

Electronic Supplementary Information

for

Oxygen dynamic exchange and diffusion characteristics of ZnO nanorods from ^{17}O MAS NMR

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Contents

1. Material Preparation
2. Material Characterization
3. ^{17}O Isotopic Labelling
4. Solid-State NMR Spectroscopy
5. Characterization of ZnO Nanomaterials
6. References

1. Material Preparation

ZnO nanorods were prepared according to Lin's method.¹ In a typical preparation procedure, 0.176 g $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ and 0.064 g NaOH were dissolved in 40 mL ethanol. The NaOH solution was then added to $\text{Zn}(\text{Ac})_2$ solution dropwise under vigorous stirring, before 1.5 mL aqueous solution containing 0.095 g ethanediamine was added to the mixture. After stirring for 0.5 h, the solution was transferred to a 100 mL Teflon lined autoclave and heated at 160 °C for 8 h before it was cooled to room temperature. The white precipitate was centrifuged, and washed with distilled water three times, before it was dried at 80 °C for 8 h to produce white ZnO nanorod powders.

2. Material Characterization

The powder XRD analysis was carried out on a Philips X'Pro X-ray diffractometer using $\text{Cu K}\alpha$ irradiation ($\lambda = 1.54184 \text{ \AA}$) operated at 40 kV and 40 mA at 25 °C. JEOL JEM-2010 type high-resolution transmission electron microscope was applied to characterize the morphology and the exposed crystal facet of the ZnO nanorods. EPR spectra were recorded on the samples by a Bruker EMX-10/12 spectrometer at room temperature. XPS measurements of ZnO nanorods subjected to desired H_2 pressure were carried out on Thermo Scientific EscaLab 250Xi equipped with an ambient-pressure preparation chamber using an $\text{Al K}\alpha$ x-ray source ($h\nu = 1486.6 \text{ eV}$).

3. ^{17}O Isotopic Labelling

For ZnO nanorods labelled with ^{17}O -enriched H_2O , the sample was first put into a glass tube, heated to 100 °C and kept at the temperature for 2 h under vacuum to remove adsorbed species. After it was cooled to room temperature, H_2^{17}O (90 % ^{17}O ,

Cambridge Isotope Laboratories), vapor was supplied through the vacuum line. The mixture was heated at 40 °C for 5 h (the sample was named as ZnO-W-40-wet), and then vacuum dried (ZnO-W-40). The samples were kept in the N₂ glove box before NMR measurements.

4. Solid-State NMR Spectroscopy

Room temperature ¹⁷O and ¹H MAS NMR spectra were measured on 9.4 T Bruker Avance III spectrometer using 3.2 and 4.0 mm MAS probes double tuned to ¹⁷O at 54.2 MHz, and ¹H at 400 MHz, respectively. All samples were packed into rotors in a N₂ glove box. ¹⁷O and ¹H chemical shifts are referenced to H₂O at 0.0 ppm and adamantane at 1.79 ppm, respectively.

