Low-Temperature Remediation of NO Catalyzed by Interleaved CuO Nanoplates

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Air pollution by automobile exhaust is becoming a global challenge; it is not limited to developing countries where traffic volumes are rapidly increasing.[1] Small vehicles, such as motorcycles and scooters with an engine displacement of 100 mL or less,[2] are one of the major causes for such air pollution; only a small percentage of these vehicles is equipped with exhaust purifiers.[3] Current exhaust purifiers comprise catalysts based on platinum-group metals (PGMs), such as Pt, Pd, and Rh.[4–7] The supply of PGMs may not be reliable for meeting the increasing demands for exhaust purification since deposits of PGMs in the Earth’s crust are limited and localized.[5] Furthermore, PGM-based catalysts are not suited to the low-temperature exhaust of small vehicles (<300 °C at the catalyst) because at temperatures less than 300 °C they exhibit poor activity toward one of the most harmful gases in the exhaust, nitrogen monoxide (NO).[9]

Abundantly available transition-metal oxides have been investigated for several decades as an alternative NO-remediation catalyst to the PGM-based catalysts.[10–14] Transition-metal oxides can exhibit good NO remediation activity in the presence of reaction intermediates of combustion, carbon monoxide (CO; Equation 1) and/or hydrocarbons.[15]

\[
\text{NO} + \text{uCO} \rightarrow \text{yN}_2 + z\text{N}_2\text{O} + \text{uCO}_2
\]  

The ever-developing transition-metal-oxide catalysts are, however, susceptible to catalytic poisoning by O\textsubscript{2} contained in the exhaust, resulting in rapid degradation in performance.[10]

Here, we report that an abundant oxide, copper(II) oxide (CuO), can exhibit better activity than Pt-nanoparticle catalysts and rival Rh-nanoparticle catalysts in NO remediation at low temperatures; as a result of a theoretically driven design, a rational preparation of interleaved nanoplates bearing the maximal active [001] facet (CuO nanoplates) is carried out. In addition, a field test using a commercial engine for small vehicles demonstrates that the CuO-nanoplate catalyst efficiently removes NO gas from the exhaust, which also contains a high concentration of O\textsubscript{2}.

CuO possesses a monoclinic crystal structure, in which the Cu\textsuperscript{2+} cations are coordinated by four oxygen atoms in an approximately square planar configuration.[16] Each low-index crystal plane or facet of CuO has a characteristic atomic arrangement at its surface (Figure 1a,b), in turn suggesting that each crystal facet of CuO should possess different catalytic properties.[17–19] Density functional theory calculations with a Hubbard potential energy U (DFT+U) (see Supporting Information, SI) indicate that the surface energy of the [001] facet (+1.70 J m\textsuperscript{−2}) is significantly higher than that of the {100} facet (+1.56 J m\textsuperscript{−2}), in turn indicating that the [001] facet is more chemically reactive. This originates from the unstable surface geometry of the {001} facet where under-coordinated oxygen atoms protrude from the surface plane as shown in Figure 1a. The surface thus becomes a suitable platform for the chemical reaction shown in Equation 1. Carbon monoxide molecules that are initially adsorbed on the surface react at the outermost oxygen atoms. This process creates oxygen vacancies (V\textsubscript{O}) which can act as reaction centers for the oxygen elimination reaction of nitrogen oxide species, NO\textsubscript{x}. A chemical reaction on the [001] facet is illustrated schematically with energy-minimized geometries for

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CO-adsorbed and oxygen-deficient surfaces in Figure 1a. This series of chemical reactions rarely occurs on the \{100\} facet due to the planar geometry of the surface (Figure 1b), which leads to lower surface energy. According to our computational results, CO molecules are tightly bound at the \{100\} surface forming stable carbonate units (CO$_3$), which suppresses desorption of CO$_2$ and inhibits the creation of the reactive centers, V$_{O}$. Hence, the oxygen vacancies necessary for N$_2$O remediation are not created. Note that N$_2$O is used as a representative NO$_x$ in this theoretical study to simplify the construction of reaction models.

 Accordingly, we attempted the synthesis of thin single crystals of CuO (CuO-1) with developed \{001\} facets by a ligand-assisted hydrothermal reaction. Ligand molecules often promote anisotropy in the kinetics of crystal growth processes, leading to fine control of nanocrystalline morphology.$^{20,21}$ CuCl$_2$, urea, and ethylene glycol (a bidentate ligand) were mixed in water and then heated at 140 °C in an autoclave for 15 h. Flowerlike assemblies of thin CuO crystals were obtained as a black powder (Figure 2a,b). If ethylene glycol was not added or if smaller quantities of ethylene glycol were used, thicker crystals of CuO were obtained due to isotropic crystal growth (SI: Figure S1). Also, when monodentate ethanol was used instead of ethylene glycol, thick crystals of CuO were obtained (SI: Figure S1). These result suggests that ethylene glycol molecules are strongly adsorbed onto the \{001\} facets and inhibit the crystal growth of CuO along the c-axis. As a result, crystals of CuO tend to grow in the a–b plane resulting in the formation of thin crystals with large surfaces predominantly composed of \{001\} facets, which is supported by the following analyses of CuO-1.

