INCREASING EFFICIENCY IN PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

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ABSTRACT

Photoelectrochemical hydrogen production promises to be a renewable, clean, and efficient way of storing the sun's energy for use in hydrogen-powered fuel cells. We use p-type $Ga_{51}In_{49}P$ semiconductor (henceforth as $GaInP_2$) to absorb solar energy and produce a photocurrent. When the semiconductor is immersed in water, the photocurrent can break down water into hydrogen and oxygen. However, before the $GaInP_2$ can produce hydrogen and oxygen, the conduction band and the Fermi level of the semiconductor must overlap the water redox potentials. In an unmodified system, the conduction band and Fermi level of $GaInP_2$ do not overlap the water redox potentials. When light shines on the semiconductor, electrons build up on the surface, shifting the bandedges and Fermi level further away from overlap of the water redox potentials. We report on surface treatments with metallated porphyrins and transition metals that suppress bandedge migration and allow bandedge overlap to occur. Coating ruthenium octaethylporphyrin carbonyl (RuOEP CO) on the $GaInP_2$ surface shifted bandedges in the positive direction by 270 mV on average, allowing the bandedges to frequently overlap the water redox potentials. Coating the $GaInP_2$ surface with $RuCl_3$ catalyzed charge transfer from the semiconductor to the water, lessening bandedge migration under light irradiation. Future work will focus on the long-term surface stability of these new treatments and quantitative applications of porphyrins.

INTRODUCTION

Current methods of energy production have substantial limitations. The pervasive use of fossil fuels creates large amounts of pollution and poses a threat to both human and ecosystem health. As demonstrated by recent fluctuations in energy prices, the United States has little control over significant portions of its energy supply. Hydrogen fuel is a leading contender to solve these energy problems.

Our work focuses on devising a domestic, renewable, and nonpolluting system for producing hydrogen. The hydrogen-production system consists of a semiconductor working electrode and a platinum counter electrode immersed in an aqueous electrolyte. When the semiconductor is irradiated with light more energetic than its bandgap, electrons in the valence band are excited into the conduction band. The excited electrons generate a photocurrent, splitting water into hydrogen at the semiconductor surface and oxygen at the platinum electrode surface.

For direct photoelectrochemical decomposition of water to occur, the hydrogen-production system must meet several requirements. First, the distance between the conduction band and the Fermi level of the semiconductor must be larger than the redox potential of water. At 25 ºC, the redox potential of water is 1.23 eV. A cathodic overpotential of 24 meV and an anodic overpotential of 96 meV are typical values for water electrolysis at a photocurrent of 20 mA/cm^2 (Khaselev et al., 2001). Therefore, water has an effective redox potential of 1.3-1.4 eV. The semiconductor must have a bandgap of at least 1.5 eV to split water.

Second, the semiconductor bandedges must overlap the conduction band and the Fermi level. The semiconductor's conduction band must be higher in energy than the water reduction potential so that the reduction of water will be energetically favorable. Similarly, the semiconductor's Fermi level must be lower in energy than the water oxidation potential so that the oxidation of water will be energetically favorable.

Third, charge transfer from the semiconductor surface to the water must occur quickly. If electrons build up on the surface of the semiconductor, they will shift the bandedges and Fermi level in a negative direction. Additionally, charge build-up on the semiconductor surface can destabilize the surface and allow the semiconductor to decay. Methods have been devised to partially catalyze charge transfer (Bansal et al., 2000).

Finally, the semiconductor must be stable during photoelectrolysis conditions in water. Inert semiconductors – such as TiO_2, $KTaO_2$, ZrO_2, and SiC – have too large a bandgap to collect a significant portion of the solar spectrum. Unfortunately, many semiconductors with smaller bandgaps are unstable under photoelectrolysis conditions. Recently, $GaInP_2$ was identified as one of the few semiconductors with an ideal bandgap that is moderately stable during photoelectrolysis (Khaselev et al., 1998).