5. Characterization of ZnO Nanomaterials

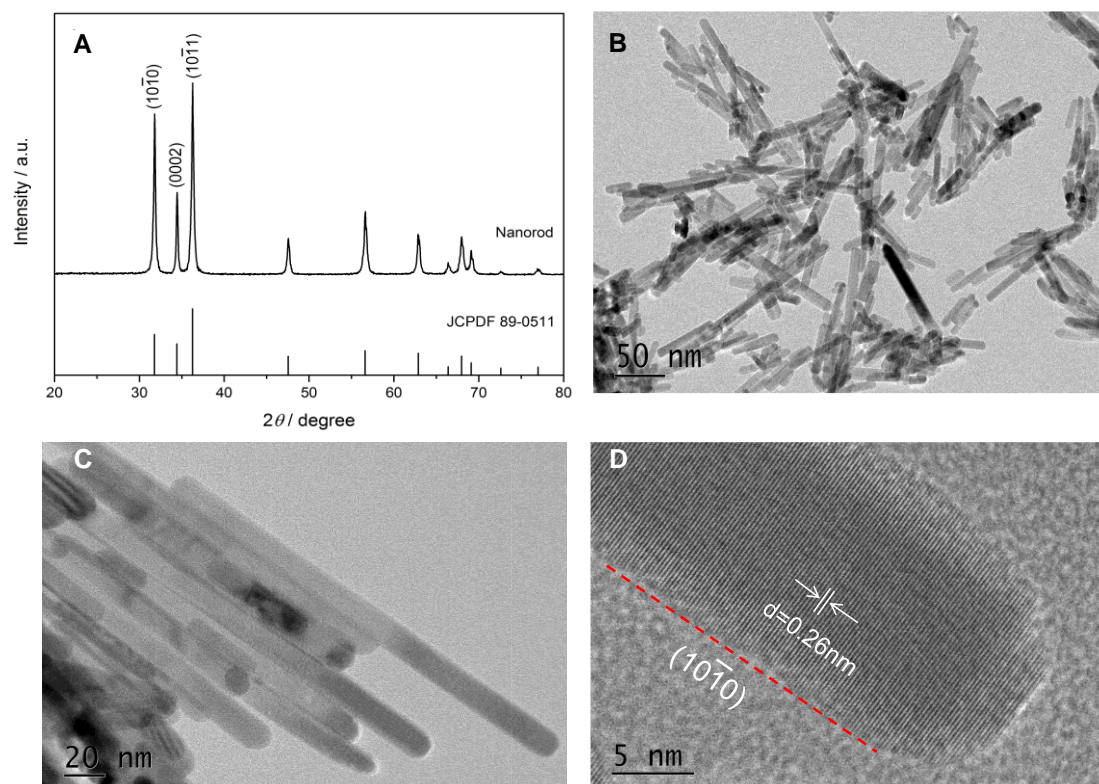


Fig. S1 Structural characterizations of the ZnO nanorod. (A) X-ray diffraction pattern.

(B), (C), (D) TEM and HRTEM images.

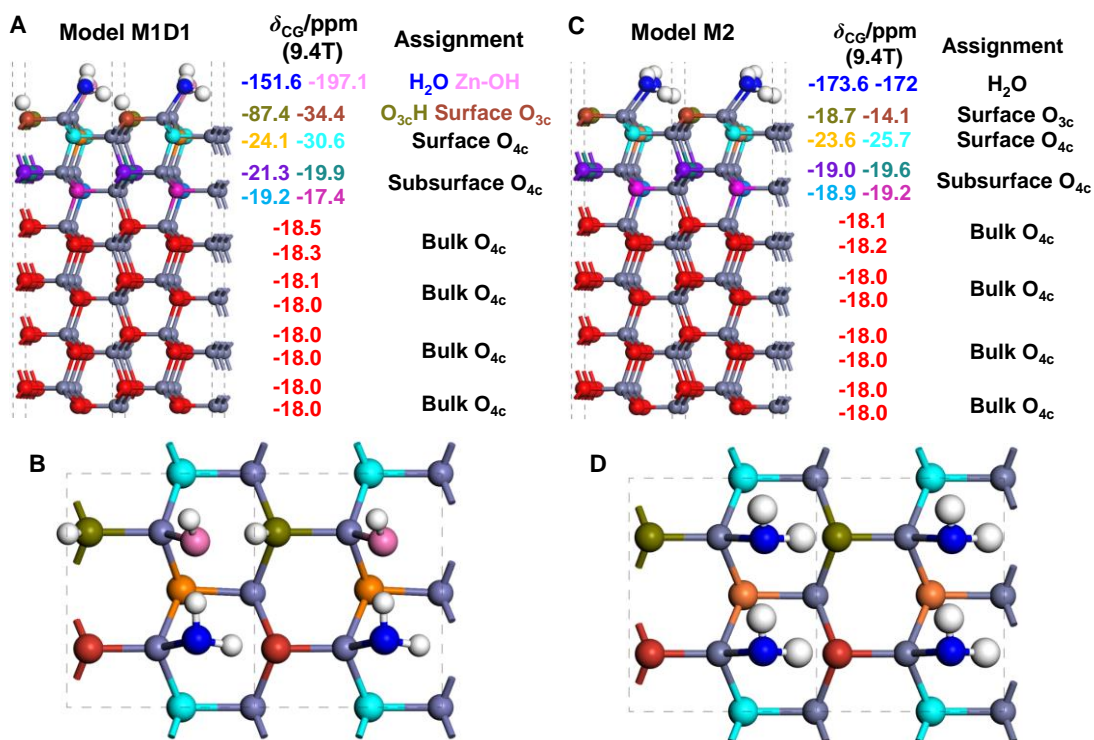


Fig. S2 The structural models of ZnO nanorods used for DFT calculations. (A) (Side view), (B) (Top view) The optimized ZnO (10 $\bar{1}$ 0) surface with a monolayer of water molecules in which half of the water molecules are dissociatively adsorbed, while the other half molecularly adsorbed (model M1D1); (C) (Side view), (D) (Top view) ZnO (10 $\bar{1}$ 0) surface with a monolayer of molecularly adsorbed water molecules (model M2).

