Supporting Information For:

Electrochemical Oxidation of Atrazine and Clothianidin on Bi-doped SnO_2-Ti_nO_{2n-1} Electrocatalytic Reactive Electrochemical Membranes

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Pages:14

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REM Synthesis. The Magnéli phase powder was synthesized from TiO_2 powder by reducing at 1050 °C under H_2 gas flow in a tube furnace (OTF-1200X, MTI) for 6 hours. After that, a certain amount of Magnéli phase powder was weighed and mixed with paraffin oil as binder (8 drops per g of powder). Then, approximately 0.6 g of the binder mixed powder was poured into a stainless steel (SS) die and pressed using a hydraulic press under a uniaxial pressure of 20.7 bar that gave a 2.5 mm thick, 1.1 cm diameter REM pellet. Then the pellet was heated in a tube furnace at 1050 ^{0}C for 6 hours under H_2 flow to remove the binder and sinter the particles.

Catalysts (BDTO) were deposited on the REMs using two different methods: pulsed laser deposition (PLD) and pulsed electrodeposition followed by thermal oxidation (EDT). The PLD method used 20 laser pulses in the presence of the BDTO precursor target to modify the REM with BDTO and the modified electrode was designated as "REM/BDTO/PLD20". Initially the PLD chamber was pumped down to 5×10^{-6} - 9×10^{-6} Torr using a turbo-molecular pump (Pfeiffer Vacuum, Germany) and the temperature in the chamber was maintained at 25 ^{0}C. The REM was placed 5.0 cm away from the BDTO target ($Sn_{0.91}Bi_{0.09}O_2$) during the PLD process. The PLD method used a krypton fluoride excimer laser (COMPexPRO201, Coherent, CA, USA) at a wavelength of 248 nm with laser frequency, number of pulses, pulse duration, energy density, and laser energy of 10 Hz, 20, 25 ns, 3 mJ cm^{-2}, and 400 mJ, respectively.

BDTO modified REM using EDT method (REM/BDTO/EDT) used pulsed electrodeposition in the presence of a precursor solution followed by thermal oxidation in DI water. The precursor solution (Sn:Bi = 10:1, mol/mol) was prepared by dissolving 2.25 g of $SnCl_2$, $2H_2O$ and 0.48 g of $Bi(NO_3)_3$, $5H_2O$ in 1000 mL 1 M HCl solution. Pulsed electrodeposition was used in the presence of the precursor solution and it was pumped through the REM cathode followed by a stainless steel anode. The parameters for pulsed electrodeposition are as follows: current density = -100 mA cm$^-$

^{2}, pulse on (t_{on}) = 10 ms, pulse off (t_{off}) = 1000 ms, and number of pulses = 3564. After electrodeposition, the metal deposited REM was heated in DI water at 80 ^{0}C for 1 hour to oxidize the metals to metal oxides. After that, the REM/BDTO/EDT was dried in an oven at 50 ^{0}C for 3 hours.

Batch Reactor.

