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# The Interplay of Corrosion and Photocatalysis During Non-Aqueous Benzylamine Oxidation on Cadmium Sulfide

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**ABSTRACT:** The photo(electro)chemical properties of bulk, nanowire, and chemical bath deposits of cadmium sulfide (CdS) for benzylamine oxidation to *N*-benzylidenebenzylamine (*N*-BB) in acetonitrile have been evaluated as a model for the activity and stability of CdS toward selective organic oxidations. CdS photocatalysts selectively deliver *N*-BB at rates ranging from 5 - 26 mM h<sup>-1</sup>. Although CdS is a capable photocatalyst, SEM imaging and XPS analysis reveal significant morphological and compositional changes to the particles upon photolysis in benzylamine. These surface changes and surface sulfide oxidation are accompanied by Cd<sup>2+</sup> leaching and hydrogen sulfide evolution, highlighting both redox and acid-base pathways of non-aqueous CdS corrosion. All facets of corrosion have been linked directly with amine reactivity, as the CdS particles are unaffected by substrate-free photolysis. A series of experiments using *N*,*N*-dimethylbenzylamine, 4,*N*,*N*-trimethylaniline, and ferrocene show that non-aqueous CdS corrosion is facilitated by acidic reaction intermediates opposed to photogenerated holes. Additionally, water and oxygen are essential components to corrosion, as photoelectrochemistry under dry/air-free conditions display higher and stable photocurrent density as well as material stability. Finally, CdS nanowires display improved corrosion resistance, suggesting that control of particle morphology and/or electronic structure is essential for developing novel chalcogenide photocatalysts.

## INTRODUCTION

Cadmium sulfide (CdS) represents a well-studied II-VI semiconductor with a band gap of 2.4 eV, which overlaps well with the solar spectrum.<sup>1</sup> Due to its impressive light absorbing properties, CdS powders and electrodes have been pursued for solar fuel prodution<sup>2–4</sup> and pollutant decomposition (organic dye degradation).<sup>5–7</sup> However, the main challenge for implementing CdS-based technologies is corrosion in aerated aqueous solutions.<sup>8</sup> Extensive studies have demonstrated that aqueous corrosion process may be initiated by either photogenerated holes<sup>9–12</sup> or by reactive intermediates, such as hydroxyl radicals.<sup>13,14</sup> Corrosion of CdS often results in the formation of water soluble CdSO<sub>4</sub>, surface dissolution, and loss of catalytic activity.

To disfavor aqueous passivation, efforts have been aimed at CdS photochemical applications in dry organic solvents. In this realm, one promising application is the selective photochemical oxidation of organic substrates,<sup>15-17</sup> in which aqueous conditions generate reactive hydroxyl radicals, leading to non-specific substrate oxidation to CO2.18-20 In order to promote selective oxidations as well as to disfavor catalyst passivation, the photochemical activity of CdS for the oxidation of electron rich benzylic amine<sup>21,22</sup> and alcohol<sup>22–27</sup> substrates in acetonitrile and trifluorotoluene solvents have been investigated. While high selectivity is observed, catalyst passivation is still apparent even in non-aqueous solvents.<sup>23-26</sup> Catalyst corrosion is identified through a loss of photocurrent, a morphological comparison by scanning electron microscopy, or detecting leached Cd<sup>2+</sup> ions by atomic absorption spectroscopy. Although past studies have not speculated on the nature of CdS corrosion, the assumption is that aqueous and non-aqueous passivation operate similarly. Compared to the extensive work on the driving forces behind aqueous CdS

corrosion,<sup>8–11</sup> there are no experimental details elucidating non-aqueous corrosion processes.

To probe the driving forces behind non-aqueous CdS corrosion, we employ the photo(electro)chemical oxidative coupling of benzylamine (BnNH<sub>2</sub>) to N-benzylidenebenzylamine (N-BB) as a test reaction. We start here because the photochemical oxidation of BnNH2 to N-BB has benchmarked a variety of photocatalysts,  $^{16,18}$  including CdS,  $^{21,22}$  BiVO<sub>4</sub>,  $^{28-30}$  Nb<sub>2</sub>O<sub>5</sub>,  $^{31-33}$  and TiO<sub>2</sub> $^{34-36}$  owing to the electron-rich amine functionality. Bulk, nanowire, and chemically deposited CdS powders and electrodes have been characterized by scanning electron microscopy and X-ray photoelectron spectroscopy before and after photolysis. Leached Cd<sup>2+</sup> ions into the solution have been determined using inductively coupled plasmaoptical emission spectroscopy (ICP-OES). Through these analytical techniques we establish that the corrosion of CdS in organic solvents is highly dependent upon the substrate identity. This insight into non-aqueous CdS decomposition pathways will aid in the design of new inorganic light absorbing platforms and target reactions.

