

METHODS

Synthesis of SmNiO_3 thin films. SmNiO_3 (SNO) was synthesized by physical vapour deposition and subsequent ultrahigh-pressure annealing in pure oxygen. Substrates were cleaned with acetone and isopropanol, followed by compressed Ar drying. SNO thin films were deposited on the substrates by magnetron co-sputtering of Sm and Ni targets at room temperature in an Ar/O_2 mixture at 0.67 Pa. To obtain the appropriate stoichiometric ratio, Sm was deposited at 160 W (radiofrequency sputtering) and Ni at 80 W (direct-current sputtering). The stoichiometric ratio of Sm and Ni was analysed using energy-dispersive X-ray spectroscopy. The substrates were rotated during deposition to ensure composition homogeneity. The deposited samples were then annealed for 24 h at 500 °C under high-pressure O_2 (10^7 Pa) in a home-built vessel to form the perovskite phase. Both epitaxial and polycrystalline SNO thin films were used in this work to demonstrate the generality of the water-mediated phase transition in SNO. Epitaxial SNO thin films were obtained on single-crystalline LaAlO_3 (001) substrates, while polycrystalline SNO thin films were grown on Si (100) wafers.

Aqueous solution preparation. To mimic the salinity of seawater, a 0.6 M NaCl aqueous solution was prepared by dissolving reagent-grade NaCl into micropure ($18.2 \text{ M}\Omega \text{ cm}$) water, which has electrical conductivity comparable to that of seawater (5 S m^{-1}). Experiments were performed at ambient temperature, unless otherwise noted. Additional aqueous solutions with a much wider pH range than seawater were studied, including standard buffers (pH = 4.0, 7.0, 10.0), a weakly acidic solution containing no salt (pH = 2.7, 0.01 M citric acid in H_2O), and a weakly basic solution (pH = 12.0, 0.01 M KOH in H_2O) (Supplementary Information section 2). These aqueous environments were designed to cover the wide ranges of temperature and pH found across Earth's oceans.

Sensing experiments in water environments. SNO thin films were incorporated into a three-terminal electrochemical cell. Platinum wire was bonded on the thin films with silver paste, and polyethylene masks (Gamry) were used to expose selected areas of SNO. The SNO film was then submerged into aqueous solutions and connected as a working electrode. The counter-electrode was a graphite rod with large surface area. A Ag/AgCl (saturated KCl) reference electrode was used to control and modulate the electric potential applied. A static electric potential was applied to SNO by a potentiostat. Cyclic voltammetry was performed on SNO samples with identical three-terminal configuration. The sensing and electrochemical tests were performed with a Solartron 1260A electrochemical analyser.

Electrical measurements. After the water-based treatment, the SNO samples were removed from the aqueous solution, rinsed with deionized water, and dried with argon gas. Contact electrodes (Pt) were patterned on the treated area. The SNO thin films were then transferred to a controlled-temperature probe station and their electrical resistance was measured with a Keithley 2635A source meter.

An ohmmeter with sensitivity of 100 n Ω is commercially available. Higher sensitivity can be obtained by utilizing a lock-in amplifier in the amplitude- or phase-sensitive mode, which is routinely used in low-temperature physics research. **Conducting AFM measurements.** To observe the propagation of the HSN phase after sensing electric potential in water, cross-sectional conducting AFM measurements were carried out on SNO films (about 500 nm thickness) grown on Si (100) substrates. The SNO was treated at a bias potential of -2.0 V (versus Ag/AgCl) for 30 min in a 0.6 M NaCl aqueous solution. After the treatment, the sample was vertically mounted in epoxy resin. The cross-sectional surface subsequently underwent multiple mechanical polishing steps, with the final polish using a 1- μm -diameter diamond suspension. The opposite cross-sectional surface was coated with silver paste to form the bottom electrode. The conducting AFM cross-sectional imaging was performed through a Pt/Ir-coated tip (Arrow-CONTPt, Nanoworld; force constant 0.2 N m^{-1}) connected to a dual-gain transimpedance amplifier (ORCA) in a commercial system (Oxford Instruments/Asylum Research Cypher ES). Topographic and current images were collected simultaneously with a bias of 5.0 V applied to the bottom Ag electrode, a setpoint of 0.06 V and a scanning rate of 1 Hz. Additional conducting AFM measurements of the top surface of a water-treated SNO sample were conducted with an Asylum MFP3D stand-alone atomic force microscope using Asylum ASYELEC-01 conductive tips (Si coated with Ti/Ir). The AFM tip was grounded and a bias of 1.0 V was applied to the sample surface. A resistor of 1 M Ω was connected in series to the SNO sample to limit the current and protect the conducting AFM tips. The current was amplified using current amplifiers (dual-gain, ORCA) with a sensitivity of 1 V μA^{-1} and 1 V nA^{-1} . The scanning rate was 1 Hz. For the top-surface conducting AFM measurement, a SNO thin film (70 nm) was grown on a Si (100) substrate. A selected area of the sample was treated at a bias potential of -4.0 V (versus Ag/AgCl) in a 0.6 M NaCl aqueous solution for 10 s.

