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Heterogeneous Photoreduction of Nitrogen to Ammonia on Tungsten Oxide

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Nitrogen was photosynthetically reduced to NH_3 with irradiated substoichiometric tungsten oxides and tungsten trioxide, WO_3. The reaction occurred with moist N_2 above WO_3 or substoichiometric WO_{3-x} or with substoichiometric tungsten oxide dispersions in N_2-saturated aqueous solutions. A decrease in the rate of NH_3 formation at WO_3 with time was attributed to tungsten bronze formation. The yields of NH_3 with WO_{3-x} and $WO_{2.96}$ were roughly proportional to time and were about 0.1 μg/h. Ammonia production for dispersions of WO_{3-x} in an aqueous phase occurred by a thermal, rather than a photochemical, reaction.

Introduction

We report here studies of the photogeneration of NH_3 from N_2 and H_2O on irradiated tungsten oxide films and dispersions. Photosynthesis of NH_3 provides an attractive application of semiconductor photoelectrochemistry for utilization of solar energy to produce useful products. Previous studies of N_2 photoreduction on semiconductors, mainly TiO_2, have appeared.[1,2] In general, these large band gap materials suffer from low yields of NH_3. The possible use of tungsten oxide materials for this purpose was suggested by a recent study of Braman et al.,[3] in which these were used as agents for the adsorption of NH_3 from the gas phase before its determination. The authors found that tubes of evaporated blue tungsten oxide filled with N_2 showed NH_3 blanks, while WO_3 did not. Photoreduction of N_2 represents a possible explanation of such blanks, and we undertook a study of various tungsten oxide preparations for this reaction. We demonstrate that substoichiometric WO_{3-x} can be used for the photoproduction of NH_3 with turnovers greater than unity.

Experimental Section

Tungsten Oxide Preparation. Table I summarizes the different films and methods of preparation. Pyrex beads and quartz tubes were pretreated for tungsten oxide coating by washing with acetone, immersing in hot 40% NaOH, washing with HNO_3, rinsing in water, and oven drying. Blue tungsten oxide (WO_{3-x}) was prepared on Pyrex beads and inside quartz tubes by vacuum deposition from a bundle of 1-mm-diameter tungsten wire (Alfa Products, 99.999%). A vacuum of approximately 0.1 Torr was maintained by leaking air or O_2 gas into the evaporation chamber. In the case of quartz tube substrates, tungsten wire was horizontally suspended in the center of the tube and heated by passing an ac current of ca. 80 A. When a thick film was necessary, cooling periods were allowed between coating intervals. Some samples were then heat-treated by passing the ac current through the tungsten wire under higher vacuum (10^{-5} Torr). Heat treatment changed the light blue color to dark blue. In the case of Pyrex bead substrates, the tube was partially filled with the beads and blue tungsten oxide was coated on them by a similar procedure. WO_3 films were prepared by annealing the WO_{3-x} films in air at 400 °C for 4 h. The resultant material was yellow.

TABLE I: Tungsten Oxide Films

film	color	preparation method
WO_{3-x}	blue	vacuum evaporation
$WO_{2.96}$	dark blue	vacuum evaporation and heating under high vacuum
WO_3	yellow	vacuum evaporation and annealing in air

Preparation of Tungsten Oxide Powders. Tungsten oxide powders were prepared by peeling off a thick tungsten oxide film, which was coated inside a Pyrex tube repeatedly in the same way, and by grinding it in an agate mortar. Pt loading on WO_{3-x} was carried out by adding WO_{3-x} powder to aqueous solutions of H_2PtCl_6 (Alfa Products). The resulting slurries were dried and reduced in flowing hydrogen at 400 °C for 4 h and then cooled to room temperature under hydrogen. The amount of loaded metal was 5 wt % of the WO_{3-x}. RuO_2-loaded (5 wt %) WO_{3-x} was prepared by grinding the mixture of WO_{3-x} powders and RuO_2 powders (Alfa Products, 99.9%) in an agate mortar.

