Abstract: Understanding the property evolution of atomically precise nanoparticles atom by atom along the size continuum is critical for selecting potential candidates to assemble nanomaterials with desired functionality, but it is very challenging experimentally for systems having mixtures of elements such as metal oxides. In this work, the capability to oxidize carbon monoxide has been measured experimentally for titania nanocluster anions of \((\text{TiO}_2)_n\text{O}^-\) \((−3 \leq m \leq 3)\) across a broad size range in the gas phase. Stoichiometric \((\text{TiO}_2)_2\text{O}^-\) exhibits superior oxidative activity over other clusters of \((\text{TiO}_2)_n\text{O}^-\) \((m \neq 1)\) even when the cluster dimensions are scaled up to \(n = 60\), indicating that each atom still influences the chemical behavior of titania nanoparticles composed of \(\approx 180\) atoms. The fascinating result not only identifies a promising building block of \(\text{Ti}_n\text{O}_{m+1}\) for devising new nanoscale titania materials with desirable oxidative activity, but also provides compelling molecular-level evidence for the Mars–van Krevelen mechanism of CO oxidation over titania supports.

Nanostructured materials have drawn increasing interest due to their potential applications in various fields such as catalysis\(^{[1]}\) sensors\(^{[2]}\), plasmonics\(^{[3]}\), and biomedicine\(^{[4]}\). The physical and chemical behavior of nanoparticles and nanoclusters is generally size- and composition-dependent\(^{[5]}\). The ability to tailor the nanoparticles at an atomic level is of crucial importance for uncovering promising candidates for the assembly of new materials with specific functionalities. To date, atomically precise metallic nanoparticles have been synthesized in solution and in the gas phase\(^{[5, 4]}\), allowing for the accurate determination of their structure–property correlations. In contrast, the information about atomically precise metal oxide nanoparticles is rather limited\(^{[7]}\) despite the widespread use of metal oxides owing to their catalytic, magnetic, and other properties.

Titanium dioxide \((\text{TiO}_2)\) is one of the most widely used metal oxide catalysts and catalyst supports for diverse reactions including CO oxidation\(^{[6]}\), water splitting\(^{[9]}\), and pollutants degradation\(^{[10]}\). In the past years, the development of solution procedures has contributed significantly to the synthesis of titania nanoclusters\(^{[11]}\). So far, the largest atomically precise cluster reported is \([\text{Ti}_3\text{O}_4]\) protected by surface organic ligands\(^{[12]}\). The hydrogen evolution activity tests demonstrated that it exhibits higher photocatalytic performance than the small cluster of \([\text{Ti}_4\text{O}_7]\). It should be noted that the atomically precise titania nanoclusters synthesized via solution methods were usually scattered over a range of discrete sizes and stoichiometric compositions\(^{[13]}\). Moreover, the introduction of various distinct types of ligands to stabilize the specific clusters inevitably influences the related properties\(^{[13]}\). It is very difficult to generalize the correlations of property evolution with cluster size and stoichiometric compositions under comparable conditions.