Figure 1. Energy-minimized geometries of ideal and CO-adsorbed surfaces of CuO with schematics describing a catalytic NO remediation cycles. a) In the case of the CuO \{001\} facet, it is more energetically favorable that oxygen atoms on the surface are removed by incoming CO molecules, resulting in the formation of CO$_2$ and an oxygen vacancy. Subsequently, the oxygen vacancy acts to remove oxygen atoms from N$_2$O, and the CuO \{001\} facet recovers its original state. Red, blue, black, and gold balls represent O, Cu, C, and N atoms, respectively. b) In the case of the CuO \{100\} facet, CO molecules are strongly bound at the surface so that the oxygen vacancies necessary for N$_2$O remediation are not created. Note that N$_2$O is used as a representative NO$_x$ in this theoretical study to simplify the construction of reaction models.

Figure 2. Characterization of single-crystalline CuO, CuO-1: a) Photograph of a powder sample. b) SEM image. c) FIB-SEM image, revealing its interior structure. d) pXRD profile. e) XPS profile in the range of 925–975 eV. Satellite signals are indicated by asterisks. f) Electron diffraction pattern of a CuO-1 fragment. The periodic diffraction pattern is characteristic of a single crystal. g) Cross-sectional HR-TEM image revealing the atomic arrangements of the CuO \{001\} facet.
is accessible to gases (SI: Table S1). The powder X-ray diffraction (pXRD) pattern of CuO-1 (Figure 2d) contains peaks that are assigned to the monoclinic phase of CuO (Joint Committee on Powder Diffraction Standards (JCPDS) 05–0661). Its X-ray photoelectron spectrum (XPS) comprised intense spin–orbit split peaks for 2p\(\frac{3}{2}\) (934.1 eV) and 2p\(\frac{1}{2}\) (954.2 eV) accompanied by satellite peaks, which are typical of pure Cu(II) valency (Figure 2e).\(^{[22]}\) The electron diffraction pattern of CuO-1 clearly indicates the presence of pristine crystalline CuO (Figure 2f). Additionally, high-resolution transmission electron microscopy (HR-TEM) as well as cross-sectional HR-TEM reveals that the atomic arrangements at the surfaces of CuO-1 are characteristic of the [001] facet (Figure 2g and S1: Figure S3, S4). Scanning microscopy measurements indicate that the [001] facet of CuO-1 is smooth with a surface roughness of less than 5 Å (SI: Figure S7). CuO-1 has a high thermal stability under inert atmosphere between 25 and 300 °C without detectable weight losses or any variation in the pXRD patterns or the morphology observed by SEM (SI: Figure S6).

Temperature-programmed desorption (TPD) of NO revealed that the surface of CuO-1 is chemically different from those of other CuOs. NO gas adsorbed on the surface of CuO-1 at 300 K desorbs with increasing temperature with most of the NO being desorbed at 379 K. An additional smaller desorption event occurred at 422 K (Figure 3a). Judging from the aforementioned unique morphology of CuO-1, desorption processes occurring at 379 and 422 K should derive from the [001] facet and other facets (i.e., edges of the thin single crystals), respectively. When CuO-1 was ground and ultrasonically treated for 60 min in water (CuO-2), the NO desorption volume at higher temperature was relatively increased due to the increased availability of edge sites (Figure 3b). Commercially available CuO nanopowder (CuO-NP), with a particle size of less than 50 nm, undergoes strong NO desorption in the range of 441–446 K (Figure 3c). These data strongly suggest that CuO-NP does not possess a large surface area of [001] facets.

Due to the large area of the [001] facet in CuO-1, it outperformed the other CuO materials tested (i.e., CuO-2, CuO-NP) for NO remediation catalysis. An equimolar mixture of NO (5.0 kPa) and CO (5.0 kPa) gases were circulated with each CuO material (10 mg) at 175 °C, and the NO remediation percentage (i.e., conversion of harmful NO to less-toxic N\(_2\) or N\(_2\)O) was monitored using gas chromatography–mass spectrometry (GC-MS) as a function of duration time (Figure 4a). As expected from theoretical calculations, CuO-1 is a much better NO remediation catalyst than the other CuO materials despite its relative surface area (15.3 m\(^2\) g\(^{-1}\)) being lower than those of CuO-2 (19.8 m\(^2\) g\(^{-1}\)) and CuO-NP (29 m\(^2\) g\(^{-1}\)). The surfaces of CuO-2 and CuO-NP are increasingly passivated by the adsorption of CO molecules without the formation of oxygen vacancies. Moreover, CuO-1 can be used repeatedly at 175 °C without deterioration of its catalytic activity because of the enhanced stability of the developed [001] facets (SI: Figure S16). HR-TEM observations demonstrated that CuO-1 retained the inherent atomic arrangement on the [001] facets even after catalysis (SI: Figure S11A). Selected-area transmission-electron diffraction (SAED) and electron-probe microanalysis (EPMA) also showed that neither the chemical composition nor the atomic ordering of the CuO-1 [001] facets was changed during the catalytic process (SI: Figure S11B,C). Conversely, the catalytic activity of CuO-2 was detrimentally affected; a significant proportion of the catalyst was reduced to Cu\(_2\)O as a result of the fact that CuO-2 is rich in unstable edges bearing the [001] facet.
facets (SI: Figure S8). In contrast to the negligible structural change on the CuO-1 {001} facets during the catalytic process, the Cu 2p photoemission peaks for CuO-1 were slightly shifted to lower binding energy, corresponding to the formation of oxygen vacancy and low-valence Cu cations on the surface (SI: Figure S10A). The oxygen vacancy on the CuO-1{001} facets, as expected from theoretical calculations (Figure 1), efficiently promotes the desired NOx remediation.

