Figure 4. ln rate of CO desorption vs. time for run B.

Suggesting that there are at least two kinds of metal–CO bonds involved which undoubtedly have different bond energies and that their approximate ratio is 5/1, the type of site greatest in quantity being that which bonds most strongly with CO. There may be other types of sites or these two kinds may actually include subtypes which have bond energies so close as to be indistinguishable by this experimental technique.

Since the room temperature rate constant for displacement for process I is about 7 times greater than that for process II, the activation energy for process II must be 1200 cal greater than that for process I. This suggests that the CO displaced in process II might be bonded to the metal 1200 cal more strongly than that which is displaced

in process I. This deduction is highly speculative, however, since when a more strongly bonded CO is displaced, the displacing molecule may also be bonded more strongly and this could have considerable influence on the activation energy for the process. At best, it is probably reasonable to assume that the process II corresponds to desorption of a more strongly bonded CO.

Runs B, D, E, and F of Table II indicate that CO on a Ni site of type I is only about 0.2 as abundant as CO on a Ni site of type II. There is considerable reason to believe that the relative abundance of the two types of sites is probably a strong function of the technique used in the evaporation and the agreement found in this work is actually somewhat surprising considering that each run was carried out on an individually prepared surface.

Note Added in Proof. One experiment was conducted to determine if argon alone would remove CO from an evaporated Ni surface. Ni was evaporated on a salt plate in the infrared cell,[11] CO was adsorbed, the spectrum was recorded, and the system was purged with argon. No change in the spectrum could be observed.

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Heterogeneous Photocatalytic Oxidation of Cyanide and Sulfite in Aqueous Solutions at Semiconductor Powders

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The photocatalytic oxidations of CN⁻ and SO₃²⁻ were studied at several semiconductor powders including TiO_2, ZnO, CdS, Fe_2O_3, and WO_3 using a xenon light source. TiO_2, ZnO, and CdS were active photocatalysts for cyanide oxidation, while no oxidation was seen for Fe_2O_3 and WO_3. The catalyzed oxidation of CN⁻ at TiO_2 using sunlight was also investigated. The rate constant for CN⁻ oxidation at TiO_2 in sunlight was 3.1×10^{-6} mol day⁻¹ cm⁻² illuminated surface. The product of the oxidation of CN⁻ at TiO_2 was quantitatively determined to be OCN⁻. TiO_2, ZnO, CdS, and Fe_2O_3 photocatalyzed the oxidation of SO_3^{2-}. The order of the catalytic activity was $Fe_2O_3 \sim ZnO \sim CdS > TiO_2$. The rates of the photocatalytic oxidations were greater for SO_3^{2-} than for CN⁻ in the cases of TiO_2, ZnO, and CdS. The chemical and photochemical stabilities for the most active catalysis were determined.

Introduction

The study of semiconductor materials as electrodes in electrochemical solar cells is currently a subject of much interest.[1] Less attention has been directed toward exploiting the photoelectrochemical properties of semi-

conductors for other purposes, however, e.g., as photocatalysts for bulk synthesis and for the conversion of pollutants in waste streams to less harmful forms. In electrochemical devices such as solar cells[2] the n-type semiconductor functions as a photoanode and a metal or

carbon counterelectrode functions as the cathode (for example, in the $TiO_2|NaOH|Pt$ cell, oxygen is photogenerated at the n-TiO_2 and is reduced at the Pt cathode). However, under certain conditions both reduction and oxidation can occur simultaneously at an illuminated semiconductor.[3-5] This process, called heterogeneous photocatalysis, bears the same relation to photoelectrochemical cells as corrosion processes relate to galvanic cells. A number of solution studies of the photocatalyzed reactions at semiconductor powders have been carried out.[3] These studies have usually involved organic reducing agents and have mainly been concerned with the production of H_2O_2 by reduction of the O_2 present in the solution. Little effort has been directed to larger scale experiments and to carrying the chemical processes to completion.

