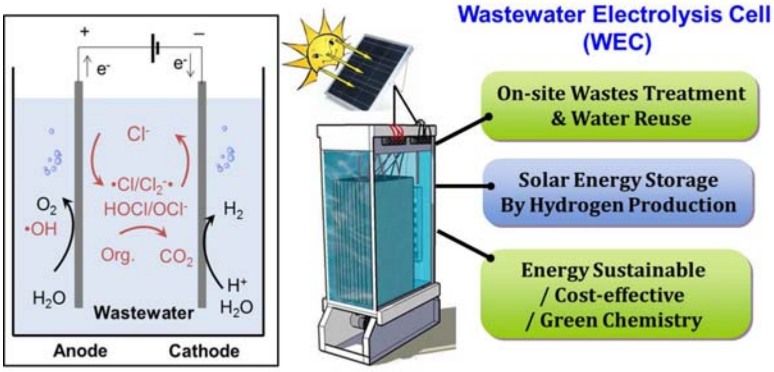
Chapter 1

INTRODUCTION



1.1. HUMAN NEEDS

Current world water crisis manifests that more than 2.5 billion people worldwide lack access to improved sanitation and waste disposal facilities, most often in developing areas such as South Asia, Indonesia and Africa.[1] In these emerging countries, human waste and open defecation are major sources of waterborne diseases. The biochemical oxygen demand (BOD) from human waste discharge into receiving waters is becoming a threat to biodiversity.[2] Consequently, there have been growing demands for research and development to find breakthroughs in on-site wastewater treatment and water reuse technologies. When considering the deficiency of underground infrastructures, water treatment and reuse practices suitable to use in the developing world should be self-contained with reduced consumptions of water, energy, and capital costs.[3,4] Even in the developed world, a growing need for sustainability and water treatment capacity along with an increase in population density has forced water treatment criteria more stringent in order to enhance livability and water use efficiency.[5] Corresponding demands for reduction in the total maximum daily loads of pollutants also drive towards on-site wastewater treatment practices due to difficulties in building or retrofitting a centralized wastewater treatment plant.[4]

On the other hand, extensive efforts are underway to develop renewable energy sources with negligible carbon footprints. Electrochemical water splitting is often used for the production of molecular hydrogen via alkaline and solid oxide electrolysis that have current efficiencies for a hydrogen production up to 67%.[6] The dominant fraction of the hydrogen production cost is coming from the electricity consumption and partially the operational costs for chemicals including potassium hydroxide or other solid electrolytes. The US department of energy[7] established a goal to reduce the total hydrogen production cost by virtually 50% in within the next 10 years. Therefore, a different strategy to finding an alternative electrolyte is required to reduce the electricity and chemical reagents consumption for molecular hydrogen production.

1.2. TECHNOLOGYCAL BACKGROUND

1.2.1. Wastewater Electrolysis Cell. A well-designed wastewater electrolysis cell (WEC, Figure 1.1) can provide a feasible approach for self-sustainable on-site wastewater treatment with simultaneous decentralized H_2 production. Chloride ion is a ubiquitous, naturally occurring anion providing electric conductivity and, when employing saline wastewater as a background electrolyte for electrochemical water splitting, the chloride ion is oxidized to reactive chlorine species (RCS, $Cl\cdot$, Cl_2, and conjugate species) to remove environmental pollutants including organics, ammonium ion, and coliform bacteria.[8] This green chemistry that acts without external chemicals can be totally driven by photovoltaic (PV) panels,[9] which makes the PV-powered WEC (PWEC) a traditional infrastructure-free approach.[10] Simultaneously with the wastewater treatment, solar energy storage is possible by cathodic production of H_2, which can be utilized as a secondary energy source for the PWEC or for other domestic living purposes.[11] By this dual-functioning approach, one can reduce the cost of electrolytic H_2 production, particularly the cost for electrolyte and electricity, by saving energy for water treatment. Recent statistics suggest that handling water and wastewater occupied up to 4% of total electricity consumption in

