variation of the surface tension) is shown in Figure 6 as a function of the distance. It is seen, however, that the layer thickness is, in this present situation, not much affected by the presence of a nonuniform surface tension gradient.

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Heterogeneous Photocatalytic and Photosynthetic Deposition of Copper on TiO$_2$ and WO$_3$ Powders

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The deposition of Cu from aqueous solutions on suspensions of TiO$_2$ and WO$_3$ under irradiation with a xenon lamp is reported. Deposition in the photosynthetic mode (Cu^{2+} + H$_2$O + 2$h\nu$ → Cu + $^1/_2$O$_2$ + 2H$^+$) led to removal of as much as 83% of the Cu(II) from a solution containing 4.2 μg of Cu/mL. In the presence of acetate the reaction is photocatalytic (Cu^{2+} + 2CH$_3$COO$^-$ + 2$h\nu$ → Cu + C$_2$H$_6$ + 2CO$_2$). A comparison is made between the photoprocesses at powders and the photoelectrochemical behavior at single crystal semiconductor electrodes.

Semiconductor powders suspended in solution can be employed to carry out heterogeneous photocatalytic and photosynthetic processes.[1,2] For example, the photocatalytic decomposition of acetic acid solutions containing suspended platinized TiO$_2$, predominantly to methane and CO$_2$, under irradiation with light of wavelengths below 420 nm was recently described.[3] A recent communication from this laboratory has dealt with the photocatalytic deposition of Pt and other metals on TiO$_2$ powders and suggested the application of this technique to the preparation of supported catalysts.[4] We describe here the photodeposition of Cu on semiconductor powders.

Wrighton and co-workers[5] in experiments with single crystal n-type TiO$_2$ and SrTiO$_3$ demonstrated that the reduction of Cu^{2+} occurs in solutions of pH 7 at potentials positive of the flat-band potential (V_{fb}) on these semiconductors. Thus irradiation of a TiO$_2$ electrode, short-circuited to a Cu-metal electrode immersed in a 0.5 M CuSO$_4$ solution, resulted in a photocurrent with gas evolution at the TiO$_2$ anode and Cu deposition at the cathode. These results, coupled with our previous experiments on photocatalytic metal deposition, suggested the use of semiconductor powders in a similar way, e.g., for removal of Cu from solutions. An important problem which arises when extending the results of photoelectrochemical experiments with large electrodes to particulate systems under photosynthetic conditions (i.e., when the back-reaction is spontaneous) is the possible "short circuiting" of the reaction on the particle. In this case the product formed at oxidizing sites (e.g., oxygen) may be preferentially reduced at reducing sites, thus hindering the desired reduction reaction (Cu^{2+} reduction) and greatly decreasing the efficiency of the process. The direct back-reaction of products must also be considered. For photocatalytic processes, where ΔG° for the overall reaction is negative, this is less of a problem, since the back-reaction cannot occur.

Experimental Section

Materials. The TiO$_2$ powder (Matheson Coleman and Bell) was 99% in the anatase form as determined by X-ray diffraction and had a surface area in excess of 15 m^2/g as determined by BET measurements. The WO$_3$ powder (99.9% pure, surface area ~15 m^2/g) was purchased from Apache Chemicals Inc. The TiO$_2$ was reduced by heating in a quartz tube under H$_2$ at 500 °C. Rutile powders were produced by heating under H$_2$ at 900 °C for 5–6 h, which resulted in about a 99% conversion. Rutile single crystals were purchased from National Lead (Niagra Falls, N.Y.). The mounting procedure for those crystals used as electrodes has been described previously.[6] Copper sulfate (Matheson Coleman and Bell), glacial acetic acid, and 8-hydroxyquinoline (Fisher Scientific Co.) were of reagent grade. Extractions were performed with spectrophotometric grade chloroform (Malinckrodt Chemical Works).

Apparatus and Procedure. Low copper concentration studies employed 100 mg of semiconductor powder suspended in 15 mL of solution. Solution conditions and illumination times are listed in Tables I and II. pH adjustments were made with Na$_2$CO$_3$. Copper concentrations following irradiation were determined spectrophotometrically by the following procedure.[7] The pH of the solution was adjusted to 5 and it was then extracted with 20 mL of chloroform containing 8-hydroxyquinoline.

