Activating low-temperature diesel oxidation by single-atom Pt on TiO₂ nanowire array

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Supported metal single atom catalysts (SACs) present an emerging class of low-temperature catalysts with high reactivity and selectivity, which, however, face challenges on both durability and practicality. Herein, we report a single-atom Pt catalyst that is strongly anchored on a robust nanowire forest of mesoporous rutile titania grown on the channeled walls of full-size cordierite honeycombs. This Pt SAC exhibits remarkable activity for oxidation of CO and hydrocarbons with 90% conversion at temperatures as low as ~160 °C under simulated diesel exhaust conditions while using 5 times less Pt-group metals than a commercial oxidation catalyst. Such an excellent low-temperature performance is sustained over hydrothermal aging and sulfation as a result of highly dispersed and isolated active single Pt ions bonded at the Ti vacancy sites with 5 or 6 oxygen ions on titania nanowire surfaces.
Effective catalytic oxidation of CO, hydrocarbons (HCs), and nitrogen oxides (NOx) at low temperature is sought for ultra-clean and energy-efficient emission control over various energy systems, including both mobile and stationary sources. The exemplary catalytic devices range from diesel oxidation catalysts (DOCs)\(^2\), three-way catalysts (TWCs)\(^3\), selective catalytic reduction (SCR) of NO\(_x\) catalysts\(^4\), to lean NO\(_x\) traps (LNT)\(^5\). Developing low-temperature emission control solutions could enable advanced energy and environmental technologies that operate in a more energy-efficient and eco-friendly environment, such as the low-temperature combustion regime engine technology\(^6\).

In search of low-temperature oxidation catalysts, promising results have been shown using gold\(^7\)-9, metal oxides, such as Co\(_3\)O\(_4\)\(^10,11\), Co-Cu-Ce mixed oxides\(^1\), and La-based perovskites\(^2\). Unfortunately, these catalysts usually are poor in hydrothermal stability and susceptible to sulfur poisoning. Recently, supported platinum-group metal (PGM) single atom catalysts (SACs) have emerged as a new type of low-temperature catalysts with high reactivity and selectivity, due to their high metal dispersion, fewer types of active sites, low-coordination environments, quantum size effects, and enhanced metal-support interactions\(^12\)-19.

However, isolated metal atoms are usually mobile and tend to aggregate into clusters or particles during synthesis or reaction. Improving SACs’ stability and maintaining their high activity is one of the grand challenges\(^20\)-22 currently. Recently, Nie et al. reported highly active and stable Pt SACs supported by CeO\(_2\) that were prepared using the atom trapping method\(^23\). The catalyst showed good CO oxidation performance with total CO conversion at 148 °C and stability up to 500 °C. However, deactivation was observed after exposure to 800 °C. Meanwhile, the studies on SACs up to now have been limited to model reactions, such as CO oxidation and water gas shift. Little success has been achieved in the supported SACs so far over hydrocarbon oxidation at low temperature. Furthermore, the reported SACs have been limited to lab-scale reactors with a small amount of powders. There has yet to be an evaluation of SACs in field-size catalytic reactors under realistic exhaust conditions, although such a real-world demonstration is necessary to translate the scientific advancement to technological applications.

In this work, durable single-atom Pt catalysts are successfully demonstrated to be anchored on titania nanowire array (nano-array, NA) forest integrated on full-size honeycomb substrates, as denoted as Pt\(_1/\)TiO\(_2\) NA catalyst. As a SAC based monolithic catalyst, it displays a sustained and remarkably high oxidation activity over CO and hydrocarbons at low temperature under simulated diesel exhaust, the industry-defined conditions protocled by USDRIVE\(^24\) and under heavy duty diesel (HDD) engine transient dynamic cycles, as illustrated and summarized in Fig. 1a. We demonstrate that the temperature of 90% conversion, \(T_{90}\), for CO and HCs in the clean diesel combustion (CDC) simulated exhaust evaluation\(^25\) approaches 160 °C, while using five times less PGM than a benchmark commercial DOC. Notably, the single-atom Pt active sites are highly robust after hydrothermal (HT) aging at 700 °C for 100 h as a result of their fixation at the five-fold coordinated Ti vacancy sites bonded with five or six oxygen ions on titania nanowire surfaces. Such a NA supported Pt SAC retains its nanowire array structure as well as abundant Pt single-atom species on the TiO\(_2\) nanowire surfaces after the hydrothermal aging and simulated exhaust test.

