Diamond photochemistry with visible light

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ABSTRACT

This project demonstrates diamond-based photochemistry using visible light. Diamond has the unique property of having a widely tunable electrochemical surface, with hydrogen terminated diamond known to have a negative electron affinity. This property enables the emission of electrons from the surface of the diamond. In this work, electrons are emitted into an aqueous solution, creating a reservoir of free, solvated electrons, that can be used to initiate energy intensive chemical reactions. We demonstrate that visible light incident on thin films of diamond on molybdenum substrates can be used to reduce nitrogen gas to ammonia via the photogenerated electrons.

Solar energy has the potential to power not only electrical systems, but also provide energy inputs for industrial chemical reactions. Using photocatalysis to split water with visible light has seen significant progress in recent decades, and may soon be a source of commercial hydrogen [1]. However, less progress has been made on using photochemistry for high energy reactions, such as the reduction of nitrogen gas to ammonia or the reduction of carbon dioxide.

The reduction of atmospheric nitrogen to ammonia for industrial or fertilizing applications is energy intensive, due to the triple nitrogen-nitrogen bond, which is one of the strongest molecular bonds in nature at 9.8 eV/bond. The production of ammonia from nitrogen in industry is typically based on the Haber-Bosch reaction, which uses high pressure and temperature to break the nitrogen bonds. Similarly, the reduction of carbon dioxide with solar energy could enable recycling carbon dioxide into useful products. Driving this reaction with visible light, as will be explained below.

Several studies have utilized the negative electron affinity of diamond for photochemistry [7] or vacuum emission studies [8,9]. In the photochemistry experiments, intrinsic or boron-doped diamond excited with ultraviolet light generates solvated electrons for the reduction of nitrogen gas to ammonia [7] or carbon dioxide gas to CO [10]. In this work, we choose to use a hydrogen-terminated, nitrogen-doped diamond layer on a conducting substrate to enable photochemistry with visible light, as will be explained below.

Compared to intrinsic or p-type diamond, n-type diamond is especially effective as an electron emitter. The vacuum emission profile of thin films of hydrogen-terminated nitrogen-doped (n-type) diamond on molybdenum has been extensively studied in prior work [8,9] (the same material is the subject of this work). These studies show that diamond plays a key role in enabling electron emission: bare molybdenum substrates emit no observable photoemission or thermionic current at energies below molybdenum’s work function (4.5 eV), but emission does occur from hydrogen-terminated, n-type diamond coated molybdenum at photon energies as low as 1.5 eV. In other words, the diamond coating produces a much lower effective work function. In this work, we demonstrate the utility of these films for photochemistry applications.

These films are anticipated to produce the band structure shown in Fig. 2, which enables visible light to be absorbed via a metal-assisted absorption process (similar to that explored in the vacuum emission work [8]). Electrons then migrate to the diamond surface where they are ejected into the aqueous solution. Based on the vacuum emission study, the Schottky barrier at the diamond-metal interface does not appreciably impact the emission [8]. This surface also potentially reduces recombination due to a lack of mobile holes [9], and the n-type...
semiconductor/metal interface presumably generates a downward bending conduction band which pushes electrons away from the molybdenum towards the water interface.

The first experiment we describe uses a hydrogen-terminated single crystal diamond plate, illuminated with ultraviolet light; this experiment confirms our results are consistent with prior studies. Next, we describe the results of illuminating the nitrogen-doped thin film diamond with ultraviolet or visible light. In all cases, we observe the formation of ammonia.

In the first experiment, a single crystal diamond plate is first hydrogenated in a hydrogen plasma. This plate is suspended in water, and illuminated with an ultraviolet light source, a Newport Hg medium pressure 100 W arc lamp filtered through a 212 nm bandpass filter. A 212 filter was chosen, as this corresponds to a photon energy of 5.8 eV, which is greater than the bandgap energy of diamond, 5.5 eV. The measured output through the filter is 1.8 mW. Nitrogen (high purity N\textsubscript{2} gas) is continuously bubbled through the water. Five samples of the water, each 5 mL, are removed after 30 min for analysis of the ammonia concentration, using Flow Injection Analysis (FIA) at ASU Goldwater Environmental Laboratory (Lachat QC8000). As seen in Table 1, the hydrogen-terminated diamond indeed generates ammonia, at a concentration of 0.027 N mg/L, and a standard error of 0.001 N mg/L. Five measurements of the concentration are averaged for this value and used to calculate the standard error. These results are qualitatively consistent with those previously reported in the literature [7]; however, due to the difference in experimental set ups, we are unable to directly compare concentration yields.