X-ray reflection and diffraction measurements. Synchrotron XRR and X-ray diffraction measurements of the SNO samples were carried out on a five-circle

diffractometer with χ -circle geometry (in which the sample can be rotated around the centre of the diffractometer), using an X-ray energy of 20 keV (wavelength $\lambda = 0.6197 \text{ \AA}$) at beamline 12-ID-D of the Advanced Photon Source of Argonne National Laboratory. The X-ray beam had a total flux of 4.0×10^{12} photons s^{-1} and was vertically focused by beryllium-compound refractive lenses to a beam profile below 50 μm . Scans along the Q_z and L directions of the HKL reciprocal space were obtained by subtracting the diffuse background contributions using the two-dimensional images acquired with a two-dimensional pixel array detector (Dectris PILATUS 100K, with a 1-mm-thick Si sensor chip and 10^5 pixels). Additional X-ray diffraction measurements over a wide range of scattering angles were carried out using the PANalytical MRD X'Pert Pro diffractometer with $\text{Cu K}\alpha$ X-rays (wavelength $\lambda = 1.5418 \text{ \AA}$). For *in situ* XRR measurements, epitaxial SNO samples with thicknesses of 70 nm were grown on a LaAlO_3 (001) substrate. Each sample was attached to an electrochemical cell (Extended Data Fig. 5) filled with a 0.01 M KOH aqueous solution. The XRR data of SNO were measured *in situ* after applying a bias potential of -1.5 V (versus Ag/AgCl) for 3 min and 9 min. Additional *ex situ* XRR measurements of SNO in various aqueous solutions were carried out. The samples were treated separately in aqueous solutions of 0.01 M citric acid and 0.01 M KOH by applying the same bias potential of -4.0 V (versus Ag/AgCl) for 5 min, and X-ray diffraction measurements were carried out after the latter treatment.

Neutron reflectivity measurements and heavy water studies. Neutron reflectometry was performed at the Center for Neutron Research of the National Institute of Standards and Technology using the MAGIK reflectometer²⁹ in air with procedures similar to those described in ref. 30. The samples were characterized in the neutron beam over the Q range $0\text{--}0.18 \text{ \AA}^{-1}$. The neutron reflectivity data were fitted with the NIST Refl1d software package (<http://www.ncnr.nist.gov/refl1d>). For the isotope substitution measurement, a SNO sample with thickness of about 70 nm was grown on a Si (100) substrate. The sample was cleaved into two pieces. The one piece was first characterized at the pristine state as a reference and was then treated at -4.0 V (versus Ag/AgCl) for 30 s in a 0.01 M KOH/ H_2O solution. To observe the contrast from isotope substitution, the other piece of SNO was treated at -4.0 V (versus Ag/AgCl) for 30 s in a 0.01 M KOH/ D_2O solution. After treatment, the samples were cleaned in isopropanol and dried in ambient conditions before the measurements.

Certain commercial equipment, instruments or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment mentioned are necessarily the best available for the purpose.

X-ray absorption spectroscopy. The XAS were measured at beamline 10ID-2 (REIXS) of the Canadian Light Source. The absorption near the Ni L_3 and O K edges was determined from the total fluorescence yield obtained with linearly polarized photons. The samples were placed in normal-incidence geometry with the electric field vector parallel to the (110) direction in a pseudocubic coordinate system. All spectra were measured at 20 K. For the X-ray absorption measurements, SNO samples with thickness of 70 nm were grown epitaxially on LaAlO_3 (001) substrates. Treatment was carried out in a 0.01 M KOH aqueous solution under a bias potential of -4.0 V (versus Ag/AgCl) for 30 s. After the treatment, the samples were rinsed with deionized water and dried with argon gas.

Optical spectra measurements. Reflection optical spectra in the near- and mid-infrared were measured using a Fourier transform infrared spectrometer and a mid-infrared microscope. For spectroscopic measurements of the transmission spectra, the samples were mounted in front of the opening of a gold integrating sphere, which captured both the direct and the diffused transmission of the samples. The signal was measured by a mercury cadmium telluride detector attached to the integrating sphere. The optical refractive indices were calculated by transfer matrix formalism (Supplementary Information section 6). To take an infrared image, a tunable mid-infrared quantum-cascade laser was used as the light source and irradiated the sample at a wavelength of 8 μm . For optical spectra measurements, SNO samples with thickness of 70 nm were grown on Si (100) substrates. The optical properties of Si substrates are well known, enabling us to quantitatively analyse the optical properties of SNO grown on Si. For infrared imaging, SNO samples with a thickness of 70 nm were grown on LaAlO_3 (001) substrates. Treatment was carried out in a 0.01 M KOH aqueous solution under a bias potential of -4.0 V (versus Ag/AgCl) for 30 s.

AIMD simulations of SmNiO_3 -water interactions. AIMD simulations were performed with the Argonne Leadership Computing Facility supercomputers (2048 cores) using the generalized gradient approximation (GGA). The Hubbard correction to treat electron localization for Ni atoms used the projector-augmented wave formalism, as implemented in the Vienna Ab initio Simulation Package (VASP)^{31,32}. The computational supercell consisted of a monoclinic SNO slab (160 atoms) with the surface normal pointing along the orthorhombic