**Results**

**Structure and stability of single-atom Pt on TiO\(_2\) nanowire arrays.** It is noted that pure rutile phase, the most thermodynamically stable among TiO\(_2\) polymorphs as typical oxidation catalyst support materials\(^26,27\), is realized in the form of TiO\(_2\) NA forest in this study. Additionally, the hierarchically structured NA forest allows efficient mass transport and good catalytic performance in supported catalysts in a honeycomb monolithic device form, with advantageous attributes, such as low pressure drop and high surface area\(^28\). In this work, densely packed forest of mesoporous rutile TiO\(_2\) NA was successfully grown onto channel surfaces of cordierite honeycombs with various sizes ranging from a size of 0.2 L (63 mm × 63 mm × 50 mm), to a full-size core of 1.2 L (Φ 145 mm × 75 mm), which was used for the measurement of CO oxidation, determined from inductively coupled plasma mass spectrometry (ICP-MS) measurement, is ~23 wt.% or ~69 g L\(^{-1}\). The T\(_{90}\) for Pt\(_1/\)TiO\(_2\) NA was grown uniformly with a height of ~3 μm, and arranged in the form of individual nanowire-bundles ~50~100 nm wide (Fig. 1b). The comprised TiO\(_2\) nanowires are ~10-20 nm wide, as revealed in the high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) image in Fig. 1d and high resolution transmission electron microscopy (HRTEM) image (Supplementary Fig. 1a). The bundled TiO\(_2\) nanowires are mesoporous, revealed by arrays of darker spots (<3 nm in diameter) in Fig. 1d, consistent with the BJH pore size distribution (Supplementary Fig. 2b). The HRTEM lattice image identified an inter-planar lattice spacing of 0.326 nm, matching the [110] planes of rutile TiO\(_2\), corroborating with the XRD pattern in Supplementary Fig. 1b (ICPDS 888-1175). We note that a thin mesoporous layer of SiO\(_2\) was also formed during the TiO\(_2\) growth process. These mesoporous SiO\(_2\) are formed due to the leaching of Al, Fe, and Mg from cordierite by hydrochloric (HCl) acid at the initial stage of the solvothermal TiO\(_2\) growth process (Supplementary Fig. 3 and Supplement Note 1). The rutile TiO\(_2\) NA integrated cordierite honeycomb has a high BET surface area of ~89.6 m\(^2\) g\(^{-1}\), equivalent to 25,984 m\(^2\) for a 1 L cordierite honeycomb core. Such a high surface area of the TiO\(_2\) NA integrated honeycomb is attributed to the unique mesoporous structures of nanowire arrays and partially etched cordierite substrate surface as discussed earlier (Fig. 1d and Supplementary Fig. 2). After Pt loading using a dip-coating method (Method section), the surface area reduces to 45.7 m\(^2\) g\(^{-1}\) (Supplementary Fig. 2b), comparable to the surface area of benchmark commercial DOC sample (49.8 m\(^2\) g\(^{-1}\)). After hydrothermal aging at 700 °C for 100 h, the surface area of the sample is further reduced to ~16 m\(^2\) g\(^{-1}\), however with the array structure well retained (Supplementary Fig. 2b). The loss of surface area after both dip-coating and HT aging processes are due to the closure of small pores within TiO\(_2\) nanowires (<7 nm), as revealed in the pore size distribution measured by N\(_2\) isotherms and by presence of fewer (dark-spot) pores revealed in the HAADF STEM image of the respective samples (Supplementary Fig. 2b). It is noted that, despite the over 60% decrease of surface area after hydrothermal aging on the Pt\(_1/\)TiO\(_2\) NA, the superb catalytic oxidation performance has been largely retained. This is due to the remarkable activity and durability found on the well-dispersed and isolated single-atom Pt catalysts anchored on the mesoporous rutile TiO\(_2\) nanowire surfaces.

During operation, oxidation catalysts may endure mechanical vibrations and high velocity multi-phase exhaust flow such as the vehicular conditions. The associated mechanical stresses might cause the separation or delamination of washcoat layers from the monolithic substrates, resulting in loss of active materials, deactivation of catalysts, and even damage of downstream functional devices\(^29\). Since the TiO\(_2\) nano-array forest was “in situ grown” instead of “wash-coated” on the honeycomb monoliths, these nano-array integrated monoliths have an improved adherence over conventional washcoated samples. Evidently, after ultrasonicing at 40 kHz in water bath at 25 °C for 4 h, both fresh and HT aged Pt\(_1/\)TiO\(_2\) NA integrated
monoliths showed little morphology change (Supplementary Fig. 4). A negligible weight loss of ~1% was observed in both fresh and aged nano-array integrated monoliths, as compared to that of >10 % weight loss for the commercial DOC after similar ultrasonication testing.

Pt was loaded on TiO2 nano-arrays, with a volumetric Pt loading of 0.53–1.73 g L\(^{-1}\) (0.18–0.58 wt.%, Supplementary Table 1) to prepare functional DOC devices, employing either microwave-assisted dip-coating or wet-incipient impregnation (WII)\(^{12}\). Aberration-corrected (ac) HAADF STEM, a powerful tool for discerning individual heavy atoms (e.g., Pt) from lighter supporting atoms (e.g., Ti, O), was employed to investigate the distribution of Pt on the TiO2 nano-array. Supplementary Fig. 5 shows ac-HAADF STEM images of Pt supported on TiO2 NA prepared using Na-promoted WII method, clearly revealing the well-dispersed Pt single atoms on TiO2 nanowire surface. High Pt dispersions of 80% and 74% were determined for the Pt loading of 0.71 and 1.73 g Pt L\(^{-1}\), respectively, by H\(_2\) chemisorption measurement, further confirming the dominant atomically dispersed Pt sites. Interestingly, without any promoter, microwave-assisted dip-coating also results in atomic dispersion of Pt on TiO2 nano-arrays shown in Fig.1e and Supplementary Fig. 6. However, the Pt dispersion of dip-coating samples is lower, 33% and 24% for the Pt loading of 0.71 and 1.73 g Pt L\(^{-1}\), respectively, due to a higher amount of Pt nanoparticles dispersed on the adjacent mesoporous SiO2 (Supplementary Figs. 3 and 6).

