

## Catalytic Converters for Water Treatment

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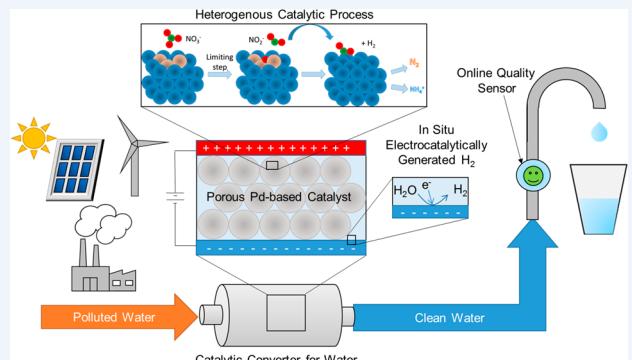
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### Supporting Information

**CONSPECTUS:** Fresh water demand is driven by human consumption, agricultural irrigation, and industrial usage and continues to increase along with the global population. Improved methods to inexpensively and sustainably clean water unfit for human consumption are desired, particularly at remote or rural locations. Heterogeneous catalysts offer the opportunity to directly convert toxic molecules in water to nontoxic products. Heterogeneous catalytic reaction processes may bring to mind large-scale industrial production of chemicals, but they can also be used at the small scale, like catalytic converters used in cars to break down gaseous pollutants from fuel combustion. Catalytic processes may be a competitive alternative to conventional water treatment technologies. They have much faster kinetics and are less operationally sensitive than current bioremediation-based methods. Unlike other conventional water treatment technologies (i.e., ion exchange, reverse osmosis, activated carbon filtration), they do not transfer contaminants into separate, more concentrated waste streams.

In this Account, we review our efforts on the development of heterogeneous catalysts as advanced reduction technologies to treat toxic water contaminants such as chlorinated organics and nitrates. Fundamental understanding of the underlying chemistry of catalytic materials can inform the design of superior catalytic materials. We discuss the impact of the catalytic structure (i.e., the arrangement of metal atoms on the catalyst surface) on the catalyst activity and selectivity for these aqueous reactions. To explore these aspects, we used model metal-on-metal nanoparticle catalysts along with state-of-the-art *in situ* spectroscopic techniques and density functional theory calculations to deduce the catalyst surface structure and how it affects the reaction pathways and hence the activity and selectivity. We also discuss recent developments in photocatalysis and electrocatalysis for the treatment of nitrates, touching on fundamentals and surface reaction mechanisms.

Finally, we note that despite over 20 years of growing research into heterogeneous catalytic systems for water contaminants, only a few pilot-scale studies have been conducted, with no large-scale implementation to date. We conceive of modular, on- or off-grid catalytic units that treat drinking water at the household tap, at a community well, or for larger-scale reuse of agricultural runoff. We discuss how these may be enhanced by combination with photocatalytic or electrocatalytic processes and how these reductive catalytic modules (catalytic converters for water) can be coupled with other modules for the removal of potential water contaminants.



### 1. INTRODUCTION

While water covers 70% of the surface of the globe, only 3% of the water on Earth is fresh enough to drink.<sup>1</sup> With growing worldwide populations, supplies of fresh water will be stressed at unprecedented levels; by 2025 half of the world's population will struggle for fresh water.<sup>2</sup> In addition to the quantity of water, water *quality* impacts its beneficial uses. Most pristine water supplies are already utilized, which is necessitating the use of increasingly impaired water qualities. This requires

efficient and low-cost treatment technologies to increase the available quantity of water.

Conventional potable water treatment technologies were largely designed to reduce the risks of water-borne diseases by removing or chemically inactivating viruses, bacteria, and protozoa. Over time, these Victorian-age treatment technolo-

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gies were modified to remove naturally occurring elements (e.g., arsenic) or anthropogenic carcinogens (e.g., BTEX petroleum products) using adsorption, air stripping, or other separation techniques. Numerous advanced oxidation techniques (AOTs) have been developed that use hydroxyl radicals ( $\cdot\text{OH}$ ) to transform nonadsorbable polar organic pollutants into less toxic or more biodegradable byproducts. However, very few electron-reduction techniques are commercially used in drinking water treatment despite growing impairment of water supplies by the presence of oxyanions (e.g., nitrate, perchlorate, hexavalent chromium) and organic pollutants (e.g., trichloroethene, perfluorinated compounds, methyl *tert*-butyl ether, *N*-nitrosodimethylamine). This Account describes our experiences with advanced reduction technologies (ARTs) that use catalysis to treat pollutants in drinking water supplies.

Our strategy is to transform toxic compounds into nontoxic products using catalytic chemistry. This contrasts with methods based on physical separation, which generate waste streams that must undergo further treatment. However, catalysis is associated with the chemical industry but not generally with the water industry. It may be more suitable than bioremediation (i.e., where bacteria are engineered to metabolically convert contaminants to inert compounds), which is operationally sensitive and has significantly lower degradation rates. Catalysis may be superior to traditional AOTs, as it is more selective, consumes less reagents, and avoids the generation of disinfection byproducts. Challenges for heterogeneous catalysis in drinking water revolve around (1) the need to add/recover catalysts that pose minimal health risks, (2) the presence of low (ppb or ppm) pollutant levels, (3) the presence of mixtures of pollutants and otherwise benign salts, organic acids (e.g., natural organic matter<sup>3</sup>), or neutral species (e.g.,  $\text{SiO}_2$ ). In this Account, we first review two contaminant classes we that have targeted for drinking water treatment: chlorinated volatile organic compounds (CVOCs) and nitrate/nitrite anions, which represent organic and inorganic contaminants, respectively. We then briefly introduce heterogeneous catalysis and motivate our use of model nanoparticle (NP) catalysts to discern the structure–activity relationships at the molecular level. We describe our development and use of new techniques to better understand these relationships and share insights that we have discovered for specific reaction systems. Finally, we offer a perspective on a futuristic modular catalytic converter for drinking water.

