Opportunities for Nanotechnology to Enhance Electrochemical Treatment of Pollutants in Potable Water and Industrial Wastewater -A perspective

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Environmental significance statement

Electro-driven technologies can be used in many applications where chemical-intensive water technology solutions are logistically difficult to deploy or are ineffective at treating emerging classes of persistent pollutants. The manipulation of current in electrodes strongly depends on material properties, and there is increasing recognition that nano-structures (pores, sieves, crystal facets, shapes, and core-shells) hold promise to improve pollutant degradation in water. The advent of two-dimensional (sub) nano-scale single-atom catalysts is leading to extremely high reactivity rates, but managing pollutant mass transport to reactor-scale architectures requires increased focus on nano-material selections and also design of nano-structured electrodes that can operate in complex water matrices without fouling or interference by solutes ubiquitously present in drinking or waste waters.

Opportunities for Nanotechnology to Enhance Electrochemical Treatment of Pollutants in Potable Water and Industrial Wastewater -A perspective

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Abstract

Based upon an international workshop, this perspective evaluates how nano-scale pore structures and unique properties that emerge at nano- and sub-nano- size domains could improve the energy efficiency and selectivity of electroseparation or electrocatalytic processes for treating potable or waste waters. An Eisenhower matrix prioritizes the urgency or impact of addressing potential barriers or opportunities. There has been little optimization of electrochemical reactors to increase mass transport rates of pollutants to, from, and within electrode surfaces, which become important as nano-porous structures are engineered into electrodes. A “trap-and-zap” strategy is discussed wherein nanostructures (pores, sieves, and crystal facets) are employed to allow localized concentration of target pollutants relative to background solutes (*i.e.*, localized pollutant trapping). The trapping is followed by localized production of tailored reactive oxygen species to selectively degrade the target pollutant (*i.e.*, localized zapping). Frequently overlooked in much of the electrode-material development literature, nano-scale structures touted to be highly “reactive” towards target pollutants may also be the most susceptible to material degradation (*i.e.*, aging) or fouling by mineral scales that form due to localized pH changes. A need exists to study localized pH and electric-field related aging or fouling mechanisms and strategies to limit or reverse adverse outcomes from aging or fouling. This perspective provides examples of the trends and identifies promising directions to advance nano-materials and engineering principles to exploit the growing need for near chemical-free, advanced oxidation/reduction or separation processes enabled through electrochemistry.

1. Introduction

Treating industrial or municipal wastewaters and potable waters continues to face significant challenges to meet regulatory mandates, ecosystem requirements, and aesthetic consumer preferences. Globally, there is growing reliance on distributed technologies in decentralized systems that enable local reuse of wastewaters or point-of-use polishing of centrally-treated potable waters.[1] Decentralized technologies should be designed with small system footprints, minimal or zero on-site chemical storage and dosing systems, minimal liquid or solid waste production, the potential for remote operation with minimal on-site expertise, and the ability to treat water of variable inorganic and organic composition or concentrations. Furthermore, there is demand for water treatment processes powered directly by renewable energy sources, even if that necessitates intermittent rather than continuous operation.[2] Several nano-enabled water treatment technologies have already been commercialized,[3] and numerous treatment systems have been conceptualized[4] to address emerging water quality challenges and satisfy decentralized system requirements. Nanoengineering material properties and architectures holds tremendous opportunity for direct use of electrical current to separate ions (electroseparation) or transform pollutants (electrocatalysis) without chemical addition.

Figure 1 portrays the emerging array of electrochemically-driven processes, including reductive or oxidative Faradaic charge-transfer pollutant transformation processes and non-Faradaic non-charge-transfer pollutant separation processes. Advanced oxidation processes (AOPs) generate powerful reactive oxygen species (ROS) that degrade organic pollutants. Common AOPs require chemical addition such as H_2O_2/UV,[5] H_2O_2/Fe(II) Fenton processes,[6] persulfate oxidation.[7]. Photocatalytic AOPs generate ROS by irradiating surfaces with ultraviolet or visible light, but a challenges related reactor design (e.g., uniformly irradiating fixed photocatalytic films on reactor walls, adding and recovering catalyst slurries to the water) remain challenges.[8,9] In contrast with chemical-based advanced oxidation processes (AOPs) that require off-site chemical production (*e.g.*, H_2O_2/UV), nano-enabled electrodes and Faradic processes can generate H_2O_2 on-site immediately upstream of ultraviolet (UV) reactors, producing reactive oxygen species (ROS) via water oxidation directly on electrode surfaces or electrogenerating other oxidant species (*e.g.*, sulfate radical, active chlorine species, *etc*.). These electrochemical processes avoid the need for chemical production, transportation, and on-site storage/feed because they generate the ROS *in-situ*. Additionally, whereas pressure-driven membrane separation processes convert electricity via pumps into mechanical work, electro-separation systems drive separation without high pressures. While debate exists regarding energy and economic comparison between pressure-driven membrane separation processes and electrochemical-driven non-Faradic ion separation methods,[10] bottom-up design of nanostructured electrodes or electrochemically-enhanced membranes offer opportunities for selective ion removal.

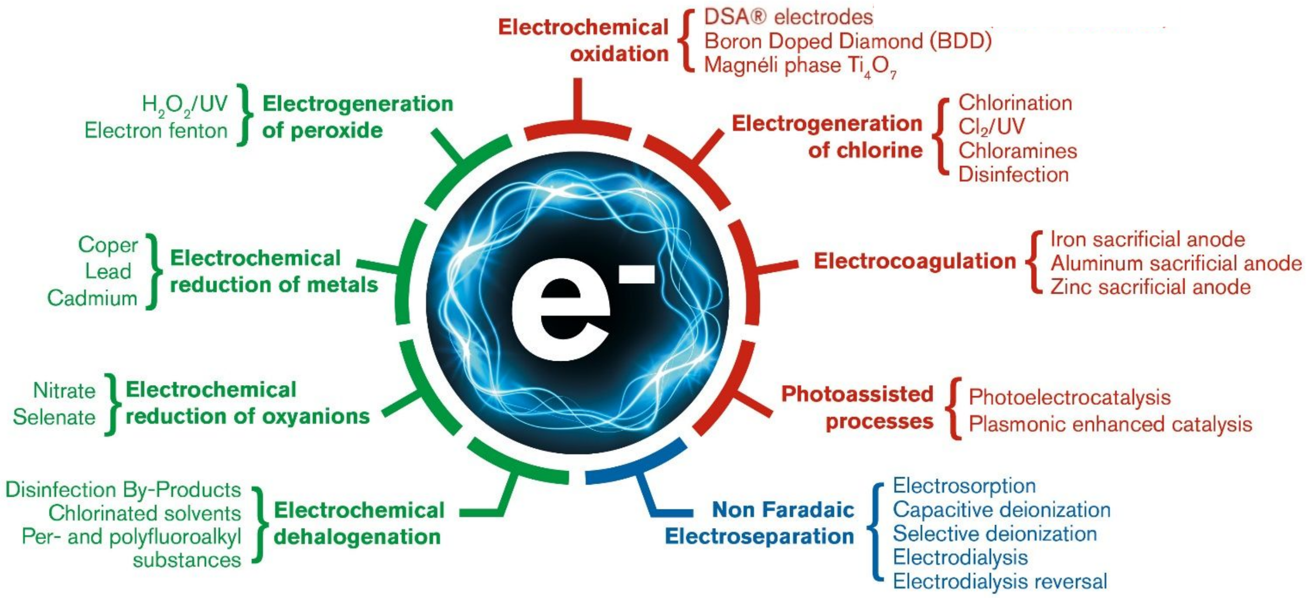

Figure 1. Electrochemically-driven processes classified as reductive Faradaic processes (green), oxidative Faradaic processes (red), and physical separation through non-Faradaic processes (blue).

Commercial electrochemical technologies are already in use in the water industry (*e.g.*, on-site hypochlorite production, electrodialysis), and interest in electrochemically-driven technologies is growing in both peer reviewed literature and commercial development. More broadly, there are roughly 18,000 publications using “electrochemical”, “electrocatalytic”, “electroseparation” and “water” between 1996 and 2018, which grew exponentially from 560 in 1996 to 5900 publications in 2018 when nearly 2800 of these publications also included the keyword “nano”. “Sensors” accounted for 850 of these publications in 2018 (see Figure SI1). Publications containing “nano” grew at a rate nearly 25% faster than papers without “nano”. There is no way to capture all the key messages in all the electrochemical-related papers, but recent reviews related to electrochemical processes for water treatment capture important findings[11–14], albeit few are nano-focused. Reviews based on electrochemical destruction methods have identified challenges associated with 1) minimizing the formation of toxic byproducts, 2) reducing loss of efficiency caused by mass transfer limitations and undesired side reactions, 3) synthesizing nontoxic, inexpensive, high surface-area electrodes that have a long operational life (*i.e.*, electrode stability[14,15]), 4) improving energy demand by improved electrode spacing or energy recovery devices, and 5) recognizing that many publications focus on investigating individual contaminant transformation pathways and mechanisms rather than reactor design considerations. While a few reviews on electrochemical processes exist for certain classes of nanomaterials (*e.g.*, 2-D[16]) or processes (*e.g.*, electro-Fenton[17]), this perspective considers the broad range of nanomaterial opportunities that emerge as a commonality to nearly all electrochemical water treatment processes.