Meanwhile, TiO2 NA and NW samples with different mesoporosity were prepared under different calcination temperatures and used to look into the support porosity in influence on the Pt SAC loading. It is noted that the Pt single-atom distribution is retained...
in all these different mesoporous TiO₂ nanowire surfaces, where few to no Pt nanoparticles were observed (Supplementary Fig. 7). This may suggest that the Pt SAC loading is relatively insensitive to the mesoporosity of TiO₂ NWs. In addition, the mesoporous NA samples maintained a similar specific surface area of 20–25 m² g⁻¹ despite the obvious evolution of mesopore size and distribution as the calcination temperature increased from 500 to 900 °C (Supplementary Fig. 8), indicating the excellent thermal stability of these rutile nano-arrays.

It was noted earlier that the single Pt atom catalysts are often not stable under the HT condition due to their tendency to agglomerate, thus hindering their practical applications³⁰. Here on the mesoporous rutile TiO₂ nanowire supports, the atomically dispersed Pt was found to retain its dispersion even after HT aging at 700 °C for 100 h and simulated exhaust treatment (Fig. 1f, g and Supplementary Fig. 9). On both dip-coating and Na-promoted WII samples, these single-atom Pt catalysts retained their dispersion after HT degreening at 700 °C for 4 h (Supplementary Figs. 10 and 11). On the contrary, Pt nanoparticles supported on adjacent SiO₂ on both samples severely sintered after HT degreening (Supplementary Figs. 10 and 11). To understand the excellent durability displayed here, a series of in situ CO oxidation studies were conducted over the Pt₁/TiO₂ SAC catalysts using synchrotron X-ray adsorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) computation (Figs. 2a–d). It is found that the strong electrostatic interactions between Pt and TiO₂ support surface are responsible for the excellent durability in these single Pt atom catalysts²¹,²²,³⁰. Specifically, on the TiO₂ nanowire surfaces, isolated and catalytically active Pt ions are predominantly located at the surface Ti vacancies, and strongly anchored by five or six neighboring O ions, thus exhibiting outstanding hydrothermal durability. Additional studies using in situ diffuse reflectance infrared fourier-transform spectroscopy (DRIFTS) and temperature programmed reduction (TPR) under hydrogen have revealed an outstanding low-temperature catalytic activity of these TiO₂ nanowire supported SAC catalysts toward CO oxidation (Figs. 2e, f).

Structure and reactivity of single-atom Pt on TiO₂ nanowire surface. The in situ XAS studies for CO oxidation were performed on 0.2 wt.% Pt₁/rutile TiO₂ nanowires (NW) for understanding the structural characteristics and low-temperature reactivity of the Pt single-atom active sites. TiO₂ NW powder, collected in the same batch with the synthesis of TiO₂ NA monolith, was employed as the support to avoid the interference from the cordierite substrates. The fourier transformed-extended X-ray absorption fine structure (EXAFS) spectrum of 0.2 wt.% Pt₁/TiO₂ at the Pt L₃ edge in r-space shows a dominant peak at 1.6 Å from the Pt–O contribution and very weak peaks at 2.6 and 3.0 Å from either the Pt–Pt or the Pt–Ti contribution (Fig. 2a), confirming that Pt is atomically distributed on TiO₂ NW surface. Structural parameters extracted from the Pt L₃-edge EXAFS fitting, summarized in Supplementary Table 2, indicates that on Pt₁/TiO₂ NW, the Pt site has 5 Pt–O coordinations, which have an interatomic distance of 1.99 ± 0.02 Å, almost the same as the Pt–O distance in PtO₂ (2.01 ± 0.02 Å). As shown in Fig. 2b, the white line intensity at ~11570 eV of Pt₁/TiO₂ NW in the normalized X-ray Absorption Near-edge Structure (XANES) is between the intensities of Pt(NH₃)₄(NO₃)₂ and PtO₂, suggesting that the Pt single atoms have oxidation states between 2+ and 4+, corroborated with the XPS analysis that the sample only contains Pt⁴⁺ and Pt²⁺ (Fig. 2c). During the CO oxidation reaction in lean conditions (2000 ppm CO and 12% O₂), the overall oxidation state of Pt decreases slightly, but remain in between 2⁺ and 4⁺, indicated by the decrease in the white line intensity of Pt₁/TiO₂ NW under the in situ XANES measurements.

DFT calculations were performed to find the most stable configurations of single-atom Pt on TiO₂ NW surfaces. The binding energy, defined as the energy needed to move a Pt atom from the TiO₂ surface to vacuum (>10 Å), is used to assess the stability of the Pt atom on the surface. We only considered configurations on rutile TiO₂ (110) with and without Ti vacancies since the [110] is the dominant surfaces and no O vacancies were detected on TiO₂ NW (Supplement Note 2). The structures and the corresponding binding energy of Pt are shown in Supplementary Fig. 12. The calculation predicts that the configuration where Pt stays in the five-fold coordinated Ti vacancy (Pt–Tiᵥ) is the most stable, with 2.3 eV higher in binding energy compared to that with Pt substituting six-fold coordinated Ti (Pt–Ti₆) and at least 1.8 eV higher than other configurations where Pt adsorbed on the TiO₂ (110). This prediction is in good agreement with XAS fine structure studies. We note that the Pt–Tiᵥ configuration has two models, with (Model A) and without (Model B) O on top (Oₖ) of Pt. In model A, Pt is fully oxidized (Pt⁴⁺) and has six Pt–O coordinations including four in-plane Pt–Oₖ, one Pt–Oₙb, and one Pt–Oₙb, where Oₖ is in-plane O, and Oₙb is O from the sub-surface layer. The Pt–Oₙb is a weak bond and can be easily activated, thus this bond is absent in the partially oxidized form (Pt²⁺) in model B, leaving 5 coordinations on the Pt sites. The binding energies of Pt in the Models A and B are close to each other (10.44 eV vs. 11.09 eV), suggesting the likely co-existence of both Pt⁴⁺ and Pt²⁺ on the TiO₂ NW surface, therefore, the average coordination number of Pt is between 5 and 6, in agreement with the experimental result from both fitting EXAFS curve (Supplementary Table 2) and XPS analyses (Fig. 2c and Supplementary Table 3).