### 1.1. Chlorinated Volatile Organic Compound Contamination

CVOCs are a class of low-molecular-weight organic chemicals such as perchloroethylene (PCE), trichloroethylene (TCE), trichloroethane (TCA), vinyl chloride (VC), and chloroform (CF) that were widely used as degreasing agents in the military, automotive, and electronic industries.<sup>4,5</sup> They currently have limited use in dry cleaning, chemicals production, and consumer products. Human health effects include liver, lung, and nervous system damage.<sup>5,6</sup> The U.S. Environmental Protection Agency has set a maximum contaminant level (MCL) for TCE at 5 ppb, for example. Mounting evidence has also linked TCE exposure to Parkinson's disease, other autoimmune diseases, and cancer. Though usage has declined, their former widespread use and relative stability in the environment make CVOCs some of the most hazardous organic contaminants. As of 2017, VC, CF, TCE, PCE, and TCA stand at the fourth, 11th, 16th, 33rd, and

117th spots, respectively, on the ASTDR Substance Priority List.<sup>7</sup> Moreover, TCE, PCE, DCE, and TCA naturally degrade to more toxic VC.<sup>8</sup> Treatment technologies to dehalogenate chlorinated, brominated,<sup>9,10</sup> and fluorinated<sup>11</sup> polar organic chemicals is a historic and growing water treatment challenge.

### 1.2. Nitrate and Nitrite Contamination

Pollution with nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ) predominantly arises from the overuse of ammonia-based fertilizers for food production.<sup>12</sup> Because of their agricultural use and the water-soluble nature of nitrate, the worst nitrate pollution is in rural areas, where drinking water systems are small-scale or individual groundwater wells. Nitrate runoff in surface waters contributes to eutrophication and the growth of large algal blooms, which harm water quality, contribute to cyanobacteria growth, impact recreational activities, and create hypoxic dead zones.<sup>13</sup> The economic damage from eutrophication alone is estimated to be \$2.2 billion in the U.S. annually.<sup>14</sup> Though they appear much lower (216 and 223) on the ASTDR list,<sup>7</sup> the World Health Organization recently declared “processed meats” as class 1 carcinogens,<sup>15</sup> partly because of the addition of nitrites/nitrates during curing. Once ingested, nitrate can metabolically be converted to nitrite, which can form suspected carcinogenic *N*-nitroso compounds. Nitrite consumption during pregnancy can cause infant methemoglobinemia, a potentially fatal blood disorder. With an MCL of 10 ppm, nitrate is among the top 10 reported water quality violations in the USA.<sup>17,18</sup>

## 2. HETEROGENEOUS CATALYSIS: AN ADVANCED REDUCTION TECHNOLOGY

As materials that accelerate chemical reactions without being consumed, catalysts can be either homogeneous (e.g., dissolved in the reaction medium) or heterogeneous (e.g., solid pellets). They are often composed of precious metals, and the heterogeneous form is preferred because they can be readily recovered for reuse. Broadly speaking, catalytic processes function by lowering the activation energy barrier of a reaction, which initiates when reactant species bind to the catalyst active site to form surface-bound transition state species. Energy barriers are lowered by (a) facilitating the encounter of reactant species, (b) donating/withdrawing electrons to create more reactive transition state species, (c) or having chemically dissimilar active sites that drive different reaction steps. These notions describe the geometric effect (i.e., the arrangement of surface catalytic atoms),<sup>19</sup> the electronic effect (e.g., d-level electronic interactions between different metals),<sup>20</sup> and the bifunctional effect, respectively. Catalytic structure is key to accelerating and controlling the selectivity of chemical reactions.

The CVOC and nitrate/nitrite drinking water pollutant classes are amenable to catalytic treatment through reduction chemistry. Figure 1 illustrates three heterogeneous catalytic processes, each of which requires an electron source: chemical ( $\text{H}_2$ ), photons ( $\text{h}\nu$ ), or an electrical current ( $e^-$ ). Common barriers exist among these ARTs: (1) mass transport limitation of molecules toward and byproducts away from the catalyst surface, (2) low activity and selectivity of the catalyst, and (3) inefficient delivery of electrons into pollutant molecules. Consequently, common water quality constituents will influence the efficiency of the ART in converting pollutants to benign byproducts (e.g., chloride salt and dehalogenated organics from CVOCs, dinitrogen gas from nitrate/nitrite).

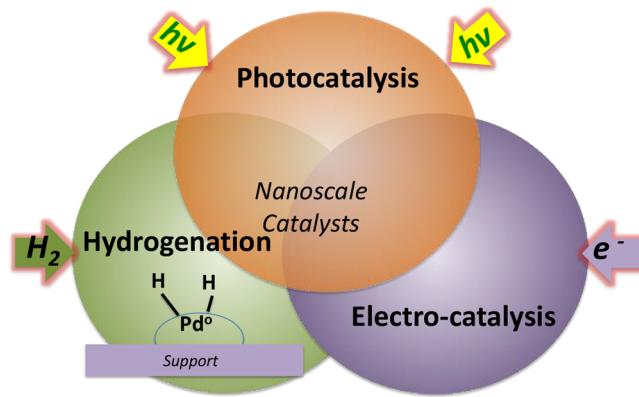


Figure 1. ART approaches for catalytic water treatment.