TABLE I: Photosynthetic Deposition of Copper

Dilute Solutions[a]

powder[b]	irradiation time,[c] h	initial $[Cu^{2+}]$, μg/mL	Cu removal, %
TiO₂ (a,u)	0	4.2	0
TiO₂ (a,u)	8	8.4	41
TiO₂ (a,r)	2	4.2	83
WO₃	3.5	4.2	45
TiO₂ (a,u)	16[d]	62.4	54

Concentrated Solutions[e]

powder	TiO₂ wt, g	initial $[Cu^{+2}]$, mg/mL	Cu deposition, mg
TiO₂ (a,u)	1.010	10.5	1.4
TiO₂ (a,r)	0.500	15.9	2.8

[a] Solution volume, 15 mL, pH 6.5. [b] 0.100 g; symbols for samples are as follows: a, anatase; r, reduced; u, unreduced. [c] Xe lamp. [d] Solar experiment, June 7–8, 1978. [e] Solution volume, 20 mL, pH 6.5. Irradiation time, 24 h.

TABLE II: Photocatalytic Copper Reduction

Dilute Solution[a]

sample[b]	acetic acid, mL	pH	irradiation time, h	initial $[Cu^{2+}]$, μg/mL	Cu removal, %
none	7.5	3.3	2	4.2	0
TiO₂ (a,u)	13	3	2.25	8.4	87
TiO₂ (a,u)	7.5	6	2	4.2	82
TiO₂ (a,u)	1.0	6	2.25	4.2	45
TiO₂ (a,r)	7.5	3.3	2	4.2	3.7
TiO₂ (R,r)	7.5	6	2	4.2	3.7
TiO₂ (a,r)	7.5	6	5	8.4	68

Concentrated Solutions[c]

sample	wt, g	acetic acid, mL	pH	initial $[Cu^{2+}]$, mg/mL	Cu deposited,[d] mg
TiO₂ (a,r)	0.462	10	3.3	10.5	47
TiO₂ (a,u)	1.006	10	3.3	10.5	47
TiO₂ (a,r)	0.495	10	3.3	10.5	54
TiO₂ (a,r)	0.500	10	5	10.5	59
TiO₂ (a,u)	0.500	10	5	10.5	17
TiO₂ (a,r)	0.495	5	5	32.8	26
TiO₂ (a,u)	1.006	10	5	10.5	8.3

[a] Solution volume, 15 mL. [b] 0.100 g; symbols for samples are as follows: a, anatase; r, reduced; R, rutile; u, unreduced. [c] Solution volume, 20 mL; irradiation time, 24 h. [d] Determined as CuO, see Experimental Section.

The absorbance of the copper 8-hydroxyquinoline complex was measured at 410 nm and the copper concentration was determined by comparison with a calibration curve prepared by treatment of standard solutions by the same procedure. Absorbance measurements were made with a Cary 14 spectrophotometer (Applied Physics Corp., Monrovia, Calif.). Studies with higher copper concentrations were performed by using from 0.5 to 1.0 g of TiO₂ powder. The suspensions were irradiated for 24 h, after which the powders were recovered, washed thoroughly with distilled water, and dried for 12–14 h at 110 °C. At this temperature the surface deposit is converted to CuO,[8] which resulted in a change in color of deposit from reddish brown to gray.

The reaction mixtures were contained in an undivided Pyrex cell with a flat window for irradiation. Nitrogen was bubbled through the solutions before and during the
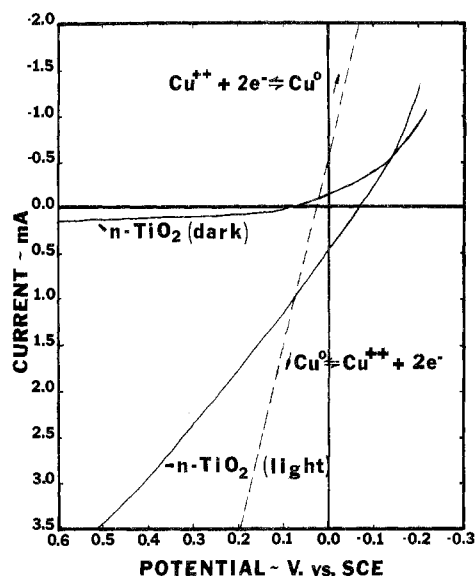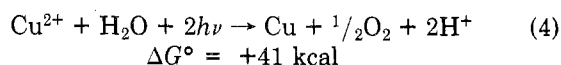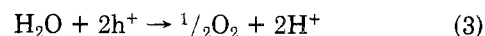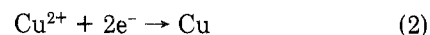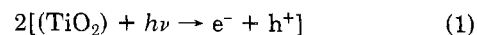