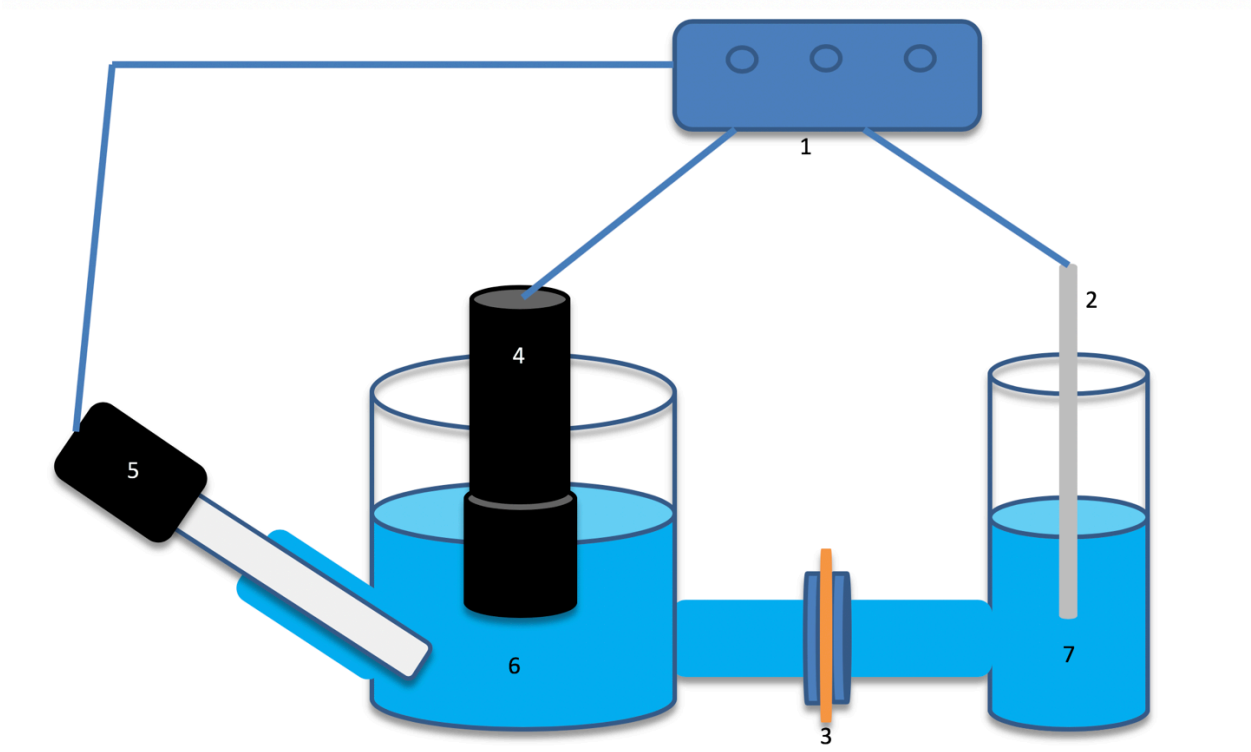


Figure S-1. Schematic of batch reactor setup. 1) Potentiostat, 2) Counter electrode (Pt), 3) Nafion membrane separator, 4) Working electrode holder with REM, 5) Reference electrode, 6) anode chamber, 7) cathode chamber

Flow-through Reactor. The flow-through cell (Figure S-2) was made of polyether ether ketone (PEEK) and contained the REM/BDTO as the working electrode, 316 SS as the counter electrode, and a 1 mm diameter Ag/AgCl/KCl (1M) as reference electrode (Harvard Apparatus, MA, USA). The reference electrode was placed at a distance of ~3.3 mm from the working electrode. Potentials and currents for all electrochemical experiments were applied by a Gamry Reference 600 potentiostat/galvanostat (Warminster, PA).

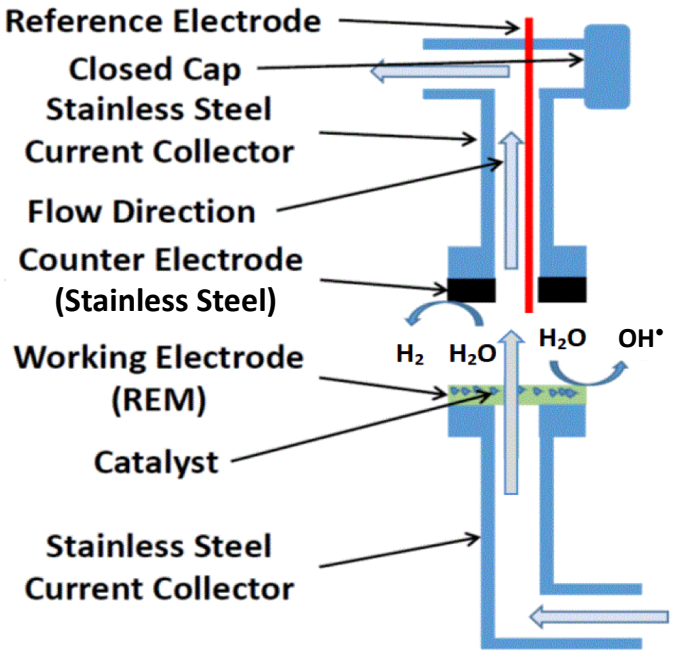


Figure S-2. Schematic of the flow-through reactor setup.

Membrane Characterization. The REMs were characterized by X-ray diffraction (XRD) (Siemens D-5000) with a Cu X-ray tube (40 kV and 25 mA). Scans were monitored and analyzed using DataScan software (MDI, v. 4.3.355, 2005) at a step size and dwell time of 0.01° and 0.5 s, respectively. The electrodes were also characterized using X-ray photoelectron spectroscopy (XPS) with a Kratos Axis-165 at the Research Resource Center at the University of Illinois at Chicago. The XPS spectrum was analyzed and deconvoluted using XPSPEAK 4.1 software. To