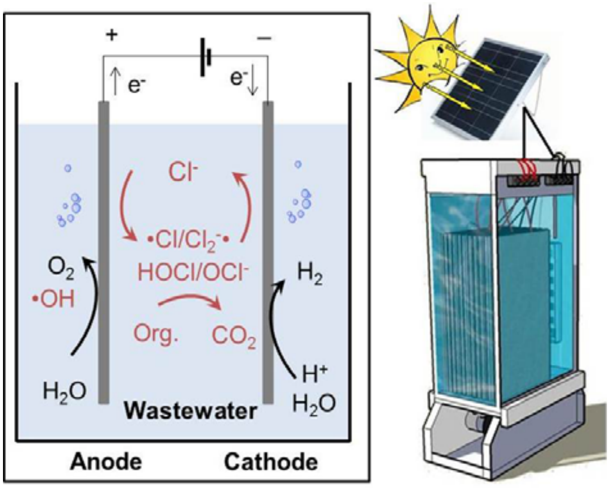


Figure 1.1. Schematic diagram of photovoltaic-powered wastewater electrolysis cell for on-site waste treatment for reuse with simultaneous solar energy storage by hydrogen production.

the US and the collection and treatment of wastewater consume up to 5 Wh of electricity per gallon of wastewater in California.[12]

1.2.2. Electrochemical Degradation of Environmental Pollutants. The electrochemical system has often been used for treatment of high-salinity wastewater such as dye (textile) wastewater, landfill leachate, olive mill wastewater, tannery wastewater, livestock industry wastewater, and reverse osmosis concentrates, among many other usages. In addition, degradations (mostly oxidative) of non-biodegradable or recalcitrant environmental pollutants (pesticides, pharmaceuticals and personal care products, polycyclic aromatic hydrocarbons, and other aliphatic/phenolic compounds) have been widely investigated in electrochemical cells, usually employing laboratory-generated electrolyte (substrates of interest in background electrolyte). More thorough reviews on the electrochemical wastewater treatment can be found in recent reports by Panizza and Cerisola,[13] Martinez-Huitle and Ferro,[14] and Chaplin.[15]

Electrochemical wastewater treatment systems with a wide array of electrodes have conventionally categorized the electro-catalytic anodes into the following two groups: active electrodes and non-active anodes. Since the non-active anodes actually do catalyze heterogeneous oxidation of environmental pollutants, these terminologies should be interpreted in terms of electro-catalytic activity for oxygen evolution reaction (OER). In other words, the most common non-active anodes include SnO_2, PbO_2, and boron-doped diamond (BDD), which show relatively high over-potential for OER. In contrast, mixed metal oxides electrodes based on IrO_2 or RuO_2 have the lowest OER over-potential and are referred to as active anodes in the field of electrochemical wastewater treatment.

Based on the mechanistic point of view, on the other hand, electrochemical pollutants oxidation is referred to either as direct oxidation or indirect oxidation. Despite some discrepancy among researchers, direct oxidation generally corresponds to heterogeneous oxidation of target pollutants on the anode surface, while indirect oxidation accounts for homogeneous oxidation of pollutants often mediated by reactive oxygen species (ROS) and the RCS. In spite of a possibility of direct electron transfer from the target pollutants to the anode, the heterogeneous direct oxidation has been almost exclusively ascribed to the surface bound ROS, particularly hydroxyl radical (·OH). When the anode surface under a potential bias is able to liberate free ROS, as reaction intermediates or byproducts of OER, the indirect oxidation can take place via mediation of homogeneous ·OH, H_2O_2, and O_3. However, it is difficult to distinguish the direct oxidation by surface-bound ROS from the indirect oxidation by free ROS, due to the short life and low yield of free ROS. Therefore, the RCS generated in the presence of a chloride ion (usually in 10 mM to 100 mM range) in the electrolyte has been appreciated as the primary mediator of indirect oxidation.