It is noted that the white line intensity of Pt₁/TiO₂ NW decreases in the CO/O₂ mixture even at room temperature, suggesting isolated Pt atoms supported on TiO₂ NW may catalyze room-temperature CO oxidation. We employed DRIFTS to obtain mechanistic insights into low-temperature CO oxidation reactivity of Pt₁/TiO₂ NA. Fig. 2e shows the in situ DRIFT spectra of CO adsorption and oxidation at 30 and 100 °C of Pt₁/TiO₂ NA. After CO is adsorbed on Pt₁/TiO₂ NA, quasi-symmetrical IR bands at 2085 and 2081 cm⁻¹ are observed for the spectra collected at room temperature and 100 °C, respectively, and ascribed to CO linearly adsorbed on isolated ionic Pt⁶⁺ sites²¹,²². The IR band at 2085 cm⁻¹ shows a reduction of 80% in peak area after O₂ was introduced for 10 min at room temperature, suggesting CO is readily oxidized at room temperature on Pt₁/TiO₂ NA. All adsorbed CO is oxidized when the temperature increases to 100 °C as the IR band at 2081 cm⁻¹ vanishes with the introduction of O₂. These evidences clearly demonstrate low-temperature reactivity of Pt₁/TiO₂ NA.

DFT calculations were also performed to elucidate the high catalytic activity for CO oxidation of Pt₁/TiO₂ NA and NW. CO can be oxidized over supported Pt catalysts in three ways, namely Langmuir-Hinshelwood (LH), Mars-van Krevelen (MvK), and Eley-Rideal (ER) mechanisms²¹–³³. On Pt₁/TiO₂ NA and NW, the ER mechanism was found to be favored due to a very low DFT derived activation energy of ~0.2 eV (~19 kJ mol⁻¹), in good agreement with the experimentally measured activation energy of 22.7 kJ mol⁻¹ (Supplementary Fig. 13). The ER catalytic cycle and the corresponding calculated energy profile of CO oxidation on Pt₁/TiO₂ NA is shown in Fig. 2d. Model A with a Pt⁴⁺ reactive center was employed as the starting configuration (Intermediate I). CO reacts with the O on top of Pt via the ER mechanism with an activation energy of 0.2 eV and exothermicity (AH) of ~3.6 eV, leaving one free coordination on Pt.
(Intermediate II). This free coordination is then filled by adsorption of an \( \text{O}_2 \) molecule (Intermediate III). The O–O bond of \( \text{O}_2 \) adsorbed on the Pt site can be easily activated when another CO coordinates with one O atom at the other end (Intermediate IV). The cycle is completed with the release of \( \text{CO}_2 \). It is worth noting that the LH mechanism is usually dominated for supported Pt nanoparticle catalysts (except for Pt/CeO\(_2\) case where MvK is dominant\(^2\))\(^1\), which involves adsorption of CO and dissociative adsorption of \( \text{O}_2 \) on metal active sites, followed by the reaction of adsorbed CO and O species to form \( \text{CO}_2 \)\(^3\). A modified LH scheme was proposed for CO oxidation on Pt single atoms supported on FeO\(_x\) (Pt\(_1/\text{FeO}_x\)), in which CO adsorbing on the Pt atom reacts with O from FeO\(_x\) support\(^1\)\(^5\). Meanwhile, the LH-based mechanisms are energetically unfavorable on Pt\(_1/\text{TiO}_2\) \( \text{NA} \) due to a high activation energy of \( \sim 1.8 \) eV (174 kJ mol\(^{-1}\)) for the dissociation of the adsorbed \( \text{O}_2 \) molecule with the help of the Pt site and one surrounding Ti site (Supplementary Fig. 14).

The redox property of Pt\(_1/\text{TiO}_2\) \( \text{NW} \) was studied using \( \text{H}_2 \)-temperature-programmed reduction (\( \text{H}_2\)-TPR) (Fig. 2f). In the \( \text{H}_2\)-TPR profile of Pt\(_1/\text{TiO}_2\) \( \text{NW} \), the peaks at 103 and 508 °C are