### 3. HETEROGENEOUS HYDROGENATION CATALYSIS

Understanding and controlling the structure of a material at the atomic level is a challenge in materials science. Traditional metallic catalysts are typically prepared by adding a metal precursor (e.g., Pd salt) to a support material (e.g., SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, C) and then reducing it. Upon reduction, the metal forms nanoparticles within the support, where the NP surface presents the catalytic active sites. While different techniques (e.g., variation of the reductant temperature, use of templating agents) can be used to control the size and shape of the formed nanoparticles, catalysts prepared in this way typically have a wide range of particle morphologies and sizes, which ostensibly have a range of catalytic activities.

On the basis of early reports that Pd catalysts degrade chlorinated solvents, we sought fundamental understanding of TCE hydrodechlorination (HDC).<sup>21–23</sup> Over a Pd-based catalyst, aqueous TCE (and other CVOCs) react with aqueous H<sub>2</sub> to form inert ethane and HCl. Instead of traditional supported Pd catalysts, we tested the reaction on Pd atoms

supported on Au NPs, or “Pd-on-Au NPs”.<sup>24,25</sup> These catalysts consist of a submonolayer amount of Pd metal layered over a Au NP core, the amount of which we call the calculated Pd percent surface coverage (sc%). They are not strictly core-shell NPs because the core is incompletely covered. To characterize the structure of the Pd-on-Au NPs, we used X-ray absorption spectroscopy (XAS),<sup>26,27</sup> which can determine the numbers of same-atom neighbors and heteroatom neighbors and metal oxidation states. These parameters are used to deduce the atomic structures of catalytic sites. At low sc%, the Pd atoms form monomers (isolated atoms diluted within the surface Au layer), and as the loading increases, two-dimensional (2D) Pd islands (or ensembles) are formed in which all of the Pd atoms are in direct contact with the Au (Figure 2a). As the Pd sc% is further increased, 3D islands (in which not all Pd atoms contact the Au) are formed, and at even higher loadings, Pd migrates to the subsurface of the NP. These results were corroborated with high-angle annular dark-field transmission electron microscopy (HAADF-TEM).<sup>28</sup> Figure 2b shows a HAADF-TEM image of one Pd-on-Au NP, where the orange circles indicate Pd monomers and green circles indicate 2D/3D Pd islands.

By normalizing by the amount of catalytically active metal (i.e., the Pd on the surface), we observed that the activity peaks at ~60 sc% Pd for many reactions, implicating the 2D/3D Pd islands as the most active species, whose extraordinary activity was likely due to geometric and electronic effects. For example, PCE hydrodechlorination over a Pd catalyst was 20 times less active on a per-Pd basis (Figure 2c). Testing the reaction over larger particles showed a particle size effect: increasing the size of the Au NP core from 4 to 7 nm led to a decrease in the rate for NPs with identical Pd sc% due to less subsurface Pd migration into the smaller NPs.<sup>28</sup> Pd-on-Au NPs were shown to be effective for a number of different CVOCs, including PCE,<sup>29</sup> CF,<sup>30,31</sup> and DCE.<sup>29</sup>

