Environmental Science and Ecotechnology 30 (2026) 100685

Contents lists available at ScienceDirect

Environmental Science and Ecotechnology

journal homepage: www.journals.elsevier.com/environmental-science-and-ecotechnology/

Commentary

Failure windows and commit points of engineered nanomaterials in the environment

Engineered nanomaterials (ENMs) rarely fail in their pristine state. I argue that functional failure can become predictable within defined boundary conditions as an ENM moves through environmental compartments and encounters rapid "commit-point" chemistry. The high surface reactivity that makes ENMs powerful also makes them exquisitely vulnerable to their surroundings. Despite our advanced synthesis capabilities, we continue to treat performance loss and safety issues as static, intrinsic properties, leading to costly lab–field discrepancies and post-hoc rationalization. In reality, functional failure is not a property but a trajectory. For environmental technologies such as nano-enabled membranes, fixed-bed sorbents, catalytic filters, and protective coatings, these same transformations decide whether systems maintain removal efficiencies and resource recovery or drift into failure modes that undermine both performance and safety. Building on established environmental transformation and corona literature, I use failure windows and commit points as function-linked descriptors for when early transformations become decision-relevant for performance or risk [1,2]. These descriptors are governed by two underappreciated determinants: the environmental sequence that an ENM traverses and the chemistry of the first moments of each new interfacial encounter [3,4]. The framework is intended primarily for chemically driven, interface-controlled irreversible changes (for example, dissolution, surface complexation, ligand exchange, redox conversion, and corona-mediated interfacial reorganisation), rather than failure modes dominated by abrasion or fracture [1,4]. Fig. 1 summarises how exposure sequence, commit points, and downstream failure trajectories connect.

Defining functional failure

Here, I define functional failure as the first irreversible structural or chemical transformation event that compromises intended performance or materially increases unacceptable risk under realistic use or release scenarios. This contextual framing is critical. For instance, a passivating oxide shell that protects a quantum dot in a biological fluid may be catastrophic for a catalyst that requires a pristine surface. Similarly, a transient dissolution burst that is negligible for material recovery could be decisive for triggering acute toxicity within an organism. Therefore, we must anchor the definition of functional failure to the application. Performance loss might manifest as a drop in catalytic turnover, electrical conductivity, or optical response; risk escalation could involve a surge in bioavailable dissolved ions from ENMs, the activation of harmful radical chemistry, or a corona-driven shift in cellular uptake that concentrates ENMs in sensitive tissues. The common thread linking these diverse outcomes is irreversibility: once early processes lock in a new surface speciation, defect structure, or adsorbed layer, the ENM's trajectory bends toward a failure outcome that is difficult to reverse. Operationally, I use failure window to mean a bounded region in sequence-time-chemistry space, defined by (i) exposure order/interface, (ii) an early-time interval, (iii) bounded medium conditions, and (iv) a pre-declared function or risk readout [4,5]. I use commit point more narrowly than a generic kinetic bottleneck: it is the earliest experimentally detectable, irreversible (or strongly hysteretic) interfacial shift that redirects subsequent behaviour under a given sequence. A system is considered to have entered a failure window when a reproducible early signal (for example, dissolution flux, redox shift, or corona change) crosses a pre-defined criterion and precedes downstream performance loss or risk escalation under the same sequence conditions [6]. Functional failure is therefore endpoint-specific, but the framework is mechanistically unifying because it asks the same question across endpoints: which early interfacial transition commits the trajectory?

Environmental hierarchy and sequence dependence

Functional failure is not random; it follows an environmental hierarchy, the ordered sequence of compartments (for example, air → freshwater → soil → biota) that an ENM encounters. This hierarchy adds a third axis to conventional space-and-time descriptions by encoding exposure order [3]. This hierarchy serves as the geography of functional failure and adds a third axis to conventional space-and-time descriptions of nanomaterial behaviour. Each environmental compartment imposes its own distinct chemical rules, but the order of exposure is a primary selector of the transformation pathway that ultimately leads to ENM functional failure. Consider a nominally simple sequence moving from the atmosphere to water. An ENM preconditioned in humid, CO_2-rich air may develop a carbonate layer that significantly buffers its subsequent dissolution upon immersion in water. If we reverse this sequence, exposing the material to water first and then to air, it might experience a rapid burst of ion release and complexation, later frozen by drying into a different solid phase. In one sequence, an ENM may passivate into a benign state; in another, it may activate into a hazardous one. The sequence is therefore not a mere nuisance variable but the fundamental geography that defines all possible failure routes.