The surface and subsurface oxygen species can be conveniently assigned according to the DFT calculation results. The observed disparity in NMR shifts (δ_{CG}) between surface OH and H₂O, when compared to the calculated values, can be attributed to the chosen calculation method, specifically the inclusion of Hubbard U corrections.²

Table S1. The assignments of different ^{17}O signals of ZnO nanorods obtained at 9.4 T.²

^{17}O shift/ppm	Assignment
-2	Sorbed water
-18.2/-18.4	Bulk O_{4c}
-18.8 (broad)	Surface O_{3c} (M2)
-18.8 (narrow)	Subsurface O_{4c}
-24.7	Surface O_{4c}
-29.5	Surface O_{4c}
~ -34	Surface O_{3c} (M1D1)
~ -52	OH

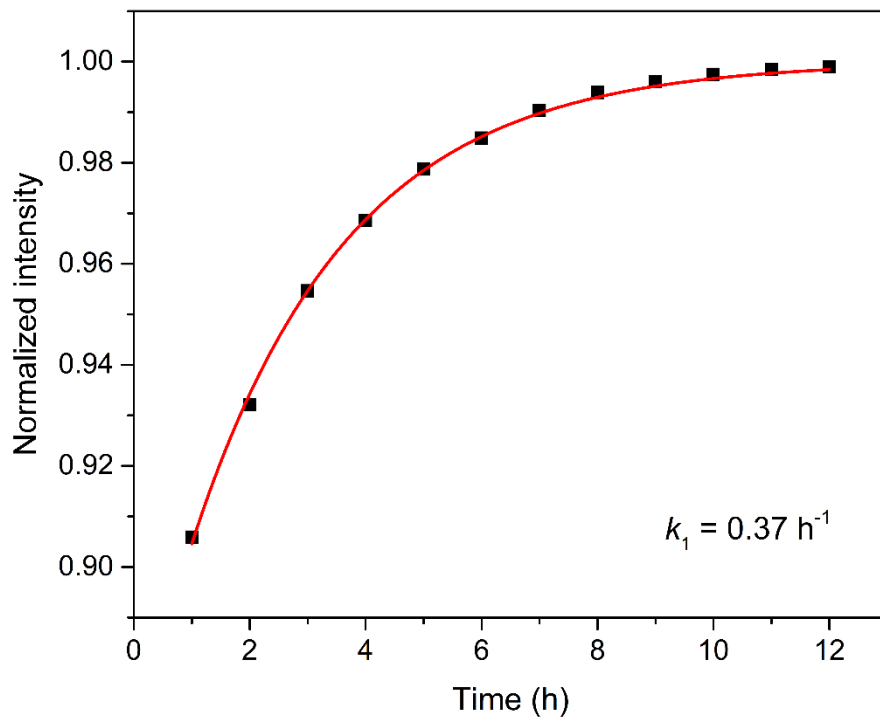


Fig. S3 The intensity sum of the peaks at -18.8, -24.7 and -29.5 ppm in the ^{17}O NMR spectra of ZnO nanorods as a function of the exposure time to water. The fitting curve uses the equation $I(t) = I(\infty) \cdot [1 - b \cdot \exp\{-k \cdot t\}]$, where $I(\infty)$ corresponds to the ^{17}O signal intensities obtained at an exposure time of 12 h.