Figure 1. Current–potential curves for (—) single crystal n-TiO₂ and (- - -) Cu electrodes in 0.025 M CuSO₄.

experiment to remove oxygen. The cell was contained in a Pyrex water bath, which absorbed IR radiation from the lamp and magnetic stirring was used to agitate the mixtures during irradiation. The samples were irradiated with a 2500-W Hg–Xe lamp (Model UR 30 KK, Christie Electric Corp., Los Angeles, Calif.), operated at 1600 W, with the light focused by a convex quartz lens between the lamp and cooling bath on to the flat window of the cell. In some experiments illumination was provided by an unfocused 6000-W Xe lamp (Model 600-WR, Weatherometer, Atlas Electric Devices, Co., Chicago, Ill.), operated at 5000 W. The large shielded chamber of this instrument allowed side-by-side experiments with reactants and controls.

Electrochemical experiments were performed with a PAR Model 173 potentiostat (Princeton Applied Research, Princeton, N.J.) and a PAR Model 173 universal programmer. Irradiation of the single crystal electrodes was accomplished with a 450-W Xe lamp (Oriel Corp., Stamford, Conn.), operated at 250–300 W. A water chamber was placed before the focusing lens to remove IR radiation.

Results

Heterogeneous Photosynthetic Copper Reduction. The current–potential behavior for a single crystal n-TiO₂ (rutile) electrode as well as a Cu metal electrode in 0.25 M copper sulfate solution (pH 6.5) is shown in Figure 1. Wrighton et al.[5] have obtained similar results. The relative positions of these curves lead to the prediction (Figure 2) that the potential of the irradiated n-TiO₂ electrode will be sufficient to promote Cu²⁺ reduction. Thus, if these results can be extended to the particulate TiO₂ systems, as has been found in previous studies,[2–5,9] irradiation of a Cu(II) solution containing TiO₂ powder should lead to the removal of the copper from the solution in a photosynthetic reaction:

$$2[(TiO_2) + h\nu \rightarrow e^- + h^+] \quad (1)$$

$$Cu^{2+} + 2e^- \rightarrow Cu \quad (2)$$

$$H_2O + 2h^+ \rightarrow {}^1/_2 O_2 + 2H^+ \quad (3)$$

$$Cu^{2+} + H_2O + 2h\nu \rightarrow Cu + {}^1/_2 O_2 + 2H^+ \quad (4)$$

$$\Delta G^\circ = +41 \text{ kcal}$$

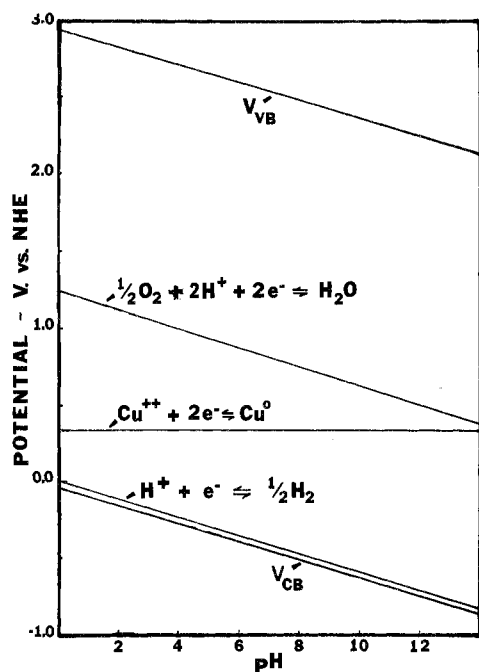Indeed Wrighton et al.[5] reported that under open circuit conditions copper deposition occurs in the dark areas of
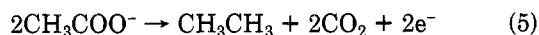
Figure 2. Potential–pH diagram relating semiconductor bands to redox couple positions.

Figure 3. Schematic diagram of the photochemical reactions at an irradiated semiconductor powder particles.

a single crystal photoelectrode surface along with oxygen production in the illuminated areas. We have confirmed this and find that, in addition, when the electrode is held at negative potentials (−0.1 V vs. SCE), where copper (II) reduction readily occurs in the dark, no copper deposits are formed on the illuminated areas of the electrode. When copper is electrodeposited on the entire crystal surface in the dark, open circuit irradiation of a small section of the electrode reoxidized the copper deposit in the illuminated region. Furthermore, when the focused beam was then moved to an adjacent area that was still plated with copper, a more rapid deposition of copper could be seen in the section from which the copper had been previously removed, i.e, the copper plating appeared to transfer from an illuminated area to a dark area of the electrode. Finally when one side of a TiO_2 crystal was illuminated, small copper deposits were visible in scratches on the illuminated face, but the major copper deposition was on the dark side of the crystal.