Characterization of WO_{3-x}. X-ray diffraction measurements of the tungsten oxide films and powders were carried out with the IBM Series 1 Automated Phillips vertical scanning X-ray diffractometer fitted with diffracted beam graphite monochromator (Cu Kα). The spectral absorbance from 300 to 800 nm was measured with a spectrophotometer (Varian Instrument, Model 17 D). The surface area of WO_{3-x} was measured by a BET surface area analyzer (Micromeritics).

Photochemical Reaction—Gas Phase. The reactor was a 25-mm-o.d., 20-cm-long quartz tube that was coated with blue tungsten oxide and tungsten trioxide or was packed with blue tungsten oxide coated Pyrex beads. The reactor was irradiated with a 1400-W ozone-free Xe lamp. A 10-cm water jacket was placed between the reactor and the lamp to absorb the IR light. The intensity at the reactor was about 250 mW/cm^2. The temperature of the reactor was ca. 50 °C under irradiation. During the irradiation, H_2O-saturated N_2 gas was passed through the reactor. The N_2 gas was purified in advance by a hot copper pellet column, chromic acid solution, a NaOH solution, and finally H_2O. The effluent gas from the reactor was bubbled through a 0.1 M HCl solution to trap products. As a blank, purified N_2 gas was also bubbled through 0.1 M HCl which bypassed the reactor. NH_3 was determined by Nessler's method.[4] N_2H_4 was determined spectrophotometrically.[5]

Photochemical Reaction—Aqueous Phase. WO_{3-x} powders were dispersed in 50 mL of water in a Pyrex cylindrical reactor. The water was freshly prepared in a Millipore Continental water system before each experiment. The sample in the reactor was stirred magnetically during the experiment. The reactor was irradiated with a 1400-W Xe lamp for 5 h. A 10-cm Pyrex water jacket was placed between the reactor and the lamp to absorb the

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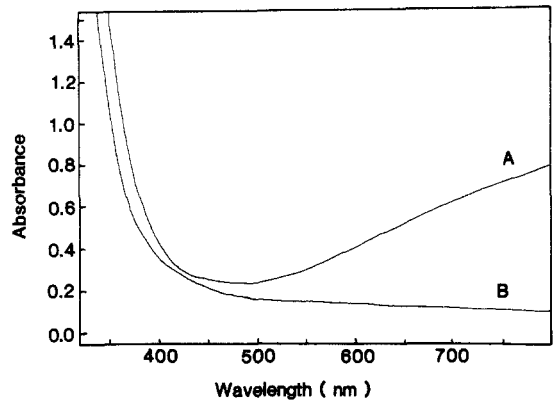

Figure 1. Absorbance spectra of (A) evaporated blue tungsten oxide and (B) WO_3.

IR light. The temperature of the solution was ca. 55 °C under irradiation. During the irradiation, H_2O-saturated N_2 gas, purified as described previously, was passed through the solution. As a reference, commercially available TiO_2 powder (Degussa P-25) was used under the same conditions. After the reaction, the dispersion was centrifuged to remove the powders. The analysis of NH_3 was done spectrophotometrically by the indophenol method.[4]

Electrochemical Measurements. Electrochemical measurements were made with a Princeton Applied Research (PAR) Model 173 potentiostat and Model 174 universal programmer. The space charge capacity was measured with a PAR potentiostat and a PAR Model 5204 lock-in amplifier.