investigate surface morphology before and after catalyst deposition, scanning electron microscopy (SEM) was performed using a variable pressure scanning electron microscope (VPSEM) (Hitachi S-3000N, Japan) at 3 to 4 kV and from 3 to 4 k magnifications. Only REM/BDTO/PLD20 was characterized by transmission electron microscope (TEM) (JEOL JEM-3010, USA). To show the elemental distribution and concentration of the BDTO catalysts within the REMs, SEM coupled with energy dispersive X-ray spectroscopy (EDS) was used on the surface as well as on the X-section of different REMs. An acid digestion method using a mixture of 2 mL H_2O_2 (30 %), 4 mL HF (10 %), 8 mL HNO_3 (70 %), and 10 mL HCl (37 %) was performed to determine the metal loading of the REM/BDTO/EDT and REM/BDTO/PLD20. The pellet (0.5 – 0.6 g) was crushed into powder and the powder with the acid mixture was introduced into a 50 mL Teflon digestion tube that was heated at 200 ^{0}C for 1 hour. Elemental concentrations of Bi and Sn were measured in these acid extracts using a Thermo iCAP 7600 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (detection limit ~ 1 - 3 ppb).

Analytical Methods. Concentrations of NO_3^- and NH_4^+ were determined using ion chromatography (IC) (Dionex ICS-2100). Anions concentrations were measured using an anion exchange column (Dionex IonPac AS18) and cations were determined using a cation exchange column (Dionex IonPac CS16). Concentrations of TA, ATZ, and CDN were determined using a Shimadzu UFLC XR HPLC with a Phenomenex Kinetex® 5 μm C18 column and a photodiode array (PDA) detector (Nexera X2, Shimadzu). HPLC with a fluorescent detector (RF-20A, Shimadzu) was used to measure 2-hydroxyterephthalic acid (HTA) concentration (λ_{ex} = 315 nm and λ_{em} = 435 nm). A mobile phase was a mixture of methanol and 0.1% formic acid in DI water (60:40) at 1.0 mL min^{-1} flow rate for TA and HTA quantification. Another mobile phase consisting of a mixture of methanol and DI water (55:45) was used at a flow rate of 1.0 mL min^{-1} for ATZ

and CDN concentration measurements. Chemical oxygen demand (COD) for TA oxidation was determined using Hach method 8000 (USEPA Reactor Digestion Method). Total nitrogen (N) for ATZ and CDN oxidation was determined through oxidative digestion of all dissolved nitrogen species present in the permeate, followed by IC detection of NO_3^-.[1]

XRD Characterization.