1.2.3. Molecular H_2 Production from (PV-Powered) Electrolysis of Wastewater. A wastewater electrolysis cell may prove to be a promising approach for decentralized H_2 production with simultaneous on-site wastewater treatment. Hoffmann and co-workers[8,9,16-18] have investigated the electrolytic H_2 production from model organics containing solutions or real wastewater (domestic or industrial wastewater) in circum-neutral pH. In these reports, inexpensive stainless steel was employed as a cathode. The cathodic current efficiency and energy efficiency of H_2 production have been reported to vary widely depending on the electrolyte composition (NaCl or Na_2SO_4 background, electrical conductivity, concentration of electron donating substrates other than water), cell configuration (distance between anode and cathode, geometric area), and operating condition (applied cell voltage). The reported values ranged from 40 to 80% for current efficiency and from 15 to 60% for energy efficiency. The major scavenging reactions for H_2 production include reduction of RCS (to chloride ion) in NaCl background and reduction of oxygen (to superoxide radical and its dissociation products). The current efficiency for H_2 production was usually higher in the $NaSO_4$ background than in the NaCl background. In the NaCl background solution, a presence of electron donating substrates enhances the current and energy efficiency of H_2 production. For example, batch injections of small amounts of organics including urea, phenol, and other oxidizable organics sharply enhanced the production of H_2. The RCS competing with water and proton to accept electrons can be readily quenched by the organics to enhance the H_2 production. The energy efficiency of H_2 production decreased as the electrical conductivity decreased or applied cell voltage (or current) increased, primarily owing to the increase in ohmic energy loss. Park *et al.*[9,17] would be the first to attempt electrolytic H_2 production from dilute aqueous solutions, which was solely powered by photovoltaic panels. In these reports, the sequential energy losses in the PV panel and the electrolysis cell resulted in net energy conversion efficiency about 1% (2.5% energy efficiency for solar light to direct current and 30~60% energy efficiency for the direct current to H_2).

1.2.4. Mixed Metal Oxides Anodes. Electrochemical water oxidation on metal oxides (MO_x) anodes has long been believed to initiate from a formation of surface bound hydroxyl radical ($MO_x(\cdot OH)$).[19] The oxygen evolution activity is largely coming from the transition of the surface bound hydroxyl radicals to the chemisorbed active oxygen (MO_{x+1}).[19] The $MO_x(\cdot OH)$ is a strong oxidant (standard redox potential of free $\cdot OH$ is 2.8 V versus Normal Hydrogen Electrode) and, as a rule of thumb, prefers oxidation of pollutants or chloride ion to the OER. Boron doped diamond, SnO_2, and PbO_2 are well known anode materials which can provide both the direct pollutants oxidation and indirect oxidation with a presence of chloride ions. Owing to the high OER overpotential for these non-active anodes, the resulting current efficiency of pollutants oxidation sometimes approached unity, which could be mitigated by mass transport limitation. However, a concomitant large kinetic barrier for the initial water discharge ($MO_x(\cdot OH)$ formation) requires relative large energy consumption and limits their application for H_2 production and energy storage purposes. On the contrary, the higher oxides favor liberation of the lattice active oxygen to molecular O_2 and a direct oxidation of pollutants is relatively sluggish. Therefore, indirect oxidation mediated by RCS plays more important roles for the anode materials undergoing facile redox oxide transition. RuO_2 or IrO_2 based metal oxides anodes have been widely employed as active anodes with relatively low OER overpotentials. Compared to the non-active anodes, the current efficiencies for the pollutants oxidation are mostly lower on the active anodes, but more pronounced energy efficiency can be achieved owing to the low kinetic barrier to the formations of MO_{x+1}. However, the high material cost for these precious metals is a major barrier for commercialization. A pictorial illustration of the direct and indirect oxidation of pollutants on metal oxide anodes is given in Figure 1.2.

