Facet engineering of oxide nanocrystals represents a powerful method for generating diverse properties for practical and innovative applications. Therefore, it is crucial to determine the nature of the exposed facets of oxides in order to develop the facet/morphology-property relationships and rationally design nanostructures with desired properties. Despite the extensive applications of electron microscopy for visualizing the facet structure of nanocrystals, the volumes sampled by such techniques are very small and may not be representative of the whole sample. Here, we develop a convenient $^{17}$O nuclear magnetic resonance (NMR) strategy to distinguish oxide nanocrystals exposing different facets. In combination with density functional theory calculations, we show that the oxygen ions on the exposed (001) and (101) facets of anatase titania nanocrystals have distinct $^{17}$O NMR shifts, which are sensitive to surface reconstruction and the nature of the steps on the surface. The results presented here open up methods for characterizing faceted nanocrystalline oxides and related materials.
Faceted oxide nanocrystals have attracted much research attention in a variety of fields, including catalysis, photocatalysis, solar hydrogen generation, photoelectrochemical application, gas sensing, and energy storage, owing to their specific surface structures. Identification of the exposed facets is thus fundamental to the preparation and applications of oxide nanomaterials. Current characterization tools for studying the surface structure of nanocrystals are mostly based on electron microscopy. At a resolution that the exposed facet can be determined, however, the field of view of microscopy techniques is often so small, or the particles may show considerable aggregation that it is possible that the region investigated is not representative of the whole sample. Therefore, the development of complementary characterization methods that can give detailed structural information concerning the nature of the exposed facets of nanocrystals is urgently required.

Solid-state NMR spectroscopy is a powerful technique that has been widely used in studying the local environments of solids. 17O NMR spectra, e.g., can give detailed structural and dynamic information of important functional oxygen-containing materials benefiting from the large 17O chemical shift range (>1000 ppm). However, few publications are available on the 17O NMR studies of nanosized oxides, in spite of their widespread applications, largely owing to the high cost of 17O and structure change during isotopic labeling. Recently, Wang et al. developed a surface-selective labeling method for oxide nanomaterials at low temperatures and revealed that the 17O species on the first few layers of ceria nanomaterials are associated with different 17O chemical shifts. However, direct experimental evidence is still missing concerning the relationship between the 17O chemical shifts and the nature of the exposed facets.

Here, we demonstrate a new approach based on NMR and surface-selective 17O labeling to determine the structures of the exposed facets on the technologically important anatase titania nanocrystals. With the help of density functional theory (DFT) calculations, oxygen species on different facets can be distinguished by their NMR shifts. The nature of surface steps and reconstructions of these surfaces, particularly on reaction with water, are also revealed.

**Results**

**Morphology of anatase TiO2 nanosheets and nano-octahedra.** Two types of anatase TiO2 nanocrystals with different tailored facets were examined, i.e., anatase TiO2 nanosheets with dominant exposed (001) facets (NS001-TiO2), and nano-octahedra preferentially exposing (101) facets (NO101-TiO2). Their crystal forms were confirmed with X-ray diffraction (XRD) (Supplementary Fig. 1). High-resolution transmission electron microscopy (HRTEM) results show that NS001-TiO2 (Supplementary Fig. 2) are nanosheets with a thickness of 6–7 nm, while NS101-TiO2 (Supplementary Fig. 3) are nano-octahedra with an average size of 14 nm. According to the statistical analysis of the data (Supplementary Figs. 2, 3), an average of 77% of the exposed surfaces of NS001-TiO2 are (001) facets, while 96% of the exposed surfaces of NO101-TiO2 are (101) (see Supplementary Table 1, Supplementary Fig. 4 and additional discussion in Supplementary Note 1). X-ray photoelectron spectroscopy (XPS) spectra (Supplementary Fig. 5) suggest that there is no evidence for the existence of CO or Cl on the surface of either sample, while the concentrations of carbon (C) or nitrogen (N) impurities in both samples are also very small according to the elemental analysis (Supplementary Table 2).

