2\text{O}_5$ , was used as purchased as the control catalysts.  $\text{Nb}_2\text{O}_5$ -supported Ni nanoparticles were also synthesized and used as a control (see ESI† for details).

Each of the catalysts was transferred into a gas-circulation reactor (see Experimental section). An aliquot consisting of 10 kPa of the reactant gas ( $\text{NO} : \text{CO} = 1 : 1$ ) was circulated through the catalyst powder at 325 °C. Fig. 1a shows the time course of the gas composition over the  $\text{Ni}_3\text{Nb}$ , Pt, Ni and Nb materials. Pt exhibited a finite NO remediation activity, reaching 7.5% NO remediation 35 min after exposure to the reactant gas. Neither Ni nor Nb promoted NO remediation in 60 min. The  $\text{Ni}_3\text{Nb}$  material exhibited a much higher NO remediation activity than that of Ni, Nb or even Pt, and a NO remediation of 96% was achieved in 11 min.

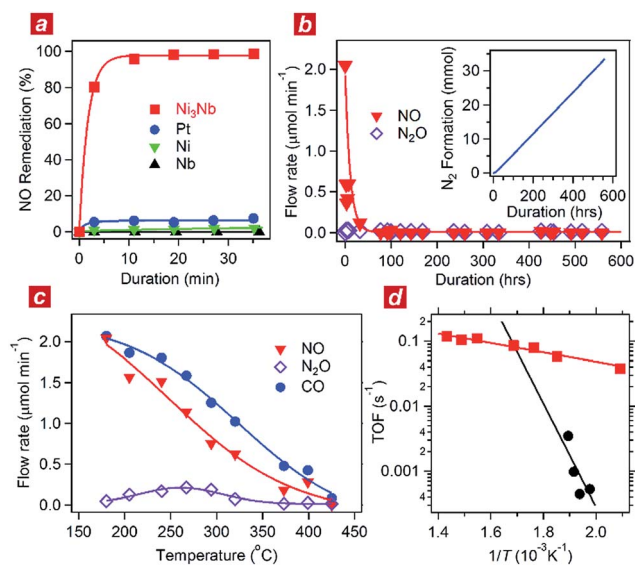
Fig. 1b shows the results of a long-duration catalytic test for the  $\text{Ni}_3\text{Nb}$  material in a steady flow of a He-balanced reactant gas (5 ml  $\text{min}^{-1}$ ;  $\text{NO} : \text{CO} : \text{He} = 1 : 1 : 98$ ; 400 °C; feeding rate = 5  $\text{cm}^3 \text{min}^{-1}$ ; space velocity = 30 000  $\text{h}^{-1}$ ). Neither NO nor  $\text{N}_2\text{O}$  was detected in the effluent gas 50 h after the exposure to the catalyst. The  $\text{Ni}_3\text{Nb}$  material promoted NO remediation for more than 500 hours, and this catalyst converted 66 mmol of NO to  $\text{N}_2$  (inset of Fig. 1b). Fig. 1c shows the result of catalytic tests conducted at different temperatures after the long-duration test. The CO concentration monotonously decreased with increasing temperature and reached zero at 425 °C. The NO concentration decreased more steeply than the CO concentration because a portion of the NO was converted to nitrous oxide ( $\text{N}_2\text{O}$ ) in a temperature range from 175 to 375 °C *via* the following reaction path:  $\text{NO} + 1/2\text{CO} = 1/2\text{N}_2\text{O} + 1/2\text{CO}_2$ . The  $\text{NO}_x$  fraction in the effluent gas disappeared at 425 °C or higher temperatures, where the reaction proceeded *via* the major path (*i.e.*,  $\text{NO} + \text{CO} = 1/2\text{N}_2 + \text{CO}_2$ ).

Fig. 1d shows the turnover frequency (TOF) of the  $\text{Ni}_3\text{Nb}$  material for NO remediation as a function of the inverse of the temperature, which was calculated from the data in Fig. 1c. The number of active sites on the sample surface was determined to be 0.47  $\mu\text{mol g}^{-1}$  by CO chemisorption at 298 K. The TOF of the  $\text{Ni}_3\text{Nb}$  material was calculated to be 0.075  $\text{s}^{-1}$  at 300 °C, which was higher than that for the commercial Pt catalysts (0.025  $\text{s}^{-1}$ ) and even higher than that reported for the state-of-the-art Pt–Rh catalysts (0.047  $\text{s}^{-1}$ ).<sup>18–20</sup> The  $\text{Ni}_3\text{Nb}$  material can be employed as a rational substitute for traditional PM catalysts for NO remediation based on the high TOF and long-term stability.