Results

Characterization of WO_{3-x} Film. X-ray diffraction analysis showed the evaporated blue tungsten oxide film to be amorphous. The heat-treated (under vacuum) tungsten oxide films showed several sharp X-ray diffraction peaks and was confirmed to be β-$WO_{2.96}$.[6] The air-annealed blue tungsten oxide also gave sharp X-ray diffraction peaks and was determined to be stoichiometric WO_3 with a triclinic lattice (ASTM 20-1323). When the oxygen pressure in the vacuum evaporator was relatively high, the color of the evaporated tungsten oxide was yellowish green or light yellow. A clear blue film was obtained when the oxygen pressure was low. Stoichiometric tungsten trioxide is yellow, but the color changes to blue by slight reduction.[6] The substoichiometric composition of $WO_{2.96}$ is known to result from the reduction of stoichiometric trioxide at high temperatures (ca. 1050–1250 °C) under high vacuum.[7] Therefore, the composition of the evaporated amorphous film was believed to be between WO_3 and $WO_{2.96}$ or a mixture of these. Heating of the amorphous blue film (WO_{3-x}) reduced it to $WO_{2.96}$, which is reported to be dark blue,[7] and enhanced its crystallinity.

Similar amorphous blue tungsten oxide films have been prepared by a radio-frequency reactive sputtering technique.[8] The films, prepared under a low oxygen sputtering atmosphere, had a blue color, n-type semiconducting properties, and much lower resistivity compared with that of WO_3.

Characterization of WO_{3-x} Powder. X-ray diffraction of WO_{3-x} powder also showed several sharp peaks, but it was difficult to identify its structure. The stoichiometry of this WO_{3-x} powder may be between WO_3 and $WO_{2.96}$. The crystal size of the WO_{3-x} powders was ca. 150 Å as calculated from the X-ray diffraction peak.[9] The surface area of the WO_{3-x} powders was 48 m^2/g (BET).

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TABLE II: Results of Photoreactions in Gas Phase

film	conditions	wt of film, mg	irradn time, h	yield, μg	yield, μg/h
WO_{3-x}	thick film on Pyrex beads	950	280	35	0.125
$WO_{2.96}$	thin film on quartz tube	27	970	106	0.109
WO_3	thin film on Pyrex	6.9	400	81	0.202

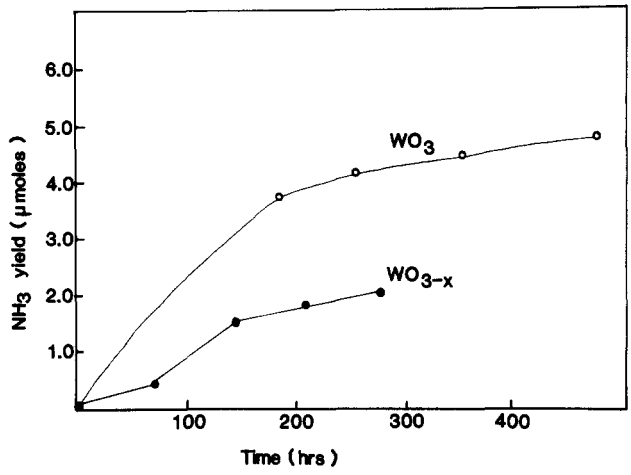

Figure 2. Yield of NH_3 vs. time for WO_{3-x} (coated beads, 0.95 g) and WO_3 (apparent surface area 100 cm^2, 1000-Å thickness).

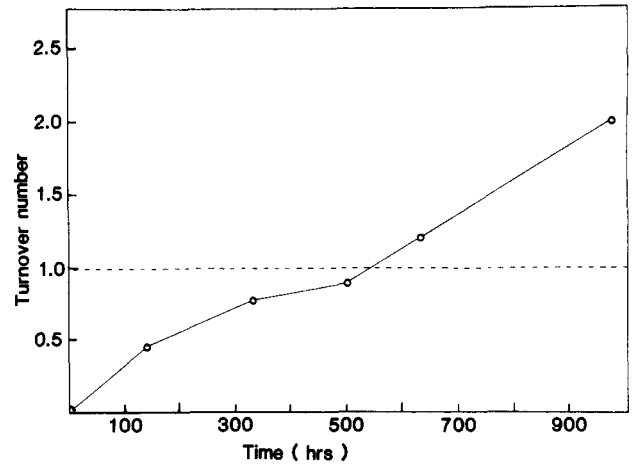

Figure 3. Yield of NH_3 vs. time for $WO_{2.96}$ (apparent surface area 113 cm^2, 3300-Å thickness).