#### **EXPERIMENTAL SECTION**

**Materials and Methods.** Cadmium sulfide bulk particles (99.995 %, trace metals basis), all solvents, and trimethylsilyl cyanide were purchased from Sigma Aldrich. All amines were purchased from Acros Organics; benzylamine and 4,*N*,*N*-trimethylaniline were further purified by vacuum distillation over zinc dust and potassium hydroxide, respectively, then subsequently stored over molecular sieves. Tetrabutylammonium hexafluorophosphate (> 98 %) was purchased from TCI America and purified by recrystallization from ethanol. Ferrocene was purchased from Sigma Aldrich and was recrystallized from hexanes prior to use: all other reagents were used without further purification.

**Preparation of CdS Nanowires.** CdS Nanowires (NWs) were prepared by adopting a previously reported hydrothermal synthesis.<sup>37</sup> Cadmium(III)nitrate tetrahydrate (751 mg, 2.4 mmol), thiourea (556 mg, 7.3 mol), and ethylenediamine (13 mL) were mixed in a 18 mL PTFE lined autoclave. The vessel was sealed and was warmed to 160 °C at a ramp rate of 10 °C/min, and was then held at 160 °C for two days. After cooling naturally to room temperature, the mixture was centrifuged at 4000 rpm for 5 minutes to isolate a bright yellow powder. This powder was washed three times with Millipore (MQ) water (3 × 15 mL), and then dried overnight in a vacuum oven.

Chemical Bath Deposition of CdS. CdS was deposited onto fluorine-doped tin oxide (FTO) substrates by adopting a previously reported procedure.<sup>38</sup> Slides of FTO  $(1 \times 4 \text{ cm})$ were rinsed and sonicated sequentially with acetone, MQ water, and acetone. These cleaned slides were fastened to the side of a beaker (FTO side facing the center, and the bottom of the FTO nearly touching the beaker bottom) containing a MQ water (25 mL) solution of cadmium sulfate (522 mg, 2.5 mmol), and warmed to 70 °C. While stirring the cadmium sulfate solution, ammonium hydroxide (28-30%, 10 mL) was added drop-wise, resulting in the evolution of a white vapor. In a separate beaker, thiourea (190 mg, 2.5 mmol) was dissolved in MQ water (25 mL). The thiourea solution was slowly added to the stirring cadmium sulfate, ammonium hydroxide mixture. The submerged FTO plates were left in the stirring solution for 15 minutes, which became a cloudy yellow suspension by the end of the deposition. The CdS-functionalized FTO electrodes were then removed from the beaker to be washed and sonicated with MO water. Any deposits that formed on the glass side of the FTO were removed by gently rubbing that side with a Kim wipe wet with 1 M hydrochloric acid followed by copious MQ water rinsing. The CdS-functionalized FTO slides were annealed in a tube furnace with flowing nitrogen at 300 °C for 30 minutes with a 10 °C/min ramp rate. After annealing, the CdS films were clear and bright vellow. Photoelectrodes were prepared from these deposits by attaching an exposed portion of the FTO slide to a copper wire using silver print (Jameco Electronics). After drying for 12 hours, the exposed wire was inserted into a Pyrex tube (length 10 cm, 3 mm ID, 4 mm OD). The exposed wire and silver paint were masked using epoxy (Loctite EA 1C, "Epoxi-patch Hysol", VWR) to give electrodes with a surface area of 1 cm<sup>2</sup>. The epoxy was allowed to cure at room temperature for a minimum of 24 hours prior to use in any experiments.

**Material Characterization.** Brunauer–Emmett–Teller (BET) surface area measurements were obtained using a NOVA4200e from Quantachrome surface area analyzer. Scanning electron microscopy (SEM) images were obtained from either a JEOL-7800FLV FE SEM or a Zeiss LEO 1455VP tungsten filament SEM at an accelerating voltage of 3 kV and working distance of 5 mm. UV-Vis spectra were recorded using a Cary 5000 spectrophotometer (Agilent) equipped with an external diffuse reflectance accessory. Spectra were recorded in reflectance mode and transformed mathematically into the Kubelka–Munk function. Powder X-ray diffraction (PXRD) data was collected on a Panalytical Empyrean diffractometer at a power of 1.8 kW (45kV, 40 mA) with Cu K $\alpha$  ( $\lambda$  = 1.5418 nm) radiation. The diffractometer was a X'Celerator Scientific, a position-sensitive 1D detector