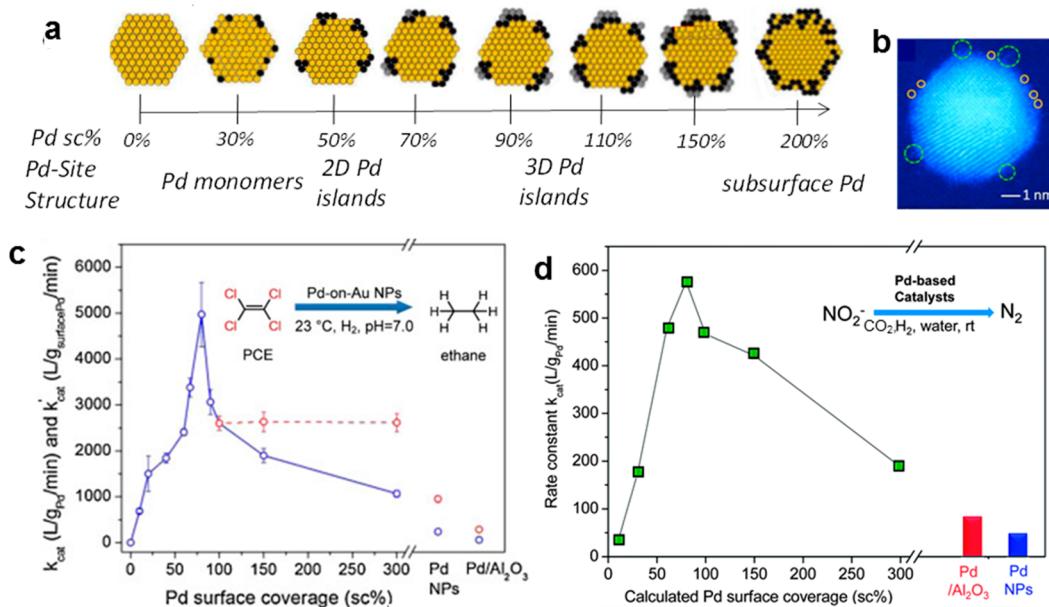
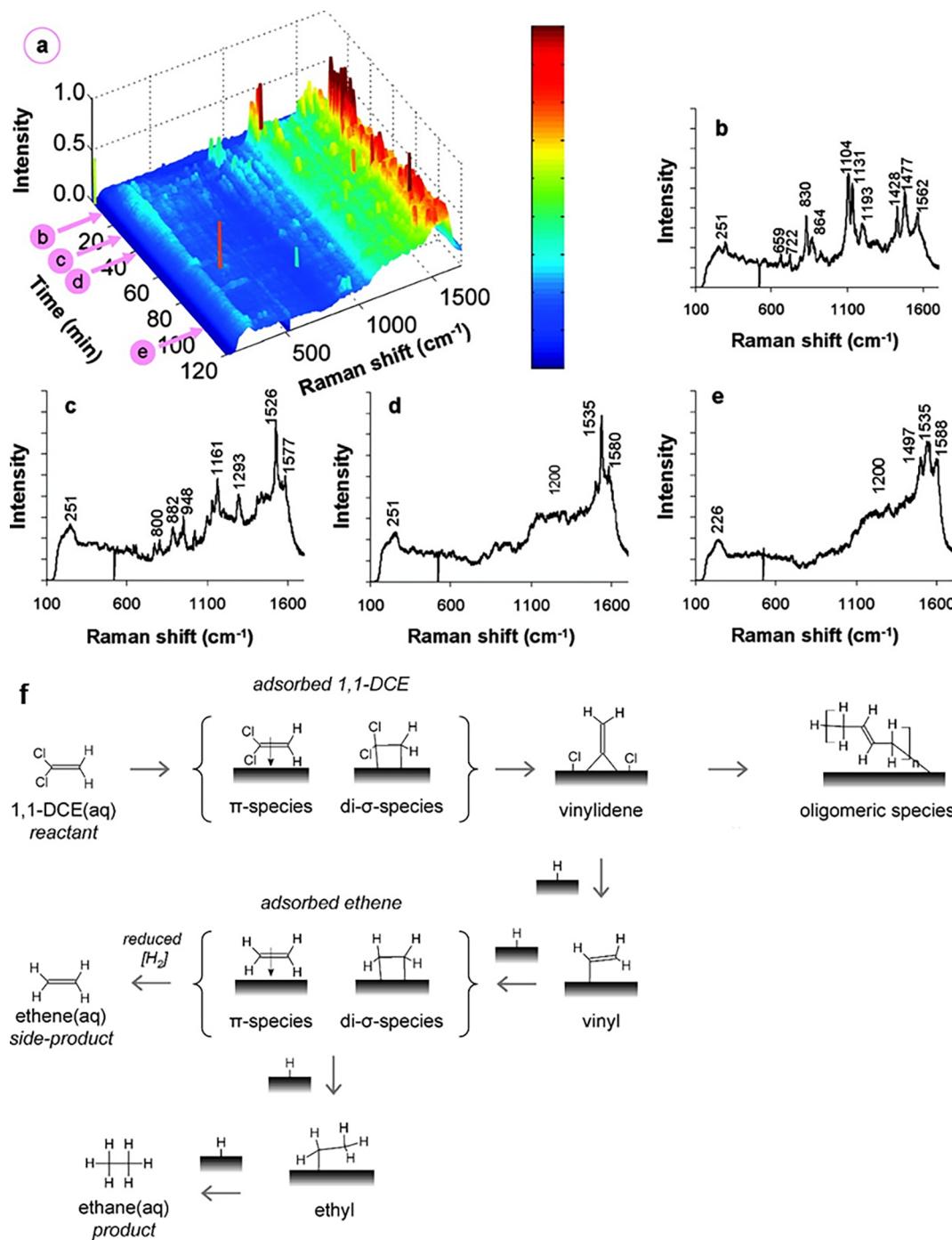


Figure 2. (a) Cartoon schematic of the change in Pd-on-Au surface sites with increasing Pd content. (b) HAADF-TEM image of a Pd-on-Au NP. Orange circles indicate Pd monomers, and green circles indicate Pd clusters. (c, d) Activity of 4 nm Pd-on-Au NPs for (c) PCE HDC and (d) nitrite reduction. Reproduced with permission from (b, c) ref 28 and (d) ref 38. Copyright 2013 Elsevier and 2014 Royal Society of Chemistry, respectively.



**Figure 3.** (a) Time-resolved SER spectra for the reaction of 1,1-DCE and (b–e) representative spectra after (b) 10, (c) 30, (d) 40, and (3) 100 min. (f) Proposed surface-reaction mechanism. Reproduced from ref 37. Copyright 2008 American Chemical Society.

Catalysis fundamentals can also be learned from the surface-bound transition species. Exploiting the plasmonic properties of nanoscale Au, we designed Pd-on-Au nanoshells (NSs) to determine the identity of the surface species involved in the HDC reaction (Figure 3). NSs consist of a submicron silica core covered with a few nanometers of gold,<sup>32,33</sup> and they can enhance the Raman signal of adsorbates by up to  $10^9$  (i.e., surface-enhanced Raman spectroscopy, SERS).<sup>34–36</sup> Exposing Pd-on-Au NSs to 1,1-dichloroethylene with a stoichiometric amount of  $\text{H}_2$  resulted in rapid dechlorination, as evidenced by growing metal–Cl peaks ( $\sim 250 \text{ cm}^{-1}$ ; Figure 3a–e) and the disappearance of C–Cl modes ( $\sim 800 \text{ cm}^{-1}$ ; Figure 3b,c),

followed by a slower hydrogenation and/or oligomerization step ( $\sim 1500 \text{ cm}^{-1}$ , typical of unsaturated oligomeric species; Figure 3c–e), in agreement with bulk concentration measurements.<sup>37</sup> These *in situ* spectroscopic measurements allowed us to propose a likely surface reaction mechanism (Figure 3f). The HDC reaction appears to be rather general over Pd-on-Au catalysts, as similar results were obtained using CF.<sup>30</sup>