Current discussion can be more elaborated on the volcano plot suggested by Trasatti[20] which describes a relation between the OER overpotential and the enthalpy change in redox transition from lower to higher oxides (Figure 1.3). It has been reported that the enthalpy change in the oxides transition is well correlated with the bond strength between the oxide ion and the central metal ion.[21] The electrodes for direct oxidation would be located in the

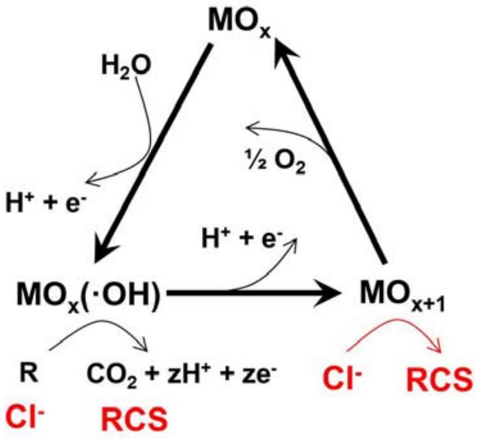


Figure 1.2. A schematic diagram of direct oxidation of organics (R) and indirect oxidation mediated by reactive chlorine species (RCS) on metal oxide (MO_x) electrodes.[19] $MO_x(\cdot OH)$ and MO_{x+1} stand for surface-bound hydroxyl radical and higher oxide, respectively.

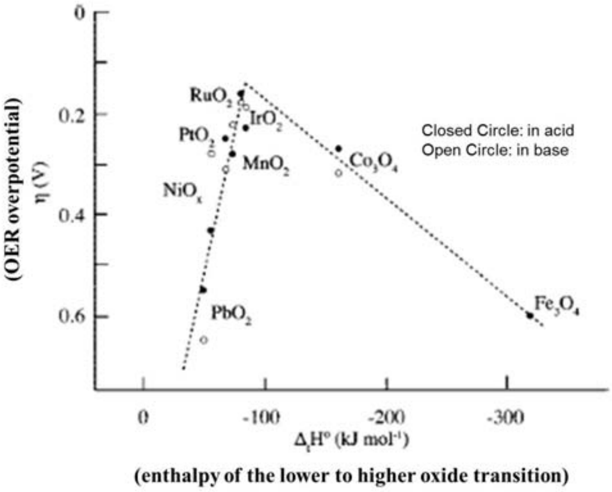


Figure 1.3. Volcano plot of the overpotential of oxygen evolution reaction (OER) for various types of metal oxide electrode as a function of enthalpy change for lower to higher oxide. Reproduced from Trasatti.[20]

left-hand side of the apex (*e.g.*, PbO_2) and the formation of the higher oxides requires large energy input. Therefore, the initial water discharge is rate determining and weakly coordinated hydroxyl radicals are subject to reactions with aqueous solutes (R or Cl^-) with relatively high current efficiencies.[22] The summit of the volcano is occupied by active anode materials (RuO_2 and IrO_2) whose nearly optimal M-O bond strengths allow for facile OER. On the other hand, the metal oxides in the right-hand side of the apex (*e.g.*, Co_3O_4 and Fe_3O_4) undergo the oxide transition too easily and the liberation of active oxygen is the rate determining step.

1.2.5. Hetero-junction Anodes with BiO_x/TiO_2 Functionalities. The core components of the wastewater electrolysis cells investigated in this study include hetero-junction anodes sequentially coated with a series of mixed metal oxides. The electrodes were prepared by sequential thermal decomposition of mixed oxides of Ti and Bi on Ti base plates pretreated with IrO_2, Ta_2O_5, SnO_2, and Bi_2O_3, as shown in Table 1.1.[23] Based on an electron probe microanalysis, the outer surface of the electrode is dominantly composed of bismuth, titanium, and oxygen, to be designated as BiO_x/TiO_2 electrode.[24] The hetero-junction electrode fabrication is expected to bring about a shift in heterogeneous kinetics. In particular, the surface BiO_x/TiO_2 functionality can provide active sites for hydroxyl radical formation while the underlying precoat layer based on IrO_2 would reduce the kinetic barrier for water discharge. Also, the hetero-junction design should minimize losses of precious IrO_2, while the seal-coat layer based on SnO_2 is believed to enhance the conductivity of the electrode.[23]