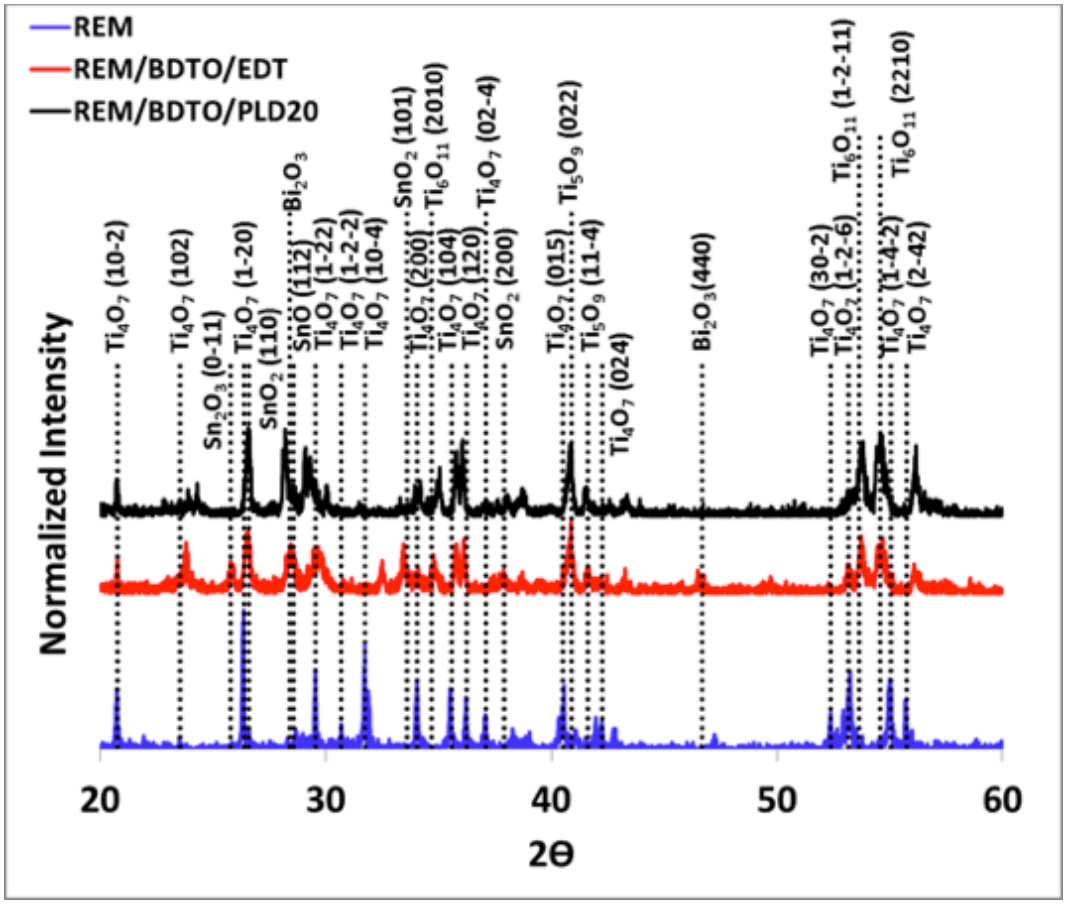


Figure S-3. XRD spectra of REM samples

XPS Results. The deconvoluted O 1s, Sn 3d and Bi 4f XPS spectra of REM/BDTO/EDT and only Sn 3d XPS spectra of REM/BDTO/PLD20 is provided in SI (Figure S-4). The peak assignments for deconvoluted Sn 3d spectra of REM/BDTO/EDT was supported by the literature, which showed the presence of SnO_2 (Sn $3d_{3/2}$ = 494.4 eV and Sn $3d_{5/2}$ = 486.0 eV) and SnO (Sn $3d_{3/2}$ = 493.7 eV and Sn $3d_{5/2}$ = 485.3 eV).[2-4] This result was also supported by the XRD results that showed the presence of Sn in the form of SnO_2 and SnO. The deconvoluted Bi 4f spectra showed the presence of only Bi_2O_3 (Bi $4f_{5/2}$ = 163.2 eV and Bi $4f_{7/2}$ = 157.9 eV) that was also supported by the XRD data (Figure S-4).[5] The Sn 3d spectra of REM/BDTO/PLD20 showed the

presence of only SnO_2 (Sn $3d_{3/2}$ = 494.2 eV and Sn $3d_{5/2}$ = 486.2 eV) without any traces of SnO. However, the Bi concentration was below the detection limit of XPS. All the results confirmed successful deposition of bismuth doped tin oxide using PLD and EDT methods.

Table S-1. Atomic Concentrations (atomic %) of Ti, O, Sn and Bi determined by XPS for REM, REM/BDTO/EDT and REM/BDTO/PLD20.

Electrode	Ti (%)	O (%)	Sn (%)	Bi (%)
REM	27.7	72.3	-	-
REM/BDTO/EDT	11.1	77.5	10.4	1.02
REM/BDTO/PLD20	27.0	71.8	1.06	Not detected

