



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 into 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 reduction with semiconductor-based photo catalysis is a challenge, since the single electron reduction from CO_2 to CO_2^- sits at just 2.3 eV under the vacuum energy level, too high for the conduction band minimum of most semiconductors [2]. The energy levels of these reduction reactions and the conduction band minimum and valence band maximum for select semiconductors are shown in Fig. 1. As can be seen, the conduction band minimums of most semiconductors are far too low to drive the reduction of carbon dioxide or nitrogen. In contrast, the conduction band of hydrogen-terminated diamond is remarkably high, making it a promising material for this application.

The extreme conduction band position of diamond is due to diamond's remarkable property of having an electron affinity that is highly sensitive to the surface treatment. Surface termination with hydrogen, fluorine, oxygen, magnesium or other adsorbates can change the electron affinity level of diamond by an astonishing 5 eV. Fluorine-terminated diamond has an electron affinity at the high end, of 2.5 eV [3]. At

the other extreme, magnesium or hydrogen terminated diamond results in a negative electron affinity, of -2 eV for magnesium-terminated diamond [4], and -1.3 eV for hydrogen-terminated diamond [5,6].

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 workfunction. 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

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H-terminated Diamond

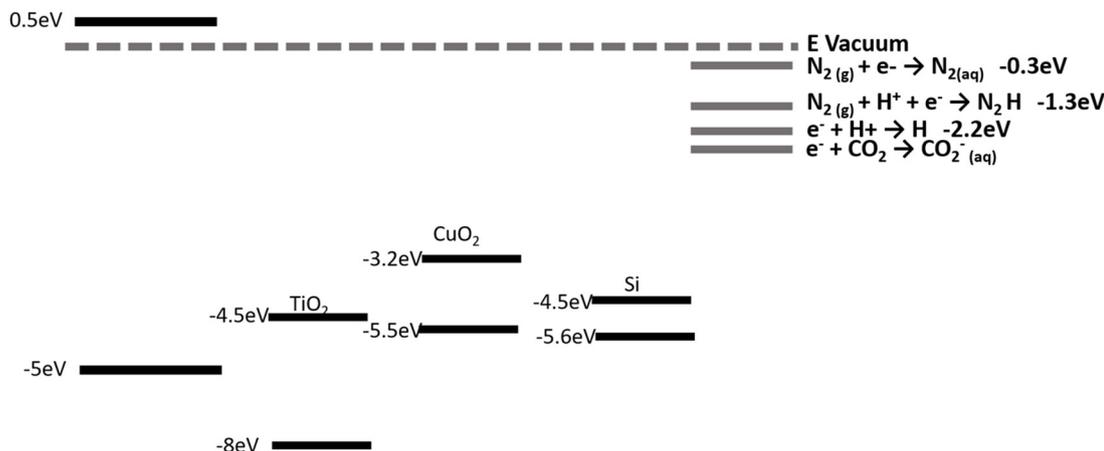


Fig. 1. Valence band maximum and conduction band minimum levels of common semiconductors and hydrogen-terminated diamond, shown vs the free vacuum energy level. Also shown are the energy levels of select redox reactions. The conduction band minimum of hydrogen-terminated diamond lies far above the conduction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

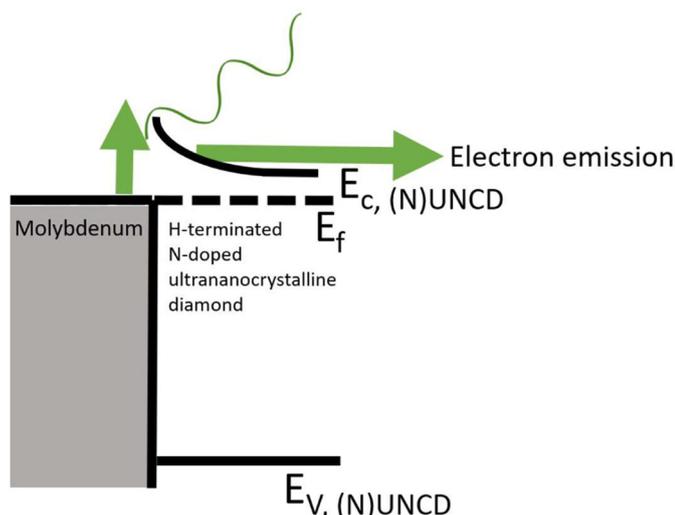


Fig. 2. Band schematic of the molybdenum substrate and N-doped ultrananocrystalline diamond film. The light is incident on the diamond side, which then gets absorbed in the diamond or molybdenum. Due to the negative electron affinity of hydrogen-terminated diamond, electrons are ejected from the diamond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

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 N₂ 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

Table 1

Ammonia concentration measured via flow injection analysis for three experiments: 1) single crystal, hydrogen-terminated diamond illuminated with ultraviolet light; 2) a hydrogen-terminated, nitrogen-doped nanocrystalline diamond film grown on molybdenum and illuminated with ultraviolet light; and 3) a hydrogen-terminated, nitrogen-doped nanocrystalline diamond film grown on molybdenum and illuminated with visible light.

Experiment	1	2	3
Photon energy (eV)	5.8	5.8	2.3
Ammonia concentration (mgN/L)	0.027	0.05	0.021
Standard error (mgN/L)	0.001	0.003	0.0003

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 Nmg/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.

