Rare earth single atoms enhance manganese oxide's electrochemical oxygen evolution

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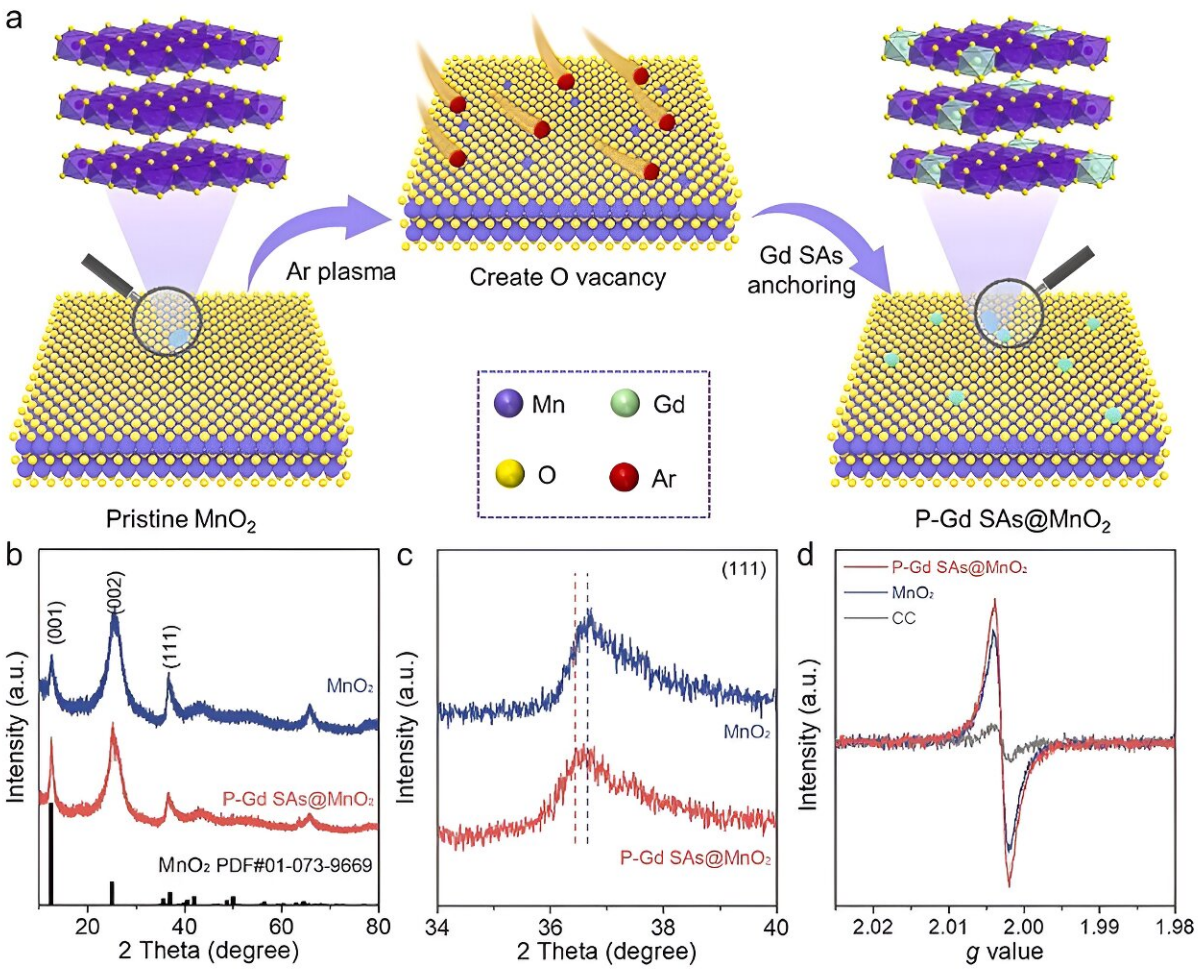


(a) The schematic route for the synthesis of P-Gd SAs@MnO_2 nanosheets; (b, c) XRD patterns of P-Gd SAs@MnO_2 and MnO_2; (d) EPR spectrum of P-Gd SAs@MnO_2, MnO_2, and blank CC. Credit: Hao Li et al.

An international group of researchers has developed a novel approach that enhances the efficiency of the oxygen evolution reaction (OER), a key process in renewable energy technologies. By introducing rare earth single atoms into manganese oxide (MnO_2), the group successfully modulated oxygen electronic states, leading to unprecedented improvements in OER performance.