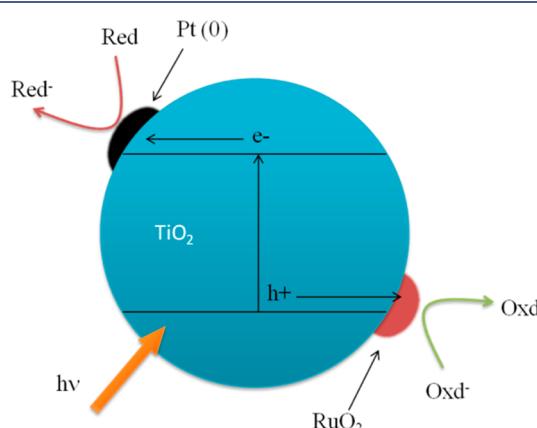
We tested Pd-on-Au NPs for the reduction of nitrite,<sup>38</sup> as Pd metal has previously been shown to be active for this reaction. This reaction also followed a volcano-shaped dependence on the Pd coverage, in which Pd ensembles were responsible for maximum denitrification activity (Figure 2d). Moreover,

regardless of composition, all of the catalysts exhibited >95% selectivity for dinitrogen. This catalyst was ineffective for reduction of nitrate, a more recalcitrant pollutant, as both monometallic Pd and Au cannot activate the  $\text{NO}_3^-$  to  $\text{NO}_2^-$  reduction step.<sup>39</sup>

Previous studies have reported nitrate degradation over supported mixed-metal catalysts containing Pd and a secondary metal (e.g., Sn, In, or Cu).<sup>40–44</sup> We developed a catalyst analogous to our Pd-on-Au NPs, except this time a Pd NP was decorated with surface indium atoms to form In-on-Pd NPs.<sup>45</sup> Using this catalyst, we determined an optimum In content for the In-on-Pd NPs of 40 sc%. To improve on the XAS data, we studied the *in situ* behavior of the In-on-Pd NP catalysts, i.e., in water, with dissolved  $\text{H}_2$ , and with nitrate, and examined the Pd and In edges following exposure. Exposure to  $\text{H}_2$ -saturated water partially reduced the In, which was surprising since In alone cannot be reduced with  $\text{H}_2$  at room temperature. Exposure to nitrate-containing water reoxidized the In. Re-exposure to the  $\text{H}_2$ -saturated water confirmed that the reduction was reversible. A bifunctional surface mechanism was proposed in which In undergoes a redox cycle where nitrate first oxidizes In to form nitrite. The role of Pd is twofold: to generate H adatoms for In rereduction and to convert the nitrite to dinitrogen. Density functional theory modeling suggested that the 40 sc% optimum loading of In on Pd was due to the large barrier to H adatom diffusion within In clusters, with only interface In-on-Pd sites active for the reaction.

#### 4. PHOTOCATALYTIC NITRATE REDUCTION

Photocatalysts are attractive because they use UV light to generate the electrons required for reduction, which avoids storage and transport issues of hazardous chemicals required for traditional catalysis. Oxidation and reduction reactions occur simultaneously on a photocatalytic surface (Figure 4).



**Figure 4.** Photocatalyst ( $\text{TiO}_2$ ) loaded with Pt (cathode) and  $\text{RuO}_2$  (anode).

Upon absorption of a photon with an energy  $E = h\nu$  greater than or equal to the band-gap energy ( $E_{\text{BG}}$ ) of the semiconductor (e.g.,  $\text{TiO}_2$ ), an electron is excited from the valence band into the conduction band, generating a positively charged hole in the valence band ( $\text{h}_{\text{vb}}^+$ ). Photocatalytic nitrate reduction was first documented in the 1930s in India,<sup>46–48</sup> but its material science fundamentals were not explored until 1987,<sup>49</sup> when Pt-loaded  $\text{TiO}_2$  irradiated with UV light showed better nitrate reduction than Pd- or Ru-loaded  $\text{TiO}_2$  ( $\text{TiO}_2$

alone resulted in little nitrate removal and formed nitrite byproduct). No nitrate removal was observed without a hole scavenger (methanol); minimal nitrate reduction occurs when the recombination rate within the catalyst exceeds that of electron transfer to the adsorbate (i.e., nitrate) (Figure 5).<sup>50,51</sup> Undesirable ammonium byproduct formation was attributed to the low hydrogen ( $\text{H}_2$ ) overpotential of Pt. Since then, many types of semiconducting materials and composites have been tested for photocatalytic nitrate reduction. To date, silver-loaded  $\text{TiO}_2$  is the most promising photocatalyst with the use of an organic hole scavenger,<sup>52,53</sup> though metal-loaded tantalates may be able to achieve nitrate reduction without using water as a hole scavenger.<sup>54</sup>