Figure 1 shows the absorbance of the evaporated tungsten blue and WO_3 films. The band gap of both the blue tungsten oxide was near 2.8–3.0 eV from the measurement of the absorbance onset. The broad absorbance for the blue tungsten oxide around 800 nm is believed to be due to the oxygen deficiency in the structure.[7,8]

Photoreaction—Gas Phase. The results are summarized in Table II. Figure 2 shows the yields of NH_3 on WO_{3-x}-coated beads (apparent surface area 200 cm^2, 0.94 g of WO_{3-x}). The yields of NH_3 were roughly proportional to the irradiation time. No N_2H_4 was detected in the HCl trap. No NH_3 was produced when the N_2 gas was passed through the reactor which was heated at 100 °C in the dark. During irradiation the blue color of WO_{3-x} changed partially to yellow, the color of WO_3. This phenomenon implied that the reaction might proceed by a simple thermal path (eq 1), rather than a photocatalytic one. To ensure that this

$$WO_{2.96} + 0.04H_2O + (0.04/3)N_2 \rightarrow WO_3 + (0.08/3)NH_3 \quad (1)$$

reaction was not the sole source of NH_3, the photoreaction was run with a thin film of heat-treated $WO_{2.96}$ (27 mg, thickness 3300 Å, apparent surface area 100 cm^2) for a sufficient time to produce a quantity of NH_3 above the maximum stoichiometric amount of eq 1, i.e., to demonstrate a turnover of catalyst greater than

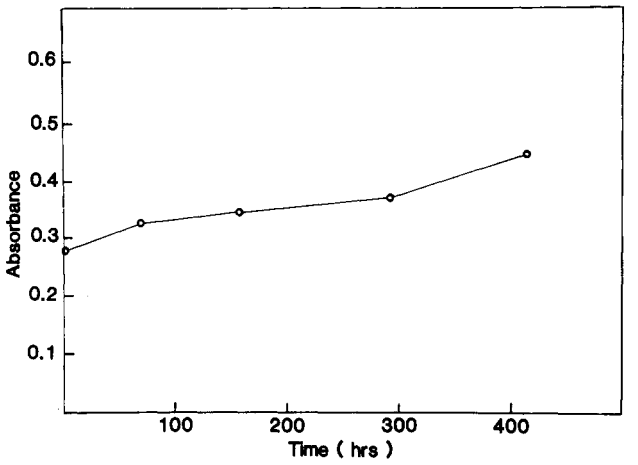

Figure 4. Absorbance of WO_3 film at 800 nm vs. time.

1. Figure 3 shows the number of turnovers of catalyst vs. irradiation time. The NH_3 yield was again roughly proportional to the irradiation time, and the number of turnovers exceeded unity. During this experiment, no color change was observed.

Irradiation of WO_3 films under a humid N_2 atmosphere also resulted in the formation of NH_3, as shown in Figure 2. In the dark, no NH_3 was produced. Analysis for N_2H_4 in the reaction vessel and trap was negative.

In another experiment, small dosages (ca. 0.05 mL/min at STP) of gaseous formaldehyde (CH_2O) were pumped through the WO_3 reaction vessel along with H_2O and N_2. It was hoped that CH_2O would serve as a hole scavenger, since it is much easier to oxidize than H_2O, and the yield of NH_3 would increase. The initial yield of NH_3 was found to decrease and the photolysis stopped. The CH_2O did scavenge the valence band holes, but the photogenerated electrons remained in the lattice and resulted in a change in morphology of WO_3 to that of a tungsten bronze:[11,12]

$$WO_3 + yH^+ + ye^- \rightleftarrows H_yWO_3 \qquad (2)$$

This reaction occurred rapidly relative to the NH_3 production rate. Irradiation for 8 h resulted in a tungsten bronze where y is about 0.1 as measured by the absorbance at 800 nm using Smakula's equation.[12] At this point, the catalyst was intensely blue. X-ray analysis confirmed bronze formation (ASTM 6-0210).