17O NMR spectra of the surface-selectively labeled samples. After exposing to 17O-water for surface-selective labeling, the anatase nanocrystals were characterized with 17O magic angle spinning (MAS) NMR spectroscopy and were compared to a non-faceted anatase TiO2 sample with a smaller surface area (denoted as NF1-TiO2, see Supplementary Fig. 6) labeled nonselectively with 17O2 at 500 °C, as shown in Fig. 1. Bulk anatase TiO2 consists of TiO6 octahedra that share 4 O–O edges (Supplementary Fig. 7a and Supplementary Table 3) and all of the O ions are 3-coordinated (OTi3, denoted as O3c) with an average Ti–O bond length of 0.195 nm. Therefore, 17O NMR spectrum of the anatase TiO2 sample enriched with 17O2 at high temperature show a single sharp peak at 558 ppm (Fig. 1), corresponding to O3c species in the “bulk” part, consistent with previous reports. It is clear that the 17O NMR spectra of surface-labeled NS001-TiO2 and NO101-TiO2 differ significantly and are also distinct from the spectrum of the nonselectively labeled anatase TiO2 (Fig. 1), reflecting their different local structures (see Supplementary Fig. 7 and Supplementary Table 3, and further discussions below), suggesting that 17O NMR spectroscopy can be a new method to distinguish faceted oxide nanocrystals.

The signals observed in the 17O NMR spectra of NS001-TiO2 and NO101-TiO2 can be categorized into three types. The resonances at 480–570 ppm should arise from O3c species on the surface of titania, since their chemical shifts are close to that of bulk O3c. The peaks at higher frequencies (600–750 ppm) can be assigned to O species with lower coordination numbers (e.g., O2c).

![Fig. 1](image-url) 17O NMR spectra of faceted anatase titania nanocrystals compared to the non-faceted sample. Anatase TiO2 nanosheets with dominant exposed (001) facets (NS001-TiO2), and nano-octahedra preferentially exposing (101) facets (NO101-TiO2) were surface-selectively 17O-labeled and vacuum dried for 2 and 12 h, respectively. The other sample, NF1-TiO2, was nonselectively 17O-labeled. All data were obtained at 9.4 T under a MAS frequency of 14 kHz. A rotor synchronized Hahn-echo sequence (\(\pi/2\rightarrow T \rightarrow \pi\rightarrow T \rightarrow \text{acquisition}\)) and optimized recycle delays (0.5 s for NS001-TiO2 and NO101-TiO2, and 50 s for NF1-TiO2, see Supplementary Fig. 8), with \(^1\)H decoupling, were used to obtain the NMR data. 120,000, 110,000, and 1200 scans were collected for NS001-TiO2, NO101-TiO2, and NF1-TiO2, respectively. The spectra are normalized according to the sample mass and the number of scans (Supplementary Table 4). Asterisks denote sidebands. The dependence of the 17O MAS NMR spectra of the two faceted samples on the vacuum-drying time is shown in Supplementary Figs. 9 and 10, and discussed in the Supplementary Notes 2 and 3. Comparison of the 17O NMR spectra of the two faceted nanocrystalline samples to a surface-selectively labeled, non-faceted anatase TiO2 nanoparticle sample with comparable surface area (denoted as NF2-TiO2 and the TEM image of the sample is shown in Supplementary Fig. 11) can be found in Supplementary Fig. 12 and Supplementary Note 4.
on the surface of titania nanostructure\textsuperscript{27}. The broad signals at lower frequencies (~150 to 300 ppm) can be attributed to hydroxyl groups in surface hydroxyls and/or water environments\textsuperscript{27, 34, 35}. The peak centered at 150 ppm in the spectrum of NS001-TiO\textsubscript{2} can also be observed in \textsuperscript{1}H→\textsuperscript{17}O cross-polarization (CP) MAS NMR spectra (Supplementary Fig. 13 and Supplementary Note 5), confirming that this signal arises from oxygen ions in close proximity to proton. Such signal is very weak in the spectrum of NO101-TiO\textsubscript{2}, while an additional peak can be found centered at ~75 ppm (Fig. 1 and Supplementary Figs. 10, 14). According to the shift, this lower-frequency resonance is assigned to adsorbed water molecules (see Supplementary Fig. 10 and Supplementary Note 3). The observation of surface OH species on the (001) facet while only water on the (011) surface, on the vacuum-dried samples, agrees with the previous DFT calculations that water prefers to dissociate on anatase TiO\textsubscript{2} (001) facet to form surface OHs\textsuperscript{36}, while it tends to adsorb molecularly on (011) surface\textsuperscript{37, 38}.