Table 1.1. Fabrication procedure of BiO_x/TiO_2 hetero-junction electrodes used in this study (Chapter 2 – 4).[23]

Layer	Nominal Composition	Precursor	Annealing[a]	Repeat
Overcoat (O)	TiO_2/Bi_2O_3 (Ti:Bi = 70:30 mol%)	175 mM Ti-Glycolate Complex + 75 mM bismuth citrate in 225 mM NH_4OH	500 °C	4
			250 °C	2
			250 °C[c]	2
Slurrycoat (Sl)	Bi-doped TiO_2 (Ti:Bi = 96:4 mol%)	300 mM Bi-doped TiO_2 (Bi:Ti = 4:96) in water (pH 11)	250 °C[b]	7
Sealcoat (S)	SnO_2/Bi_2O_3 (Sn:Bi = 90:10 mol%)	225 M $SnCl_4 \cdot 5H_2O$ + 12.5 mM Bi_2O_3 in 0.5 M HCl	425 °C	4
Precoat (P)	IrO_2/Ta_2O_5 (Ir:Ta = 67:33 mol%)	73 mM $H_2IrCl_6 \cdot nH_2O$ + 27 mM $TaCl_5$ in 4 M HCl	525 °C	6

[a] Annealing time is 10 min except for the final annealing (1 h).

[b] Brush of Sl precursor and 4 V% O precursor before annealing.

[c] Brush 50 V& O precursor before annealing.

A series of investigations on the BiO_x/TiO_2 anodes noted reliable indirect oxidation of various types of environmental pollutants (model phenol compounds,[8,9,17,18] urea,[25] arsenite,[26] industrial wastewater,[18] and domestic wastewater[16]) and stability during a long-term electrolysis in circum-neutral pH. Nevertheless, the preparation procedure is actually the outcome of technical trial-and-error, and somewhat complicated, as shown in Figure 1.4. Therefore, it needs further modification to be a simplified preparation method. In addition, the core nature of each layer relevant to the activity and stability is not fully understood.