To elucidate the origin of the catalytic performance of the  $\text{Ni}_3\text{Nb}$  material, we conducted microscopic investigations including *in situ* transmission electron microscopy.<sup>21</sup> As shown in Fig. 2a, a low-contrast phase propagated from both the top-left and bottom-right corners of the  $\text{Ni}_3\text{Nb}$  material after exposure to the reactant gas ( $\text{NO} : \text{CO} : \text{Ar} = 1 : 1 : 98$ ) at 400 °C (red arrows show the propagation direction of the low-contrast phase; see ESI† for the *in situ* TEM observation). This low-contrast phase consisted of Ni metal and low-crystalline, oxygen-deficient  $\text{NbO}_x$  ( $x < 5/2$ ) with a crystal structure that was identical to that of  $\text{Nb}_2\text{O}_5$  (see Fig. S3 and S4† for HAXPES and Fig. S5† for pXRD<sup>22</sup>).

The  $\text{Ni}_3\text{Nb}$  material after the catalysis was further characterized using high-resolution transmission electron microscopes (TEM and STEM). As expected from the HAXPES and pXRD analyses, the surface layer of the material was consisted of Ni metal and low-crystalline  $\text{NbO}_x$  after the gas exposure. Importantly, the Ni phase was not dispersed as isolated nanoparticles on the  $\text{NbO}_x$  surface (Fig. 2b, see also Fig. S6†). As shown in the elemental-mapping images using electron energy loss spectroscopy (EELS; Fig. 2c), Ni formed a nanometer-thick filamentous network inside the bulk and/or over the surface to result in a nanophase-separated  $\text{Ni}_3\text{Nb}$ , and the distribution of this network was exclusive to the distributions of Nb or O.

Based on the TEM characterizations, a structural model of the catalytic centre of the nanophase-separated  $\text{Ni}_3\text{Nb}$  catalyst has been determined (Fig. 2d). When exposed to the reaction atmosphere, the intermetallic  $\text{Ni}_3\text{Nb}$  evolves into a nanophase-



**Fig. 1** Catalytic performance of the  $\text{Ni}_3\text{Nb}$  catalyst. (a) Time course of NO remediation at 325 °C over the  $\text{Ni}_3\text{Nb}$  (red), Pt (blue), Ni (green) and Nb (black) catalysts. (b) Long-term NO remediation over the  $\text{Ni}_3\text{Nb}$  catalyst at 400 °C in a steady flow of the He-balanced reactant gas. Inset shows the generation of  $\text{N}_2$  as a function of duration. (c) Concentrations of NO (red),  $\text{N}_2\text{O}$  (purple) and CO (blue) in the effluent gas presented as functions of temperature. (d) Turnover frequencies (TOFs) of the  $\text{Ni}_3\text{Nb}$  catalyst (red) and commercial Pt catalysts (black) for NO remediation plotted as functions of inverse temperature.