Surface reconstruction of anatase TiO\textsubscript{2}(001). In order to help the spectral assignment, DFT calculations were performed on anatase titania structures with different exposed facets. Since water molecules prefer to dissociate on the high-energy (001) facets\textsuperscript{36}, and surface reconstructions are likely to occur on (001)\textsuperscript{39}, four possible surface models were constructed for NS001-TiO\textsubscript{2}, including the un-reconstructed clean TiO\textsubscript{2}(001) (CL), hydrated TiO\textsubscript{2}(001) at a water coverage of $\frac{1}{2}$ ML (dissociative adsorption, DA), $1 \times 4$-reconstructed clean TiO\textsubscript{2}(001) (RC-CL), and hydrated $1 \times 4$-reconstructed TiO\textsubscript{2}(001) (RC-DA) (see Fig. 2 and Supplementary Figs. 15–18 for details). $\frac{1}{2}$ ML means that every two surface Ti\textsubscript{Sc} take one water molecule, and it also corresponds to a fully hydrated surface state\textsuperscript{40}. The calculated isotropic chemical shifts of each oxygen sites ($\delta_{\text{iso}}$), quadrupolar coupling constant ($\eta_{Q}$), asymmetry parameter ($\eta$), and center of gravity of the NMR signals ($\delta_{\text{CG}}$) are given in Supplementary Tables 5–8. In all the models investigated, the calculated chemical shifts ($\delta_{\text{CG}}$) of oxygen ions in the “bulk” part (middle layers) of the anatase structures are close to 558 ppm, which is the observed chemical shift of O\textsubscript{Sc} in the nonselectively labeled anatase TiO\textsubscript{2}. The chemical shifts of the oxygen species in the first few layers, however, deviate noticeably from the “bulk” values and depend on the specific local structure.

The calculated results were used to simulate the \textsuperscript{17}O NMR spectra at different external magnetic fields (Fig. 2 and Supplementary Fig. 19) by considering the surface oxygen species only, whose isotropic chemical shifts have been marked in the structural models in Fig. 2. The simulated signals arising from the OH species generated in the DA and RC-DA structures give a fair match with the experimental data (450–0 ppm), further supporting that water dissociates on the (001) facets. Furthermore, they also allow us to assign a weak peak centered at approximately 400 ppm that overlaps with the sidebands from the surface oxygen sites to another OH environment. The calculation results also show that the majority species that give rise to the signals at 600–760 ppm in the experimental data are actually the O\textsubscript{Sc} environments, rather than the O\textsubscript{Sc} site, and that these species can only be ascribed to reconstructed surfaces (i.e., contributions from the RC-CL and/or RC-DA structures). Therefore, these results provide compelling evidence that structure reconstruction does indeed occur on the (001) surface. On the basis of the \textsuperscript{1}H NMR results (Supplementary Fig. 20 and Supplementary Table 9), the water coverage on this sample is 0.3 ML, indicating that a reconstructed surface is energetically favored at this state\textsuperscript{36}, and both RC-CL and RC-DA surface conditions should exist, due to the insufficient water coverage. Therefore, it can be concluded that, at this specific water coverage (0.3 ML), surface reconstruction occurs on (001) surface of anatase titania, and water dissociates on this surface.