Tunable nanomaterial properties offer unprecedented opportunities for electrochemical water treatment. For electrocatalysis, desirable features include (i) increasing pollutant selectivity for removal with higher precision and efficiency, (ii) high production rate of specific redox mediators capable of degrading pollutants, and (iii) increasing the mass transfer rate. In contrast, for electroseparations, two important desirable design functions are (i) maximizing electrode surface area to adsorb charged ions and (ii) reducing mass transfer limitations from bulk solution to electrode surfaces to lower adsorption-desorption cycling times. In both processes, nanoparticles, nanotubes, and hybrid nanomaterials can be integrated into electrodes and used in different reactor architectures. Higher surface area improves reaction rates that occur on the electrode surface (i.e., heterogeneous processes). Compared against monolithic or only “rough” macro-scale surfaces, nanotechnology is allowing unprecedented control of surface morphology, pore geometry and structures that exponentially increase the amount of surface area available for electrochemical reactions.

This perspective also explores opportunities to use nano-structured electrodes, whose unique and tunable properties (*e.g.*, surface morphology, crystalline structure, facets and porosity) combined within novel reactor geometries form an emerging class of electrochemical water treatment technologies. Each section is motivated by a question that the authors addressed during a workshop. First, we describe how existing electrochemical processes have benefited from incidental use of nanotechnology. Second, we discuss opportunities for nanomaterials in next generation electrodes to overcome barriers facing existing anodes or cathodes: (i) enabling unique nano-scale properties, (ii) utilizing highly selective surfaces and unique geometries, (iii) reducing reliance on noble metals or non-earth abundant elements. Third, we introduce the concept of sub-nano structures and single atom catalysis as future trends. Fourth, we discuss the role of nanotechnology in improving pollutant selectivity over other solutes present in complex water matrices and how nanotechnology can enhance the competitiveness of electrochemical technologies. We consider enhancing selective yield of oxidants and selective final product formation (i.e. innocuous nitrogen gas from nitrate reduction). In addition, we propose emerging operation strategies to increase target pollutant transformation over scavengers and competitive species using a simultaneous adsorption-destruction approach (*i.e.*, “trap-n-zap”). Fifth, we highlight the relevance of aging and fouling effects on electrodes stability, as well as discussing their effects on nano-enabled electrodes. Sixth, we explore how nanomaterials can lead to different reactor designs through improving mass transfer towards electrodes. Seventh, we describe how capital and energy costs (*e.g.*, techno-economic analyses) can be used to drive innovation in electrochemical technologies and how the concept of “cost learning curves” will continue to decrease system expenses over time. We discuss how early development considerations of nanomaterial durability, safety, toxicity, or scalability are important for electrochemical systems, as with any other new technologies. Finally, a perspective on how to prioritize research barriers and opportunities where nanotechnology offers the greatest potential

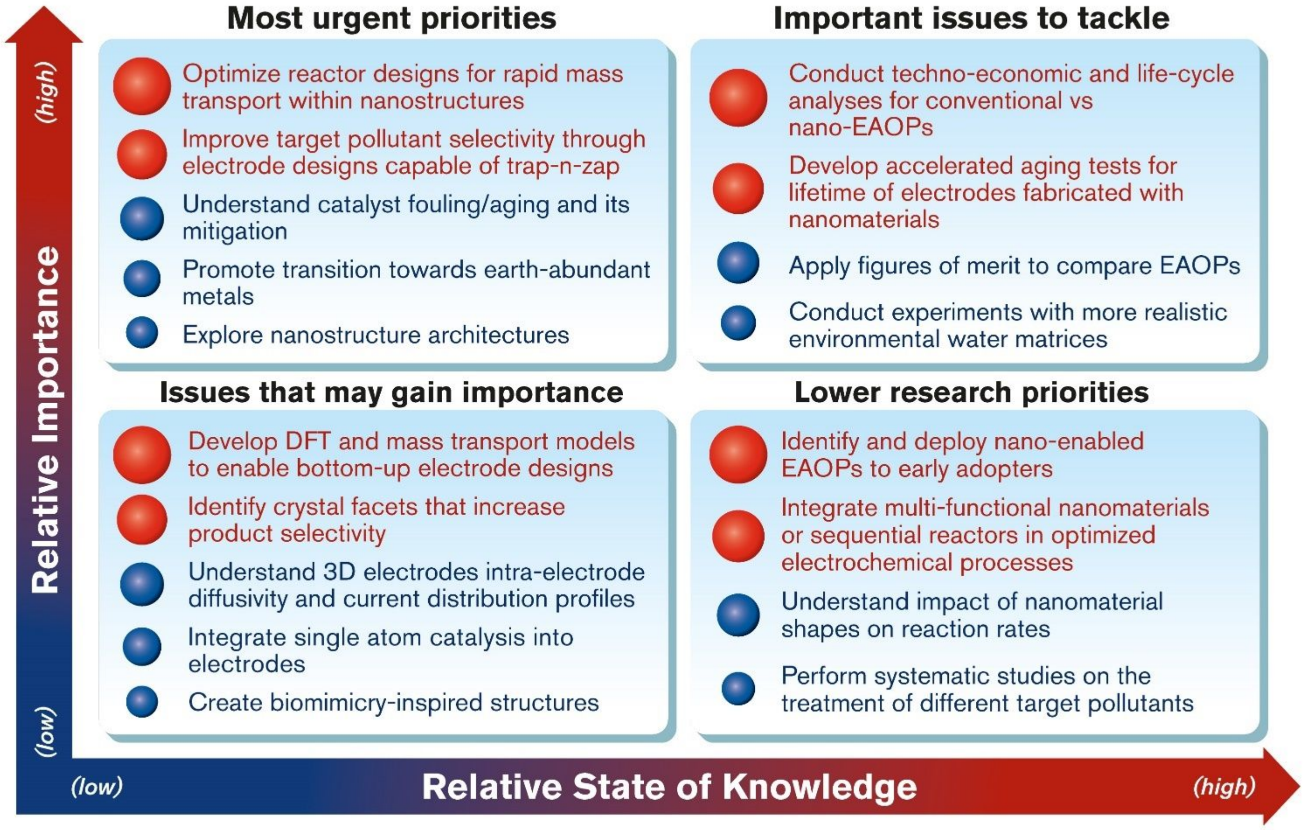

Figure 2. Eisenhower matrix of prospective research needs. Red text and larger bullets signify higher importance.

2. Current reliance on nanotechnology in electron-mediated chemical separation, production, or destruction in commercial applications

Has nanotechnology always been part of electrochemically driven technologies? Whether intentional or not, the answer is yes. Commercial electrodes used in industrial processes *de facto* contain nanostructured materials. DSA® anodes that incorporate nanostructured metal oxide coatings on electrodes were pioneered by Oronzio De Nora in 1923[18] and revolutionized the chloro-alkali industry enabling electrochemical generation of chlorine (Figure SI2). DSA® electrodes are now widely used in water treatment applications for on-site electrochemical production of hypochlorite[19–21]. These electrochlorination systems use titanium-based electrodes coated with a few hundred microns of nanostructured ruthenium, niobium, indium, tin, titanium, and/or other metal doped-oxides. They are highly efficient. However, the electrode coatings electrochemically and mechanically degrade over a few years, at which time the base electrodes are removed, shipped to central facilities, and can be recoated with metal-oxides are returned for use. To further enhance coating stability and reduce catalyst leaching or erosion in other applications, the industry is beginning to use conformal and non-line-of-sight coating technologies. This is especially important to create robust and uniform coatings on porous substrates, such as membranes. Developed by materials scientists, two manufacturing methods stand out: liquid solution combustion (LSC)[22] and liquid-phase atomic layer deposition (L-ALD).[23] Based on different solution deposition chemistry, these readily-scalable methods could yield robust oxide or mixed oxide conforming coatings on the inner pore walls of ceramic membranes with micron-scale and even nano-scale pores. The coatings are robust, and their thickness uniformity can be controlled at sub-nanometer precision. Furthermore, atomic level lattice doping is achievable for intrinsic band-gap tuning of the semiconductor oxide coatings.[24] In addition, nanoporous carbon electrodes are being used successfully in commercial-scale in electrodialysis reversal (EDR) and capacitive deionization (CDI) systems.

