OPEN ACCESS

Materials Chemistry COMMENTARY

Coordination purification unlocks Co oxide for acidic water electrolysis

Peipei Du,[1] Yongqiang Yang,[2,3,*] Yuxuan Peng,[1] Dunyu Sun,[1] Jing Wei,[1,*] and Gang Liu[2,3]

[1]Nanjing Institute of Environmental Sciences, Ministry of Ecology and Environment, Nanjing 210042, China

[2]Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

[3]School of Materials Science and Engineering, University of Science and Technology of China, Shenyang 110016, China

*Correspondence: yqyang@imr.ac.cn (Y.Y.); weijing@nies.org (J.W.)

Received: August 23, 2026; Accepted: October 10, 2026; https://doi.org/10.59717/j.xinn-mater.2026.100247

© 2026 The Author(s). This is an open access article under the CC BY license (https://creativecommons.org/licenses/by/4.0/).

Citation: Du P., Yang Y., Peng Y., et al. (2026). Coordination purification unlocks Co oxide for acidic water electrolysis. *The Innovation Materials* **4**:100247.

Proton-exchange-membrane water electrolysis (PEMWE) relies on scarce Ir/Ru-based oxides for the anodic oxygen evolution reaction (OER), while non-noble alternatives suffer from a severe activity-stability trade-off in acidic, oxidizing media.[1] In a recent study, Wang et al. tackled this by modifying the coordination architecture of Co_3O_4.[1] Their trigonal phase (Tri-Co_3O_4) consists exclusively of edge-shared [CoO_6] octahedra, eliminating tetrahedral Co sites that are poorly active and prone to dissolution in the conventional spinel.[1,2] Here, we refer to this design logic as "coordination purification": the deliberate use of phase engineering to eliminate intrinsically underperforming or unstable coordination sites and thereby create a more uniform catalytic architecture. As a result, this coordination purification endows the Co oxide with enhanced acidic OER activity, significantly reduced Co leaching, and practical viability in PEMWE devices. More importantly, however, it points to a general design principle: when a crystallographic site proves intrinsically unfavorable, phase engineering offers a direct route to eliminate it entirely, rather than relying on iterative adjustments to its local chemical environment.

Conventional cubic spinel Co_3O_4 contains tetrahedral Co^{2+} and octahedral Co^{3+} sites with distinct catalytic and dissolution behaviours. Wang et al. synthesized a distinct trigonal (P-3m1) phase via a vacuum-assisted molten-alkali mechanochemical route.[1] In this 2D trilayer structure (Figure 1A), both Co^{2+} and Co^{3+} occupy octahedral sites, with Co^{3+} in the outer layers and Co^{2+} in the central layer at a ~1:2 ratio as confirmed by Co-*K*/*L* XAFS, Raman and electron microscopy, establishing an all-octahedral edge-sharing framework. This structural change dramatically improves OER performance (Figure 1B):