P-type $GaInP_2$ has a bandgap of 1.8-1.9 eV, ideal for splitting water (Kocha et al., 1994). However, the conduction band and Fermi level are 300-450 meV too negative to overlap the water redox potentials when overpotentials are taken into account. Additionally, $GaInP_2$ does not catalyze charge transfer well. This research focuses on correcting these problems by modifying the inner Helmholtz layer. Previous research has shown that adsorbing organic molecules onto the $GaInP_2$ surface can shift bandedges (Kocha et al., 1995, August), while adsorbing transition metals

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(particularly Ru and Rh) can partially catalyze charge transfer (Bansal et al., 2000). With the hope of combining these effects, we studied a wide range of metallated porphyrins.

In this paper, we report on our results using capacitance-voltage and current-voltage measurements. We performed kinetics studies to determine charge catalysis on those porphyrins that succeeded in shifting band edges in the positive direction. We also combined porphyrin treatments with transition metals to bolster charge transfer kinetics.

MATERIALS AND METHODS

We used all chemicals as received. The chemicals included H_2SO_4 (J. T. Baker), HNO_3 (J. T. Baker) and dichloroethane (DCE) (Aldrich). The porphyrins used in this study were manufactured by Midcentury and are listed in Table 1. All porphyrins were made to 0.1 mM in DCE. Phthalate buffer and carbonate buffer (pH 4 and 10) (Beckman), Hydrion buffers (pH 2 - 12) (Metrepak) and dilute sulfuric acid were the electrolytes in our three-electrode cell. A 0.010 M $RuCl_3$ (Strem) solution in pH 1.5 HCl was used from a previous study (Bansal et al., 2000). We also used a platinum sol (colloid size ranging from 50 - 100 Å) made by refluxing hydrogen hexachloroplatinate hydrate (Aldrich) with citric acid.

Our materials included zinc-doped 3 μm thick p-type $Ga_{.51}In_{.49}P$ epilayers (henceforth, $GaInP_2$). It was grown by atmospheric-pressure metal organic chemical vapor deposition (MOCVD) epitaxy on zinc-doped GaAs substrates approximately 350 μm thick and misoriented from the (100) surface by 2° toward (110). A growth temperature of 700 °C and growth rate of 4.4 μm/h were used (Kurtz et al., 1992). The carrier concentration in the sulfuric acid-etched $GaInP_2$ layer was (5-7) x 10^{16} cm^{-3}. Electrodes were made from the $GaInP_2$ using a previously published technique (Bansal et al., 2000). Exposed surfaces of the electrodes ranged from 0.02 to 0.13 cm^2. Prior to use, the electrode was etched in concentrated sulfuric acid, rinsed in deionized water, and dried in nitrogen gas. After drying, the electrode surface was chemically modified using the methods discussed below: porphyrin drop evaporation, porphyrin spray application, and metal-ion dip-coating.

Using the porphyrin drop evaporation method, we placed a 50 μL drop of the 0.1 mM porphyrin solution in DCE on the surface of the $GaInP_2$ electrode. The DCE evaporated under a stream of nitrogen gas, leaving a layer of the porphyrin on the electrode surface.

In the porphyrin spray application, we used a chromatography sprayer to apply 0.1 mM porphyrin solutions in DCE to the surface of the $GaInP_2$ electrode. The spraying occurred in half-second pulses to allow the DCE to evaporate before spraying again. The spray time ranged from 5 to 80 seconds.

We performed metal-ion chemisorption using a previously published method (Bansal et al., 2000). Electrodes were immersed in the $RuCl_3$ solution for 60 seconds and in the Pt sol for 1 - 3 hours. In combination treatments of porphyrins with metal ions, the metal ion was adsorbed first. Then, a layer of the porphyrin was adsorbed.

Capacitance-voltage (C-V) and current-voltage (I-V) measurements were performed in a three-electrode cell. The setup consisted of a $GaInP_2$ semiconductor, a platinum mesh counter electrode (~2 cm^2) and a saturated calomel reference electrode (SCE). We irradiated the $GaInP_2$ electrode with a Cole-Parmer 41500-50 Fiber Optic Illuminator housing a 150 W quartz halogen bulb. Data were collected using a Solartron 1286 Electrochemical Interface connected to a Solartron SI 1260 Impedance/Gain-Phase Analyzer. We used ZPlot 2 and ZView 2 software to collect and analyze C-V data and CorrWare 2 and CorrView to collect and analyze I-V data. Measurements were made at a frequency of 10 kHz with a 10 mV rms amplitude. Scan rates ranged from 5 to 10 mV/s. For measurements in the dark, data was collected between –1.0 V and +0.2 V vs. SCE and the current range was automatically selected by ZPlot. For measurements in the light, the negative end of the scan range extended to –2.2 V vs. SCE and the current range was fixed at 0.2 or 2.0 mA, depending on the photocurrent.