and was equipped with a Bragg-Brentano<sup>HD</sup> X-ray optic delivering only K $\alpha$  radiation. Patterns were collected with a sampling step of 0.017 ° and a scan rate of 6 °/min while spinning at a rate of 0.25 Hz. X-ray photoelectron spectroscopy (XPS) was conducted using a Kratos Axis Ultra X-ray Photoelectron Spectrometer. The X-rays used were monochromatic Al K $\alpha$  X-rays (1486.7 eV). All data collected while the analysis chamber pressure was ~  $1 \times 10^{-9}$  torr. The charging effects of the semiconducting substrates were compensated using an electron flood gun. High-resolution spectra were collected at a pass energy of 20 and a step size of 0.1 eV. XPS spectra interpretation was performed using Casa XPS with a Shirley-type baseline to calculate peak areas. Binding energies were calibrated by positioning the adventitious carbon signal at 248.8 eV.

Photochemistry. CdS (bulk or nanowire, 10 mg) was suspended in acetonitrile (2 mL) in a borosilicate test tube (13  $\times$ 100 mm) equipped with a stir bar. The concentration of any substrate employed was 250 mM. The test tube was capped with a septum and vented using a needle. The reaction mixture was placed in a blue LED photolysis reactor composed of LED strips (Creative Lighting Solutions, flex LED strip 5050 High Density 12vDC, CL-FRS5050-12WP-12V) wrapped around a water jacketed beaker (Figure S1) to deliver 5-10 mW/cm<sup>2</sup> of 470 nm blue light. Substrate concentrations were measured by periodically removing an aliquot (10  $\mu$ L) from the reaction mixture and combining with a chlorobenzene standard (50 µL of a 21.6 mM standard) and acetonitrile (940 uL). The samples were analyzed on either a Shimadzu OP-2010 GC/MS or Thermo Fisher Trace 13-10 gas chromatograph equipped with a capillary column and a FID detector. Quantification was enabled by the integration ratio of the analyte and chlorobenzene signals in relation to an obtained calibration curve. For dry photochemistry experiments, the samples were prepared inside of a nitrogen glove box using acetonitrile that was distilled over calcium hydride and stored over molecular sieves. The sealed samples were brought outside of the glove box and saturated with dry air.

**Leached Cadmium Detection.** The post photolysis solutions were analyzed for leached cadmium via inductively coupled plasma optical emission spectrometry (ICP-OES) using a Perkin-Elmer Optima 2000DV. Samples were prepared by removal of the volatile organics via rotary evaporation, digestion in a 5 % nitric acid solution, followed by filtration through a syringe filter (VWR). Samples were referenced to a yttrium internal standard (1 ppm) and concentrations of cadmium were determined via a series of standard cadmium solution prepared from a 1000 ppm Cd reference solution (Sigma Aldrich).

**Hydrogen Sulfide Detection.** A bismuth hydroxide hydrogen sulfide (H<sub>2</sub>S) chemical sensor was employed to verify the production of H<sub>2</sub>S during photochemical amine oxidation.<sup>39</sup> Bismuth(III) nitrate pentahydrate (100 mg) was suspended in acetone (10 mL) and sonicated for 10 minutes. The resulting white suspension was filtered through celite to give a clear colorless solution that was syringed (100  $\mu$ L) onto the center of a Kim wipe twice, with a minute delay between each dose to allow for acetone evaporation. Once dry, a sodium hydroxide solution (1 M, 100  $\mu$ L) was dropped onto the same spot, generating the bismuth(III) hydroxide sensor. While wet, the

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Table 1. Metrics for Photochemical Catalysis and Corrosion of CdS Particles Under the Specified Conditions

Conditions	Conversion / %	Rate / mM h <sup>-1</sup>	Solvated [Cd <sup>2+</sup> ] / ppm	Surface SO <sub>4</sub> <sup>2-</sup> / % <sup>a</sup>
1. CdS, BnNH <sub>2</sub> , LED	$63 \pm 14$	$5 \pm 1$	$2.0 \pm 0.03$	95
2. BnNH <sub>2</sub> , LED	0	0	N/A	N/A
<b>3.</b> CdS, LED	N/A	N/A	0	14
4. CdS, BnNH <sub>2</sub>	0	0	0	5
5. CdS, BnNH <sub>2</sub> , LED, N <sub>2</sub>	0	0	0	6
6. CdS, BnNH2, LED, Dry	< 0.1	N/A	0	17
7. CdS, BnNH <sub>2</sub> , <sup><i>t</i></sup> BuOH, LED	$60 \pm 11$	$3.0 \pm 0.1$	$1.6\pm0.07$	83
8. CdS, BnNMe2, LED	0	0	$4.7\pm0.6$	19
9. CdS, TMA, LED	0	0	0	18
10. CdS, Fc, LED	N/A	N/A	0	16
11. CdS NWs, BnNH2, LED	100	$26 \pm 5$	$5\pm0.9$	55

<sup>a</sup>Calculated as the percentage of total surface sulfur that exists as sulfate; all HR S2p XPS spectra are provided in Figure S11.