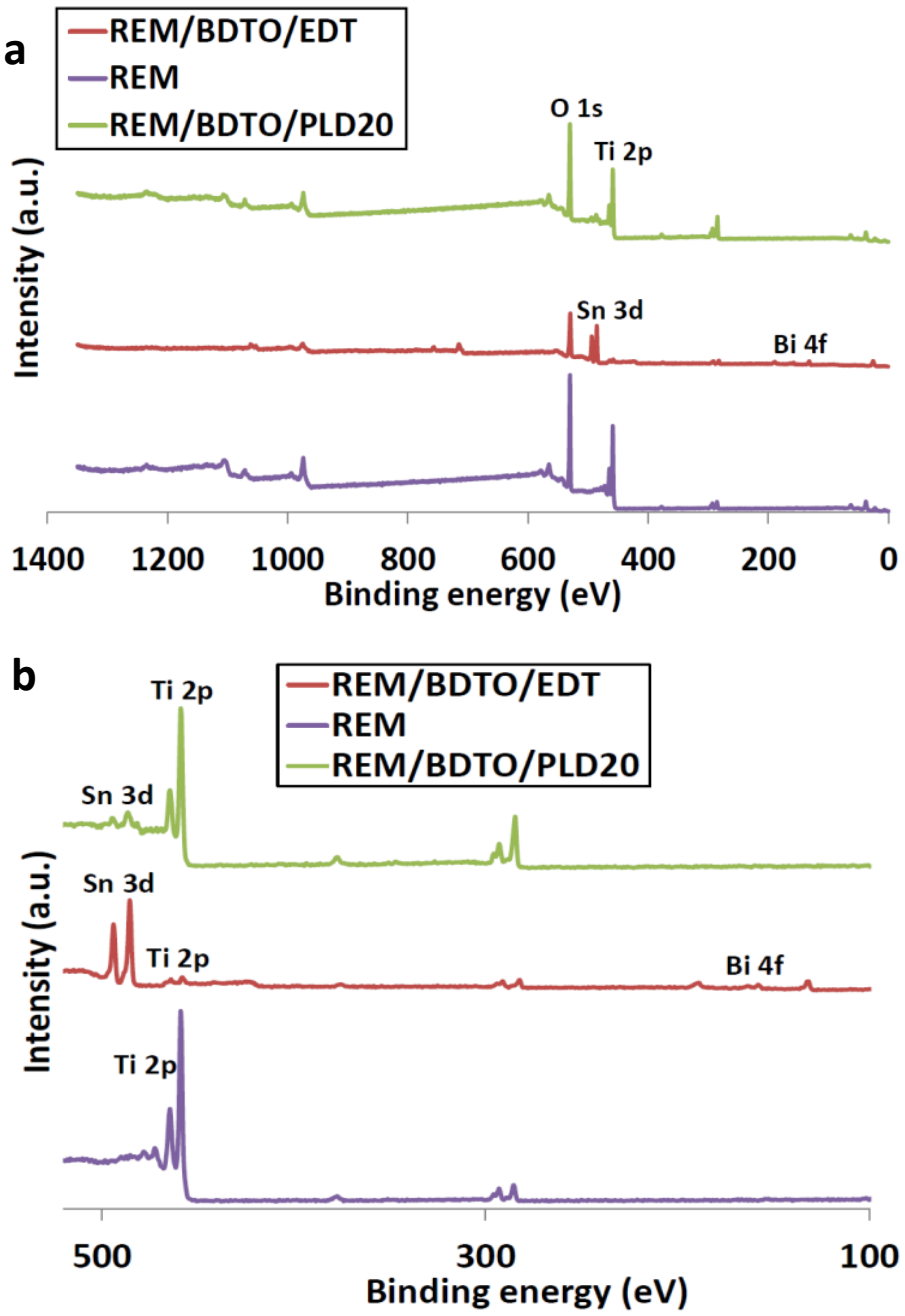


Figure S-4. XPS of REM, REM/BDTO/EDT and REM/BDTO/PLD20 at a) 0-1350 eV and b) 100-520 eV.

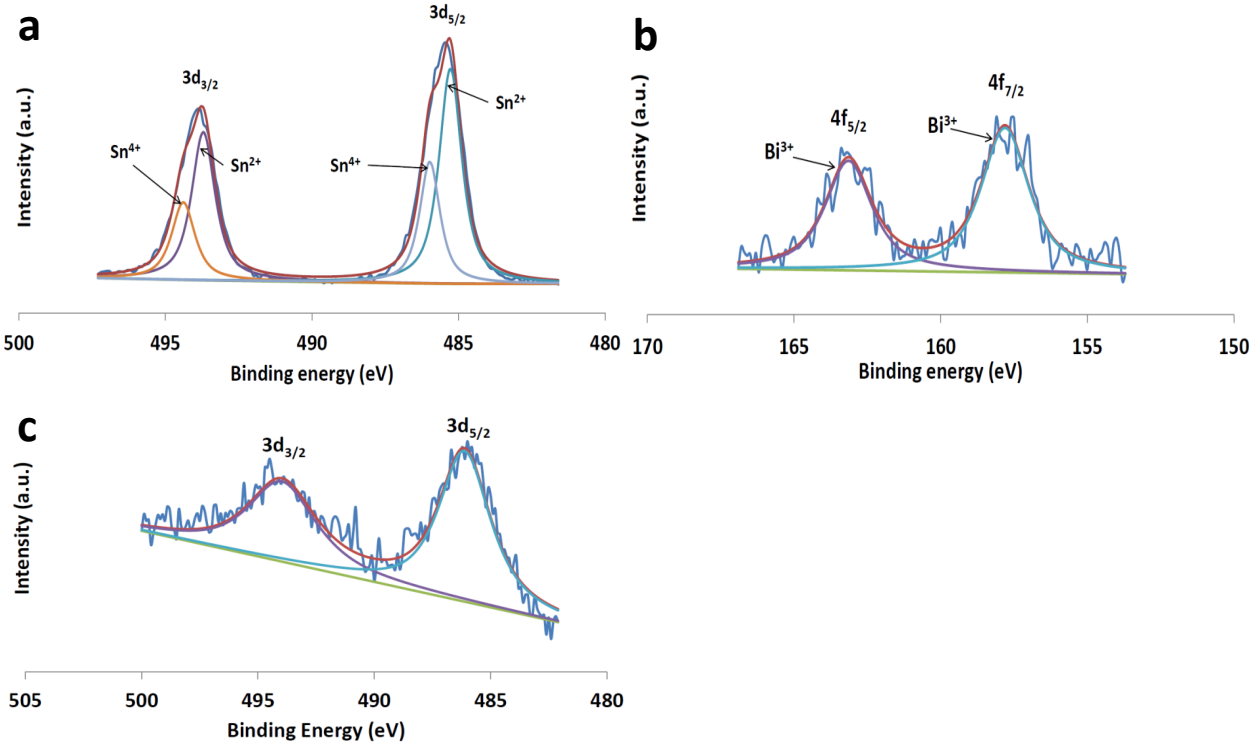


Figure S-5. Deconvoluted XPS of a) Sn 3d and b) Bi 4f spectra of REM/BDTO/EDT and c) Sn 3d spectra of REM/BDTO/PLD20.