The results of irradiation of suspensions of TiO_2 immersed in aqueous copper(II) solutions are given in Table I. The individual TiO_2 particles act as short-circuited anodes and cathodes and carry out the reaction in (4) with a net storage of radiant energy (Figure 3). A steady state for deposition is attained, since, as demonstrated in the single crystal studies, oxidation of Cu occurs more easily than water oxidation on the illuminated areas, and thus some photoinduced stripping occurs, either directly, or by oxygen itself or intermediates in the water oxidation step (e.g., hydroxyl radicals).

Heterogeneous Photocatalytic Copper Reduction. Previous studies in this laboratory of the current–potential behavior of n-TiO_2 (rutile) electrodes in aqueous solutions containing acetate/acetic acid buffers have demonstrated that the photooxidation of acetate, reaction 5, competes

$$2CH_3COO^- \rightarrow CH_3CH_3 + 2CO_2 + 2e^- \qquad (5)$$

with water oxidation as the potential is swept in a positive direction (the photo-Kolbe reaction).[6] Although no significant change in V_{fb} occurs upon the addition of acetate to an aqueous solution at a given pH, a photooxidation wave which preceeds that for solvent oxidation is seen
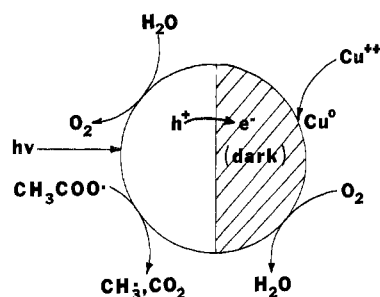
when acetate is added to the solution. Photocatalytic decomposition of acetate has also been carried out with irradiated suspensions of platinized TiO_2.[3] In this case, the major products are methane and carbon dioxide, presumably due to the low surface concentration of methyl radicals, produced near reducing sites. The irreversible oxidation of acetate (reaction 5) is a more favorable reaction, since the products are unable to oxidize copper and the net reaction is spontaneous:

$$Cu^{2+} + 2CH_3COO^- \rightarrow Cu^0 + CH_3CH_3 + 2CO_2 \quad (6)$$
$$\Delta G^\circ = -34 \text{ kcal/mol}$$
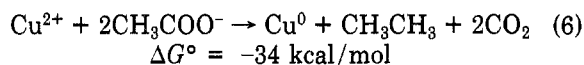
While the homogeneous reaction is very slow, n-TiO_2 serves as a heterogeneous photocatalyst for the redox process. The rate of copper reduction in the dark areas of the partially illuminated crystal is visibly enhanced over that observed in the absence of acetate. Although reoxidation of copper on the illuminated areas of the crystal is still observed, the oxidation of acetate competes more favorably with the copper reoxidation process than does water oxidation, so that the net reduction of copper proceeds more completely. This is supported by the increase in the amount of copper reduced on the back side of a flat rutile single crystal at open circuit irradiated for a given time interval, and by the higher net copper content of powders recovered after irradiation in copper solutions buffered with acetate (Table II). In these solutions, the redox reaction exhibits a pH dependence, with pH values from 5 to 6 providing the most favorable range. The CO_2 generated by the oxidation of acetate was collected in 1 M NaOH saturated with $Ba(OH)_2$ and determined as $BaCO_3$. The ratio of Cu to CO_2 predicted in eq 6 is 1:2, and a ratio of 1:2.2 was obtained experimentally at pH 3.3. At a pH of 5, the ratio increased to 1:7, suggesting that the photo-Kolbe reaction leading to CH_4 or H_2 is contributing significantly to the total CO_2 production. Recovered powders were analyzed by electron spectroscopy with a Physical Electronics Model 548 electron spectrometer. Because of the small shifts in binding energy which result from oxidation state changes in Cu and a large charging current of the TiO_2 powders, the oxidation state of copper could not be established by these methods. The results did confirm the presence of copper on the powder surface, with no other solution species being detected.