The second experiment utilizes thin diamond film on molybdenum for ultraviolet-driven photochemistry. The diamond film is a nitrogen-doped nanocrystalline diamond film, grown on a molybdenum substrate by microwave enhanced chemical vapor deposition. The nature of the deposition results in a film with hydrogen termination. Because this sample is grown on a conducting substrate, it is possible to use an H-cell configuration to maintain charge neutrality. A schematic of this experiment is shown in Fig. 3. Briefly, the diamond sample is placed in a waterproof sample holder with a window that exposes only the diamond surface (not the molybdenum back surface). This is submerged in water, which is contained in a quartz tube. Nitrogen is continuously bubbled into the water for the duration of the experiment. A salt bridge, made of agar gel soaked with magnesium chloride, connects this chamber to a second chamber, which contains an aqueous solution of potassium iodine; in this solution hangs a platinum foil which is connected via a copper wire to the molybdenum substrate of the diamond film. As described previously, ammonia concentration is measured with FIA for five samples. The results of this experiment show an ammonia concentration of 0.05 mgN/L, with a standard error of 0.003 mgN/L.

In the third experiment, the ultraviolet lamp is replaced with a green laser pointer (wavelength 532 nm), with a power output of 2 mW.

In all cases, we observe the formation of ammonia.

![Fig. 1. Valence band maximum and conduction band minimum levels of common semiconductors and hydrogen-terminated diamond, shown vs the free vacuum energy level. Also shown are the energy levels of select redox reactions. The conduction band minimum of hydrogen-terminated diamond lies far above the conduction band minimum of most semiconductors, enabling it to be used as a source of solvated electrons that can drive high energy reactions.](image1)

![Fig. 2. Band schematic of the molybdenum substrate and N-doped ultrananocrystalline diamond film. The light is incident on the diamond side, which then gets absorbed in the diamond or molybdenum. Due to the negative electron affinity of hydrogen-terminated diamond, electrons are ejected from the diamond surface. Visible light and ultraviolet photons are capable of generating free solvated electrons for use in reduction reactions.](image2)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photon energy (eV)</td>
<td>5.8</td>
<td>5.8</td>
<td>2.3</td>
</tr>
<tr>
<td>Ammonia concentration (mgN/L)</td>
<td>0.027</td>
<td>0.05</td>
<td>0.021</td>
</tr>
<tr>
<td>Standard error (mgN/L)</td>
<td>0.001</td>
<td>0.003</td>
<td>0.0003</td>
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</table>
Once free electrons are ejected from the conduction band of diamond into the solution, they can be thought of as solvated electrons. Multiple reactions are then required to generate the ammonia [7]. The intermediate chemical steps of this process are difficult to measure, but are thought to involve the following [11]. Water is spontaneously dissociated into \( H^+ \) and \( OH^- \), which provides a supply of free protons. The solvated electrons react with these protons to form neutral hydrogen atoms which in turn react with the nitrogen gas to form \( N_2H \). This is the most high energy intermediate in the process. \( N_2H \), by the spontaneous addition of \( H^- \), will form \( NH_3 \).

\[
\begin{align*}
    e^-_{(aq)} + H^+ & \rightarrow H \\
    H + N_2 & \rightarrow N_2H \\
    N_2H + H & \rightarrow N_2H_2
\end{align*}
\]

In conclusion, we demonstrate that visible light can be used to drive the high energy reduction reaction of nitrogen to ammonia. It is also worth noting that the energy barrier to form \( NH_3 \) from \( N_2 \) is 3.1 eV, which is greater than the energy of the green laser photons used in the visible light experiment; however, it is achieved by a multi-step process. The generation of ammonia from nitrogen gas with visible light is a promising result and will be explored further.

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References