Pore Size Determination. Average pore size/pore radius (r_p) using the Hagen-Poiseuille equation (S-1) by varying flow rate and trans-membrane pressure (ΔP) (Figure S-2).

$$u = \frac{r_p^2 \Delta P \varepsilon}{8 \eta \Delta x} \qquad \text{(S-1)}$$

In equation S-1, u is the linear pore velocity, which was determined from the measured flow rate and cross-sectional surface area; ε is the porosity (0.3), which was determined from past work with the same material;{Nayak, 2018 #4991} η is the fluid viscosity of pure water (9.78×10^{-4} Pa s (21 ^{0}C)){Haynes, 2010 #1142}; and Δx is the membrane thickness (2.5 mm). The pore radius was determined as 0.41 ± 0.03, 0.36 ± 0.02, and 0.40 ± 0.04 µm for REM, REM/BDTO/EDT, and REM/BDTO/PLD20, respectively.

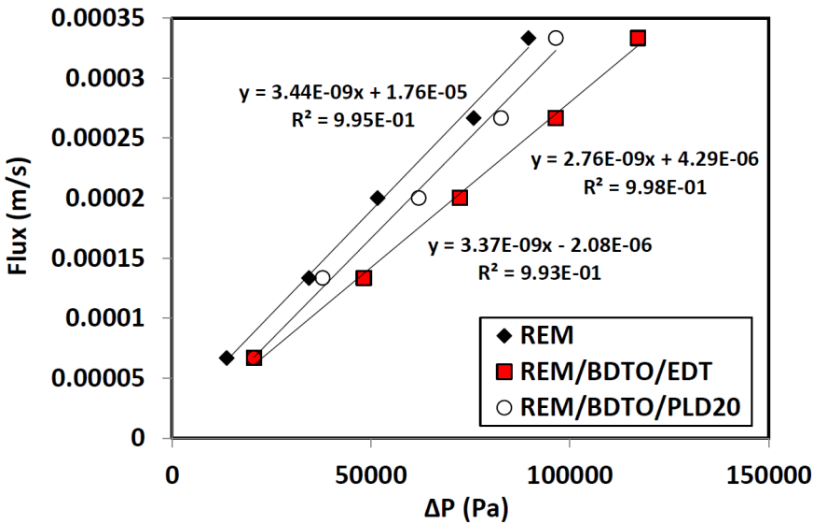


Figure S-6. Flow velocity (u) with pressure drop (ΔP) for REM, REM/BDTO/EDT and REM/BDTO/PLD20.

HTA Concentration Profile.

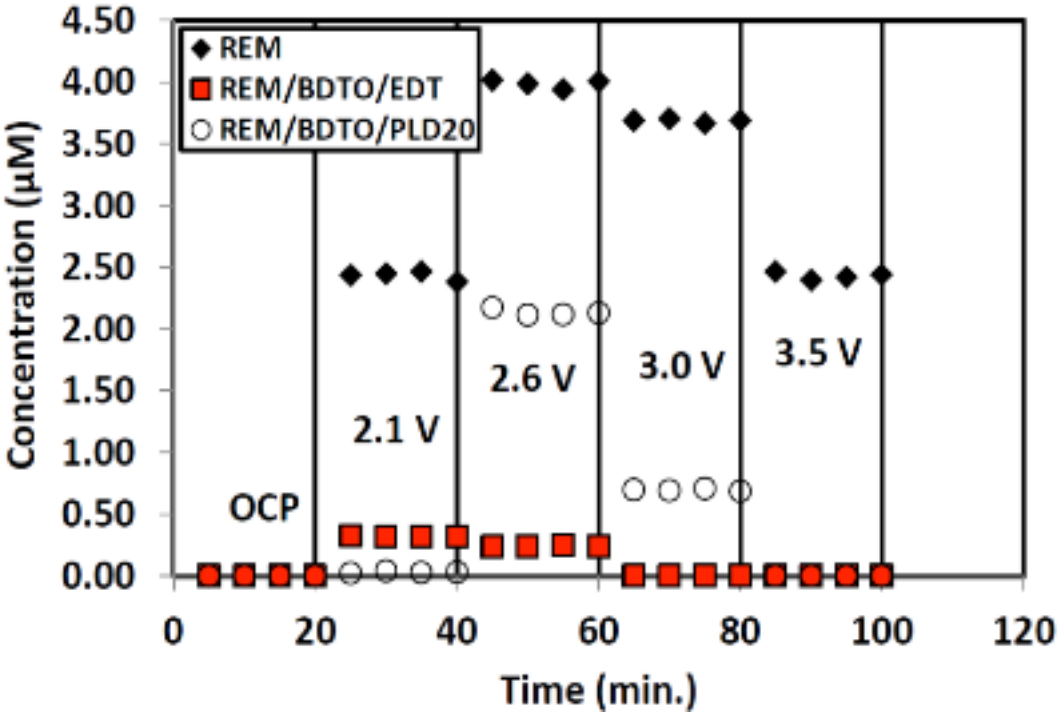
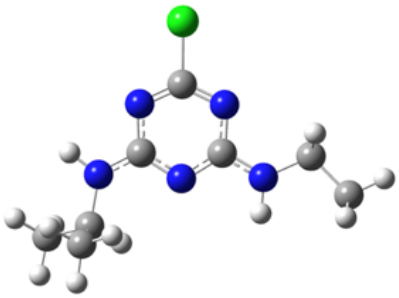