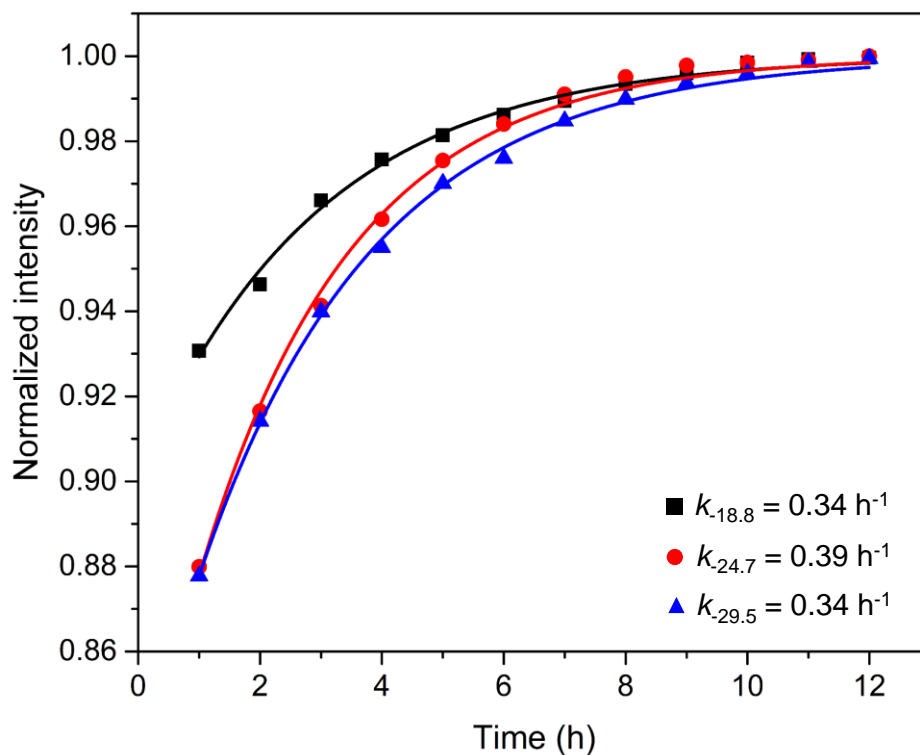


Fig. S4 The spectral intensities for the three individual peaks at -18.8, -24.7 and -29.5 ppm in the ^{17}O NMR spectra of ZnO nanorods as a function of the exposure time to water. The fitting curve uses the equation $I(t) = I(\infty) \cdot [1 - b \cdot \exp\{-k \cdot t\}]$, where $I(\infty)$ corresponds to the ^{17}O signal intensities obtained at an exposure time of 12 h.

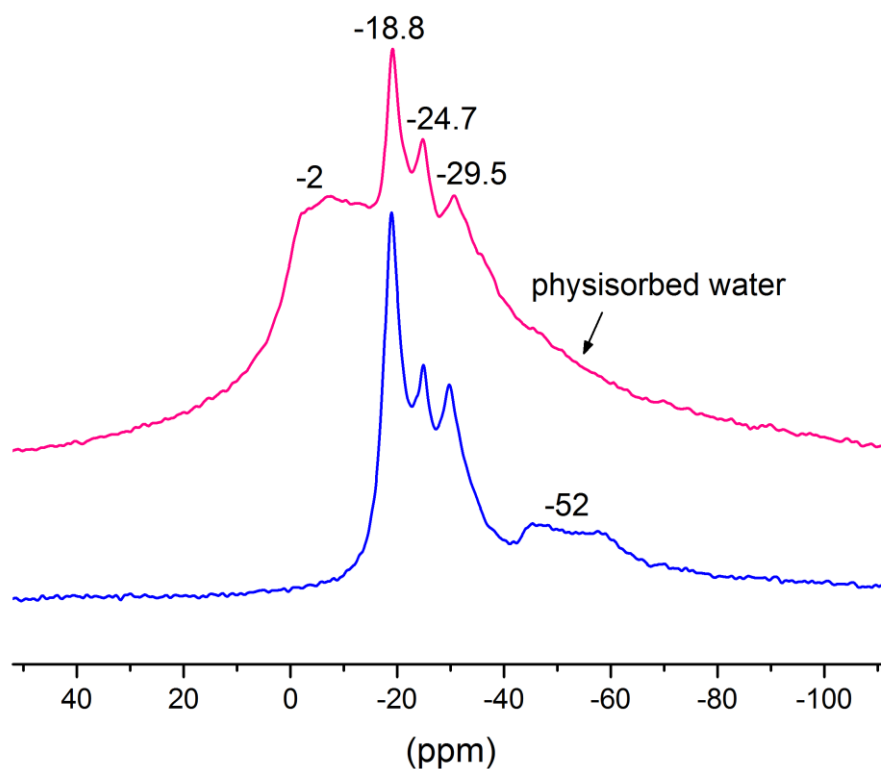


Fig. S5 ^{17}O NMR spectra of the ZnO nanorods labelled with H_2^{17}O at 40°C before (top, named as ZnO-W-40-wet) and after (bottom, named as ZnO-W-40) vacuum dried. Spectra were obtained at 9.4 T under a MAS rate of 14 kHz, and recycle delay 5 s was used.

Compared the two ^{17}O NMR spectra of ZnO nanorods, the resonance at ca. -2 ppm of ZnO-W-40-wet disappears after vacuum dried, indicating that this peak arises from sorbed water. In addition, the low-frequency signals ($< \sim -40$ ppm) of ZnO-W-40-wet is broader than ZnO-W-40, this may also attribute to water molecules considering that the ZnO nanorods were exposed to ^{17}O -enriched water without vacuum dried (see following discussions).