In a previous communication we reported the photocatalyzed oxidation of CN^- in aqueous solutions at TiO_2 powders.[4] Here we extend these studies to the photocatalyzed oxidation of CN^- at other semiconductors such as ZnO, CdS, and Fe_2O_3. We also studied the oxidation of CN^- at TiO_2 under solar radiation at concentrations and solution volumes which would be useful in gauging the applicability of this reaction to large scale processes. The effect of varying the solution redox level was explored by measuring the rate of the photocatalyzed oxidation of sulfite ion (SO_3^{2-}) at the same semiconductor materials.

Experimental Section

The following were the sources of the semiconductor powders: TiO_2 [anatase, Matheson Coleman and Bell (MCB)]; ZnO (Fischer); α-Fe_2O_3 (MCB); all were used without further pretreatment. Two samples of CdS powder were used. One was prepared in this lab by precipitating CdS by heating a solution of $Cd(NO_3)_2$ and thioacetamide. The other was a commercial powder of unknown origin. Electron micrographs showed that the particle size of all of the powders was less than 1 μm. Other chemicals were of reagent grade. Solutions were prepared with low conductivity water.

Typical experiments consisted of illuminating 10-mL aliquots of CN^- or SO_3^{2-} in quartz tubes containing 0.1 g of semiconductor powder (except where noted) kept in suspension by bubbling O_2 through the solution. These tubes were positioned in a standard fashion in order to maintain a constant photon flux from run to run. The light source was a 450-W xenon lamp (Oriel, Stamford, Conn.) powered with an Oriel Model 6242 arc lamp power supply.

Polarographic analysis was carried out with a PAR Model 170 electrochemistry system (Princeton Applied Research, Princeton, N.J.) at a dropping mercury electrode utilizing a PAR 172 drop knocker.

Unreacted CN^- was determined by potentiometric titration with $AgNO_3$, cyanate, by spectrophotometry,[6] and SO_3^{2-}, by titration with iodine to a starch endpoint. In some determinations, such as SO_3^{2-} in the presence of CdS, the semiconductor interfered with the titration with iodine. In these cases the semiconductor powder was removed by centrifugation before the determination.

Results

Photocatalyzed Oxidation of Cyanide at TiO_2. The photocatalyzed oxidation of CN^- at TiO_2 was reported previously.[4] Since the most active form of TiO_2 was found to be the undoped anatase, all work reported here used this material. In the previous report the rate of CN^- oxidation as a function of concentration was investigated in the range of 1 mM to 0.1 M. In this range the rate of oxidation (i.e.,
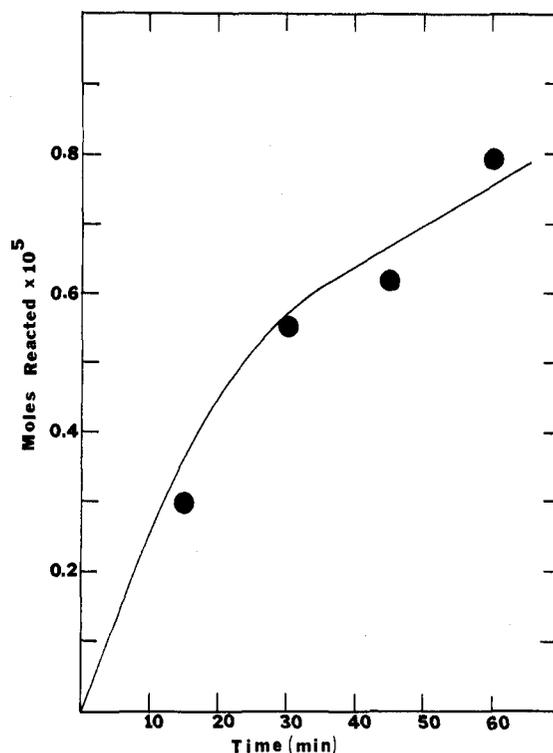
Figure 1. Number of mol of CN^- that reacted following irradiation with 450-W xenon lamp while bubbling O_2. Solution initially 1 mM CN^-. 0.1 M KOH electrolyte containing 0.1 g of anatase TiO_2. Solution volume 10 mL.