Kimwipe was affixed to the top of the test tubes and photochemistry was performed as described above. Intermittently, MQ water was used to gently wet the Kim wipe to improve the gas sorption. The response of this sensor was verified by affixing a Bi-loaded Kim wipe onto a vial containing bulk CdS and 6 M hydrochloric acid; upon exposure to the H<sub>2</sub>S vapors, a yellow spot formed on the Kim wipe, indicative of bismuth(III) sulfide formation (Figure S2).

Photoelectrochemistry. Chemical bath deposits of CdS on FTO substrates were used as the working electrode, a polished silver wire (CH instruments) as the reference, and a platinum mesh (CH instruments) as the counter electrode in a custom build two-compartment photoelectrochemical cell (Figure S3). All electrochemical solutions contained 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> supporting electrolyte. A Nafion (NRE-212, Fuel Cell Earth) membrane was used to separate the anode and cathode compartments. The photoelectrodes were back illumined using the same LEDs described above for the photochemical experiments (5 mW/cm<sup>2</sup> of 470 nm blue light). Linear sweep voltammetry (LSV) and bulk electrolysis in the dark and under illumination were conducted using a CH instruments electrochemical workstation 1000A. LSVs were performed on quiescent solutions while the electrolyte was vigorously stirred during bulk electrolysis All potentials are reported versus the ferrocenium/ ferrocene (Fc<sup>+/ $\bar{0}$ </sup>) couple by acquiring cyclic voltammograms of ferrocene in the electrolytes used (Figure S4). The solution-phase products were analyzed by gas chromatography, by first concentrating the catholyte and precipitating the electrolyte using diethyl ether. The electrolyte was filtered through celite and washed with diethyl ether. The organic filtrates were combined and concentrated in vacuo to a yellow oil. This oil was combined with a chlorobenzene standard (50 µL of a 21.6 mM standard) and diluted to 1 mL. For the dry and air-free photoelectrochemistry, the cell was assembled inside of a nitrogen glove box using dry solvents and reagents. Activated molecular sieves (4A, Alfa Aesar) were added to the anode compartment prior to brining the sealed cell outside of the glove box. To maintain an air-free environment during photoelectrolysis a gentle stream of nitrogen was introduced into the anode compartment.

### **RESULTS AND DISCUSSION**

The photochemical activity and stability of bulk cadmium sulfide was assessed in 250 mM solutions of benzylamine (BnNH<sub>2</sub>) in acetonitrile illumined by  $5 - 10 \text{ mW/cm}^2 470 \text{ nm}$ blue LEDs for two days. The concentrations of BnNH2 starting material and the coupled product, N-benzylidenebenzylamine (N-BB) were quantified periodically using gas chromatography (GC). Analysis of the products by GC reveals N-BB to be the only product formed under these conditions (Figure S5) at a rate of  $5 \pm 1 \text{ mM h}^{-1}$  (Table 1, entry 1; Figure S6). Repeating the experiment in the absence of any photocatalyst material yields no conversion, highlighting the heterogeneous catalytic activity of CdS (Table 1, entry 2). By measuring the photochemical rate as a function of concentration, we have confirmed that the catalysis is first order in both CdS and BnNH<sub>2</sub> (Figure S7). During the extended illumination of bulk CdS particles necessary for full BnNH<sub>2</sub> conversion, the first order constant changes from  $1.6 \times 10^2 \,\text{h}^{-1}$  to  $6.9 \times 10^{-3} \,\text{h}^{-1}$  (Figure S8). We attribute the decreased activity of bulk particles throughout long photolysis experiments to photocatalyst corrosion.