In agreement with a previous study, we successfully modeled the $GaInP_2$/water system as a series RC circuit (Kocha et al., 1996). In this model, R_S is the series resistance of the circuit and C_{SC} is the capacitance of the space charge region (see Figure 1). By modeling the space charge layer of the semiconductor in this manner, we were able to determine the flatband potential using Mott-Schottky plots.

RESULTS

Table 1 displays the flatband potentials for drop-evaporated porphyrin treatments and drop-evaporated porphyrins combined with transition metals. The porphyrins were drop-evaporated onto a new $GaInP_2$ electrode after initial characterization and etching
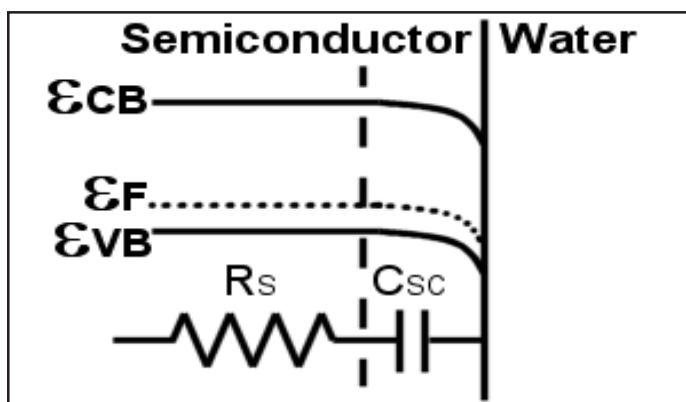

Figure 1. Modeling a p-type semiconductor as a series resistor and capacitor. R_S = System resistance. C_{SC} = Semiconductor capacitance.

Table 1. Results of Mott-Schottky plots in pH 4 buffer.
OEP = Octaethylporphyrin, TPP = Tetraphenylporphyrin.
V_{FB} = Flatband potential, which is a measure of the bandedge positions.

Treatment	V_{FB}	Standard Deviation
CoOEP	0.117	0.017
CoTPP	0.121	0.053
FeOEP Cl	0.102	0.058
FeTPP Cl	0.100	0.043
Pt sol + RuOEP CO	0.481	0.012
RhOEP Cl	0.138	0.082
$RuCl_3$ + RuOEP CO	0.488	0.207
RuOEP CO	0.266	0.182
RuTPP CO	0.161	0.091

with concentrated sulfuric acid. The testing was done in pH 4 buffer. Repeated scans were performed in the cathodic and anodic directions to determine the stability of the surface treatment. The results in Table 1 are the average of all of the scans in both cathodic and anodic directions. All of the porphyrins show a statistically significant shift in flatband potentials, with the ruthenated porphyrins showing the greatest shift. The bandedges shifted into overlap conditions about 20% of the time with the RuOEP CO treatment. Both of the combination treatments of RuOEP CO with either Pt sol or $RuCl_3$ showed substantial shifts in bandedge position. These combination treatments allowed overlap of the water redox potentials to occur in the dark

Figures 2 and 3 show the results of charge transfer catalysis testing in pH 4 buffer. The porphyrins were applied to new electrodes. At higher light intensities, the potential scan range was shifted negative as the flatband potential shifted negative. Of the molecules tested, only the RuOEP CO shifted the conduction band and Fermi level into the correct positions under light irradiation.
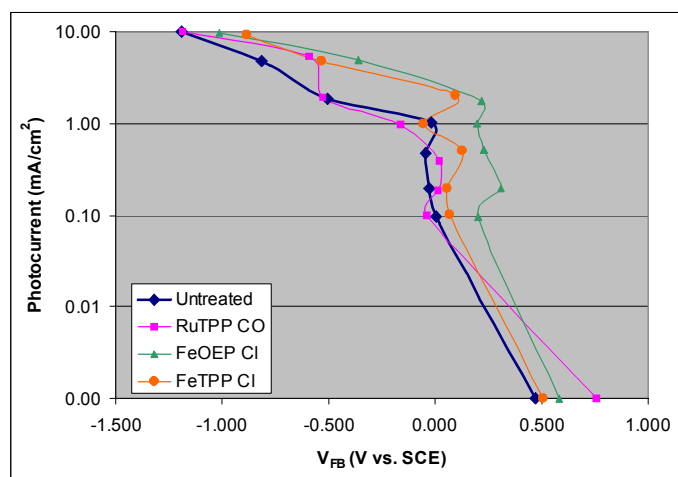
Figure 4 demonstrates the effect of a combined porphyrin-metal ion treatment. Dip-coating a RuOEP CO-treated electrode with $RuCl_3$ vastly improves charge catalysis properties up to a photocurrent of 1 mA/cm^2. Testing is in pH 4 buffer.