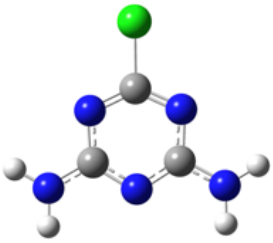
Figure S-7. Concentration profile for HTA during TA oxidation.

a) Atrazine (ATZ)



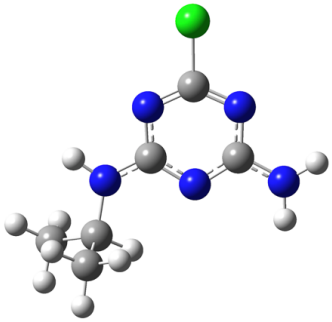
b) Clothianidin (CDN)

c) Desethyl Deisopropyl Atrazine (DEDIA)

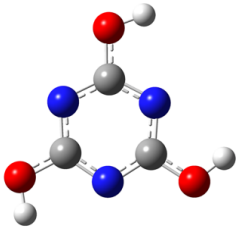


d) Desisopropyl Atrazine (DIA)

e) Desethyl Atrazine (DEA)



f) Cyanuric Acid (CA)



g) 2-chloro-1,3-triazole (CTA)

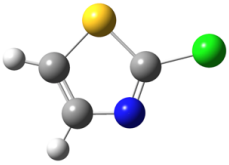


Figure S-8. DFT geometrically optimized structures. Atom key: C = grey; H = white; N = blue; O = red; Cl = green; S = yellow.