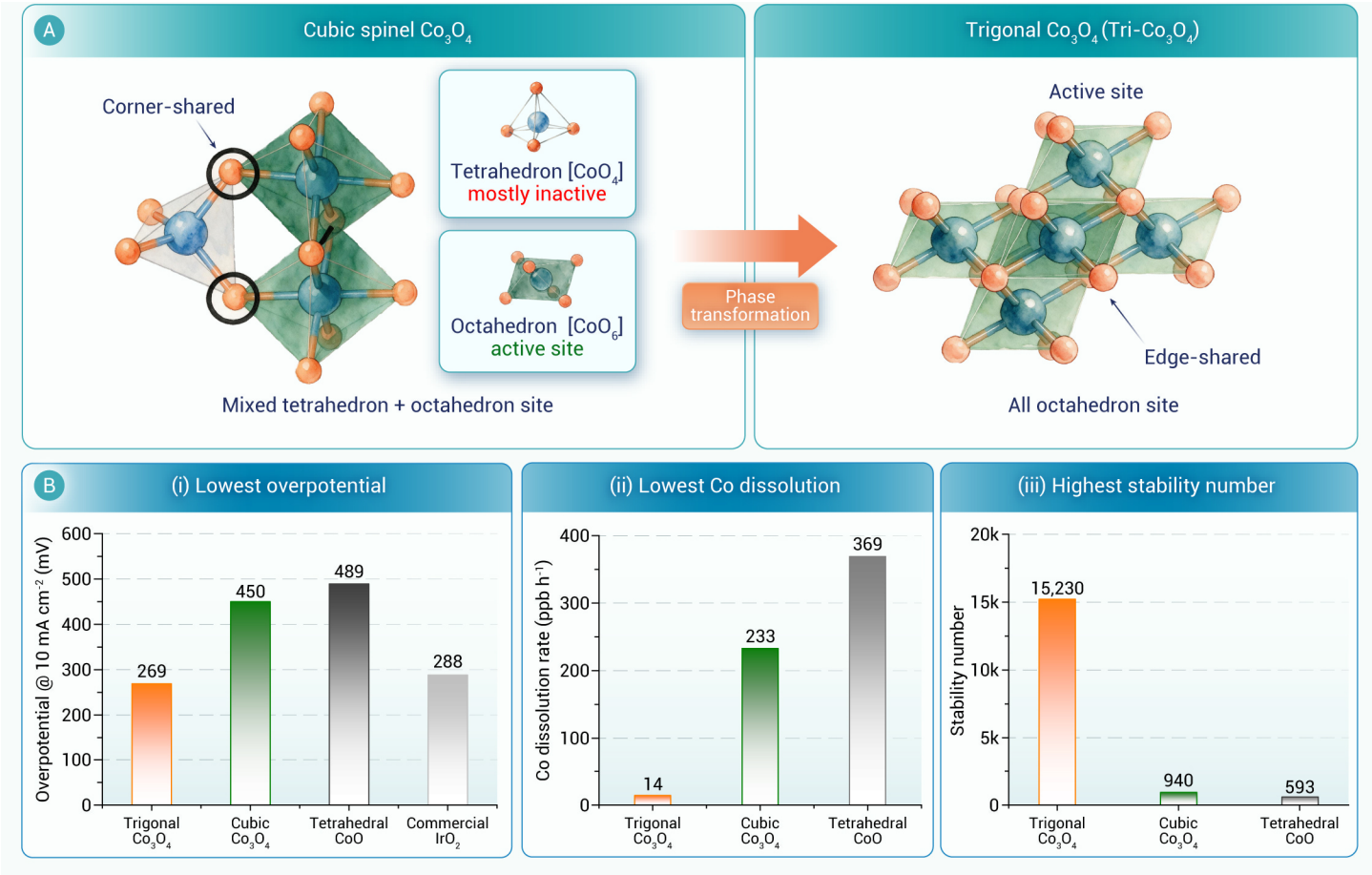


Figure 1. Phase-engineered coordination purification of Co_3O_4 (A) Structural transition from cubic spinel Co_3O_4 to trigonal Tri-Co_3O_4. (B) Enhanced acidic OER activity, suppressed Co leaching, and highest stability number by the all-octahedral coordination. Structural and electrochemical data adapted from Wang et al.[1]

Tri-Co_3O_4 requires an overpotential of only 269 mV to reach 10 mA cm^{-2} in 0.5 M H_2SO_4, 181 mV lower than cubic Co_3O_4 and slightly lower than commercial IrO_2. At 1.60 V versus RHE, it delivers a mass activity of 207 A g^{-1} and a TOF of 8.10 s^{-1}, while maintaining an exceptionally low Co dissolution rate of only 14 ppb h^{-1}. Its reported stability number reaches 15,230 after 120 h, substantially exceeding cubic Co_3O_4 (940, 12 h) and hexagonal CoO (593, 7 h), although it remains two to three orders of magnitude below benchmark crystalline rutile IrO_2, whose reported stability numbers are typically on the order of 10^6–10^7. As a separate Co-based device benchmark, La/Mn-doped cobalt spinel has previously demonstrated 360 h acidic OER durability and PEMWE operation.[3,4]

The activity and stability improvements arise from the all-octahedral struc-

ture and are robustly supported by multiple orthogonal techniques. In situ Co *K*-edge XAFS shows only a modest increase in Co valence under OER potentials, while the local coordination structure remains largely preserved. Density-functional-theory calculations further identify the exposed Co site on the Tri-Co_3O_4 (10-10) facet as having moderate binding strength toward oxygenated intermediates with a calculated OER overpotential of 0.36 V. The trigonal phase therefore improves catalytic energetics by placing its exposed octahedral Co sites in a more favorable adsorption regime and lowering the free-energy penalty of the rate-determining step. Coordination geometry also influences resistance to dissolution. The trilayer structure assigns different structural environments to Co^{3+} in the outer layers and Co^{2+} in the middle layer, with the latter proposed to contribute to lattice stabilization under acidic OER conditions. Calculated Co dissociation energies suggest that tetrahedral Co in cubic spinel Co_3O_4 is more readily detached and solvated than Co in the trigonal phase, supporting a proposed pathway where preferential loss of tetrahedral Co initiates framework destabilization. Eliminating these sites may therefore suppress this dissolution pathway. Importantly, however, all-octahedral coordination alone should not be regarded as sufficient for acid stability, because cobalt-oxide dissolution and reconstruction can be strongly phase-, time- and protocol-dependent. This uncertainty motivates spatially and temporally resolved operando measurements capable of distinguishing persistent bulk coordination from transient surface reconstruction and dissolution.[5]

This connection gives the work significance beyond Co_3O_4. Doping, vacancy engineering and surface modification tune the electronic structure or chemical environment of sites already present in a material. Phase engineering addresses a different question: whether an unfavorable crystallographic site needs to remain in the lattice at all. Tri-Co_3O_4 illustrates a transition from site optimization to site elimination. Such a strategy could be valuable for other mixed-site oxides in which one coordination environment is catalytically less productive, chemically fragile, or both. Metastable phases are especially interesting in this context because they provide access to coordination motifs and atomic connectivities that are unavailable in thermodynamically preferred bulk structures. Their value therefore depends not simply on metastability itself, but on whether the new phase creates a more favorable distribution of catalytic and structural functions.