Most electrodes, while nanostructured, rely on traditional trial-and-error synthesis rather than bottom-up designs. Historically, density functional theory (DFT) has been utilized to explain experimental results by understanding energetics within materials or between ions and surfaces. Now, DFT is emerging as a material discovery tool to *a priori* select elements and design specific crystal facets into electrodes. Applying machine learning to material discovery involves creating feedback loops between experimental synthesis and characterization with DFT or other molecular simulations[25,26] and holds tremendous promise to improve efficiency and selectivity of electrodes. However, we currently lack the ability to scale electron mobility from the atomistic equilibrium conditions predicted by DFT to dynamic processes within nanostructures (*e.g.*, tubes or other geometries). The next wave of innovation will likely occur through filling this fundamental knowledge gap to enable bottom-up designs, which could eventually diminish capital costs of electrodes (*i.e.*, efficient use of non-earth-abundant (aka, endangered) elements[27]) and reduce electrical operational costs by enabling more efficient use of delivered electrons towards desirable target reactions rather than competing side-reactions.

3. Moving up the periodic table

Do electrodes always need to utilize noble metals to be cost-efficient? Most electrocatalysts reported in academic publications focus on expensive noble metals (*e.g.*, Pd, Pt, Ir, *etc.*). Figure SI3 identifies endangered elements due to their excessive use or limited resources on the planet.[28] Earth-abundant alternatives to precious/critical metal electrocatalysts likely exist for many water treatment applications but have not been a main research focus[27]. The reasons may be numerous but could be related to the probability that earth-abundant catalysts may be less reactive or degrade easily when compared to precious elements used in catalysis – and thus *a priori* less attractive to pursue. But reaction kinetics of pollutants within electrochemical systems may not always control net costs of a water treatment system. Techno-economic assessments (TEAs) of electrochemical treatment systems show that electrode materials are a major cost driver, and as such significant reductions in system costs can be achieved either by improving efficiency of costly electrodes or by using lower cost electrodes even if they have slower reaction rates. We suggest that taking a systems level view of major environmental and/or cost-drivers rather than focusing only on electrode performance for pollutant removal will reveal that alternatives to using noble metal-based electrodes are needed. [29,30] Even if electrodes fabricated using earth abundant elements are only 10% as efficient as noble metals, if they are 1000x less expensive, then they emerge as better choices within the overall electrochemical system.

Moving up the periodic table (*i.e.*, elements with lower atomic numbers) usually indicates the elements are more earth-abundant. Specifically, moving up the periodic table will drive innovation to find homogeneous and heterogeneous catalysis that substitute first-row earth abundant transition metals for precious metals. A complimentary philosophy could suggest that by going down to the nano-scale, the reactivity per atom increases, and hence perceived inefficiencies of non-noble metal catalysts can be overcome when viewed at a system-level of a water treatment unit. Few life cycle assessments exist for electrodes with endangered elements. In the related field of hydrogen catalysis, similar concerns were recently examined for hydrogenation (H_2) catalysts for heterogeneous pollutant destruction,[31] where Pd was determined to be a major driver of adverse environmental impacts.[32] However, reducing Pd to 2.5% by using nano-Pd allows treating nitrate in ion exchange brines while considerably diminishing the environmental footprint of conventional nitrate treatment systems.[32] By nano-engineering non-traditional earth abundant materials (*e.g.,* control of crystal facets, nanoparticles shape, *etc*.), we hypothesize that opportunities may exist to replace endangered and expensive materials.[33] Carbon based electrodes offer one potential pathway for non noble metal electrode designs. Carbon is one of the most earth-abundant elements, and its electrocatalytic properties can be drastically modified with very low doping of other elements such as boron (e.g. ~0.5-3.0 wt% (~1 to 3 x10^{20} atoms per cm^3) or more abundant dopants such as nitrogen.[34,35] Doping affects the sp^3/sp^2 ratio and surface termination of the diamond structure, and boron-doped diamond (BDD) electrodes are often considered a gold-standard in terms of their performance and stability.[35,36] However, BDD electrodes are among the most costly because chemical vapor deposition (CVD) is needed for their synthesis. Sensing applications have been proposed using nano-BDD films or rods that leverage increased surface areas and material durability,[37,38] showing how nano-BDD is just one example of the potential opportunities to use earth-abundant electrode materials in electrochemical water treatment processes.

4. Sub-nano and single-atom catalysis

What are the benefits of going smaller than nano-scale? Figure 3 illustrates that an important design space with enhanced reactivity may exist below a few nanometers. Depositing metals on the electrode surface as sub-nanometer clusters or single atoms presents an untapped opportunity for new electrode development. Single-atom catalyst (SAC) morphology is the theoretical limit in the endeavor to maximize atomic efficiency of metals (*e.g*., catalytic activity, specific surface area, *etc*.) and minimize the use of noble metals and other non-earth abundant elements.[39] Metal atoms in the SAC form behave differently from their nanostructured counterpart because the valency changes, often exhibiting behaviors in between homogeneous and heterogeneous catalysts. Within the past decade, SAC has been rapidly advancing from gas phase catalysis to electrocatalysis in driving oxygen evolution reaction (OER), hydrogen evolution reaction (HER), nitrogen conversion to ammonia, CO_2 conversion to methanol, as well as oxygen reduction reaction (ORR) and hydrocarbon oxidation for fuel cells.[40–45] While not widely studied for pollutant remediation in water, SACs may be relevant for water treatment reactions (*e.g.*, oxyanion reduction, hydrodehalogenation, or oxidant generation) at high selectivity and efficiency. SACs allow significant reduction in use of non-earth abundant elements due to their low mass requirements and implicitly high surface area. SAC might bring catalysis to an era where material cost or availability would no longer be a concern. However, directly translating findings of recent SAC research to redox reactions in water is challenging because the mechanism of SAC appears to vary depending on the types of metal(s), their surrounding environment (*i.e.*, substrate, aqueous matrix at the boundary layer), and target reactions. For example, SACs using Pt/Ti have been studied for electrochemical H_2O_2 production.[45]

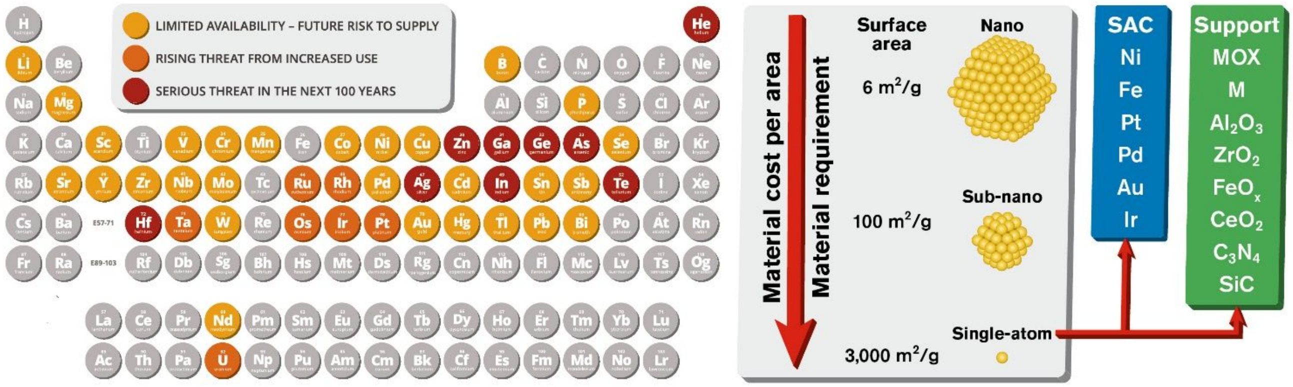

Figure 3. a) The periodic table of endangered elements (Source from ACS Green Chemistry Institute by Andy Brunning shared under a Creative Commons BY-NC-ND 4.0 International license). b) Definition of sub-nano and single-atom catalysis (SAC) and the implication of using these novel structures for electrocatalytic applications in terms of increased available surface area.