TABLE I: Removal of CN^- Under Irradiation in the Presence of Several Semiconductor Powders[a]

μmol of CN^- reacted	Initial CN^- concn, mM	illumination time, min	Semiconductor powder
7.7	1	60	TiO_2 (anatase)
6.3	1	45	TiO_2 (anatase)
5.5	1	30	TiO_2 (anatase)
9.5	1	60	ZnO
7.8	1	30	ZnO
<0.1	1	30	Fe_2O_3
<0.3	1	45	WO_3
0.6	3	60	CdS
<0.1	3	60	Fe_2O_3
15.8	3	60	TiO_2
22.5	3	60	ZnO

[a] The solution was 10 mL of 0.1 M KOH containing the indicated amount of KCN and 0.1 g of semiconductors contained in a quartz tube, illuminated with a 450-W Xe lamp with continuous O_2 bubbling.

the moles of CN^- removed per second at a given irradiation intensity) was nearly independent of the CN^- concentration. We extended these measurements to lower concentrations, since these could be of significance in the removal of CN^- from waste streams to sub parts per million levels. The number of mol of CN^- removed as a function of time from 10 mL of a solution initially containing 1 mM CN^- illuminated with a 450-W xenon lamp is shown in Figure 1. Note that the oxidation rate decreased by about one-half when the CN^- concentration fell below ca. 0.5 mM. A similar conclusion is reached by comparing the results for removal of CN^- from 1 and 3 mM solutions at TiO_2 (Table I), where significantly less CN^- was removed from the 1 mM solution than from the 3 mM solution during the same length of time, 1 h. At shorter times, when less CN^- is removed and the concentration of CN^- is higher, the rates were more nearly the same (e.g., for 60 min, 7.7
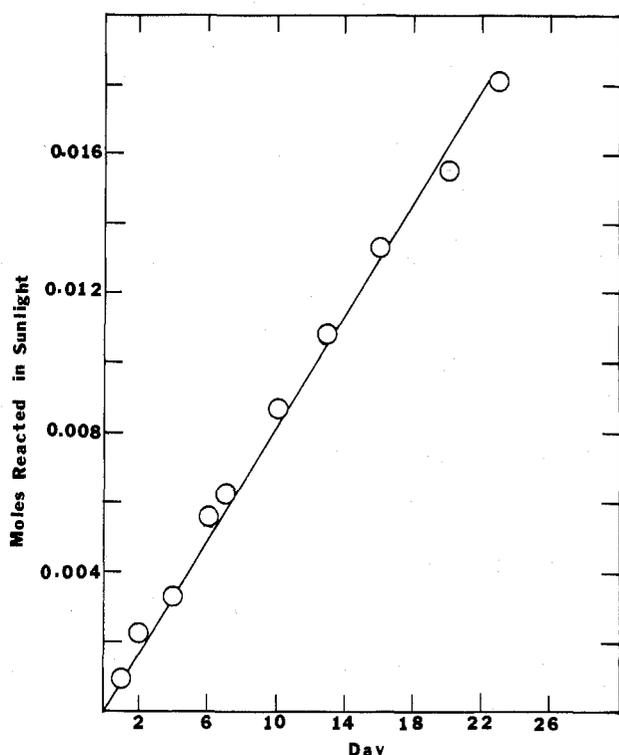
Figure 2. Number of mol of CN⁻ that reacted in 750 mL of a 30 mM KCN solution (0.1 M KOH) containing 7.5 g of anatase TiO₂ illuminated with unfocused sunlight. The solution was unstirred.

$\times$ 10⁻⁶ mol vs. 15.8 $\times$ 10⁻⁶ mol and for 30 min 5.5 $\times$ 10⁻⁶ mol vs. 7.9 $\times$ 10⁻⁶ mol removed from the 1 mM vs. 3 mM solutions, respectively). The vigorous solution agitation and relatively long times employed suggest that the decrease in rate at low CN⁻ concentrations cannot be attributed to difference in the rate of mass transfer of CN⁻ to the catalyst particles. It probably represents a decrease in efficiency of CN⁻ oxidation with respect to electron–hole recombination (see Discussion) at low concentrations.[8]

Product of the Oxidation of CN⁻ at TiO₂. In the previous investigation[4] we reported that a spot test indicated that OCN⁻ was one of the products of CN⁻ oxidation. In order to determine quantitatively the final oxidation product of CN⁻ at TiO₂, we measured the amount of OCN⁻ in a 20 mM CN⁻ solution containing TiO₂ following 10 h of illumination with a 450-W xenon lamp by spectrophotometry by measuring the absorbance of the copper(II)–pyridine–OCN⁻ complex following extraction with chloroform.[6] The analysis showed that at least 90% of the CN⁻ decomposed to form OCN⁻ as a stable final product of the oxidation.