Benefitting from state-of-the-art mass spectrometry and spectroscopy methods coupled with various cluster sources, gas-phase experiments offer an excellent opportunity to study the variation in cluster properties systematically atom by atom.\(^{[14]}\) Early in 2007, an investigation of the electronic structures of \((\text{TiO}_2)_n\) clusters \((n = 1–10)\) identified that the band gap of \((\text{TiO}_2)\) rapidly approaches the bulk limit at \(n = 7\) due to the small exciton radius of bulk \(\text{TiO}_2\) \((\leq 3\) nm\)\(^{[15]}\). In sharp contrast, our study\(^{[16]}\) revealed that when the clusters were upsized to \((\text{TiO}_2)_2\text{O}^-\) \((−3 \leq m \leq 3)\), the chemical reactivity still exhibited cluster behavior: Clusters of stoichiometric \((\text{TiO}_2)_2\text{O}^-\) were reactive for CO oxidation at room temperature, whereas other clusters of \((\text{TiO}_2)_m\text{O}^-\) \((m \neq 1)\) were inert. To pursue the bottom-up strategy\(^{[17]}\) that uses potential clusters as building blocks for tailoring the properties of new materials with nanoscale dimensions, it is highly desirable to investigate much larger titania nanoclusters to determine which individual characteristics might be retained when they assemble into extended materials. However, it is experimentally challenging to 1) prepare such large nanoclusters in significant quantities for characterization and 2) build a compatible mass spectrometer with high resolution to resolve the nanocluster ions. Herein, by using a homemade high-resolution time-of-flight (TOF) mass spectrometer coupled with a nanocluster source,\(^{[18]}\) we prepared large negatively charged titania nanoclusters \((\text{TiO}_2)_n\text{O}^-\) \((−3 \leq m \leq 3)\) covering a broad size range of \(n = 26–60\). Their reactivities toward CO oxidation were studied under comparable con-
ditions, which provided a good opportunity to uncover the reactivity evolution of titania nanoclusters atom by atom along the size continuum.

The five stable isotopes of Ti occur with the following natural abundance: $^{46}$Ti 8.25%, $^{47}$Ti 7.44%, $^{48}$Ti 73.72%, $^{49}$Ti 5.41%, and $^{50}$Ti 5.18%. In order to eliminate the isotopically overlap of adjacent clusters in a mass spectrum, a monoisotopic $^{48}$Ti sample was used to prepare the atomically precise titania nanocluster anions of (TiO$_2$)$_n$O$_m^-$ with $n$ up to 60 via a laser ablation method. Selected TOF mass spectra for the interactions of Ti$_n$O$_m^-$ (n = 40–42) with background gas (N$_2$) for reference and reactant gas (CO) in a fast-flow reactor are shown in Figure 1a,b, respectively.

Figure 1. Selected TOF mass spectra for reactions of $^{48}$TiO$_m^-$ with 1.3 Pa N$_2$ (a) and 1.3 Pa CO (b). The difference spectrum between (a) and (b) is shown as (c). The peaks marked with asterisks originate from the Ca impurities in the sample of $^{48}$Ti powder. The detailed assignments of CaTi$_n$O$_m^-$ cluster anions are shown in Figure S1 in the Supporting information.

(calibration details are given in the Supporting Information).

It can be seen that upon reaction with 1.3 Pa CO, the signal magnitudes of Ti$_4$O$_{11}^-$ [(TiO$_2$)$_4$O$^-$], Ti$_5$O$_{12}^-$ [(TiO$_2$)$_5$O$^-$], and Ti$_6$O$_{18}^-$ [(TiO$_2$)$_6$O$^-$] clusters decrease significantly concomitant with the signal increase of the clusters with one less oxygen: Ti$_3$O$_{11}^-[(TiO$_2$)$_3$O$^-],$ Ti$_4$O$_{12}^-[(TiO$_2$)$_4$O$^-],$ and Ti$_5$O$_{18}^-[(TiO$_2$)$_5$O$^-]$. In sharp contrast, the signal intensities of more oxygen-rich clusters such as Ti$_6$O$_{24}^{3-},$ Ti$_7$O$_{34}^{-6},$ and Ti$_8$O$_{36}^{-8}$ do not change within the experimental uncertainty. The difference spectrum (Figure 1c; spectrum in Figure 1b minus that in Figure 1a) clearly shows that the signal depletion of (TiO$_2$)$_n$O$^-n$ results in the signal increase of (TiO$_2$)$_{n-2}$O$^-n$.