Step edges of anatase TiO\textsubscript{2}(101). For NO101-TiO\textsubscript{2}, three defect-free structure models, including clean anatase TiO\textsubscript{2}(101) (CL), hydrated anatase TiO\textsubscript{2}(101) under a water (molecular adsorption) coverage of $\frac{1}{2}$ ML (MA), and hydrated anatase TiO\textsubscript{2}(101) with dissociatively adsorbed water under the coverage of $\frac{1}{2}$ ML (DA, which is energetically less favorable\textsuperscript{37, 38}), were constructed first to calculate the NMR parameters (Supplementary Figs. 21–23 and Supplementary Tables 10–12). However, the simulated spectra do not match the experimental data (for surface O\textsubscript{Sc} sites in particular) (Supplementary Fig. 24). Surface defects, however, often occur on the (101) facets according to scanning tunneling microscopy investigations\textsuperscript{40, 41} as well as first-principles calculations\textsuperscript{41}. Particularly, “step edges”, associated with higher reactivity\textsuperscript{41}, are considered as the most common defects on this surface. Gong et al. have proposed several types of step-edge defects\textsuperscript{42} with monoatomic height along trapezoidal or triangular islands on (101) surface\textsuperscript{40, 43}. The so-called type-D steps occur along two nonparallel sides of the trapezoidal islands (or two sides of the triangular ones), and they are also the most prevalent ones among all the steps. Accordingly, in the current work, an anatase TiO\textsubscript{2}(134) vicinal surface with such type-D steps...
and Supplementary Fig. 27b), except for the center of gravity of the NMR signal for the adsorbed water species (Fig. 3b, peak 1).

The experimental line width of this peak is smaller than the calculated one, which can be attributed to the motion of the adsorbed water molecules (see Supplementary Fig. 28 and Supplementary Note 6). Other signals from surface sites probably originate from the dissociation of H\textsubscript{2}\textsuperscript{17}O at oxygen vacancies generated in the vacuum-drying pretreatment at 100 °C (see Supplementary Fig. 29 and Supplementary Note 7) and possible subsequent migration of oxygen ions within the structure of TiO\textsubscript{2}, since water molecules are not expected to dissociate on type-D step edges\textsuperscript{37, 44}. The major resonance at 730 ppm (peak 3) arises from O\textsubscript{2c} species at the step edges (Fig. 3). In comparison, peak 2, corresponding to O\textsubscript{2c} species at the middle of (101) plane, has much smaller intensity. Considering the fact that there is only a small fraction of oxygen ions at step edges (4 ± 1.5%\textsuperscript{35}), the much stronger intensity of peak 3 implies that O\textsubscript{2c} at the step edge has higher activity in the initial labeling process than the species on (101) plane. The other relatively strong peak owing to O\textsubscript{2c} ions occurs at 640 ppm (peak 5). Such oxygen species is at flat terraces below the adjacent step edge and is attached with the adsorbed water through hydrogen bond. The signals at 480–560 ppm can be assigned to surface and subsurface O\textsubscript{2c} species. The much stronger intensity of the O\textsubscript{2c} species compared to the O\textsubscript{2c} ones confirms that the \textsuperscript{17}O-enrichment method adopted in this work does achieve an effective surface-selective labeling.

### Discussion

\textsuperscript{17}O solid-state NMR spectroscopy, in combination with DFT calculations, can be used to distinguish two anatase TiO\textsubscript{2} nanocrystals with different exposed facets and explore the details of their unique surface local environments. The \textsuperscript{17}O NMR spectra provide definitive evidence that surface reconstruction occurs when (001) faceted anatase TiO\textsubscript{2} nanosheets adsorb a small amount of water, while “step edges” are the main defects present on the anatase TiO\textsubscript{2}(101) surface. The results indicate that \textsuperscript{17}O solid-state NMR spectroscopy is a sensitive method to probe the local environments of the exposed facets of oxide nanocrystals, the structures of these facets playing a vital role in determining their properties. Further studies based on this approach can be readily envisaged to study possible changes that may occur on the faceted oxide nanocrystals in catalytic processes and other related applications.