NO remediation activity of CuO-1 exceeds that of an equal weight of Pt nanoparticles immobilized on alumina, and is comparable to the activity of an equal weight of Rh nanoparticles on alumina (Figure 4a). Considering that the relative surface area of CuO-1 is several times lower than that of the PGM nanoparticles (with an average particle size of 2.5 nm), the NO remediation activity of CuO-1 per unit surface area must be considerable. Note that during its early stage, CuO-1 catalysis leads to the production of a considerable quantity of N2O (Figure 4b). N2O is less harmful than NO (it has been used as an anesthetic) although it has recently been recognized as a potent green-house-effect gas\(^\text{[26]}\) as well as an ozone-depleting agent. CuO-1 further converts N2O gas to N2 through a sequential/concurrent reaction (see Equation 2 so that the selectivity of the catalyst, which is defined as the ratio of N2O to remediated gases (i.e., N2 + N2O) produced, exhibits a parabola-like curve only in the case of CuO-1 and Rh nanoparticles.

Thus, at the final stage of catalysis, the quantity of N2O relative to remediated gases is less than those for other CuO materials and Pt nanoparticles.

\[
\text{N}_2\text{O} + \text{CO} \rightarrow \text{N}_2 + \text{CO}_2 \tag{2}
\]

The CuO-1 catalyst efficiently remediates NO not only in the simulated exhaust corresponding to Equation 1 and/or 2, but it can also remove NO contained in the real exhaust of small vehicles (Figure 4c). An aliquot of 100 mL min\(^{-1}\) of exhaust from a commercial gasoline engine (SUBARU EH09, 86 mL displacement) was passed over CuO-1 at 170 °C. The NO concentration in the exhaust was initially 600 ± 50 ppm, but it quickly decreased to the detection limit of the gas sensor, 400 ± 50 ppm, upon exposure to the catalyst (denoted by ON in Figure 4c). When the exposure was terminated by bypassing the exhaust, the NO concentration went back to the initial value (denoted by OFF in Figure 4c). Note that the exhaust contained 10, 4, and 1 vol% of CO2, H2O, and O2, respectively (SI: Figure S18). The CuO-nanoplate catalyst can remediate NO in the presence of certain amounts of H2O and O2.

In summary, we have demonstrated that transition-metal oxides can perform as an effective, PGM-free catalyst for the exhaust of small vehicles, following the theoretical identification of its most reactive surface and after synthesizing it with a maximized amount of reactive surface. We believe that our approach is applicable to various substances such as metals, metal oxides, and alloys, leading to a promising approach for the development of effective catalysts from abundantly available resources.

**Experimental Section**

**Synthesis of CuO-1:** Equal amounts of CuCl\(_2\) (100 mg) and urea (100 mg) were dissolved in a mixture of water (9 mL) and ethylene glycol (6 mL), and the subsequent solution was stirred to obtain a clear solution. The solution was then transferred to a 25-mL Teflon-lined stainless-steel autoclave, sealed, and heated at 140 °C for 15 h in an electric oven. After the reaction, the autoclave was naturally cooled to room temperature. The product was collected by centrifugation at 3000 rpm for 3 min and washed with distilled water twice and ethanol to remove excess reactants. Finally, the product, CuO-1, was dried under vacuum and collected for characterization. Yield: 20 mg (34%).

**NO-Remediation Catalysis Test:** The NO-remediation reaction was performed over the catalyst in a circulating-gas reactor equipped with a gas chromatograph (Shimadzu GC-8A). The catalyst was vacuum-dried in the reactor prior to the reaction. A mixture of NO (5.00 kPa) and CO (5.00 kPa) was then circulated through the catalyst at different temperatures. The formation of N2O and CO2 was monitored at each temperature with the gas chromatograph. The practical feasibility of the catalyst was tested by using a commercial engine (SUBARU EH09, 4-cylinder, gasoline, 2.4 HP, 3600 rpm, 86 mL displacement). Exhaust from the engine was passed over 10 mg of the catalyst at a flow rate of 1000 mL min\(^{-1}\).
100 mL min⁻¹, in which the catalyst temperature was kept at 170 °C. The composition of the exhaust with and without the exposure to the catalyst was monitored with a quadrupole mass-spectrometer (Q-mass, ULVAC Qulee YTP-50M) and a Fourier-transform IR spectrometer (Shimadzu Prestige 21).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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