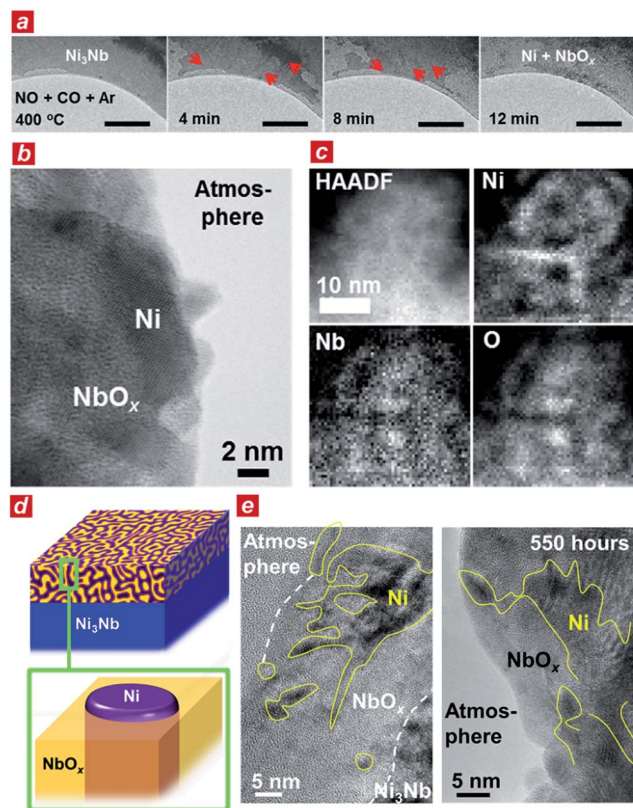


Fig. 2 Microscopic characterizations. (a) Evolution of nanophase-separated structures on the  $\text{Ni}_3\text{Nb}$  surface exposed to the Ar-balanced reactant gas at 400 °C. The scale bars correspond to 200 nm. (b) Scanning transmission microscope (STEM) image of the nanophase-separated  $\text{Ni}_3\text{Nb}$  catalyst. (c) Annular-dark field (HAADF) image and elemental-mapping images of the nanophase-separated  $\text{Ni}_3\text{Nb}$  catalyst. (d) Structural model of the nanophase-separated  $\text{Ni}_3\text{Nb}$  catalyst. (e) Cross-sectional transmission electron microscope (TEM) images of the nanophase-separated  $\text{Ni}_3\text{Nb}$  catalyst after 0.5 h (left) and 550 h of exposure to the reactant gas at 400 °C (right).

separated structure that consists of filamentous Ni and a  $\text{NbO}_x$  matrix ( $x < 5/2$ ). The filamentous Ni is ingrained in the  $\text{NbO}_x$  matrix and partially exposed to the atmosphere. Importantly, the filamentous Ni on the catalyst surface retained both the network structure and thickness even after the 550 h of gas exposure (Fig. 2e, see high-quality images in Fig. S7†). The long-term catalytic performance of the  $\text{Ni}_3\text{Nb}$  catalyst (see Fig. 1b) is ultimately due to the stability of the nanophase-separated structure on the surface, where filamentous Ni was immobilized in the  $\text{NbO}_x$  matrix, preventing thermal agglomeration. Indeed, artificially prepared  $\text{Nb}_2\text{O}_5$ -supported Ni nanoparticles exhibited lower NO remediation activity and shorter lifetime (Fig. S8†) because the Ni nanoparticles are dispersed over the support surface and not embedded by the  $\text{Nb}_2\text{O}_5$  matrix.

In addition, we performed *in situ* Fourier transform infrared spectroscopy (FTIR) and *in situ* XPS to elucidate the reaction kinetics behind the activity of the nanophase-separated  $\text{Ni}_3\text{Nb}$  catalyst. As shown in Fig. 3a, when subjected to the reaction atmosphere ( $\text{NO} : \text{CO} : \text{He} = 1 : 1 : 98$ , 400 °C), the Ni catalyst accepted oxygen adatoms to form  $\text{Ni}^{2+}\text{O}$ - and  $\text{Ni}_2^+\text{O}$  species on

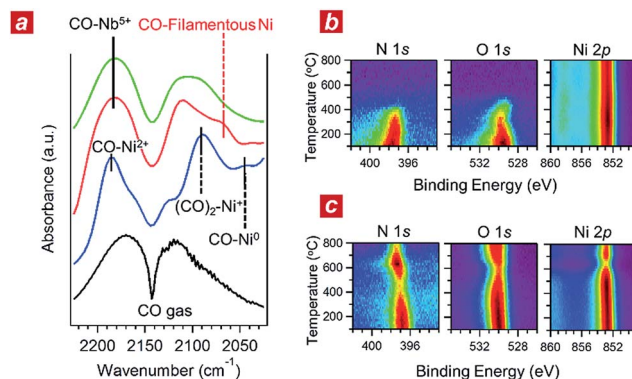


Fig. 3 *In situ* investigations of the reaction kinetics. (a) *In situ* Fourier transformation infrared (FTIR) spectra of the Ni (blue), nanophase-separated  $\text{Ni}_3\text{Nb}$  (red) and  $\text{Nb}_2\text{O}_5$  (green) acquired in the He-balanced reactant gas at 400 °C. (b) *In situ* X-ray photoemission (XPS) spectra for the (111) surface of single-crystalline Ni that was exposed to a monolayer of NO adsorption under ultra-high vacuum (UHV). The measurement temperature ranged from 100 to 800 °C. (c) *In situ* XPS spectra for the  $\text{Ni}_3\text{Nb}$  surface acquired under the same conditions as those in (b).