The photocatalyzed oxidation of CN⁻ at TiO₂ in sunlight was also reinvestigated. In this experiment 750 mL of a 30 mM KCN solution was placed in a large crystallizing dish so that the solution depth was about 3 cm and the area about 254 cm². A quantity of TiO₂ (7.5 g) sufficient to cover the bottom of the crystallizing dish with a thin layer of powder was added and the top of the crystallizing dish was covered with Saran Wrap, which is transparent to UV radiation in the range where TiO has a high absorbance. The amount of CN⁻ removed when the crystallizing dish was placed on the roof where it was exposed to sunlight for most of the day, with the solution unstirred, is shown in Figure 2. The experiment was carried out from late September through October. About 65% of the days were clear to partly cloudy. The remainder of the days were cloudy, some with rain. The variation in the weather was such, however, that there was no significant nonlinearity in the plot due to a number of cloudy days

in succession. For a control prepared in exactly the same way, but not containing TiO₂, which was placed beside the first dish, no loss of CN⁻ was observed. From the slope of the plot in Figure 2 the rate of CN⁻ removal was 3.1 $\times$ 10⁻⁶ mol day⁻¹ cm⁻² irradiated surface.

Oxidation of Cyanide at Other Semiconductors. The amount CN⁻ that reacted in 1 mM solutions at several other semiconductors under irradiation with the Xe lamp is given in Table I. Several experiments were attempted with SrTiO₃, FeTiO₃, BaTiO₃, and Eu₂O₃ as catalysts but no evidence of any reaction was found with these. Of the semiconductors listed in Table I, ZnO was the most active and only a small amount of catalytic activity was seen with both forms of CdS. No reaction of CN⁻ was detected with either Fe₂O₃ or WO₃. No reactions were observed with any of the powders listed in Table I in the dark, or in the absence of catalyst or oxygen. The results were independent of the amount of powder over a considerable range as long as all the light that impinged on the sample tube was absorbed (i.e., opaque solutions).

The photocatalyzed oxidation of CN⁻ at ZnO has been reported previously.[7] The greater activity of ZnO as compared to TiO₂ cannot be explained by absorption of more light quanta since the band gap of ZnO (3.2 eV) is greater than that of TiO₂ (3.0 eV). At TiO₂ the quantum efficiency for the oxidation of CN⁻ was estimated to be about 0.06.[4] A similar estimate for ZnO could not be made, since data on the quantum efficiency and current–potential curve of a single crystal ZnO electrode for the xenon lamp used in these experiments were not available. However, the quantum efficiency of the ZnO powder must be significantly larger than that of the TiO₂ powder. Efficiencies higher than 0.06 have been reported for ZnO[3] as well as for TiO₂[9] with other reducing agents. The much lower catalytic activity for the smaller band gap CdS suggests a quantum efficiency much less than 0.06 for this material.

A decrease in the rate of CN⁻ removal was found with ZnO just as with TiO₂ at lower concentrations of CN⁻ (Table I). The 60-min result for ZnO in Table I corresponds to nearly complete removal of CN⁻ from solution so that it cannot be compared to the 60-min TiO₂ result. However comparison of rates at shorter times or higher CN⁻ concentrations shows that the catalytic activity of TiO₂ is about 0.7 that of ZnO at all concentrations.