### Methods

#### Sample preparation.

The anatase TiO\textsubscript{2} nanosheets, mainly dominated by exposed (001) facets, i.e., NS001-TiO\textsubscript{2}, were prepared according to Han’s work\textsuperscript{45}. (101) facets dominated anatase nano-octahedra (NO101-TiO\textsubscript{2}), and non-faceted anatase TiO\textsubscript{2} nanoparticles (NF2-TiO\textsubscript{2}) were prepared hydrothermally according to Liu’s work\textsuperscript{44}. The obtained materials were washed thoroughly with NaOH aqueous solution and water to remove F\textsuperscript{−} or Cl\textsuperscript{−} on the surface, which were introduced in the preparation. Experiment details are given in the Supplementary Methods. Another non-faceted anatase TiO\textsubscript{2} sample with smaller surface area, NFI-TiO\textsubscript{2}, was purchased from Sigma-Aldrich Corporation, and used as received.

#### Characterization.

The powder XRD analysis was carried out on a Philips X’Pert X-ray diffractometer using Cu K\textsubscript{α} irradiation (λ = 1.54184 Å) operated at 40 kV and 40 mA at 25 °C. High-resolution TEM images were obtained on an FEI Titan 80/300 STEM with an acceleration voltage of 200 kV. Electron paramagnetic resonance (EPR) spectra were recorded on the samples with the same mass (50 mg) by a Bruker EMX-10/12 spectrometer at room temperature. The Brunauer–Emmett–Teller specific surface areas of the samples were measured by nitrogen adsorption at 77 K using a Micromeritics tristar ASAP 2020 instrument. The contents of C and N impurities of the samples were analyzed using a Heraeus CHN-O-Rapid analyzer. XPS spectra of both faceted samples were obtained on an Ulvac-PHI PHI 5000 VersaProbe instrument.

#### \textsuperscript{17}O enrichment.

Faceted NS001-TiO\textsubscript{2}, NO101-TiO\textsubscript{2}, and non-faceted NF2-TiO\textsubscript{2} nanocrystalline samples were surface-selectively \textsuperscript{17}O-labeled through a vacuum line
using 90% 17O-enriched H2O (Cambridge Isotope Laboratories). The sample (typically 300 mg) was first activated in a glass tube by vacuum drying at 100 °C for 1.5 h. After the sample was cooled to 25 °C on room temperature, it was exposed to the saturated vapor of 17O-enriched H2O for 10 min for adequate adsorption. Then the sample was sealed in the glass tube, heated to 40 °C and kept at this temperature for 5 h to achieve an optimized 17O labeling of the surface oxygen species. The other non-faceted anatase TiO2 sample NFI-TiO2, with a smaller surface area, was 17O labeled nonselectively by calcining in 17O2 (70% 17O, Cambridge Isotope Laboratories) within a sealed glass tube at 500 °C for 12 h.

### Solid-state NMR measurement.
17O MAS NMR spectra were measured on 9.4 and 14.1 T Bruker Avance III spectrometers using 4 mm MAS probes doubly tuned to 1H and 17O at 54.2 and 81.3 MHz, and H at +4000 and 600.0 MHz, respectively. All samples were packed into rotors in a N2 glove box. 17O chemical shift is referenced to H2O at 0.0 ppm.

### DFT calculations.
Spin-polarized DFT calculations were performed with the Perdew–Burke–Ernzerhof functional by using the Vienna Ab initio Simulation Package (VASP). The 17O chemical shifts were calculated by using the linear response method. We used the project-augmented wave method to describe the core-valence electron interactions in structure optimization, chemical shift, and electric field gradients (EFGs) calculations at a kinetic energy cutoff of 500 eV with Ti (3s, 3p, 3d, 4s), O (2s, 2p), and H (1s) electrons being treated as valence electrons. All of the atoms were allowed to relax during structure optimization with a force cutoff of 0.02 eV/Å. During optimization, we used an extremely high stopping criterion of 10−8 eV for all the calculations. With a 3 × 3 × 3 k-point mesh, we obtained optimized lattice parameters of a = 3.80 Å and c = 9.51 Å for bulk anatase TiO2, which is very close to the experimental values (a = 3.78 Å and c = 9.50 Å). It should be noted that the on-site Coulomb interaction of localized electrons was also considered by using the DFT+U approach with an optimum Hubbard U value of 4.0 eV48, and lattice parameters of a = 3.86 Å and c = 9.53 Å was obtained. This indicates pristine DFT method can give reliable structural information. Since correct structural information is crucial to chemical shift calculations, we then used the pristine DFT method to do all the calculations.