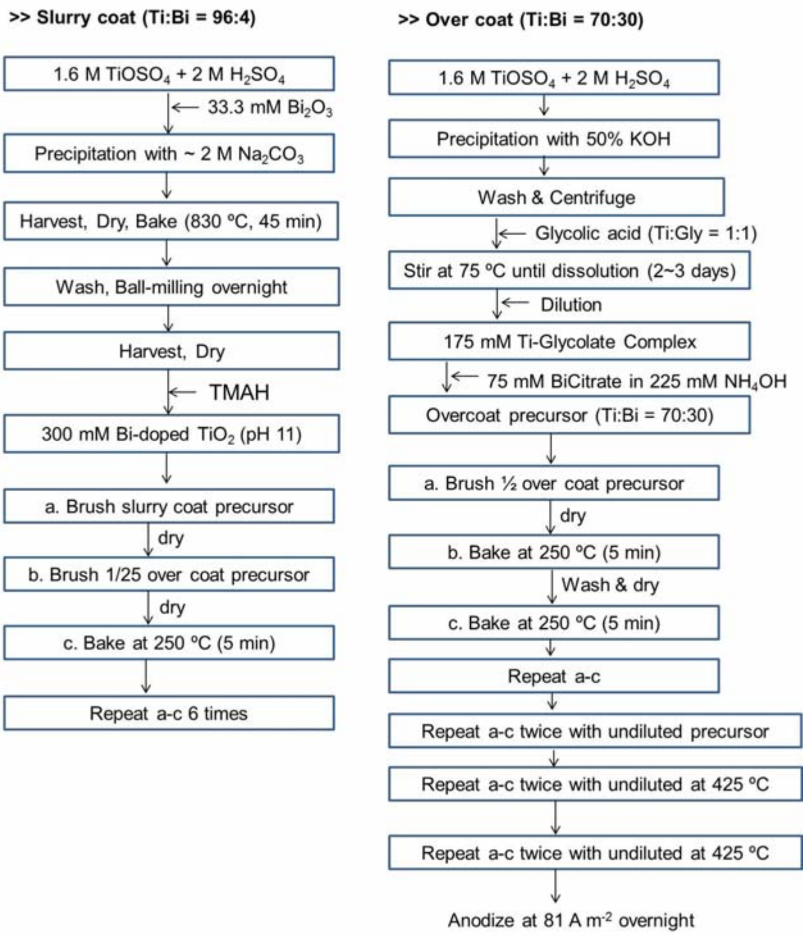


Figure 1.4. Detailed fabrication procedure for slurry coat and overcoat described in Table 1.1.[23]

1.3. OBJECTIVES AND POTENTIAL CONTRIBUTIONS OF THE THESIS

The objectives of this study are to develop a wastewater electrolysis cell which includes hetero-junction anodes as core components for potential application to toilet wastewater treatment, and to provide an underlying scientific background particularly for the redox transformation of environmental pollutants and molecular hydrogen production.

This study can be distinguished from the previous works by using bismuth doped titanium dioxide (BiO_x/TiO_2) anode, which shows reliable electrocatalytic activity and stability in long-term operation. In addition, simultaneous molecular hydrogen production along with waste treatment is another unique feature of this study, and the multi-functional approach of the electrochemical system can be denoted as wastewater electrolysis cell. In the electrochemical wastewater treatment system, the complex reaction networks involve heterogeneous and homogeneous ROS and RCS depending on the operating condition. Therefore, there has been a controversy on the primary oxidants which account for the mineralization of environmental pollutants. While the previous reports generally infer the existence of various reactive oxidants based on the cell voltage, this study employs potentiostatic electrolysis with precise monitoring of anodic potential and ohmic loss. The experimental approach of this study allows more plausible explanations for the role of various oxidants in comparison with their thermodynamic redox potentials. Comprehensive environmental analyses coupled together with kinetic models are expected to provide in-depth knowledge related with various redox reactions mediated by the chloride ion present in human waste.

1.4. THESIS OVERVIEW

This thesis consists of the following six chapters. The overall composition of the thesis is illustrated in Figure 1.5.

- Chapter 1 – Introduction
- Chapter 2 – Urea degradation by electrochemically generated reactive chlorine species: Products and reaction pathways
- Chapter 3 – Effects of anodic potential and chloride ion on overall reactivity in electrochemical reactors designed for solar-powered wastewater treatment
- Chapter 4 – Electrochemical treatment of human waste coupled with molecular hydrogen production
- Chapter 5 – $Bi_xTi_{1-x}O_z$ functionalized hetero-junction anode with an enhanced reactive chlorine generation efficiency in dilute aqueous solutions
- Chapter 6 – Outlook for the future