Passivation of CdS catalysts by forming CdSO<sub>4</sub> that leaches Cd<sup>2+</sup> into solution has been well established for aqueous photochemistry.9-12 Two mechanisms of CdS corrosion are often evoked: acidic dissolution and sulfide oxidation. Under acidic conditions, as predicted by the cadmium sulfide Pourbaix diagram,<sup>40</sup> sulfide is thermodynamically unstable relative to hydrogen sulfide (H<sub>2</sub>S); upon gaseous H<sub>2</sub>S evolution, Cd<sup>2+</sup> leaches out into the aqueous electrolyte.41,42 Alternatively, sulfide may be oxidized to sulfate either by photogenerated holes<sup>9-12</sup> or by hydroxyl radicals formed during water oxidation.<sup>13,43</sup> Non-aqueous examples of CdS corrosion have also been reported during benzyl alcohol oxidations, but with no discussion of how the non-aqueous solvent affects the corrosion mechanism.<sup>23–25</sup> In order to determine the extent of CdS corrosion and its role in non-aqueous photochemical transformations, we quantified Cd<sup>2+</sup> dissolution as well as the surface composition and morphology under a variety of photolysis conditions. ICP-OES analysis detects  $2.0 \pm 0.3$  ppm dissolved Cd<sup>2+</sup> in the solution after photolysis. SEM imaging revealed the bulk CdS to contain large, smooth particles that are 20 -50 µm in size (Figure 1a). XPS of this



**Figure 1.** SEM images and HR-S2p XPS spectra of CdS (a,b), post  $BnNH_2$  photolysis (c,d), and a substrate-free post-photolysis control experiment (e,f). The blue components of the XPS fit represent sulfide and the red components represent sulfate.

material displayed one major sulfur signal in the S2*p* high-resolution (HR) region at  ${}^{2}P_{3/2} = 161.8$  eV, with a small (6 % of all surface sulfur) amount of sulfate at  ${}^{2}P_{3/2} = 168.8$  eV (Figure 1b). The smooth pre-photolysis surface predominately comprised of sulfide, is contrasted with the highly textured surface post photolysis that is 95 % sulfate (Figure 1c,d). Sulfate assignment was based on cadmium sulfate standard spectra (Figure S9). Although Cd<sup>2+</sup> reduction to metallic Cd by photogenerated electrons has been reported on other CdS materials,<sup>12,14</sup> energy dispersive X-ray mapping of the post photolysis particles shows no Cd localization and HR Cd3*d* XPS shows no shift in the binding energy of the  ${}^{2}D$  components or any deviations from a Cd:S atomic ratio of one (Figure S10).

To understand the nature of catalyst corrosion during BnNH<sub>2</sub> photolysis, we carried out a control experiment in which we illuminated a substrate-free CdS suspension in acetonitrile. To our surprise, the pre- and post-photolysis materials were morphologically indistinguishable; only a small particle size decrease due to the mechanical force of the stir bar is observed (Figure 1e). In addition to the lack of morphological change, XPS revealed only a minor increase in surface sulfate from 6 % to 14 % (Figure 1f), contrasted with the 95 % sulfate present after BnNH<sub>2</sub> photolysis (Figure 1d). Finally, ICP-OES detected no leached Cd<sup>2+</sup> in the post photolysis solution (Table 1, entry 3). The lack of corrosion upon amine-free photolysis suggests that non-aqueous CdS passivation occurs though a substrate-mediated pathway, rather than by photogenerated holes.

To probe the interplay between amine oxidation and CdS corrosion, we performed a variety of additional control exper-

iments in which we react BnNH<sub>2</sub> substrate on CdS in the absence of either light, oxygen, or water. Under conditions where any one of the listed variables was removed, no conversion of BnNH<sub>2</sub> was detected, nor was any evidence for corrosion detected by ICP-OES or XPS (Table 1, entries 4 - 6, Figure S11). The lack of catalysis under either dark, nitrogen, or dry conditions highlights: 1) the photochemical nature of catalysis; 2) that oxygen serves as the sacrificial oxidant for this system; 3) that, water is mechanistically involved through a hydrolysis step as has been previously proposed, respectively.<sup>35,44</sup> Interestingly, under dry conditions, a small increase in surface sulfate is observed from 6.3 to 17 %, similar to that seen under substrate-free conditions, further demonstrating the slow nature of sulfide to sulfate oxidation, by photogenerated holes.

The control experiments described above begin to link oxidative amine-coupling catalysis with both Cd<sup>2+</sup> leaching and sulfide oxidation. To understand how reaction intermediates may be playing a part in these corrosion events, we propose the amine oxidation mechanism suggested by others and shown in Scheme 1.35,44 Principally, one-electron amine oxidation generates a nitrogen-centered radical cation (Scheme 1, reaction 1). This oxidized intermediate contains acidic  $\alpha$ hydrogens in comparison to native BnNH2.44,45 Deprotonation of the amine cation radical yields a neutral carbon-centered radical intermediate (Scheme 1, reaction 2), which following additional oxidation and deprotonation steps, produces an imine (Scheme 1, reaction 3). In the presence of water, this imine hydrolyzes to benzaldehyde (Scheme 1, reaction 4), which undergoes a facile condensation reaction with BnNH<sub>2</sub>, yielding N-BB (Scheme 1, reaction 5).