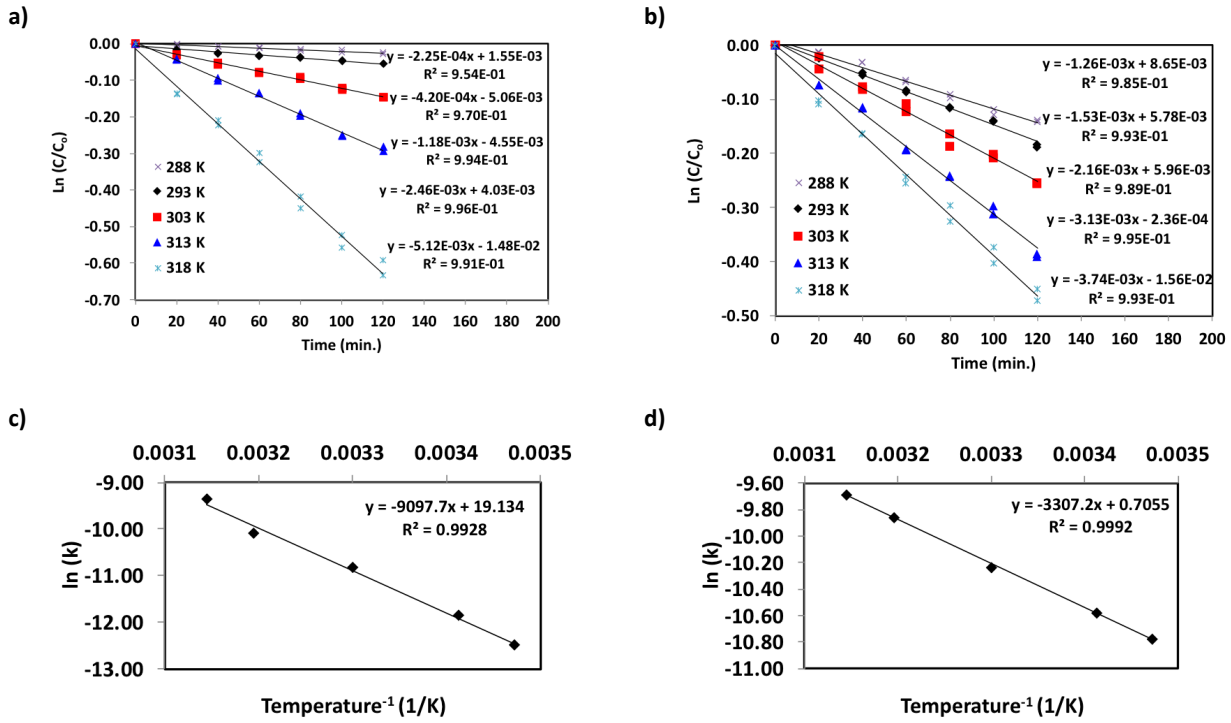


Figure S-9. Concentration profiles for oxidation of a) ATZ at 1.5 V/SHE, b) ATZ at 1.8 V/SHE, c) Arrhenius plot for ATZ oxidation at 1.5 V/SHE, c) Arrhenius plot for ATZ oxidation at 1.8 V/SHE. Error bars contained within data points (c, d).

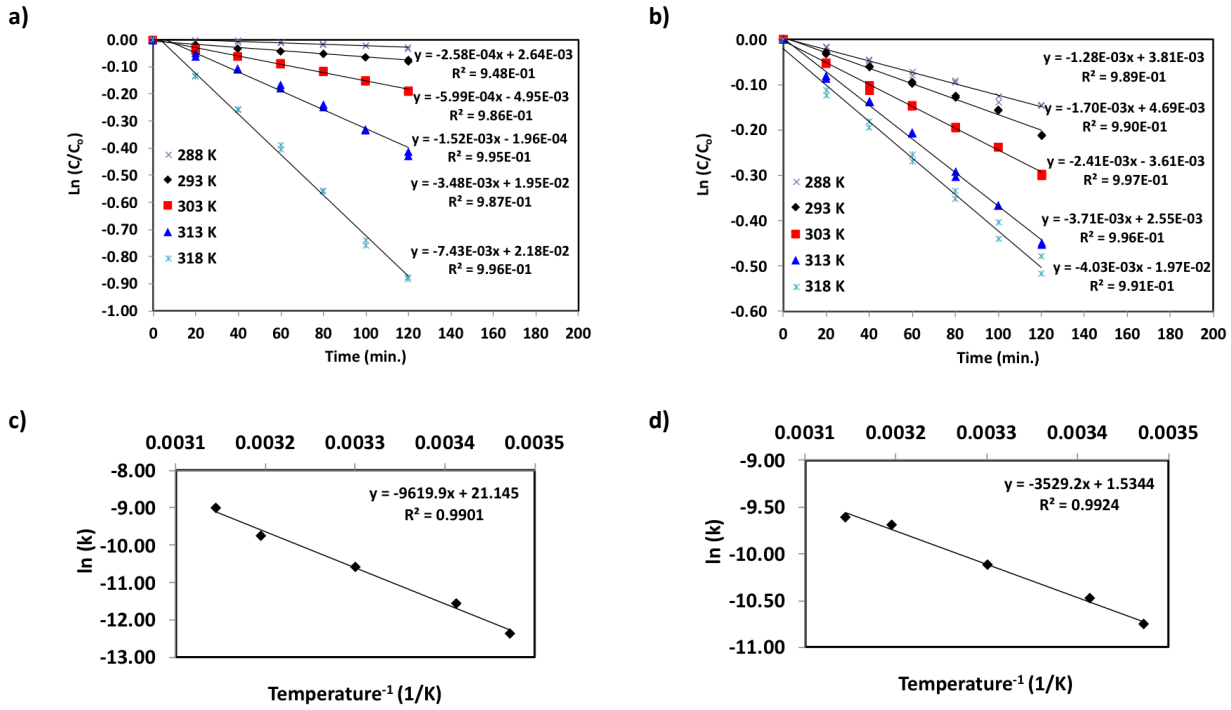


Figure S-10. Concentration profiles for oxidation of a) CDN at 1.14 V/SHE, b) CDN at 1.5 V/SHE, c) Arrhenius plot for CDN oxidation at 1.14 V/SHE, c) Arrhenius plot for CDN oxidation at 1.5 V/SHE. Error bars contained within data points (c, d).

References.

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