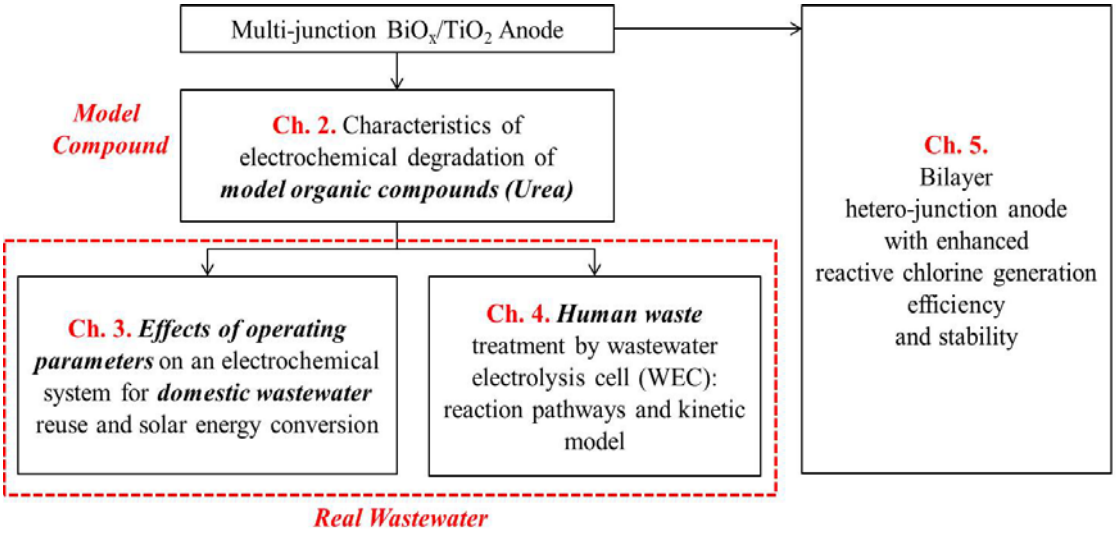


Figure 1.5. Overall composition of this thesis

1.5. REFERENCES

(1) *UN-water global annual assessment of sanitation and drinking-water (GLAAS) 2012 report: the challenge of extending and sustaining services*; World Health Organization: Switzerland, 2012.; http://www.un.org/waterforlifedecade/pdf/glaas_report_2012_eng.pdf.

(2) Grant, S. B.; Saphores, J. D.; Feldman, D. L.; Hamilton, A. J.; Fletcher, T. D.; Cook, P. L. M.; Stewardson, M.; Sanders, B. F.; Levin, L. A.; Ambrose, R. F.; Deletic, A.; Brown, R.; Jiang, S. C.; Rosso, D.; Cooper, W. J.; Marusic, I. Taking the "Waste" out of "Wastewater" for human water security and ecosystem sustainability. *Science* **2012,** *337* (6095), 681-686.

(3) *Onsite wastewater treatment systems manual*; EPA/625/R-00/008; United States Environmental Protection Agency: Washington, D.C., 2002.; nepis.epa.gov/Adobe/PDF/P100FS7K.pdf.

(4) *Guidelines for water reuse*; EPA/600/R-12/618; United States Environmental Protection Agency: Washington, D.C., 2012.; nepis.epa.gov/Adobe/PDF/P100FS7K.pdf.

(5) *Clean Watersheds Needs Survey: Report to Congress*; EPA-832-R-10-002; United States Environmental Protection Agency: Washington, DC., 2008.; water.epa.gov/scitech/datait/databases/cwns/upload/cwns2008rtc.pdf.

(6) *The Fuel Cell Technologies Program Multi-Year Research, Development, and Demonstration Plan*; United States Department of Energy: Washington, D.C., 2012.; http://energy.gov/eere/fuelcells/fuel-cell-technologies-office-multi-year-research-development-and-demonstration-plan.

(7) *2013 Annual Progress Report: DOE Hydrogen and Fuel Cells Program*; DOE/CO-102013-4260; United States Department of Energy: Washington, D.C., 2013.; http://www.hydrogen.energy.gov/annual_progress13.html.

(8) Park, H.; Vecitis, C. D.; Hoffmann, M. R. Electrochemical water splitting coupled with organic compound oxidation: The role of active chlorine species. *J Phys Chem C* **2009,** *113* (18), 7935-7945.