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**Fig. 2 Characterization of the Pt single-atom species on TiO\(_2\) NW and NA surfaces.**

a k\(^2\)-weighted Fourier-transformed EXAFS spectra of Pt\(_1/\text{TiO}_2\) \( \text{NW} \). Pt NP/\( \text{TiO}_2\) \( \text{NA} \), Pt foil, and PtO\(_2\) are employed as references. b Normalized XANES spectra at the Pt L\(_3\) edge of Pt\(_1/\text{TiO}_2\) \( \text{NW} \) under in situ CO oxidation. c Core Pt 4\( \text{f}\) XPS spectrum of the Pt\(_1/\text{TiO}_2\) \( \text{NW} \). d The proposed Eley-Rideal mechanism for CO oxidation on Pt\(_1/\text{TiO}_2\) \( \text{NA} \). The reaction cycle shows the structure of intermediates and transient state (TS) of the key elementary steps. The inset shows the calculated energy profile. e In situ DRIFT spectra of CO adsorption and oxidation at 30 and 100 °C of Pt\(_1/\text{TiO}_2\) \( \text{NA} \), and f, \( \text{H}_2\)-TPR profile of Pt\(_1/\text{TiO}_2\) \( \text{NW} \).
assigned to the reductions of isolated Pt atoms and bulk TiO$_2$, respectively. We observed an additional H$_2$-consumption peak at 186 °C for Pt$_1$/TiO$_2$ NW, which is absent in the profile of Pt NP/ TiO$_2$ NA. This peak can be assigned to the reduction of TiO$_2$ induced by isolated Pt atoms. It has been reported that the presence of single-atom Pt can lower the reduction temperature of metal oxide support due to the strong metal-support interaction. The enhanced reducibility of Pt$_1$/TiO$_2$ NA compared to other TiO$_2$ based-DOCs might allow excursions into fuel-rich and fuel-lean conditions although more thorough evaluation is necessary.

**Low-temperature diesel oxidation over single-atom Pt on TiO$_2$ nanowire arrays.** To evaluate their catalytic oxidation activity, the Pt$_1$/TiO$_2$ NA monoliths were tested under simulated engine exhausts based on clean diesel combustion (CDC) and low-temperature diesel combustion (LTC-D) protocols developed by US DRIVE$^{24}$. The samples were tested at a high gas hourly space velocity (GHSV) of 60,000 h$^{-1}$ to assess their close-to-reality performance under these protocolled conditions. We note that in both conditions, the composition of total hydrocarbons (THC) on a C$_1$ basis in the exhausts is ~56% C$_2$H$_6$, 33% C$_3$H$_6$, and 11% C$_2$H$_4$. Samples were hydrothermally degreened at 550 °C for 4 h and at 700 °C for 4 h for evaluation in the CDC and LTC-D conditions, respectively, representing a ~5000 mile-on-road condition.

Fig. 3a shows the light-off curves for Pt$_1$/TiO$_2$ NA with Pt loading of 0.71 g L$^{-1}$ in the CDC simulated exhaust. The $T_{90}$ temperatures of CO, C$_2$H$_4$, C$_3$H$_6$, and THC are 164, 172, 173, and 178 °C, respectively, all well below 200 °C, at which most catalyst systems in today’s vehicles are ineffective.$^{34}$ For benchmark, we employed a commercial DOC sample with PGM loading of 4.66 g L$^{-1}$, obtained from a brand new heavy-duty pick-up truck (year model 2012). The temperature $T_{90}$ for THC of Pt$_1$/TiO$_2$ NA is ~172 °C lower than that of the commercial DOC (350 °C), despite ~5 times less PGM loading (Supplementary Fig. 15). On Pt$_1$/TiO$_2$ NA, both ethylene and propylene oxidation occur almost simultaneously. On the other hand, the oxidation of ethylene, the main hydrocarbon component in the simulated exhausts (56%), on the commercial DOC sample is sluggish, leading to the slow conversion of THC and consequently a much higher $T_{90}$ than that of Pt$_1$/TiO$_2$ NA. Additionally, the conversions of both C$_2$H$_4$ and C$_3$H$_6$ on the Pt$_1$/TiO$_2$ NA integrated monoliths quickly reach more than 99% with no plateau in the high conversion region that was observed in the commercial DOC, suggesting that the catalytic reaction kinetics over Pt$_1$/TiO$_2$ nano-array are not mass-transfer limited even at a high space velocity of 60,000 h$^{-1}$. $^{135}$

A secondary function of a DOC catalyst is to oxidize NO to NO$_2$ to help downstream functionalities such as NO$_X$ selective catalytic reduction (SCR) catalyst and regeneration of diesel particulate filters. In this regard, the Pt$_1$/TiO$_2$ NA also outperforms the commercial sample, with a maximum NO-to-NO$_2$ conversion of 47% for the Pt/TiO$_2$ nano-array at a low temperature 291 °C as compared to 27% at 427 °C for the commercial DOC (Supplementary Fig. 15).

To evaluate and validate the practical diesel oxidation reactivity of isolated Pt atom active sites, we employed Pt-nanoparticle (NP) supported on mesoporous SiO$_2$ monolith and TiO$_2$ NA monolith (Supplementary Fig. 16) as two references. These reference catalysts were prepared by etching of cordierite honeycombs followed by Pt dip-coating, and atomic layer deposition of Pt over TiO$_2$ NA monolith$^{38}$, respectively. It is noted the low-temperature DOC activity of Pt NP/TiO$_2$ nano-array is good, but inferior to Pt$_1$/TiO$_2$ NA, despite a 2.5-time higher PGM loading (Fig. 3b). The temperatures $T_{90}$ of Pt NP/ TiO$_2$ NA for CO, C$_2$H$_4$, C$_3$H$_6$, and THC are 193, 196, 196, and 223 °C, respectively, ~23–45 °C higher than that of Pt$_1$/TiO$_2$ NA. When using a Pt NP loading of 0.71 g Pt L$^{-1}$ on the etched cordierite substrate that spontaneously created a layer of mesoporous SiO$_2$ support, similarly inferior catalytic oxidation performances were observed over CO and C$_3$H$_6$ with ~35–45 °C higher $T_{90}$ temperatures than those of the Pt$_1$/TiO$_2$ NA sample of the same Pt loading (Supplementary Fig. 16c). This evidence clearly illustrates the improved reactivity for CO and HC oxidation of isolated Pt atoms, compared to Pt NP active sites although direct turnover frequency (TOF) measurements are difficult or impossible with these steep light-off curves and under the complex flow conditions.