Figure 5 compares the drop-evaporation method with the spray application method. The drop-evaporation method is capable of adsorbing greater amounts of porphyrins on the GaInP$_2$ surface than the spray application method.

Displayed in Figure 6 are the effects of testing in a range of pHs on a treated and untreated electrode. The most substantial shift in flatband potential occurs at pH 4, hence the testing at that pH.

Figure 7 shows the possible desorption of CoTPP in pH 4 buffer over a period of days. The flatband potential decreases by 50 mV after 23 hours and by another 25 mV after another 70 hours.

Table 2 shows the doping densities in an untreated electrode (and hole concentrations in a treated electrode). The combination metal-RuOEP CO treatments show a statistically significant decrease in doping density as compared with untreated electrodes.
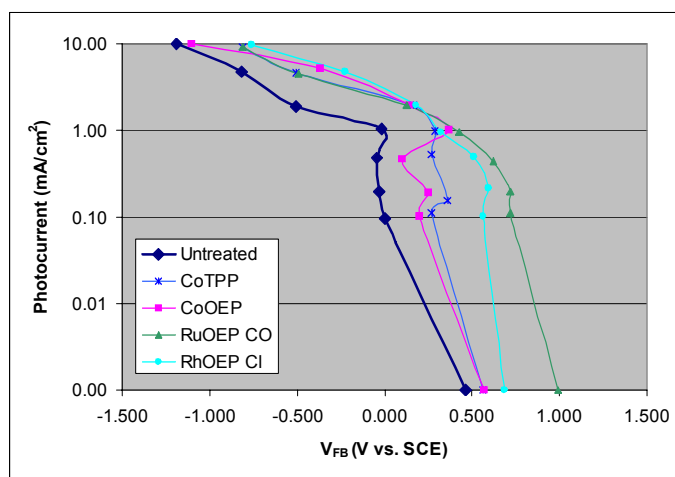

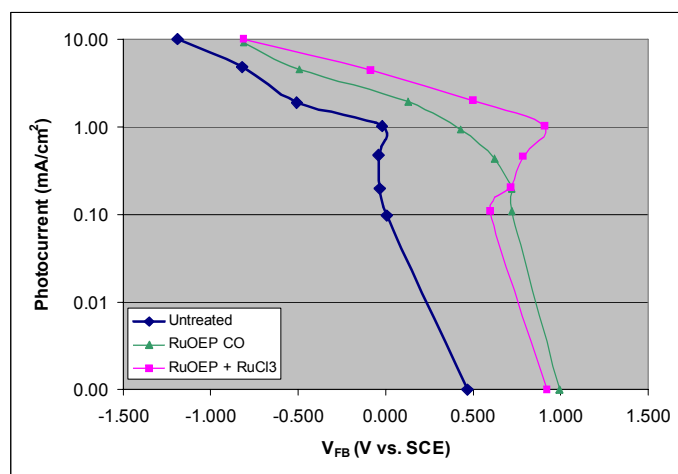**Figure 2**. Charge transfer catalysis testing under increasing light intensities. Testing performed in pH 4 buffer. V_{FB} = Flatband potential, which is a measure of the bandedge positions.

Figure 3. Charge transfer catalysis testing under increasing light intensities. Testing performed in pH 4 buffer.