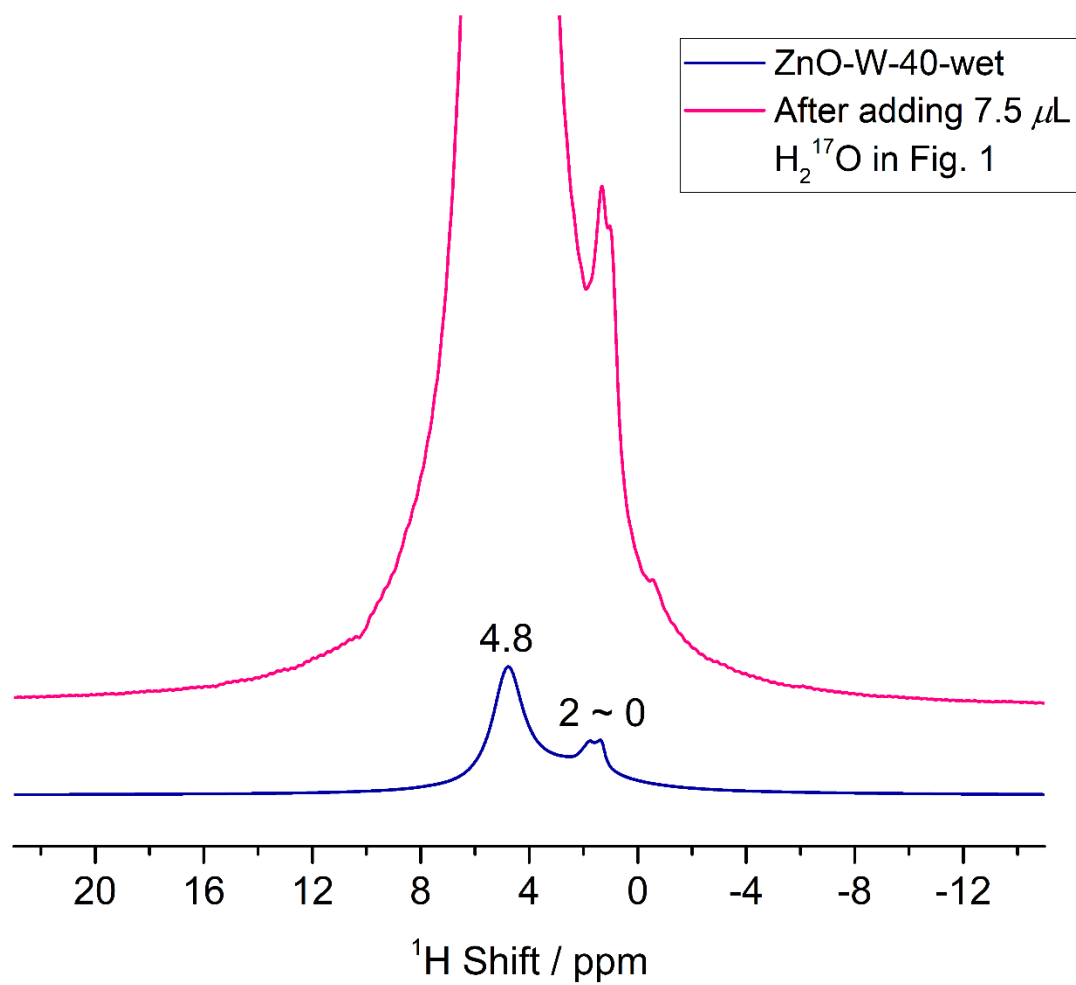


Fig. S6 ^1H NMR spectra of ZnO-W-40-wet and ZnO nanorods after adding 7.5 μL H_2^{17}O in Fig. 1.

Table S2. The corresponding integral areas in ^1H NMR spectra between 15 ~ -12 ppm in Fig. S6.