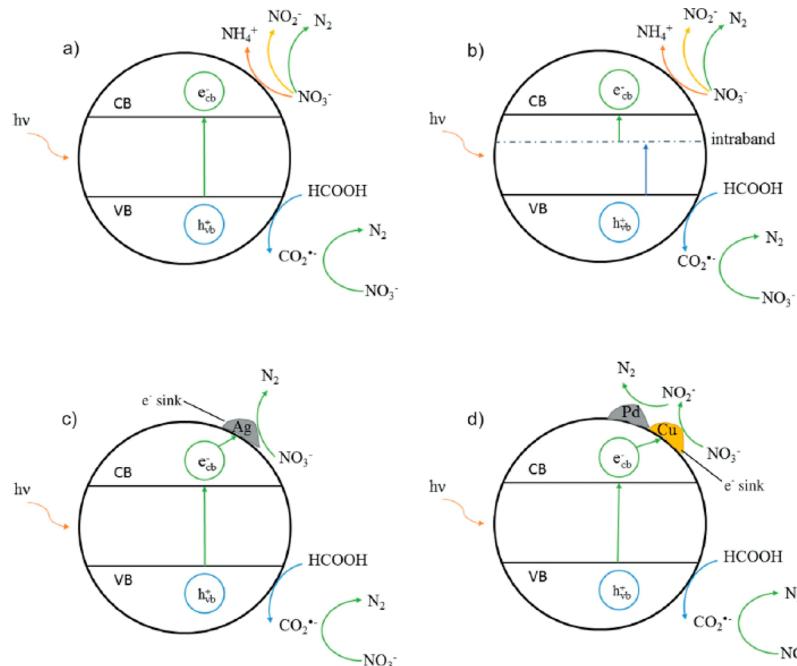
Photocatalytic nitrate conversion to byproducts involves multiple steps (Figure 6).<sup>55</sup> The rate-limiting step is the initial first electron loss from  $\text{NO}_3^-$ , which can be enhanced by using bimetallic composite photocatalysts. While direct photolytic processes can initiate conversion of  $\text{NO}_3^-$  to reactive byproducts (e.g.,  $\text{NO}_2^*$ ,  $\text{HNO}_2/\text{NO}_2^-$ ) to  $\text{NO}^*$ , these reactions depend upon the available wavelengths of light, the absorption spectrum of the photocatalyst, and the quantum yield of the reaction.<sup>56</sup> Consequently, polychromatic light sources can improve rates and selectivity toward desirable byproducts. We have observed the best nitrate removal rates and selectivity using silver– $\text{TiO}_2$  composite photocatalysts with formic acid as an external electron donor and polychromatic light sources at low pH ( $\text{pH} < 3$ ), where  $\text{HNO}_2$  predominantly exists. Such low-pH conditions are not feasible in drinking water directly; one approach for incorporating photocatalysis into drinking water treatment would be to treat ion-exchange brines,<sup>57</sup> which can be pH-adjusted, thereby improving the cost effectiveness of nitrate treatment.<sup>58</sup>

#### 5. ELECTROCATALYTIC NITRATE REDUCTION

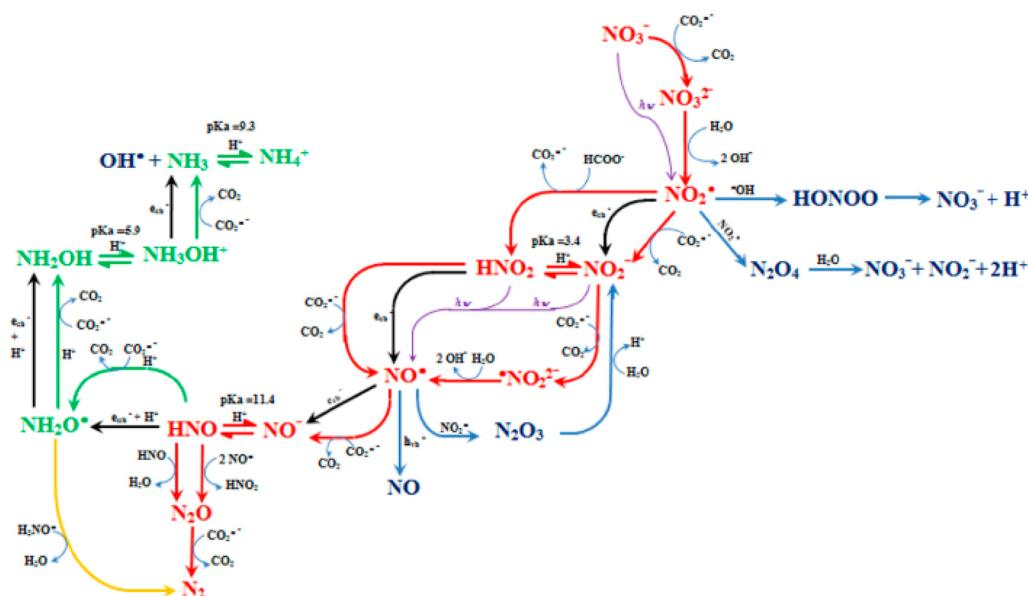
Electrocatalysts are an intriguing alternative as well, as they also do not require outside chemicals but directly reduce contaminants and/or generate reactive oxidant or reductant chemicals *in situ* using electricity. Electrochemical processes catalyze charge transfer reactions at the electrode–solution interface under the application of electrical current to reduce nitrate at the cathode surface.<sup>58</sup> Similar to catalytic hydrogenation, the kinetics and selectivity are related to the electrocatalytic material and its structure.<sup>58,59</sup> The electrode potential defines thermodynamically which charge transfer reactions occur. Elementary charge transfer reactions involve solely one electron per step. Nitrate conversion involves several adsorbed short-lived intermediates (Figure 7).