To evaluate the durability of Pt$_1$/TiO$_2$ NA during reactive conditions, the catalyst was tested under simulated exhaust at 330 °C with cyclic exposures to 820 °C for 10 min (Fig. 3c). No deactivation was observed of the catalyst with the conversions of CO and THC remaining at 100% and >90%, respectively, during ~36 h evaluating period. The excellent durability of Pt$_1$/TiO$_2$ NA is attributed to the stable atomically distributed Pt sites, which even retained after hydrothermal aging at 700 °C for 100 h and the CDC simulated exhaust treatment, as revealed in the single-atom structural analyses earlier (Fig. 1f, g).

Sulfur-containing compounds, present in most vehicle fuels and lubricants, can be oxidized to SO$_2$ during combustion, interacting with and deactivating PGM supported catalysts. Therefore, it is necessary to test sulfur-poisoning effects on Pt$_1$/ TiO$_2$ NA for the practical DOC applications. The sample Pt$_1$/ TiO$_2$ NA with Pt loading of 1.73 g L$^{-1}$ was chosen for the USDRIE’s testing protocol for sulfur tolerance based on the LTC-D simulated exhaust$^{24}$. Under the LTC-D condition, this sample performed better than the commercial DOC sample (5 °C lower in $T_{90}$ for THC oxidation and much higher max NO-to-NO$_2$ conversion (71% vs. 25%) despite 2.7 times lower in PGM loading (1.73 vs 4.66 g L$^{-1}$) (Supplementary Fig. 17). After an exposure to 1 g g守土 L$^{-1}$ of SO$_2$, the sample showed only a slight deactivation for CO and unsaturated HC with a $T_{90}$ increase of ~19 °C (Fig. 3d, e and Supplementary Fig. 18). Interestingly, low-temperature catalytic propane oxidation was improved, likely due to the formation of interfacial sulfate species that facilitate propane chemisorption on Pt$^{36}$, thus decreasing $T_{90}$ of THC by 9 °C (Fig. 3e and Supplementary Fig. 18). Under simulated exhaust, propane contributes to 11% of THC and propane oxidation often starts after unsaturated HCs. Therefore, $T_{90}$ of THC of a DOC is largely dependent on low-temperature propane oxidation activity, as reflected by increased $T_{88}$ but decreased $T_{90}$ of THC after S-poisoning (Supplementary Fig. 18). After de-sulfation in H$_2$ stream, the oxidation catalytic activity for CO was even better and that for unsaturated HCs was almost fully recovered.

To demonstrate the scalability for practical conditions, a full-size Pt$_1$/TiO$_2$ NA monolith with a Pt loading of 0.53 g L$^{-1}$ and dimensions of Φ 5 cm × 7.5 cm was evaluated under highly transient feed gas conditions, mimicking a heavy-duty diesel (HDD) federal test procedure (FTP) as running on a HDD certified 2010 Cummins ISB (6.7 L) 320 hp engine. The transient feed gas composition is listed in Supplementary Fig. 19. The Pt$_1$/ TiO$_2$ NA sample was aged at 650 °C for 100 h in 10% steam/air flow to a representative end of life condition for a North American HDD application. Fig. 3f and Supplementary Fig. 20 show the transient response and cumulative emission of THC and CO, respectively, for the fresh and aged Pt$_1$/TiO$_2$ samples. The Pt$_1$/TiO$_2$ samples do not show reactivity during the first 200 s because of low temperature, high exhaust flow rate, and high concentration of HCs and CO. When the temperature increases,
both fresh and aged samples showed good activity despite the drastic changes in both concentration and flow rate of emissions. It is noted that the HC oxidation activity of the aged sample is almost as good as the fresh sample, with only a small difference observed in the transient and cumulative HC emissions. The performance of the aged sample is mainly due to the stable single-atom Pt sites. As revealed by HAADF STEM (Fig. 1f, g and Supplementary Fig. 9), we observed a high density of isolated Pt atoms on the surface of TiO2 nanowires even after hydrothermal aging at 700 °C for 100 h followed by the simulated exhaust treatment. However, some small pores (<7 nm) are closed during hydrothermal aging, as indicated by HAADF STEM and N2 isotherms, thus access is inhibited on a portion of Pt sites (Supplementary Fig. 2). Such loss of Pt active sites leads to slow response to CO at high flow rate and concentration (at 500, 930, and 1100 s), and consequently an increase in the CO emission.
The remarkable low-temperature performance of the isolated Pt single atoms supported on TiO₂ nano-arrays can be attributed to the combination of atomically dispersed Pt and the unique structure of long-range ordered mesoporous TiO₂ arrays. Single Pt atoms clearly show better diesel oxidation activity than the Pt NP counterpart, as demonstrated in the reactivity comparison under the simulated CDC exhaust conditions (Fig. 3b and Supplementary Fig. 15). First, the enhanced low-temperature reactivity of Pt single-atom catalyst is explained by the distinct electronic structures that modify interaction with adsorbate molecules or by the involvement of supports that may alter reaction pathways. The LH and MvK mechanisms are often reported for supported Pt catalysts. However, low-temperature CO oxidation on Pt/TiO₂ NA favors the ER mechanism with very low activation energy. Second, the introduction of macro-pores in the mesoporous NW structures improves mass transport properties. In the Pt/TiO₂ NA, the space between the mesoporous nanobundles acts as a large channel for fast transport of the reactants along the bundles before the reactants diffuse into the reactive area. Well-spaced support also helps to inhibit sintering of Pt, contributing to the hydrothermal robustness. The Pt/TiO₂ NA structures, which combine durable and reactive single Pt atoms and hierarchically porous NA support, are expected to have broader applications in the field of catalysis and materials science.