At the heart of each transition between these environmental compartments lies a critical juncture I call a commit point [4].

https://doi.org/10.1016/j.ese.2026.100685

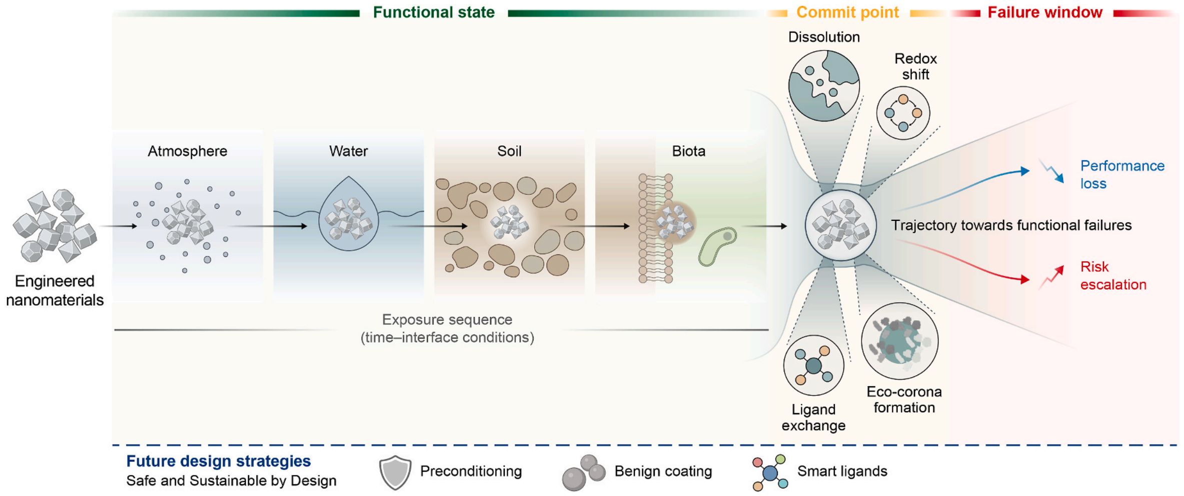

Fig. 1. Failure windows and commit points of engineered nanomaterials in the environment. Engineered nanomaterials experience an ordered exposure sequence (atmosphere → water → soil → biota or atmosphere → water → biota or atmosphere → soil → biota), in which rapid, early interfacial processes can reach a commit point—an irreversible (or strongly hysteretic) transformation that redirects the subsequent trajectory. Illustrative commit-point processes include dissolution, redox shift, ligand exchange, and eco-corona formation, which together define a bounded failure window (sequence-time-chemistry space) leading to performance loss and/or risk escalation. The figure also highlights forward-looking Safe and Sustainable by Design levers—preconditioning, benign coatings, and smart ligands—to steer first-contact chemistry towards stable, lower-risk states.

This is a narrow window, spanning the first seconds after contact, during which a small set of rapid processes dominates and sets the long-term trajectory toward or away from functional failure. During this brief period, hydration and counter-ion uptake instantly set the interfacial charge and local acidity. Concurrently, ion release and complexation establish steep near-surface gradients that can either nucleate protective shells or propagate destructive etching. For coordination solids such as metal–organic frameworks, ligand or linker exchange can create defects that seed subsequent restructuring. Most notably, the competitive adsorption of biomolecules forms an initial corona that reprogrammes the particle's identity, masking active sites and dictating its subsequent adhesion and uptake. These initial signals—such as early ion speciation, nascent secondary phases, and corona composition—are not merely ephemeral events; they are prognostic markers that can improve predictions under defined boundary conditions, including medium composition, sequence history, timescale, and endpoint, rather than guarantees across all heterogeneous systems. Capturing them still requires high-time-resolution operando measurements; without such measurements, causal attribution remains weak, and the opening of a failure window is inferred only retrospectively.

Sequence effects become clearer when examples are presented in a common format. For silver nanoparticles, this framework comprises: (i) contrasting oxic aqueous conditions and sulphide-reactive conditions, (ii) commit-point chemistry in early Ag speciation and sulfidation/passivation, (iii) earliest measurable signal in rapid dissolved/surface Ag species evolution, and (iv) downstream differences in persistence and hazard potential [7]. For copper oxides, it includes: (i) direct exposure to acidic or complexing media versus buffered/preconditioned exposure, (ii) commit-point chemistry in early dissolution and re-speciation, (iii) earliest measurable signal in the initial dissolved-Cu rise, and (iv) altered performance and toxicity trajectories [8]. For metal–organic frameworks, it includes: (i) simple electrolyte media versus organic- and biopolymer-rich media, (ii) commit-point chemistry in early interfacial adsorption and ion/linker competition, (iii) earliest measurable signal in pore-masking and surface-potential change, and (iv) loss of adsorption efficiency or altered biointeractions [9]. Here, eco-corona denotes an environmentally formed adsorbed layer of natural organic matter, ions, extracellular polymers, and/or organism-derived biomolecules; it is conceptually related to the biomolecular corona but is specific to ecological media [10].

Recognising these conditionally predictable functional failure windows allows us to reframe the Safe-and-Sustainable-by-Design (SSbD) paradigm from a static, material-centric exercise to a dynamic, trajectory-aware one. If the first environment encountered so strongly steers the ultimate fate, we should deliberately precondition that first contact. This can be achieved through intelligent packaging and formulation designed to seed benign commit points, such as carbonate priming for oxide particles or controlled atmospheres for nano-enabled filters and catalysts. We can design sacrificial ligands that outcompete hazardous complexation routes in the critical first seconds. We can even programme the corona by pre-adsorbing benign macromolecules to steer cellular uptake away from sensitive tissues or to reduce fouling in engineered treatment units. These are not exotic chemical concepts but practical design levers that simply require a new clarity about when and where to intervene along the ENM's journey.