## Scheme 1. Proposed photochemical oxidation mechanism



We suspect that oxidized BnNH<sub>2</sub> intermediates, such as the amine radical cation may serve as an oxidizing agent to corrode sulfide to sulfate, as the hydroxyl radical does in aqueous solutions.13,43 The BnNH2-mediated corrosion of CdS is thermodynamically allowed as the BnNH2 standard reduction potential (0.9 V vs. NHE)<sup>46</sup> is sufficiently positive to oxidize CdS (0.3 V vs. NHE).<sup>47</sup> Similar amine redox mediators have been used in oxidative organic electrosynthesis, where an electrochemically generated amine radical cation performs homogenous oxidation chemistry.<sup>48,49</sup> We propose that the amine-radical cation serves as a similar mediator for nonaqueous sulfide oxidation as shown in Figure 2. CdS photogenerated hole corrosion is slow, demonstrated by the control experiments discussed above. In addition to serving as an oxidizing agent, the acidic benzylic hydrogens formed upon photolysis may serve as a source of protons for H<sub>2</sub>S evolution, resulting in the observed Cd<sup>2+</sup> leaching. We have confirmed the production of H<sub>2</sub>S during amine oxidation using a bismuth hydroxide chemical sensor (Figure S2).<sup>39</sup> To ensure that hydroxyl radicals ('OH) are not involved in either the observed catalysis or corrosion, we illuminated BnNH2



Figure 2. Benzylamine-mediated oxidation of sulfide to sulfate.

solutions with the 'OH scavenger 'BuOH.<sup>13,50</sup> No change in *N*-BB production, Cd<sup>2+</sup> leaching, or sulfate formationdemonstrates that trace water oxidation to 'OH is not a significant contributor to the observed chemistries (Table 1, entry 7; Figure S11).

To elucidate the role of substrate in sulfide oxidation and  $Cd^{2+}$  leaching, we performed photolysis experiments on N.Ndimethylbenzylamine (BnNMe2). This tertiary amine is incapable of producing a coupled product, yet reversible amine oxidation may still occur to generate reactive intermediates akin to those of BnNH<sub>2</sub>. Illuminating BnNMe<sub>2</sub> in the presence of CdS consumes a small amount of amine  $(14 \pm 6 \%)$ , but yields no detectable products. While ICP-OES suggests Cd<sup>2+</sup> leaching  $(4.7 \pm 0.6 \text{ ppm})$ , the surface sulfur composition appears unchanged (Table 1, entry 8; Figure S11). Given that tertiary radicals are stabilized compared to primary ones, we propose that BnNMe2 radical cations are not sufficiently reactive to corrode sulfide. Through a series of LSVs, we have confirmed that the tertiary amine/radical cation couple is ~300 mV more negative than that of BnNH<sub>2</sub> (Figure S12). Instead, the stabilized radical provides protons from its  $\alpha$ -hydrogens, leading to the observed Cd<sup>2+</sup> leaching with concomitant H<sub>2</sub>S evolution (Figure S2). The resulting deprotonated species is likely prone to decomposition, accounting for the reduced post photolysis BnNMe2 concentration. Homogeneous photocatalysts (e.g. [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>) have successfully oxidized similar tertiary amines, to give unique reactions involving oxidized intermediates trapped by an appropriate nucleophile or electrophile.<sup>51-54</sup> In light of these studies, we propose that iminium cation formation (tertiary analogue to Scheme 1, reaction 3) occurs upon tertiary amine oxidation and may be responsible for BnNMe<sub>2</sub>-enabled Cd<sup>2+</sup> leaching. To verify iminium cation formation, we carried out photochemical trapping experiments using trimethylsilyl cyanide (Equation 1). Cyanide nucleophiles have been used to trap similar iminium cation intermediates from tertiary amine oxidations.55,56 We were pleased to find that illuminating BnNMe2 with Me3SiCN produced the expected  $\alpha$ -cyanated species (68 ± 7 % conversion, Figure S13), confirming the formation of reactive intermediates upon BnNMe<sub>2</sub> photolysis.