In summary, we demonstrate a single-atom Pt catalyst anchored on a highly stable mesoporous rutile titania nanowire array forest grown in field-size honeycomb monolith. With over 80% PGM usage reduction compared to that of the commercial benchmark, such a single-atom Pt catalyst has displayed remarkable oxidation activities for CO and hydrocarbons with 90% conversion at temperatures as low as ~160 °C under simulated exhaust conditions. Such excellent low-temperature activities are sustained over hydrothermal aging and sulfation as the active single-atom Pt species retain on the stable titania nanowire arrays, as a result of a strong electrostatic interaction between Pt single-atom species and TiO₂ nanowire surface. A simple and cost-effective solvothermal process in conjunction of dip-coating and impregnation methods provides a viable strategy for scalable manufacturing of durable Pt single-atom catalysts on the nanowire-integrated monoliths.

**Catalytic activity evaluation.** The catalytic activity measurements were performed in a continuous flow reactor equipped with a gas chromatography. The monolithic catalysts (5 × 5 channels × 2.5 cm long) were placed in a tubular quartz reactor with a surrounding electrical heating coil. The inlet temperature was measured using a 0.16-mm K-type thermocouple, which was fixed at ~5 mm in front of the monolith. The composition of the small thermal pulse (0.16 ms) is uninterrupted disruption of gas flow. Typically, the catalytic activity of each sample was evaluated through total six reaction cycles, in which the inlet temperature was ramped up from 100 to 525 °C at 2 °C min⁻¹ and naturally cool down to 100 °C before next testing cycles. The feed gas mixtures were controlled by mass flow controller before entering the fixed bed reactor. The feed space velocity was varied between 0.5 and 20000 ppmv. The feed gas always contains 12% O₂ to mimic the O₂ concentration in the CDC and LTC-D simulated exhausts, but varies CO and C₂H₄ concentrations (also were chosen to reflect the CO and total hydrocarbon concentration in the CDC and LTC-D simulated exhausts) in each cycle such that cycle 1 and 2 contain 2000 ppm CO and 2000 ppm C₂H₄ cycle 3 contains 2000 ppm CO; cycles 4 contains total 100 ppm C₂H₄ cycle 5 contains 500 ppm C₂H₄; and cycle 6 contains 500 ppm CO and 500 ppm C₂H₄ all are balanced by N₂. Sample Array-50-D was evaluated in an additional sequence (cycle 3 → 4 → 5 → 6 → 1 → 2), showing negligible difference in the catalytic activity, thus confirming the sequence of the tests does not affect the catalytic activity of TiO₂ nano-array supported Pt catalysts.

The catalytic diesel oxidation activity of catalysts under simulated exhaust conditions was evaluated according to the protocol developed by the Advanced Combustion and Emission Control (A2EC) Team of USDRIVE. The light-off measurements were conducted on a customized plug-flow reactor system. Monolithic catalyst samples were cut and loaded into a quartz tubular reactor using a wrapping in order to ensure no gas could bypass the catalyst channels. The catalytic activity was measured using two thermocouples, one measuring the inlet temperature while located ~2 cm from the catalyst front, the other measuring the mid-catalyst temperature and located from the rear into the middle of the channel of the micro-core. Space velocity was kept at 60,000 h⁻¹ throughout all the tests. Gas concentrations were determined per A2EC Tech Team (USDRIVE) protocol. The composition of the “LTC-D” and “CDC” simulated exhausts is [O₂] = 12%, [H₂O] = 6%, [CO₂] = 6%, [H₂] = 400 ppm, [CO] = 2000 ppm, [NO] = 100 ppm, [C₂H₄] = 833.5 ppm, [C₂H₆] = 333 ppm, [C₃H₆] = 111 ppm, and Ar balance (31). The composition of the “LTC-D” simulated exhaust is [O₂] = 12%, [H₂O] = 6%, [CO₂] = 6%, [H₂] = 100 ppm, [CO] = 500 ppm, [NO] = 500 ppm, [C₂H₄] = 389 ppm, [C₂H₆] = 233.5 ppm, [C₃H₆] = 51.7 ppm, and Ar balance. Water was introduced via argon flow through a bubbler and heated lines held at 200 °C. Product gas stream was measured via MKS FTIR. Experiments were conducted in a step with a degassing step in only the O₂, CO, and H₂O components of the gas stream at 700 °C for 4 h for LTC-D and 550 °C for 4 h for CDC protocols, followed by an evaluation step from 100 to 500 °C at a rate of 2 °C min⁻¹. Besides the regular simulated exhaust test, catalyst samples were also treated using the following simulated exhaust test treatment protocol to look into the single Pt atom species fate before and after experiencing the treatment on the Pt/TiO₂ NA samples with both fresh state and hydrothermal aged condition. CDC simulated gas treatment: 12% O₂ + 6% H₂O + 6% CO₂ + 100 ppm H₂ + 500 ppm CO + 200 ppm NO + 1400 ppm H₂O, with a ramp rate of 5 °C min⁻¹ from room temperature to 500 °C, and then keeping at 500 °C for 1 h. The catalyst performance was evaluated following USDRIVE’s protocol. The catalyst was exposed to 5 ppm SO₂ added to the full simulated exhaust at a space velocity of 30,000 h⁻¹ and 300 °C catalyst inlet temperature for 5 h. A total sulfur exposure level of 1 g sulfur per liter of catalyst was estimated following this exposure condition. Poisoning was conducted following the pretreatment in which the catalyst was annealed at 600 °C for 20 min before cooled down to 300 °C in 12% O₂, 6% H₂O, 6% CO₂, and N₂ balance. After sulfur exposure, SO₂ was removed from the feed and the sample cooled to 100 °C at which point the catalyst performance was evaluated. For de-sulfation, the catalyst was annealed at 700 °C in 3% H₂ and 1% CO in N₂ for 30 mins, followed by calcination in air at 500 °C for 2 h.