A minimum viable sequence-aware workflow

To translate this vision into practice without overburdening a commentary, I propose a minimum viable sequence-aware workflow and an Atlas trajectory for future harmonisation. For each material–function pair, studies should record exposure order and residence time, core medium descriptors (pH, ionic strength, key ions, and organic matter/biomolecule source), and the timing of the first functional measurement. At minimum, one order-swapped comparison and one early-time assay (for example, dispersion stability, dissolution/speciation, or redox/interfacial adsorption) should be included as a reference commit-point test [5,6]. These data can seed an open Transformation & Functional Failure Atlas while directly informing SSbD decisions on preconditioning, formulation, and deployment windows. This is not a full standard but a practical starting point that is compatible with existing testing approaches developed by the Organisation for Economic Co-operation and Development and with the emerging European Commission's SSbD implementation.

Conclusion

The longstanding inability to anticipate functional failure has remained a major bottleneck in ENM innovation and deployment. By shifting attention to failure windows shaped by environmental sequence and commit-point chemistry, I propose a framework that can improve prediction and support more decision-relevant assessment within defined boundary conditions. Used in this way, the framework may help reconcile lab-field discrepancies, clarify design trade-offs, and inform safer and more reliable nanomaterial development, while recognising that outcomes remain dependent on medium composition, exposure history, timescale, and endpoint. Progress will therefore depend on testing, modelling, and design strategies that account not only for what a nanomaterial is, but also for the journey it takes and the early interfacial events that can redirect its subsequent trajectory.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

SC acknowledges UKRI NERC Independent Research Fellowship (Grant number- NE/B000187/1) for supporting this work.

References

[1] G.V. Lowry, K.B. Gregory, S.C. Apte, J.R. Lead, Transformations of nanomaterials in the environment, Environ. Sci. Technol. 46 (2012) 6893–6899, https://doi.org/10.1021/ES300839E.

[2] M.P. Monopoli, C. Åberg, A. Salvati, K.A. Dawson, Biomolecular coronas provide the biological identity of nanosized materials, Nat. Nanotechnol. 7 (2012) 779–786, https://doi.org/10.1038/NNANO.2012.207.

[3] S. Chakraborty, Environmental hierarchy as the third dimension of nanomaterial transformation science, Eco-Environ. Health (2025) 100195, https://doi.org/10.1016/J.EEHL.2025.100195.

[4] S. Chakraborty, S.K. Misra, J.R. Lead, I. Lynch, Capturing rapid nanomaterial transformations with cross-platform operando characterization, Nat. Rev. Mater. 2025 (2025) 1–3, https://doi.org/10.1038/S41578-025-00844-9.

[5] OECD, Test no. 318: dispersion stability of nanomaterials in simulated environmental media. OECD Guidelines for the Testing of Chemicals, Section 3, 2017, https://doi.org/10.1787/9789264284142-en.

[6] R.K. Cross, D. Spurgeon, C. Svendsen, E. Lahive, S. Little, F. von der Kammer, F. Loosli, M. Matzke, T.F. Fernandes, V. Stone, W.J.G.M. Peijnenburg, E.A.J. Bleeker, An integrated approach to testing and assessment (IATA) to support grouping and read-across of nanomaterials in aquatic systems, Nano Today 54 (2024) 102065, https://doi.org/10.1016/j.nantod.2023.102065.

[7] B. Thalmann, A. Voegelin, B. Sinnet, E. Morgenroth, R. Kaegi, Sulfidation kinetics of silver nanoparticles reacted with metal sulfides, Environ. Sci. Technol. 48 (2014) 4885–4892, https://doi.org/10.1021/es5003378.

[8] R.D. Kent, P.J. Vikesland, Dissolution and persistence of copper-based nanomaterials in undersaturated solutions with respect to cupric solid phases, Environ. Sci. Technol. 50 (2016) 6772–6781, https://doi.org/10.1021/acs.est.5b04719.

[9] S. Chakraborty, P. Dhumal, I. Mikulska, S. Pham, L.-J.E. Bradford), D. Menon, S.K. Misra, I. Lynch, Biotic transformation of abiotically stable nanoscale UiO-66 metal–organic framework by Daphnia magna results in chronic reproductive toxicity, ACS Nano (2025), https://doi.org/10.1021/ACSNANO.5C16532.

[10] K.E. Wheeler, A.J. Chetwynd, K.M. Fahy, B.S. Hong, J.A. Tochihuitl, L.A. Foster, I. Lynch, Environmental dimensions of the protein corona, Nat. Nanotechnol. 16 (2021) 617–629, https://doi.org/10.1038/S41565-021-00924-1.

Swaroop Chakraborty
School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, B15 2TT, UK
E-mail address: s.chakraborty@bham.ac.uk.

30 December 2025