A significant knowledge gap exists in the area of sub-nano to single-atom electrocatalysis, related to the SAC itself as well as methods to integrate SAC into supportive substrate architectures. On one hand, these opportunities are exciting, but on the other hand, elemental selections and material designs should be approached strategically. Enabling machine learning algorithms between elemental selection and material designs *in silico* and through material synthesis and testing may emerge as a potential strategy to reduce the design space.[46,47] There are several synthetic challenges, specifically avoiding aggregation of the single atom catalysts and dispersion across the supports. Preliminary synthetic methodologies exist in literature but are not well established. Full-scale applications of SAC in the water industry have not been reported, and very few reactor designs are envisioned wherein inherent mass transport limitations of SAC could be overcome. It is still early to evaluate techno-economic implications at such low technology readiness level, but breakeven costs evaluation between material cost of macroelectrodes and the manufacturing costs of SAC-based electrodes will have to be conducted. Hence, the critical need in the shorter-term is to improve our mechanistic understanding of SAC to assess the upper range potential to improve performance, and then in the mid- to longer-term to envision and model potential SAC-enabled electrocatalytic reactors that can provide a framework for performing TEAs. Simultaneously there is a need to compare LCAs for different SAC synthesis techniques and manufacturing processes. Hence, the central opportunities today are to improve our mechanistic understanding of SAC and to begin envisioning and modeling potential electrocatalytic reactors enabled by SACs. As breakthroughs in SACs occur, there will be a need to consider a system-level view.

5. Improving pollutant selectivity through nanomaterial selection and process design

How can nanotechnology design principles improve degradation of target pollutants that occur in complex mixtures, often at orders of magnitude lower concentrations than background solutes? Nano-engineering does not "reinvent" electrocatalytic principles of charge transfer processes. However, controlling the flow of electrons can improve the selective removal of target pollutants over other (more abundant) solutes or shift formation towards more favorable by-products that are less toxic or easier to remove in downstream processes (*e.g.*, low solubility and innocuous N_2 versus NH_4^+). Materials science efforts have focused on bandgap engineering to control catalytic activity of semiconductor electrocatalysts, but the frontier of nano-engineering is on controlling nano-shapes and nano-morphologies. Transitioning from traditional bulk or monolithic electrodes, nanomaterials increase the possible design envelop of electrochemical water treatment technologies by playing along two novel pathways: (i) tunable recognition for selective removal of target pollutants in the water matrix and (ii) tunable electrogeneration of specific reactive radical species.

Controlling reaction pathways is one of the greatest challenges of any oxidative or reductive water treatment process, including faradaic electrocatalytic processes. The fate of the organics in water needs to be identified. Due to complex water chemistry, different degradation pathways with different degradation intermediates may exist even for the same organic pollutant.[17,48] Therefore, a comprehensive mechanistic understanding of compound transformation pathways is critical for all chemical and catalytic degradation processes during water treatment. Natural waters and industrial wastewaters contain complex mixtures of inorganic and organic solutes. These background solutes often compete with the target pollutant and decrease Faradaic efficiencies of electrocatalytic processes (*e.g.*, oxidation of natural organic matter by electrogenerated ROS). Nano-engineering design strategies can enhance selective treatment. For example, Figure 4 illustrates a concept termed "trap-n-zap". The concept first involves modifying electrodes to selectively "trap" pollutants on the electrode surface, which increases their localized surface concentrations. Second, heterogeneous catalysis achieves the "zapping" step of the selectively adsorbed pollutant on the catalyst surface via direct charge transfer or indirect oxidation/reduction of redox mediators. This approach is likely superior to production of oxidants (e.g., hydroxyl radicals) on the catalyst surface which would diffuse back into solution and non-selectively oxidize pollutants that occur at low concentrations relative to background solutes. Generally, electrochemical advanced oxidation processes (EAOPs) enable ROS to react with pollutants in the boundary layer (and on the surface), therefore the trapping approach should employ materials that are stable under oxidative processes. However, when implementing the trap-n-zap concept for electrode surface reactions, caution is also needed to avoid creating sites that lead to irreversible sorption of by-products (*e.g.*, adsorbed NO_2), because the result would be "poisoning" the electrocatalytic sites (*i.e.*, fouling or aging).

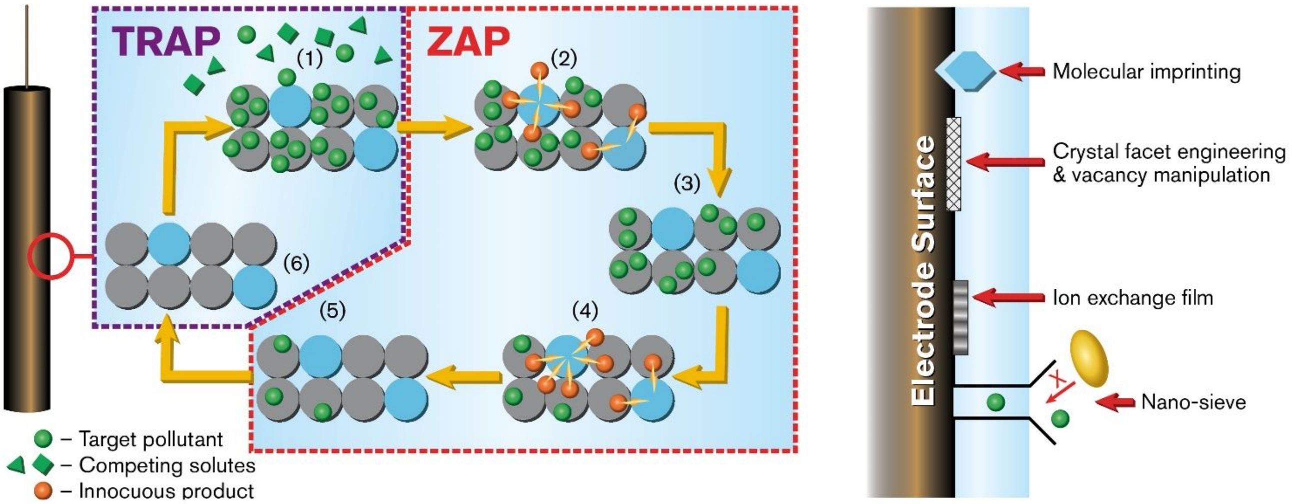

Figure 4. a) Tap-n-zap schematic for selective pollutant transformation. b) Selective target pollutant recognition strategies at the interfacial nano-scale. In the left image step 1 illustrates how the target pollutants are selectively attracted to an electrode via a non-faradaic process, molecular imprinting, or molecular sieving. This "trap" stage selectively increases the target pollutant concentration close to the electrode surface, which overcomes mass transfer limitations and decreases the extent of competitive/scavenging reactions. In steps 2–6, trapped target pollutants undergo direct or indirect electrochemically induced transformations (*i.e.,* direct charge transfer, radical mediated redox reactions),

or the so-called "zapping". After trapping and zapping target pollutants, the by-products must diffuse away from the surface – thus regenerating the surface (step 7).

Figure 4b illustrates possible nano-engineering strategies to facilitate selective "trapping" of pollutants. The first group of approaches utilizes enhanced molecular recognition on electrode surfaces nano-engineering. Molecular imprinting is a biomimicry-based strategy that emulates the selectivity of enzymatic catalytic centers. Molecular dynamic modeling can inform crystal facet engineering by identifying metal oxides that have vacancies capable of selectively coordinating with pollutants (*e.g*., oxyanions). Alternatively, redox-active nano-materials (such as poly(vinyl)ferrocene (PVF)) can be applied as a promising platform for selective separations and in-situ reduction due to their molecular selectivity and electronic tenability.[49]

The second group of approaches utilizes physical exclusion of competing species. For example, similar to how ion selective electrodes can be enhanced for selective analyte detection, nano-scale ion exchange films or porous particle coatings have shown increased selectivity in non-faradaic electrosorption processes.[50,51] Organic and inorganic molecular selection can be considerably improved with nano-sieves that become highly selective "nanoreactors". Nanoreactors can reduce competition for electrogenerated ROS by decreasing scavenging and lengthening reactant lifetime within close proximity to the electrode surface. For example, Figure 5 shows a yolk-shell nanoarchitecture with a mesoporous shell and a catalytic core that provides molecular sieving to exclude competing solutes (e.g., humic acids (HA)) while allowing a target pollutant (*e.g*., bisphenol-A) to enter the nanoreactor. Once the pollutant is within the nanoreactor, nano-Co_3O_4 can produce persulfate radicals ($SO_4^{\bullet-}$) from peroxymonosulfate (PMS) that then selectively react with BPA. These unique nanoreactors might be engineered to also avoid undesirable reactions that produce non-targeted oxidizing radicals (*e.g*., $Cl^{\bullet}$), which can react with HA to produce halogenated disinfection by-products.