The absorbance of the WO_3 catalyst irradiated at 800 nm under the N_2/H_2O atmosphere in the absence of CH_2O also increased, but very slowly compared to the rate when the hole scavenger was present (Figure 4). This again indicates bronze formation.

Electrochemical Measurements. A number of electrochemical measurements of polycrystalline tungsten oxide materials have been reported.[10] Figure 5 is a typical current–potential curve for heat-treated WO_{3-x} (evaporated on W foil) in 1 M HCl. During anodic polarization the current was limited to a very low level. During cathodic polarization the WO_{3-x} electrode was further reduced to lower oxidation states[13] or to a hydrogen tungsten bronze,[11,14] which could be reoxidized by a subsequent anodic sweep. During these polarizations, the blue color of the WO_{3-x} did not change.

Figure 6 shows the Mott–Schottky plot of the heat-treated WO_{3-x} electrode. The capacitance measurements demonstrate that this material is a degenerate semiconductor. Mott–Schottky plots were frequency dependent and nonlinear. The capacitance values obtained were very large and of the order of the Helmholtz layer capacitance. This can probably be attributed to the complexity of the evaporated WO_{3-x} film, e.g., polycrystalline structure, presence of surface states arising from oxygen deficiencies,[15] and

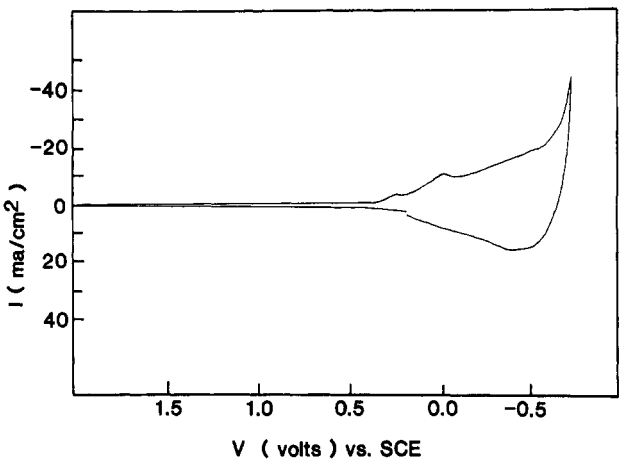

Figure 5. Current–potential behavior for a heat-treated WO_{3-x} electrode in 1.0 M HCl at 20 mV/s.

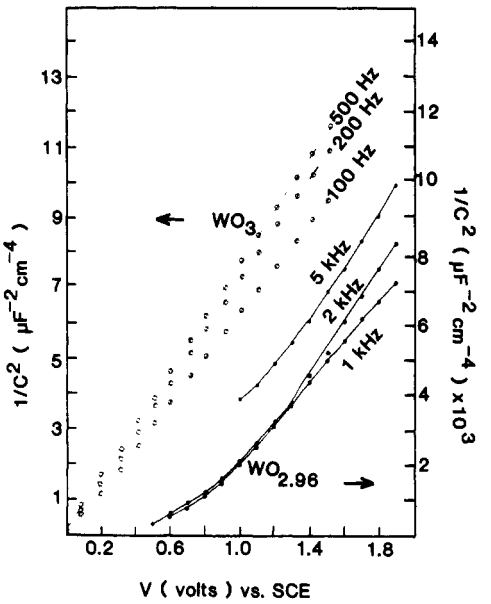

Figure 6. Mott–Schottky ($1/C^2$ vs. V) plot for $WO_{2.96}$ (closed circles) and WO_3 (open circles) in 1.0 M HCl. Note the different scales.

nonuniform dopant density. Capacitance measurements on a WO_3 electrode did give linear Mott–Schottky plots (Figure 6) suitable for determining the flat band potential. The flat band potential (V_{fb}) was estimated to be ca. +0.2 to +0.3 V vs. NHE at pH 0 from extrapolation of the capacitance curves. Note that, for WO_3 and the tungsten blue oxides, the band gap energy and flat band potential depend upon the method of preparation.[16–19]