High activation energy is required to initiate nitrate electrocatalytic reduction, which results in sluggish kinetics.<sup>58,60</sup> Similar to heterogeneous hydrogenation and photoreduction processes, nitrate to nitrite reduction is the rate-limiting step (Figure 7). The slow kinetics is attributed to the high energy of the lowest unoccupied molecular orbital of nitrate, a  $\pi^*$  orbital, which makes the charge injection required for reduction difficult. The highest catalytic activities have been reported for metals with highly occupied d subshells (Cu, Pt, Pd, etc.) because of the similarity between energies of the d orbitals and the nitrate  $\pi^*$  orbital (Figure 8).<sup>58,61</sup> Electrocatalytic materials are quite similar to heterogeneous catalysts used in hydrogenation such as Cu–Pt, Cu–Pd, and Sn–Pt.

Promising electrocatalytic/hydrogen synergies have been barely explored. Electrocatalytic materials based on Pt/Pd



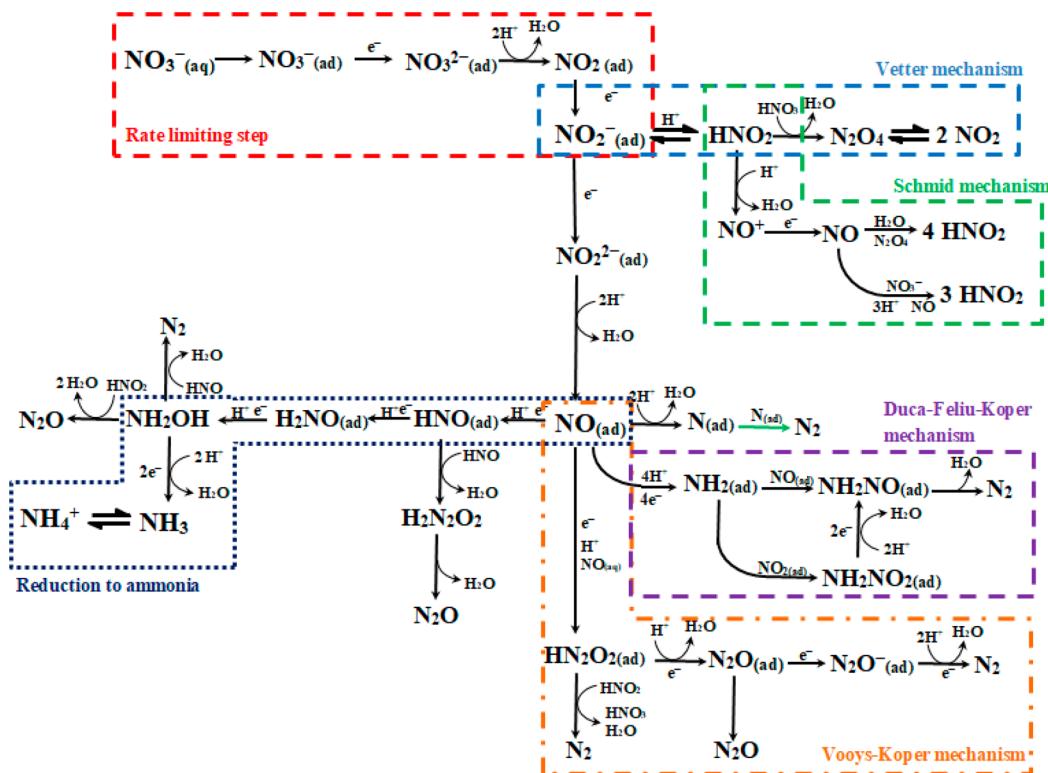
**Figure 5.** (a) Use of organic hole scavengers increases nitrate reduction. (b) Doping of metals into the photocatalyst lattice introduces intraband levels and requires less irradiation energy to form charge carriers. (c, d) Composite photocatalysts modify the charged region near the surface, and the lower work function of the metal compared with the electron affinity of common photocatalysts (e.g., TiO<sub>2</sub>) allows the metal to behave as an electron sink, forming a Schottky barrier potential that enables nitrate conversion.



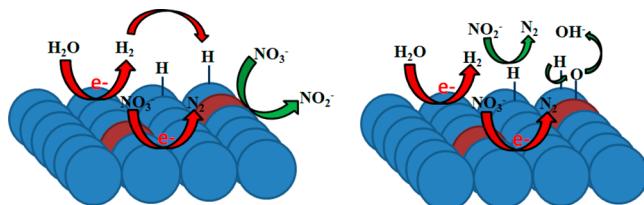
**Figure 6.** Photocatalytic nitrate conversion. Pathways selective for N<sub>2</sub> are highlighted in red, and pathways yielding NH<sub>4</sub><sup>+</sup> are shown in green; other colors show minor reactions leading to other products. Reproduced with permission from ref 55. Copyright 2017 Elsevier.

reduce nitrate at cathodic potentials overlapped with hydrogen evolution from water reduction.<sup>61</sup> As in hydrogenation catalysis, dissociative adsorption of hydrogen yields highly reductive H adatoms (H<sub>(ad)</sub>). Thus, the reduction mechanism involves both direct charge transfer via electrocatalysis with catalytic reduction by H<sub>(ad)</sub> ( $E^\circ(H^+/H) = -2.31$  V vs SHE). Electrolytic reactors are composed of at least two electrodes: (i) the cathode, where nitrate reduction take place, and (ii) the anode, where oxidation reactions occur. Electrocatalytic reactors can benefit from both reactions.