Sample	Integral areas
ZnO-W-40-wet	4.9×10^8
After adding $7.5 \mu\text{L H}_2^{17}\text{O}$ in Fig. 1	1.7×10^{10}

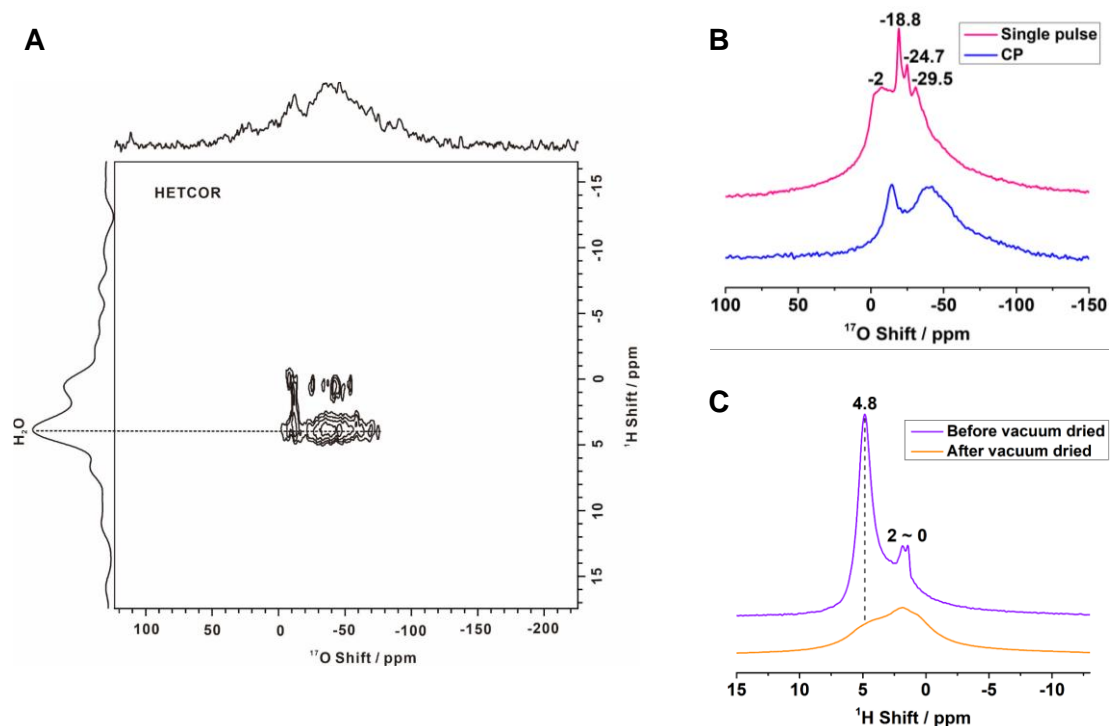


Fig. S7 ^{17}O and ^1H NMR spectra of ZnO nanorods. (A) 2D ^1H - ^{17}O HETCOR NMR spectrum of ZnO-W-40-wet. (B) ^{17}O single pulse and ^1H - ^{17}O cross polarization (CP) NMR spectra of ZnO-W-40-wet. (C) ^1H NMR spectra of ZnO nanorods before and after vacuum dried.

For ^1H NMR spectra in Fig. S7C, the sharp and intense resonance at 4.8 ppm dramatically decreases after vacuum drying, indicating that this high-frequency signal arising from adsorbed water, which corresponds to the broad ^{17}O signals in the lower part of ^{17}O NMR spectra ranging from -20 to -80 ppm ($\delta(^1\text{H}) = 4.8$ ppm) as shown in Fig. S7A. This further confirms that adsorbed water also contributes to the low frequencies (ca. < -40 ppm) (Fig. S5).