With reduction of N_2 to NH_3, there is concomitant oxidation of H_2O to O_2. The overall reaction of NH_3 with O_2 at the illuminated semiconductor is a possible back-reaction that would result in lower yields of NH_3.[20] This photocatalytic (thermodynamically downhill) reaction occurs via reaction of the NH_3 with photogenerated holes with reduction of O_2 by electrons. To investigate this reaction, a sealed reaction vessel with an atmosphere of H_2O-saturated O_2 and about 2.0×10^{-6} mol of NH_3 was illuminated by using a WO_3 catalyst under the same conditions as in the NH_3 synthesis studies. After 20 h, only about 40% of the NH_3 remained. In the dark, there was no loss of NH_3. Thus, the NH_3/O_2 back-reaction undoubtedly results in lower yields of NH_3. This experiment demonstrates the importance of removal

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TABLE III: Results of Dark and Photoreactions in Aqueous Phase

catalyst	catalyst wt, g	NH_3/yield, μg irradiated	dark	remarks
WO_{3-x}	0.58	12.2		as evaporated
WO_{3-x}	0.20		3.0	as evaporated
WO_3	0.58	<1.0		oxidized in air at 500 °C for 4 h
WO_{3-x}	0.20	3.5	3.4	reduced in H_2 at 400 °C for 4 h
WO_{3-x}	0.20	2.5	2.3	reduced in H_2 at 500 °C for 4 h
Pt/WO_{3-x}	0.20	20.7	18.7	H_2PtCl_6 impregnated H_2 reduction at 400 °C for 4 h
RuO_2/WO_{3-x}	0.20	24.3	21.4	RuO_2 ground in mortar
$RuO_2 + Pt/WO_{3-x}$	0.20	35.9	36.2	RuO_2 + Pt/WO_{3-x} ground in mortar
TiO_2	0.20	<1.0		reference system, P25 Degussa

of the products from the vicinity of the catalyst surface to prevent recombination when carrying out a thermodynamically uphill (photosynthetic) process.

Photoreaction—Aqueous Phase. Experimental results are summarized in Table III. To compare the yields to those in previous reports, TiO_2 (anatase) powder was also tried. Although the apparent NH_3 yields with WO_{3-x} were much higher than that found with TiO_2, the yields in the dark were about the same. Oxidation of the WO_{3-x} powder diminished the ammonia yield. If the reduced tungsten oxide was loaded with Pt, RuO_2, or both, the NH_3 yield increased significantly. However, again the yield in the dark was essentially the same.

Discussion

Gas Phase. For the heterogeneous photoreduction of N_2 on TiO_2, the following mechanism was proposed.[1,2a] First, H_2O molecules adsorbed on TiO_2 are split into hydrogen and oxygen on irradiation with near-UV light, followed by reaction of the N_2 with hydrogen to produce NH_3 (or N_2H_4). The formation of NH_3 on irradiated tungsten oxide can be interpreted by a similar mechanism, with N_2 reacting with H_2 formed from water under illumination.

$$^1/_2N_2 + {}^3/_2H_2 \rightleftarrows NH_3 \quad (2)$$

The equilibrium constant of eq 2, K_p, can be calculated from $\Delta G°$ for this reaction (−3.94 kcal/mol)[21] to yield

$$K_p = \frac{p_{NH_3}}{p_{H_2}^{3/2} p_{N_2}^{1/2}} = 773 \quad (3)$$

Therefore, $p_{NH_3} = 773 \times p_{H_2}^{3/2}$, where $p_{N_2} \simeq 1$ atm. Based on our measurement, the flat band potential of WO_{3-x} is about +0.2 V vs. NHE at pH 0. We assume the activity of proton on the catalyst surface is unity, since the valence band energy of WO_3 is positive enough to oxidize water to O_2 and H^+. We further assume that the V_{fb} measured in solution is representative of the gas-phase V_{fb}, since the pzzp (point of zero zeta potential) for WO_3 is at approximately pH 0.[22] The hydrogen equilibrium pressure at +0.2 V vs. NHE can be calculated by the Nernst equation