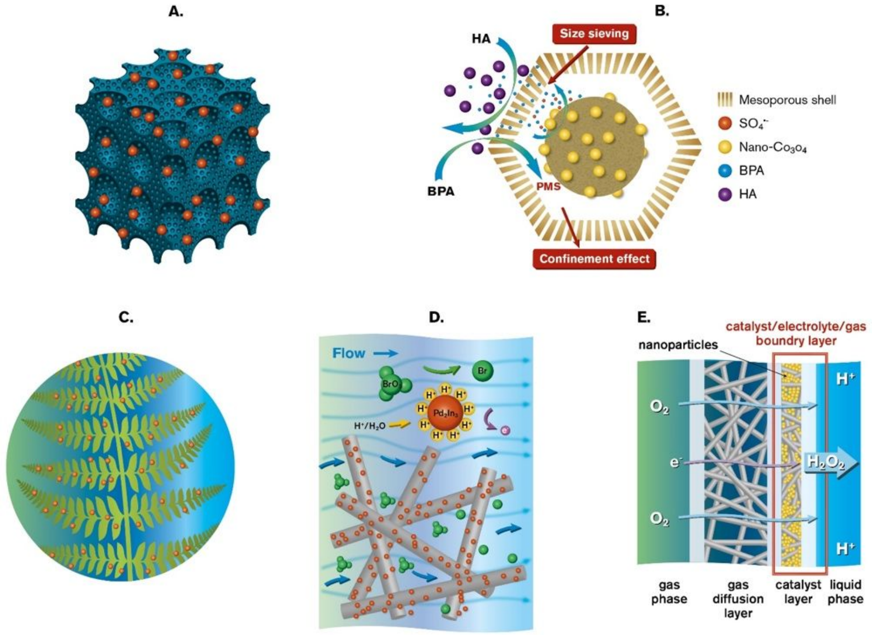

Figure 5. a) Bottom-up design of 3D-porous carbon electrode supports, b) size sieving nano-reactors for selective electrocatalytic conversion of target pollutants, c) biomimetic fern-like micro-leaves of ZnO in comparison to Fern leaves physiology,[52] d) schematic of flow-through cell of Pd-In nano-enabled graphite fiber cloth electrodes, e) air diffusion electrode with a nano-enabled catalyst layer.

Carbon nanostructures can be exploited to nano-confine reactions. Nano-engineering the interconnected hierarchical ultramicropores (<1 nm) in monolith carbon aerogel electrodes allows selective transport and adsorption of target pollutants over competing ions. For example, aerogels can be shaped and sized to allow entry based on the more planar hydrated ion geometry of a target pollutant (*e.g.*, nitrate) while excluding competing ions (*e.g.*, sulfate) for adsorption sites.[53] Hollow carbon spheres and metal-organic frameworks (MOFs) have also been envisioned to trap target pollutants near reactive centers.[54] A risk of very efficient trapping mechanisms can be irreversible adsorption of reaction (by)products. Incorporating electric potential fields in addition to hierarchical ultramicropore geometries can reduce risks from irreversible adsorption reactions. Pollutant transport efficiencies through all these physical geometries are simultaneously influenced by electro-potential fields within electrodes. As such, biomimicry also offers opportunity to become a paradigm shift in selective pollutant transport towards electrocatalytic surfaces. Biomimetic ionophore channels are controlled by voltage gates and may selectively allow target pollutants to enter confined nanoreactors similar to selective transport in cells.

The above “trapping” approaches will create high localized surface concentrations that help overcome otherwise low Fickian mass transport by increasing concentration close to the electrocatalytic surface when low pollutant concentrations exist in solution. Then, the role of electrocatalytic “zapping” will define selectivity in terms of desired radical species electrogeneration or products yielded from target pollutants.

Free and surface-bound ROS are produced at the anode via not only oxidation of water (*i.e.*, HO, O_2^-, O_3, O_2), but also from other solutes that yield persulfate or sulfate radicals, active chlorine or bromine species, or high valence metals. ROS act as redox mediators to oxidize organic pollutants, but each has unique standard reduction potentials. Preferential electrogeneration of specific ROS over less desirable ROS can be achieved through selection of electrode materials and control of applied current/voltage. While we know that electrode materials should have a high oxygen overpotential to behave as non-active electrocatalytic centers that stabilize $^{\bullet}OH$, further material and current control advances are required to maximize $^{\bullet}OH$ in the presence of common ions in water (*e.g.*, chloride) that yield chlorine radical species and produce chlorinated by-products. Faradaic efficiencies of other electrocatalytic processes (*e.g.*, hydrogen oxidation in fuel cells) are defined by electrocatalyst crystalline structures, nanoparticle shape, and accessible/preferential crystallographic planes. Other material properties that enhance electrocatalytic treatment are the introduction of defects (*e.g.*, increased number of terrace steps, vacancies, doping) or the presence of heterogeneous catalytic centers resulting from nanocomposites and bimetallic nanoalloys.[55] Similar advances for electrocatalytic water treatment are achievable through tailored synthesis of nanomaterials, guided by DFT calculations. However, research should focus on both desirable and undesirable ROS in realistic water chemistries rather than the typical approach of employing model waters with only one target pollutant present.

Many pollutants undergo surface-bound reactions. Using electro-active materials to degrade nitrate on electrode surfaces is perhaps one of the more well studied processes. Specifically, effects of different crystalline planes on faradaic efficiencies and product selectivity have been reviewed.[56] As a prime example, selectively reducing nitrate towards innocuous N_2 is not a trivial matter due to the wide range of nitrogen oxidation states (from -III up to +V). However, seminal work by Feliu and Koper's groups show tunability using single crystal electrodes of defined crystallographic planes.[57] Crystallographic terraces of Pt (100) are responsible for driving electrocatalytic reduction towards N_2 evolution. Meanwhile, symmetry defects in these [(1 0 0) x (1 1 0)] and [(1 0 0) x (1 1 1)] surfaces may increase yield of other by-products such as ammonia or nitrite. Thus, nanoengineering macroscopic electrodes populated with preferential (100) facets can increase reduction kinetics due to the larger electroactive surface area of nano-enabled cathodes and also enhance the yield of the innocuous by-product (N_2).

Beyond material selection or electrode geometries to tune ROS, an emerging research area involves synergistic application of electrons and photons (*i.e.*, photoelectrocatalysis). Emerging reactor and material approaches aim to maximize co-availability of ROS and pollutants on electrode surfaces. Here, the high surface area and ability to decorate surfaces with different materials is a key attribute for nanotechnology. For example, reactors that integrate solar or artificial light with photo-active electrodes have been effective for preventing excited electrons and holes from recombining, which enhances hydroxyl radical production.[58,59] Hierarchical nanostructures depicted in Figure 5 are crucial to ensure efficient light transport, homogeneous current distribution, and large surface availability to generate ROS. Nanotubes and geometrically-shaped nanorods have proven to be effective nano-strategies for enabled photoelectrocatalytic response. Looking further into the future, exploring biomimetic light-harvesting nanostructures that emulate plants' physiology may enhance radical generation due to increased photon-excitation[60,61] and could emerge in next-generation electrochemical systems.

Nanocomposites or nanodecorations can enhance electrocatalytic performance by combining dual roles. For example, Pt/Cu bimetallic electrocatalysts have higher nitrate reduction performance as they combine (i) the faster nitrate electrocatalytic reduction by copper, with (ii) the high selectivity of Pt towards nitrogen evolution. Similarly, novel nanocomposite electrodes can promote per- and polyfluoroalkyl substances (PFAS) degradation by enabling (i) faster activation via direct charge transfer followed by (ii) mineralization through electrogenerated ROS.

Cathodic reduction reactions can be designed into novel reactor configurations to maximize targeted ROS yields. For example, separate cells in a reactor can first electrogenerate H_2O_2, which subsequently drives AOPs (*e.g.*, electro-Fenton, H_2O_2/UV)[17,62]. The *in-situ* H_2O_2 production eliminates safety risks associated with transport, handling, and on-site storage of liquid H_2O_2. Moreover, H_2O_2 concentrations can be controlled by the applied electrical current/potentials, oxygen fed, and electrolysis time electrolysis time.[63] Modification of cathodes with Fenton-like nanocatalysts can also provide unique opportunities for catalytic generation of hydroxyl radicals from H_2O_2 without the pH limitations associated with conventional Fenton chemistry; conventional Fenton chemistry is usually optimal within a narrow acidic pH range 3.0-4.0. As illustrated in Figure 5, nanomaterial coatings on carbonaceous electrodes (*e.g.*, conductive fibers, carbon felt, carbon sponge) can increase H_2O_2 yield when used in air-diffusion cathodes. Integrating cathodic H_2O_2 production ahead of a UV reactor enables AOPs for decentralized pollutant oxidation, while the anode aided in direct surface oxidation of pollutants, which reduced residual H_2O_2 and stabilized solution pH.