the surface. The FTIR peak at  $2044\text{ cm}^{-1}$ , which was assigned to the CO ad molecules on the metallic  $\text{Ni}^0$  sites, was much less intense than the peaks at  $2091$  or  $2183\text{ cm}^{-1}$  that corresponded to the CO ad molecules on the  $\text{Ni}^+$ - or  $\text{Ni}^{2+}$  sites, respectively.<sup>23,24</sup>

In contrast, CO molecules were adsorbed on the nanophase-separated  $\text{Ni}_3\text{Nb}$  at metallic  $\text{Ni}^0$  sites, resulting in an intense IR absorption at  $2071\text{ cm}^{-1}$ . No peaks corresponding to either  $\text{Ni}^+$ -CO or  $\text{Ni}^{2+}$ -CO were observed, instead, a single peak corresponding to  $\text{Nb}^{5+}$ -CO was recognized at  $2183\text{ cm}^{-1}$ .<sup>25</sup> It is important to note that the  $\text{Ni}^0$ -CO band for the nanophase-separated  $\text{Ni}_3\text{Nb}$  catalyst had a higher wavenumber ( $2071\text{ cm}^{-1}$ ) than the reported  $\text{Ni}^0$ -CO band for the pure Ni surface ( $2044\text{ cm}^{-1}$ ). The CO ad molecules are more weakly adsorbed on the filamentous Ni than those on the pure Ni surface. These weakly adsorbed CO molecules can migrate over the surface of the filamentous Ni to efficiently scavenge oxygen adatoms.

Fig. 3b shows the results of *in situ* XPS analysis for a single-crystalline Ni(111) surface (purchased from Surface Preparation Laboratory Co.) subjected to a monolayer of NO adsorption in an ultra-high vacuum (UHV). Intense N 1s- and O 1s photoemission peaks, which correspond to the dissociative adsorption of NO, were observed at 100 °C at binding energies of 397.7 eV and 529.6 eV, respectively.<sup>26</sup> Both the N 1s- and O 1s peaks became weak with increasing temperature and disappeared at around 400 °C due to the desorption of nitrogen and oxygen adatoms, respectively. The Ni 2p emission retained the peak position at 852.8 eV and became more intense as the adatoms desorbed from the surface.

The trend in the NO ad/desorption on the  $\text{Ni}_3\text{Nb}$  surface was the NO-adsorbed  $\text{Ni}_3\text{Nb}$  surface was located at a binding energy of 396.9 eV at 100 °C, indicating that the NO ad molecules dissociated into nitrogen and oxygen adatoms. This N 1s binding energy (*i.e.*, 396.9 eV) is consistent with that for niobium nitride ( $\text{NbN}$ ), which indicates that the nitrogen adatoms are not bound to Ni atoms but to Nb atoms.<sup>27</sup> The N 1s



emission became weaker as the temperature increased from 100 to 400 °C. However, this emission increased in intensity again at higher temperatures with a maximum at 600 °C.

This behaviour in the N 1s emission indicates that in contrast to those on the Ni surface, the nitrogen adatoms on the Ni<sub>3</sub>Nb surface can migrate more deeply into the bulk at approximately 400 °C than the probing depth of XPS (*i.e.*, <1 nm). The O 1s and Ni 2p emissions exhibited different behaviours than that observed for the N 1s emission. The O 1s and Ni 2p emissions were weakened at 600 °C and became intense again at higher temperatures. This trend was due to the nitrogen atoms, which migrate into the NbO<sub>x</sub> matrix at 400 °C, being donated back to the surface of the filamentous Ni at higher temperatures, resulting in decreased Ni and O emissions.

Based on the *in situ* spectroscopic results, we propose a possible reaction mechanism for the nanophase-separated Ni<sub>3</sub>Nb catalyst (Fig. 4). First, dissociative adsorption of NO on the surface of the filamentous Ni generates nitrogen and oxygen adatoms, which coat the exposed surface of the filamentous Ni (Fig. 4a). The nitrogen adatoms spill over to the surrounding NbO<sub>x</sub> matrix at the metal/oxide interface, creating active Ni<sup>0</sup> sites for adsorption of CO molecules. The oxygen vacancy of the NbO<sub>x</sub> matrix, the existence of which was demonstrated by HAXPES (Fig. S3†), accommodates the nitrogen atoms due to the ability of Nb to form N–Nb bonds that are as strong as O–Nb bonds, resulting in the formation of stable oxynitrides (NbON) (Fig. 4b).<sup>28</sup> The nitrogen atoms migrate through the NbO<sub>x</sub> matrix and are donated back to the perimeter of the filamentous Ni to promote N<sub>2</sub> formation. This process occurs in an analogous fashion to hydrogen spillover from metal nanoparticles to migrate through the supporting materials (*e.g.*, hydrogen atoms