(9) Park, H.; Vecitis, C. D.; Hoffmann, M. R. Solar-powered electrochemical oxidation of organic compounds coupled with the cathodic production of molecular hydrogen. *J Phys Chem A* **2008,** *112* (33), 7616-7626.

(10) Cho, K.; Qu, Y.; Kwon, D.; Zhang, H.; Cid, C. A.; Aryanfar, A.; Hoffmann, M. R. Effects of anodic potential and chloride ion on overall reactivity in electrochemical reactors designed for solar-powered wastewater treatment. *Environ Sci Technol* **2014,** *48* (4), 2377-2384.

(11) Cho, K.; Kwon, D.; Hoffmann, M. R. Electrochemical treatment of human waste coupled with molecular hydrogen production. *Rsc Adv* **2014,** *4* (9), 4596-4608.

(12) *Energy Demands on Water Resources: Report to Congress on the Interdependency of Energy and Water*; United States Department of Energy: Washington D.C., 2006.

(13) Panizza, M.; Cerisola, G. Direct and mediated anodic oxidation of organic pollutants. *Chem Rev* **2009,** *109* (12), 6541-6569.

(14) Martinez-Huitle, C. A.; Ferro, S. Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes. *Chem Soc Rev* **2006,** *35* (12), 1324-1340.

(15) Chaplin, B. P. Critical review of electrochemical advanced oxidation processes for water treatment applications. *Environ Sci-Proc Imp* **2014,** *16* (6), 1182-1203.

(16) Park, H.; Choo, K.; Park, H.; Choi, J.; Hoffmann, M. R. Electrochemical oxidation and microfiltration of municipal wastewater with simultaneous hydrogen production: Influence of organic and particulate matter. *Chemical Engineering Journal* **2013,** *215-216* (15), 802-810.

(17) Park, H.; Vecitis, C. D.; Choi, W.; Weres, O.; Hoffmann, M. R. Solar-powered production of molecular hydrogen from water. *J Phys Chem C* **2008,** *112* (4), 885-889.

(18) Choi, J.; Qu, Y.; Hoffmann, M. R. SnO_2, IrO_2, Ta_2O_5, Bi_2O_3, and TiO_2 nanoparticle anodes: electrochemical oxidation coupled with the cathodic reduction of water to yield molecular H_2. *J Nanopart Res* **2012,** *14* (8).

(19) Comninellis, C. Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste-water treatment. *Electrochim Acta* **1994,** *39* (11-12), 1857-1862.

(20) Trasatti, S. Electrocatalysis in the anodic evolution of oxygen and chlorine. *Electrochim Acta* **1984,** *29* (11), 1503-1512.

(21) Rossmeisl, J.; Qu, Z. W.; Zhu, H.; Kroes, G. J.; Norskov, J. K. Electrolysis of water on oxide surfaces. *J Electroanal Chem* **2007,** *607* (1-2), 83-89.

(22) Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q. X.; Santori, E. A.; Lewis, N. S. Solar water splitting cells. *Chem Rev* **2010,** *110* (11), 6446-6473.

(23) Weres, O. Electrode with surface comprising oxides of titanium and bismuth and water purification process using this electrode. U.S. Patent 7,494,583 B2, Feb. 24, 2009.

(24) Park, H.; Bak, A.; Ahn, Y. Y.; Choi, J.; Hoffmannn, M. R. Photoelectrochemical performance of multi-layered BiO_x-TiO_2/Ti electrodes for degradation of phenol and production of molecular hydrogen in water. *J Hazard Mater* **2012,** *211*, 47-54.

(25) Kim, J.; Choi, W. J. K.; Choi, J.; Hoffmann, M. R.; Park, H. Electrolysis of urea and urine for solar hydrogen. *Catal Today* **2013,** *199*, 2-7.

(26) Kim, J.; Kwon, D.; Kim, K.; Hoffmann, M. R. Electrochemical production of hydrogen coupled with the oxidation of arsenite. *Environ Sci Technol* **2014,** *48* (3), 2059-2066.