

# Perovskite nickelates as electric-field sensors in salt water

Zhen Zhang<sup>1\*</sup>, Derek Schwanz<sup>1\*</sup>, Badri Narayanan<sup>2†</sup>, Michele Kotiuga<sup>3</sup>, Joseph A. Dura<sup>4</sup>, Mathew Cherukara<sup>2</sup>, Hua Zhou<sup>5</sup>, John W. Freeland<sup>5</sup>, Jiarui Li<sup>6</sup>, Ronny Sutarso<sup>7</sup>, Feizhou He<sup>7</sup>, Chongzhao Wu<sup>8</sup>, Jiaxin Zhu<sup>9</sup>, Yifei Sun<sup>1</sup>, Koushik Ramadoss<sup>1</sup>, Stephen S. Nonnenmann<sup>9</sup>, Nanfang Yu<sup>8</sup>, Riccardo Comin<sup>6</sup>, Karin M. Rabe<sup>3</sup>, Subramanian K. R. S. Sankaranarayanan<sup>2</sup> & Shriram Ramanathan<sup>1</sup>

**Designing materials to function in harsh environments, such as conductive aqueous media, is a problem of broad interest to a range of technologies, including energy, ocean monitoring and biological applications<sup>1–4</sup>. The main challenge is to retain the stability and morphology of the material as it interacts dynamically with the surrounding environment. Materials that respond to mild stimuli through collective phase transitions and amplify signals could open up new avenues for sensing. Here we present the discovery of an electric-field-driven, water-mediated reversible phase change in a perovskite-structured nickelate,  $\text{SmNiO}_3$ <sup>5–7</sup>. This prototypical strongly correlated quantum material is stable in salt water, does not corrode, and allows exchange of protons with the surrounding water at ambient temperature, with the concurrent modification in electrical resistance and optical properties being capable of multi-modal readout. Besides operating both as thermistors and pH sensors, devices made of this material can detect sub-volt electric potentials in salt water. We postulate that such devices could be used in oceanic environments for monitoring electrical signals from various maritime vessels and sea creatures.**

Pristine  $\text{SmNiO}_3$  (SNO), a quantum material in the family of strongly correlated electron systems<sup>5,6</sup>, is a perovskite-structured rare-earth nickelate<sup>7</sup>. The high ionic conductivity that has been noted in SNO solid-state fuel cells, comparable to that of the best-performing proton conductors, is due in part to their covalent ground state and low-energy phonon modes<sup>8</sup>. Figure 1a illustrates SNO submerged in water in the presence of an electric bias generated by a counter electrode. Under negative electric potentials, protons intercalate into the SNO lattice, accompanied by an uptake of electrons released by oxidation at the counter-electrode. As a result, a saltwater-mediated transition from pristine SNO to hydrogenated SNO (HSNO) occurs under bias. This proton influx accompanies a modification of the electronic configuration of the Ni 3d orbitals, unlike in electrochromic oxides such as  $\text{WO}_3$ , where transition to a metallic state occurs upon cation doping (Supplementary Information section 1). The doping-driven resistance change for the uptake of one electron per formula unit is about 10,000 times larger for SNO than for  $\text{WO}_3$ . As Fig. 1b, c shows, the partially filled  $e_g$  orbital with small transport gap for charge carriers in SNO becomes half-filled in HSNO, where strong Mott–Hubbard electron–electron interaction arises and localizes the charge carriers.

To demonstrate the response of the perovskite devices when encountering an electric bias in salt water, SNO thin films were incorporated into a three-terminal electrochemical cell and served as working electrodes. An electric potential was applied across the aqueous solution

using a graphite counter-electrode referenced to a standard Ag/AgCl reference electrode. Because water is generally a harsh environment for oxides<sup>9</sup> and the formation of hydroxides can be accompanied by massive crystal structure changes (for example, in hydrated cobaltites<sup>10</sup>), the stability of SNO in aqueous solution was first investigated without electric potentials. Figure 1d compares the temperature-dependent electrical resistivity of pristine SNO with that of a SNO thin film submerged for 24 h in a 0.6 M NaCl solution at room temperature. Nearly identical resistivity–temperature curves are observed in both samples, indicating stability. The expected thermally induced insulator–metal transition in submerged SNO at about 130 °C is still present, which is often used as an indicator of film quality (Extended Data Fig. 1a). SNO is robust in both weakly acidic (0.01 M citric acid, pH = 2.7) and basic (0.01 M KOH, pH = 12) solutions (Extended Data Fig. 1b) over 180 min. This stability of SNO in aqueous environments over a range of pH values enables us to study its response to electric bias in a systematic manner (Supplementary Information section 2). Moreover, the open-circuit potential of SNO relative to the standard Ag/AgCl electrode varies with the pH value of the aqueous solutions; this feature of SNO, together with its temperature-dependent electrical resistivity, enable it to operate as a local environmental sensor (Extended Data Fig. 2a, b).

Figure 1e shows the electrical resistivity of SNO after applying negative electric potential up to  $-4.0$  V (versus the Ag/AgCl electrode) in a 0.6 M NaCl solution, the salinity of which is similar to that of sea water. Upon application of negative electric potential, the electrical resistivity of SNO exhibits an increase by more than five orders of magnitude along with a noticeable colour change (Fig. 1e). The resistivity of water-treated SNO (Fig. 1d, red curve) decreases smoothly with increasing temperature, indicating an insulating state with localized electrons. The substantial change of the electrical properties of water-treated SNO is non-volatile at ambient conditions (Extended Data Fig. 1c), indicating that it is not a simple electrostatic field effect induced by charge accumulation at the surface, but a water-mediated phase transition. The observed phase change occurs regardless of the aqueous solution (examples include 0.01 M KOH, 0.6 M NaCl and 0.01 M citric acid) and substrate (for example,  $\text{LaAlO}_3$  (001) and Si (100)) used. A cross-sectional conducting atomic force microscopy (conducting AFM) image of SNO, which was acquired after the film was used for sensing an electric potential in aqueous solution (Fig. 1f, topography), shows that no corrosion occurs beneath the SNO–water interface and the thin film retains structural integrity. The cross-sectional conducting AFM image of the current reveals that the insulating phase (black

<sup>1</sup>School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907, USA. <sup>2</sup>Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, USA. <sup>3</sup>Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA. <sup>4</sup>NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA. <sup>5</sup>X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA. <sup>6</sup>Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA. <sup>7</sup>Canadian Light Source, University of Saskatchewan, Saskatoon, Saskatchewan S7N 2V3, Canada. <sup>8</sup>Department of Applied Physics and Applied Mathematics, Columbia University, New York 10027, USA. <sup>9</sup>Department of Mechanical and Industrial Engineering, University of Massachusetts – Amherst, Amherst, Massachusetts 01003, USA. <sup>†</sup>Present address: Materials Science Division, Argonne National Laboratory, Lemont, Illinois 60439, USA.

\*These authors contributed equally to this work.