As described above and illustrated in Figure 5, the trap-n-zap concept can enable endless creative designs. While these approaches hold promise to "trap" pollutants, the very same design decisions may prevent by-products from exiting ultramicropores or other "traps", thus resulting in irreversible fouling of electrode reactive sites. Thus, it is essential for researchers to *a priori* understand processes that lead to electrode aging and fouling.

6. Electrode aging and fouling

Why have so few studies addressed reversible and irreversible deterioriation of electrode performance over time? The stability of electrodes is often reported in academic studies for only a limited number of operational cycles over only a few hours. However, in actual operation, electrochemical system performance can decrease with time (Figure 6) due to fouling and aging of electrodes, which may be exacerbated for nano-enabled electrodes with high surface area of nano-confinement. Catalyst performance is often judged upon three criteria (activity, selectivity, and productivity), where the lifetime of the catalyst controls its productivity.[64] Aging and fouling of catalysts reduce this lifetime through deactivating the surface, and hence lowers the catalysts' productivity, but is often lacking in many peer reviewed studies.[64,65] Fouling is the accumulation of unwanted material (*e.g.*, microorganisms, inorganic scales) on electrode surfaces that diminishes their electrocatalytic activity. Fouling includes formation of both biological and inorganic scales.[66] Foulants may isolate electrodes from solution and may also increase electrical resistivity of the system, which increases cost and diminishes performance. Aging is the detrimental modification of electrocatalyst surface structure and composition during operation, which decreases electrocatalytic properties. In practice, it is hard to differentiate fouling from aging because they occur at the same time but have different impacts on the longevity of electrocatalytic systems. Fouling rapidly decreases performance, but it may be fully or partially restored with appropriate antifouling strategies (*e.g.*, reverse polarity) or periodic cleaning. In contrast, aging leads to permanent electrode damage, thus necessitating electrode replacement. The aging mechanisms and rates for nanomaterials is limited, and to our best knowledge, there have not been any in-depth research or review papers focusing on nanoparticle aging in electrochemical systems. While the high surface area and microporous structures of nanomaterials may enhance pollutant degradation, their high reactivity and nano-geometries may also make them more susceptible to aging and fouling challenges.

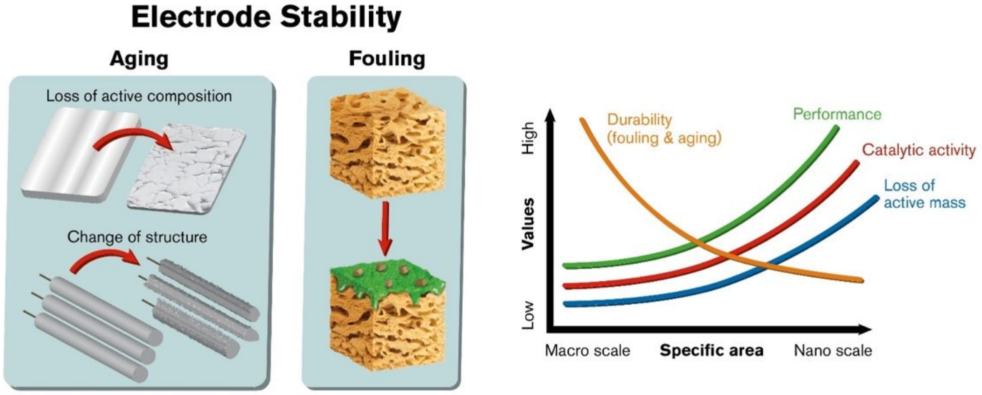

Figure 6. a) Structural and surface impacts of aging and fouling on electrode stability. (b) Impact of aging and fouling on electrode durability and long-term performance as a function of specific area transition from macroscale to nano-scale.

Research is needed for substrates or matrices used to support nanomaterials. Polymers (*e.g.*, polymeric binders such as (3-Aminopropyl)triethoxysilane (APTES) and polyethylene glycol (PEG) and ion exchange membranes) may slowly decompose (*i.e.*, age) upon exposure to ROS generated *in situ*. [67]

Some of the more “durable” electrically-conductive membrane materials (*e.g.*, fluorinated membranes) are also raising concern because of potential release of fluorinated organic by-products. With most research having been conducted at the bench-scale, where fewer than 20 operational cycles are often reported, there is a need to understand performance over the lifetime of supporting materials, including reactivity loss due to release of catalytic nanomaterials. Health risks associated to leaching or wear-off of nanostructures will have to be analyzed for each specific electrocatalytic material, although there is low risk posed by engineered and incidental nanoparticles in drinking water.[68] Not only does release of nanoparticles or degradates of nanostructured materials pose potential health risks, such losses that occur during electrode aging compromises the electrode productivity and as requires concerted focus as highlighted in prominent Perspective articles.[64,65] There is a need to develop accelerated life tests to evaluate possible application of electrodes in water treatment. Some attention has been given to porous ceramic membranes to be used instead of electrically-conductive polymers. However, industry currently avoids organic membranes or linkers in many electrodes that require highly oxidative conditions and instead prefers to use solid support matrices (*e.g.*, titania) that can be spray-coated, electrolyzed, or coated with sacrificial pastes to deposit porous reactive coatings.

Passivating films can also be added to electrodes to improve long-term stability and overcome aging. For example, nano-scale Magnéli phase titanium (Ti_4O_7) efficiently produces $^{\bullet}OH$[69,70] but is unstable over time. Magnéli phase can be difficult to fabricate, and only recently have proprietary nano-scale passivation layers been added to Ti_4O_7 that appear to remain stable and able to treat recalcitrant pollutants such as PFAS.

Commonly occurring ions in water can contribute to fouling and/or aging. For example, because the pH of water tends to increase at the cathode surface, precipitation of insoluble carbonates and/or hydroxides often occurs on the cathode surface, forming inorganic scale. Electrocatalyst poisoning is described as the partial or total deactivation of catalytic electrode centers by a strong interaction with a chemical compound. Oxidation or reduction of iron and other common metals can occur during operation and foul electrodes. Sulfides can be more damaging to electrodes, permanently poisoning their surfaces. Tradeoffs exist between electrode anti-fouling characteristics and electrocatalytic performance. For example, Pd-Au-SiO_2 catalysts with greater proportions of Au reduced loss in catalytic activity due to sulfide fouling.[71]

High surface area and charge density of nanomaterials may accelerate their susceptibility to fouling. Correlations also likely exist between fouling and aging. For example, fouling may change the local conditions (*e.g.*, pH, solution properties, and gas production) that lead to aging of nanoparticles. Structural damage and/or aggregation of nanoparticles will create deposition of inert materials as foulants (Fig. 6b). Our limited predictive capabilities have restricted the development of appropriate methods to prevent nanoparticle aging. Therefore, the first step for developing anti-fouling or anti-aging protocols starts by understanding fundamental mechanisms that govern these electrocatalyst deteriorating effects.

A potential path to limit nanomaterial fouling and aging on electrodes could emerge from new material discovery or optimization of electron fluxes.

Nanotechnology is often considered as a panacea for fouling control. Hydrophobic surfaces are well known to limit attachment of microorganisms, but this may only be a short-term benefit in “real” waters where deposition of soluble microbial products (SMPs) may quickly negate the hydrophobic properties. However, one study showed that on a hydrophobic surface could serve as an electrode wherein ROS electrogeneration and gas nanobubble evolution disrupted and removed *Pseudomonas aeruginosa* biofilms from the surface.[72] Electrode self-cleaning properties can exert a key role to control and prevent fouling.[72,73] Unfortunately, the high surface area and reactivity of nanoparticles or nanopores may be more susceptible to fouling than macroscale electrode counterparts. For example, the migration, shedding, and corrosion of nanoparticles can shorten electrode lifetime.[33] Cation aggregation can cause obvious accumulation of gypsum scaling on electrode surfaces.[74] The blockage of nano-size pore channels can rapidly decline catalytic ability. Ex-situ removal of divalent cations prior to electrocatalysis may be necessary to avoid inorganic scaling on electrodes.[75,76] Alternatively, it may be possible to avoid scale formation through in-situ cleaning, potentially involving electrophoretic mixing induced by polarity reversal on electrodes; it is largely unknown how rapid and frequent cycling may accelerate aging and deterioration of high surface area nano-enabled electrodes. Some electrodes postulate design of self-cleaning properties on electrodes can exert a key role to control and prevent fouling.[72,73] Finally, in some cases it may be necessary to intermittently clean electrodes with chemicals (e.g., acetic acid), but few peer reviewed studies examine the stability of nano-structured electrodes in such cleaning agents. But, it is unclear if operational strategies such as relaxation (periodic operation) and polarity reversal employed in conventional electrodes to alleviate fouling/aging would also work in nano-structured electrodes where charge distributions may be very different.