The Pt/TiO₂ nano-array sample with a Pt loading of 0.53 g L⁻¹ and dimensions of Φ 2 × 3 cm were tested under highly transient feed gas conditions mimicking a heavy-duty diesel (HDD) federal test procedure (FTP) as running on a HDD certified 2010 Cummins ISB (6.7 L) 320 hp engine. The characteristic of the transient feed gas is provided in Supplementary Fig. 19. The Pt/TiO₂ nano-array...
Pt foil and PtO2 were used as reference samples. Using Si (111) double-crystal at the BL14W1 station at the Shanghai Synchrotron Radiation Facility (SSRF). The Catalyst characterization representative end of life condition for a North American HDD application.

The EXAFS data was analyzed and fitted using the ATHENA module in the IFEFFIT software packages. Each k2-weighted EXAFS spectrum was processed by a two-step procedure: (i) subtraction of post-edge background from overall absorption; and (ii) normalization with respect to the edge-jump step. The k2-weighted y(k) data of Pt L2-edge were then Fourier transformed to real (R) space through a hanning windows (Δk = 1.0 Å–1) in order to separate the EXAFS contributions from different coordination shells. To determine the quantitative structural parameters around central atoms, the ARTEMIS module of IFEFFIT software packages was employed for least-squares curve parameter fitting.

A Tecnai F30 STEM. The aberration-corrected HAADF STEM images were acquired after evacuation for 2 h showed the channel walls.

The pressure range of isotherms was controlled at 0–1.05 MPa (winter) and 0.1–1.0 MPa (summer) at 70°C. The adsorption isotherm was measured by a Quantachrome (model NOVA 4200e) automated 305°C temperature programmed reduction (TPR). The samples were degassed in helium at ambient temperature for 20 min. TPR condition: 10% H2 balance Ar, 50 ml min–1, 10 °C min–1. To determine the surface area and pore size distribution of the catalysts, N2 adsorption–desorption isotherms and H2 chemisorption were carried out using a Micromeritics ASAP 2020 Physisorption analyzer. The liquid nitrogen temperature. Brunauer–Emmett–Teller (BET) and Barret–Joyner–Halenda (BIFH) method were used to calculate the specific surface area and pore size, respectively. The samples to be measured were degassed at 350 °C for 4 h in vacuum before the measurement of N2 adsorption–desorption isotherms.

To evaluate the mechanical stability of TiO2 nano-array integrated cordierite monolith systems to be modeled involve isolated molecules like CO2 and O2, the long-range van der Waals interactions was included into the calculations using the scheme of Grimme. Reaction pathways were searched using the nudged-elastic band method by Henkelman and Jónsson.

Data availability
All data generated or analyzed during this study are included in this published article (and its supplementary information files).

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Author contributions
P.X.G. conceived the research. P.X.G. and S.H. designed the experiments and co-wrote the paper. S.H. synthesized and characterized the samples. Y.G. and S.H. performed most of the catalyist evaluation, data collection, and analyses. A.J.B., E.A.K., S.H., X.L., and T.J.T. conducted the bench reactor simulated exhaust testing and in situ DRIFTS, W.T. and X.L. performed temperature programmed testing and physico-chemical characterization, S.W helped with the probe catalytic reaction testing. J.L conducted the aberration-corrected STEM characterization. T.D.H. and R.R. performed the density functional theory calculation. Y.W. carried out the XANES and EXAFS measurements. X.L. and Y.D. performed the high resolution TEM and XPS characterization. J.Y. helped with the XANES and EXAFS sample preparation, T.J.P. was responsible for the transient cyclic dynamic testing. All the authors discussed the results and provided input on the paper.

Competing interests
A U.S. non-provisional patent (Application No.: 16/465,981) on catalyst methods of making, with P.-X.G. and S.H. as co-inventors, has been filed by the University of Connecticut.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41467-020-14816-w. Correspondece and requests for materials should be addressed to P.-X.G.

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