The complete difference spectra for the reactions between CO/N$_2$ and (TiO$_2$)$_n$O$_m^-$ clusters with $n$ ranging from 5 to 60 are shown in Figure 2 (see Figures S2–S10 in the Supporting Information for complete spectra). It turns out that the overall reactivity patterns of (TiO$_2$)$_4$O$^-$ and (TiO$_2$)$_5$O$_{12}^- (m \neq 1)$ with $n$ up to 60 are very similar to those of (TiO$_2$)$_4$O$^- n$ and (TiO$_2$)$_5$O$_{12}^- (m \neq 1)$, respectively. It should be noted that the titania clusters were generated by using a $^{18}$O oxygen source. Because $^{48}$Ti and $^{48}$O have the same mass number, the peaks corresponding to Ti$_n$O$_m^-$ may also be assigned as the oxygen-rich clusters of Ti$_n$O$_m^-n$ as marked in Figure 1a (e.g. Ti$_6$O$_{11}^-$ and Ti$_7$O$_{18}^-$. Taking into account that the unique oxygen atom transfer (OAT) activity of small- and medium-sized (TiO$_2$)$_n$O$^-$ clusters ($n = 3–25$) had been previously confirmed in experiments with natural abundance Ti,$^{[16]}$ it is evident that the OAT activity of large-sized (TiO$_2$)$_n$O$^-$ ($n = 26–60$) clusters toward CO also originates from Ti$_n$O$_{2n+1}^{-}$ rather than Ti$_n$O$_{2n+4}^-$. Thus, the experiments suggest that regardless of the size of the titania clusters, only the stoichiometric (TiO$_2$)$_4$O$^-$ cluster exhibits good OAT activity toward CO [Eq. (1)].

$$(TiO_2)_4O^- + CO \rightarrow (TiO_2)_4O^- + CO_2 \quad (n = 3–60) \quad (1)$$

Besides, our experiments indicate that when one of the Ti atoms in the (TiO$_2$)$_n$O$^-$ clusters was replaced by a Ca atom (originating from impurities in the $^{48}$Ti sample), CaO-(TiO$_2$)$_n$O$^-$ clusters form and such clusters can also exhibit unique OAT activity in CO oxidation, as denoted with asterisks in Figure 1c.

The pseudo-first-order rate constants ($k_i$) for the reactions between each of the (TiO$_2$)$_n$O$^-$ and CO in the fast-flow reactor were estimated (Figure S12 in the Supporting Information) by using Equations (2) and (3).

$$\ln \frac{I_k - I_{\text{inert}}}{I_T - I_{\text{inert}} - I_{P1}} = -k_i \frac{p_{CO}}{R_k T} t$$

(2)

$$\ln \frac{x_P - x_{\text{inert}} - x_{P1}}{1 - x_{\text{inert}} - x_{P1}} = -k_i \frac{p_{CO}}{R_k T} t$$

(3)

Here, $I_k$ is the intensity of reactant (TiO$_2$)$_n$O$^- /Ti$_{n-1}$O$_{2n+4}^-$ ions after reaction, $I_{\text{inert}}$ is the intensity of inert component (TiO$_2$)$_n$O$^- /Ti$_{n-1}$O$_{2n+4}^-$ ions, $I_T$ is the total intensity including product ion [(TiO$_2$)$_n^-$] contribution, $I_{P1}$ is the background intensity of product ions before reaction, $p$ is the CO pressure.
in the reactor, \( t_R \) is the reaction time, \( k_g \) is the Boltzmann constant, and \( T \) is the temperature (300 K). Equation (2) can also be rewritten as Equation (3), in which \( x_R = I_R/I_0 = I_{net}/I_0 \) and \( x_{pt} = I_{pt}/I_0 \). Figure 3 plots the relative rate constant \( k_n[\text{TiO}_2]_n\text{O}^+ + \text{CO} \rightleftharpoons k_n[\text{TiO}_2]_n\text{O}^+ + \text{CO} \) versus cluster size. It demonstrates that the activities of \((\text{TiO}_2)_n\text{O}^-\) clusters across such the broad size range of \( n = 6-50 \) are almost in the same order of magnitude.