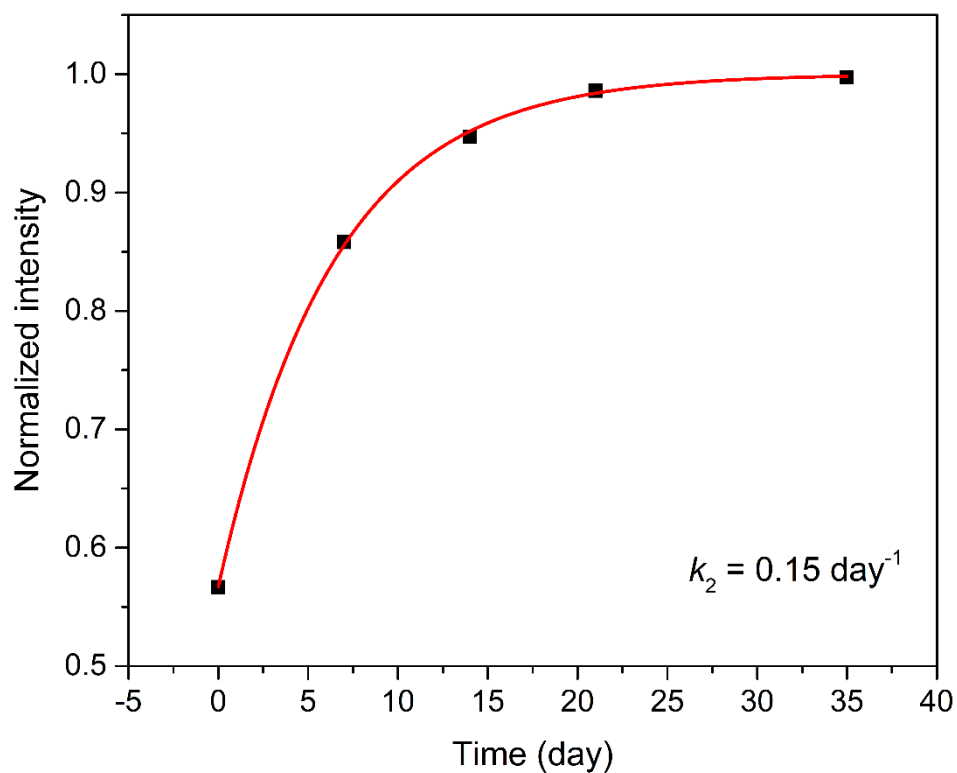


Fig. S8 The global ^{17}O signal intensities of peaks at -18.8, -24.7 and -29.5 ppm of ZnO nanorods as a function of the contact time to H_2^{17}O molecules. The fitting curve uses the equation $I(t) = I(\infty) \cdot [1 - b \cdot \exp\{-k \cdot t\}]$, where $I(\infty)$ corresponds to the ^{17}O signal intensities after exposing to H_2^{17}O molecules for 35 days.

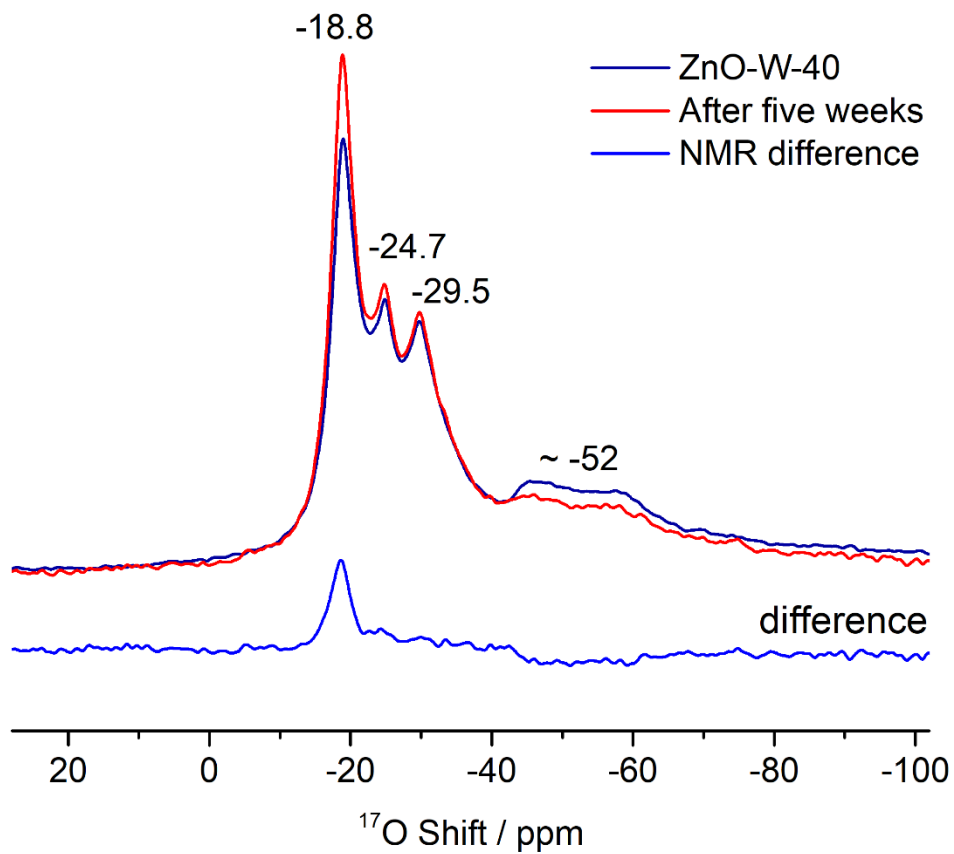


Fig. S9 ^{17}O NMR spectra of ZnO-W-40 and ZnO-W-40 after packed in a closed container at ambient temperature for five weeks.