Conclusions

The deposition of copper by irradiation of TiO_2 or WO_3 suspensions occurs in the photosynthetic or photocatalytic mode. The method appears effective in the removal or recovery of copper, even from dilute solutions (below 10 ppm), under oxygen-free conditions. Copper occurs in several industrial effluents, resulting in the significant loss of metal (e.g., ~10000 ton/yr in the U.K.[9]) as well as destruction of organisms exposed to these streams. Removal is carried out by electrolysis, ion exchange, chemical

precipitation, reverse osmosis, or solvent extraction, although these methods become less effective at low concentrations of copper ions. The photodeposition procedure described here may be applicable to treatment of waste streams, although the effect of other substances in the streams which might interfere with the process must be considered. Treatment of waste streams for removal of CN$^-$ and SO$_2$ by photocatalytic methods has previously been suggested.[10] The method may also find application in the photodeposition of copper contacts on semiconductor substrates and for the preparation of catalyst materials, as previously described for Pt catalysts.[4]

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NH$_3$ Oxidation over UV-Irradiated TiO$_2$ at Room Temperature

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NH$_3$ oxidation into N$_2$ and N$_2$O by O$_2$ in the 30–250-torr pressure range has been carried out over UV-irradiated TiO$_2$ (anatase) at room temperature. It has been checked that photons of energy greater than the band gap of TiO$_2$ are needed and that the formation rates, r_{N_2} and r_{N_2O}, in N$_2$ and N$_2$O are both proportional to UV light intensity. The electrical photoconductivity of TiO$_2$ is not affected by NH$_3$, N$_2$ and N$_2$O, i.e., these compounds do not compete with O$_2$ for surface free electrons. A kinetic study showed that r_{N_2} and r_{N_2O} both depend on O$_2$ pressure, whereas NH$_3$ pressure influences only r_{N_2}. The selectivity is not affected by P_{O_2}, the ratio r_{N_2}/r_{N_2O} being ~4 for 100-torr NH$_3$ pressure. The formal kinetics corresponds to a Langmuir–Hinshelwood model with reaction between O$_2$ and NH$_3$ adsorbed on different types of sites for N$_2$ formation, and with reaction between O$_2$ and a nitrogen-containing intermediate for N$_2$O formation. A step mechanism taking into account the activation of the catalyst by photons is tentatively proposed.

Introduction

The oxidation of ammonia has been extensively studied owing to its use for HNO$_3$ synthesis when NO is selectively obtained, as well as because NH$_3$ is an atmospheric pollutant and is also formed during engine operation in the rich mode. It has also been examined in connection with ammoxidation reactions. It forms N$_2$, N$_2$O, and NO in various ratios over a variety of catalysts (metals and oxides).

The photochemical oxidation of NH$_3$ occurs at wavelengths below 220 nm,[1] which are shorter than those employed for photocatalysis over oxides.

Relatively little work has been published on the photocatalytic oxidation of NH$_3$. Over TiO$_2$ in aqueous solutions, NO$_2^-$ ions were formed.[2] In the presence of dry TiO$_2$ at room temperature a mixture of gaseous NH$_3$ and O$_2$ produced small amounts only of N$_2$O and of surface NO$_2^-$ ions but no N$_2$.[3] Over ZnO at 25 °C, N$_2$O and H$_2$O were photocatalytically formed and a mechanism involving O$_2^-$ ions reacting with NH$_3$ to yield HNO species was proposed.[4] Nitrate surface ions, resulting from the photocatalyzed oxidation of NH$_3$ by O$_2$ in the −183–25 °C temperature range over γ-Al$_2$O$_3$ pretreated at 700 °C, were observed by IR spectroscopy; however, the gas phase was not analyzed.[5]

In this laboratory, the properties of UV-irradiated TiO$_2$ at room temperature have been used for the oxidation by O$_2$ of organic[6-9] and inorganic molecules,[6] and for O$_2$ isotopic exchange.[10] To improve the understanding of these reactions, this article presents a kinetic study of the already pointed out photocatalytic oxidation of NH$_3$ over TiO$_2$,[6] as well as the effect of NH$_3$ and of its oxidation products, N$_2$ and N$_2$O, upon TiO$_2$ electrical photoconductivity. The various kinetic models, the role of UV light and oxygen species, are discussed.

Experimental Section

Apparatus and Catalyst. The photocatalytic activities were measured in a differential flow-photoreactor described previously.[7,11] The catalyst powder was spread as a thin uniform layer onto a porous fiberglass membrane perpendicular to the UV beam and located at ca. 6.5 cm below the axis of a Philips HPK 125-W lamp. A water-containing cuvet removed the infrared part of the beam. The catalyst received ca. 25 mW cm^{-2} in the spectral range thus obtained. The reaction mixture flowed through the catalyst layer. The effluents were analyzed by gas chromatography. More details may be found in ref 11.

The photoconductivity of TiO$_2$ was measured under static conditions, in another cell, as in ref 12. TiO$_2$ (50 mg)