Upon establishing a link between amine radical reactivity and sulfide oxidation, we next sought to confirm that Cd<sup>2</sup> leaching is due to sulfide protonation by acidic  $\alpha$ -hydrogens. 4,N,N-Trimethylaniline (TMA) was chosen as an appropriate substrate, as it does not possess  $\alpha$ -hydrogens, and single electron oxidation yields a resonance-stabilized benzylic radical with oxidizing power similar to that of BnNMe<sub>2</sub> (Figure S12). In agreement with the formation of stabilized oxidation intermediates without  $\alpha$ -hydrogens, the CdS morphology and composition are unaffected by TMA photolysis and no Cd<sup>2+</sup> is leached into solution (Table 1, entry 9; Figure S11). We have further demonstrated that sulfide oxidation and Cd<sup>2+</sup> leaching is substrate dependent by performing photolysis experiments in ferrocene (Fc) solutions. After two days of illumination, the Fc solution was found to be nearly completely bleached, indicating metal centered Fc/Fc<sup>+</sup> oxidation followed by irreversible cyclopentadienyl oxidation (Figure S14).<sup>57</sup> Analogous experiments performed in the absence of CdS confirm that the oxidative decomposition of Fc is a heterogeneous photochemical process. Although CdS oxidation has occurred in these solutions, no Cd<sup>2+</sup> leaching or any significant increase in surface sulfate concentration was detected (Table 1, entry 10; Figure S11). Based on the lack of Cd<sup>2+</sup> leaching and sulfide oxidation detected upon illuminating CdS in substratefree acetonitrile solution or in ferrocene solutions, we conclude that non-aqueous CdS stability is dictated by the acidity and oxidation potential of the organic radical intermediates.

To highlight how particle morphology affects radical-based corrosion processes, we investigated the activity and stability of CdS nanowires (NWs). Both the bulk particles and NWs were found to contain crystalline wurtzite-phase CdS, with comparable UV-Vis absorption spectra, and although the bulk CdS absorption displays an Urbach tail characteristic of defect-based absorption (Figure S15), Tauc analysis reveals both materials to have similar direct bandgap transitions (Figure S16).58 The CdS NWs oxidize BnNH2 to N-BB (Figure S6) at a faster rate ( $26 \pm 5 \text{ mM h}^{-1}$ , Table 1, entry 11) than bulk particles (5  $\pm$  1 mM h<sup>-1</sup>, Table 1, entry 1), as expected for the higher surface area (Figure S17). In accord with the faster rate (as the faster reaction generates more of the acidic intermediate), the CdS NW post-photolysis solutions contain a higher concentration of leached  $Cd^{2+}$  (5.0 ± 0.9 ppm) compared to solutions of bulk CdS ( $2.0 \pm 0.3$  ppm). However, while the NW data in Figure 3 show morphological and compositional evidence for corrosion, post photolysis sulfate formation is suppressed: 55 % surface sulfate for NWs, compared to 95 % for bulk particles. In addition, the first order rate constant remains unchanged through the course of NW photocatalysis (Figure S8). We surmise that for a second, slower first-order rate constant to be observed, a majority of the surface must corrode to sulfate. Indeed, by illumining bulk CdS in BnNH<sub>2</sub> for 6 - 12 hours (times within the first rate constant region) sulfate concentrations between 20 - 60 % were detected (Figure S18). Future iterations of sulfide-based photocatalysts may make use of the correlation between a stable first-order rate constant and the lack of significant corrosion as a first approximation of material stability. The decreased surface oxidation and stable rate constant suggest that the nanowire morphology disfavors amine-based corrosion. Further experiments are required to elucidate fully how the NW morphology affects corrosion; one possible explanation is that the NW defects

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**Figure 3.** SEM images and HR S2*p* XPS spectra of CdS NWs pre- (a,b) and post- BnNH<sub>2</sub> photolysis (c,d).

and band positions may be different from commercial CdS, minimizing orbital overlap between sulfide and amine radicals.

To assess the photoelectrochemical activity and stability of CdS during non-aqueous amine oxidation, CdS photoelectrodes were prepared from a chemical bath deposition procedure.<sup>38</sup> With these chemically deposited photoelectrodes, a series of linear sweep voltammograms (LSVs) was obtained in 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>N PF<sub>6</sub>) in acetonitrile solutions. As shown in Figure 4a LSVs obtained under illumination display an anodic current onset at -0.4 V vs.  $Fc^{+/0}$  (all potentials referenced to  $Fc^{+/0}$ ) that we attribute to the photoelectrochemical corrosion of sulfide. This current is not reproduced in the dark (Figure 4a), confirming that this oxidation is due to photogenerated holes. In agreement with the photochemical stability of CdS powders in the absence of substrate (vide supra) there is a ~100 mV separation between the measured open circuit potential (-0.54 V)and the anodic current onset; an additional potential is necessary for acetonitrile-based CdS corrosion to occur.