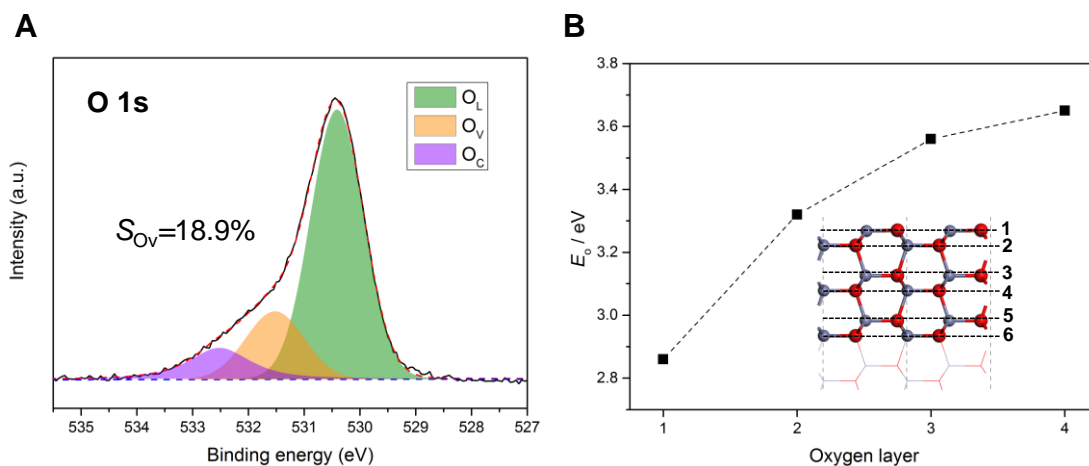


Fig. S10 (A) High-resolution O 1s XPS spectrum of ZnO-W-40. The O_L peak is attributed to O_2^- in the ZnO wurtzite structure. The O_V peak is assigned to the O_2^- ion in the oxygen-deficient region, which is related to oxygen vacancy in ZnO. The O_C peak can be assigned to chemisorbed oxygen at the surface, such as OH and H_2O . (B) Calculated energy of O vacancies formed in different layers of ZnO nanorods. The DFT calculations were performed using the Vienna ab initio Simulation Package (VASP).^{3,4} The Perdew-Burke-Ernzerhof (PBE) functional⁵ with a Hubbard U correction⁶ was used. Effective U values of 7.0 eV and 10.0 eV were applied to O $2p$ and Zn $3d$ orbitals, respectively, as suggested by Ma et al.⁷ The projector augmented wave (PAW)⁸ method was used to describe the valence-core interactions.

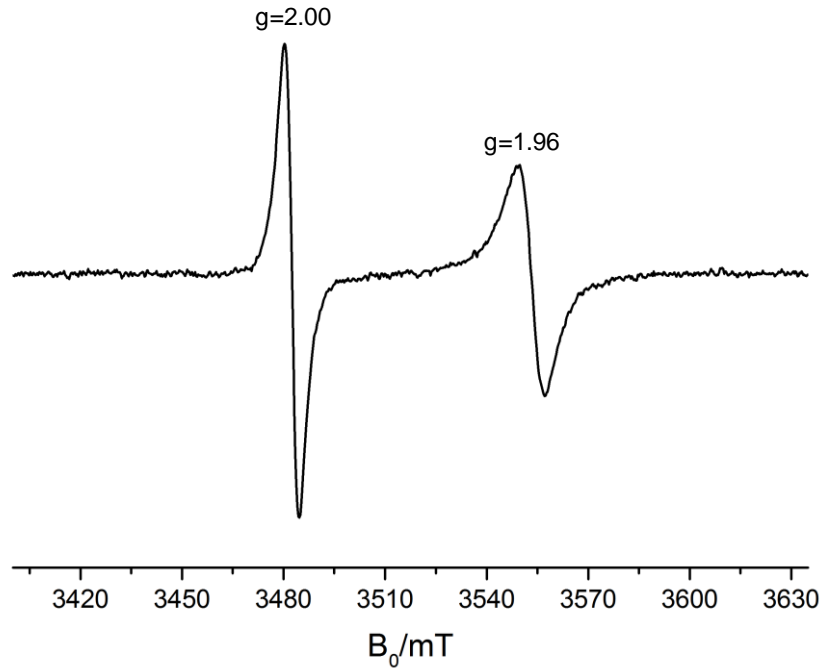


Fig. S11 Room-temperature electron paramagnetic resonance spectrum of ZnO-W-40. The signal at $g = 2.00$ has commonly been assigned to the unpaired electrons deeply trapped in oxygen vacancies, and the signal at $g = 1.96$ represents unpaired electrons trapped from the conductive band (CB) by shallow donors or impurities.

6. References

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