Figure 4. Charge transfer catalysis of various treatments. Testing performed in pH 4 buffer.
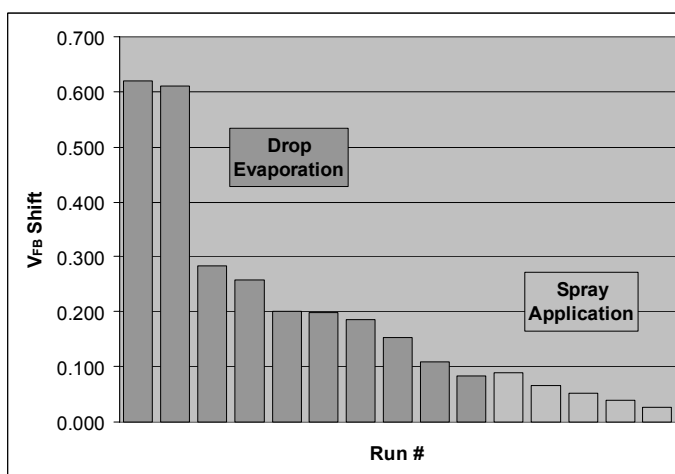

Figure 5. Comparison of drop evaporation and spray application of RuOEP CO. The magnitude of the shift in bandedge position correlates well with the thickness of the RuOEP CO application. V_{FB} Shift is the change in flatband potential between a treated and untreated electrode.

DISCUSSION AND CONCLUSION

In order to photoelectrochemically split water into hydrogen and oxygen, the conduction bandedge must be higher in energy than the water reduction potential and the Fermi level must be lower in energy than the water oxidation potential. Our survey of porphyrins as bandedge-shifting agents showed that RuOEP CO shifts bandedges a substantial amount in the correct direction. When combining the RuOEP CO with a transition metal, such as ruthenium or platinum, the bandedge shift increases.

The large standard deviation in the flatband potential is caused by two factors. The first is the varying application thickness. As we increase the porphyrin application thickness on the $GaInP_2$ surface, the shift in flatband potential increases (see Figure 5). With the RuOEP CO drop-evaporation treatment, the flatband potential shifted as much as 600 mV when a large amount of porphyrin was applied to an electrode with a small surface area. Conversely, the flatband potential shifted as little as 100 mV when a small amount of porphyrin was drop-evaporated onto a larger surface area. The RuOEP spray application applied only minute amounts of the porphyrin to the electrode surface, causing only slight shifts in flatband potentials. The flatband potential shifted as little as 26 mV when we sprayed the electrode for 5 seconds, and as much as 90 mV when we sprayed the electrode for 80 seconds.

The second factor causing a large standard deviation in the flatband potential is the electrode age. After several etchings in concentrated sulfuric acid, the response to porphyrin treatments decays. We hypothesize that the decrease in response is due to the decrease in surface defects (and an increase in the surface smoothness) of the $GaInP_2$ as the electrode is etched more. A previous study showed that the photoluminescence of $GaInP_2$ increases as the etch time increases (Kocha et al., 1995). In fact, the photoluminescence increases the fastest when etched in concentrated sulfuric acid, as compared with the other etchants studied. The increase in photoluminescence is indicative of fewer surface states, suggesting that the $GaInP_2$ has a cleaner surface with fewer defects. As the number of surface states and defects decrease, there is less opportunity for the porphyrin to attach to the surface. Thus, with less porphyrin attached to the surface, the bandedge shift substantially decreases.

We also performed testing with HNO_3 as the etchant. Nitric acid etches the surface at a much faster rate, creating a relatively rough $GaInP_2$ surface. This allows more porphyrin to attach to the surface, regardless of etching time. In accordance with prediction, etching in HNO_3 increased the repeatability of flatband potential measurements and decreased the decay in response as the electrode was used more.

Testing of charge catalysis at the GaInP2 surface showed that the RuOEP CO and the RhOEP Cl catalyze charge transfer up to a photocurrent of 0.2 mA/cm2. However, the conduction band and Fermi level are not in water-splitting position in either of these cases. However, adding a platinum sol or ruthenium metal to the surface substantially increased flatband potential and charge catalysis. A charge catalysis study was performed on an electrode treated with ruthenium metal and RuOEP CO (as shown in Figure 4). This treatment placed bandedges in a water-splitting position up to a photocurrent of 1 mA/cm^2, or about one tenth of the intensity of the sun.

Testing was performed almost entirely in pH 4 buffer because we saw the greatest shifts in flatband potential with porphyrin

Table 2. Doping densities (N_D) for untreated (etched) and treated electrodes.