The lack of knowledge in electrode fouling and aging will greatly hinder full-scale adoption of electrochemical technology. Inability to prevent or troubleshoot electrochemical breakdowns will render these promising systems unreliable under market and final users' perception. Major advances could be made if standard aging methods were developed, validated in inter-laboratory studies, and then used to cross-reference between different materials and systematically study how different nano-decorated electrodes foul or age over time. Similar standard aging protocols have been invaluable in advancing fundamental insights and remedial actions for other water processes (*e.g.*, membranes) and electrochemical sensitive systems (*e.g.*, copper and lead pipe corrosion, fuel cells).

7. Nano-enabled reactor designs to overcome pollutant mass transport limitations

Do we understand when going really small makes mass transport of pollutants or reactive species rate-limiting over heterogeneous reactions themselves? Electrochemical water treatment processes (Figure 1) implicitly involve heterogeneous reactions on the electrode surface, wherein pollutant removal efficiency can be mass transport limited based on reactor design and electrode. Electrochemical reactors can be classified as (i) conventional flow-by, (ii) flow-through, or (iii) flow-electrodes (see Figure 7). Flow-by electrodes are widely commercialized in electrocatalytic (*e.g.*, chlorine production) and electroseparation (*e.g.*, CDI, electrodialysis) applications, whereas flow-through and flow-electrodes are currently mostly pre-commercial.

Unfortunately, most electrochemical publications focus on novel electrode materials rather than recognizing the significant influences of mass transport on observed pollutant degradation experimental findings. Consequently, many reported empirical rate constants may actually be mass transport limited rather than surface reaction rate limited. To advance from this practice, material science and engineering researchers should include figures of merit that describe mass transport conditions within the reactors (*e.g.*, Peclet, Reynolds, Schmidt, and Sherwood numbers) and at the boundary layer (*e.g.*, Hatta number, Taylor dispersion) in addition to reporting percentage removals and reactor residence times. Without this information, mass transfer limitations may be misinterpreted as heterogeneous surface reactions. The effect of nanostructures and nano-modified electrodes on reactor design and operation will require mechanistic mass transport models for electrochemical reactor designs.

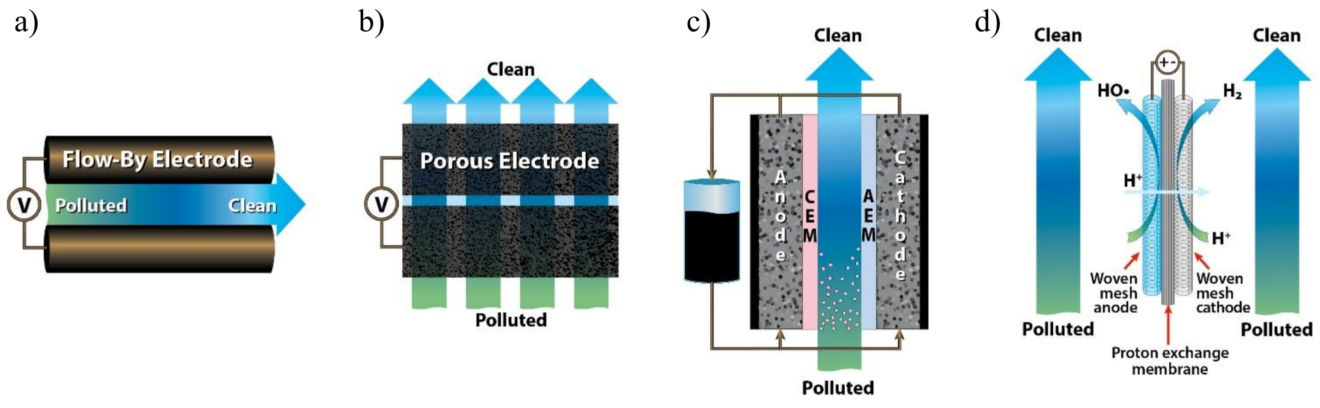

Figure 7. Scheme of different electrochemical reactors with different hydrodynamic operation conditions a) flow-by electrode, b) flow-through electrode, c) flow-electrode, and d) proton exchange membrane enabled cell.

Comparing reactor designs for electrochemical separation by non-Faradaic processes (*i.e.,* EDR and CDI) shows that nanostructured CDI electrodes in flow-through systems outperform flow-by systems for salt adsorption rates.[77] This implies the relevant factors were mass transport improvements, including Taylor dispersion, and lower current density. However, we should not discount potential innovations in flow-by electrode-based systems where nano-structured electrodes enable substantial improvements in pollutant destruction. For example, solute transport to monolithic coated electrodes is often controlled by surface film diffusion. Microporous electrodes increase surface area but can impart pore diffusion mass transfer limitations. Fluid mixing is often the principal reactor design tool available to reduce this type of mass transport limitation, and rethinking electrode configuration may have greater benefits. Traditional flat-plate designs separate the anode and cathode by a flow-channel, in which hydraulic conditions are controlled. A novel cell scheme designed by Crittenden et al. uses meshes coated with tin nanomaterials as DSA® electrodes packed around a proton exchange membrane.[78] This alternative flow-by electrode system inverted the conventional flow-by electrode configuration, thus enhancing mass transfer and reducing electropotential resistance within the system. These porous electrodes utilize novel materials in the highly permeable 3D electrode that consists of a blue TiO_2 wire mesh decorated with tin and antimony oxide nanoparticles. When working with electrodes that include elements regulated in drinking water (*e.g.*, antimony has a maximum contaminant level [MCL] of 0.006 mg L^{-1}), leaching risk must be carefully considered. Consequently, the novel flow-by 3D electrode systems achieve the energy per order of pollutant removal (E/EO; see below) that is 5-fold lower than conventional flow-by systems, even at the low solute concentrations found in realistic environmental water conditions that normally limit diffusion mass transport to electrode surfaces.

With the desire to increase electrode surface area for Faradaic processes, the advent of other 3D electrodes has also blossomed, although with new challenges and severe knowledge gaps. Figure 5 shows several 3D electrode examples. Porous Ti_4O_7 electrodes have shown the ability to obtain extremely fast reaction rates for many contaminants (*e.g.,* atrazine, PFAS, nitrate), which was facilitated by the high surface area and efficient mass transport in the micro-scale flow channels.[79,80] However, intra-electrode diffusivity becomes a rate limiting step for solute transport to the inner surface of nanoporous 3D electrodes. Hierarchical organization of macro- to meso- and micro-pores has been integrated into electrodes to facilitate mass transport while providing large surface areas. Many 3D electrodes are engineered using bottom-up nanotechnology design concepts where micro- to macro-pores are deliberately formed, and the surfaces are decorated with catalytic nanoparticles. Because bimetallic nanoparticles (*e.g.*, Pd-In, Pt-Cu) have shown outstanding electrocatalytic properties to reduce oxyanions such as nitrate,[56,81] they have been grown on microporous graphite fiber cloth electrodes. The porous 3D electrodes essentially eliminate intraparticle diffusion and expose high surface area nanoparticles (5–10 nm) on the surface of the cloth fibers.

Selecting the flow direction in 3D flow-through reactors emerges as a viable strategy to improve performance. Nano-enabled Magnéli-phase titanium suboxide decorated with bimetallic nanoparticles has excellent selective electrocatalytic reduction of nitrate to nitrogen gas.[82,83] Using anode-to-cathode flow (instead of cathode-to-anode flow) controls undesirable side reactions (*e.g.*, reduction towards

NH_4^+, H_2 evolution) and consequently has higher yield and selectivity towards desired innocuous N_2. This configuration also reduces risk of re-oxidation of already reduced products (*e.g.*, NO_2^-, NO).

Despite the rise of interest in 3D and flow-through reactors, there is a severe lack of understanding of not only pore diffusion of pollutants but also current distribution profiles inside the 3D electrodes. Little research has been conducted with modeling studies of electric current profiles and the impact of electrical resistance on the potential distribution of electrodes.[84–86] Uneven current distribution may result in different kinetic reaction zones as well as different electric potential distribution. Different regions achieve different efficiencies, and electrocatalytic "dead zones" likely exist and essentially become a waste of high-cost materials (*e.g.*, Pd) and reduced energy efficiency. In this frame, the different electric potential may result in electrode areas at the nano-scale that behave as active electrode (dominated by charge transfer processes) and areas that behave as non-active electrode (production of radicals). Furthermore, uncontrolled electro-potential regions could initiate undesired organic polymerization reactions on the electrode surface areas behaving as active electrode that may rapidly form passivating layers or even blockage of inter-diffusion channels.