on Ru/[Ca<sub>24</sub>Al<sub>28</sub>O<sub>64</sub>]<sup>4+</sup>(e<sup>−</sup>)<sup>4</sup>).<sup>29</sup> Then, two CO molecules are adsorbed by the free Ni<sup>0</sup> sites created by N<sub>2</sub> generation (Fig. 4c) and further oxidized by neighbouring oxygen adatoms to form two CO<sub>2</sub> molecules (Fig. 4d). The CO<sub>2</sub> formation creates four free Ni<sup>0</sup> sites at the perimeter of the Ni/NbO<sub>x</sub> interface where dissociative adsorption of two NO molecules occurs to complete the catalytic cycle.

## Conclusions

In conclusion, we have found that nanophase-separated Ni<sub>3</sub>Nb exhibits superior catalytic performance compared to that of Pt for NO remediation in the presence of CO. This nanophase-separated Ni<sub>3</sub>Nb efficiently catalyses NO remediation through the promoted absorption/back-donation of nitrogen atoms at the metal/oxide interface. It is also worth of noting that the Ni@NbO<sub>x</sub> can promote the desired NO remediation even in the presence of oxygen (Fig. S9†). The nanophase-separated Ni<sub>3</sub>Nb is highly tolerant to thermal agglomeration even during long-term catalysis at elevated temperatures because the filamentous Ni phase is stably incorporated in the NbO<sub>x</sub> matrix. The evolution of the nanophase-separated structures and catalytic functionalities may not be limited to Ni<sub>3</sub>Nb but could be expanded to a broad range of alloy systems containing elements with different affinities to oxidative atmospheres, such as Cu and Ni/Mn alloy materials,<sup>30</sup> to produce more earth-abundant and high-performance automobile catalysts to help us meet current environmental challenges.

## Notes

T. Tanabe and T. Fujita conducted TEM/STEM characterizations. T. Tokunaga and S. Arai and Y. Yamamoto carried out *in situ* TEM characterization. S. Ueda conducted HAXPES measurements. Catalytic performance tests were done by T. Tanabe, T. Imai and H. Abe. T. Tanabe and G. V. Ramesh prepared control catalysts. *In situ* XPS was carried out by S. Nagao, H. Hirata and S. Matsumoto. T. Fujita and H. Abe equally contributed to this work through direction of whole of the research and edition of the manuscript.

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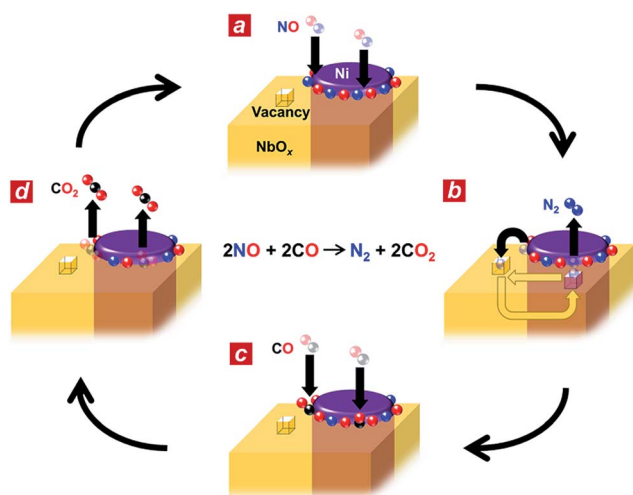


Fig. 4 Possible reaction mechanism for the Ni<sub>3</sub>Nb catalyst. (a) Nanophase-separated Ni<sub>3</sub>Nb catalyst in the exhaust atmosphere. Both the Ni surface and metal/oxide interface perimeter are occupied by dissociative NO ad molecules. (b) Oxygen vacancies on the NbO<sub>x</sub> matrix adopt nitrogen adatoms. The nitrogen atoms are donated back to the metal/oxide perimeter to generate N<sub>2</sub> molecules. (c) CO molecules are adsorbed at the free perimeter and (d) oxidized to CO<sub>2</sub> by the neighbouring oxygen adatoms.

Voltage Electron Microscope Laboratory at Nagoya University, and the Institute for Material Research at Tohoku University for XPS measurements.

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