Anodic materials with a high overpotential for oxygen evolution can electrogenerate in situ hydroxyl radicals or active chlorine species to degrade organic pollutants to low-molecular-weight organic acids and CO<sub>2</sub>.<sup>62,63</sup> Combination of nitrate reduction with electrochlorination can enhance water quality for urban and rural applications. Active chlorine species are used widely in water reclamation processes to reduce the concentration of ammonia (a common undesired byproduct of catalytic reduction). Chlorination of ammonia forms chloramines, which are used as microbial disinfectants for nearly half of the U.S.<sup>64</sup> The combination of the two processes could not



**Figure 7.** Electrocatalytic reduction pathways of nitrate. Reproduced with permission from ref 58. Copyright 2018 Elsevier.



**Figure 8.** Direct charge transfer electrocatalytic reactions (red arrows) and catalytic hydrogenation reactions (green arrows). Blue atoms represent Pt/Pd, while brown atoms represent Cu, Sn, or In redox sites.

only reduce hazardous nitrate in water but also produce in situ disinfectant species required in drinking water applications.

## 6. IMPLEMENTATION AND PERSPECTIVE

Despite the years of development of catalysts to treat contaminated waters, to date there are currently no established large-scale processes. Attempts by others have been made to scale up heterogeneous catalytic treatment processes, including a pilot-scale pump-and-treat system incorporating alumina-supported Pd catalyst that has been tested for TCE-contaminated groundwater<sup>65</sup> and PdCu catalysts to treat nitrates in drinking water.<sup>66</sup> Electrocatalytic processes are already used at a commercial scale in water treatment, albeit to produce aqueous chlorine species from NaCl brines. This permits on-site chlorine production instead of delivery and storage of hazardous pressurized tanks of chlorine gas.

A challenge in treating “real” waters (i.e., not ultrapure) with catalysts is the presence of a multitude of different solutes, some of which can strongly adsorb to and block catalytic sites, slowing the reaction.<sup>21,67,68</sup> We assessed the effect of Cl<sup>-</sup> and bisulfite, common water solutes and known Pd poisons, on our

Pd-on-Au NPs. The catalysts were completely resistant to deactivation from 1 M chloride, and 2 times more resistant to bisulfide compared with Pd.<sup>69</sup> We also tested Pd supported on alumina (“Pd/Al<sub>2</sub>O<sub>3</sub>”) and PdAu/Al<sub>2</sub>O<sub>3</sub> catalysts on CF-contaminated groundwater. Because the HDC reaction generates HCl, a combination of lower pH and generation of Cl<sup>-</sup> initially led to catalyst fouling,<sup>31</sup> which was amended with citrate additive. While deactivation was observed, it was reversible via exposure to bleach followed by reduction with aqueous H<sub>2</sub>. From these findings, we developed a protocol to continuously treat groundwater for 42 days. We also studied the use of formic acid to replace hazardous H<sub>2</sub> gas<sup>70</sup> and found that formic acid decomposes on a Pd-on-Au catalyst with >99% selectivity for hydrogen.<sup>71</sup>

The failure of the use of catalysts for large-scale treatment of water may be due to many factors, including variation of water quality and characteristics and the need for a hydrogen reductant. Instead, we suggest the development of smaller reactors that could, for example, be used to treat water for a multiunit dwelling or at a village well or even fit under the kitchen sink to treat water at the point of use. These catalytic converters for water could be tailored to treat target pollutants of interest in the affected water and could combine one or more aspects of heterogeneous catalysis, photocatalysis, or electrocatalysis. Heterogeneous catalysts can be integrated into electrochemical cells to use byproduct hydrogen produced on the cathode, or bimetallic catalysts can be integrated in packed-bed cathode cells to exploit direct both reduction mechanisms (Figure 8). Halides (Cl<sup>-</sup>, Br<sup>-</sup>) present in water can react at the anode to produce inorganic (e.g., ClO<sub>4</sub><sup>-</sup>, BrO<sub>3</sub><sup>-</sup>) and organic (e.g., THM, HAA) disinfection byproducts of health concern. However, 3D electrodes and sorbent integration into electrocatalytic reactors may avoid these unintended consequences.<sup>72</sup> Electricity could potentially be supplied by solar panels or wind

turbines<sup>73</sup> for remote or rural use. Inclusion of UV light sources could also drive selectivity while inactivating microorganisms. These catalytic converters for water may be especially suited for treatment of CVOCs, which are predominantly found in groundwater wells, and nitrates and nitrites, as ~90% of nitrate pollution occurs in small drinking water systems (<500 users).<sup>18</sup> Though precious metals are used, the modules need not be prohibitively expensive. To remove nitrate from water used by a typical U.S. household (80 gal/day), one needs 2 g of an alumina catalyst containing 1 wt % Pd and 0.13 wt % In, which costs less than 1 U.S. dollar (as of January 2018). We previously estimated that \$1.80 of electrically generated H<sub>2</sub> would treat 1 m<sup>3</sup> of water containing 100 mg/L contaminant. For a “high” concentration of 10 mg/mL NO<sub>3</sub><sup>-</sup> in drinking water, this cost falls to US\$0.0019 per gallon (see the Supporting Information). A technoeconomic analysis that accounts for all capital and operating costs for a given-size module has not yet been applied to estimate treatment costs.

## ■ ASSOCIATED CONTENT

### S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.accounts.8b00642](https://doi.org/10.1021/acs.accounts.8b00642).

Calculation of catalyst cost and hydrogen cost ([PDF](#))

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### Notes

The authors declare no competing financial interest.

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