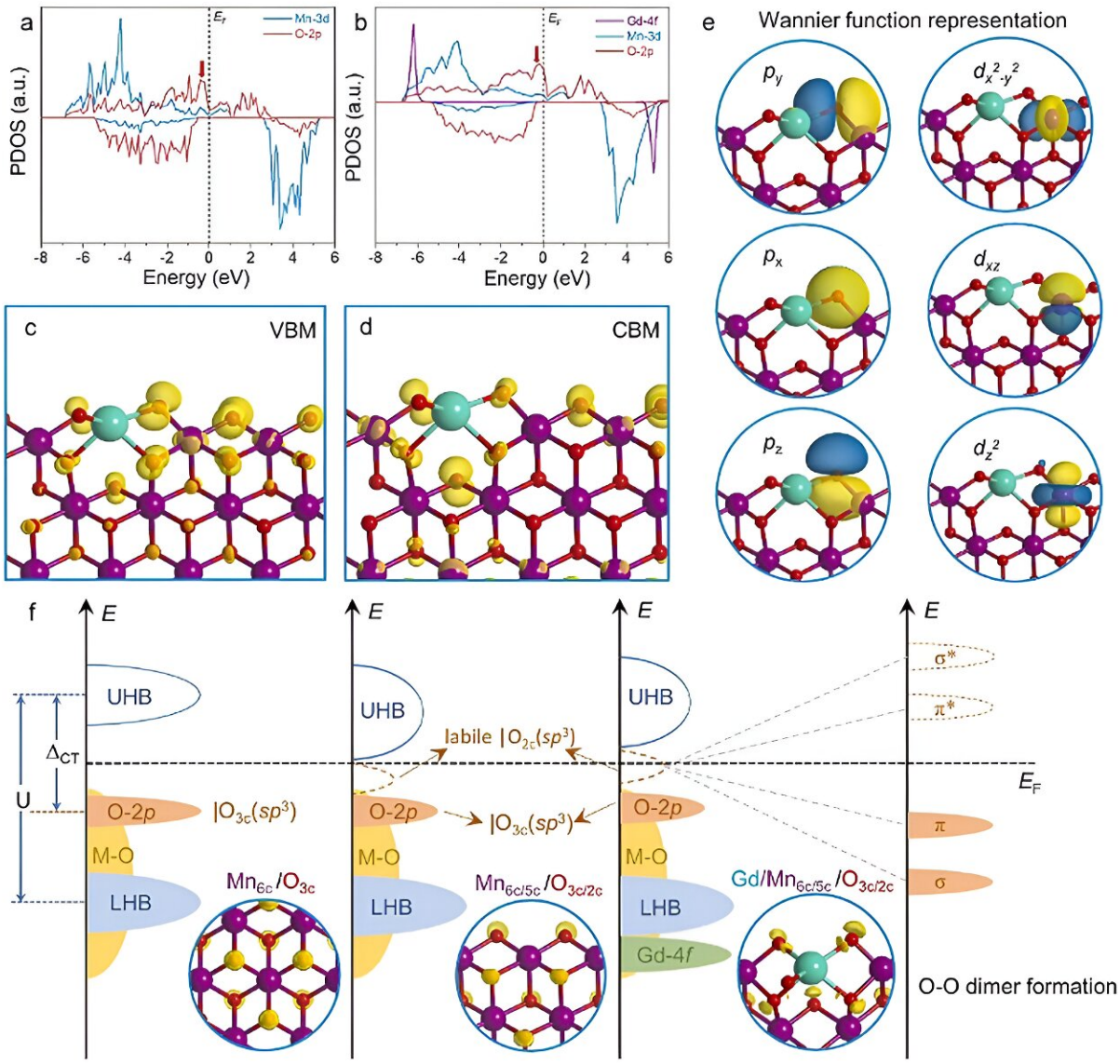
Their findings are published in the journal *Nano Energy*.

Transition-metal-based oxides have been widely explored for their potential as active OER catalysts. However, the capacity of these catalysts is hindered by the adsorbate evolution mechanism, which limits the effective release of oxygen (O_2) during the reaction.