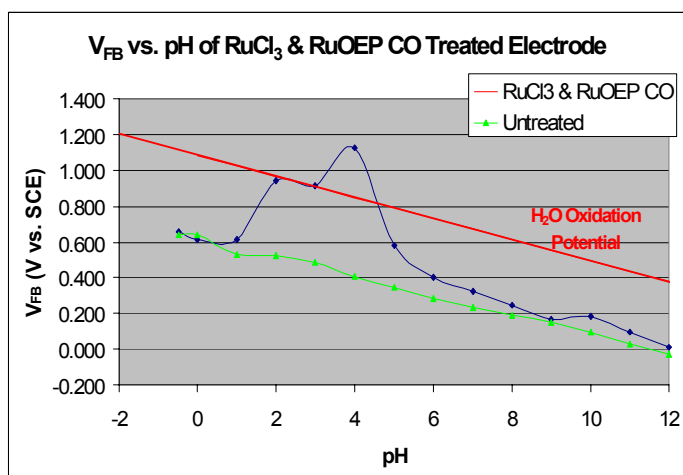|	Etched	Porphyrins Only	Metals Only	RuOEP CO	$RuCl_3$ + RuOEP	Pt sol + RuOEP
N_D	5.89E+16	5.17E+16	5.56E+16	5.29E+16	4.27E+16	3.36E+16
Std. Dev.	1.39E+16	1.48E+16	1.02E+16	2.08E+16	9.23E+15	1.60E+16

Figure 6. The effect of pH on flatband potential on an untreated and $RuCl_3$ + RuOEP CO-treated electrode.
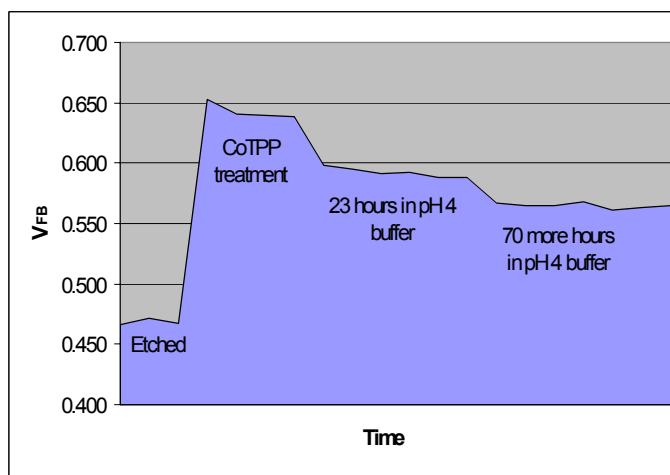

Figure 7. Possible desorption of CoTPP after immersing a CoTPP-modified electrode in pH 4 buffer for extended lengths of time.

treatments at that pH (see Figure 6). However, the short circuit current (SSC) is substantially improved at lower pHs. Further testing will focus on improving porphyrin response at lower pHs so as to improve the photocurrent and water-splitting efficiency.

Another area for improvement is the stability of the porphyrin on the $GaInP_2$ surface. As shown in Figure 7, CoTPP desorbs from surface after extended periods in pH 4 buffer. Further work will be performed on improving the porphyrin stability. Increasing the surface roughness or covalently attaching the porphyrins to the $GaInP_2$ surface are options worth exploring.

An interesting result of the metal-RuOEP CO combination treatments was the decrease in hole concentration in the $GaInP_2$. This suggests that the metal-RuOEP CO treatment donates electrons into the semiconductor. The role of electron donating porphyrins in decreasing the doping density and shifting the flatband potential in a positive direction is yet to be studied.

In this research, we have substantially improved the prospects of $GaInP_2$ for photoelectrochemical hydrogen production. With further work, we will hopefully develop a system capable of splitting water powered by the sun's light. Our research has shifted flatband potentials into water-splitting condition and catalyzed charge transfer. We have the goal of further catalyzing charge transfer to meet our goal of creating a sun-powered hydrogen production system. In this work, we have come closer to our goal of replacing fossil fuels with a clean fuel, decreasing our dependence on foreign energy sources, improving livability within cities, and creating a healthier environment for the earth's ecosystems.

ACKNOWLEDGMENTS

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