Another appealing aspect of this work is its conceptual simplicity. A relatively straightforward synthetic route produces a structurally clean metastable phase in which all Co ions occupy octahedral environments, without relying on elaborate compositional engineering. This structural simplicity, established by complementary yet conventional characterization methods, leads in turn to a comparatively clear mechanistic picture linking coordination, catalytic activity and metal dissolution. Such simplicity is particularly valuable given the exceptional acidic OER stability achieved by a transition-metal oxide, which provides the essential performance basis for appreciating the conceptual elegance of the work.

This simplicity also raises an important question for future study: why can such a seemingly simple synthetic process generate such a fundamentally different and phase-pure coordination architecture? Clarifying the respective roles of the vacuum environment, molten-alkali chemistry, mechanochemical activation and reaction kinetics could reveal how this unusual all-octahedral phase is selected. More importantly, establishing these structure-formation principles could turn the present synthesis from a material-specific recipe into a general synthetic strategy, potentially guiding the discovery of acid-stable OER catalysts based on more earth-abundant metals than Co and inspiring metastable nanomaterials for other catalytic and functional applications. Metastable phase engineering becomes particularly attractive when an unfavorable crystallographic site is intrinsic to the thermodynamically preferred lattice and therefore cannot be selectively removed by modest doping or vacancy regulation. Whereas these conventional approaches perturb the chemistry of an existing framework, phase selection can access a different site-occupancy topology in which the unfavorable coordination environment is absent altogether.

The next step is to determine how broadly this coordination-purification principle can be extended. Scaling up Tri-Co_3O_4 will require reproducible control over phase purity, layer thickness and exposed facets, while PEMWE testing under start-stop cycling, variable current loads, differential pressure, water impurities and lower catalyst loadings will help establish its stability under more demanding operating conditions. Spatially and temporally resolved operando measurements could further reveal whether minor reconstructed, dissolved or redeposited Co species contribute to catalysis while the average octahedral framework remains intact. More fundamentally, the key question is what combination of coordination geometry, electronic structure and dissolution thermodynamics allows removal of an unfavorable crystallographic site to improve activity and stability simultaneously. Testing whether the same principle applies to Mn-, Ni-, Fe- and multimetal oxides will determine whether coordination purification can develop from a distinctive feature of Tri-Co_3O_4 into a broader strategy for acid-stable electrocatalyst design.

Wang et al. show that coordination geometry can govern both catalytic activity and corrosion resistance by transforming Co_3O_4 from a mixed tetrahedral-octahedral spinel into an all-octahedral 2D trigonal phase.[1] More broadly, their work shows that metastable phase engineering can redefine which catalytic sites are present in a material, rather than simply tune the properties of an existing lattice. In Tri-Co_3O_4, eliminating an unfavorable coordination environment improves intermediate adsorption while suppressing Co dissolution, allowing activity and structural stability to emerge from the same crystallographic redesign. This shift from optimizing existing sites to selecting which sites should exist provides a compelling design principle for reducing Ir dependence in acidic water electrolysis.

REFERENCES

1. Wang, Y., Ji, Y., Zhou, J., et al. (2026). Octahedral-coordinated Co_3O_4 for water electrolysis in acid. *Nature* **656**:370–375. DOI:10.1038/s41586-026-10851-7
2. Li A., Kong S., Guo C., et al. (2022). Enhancing the stability of cobalt spinel oxide towards sustainable oxygen evolution in acid. *Nat. Catal.* **5**:109–118. DOI:10.1038/s41929-021-00732-9
3. Geiger S., Kasian O., Ledendecker M., et al. (2018). The stability number as a metric for electrocatalyst stability benchmarking. *Nat. Catal.* **1**:508–515. DOI:10.1038/s41929-018-0085-6
4. Chong L., Gao G., Wen J., et al. (2023). La- and Mn-doped cobalt spinel oxygen evolution catalyst for proton exchange membrane electrolysis. *Science* **380**:609–616. DOI:10.1126/science.ade1499
5. Priamushko T., Franz E., Logar A., et al. (2025). Be aware of transient dissolution processes in Co_3O_4 acidic oxygen evolution reaction electrocatalysts. *J. Am. Chem. Soc.* **147**:3517–3528. DOI:10.1021/jacs.4c14952

FUNDING AND ACKNOWLEDGMENTS

This work was supported by the Special Fund of the Chinese Central Government for Basic Scientific Research Operations in Commonweal Research Institute (No. ZX2026GYZX00018), the Central Government Guided Local Science and Technology Development Fund Projects (No. ZYYD2026QY27), and the Excellent Young Scientists Fund Program of NIES, MEE (No. ZX2024SZY079). The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.