8. Costs and learning curves for electrocatalytic treatment

Why do researchers need to know something about economic feasibility for nanotechnology-based innovations to succeed in the marketplace? Nanotechnology has the potential to enhance the performance and competitiveness of electrochemical technologies through the aspects discussed in this perspective. However, figures of merit are required in order to benchmark and evaluate costs. Failure to utilize figures of merit hampers direct comparisons of materials and reactor designs.

Amongst the most common figures of merit is the International Union of Pure and Applied Chemistry (IUPAC) defined electrical energy per order (E/EO), which enables comparing AOPs using the energy requirements to reduce target pollutant concentration by one order of magnitude. E/EO (kWh

m^{-3}) is a commonly used figure of merit to compare operational efficiency of water treatment processes, and to provide equivalent comparisons against electrocatalysis it is necessary to account for embedded energy costs associated with chemicals (e.g., H_2O_2, persulfate) associated with conventional AOPs. E/EO implicitly accounts for pollutant removal efficiency (e.g., percentage removal) and electrochemical efficiency (e.g., Faradaic efficiency), and is usually more scalable over large ranges in pollutant concentrations for electocatalysis compared against conventional AOPs.[78] Many EAOPs have pseudo-first order reaction rates; consequently, if you supply 1, 2, and 3 times the E/EO then you will get 90%, 99%, and 99.9% reduction of the parent compound for plug flow and completely mixed reactors. This figure of merit can be translated to evaluate electrochemically-driven water treatment technologies for batch and continuous-flow operation according to equations (1) and (2), respectively.[87,88]

$$\text{E/EO (kWh m}^{-3}\text{ order}^{-1}) = \frac{E_{cell} I t}{V_s \log{(c_i/c_f)}} \tag{1}$$

$$\text{E/EO (kWh m}^{-3}\text{ order}^{-1}) = \frac{E_{cell} I}{Q_v \log{(c_i/c_f)}} \tag{2}$$

where the E_{cell} is the cell potential (V), I is the current (A), t is the batch treatment time (h), V_s is the batch volume of the solution (L), Q_v is the continuous-flow volumetric flow rate (L h^{-1}), c_i is the initial or influent pollutant concentration (mol L^{-1}), and c_f is the final or effluent pollutant concentration (mol L^{-1}). Note that E/EO equations implicitly assume first-order kinetics according to the relationship $\log(c_i/c_f) = 0.4343 k_1 t$.

Competitive systems should minimize E/EO, if possible, to 5.0 kWh m^{-3} order^{-1} for drinking water and 25 kWh m^{-3} order^{-1} for industrial wastewaters.[78,89] Higher values are acceptable provided the associated cost is justified by the need to treat certain pollutants (*e.g.*, PFAS) or the lack of alternative technologies. Note that with the increased use of renewable energies and the diminishing cost of electrical energy, treatments with higher E/EO would become more competitive due to the positive attributes of electrochemically-driven processes.

Crittenden and co-workers used E/EO to compare several AOPs as a function of initial pollutant concentrations.[21,78] Common chemical-based AOPs (*e.g.*, UV/H_2O_2) exhibit 10x to >1000x higher E/EO as initial pollutant concentrations increase from 20 to 2000 mg/L. In contrast, while their EAOP 2D electrode reactor was marginally competitive on an E/EO basis at low pollutant concentrations, the EAOP depended less on initial pollutant concentrations than chemical-based AOPs and had roughly an order of magnitude lower E/EO at the highest pollutant concentration. Furthermore, whereas the 2D electrode system showed a strong dependence upon initial pollutant concentration, their 3D reactor was nearly independent of this parameter. The 3D system consisted of a composite wire mesh anode (composed of blue TiO_2 nanotubes covered with SnO_2− Sb_2O_3), a proton exchange membrane, and a stainless-steel wire mesh cathode, which were compressed firmly together. By interpreting performance using an E/EO figure of merit rather than typical parameters such as fractional removal, we gained significant insight in both chemical transformation mechanisms and electron flow, consequently increasing our understanding of advancing a promising EAOP reactor design.

Estimating electrical costs is a first step in the evaluation of technology translation capabilities. However, these evaluations only shed light on *operational expenditures (OPEX)* . Most publications on electrocatalysis focus on material synthesis and performance, but rarely discuss capital expenditures (*CAPEX*) of the electrodes or device required to enable the technology. There is a clear need to integrate TEA across different electrodes and reactors to understand where innovation can lower overall *OPEX* and *CAPEX*. TEA links manufacturing cost estimation techniques with device performance to evaluate total costs of ownership, which informs a holistic understanding of technology costs. A recent preliminary TEA of an EAOP as point-of-use technology to treat atrazine in groundwaters evaluated market competitiveness using amortized *CAPEX* and *OPEX* impacts on the device's total cost of ownership[90] which lead to key important conclusions. First, the cost-competitiveness is highly sensitive to process efficiency and selectivity.[90] Higher kinetic constants would ensure lower costs and more efficient system performance. This challenge can be overcome by nanotechnology (*e.g.*, trap-n-zap approach). Reducing E/EO using nanostructured and nano-enabled electrodes would lower operational costs. For example, Chaplin and co-workers showed E/EO of 5.1–6.7 kWh m^{-3} $order^{-1}$ to degrade recalcitrant PFAS to below the detection limits. These values are the lowest reported for electrochemical oxidation and approximately an order of magnitude lower than those reported for other technologies (*i.e.*, ultrasonication, photocatalysis, vacuum ultraviolet photolysis, and microwave-hydrothermal decomposition), demonstrating the promise of electrochemical technology for water treatment applications. Second, one of the main cost drivers identified is the electrode material cost.[90] A 10-fold reduction in BDD electrodes has a substantial impact on the final cost of ownership of the device. This challenge can be overcome with nano-sized and nanostructured electrodes, thus reducing capital costs. TEA is a tool to quantify whether potential benefits of nanocatalysts (*e.g.*, increased selectivity, increased kinetics), which may result in smaller devices and more efficient electrical energy use, outweigh the increased capital cost when using nanocatalysts.

Technology translation from early phase discovery (Technology Readiness Levels [TRLs] 1–5), through early adoption (TRL 5–8), to wide-spread usage (TRL9) is affected by cost learning curves,[91] which usually follow power-function declines in costs as the number of units produced increase. The per-unit cost reductions are attributed to knowledge and learning during scale-up towards mass production and other economies-of-scale. This trend is due to labor increasing their skills and familiarity with the production process, which leads to production efficiency improvements. This would impact nano-enabled electrode manufacturing costs as well as reactor assembly and operation costs. Despite publications on cost learning curves being applied to seawater desalination, wind power, solar photovoltaics, and hydrogen generation, there are no apparent analogous publications related to nanotechnology. The progress ratio ($pr = 2^{-\alpha}$*; where* α is the learning index) is related to the more commonly used learning rate ($lr = 1 - pr$), and both are usually expressed in percentages. Learning rates of 15% and 18%,[92] which are at the lower range of commonly reported *lr* values, were reported for seawater desalination and water electrolysis equipment associated with hydrogen generation, respectively. It is likely that similar ranges will be observed for decentralized electrochemical treatment technologies. Consequently, learning curves should be considered when comparing EAOPs against well-established water treatment technologies, rather than directly comparing E/EO values today for electro-oxidation processes versus commercial technologies (*e.g.*, UV/H_2O_2). However, researchers should realize that focusing only on electrode material will not accelerate learning curves, and there is a need for multiple forms of engineering design, manufacturing, and process optimization (*e.g.*, overcoming aging or fouling, enabling energy recovery from electroseparation systems, etc.).

9. Conclusions and research priorities

Figure 2 summarizes the relative state of knowledge and importance for the topics discussed in this perspective by identifying urgent research needs. Focusing on the treatment of unrealistic synthetic waters alone can be misleading and lead to false technology evaluations that harm the entire field of electrochemical water technologies. Research must identify feasible water matrices to avoid hype associated to reiterative works that do not provide answers to TRL translational challenges. Among the most urgent priorities limiting adoption of nano-enabled electrochemical systems is the lack of quantitative knowledge and tools for understanding and designing appropriate nanostructured architectures within macroscale electrodes, and the extent to which such electrodes are more or less prone to fouling and aging under real world operational conditions. More widespread application and reporting of operational figures of merit will likewise aid in direct comparisons among different materials and electrode configurations. Figure of merit concepts can then enable meaningful comparisons among emerging electrode designs (*e.g.*, trap-n-zap). Longer-term, quantitative DFT and other material discovery strategies will be valuable in finding low-cost and earth-abundant electrode materials and nano-scale geometries that can modulate the selectivity to produce targeted ROS capable of driving reactions of pollutants towards desirable end-products.

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