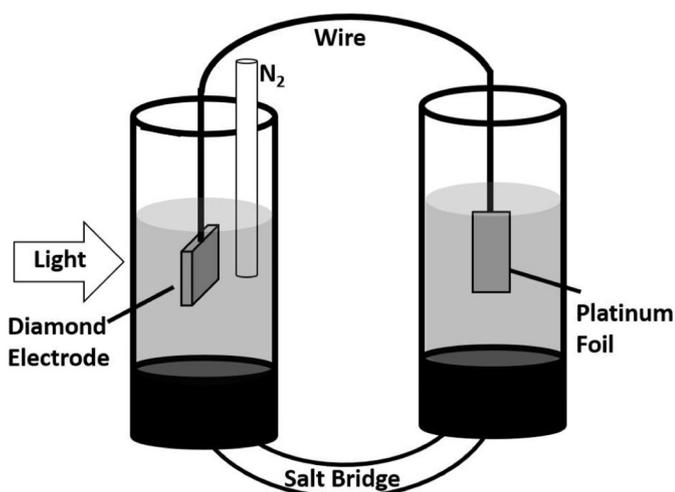


Fig. 3. Schematic of the experiment for H-cell configurations. The diamond film on the molybdenum substrate is suspended in water. A waterproof sample holder exposes just the diamond surface to water, and protects the back side of the sample from water exposure. Nitrogen gas is continuously bubbled through during the experiment. The diamond is electrically connected to a platinum foil electrode in a counter cell, which is also connected to the diamond cell via a salt bridge. In this way, charge neutrality of the diamond sample is maintained. To measure the concentration of ammonia produced by this process, samples of the aqueous solution are removed for flow injection analysis.

In all other ways, the experiment is identical to the second experiment, in that the H-cell configuration is used. We note that we use a different sample of nitrogen-doped UNCD diamond film on molybdenum for each experiment, and both samples were grown with the same technique. The result of this experiment is an ammonia concentration of 0.021 mgN/L, with a standard error of 0.0003 mgN/L.

The results from these experiments are summarized in Table 1, which gives the ammonia concentration and standard error of the measurement. All experiments use the same flow-injection analysis system. These results show that visible light is indeed able to be used to stimulate photochemistry with diamond films. For all experiments, the concentration of ammonia measured exceeds the standard error of the measurement by at least 10 times.

The electron generation process and band structure are shown schematically in Fig. 2. When visible light is used to simulate photochemistry, the yield is approximately half that for when ultraviolet light is used, despite a similar power output of the source at the wavelengths used. Taking into account the wavelengths of the sources to normalize the photon energies, the green laser has about 2.8 times the photon flux as the ultraviolet lamp. Since the ammonia production can be thought of as a proxy for solvated electron generation [7,11], the results imply that the electron emission current increases with the energy of the incident photons. This is qualitatively consistent with vacuum emission work [8] and theoretical free electron emission [12] models which describe the emission probability as depending on the difference between an electron's energy (which is increased by the photon absorption) and the effective work function of the surface.

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 .



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

- [1] S. Y. Tee, K. Y. Win, W. S. Teo, L.-D. Koh, S. Liu, C. P. Teng, and M.-Y. Han, "Recent progress in energy-driven water splitting," *Advanced Science*, vol. 4, no. 5, p. 1600337.
- [2] H. Schwarz, R. Dodson, Reduction potentials of CO_2 and the alcohol radicals, *J. Phys. Chem.* 93 (1) (1989) 409–414.
- [3] K.J. Rietwyk, S. Wong, L. Cao, K. O'Donnell, L. Ley, A. Wee, C. Pakes, Work function and electron affinity of the fluorine-terminated (100) diamond surface, *Appl. Phys. Lett.* 102 (9) (2013) 091604.
- [4] K. M. M.T. Edmonds O'Donnell, A. Tadich, L. Thomsen, A. Stacey, A. Schenk, C.I. Pakes, L. Ley, Extremely high negative electron affinity of diamond via magnesium adsorption, *Phys. Rev. B* 92 (3) (2015) 035303.
- [5] J. Cui, J. Ristein, L. Ley, Low-threshold electron emission from diamond, *Phys. Rev. B* 60 (23) (1999) 16135.
- [6] F. Maier, J. Ristein, L. Ley, Electron affinity of plasma-hydrogenated and chemically oxidized diamond (100) surfaces, *Phys. Rev. B* 64 (16) (2001) 165411.
- [7] D. Zhu, L. Zhang, R.E. Ruther, R.J. Hamers, Photo-illuminated diamond as a solid-state source of solvated electrons in water for nitrogen reduction, *Nat. Mater.* 12 (9) (2013) 836.
- [8] T. Sun, F.A. Koeck, C. Zhu, R.J. Nemanich, Combined visible light photo-emission and low temperature thermionic emission from nitrogen doped diamond films, *Appl. Phys. Lett.* 99 (20) (2011) 202101.
- [9] T. Sun, F.A. Koeck, A. Rezikyan, M.M. Treacy, R.J. Nemanich, Thermally enhanced photoinduced electron emission from nitrogen-doped diamond films on silicon substrates, *Phys. Rev. B* 90 (12) (2014) 121302.
- [10] L. Zhang, D. Zhu, G.M. Nathanson, R.J. Hamers, Selective photoelectrochemical reduction of aqueous CO_2 to CO by solvated electrons, *Angew. Chem. Int. Ed.* 53 (37) (2014) 9746–9750.
- [11] J.A. Bandy, D. Zhu, R.J. Hamers, Photocatalytic reduction of nitrogen to ammonia on diamond thin films grown on metallic substrates, *Diam. Relat. Mater.* 64 (2016) 34–41.
- [12] J.W. Gadzuk, E. Plummer, Field emission energy distribution (feed), *Rev. Mod. Phys.* 45 (3) (1973) 487.