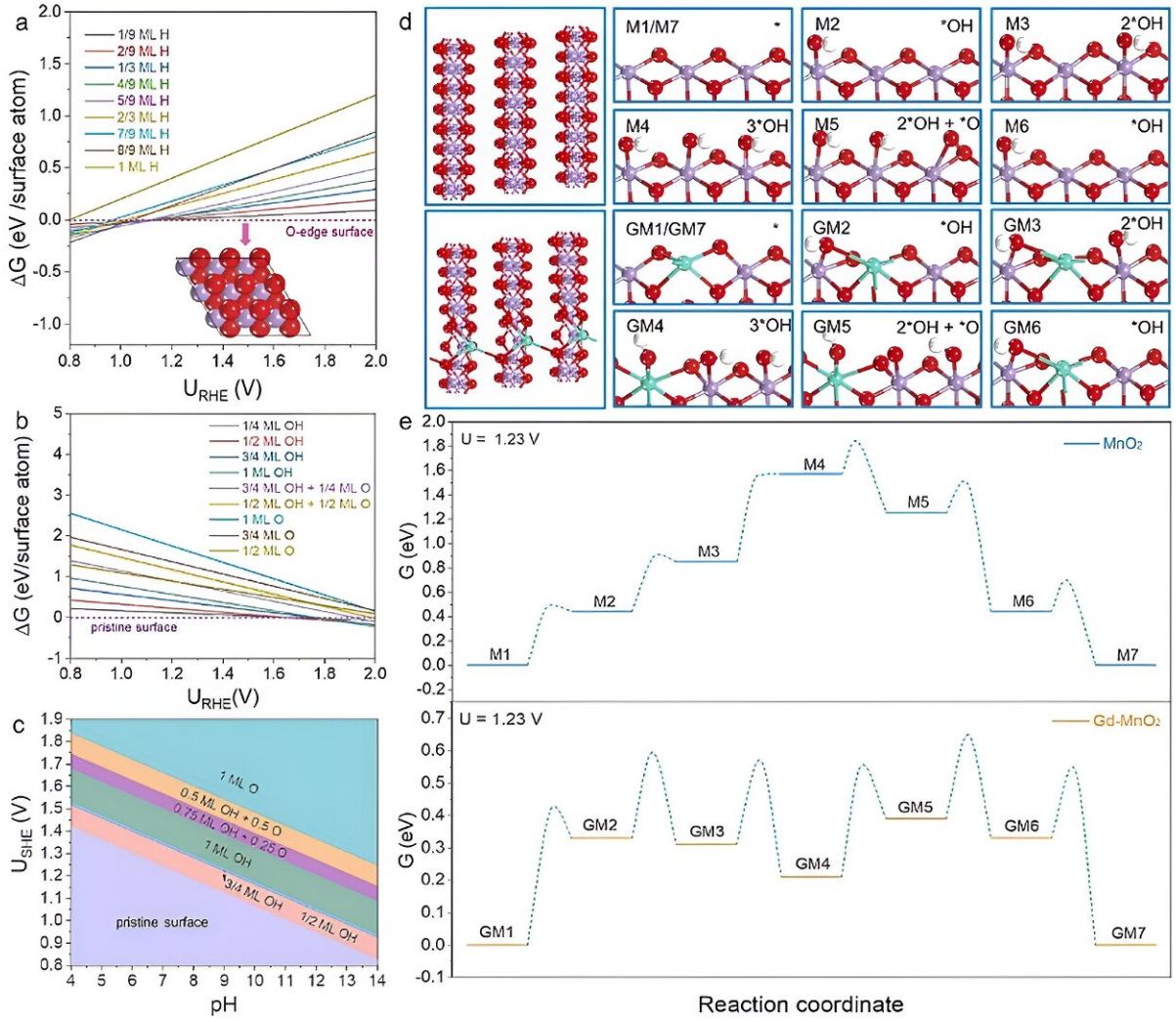
"We constructed localized asymmetric gadolinium-oxygen-manganese units on MnO_2, which helps accumulate electrons at oxygen sites," notes Hao Li, corresponding author of the paper and an associate professor at the Advanced Institute for Materials Research (WPI-AIMR) at Tohoku University.

"By doing this, the catalysts achieve a lower overpotential and maintain stability over time, making it a suitable alternative to traditional catalysts such as ruthenium dioxide (RuO_2)."

Hao Li and his colleagues employed an argon plasma-assisted strategy to introduce rare earth elements on the catalyst surface. In this strategy, argon gas is ionized, energizing and helping break the argon atoms into ions and electrons, thereby making it easier to interact with and modify materials.



PDOS diagrams of (a) MnO_2 slab model and (b) Gd-MnO_2 slab model with [Gd–O–Mn] unit site. (c)-(d) VBM and CBM diagrams of Gd-MnO_2 with Kohn-Sham orbital population (iso-surface 0.002 e/Å^3). (e) Projected MLWF plots of O_2c and Mn_5c sites in [Gd–O–Mn] unit (iso-surface 1.5 e/Å^3). (f) Mechanism of (O-O) dimer formation for OER catalysis, showing ELF plots for bulk MnO_2, slab MnO_2 model, and Gd-MnO_2 slab model (iso-surface 0.7 e/Å^3). Pink, green, red, and white spheres denote Mn, Gd, O, and H, respectively. Credit: Hao Li et al.



Surface Pourbaix diagrams: (a) H coverage for MnO_2 slice with Mn_6c-O_3c chain, (b) oxygen species coverage for MnO_2 slab with Mn_5c and O_2c sites. (c) 2D surface Pourbaix diagram showing URHE vs. pH. (d) Geometric structures of MnO_2 and Gd-MnO_2 with various oxygen intermediates. (e) OER free energy diagrams for MnO_2 and Gd-MnO_2 at 1.23 V. Pink, green, red, and white spheres denote Mn, Gd, O, and H, respectively. Credit: Hao Li et al.

"We have addressed the challenges associated with the adsorbate

evolution mechanism that limits the performance of transition-metal-based oxides like MnO_2," adds Di Zhang, co-author of the study and a Specially Appointed Assistant Professor at WPI-AIMR.

"By improving the understanding of the structure-activity relationship under the lattice oxygen mechanism, the research provides a foundation for more effective catalyst design."

Building on the success of this study, the group plans to extend their methodology to a variety of electrochemical reactions. This approach will help further decipher unique structure-activity correlations, ultimately contributing to the design of even more effective and high-performance electrocatalysts.

More information: Meng Li et al, Atomic rare earths activate direct O-O coupling in manganese oxide towards electrocatalytic oxygen evolution, *Nano Energy* (2024). DOI: 10.1016/j.nanoen.2024.109868

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