$$E = E° + 0.059 \log (a_{H^+}/p_{H_2}) \quad (4)$$

where $E = +0.2$ V vs. NHE, $E° = 0.00$ V, and $a_{H^+} \simeq 1$. Under these conditions $p_{H_2} = 4 \times 10^{-4}$ atm. If the equilibrium in eq 2 is attained during the experiment, the equilibrium pressure of NH_3 would be about 6×10^{-3} atm. The NH_3 yield on $WO_{2.96}$ for 100-h irradiation was 16 μg at a N_2 flow rate of 36 mL/min. The maximum (equilibrium) NH_3 yield calculated as the equilibrium pressure × total N_2 volume, would be much larger, ca. 1 g of NH_3. Thus, although V_{fb} is several tenths of a volt positive of the $E°$ for the H^+, H_2 (or N_2, NH_3) reaction, the yields found are well within the expected values for a flow system. The low yield of NH_3 in the gas-phase photoreaction can be attributed to several factors. Since there are no available counterions (as there are in solution) to compensate for the charge of photogenerated electrons and holes, e^-h^+ recombination is probably extensive. Moreover, even with a continuous flow of N_2, some oxidation of NH_3 with photogenerated holes must occur. During the photoreduction of NH_3 on WO_{3-x}, the color of the amorphous WO_{3-x} film became slightly more yellow, while the color of the $WO_{2.96}$ crystalline film did not. Charge transport through an amorphous WO_{3-x} film is more rapid than through crystalline $WO_{2.96}$. For example, amorphous WO_{3-x} films on electrode surfaces show electrochromic behavior and can be rapidly reduced to a blue coloration, while annealed and more crystalline films cannot.[10] Thus, WO_{3-x} is less stable and may be gradually oxidized to WO_3 by holes or by generated O_2 irradiation. On the other hand, crystalline $WO_{2.96}$ should be more stable and the oxidation of $WO_{2.96}$ should be much slower. The yield of NH_3 from illuminated WO_3 slowly decreased with time (Figure 2). This is attributed to tungsten bronze formation, since the rate approached that of WO_{3-x}. In our experiments, no N_2H_4 was detected. Since N_2H_4 is known to be unstable and easily oxidized, any N_2H_4 would probably readily decompose on the irradiated $WO_{2.96}$ or WO_3.

Aqueous Systems. In our studies the apparent ammonia yields with WO_{3-x} were much higher than those with TiO_2. However, the yields of NH_3 on WO_{3-x} in the dark were essentially the same as under illumination, except for amorphous WO_{3-x}. Loading the WO_{3-x} with Pt or RuO_2 significantly increased the apparent NH_3 yields, but again the yields in the dark were about the same. Therefore, the ammonia synthesis reaction in aqueous solution occurs predominantly by a thermal path (1), rather than by a photosynthetic one. Since the stoichiometry of evaporated WO_{3-x} powder is considered to be between $WO_{2.96}$ and WO_3, it may not be stable under oxidation conditions like the amorphous WO_{3-x} film in gas phase, and the thermal reaction (1) may become dominant. Moreover, the state of surface water on WO_{3-x} is very different for dispersed powders in the aqueous phase than for films in the gas phase; this might also affect the rate of WO_{3-x} oxidation.

Conclusion

The photoreaction of moist N_2 and water produces NH_3 on irradiated blue tungsten oxides and tungsten trioxide in the gas phase. The photoreaction showed a larger production of NH_3 than could be accounted for by the degree of reduction of the tungsten oxide (i.e., turnover greater than one). The active species was $WO_{2.96}$. This photoreduction can account for the ammonia blanks found when tungsten oxide is used as an adsorbent for NH_3.[3] With an aqueous dispersion of WO_{3-x} powder, N_2 was reduced to ammonia through a thermal chemical (not photochemical) reaction.

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