The very distinct situation in the electron transfer \( \text{O}^2- \rightarrow \text{M}^{+} \) between titania and vanadia nanoclusters well correlates with the reductive potentials of \( \text{Ti}^{4+}/\text{Ti}^{3+} \) versus \( \text{V}^{3+}/\text{V}^{2+} \). The less positive reduction potential of \( \text{Ti}^{4+}/\text{Ti}^{3+} \) (\(-0.1 \text{ V}\)) relative to that of \( \text{V}^{3+}/\text{V}^{2+} \) leads to the low electron affinity of \( \text{Ti}^{4+} \) and its weak tendency to be reduced. Therefore, the generation of \( \text{O}^- \) radicals in the nanosized \((\text{TiO}_2)_n\text{O}^- \) clusters (\( m \neq 1 \)) with \( \Delta \neq 1 \) is substantially unfavorable compared to that in the vanadia systems under similar conditions.

As to the oxidative reactions of \((\text{TiO}_2)_n\text{O}^- \) (\( \Delta = 1 \)) with \( \text{CO} \), significantly size-dependent reactivity appears over the size range \( n = 6-50 \) (Figure 3). Extensive studies on small metal oxide clusters have found that the bonding character of \( \text{O}^- \) radicals (terminally bonded \( \text{O}^- \) or bridging \( \text{O}^- \)) as well as the distribution of spin densities[10b] and local charges[10b] around \( \text{O}^- \) can profoundly affect cluster reactivity. The electron affinity of small \((\text{TiO}_2)_n \) (\( n \leq 8 \)) clusters has also been proposed to positively correlate with the relative reactivity of \((\text{TiO}_2)_n\text{O}^- \) clusters, which have \( \text{O}^- \) radicals with localized spin densities.[10b] Despite the lack of structural information for large \((\text{TiO}_2)_n\text{O}^- \) clusters in the literature, the structures of \((\text{TiO}_2)_n \) nanoclusters have been widely studied. It was predicted that the energetically stable (\( \text{TiO}_2)_n \) nanoclusters, especially for \( n > 18 \), are either fully coordinated (e.g., \( n = 23, 28, 35 \)) or have at most one \( \text{O}^- \) atom (e.g., \( n = 22, 38 \)).[23b] The anionic \((\text{TiO}_2)_n\text{O}^- \) nanoclusters can be regarded as neutral \((\text{TiO}_2)_n \) clusters bonded with \( \text{O}^- \) radicals. Thus, the \( \text{O}^- \) radicals anchored on the \((\text{TiO}_2)_n \) nanoclusters may be \( \text{O}^- \) or \( \text{O}^- \). Taking into account that the metal oxide clusters with an \( \text{O}^- \) center are usually more reactive than those with an \( \text{O}^- \) center,[10b] the \((\text{TiO}_2)_n\text{O}^- \) nanoclusters with high oxidative reactivity (e.g., \( n = 35 \) in Figure 3) are likely to have \( \text{O}^- \) radicals, whereas \( \text{O}^- \) radicals may appear in the \((\text{TiO}_2)_n\text{O}^- \) nanoclusters with relatively low reactivity. Different distributions of spin densities and local charges around the \( \text{O}^- \) radicals may also cause the size-dependent reactivity.