The anatase TiO2 structures were modeled by surface slabs that are thick enough to maintain trivial fluctuations of chemical shift values in their middle layers (see Supplementary Figures 15–18 and 21–23 for details). For un-reconstructed TiO2(001) surface, 1 × 4-reconstructed TiO2(001) surface5, TiO2(101) surface, and TiO2(134) (vicinal) surface consisting of type-D steps and (101) planes52, we used a 1 × 2, 2 × 4, 1 × 2, and 1 × 1 surface cell, respectively, with a corresponding 4 × 2 × 2, 2 × 1 × 1, 1 × 2 × 1, and 2 × 3 × 1 k-point mesh, respectively, for the Brillouin zone integration. All the slabs also contain a large vacuum gap (~12 Å for un-reconstructed anatase TiO2(001), 1 × 4-reconstructed anatase TiO2(001), anatase TiO2(101) surfaces, and ~13 Å for anatase TiO2(134) vicinal surfaces) to remove the slab–slab interactions.

The isotropic chemical shift (δiso) can be computed as

\[ δ_{iso} = δ_{sub} + δ_{surf}, \]

where \( δ_{iso} \) is the chemical shift obtained in VASP, \( δ_{sub} \) is the reference chemical shift. Considering the fact that bulk oxides have more regular arrangements than those near the surfaces, all the \( δ_{surf} \) for each model (except TiO2(134) vicinal surface) were determined by aligning the average \( δ_{surf} \) of middle four layers to the experimental \( δ_{surf} \) of bulk O3c (561 ppm, Supplementary Figs. 15–19a). We used the experimental quadrupole moment (Q) of ~0.02558 barn53 for 17O.

The adsorption energy of H2O (\( E_{ads} \)) was calculated as follows:

\[ E_{ads} = E_{H2O} + E_{sub} - E_{H2O\_sub}, \]

where \( E_{H2O} \), \( E_{sub} \), and \( E_{H2O\_sub} \) are the DFT total energies of the gas phase H2O, the TiO2 substrate, and the adsorption complex, respectively.

### 17O NMR spectra simulation.
Wisdols package developed by Dr. K. Eichele was used to simulate the 17O NMR spectra using the NMR parameters obtained with DFT calculations, as shown in Fig. 2. 3b and Supplementary Figs. 19b, 24, 27, 28. For the simulated spectra from the models of (001) facet (Fig. 2 and Supplementary Fig. 19b), only surface oxygen sites were considered, whose isotropic chemical shifts have been marked in the structural models in Fig. 2. The \( O_{2s} \) and \( O_{3s} \) sites have been given the same weight of peak area in the calculated spectra. Twice of the weight has been given to the hydroxyl groups centered around 420 ppm, and four times of the weight has been given to the hydroxyl groups centered around 130 ppm, for the sake of presentation. For simulating the NMR spectra of the defect-free (011) facet (as shown in Supplementary Fig. 24), a similar approach was used. Surface sites, i.e. sites 1–3 in Supplementary Fig. 21 and sites 1–7 in Supplementary Figs. 22 and 23, respectively, were considered. Twice the weight of the peak areas have been given to the signals of hydroxyl groups and adsorbed water, in comparison to those of the surface \( O_{2s} \) and \( O_{3s} \) sites. For simulating the spectra of (011) facet with type-D steps (Fig. 3b and Supplementary Fig. 27b), NMR parameters of surface and subsurface oxygen sites (1–14) in Supplementary Tables 13 and 14 were adopted, only with their percentage adjustable to achieve the best fitting. Furthermore, in Supplementary Fig. 28, C6 of the adsorbed water in both adsorption orientations were also allowed to change in simulation, in order to examine the influence of the motion of the adsorbed water on its NMR signal.

### Data availability.
All relevant data are available from the authors.

Received: 20 December 2016 Accepted: 12 July 2017
Published online: 18 September 2017

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