To determine the extent of corrosion during amine oxidation, a series of LSVs were recorded BnNH<sub>2</sub> solution. LSVs recorded under blue LED illumination display anodic current at -0.8 V, while the analogous dark LSVs display no current, confirming the photoelectrochemical nature of BnNH2 oxidation on CdS (Figure 4a, red traces). Amine oxidation appears to be resolved from the photocorrosion of sulfide by ~600 mV, however upon bulk photoelectrolysis either at -540 or -240 mV (Figure 4b; dashed blue and black lines, respectively) significant current loss is observed within the first five minutes. In addition to a loss in current, Figure 5 shows that the surface morphology changes significantly from flat and featureless to highly textured, while the film composition changes from largely sulfide material to one that is nearly all sulfate (80 %). These corrosion results suggest that even under photoelectrochemical conditions, amine oxidation engenders corrosion at potentials where the material would otherwise be stable.

Since both water and oxygen are involved in the oxidation of sulfide to sulfate, removing these species is expected to



**Figure 4.** LSVs obtained on CdS photoelectrodes in acetonitrile solutions of 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> with and without 0.25 M BnNH<sub>2</sub> at a scan rate of 10 mV s<sup>-1</sup>, (a). Bulk photoelectrolysis performed at the specified potential with blue LED illumination of 0.25 M BnNH<sub>2</sub> (b), the dashed data is performed under ambient conditions, while the solid data was collected in the absence of air and moisture (inert).

minimize corrosion. Dry and air free photoelectrochemistry performed at either -0.54 or -0.24 V (Figure 4b solid lines) resulted in photocurrents with significantly improved stability. Analysis of the surface morphology and composition revealed the photoelectrodes to be largely unchanged (Figure 5 e,f). Although stable photocurrents are obtained under dry and inert conditions, the Faradaic efficiency for *N*-BB generated is only ~20%. The suppressed formation of *N*-BB under these conditions may be linked to the requisite dry reaction conditions. The mechanism for BnNH<sub>2</sub> oxidation outlined in Scheme 1 requires water to hydrolyze the intermediate imine bond; under dry conditions an alternative mechanism (Scheme S1) may occur where BnNH<sub>2</sub> acts as a nucleophile towards the intermediate imine. This work is ongoing in the lab.

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**Figure 5.** SEM images and HR S2*p* XPS spectra of CdS photoelectrodes pre- (a,b), post-ambient (c,d), and post- dry/free free (e,f) BnNH<sub>2</sub> photoelectrolysis.

## CONCLUSIONS

Cadmium sulfide catalyzed photochemical and photoelectrochemical BnNH2 oxidation is accompanied by corrosion to CdSO<sub>4</sub> as well as Cd<sup>2+</sup> leaching into the photolysis solution. Through a series of amine photolysis experiments, we have identified a link between the oxidizing strength and acidity of amine radical intermediates with CdSO<sub>4</sub> formation and Cd<sup>2+</sup> leaching. The corrosion of CdS under non-aqueous conditions appears to be driven largely by choice of substrate, rather than by photogenerated holes. This is highlighted by CdS particles unaffected by illumination in acetonitrile as well as by the measured open circuit potential of photoelectrodes to be 100 mV more negative than the sulfide corrosion onset. Further, corrosion is only observed when organic radicals of sufficient reactivity are generated, as the photochemical oxidation of 4,N,N-trimethylaniline and BnNMe<sub>2</sub> does not affect sulfate formation. When Brønsted acid intermediates are formed, as in the case of BnNH2 or BnNMe2, sulfide protonation may occur to evolve H<sub>2</sub>S and leach Cd<sup>2+</sup>. Performing photoelectrochemical organic oxidations under dry and air-free conditions disfavors sulfate formation via removal of potential oxygen sources vet results in poor product selectivity. Preliminary evidence suggests that surface morphology and electronic structure has an impact on photocatalyst stability, as shown by the improved corrosion resistance of CdS NWs. These photochemical results suggest that future designs of CdS materials for organic oxidation must account for both the oxidizing power and acidity of the resulting organic radical intermediates.

#### ASSOCIATED CONTENT

**Supporting Information.** A photograph of the LED photolysis setup, images of the H<sub>2</sub>S sensor results, rate data, total ion chromatographs, SEM images, EDX maps, additional XPS data, LSV traces, UV-Vis data, XRD data, and a potential mechanism for dry BnNH<sub>2</sub> photoelectrochemical oxidation. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors.

### Notes

The authors declare no competing financial interest.

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