In heterogeneous catalysis bulk titania is inert toward \( \text{CO} \) oxidation,[24] its catalytic activity can be surprisingly activated even at very low temperatures (\(-160 \text{ °C}\)) when noble metals are supported.[8,25] Considerable efforts have been devoted to uncovering the active oxygen species and reaction mechanisms governing \( \text{CO} \) oxidation over \( \text{M}/\text{TiO}_2 \) catalysts. The surface lattice oxygen[26] (\( \text{O}^- \)) as well as molecularly adsorbed oxygen[27] (superoxide\( \text{O}_2^\cdot^- \) and peroxide\( \text{O}_2^{2-} \)) that are located at the periphery of the \( \text{M}/\text{TiO}_2 \) interface have been proved spectroscopically to participate in \( \text{CO} \) oxidation at different operating temperatures.[28] At low temperatures \( \leq -90 \text{ °C} \), the \( \text{CO} \) molecule is preferably oxidized through the Langmuir–Hinshelwood mechanism via a [\( \text{CO}^-\text{O}_2 \)] co-adsorption complex; when the operating temperature is \( \geq 80 \text{ °C} \), the removal of \( \text{TiO}_2 \) surface lattice oxygens by reaction with \( \text{CO} \) following the Mars–van Krevelen mechanism becomes dominant. However, the involvement of the \( \text{O}^- \) radicals, one of the typical reactive oxygen species formed during \( \text{O}_2 \) dissociation (\( \text{O}_2 \rightarrow \text{O}^- + \text{O}^{2-} \)),[23b] responsible for \( \text{CO} \) oxidation over \( \text{Au}/\text{TiO}_2 \) catalysts has not been experimentally determined so far. It has been frequently demonstrated that the scaling down of bulk systems to discrete and well-defined nanoparticles could significantly
influence the surface electronic properties and consequently the catalytic performance.\[30\] Herein, benefitting from the systematic investigation of the reactivity of unsupported titania cluster anions by a “bottom-up” strategy, we definitively identify that the O\(^{2-}\) radicals that are highly reactive in CO oxidation are inherently present in the stoichiometric clusters of \((\text{TiO}_2)_n\text{O}^{-}\) over a rather broad size range \((n = 3–60)\). Furthermore, our experimental observation of the removal of single oxygen atoms from isolated titania nanoparticles \((\text{TiO}_2)_n\text{O}^{-} (\approx 1.6 \text{ nm})\) by CO molecules provides compelling molecular-level evidence for the Mars–van Krevelen mechanism of CO oxidation over titania supports. These results indicate the stoichiometric titania clusters \([\text{Ti,O}_{2n+1}]^{-}\) can be potential building blocks for devising new nanoscale titania materials with special electronic structures. Note that the reactive \((\text{TiO}_2)_n\text{O}^{-}\) nanoparticles identified in this study are negatively charged. It has been shown that heterometal doping with the elements that have one less or one more valence electron relative to the host metal is an effective way to engineer neutral metal oxides with electronic structures closely resembling the positively or negatively charged ones.\[33\] Thus, we suppose that by doping stoichiometric \(\text{Ti}_n\text{O}_{2n+1}\) clusters (e.g., \(n = 60\)) with heterometals of group VB, it would be possible to generate the neutral titania nanoparticles with highly reactive O\(^{2-}\) radicals and create novel noble-metal-free titania materials with strong oxidative activity.

In summary, our experimental investigation on the reactions of carbon monoxide with atomically precise titania nanocluster anions of \((\text{TiO}_2)_n\text{O}^{-} (\approx 3 \leq m \leq 3)\) that have different stoichiometric compositions and cover a rather broad size range \((n = 60)\) indicates that only the stoichiometric clusters of \((\text{TiO}_2)_n\text{O}^{-}\) exhibit good oxidative activity even when the dimensions approach that of \((\text{TiO}_2)_6\text{O}^{-}\) \((\approx 1.6 \text{ nm})\). This observation implies that the reactive atomic oxygen radicals \((O^\cdot)\) that had been proved to be present in the small titania clusters (e.g., \(\text{Ti}_n\text{O}_{2n}\)) are well-preserved in the titania nanoparticles, and also identifies a potential building block for incorporation into cluster-assembled titania nanoparticles. The Mars–van Krevelen mechanism of CO oxidation that was frequently proposed recently is demonstrated by our finding of \((\text{TiO}_2)_n\text{O}^{-}\) \((\approx 1.6 \text{ nm})\) at strictly molecular level by the reaction of CO with isolated \((\text{TiO}_2)_{3\pm2}\text{O}^{-}\) nanoparticles.

**Acknowledgements**

This work was financially supported by the National Natural Science Foundation of China (Nos. 21573247 and 91545122), the Youth Innovation Promotion Association CAS (No. 2018041), the Beijing Natural Science Foundation (No. 2182092), and the Fundamental Research Funds for the Central Universities (JB2015RCY03).

**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** CO oxidation · mass spectrometry · nanoparticles · titania

**How to cite:** Angew. Chem. Int. Ed. 2019, 58, 8002–8006

Angew. Chem. 2019, 131, 8086–8090