Dissolution of Semiconductor Powders. For single crystal semiconductor electrodes dissolution of the semiconductor lattice is an important reaction path in the absence and often even in the presence of reducing agents[10] when the semiconductor is illuminated with band gap radiation. The instability of the semiconductor material when illuminated or when exposed to certain chemicals even in the dark is a potential complication to the interpretation of the experimental results and in the application of these reactions in practical systems. TiO₂ is well known to be stable under a wide variety of conditions,[11] although decomposition in H₂SO₄ solutions under irradiation has been reported.[12] ZnO and CdS are known to decompose as photoanodes under some conditions, so their stability in the presence of 0.1 M KOH with and without CN⁻ in the dark and following illumination with the xenon lamp was investigated. These experiments were carried out by treating the ZnO or CdS with the solutions for different time periods and then removing the powders by centrifugation, deaerating, and analyzing the resulting solution for Zn or Cd using polarographic methods.[13] Some dissolution of the ZnO powder was noted after stirring with 0.1 M KOH in the dark for several minutes yielding an equilibrium concentration of ZnO₂²⁻ of about 0.2 mM. The

same concentration was found when the ZnO was illuminated.

When 5 mM KCN was present, the dark dissolution of ZnO increased and a total Zn(II) solution concentration of about 1 mM resulted. When the ZnO suspension in this solution was illuminated by the xenon lamp, no increase in the Zn(II) concentration was detected but a much larger wave attributable to H_2O_2 reduction was observed. H_2O_2 is known to be the product of oxygen reduction at the ZnO powder. Thus in these solutions ZnO is photochemically stable but is subject to some chemical attack. No chemical attack was observed for the CdS in the dark. When CdS in a CN^- solution was illuminated and the resulting solution analyzed, a H_2O_2 reduction wave, smaller than the one seen with ZnO, was observed. A shoulder on the rising portion of this wave was seen. Although the location of this wave is not the same as that found for a solution containing Cd^{2+} and CN^-, the photochemical stability of CdS in the presence of CN^- is still suspect.

Photocatalyzed Oxidation of Sulfite. A study of the photocatalytic oxidation of SO_3^{2-} in acidic solutions was undertaken to investigate the effect of location of the solution species energy levels on the reaction rate for the different semiconductor powders. The standard electrode potential, E°, of the $OCN^-|CN^-$ couple in base is -1.21 V vs. SCE, while that for the $SO_4^{2-}|SO_3^{2-}$ couple in acid is -0.07 V vs. SCE.[14] Taking into account the variation of the flat band potential, V_{fb}, with pH, there is at least a 0.4 V difference between the relative locations of the standard potentials of the CN^- and SO_3^{2-} systems and the location of the conduction band edges of the semiconductors. Significantly different interactions between CN^- and SO_3^{2-} with the semiconductor surfaces is also expected.

The solution conditions for the SO_3^{2-} experiments (10 mM acetic acid) were selected to mimimize solution losses of SO_3^{2-} due to spontaneous oxidation of sulfite by oxygen and to volatilization as SO_2. At this level of acid all of the semiconductors, except ZnO, were stable; some dissolution of ZnO with subsequent neutralization of the solution occurred. However, the duration of the experiments with ZnO was sufficiently short that significant spontaneous oxidation of SO_3^{2-} did not occur. Blank experiments showed significant (i.e., up to 30%) losses of SO_3^{2-} from ZnO- and CdS-containing solutions in the dark. This loss was greatest for the first few seconds following addition of catalyst powder and was larger for the CdS prepared in this laboratory, which seemed to have a larger surface area (i.e., a smaller particle size was found by scanning electron micrography) than the commercial CdS. The time dependence and apparent surface area effect suggests a possible irreversible adsorption of SO_3^{2-} onto the semiconductor surfaces, perhaps forming adsorbed SO_4^{2-}. Although this effect was not studied, all results under illumination were corrected for the relatively large initial loss of SO_3^{2-} with ZnO and CdS. No dark reaction of SO_3^{2-} with TiO_2 or Fe_2O_3 was found.

The results of the photocatalyzed oxidation of SO_3^{2-} at TiO_2, ZnO, CdS (both sources), and Fe_2O_3 is shown in Figure 3. The rates of oxidation of SO_3^{2-} at illuminated ZnO, Fe_2O_3, and CdS (lab prepared) were highest and about the same. The bending over of the curves for Fe_2O_3 and CdS presumably result from a depletion of SO_3^{2-} from the solution. This occurs for CdS after less SO_3^{2-} has photoreacted than for Fe_2O_3 because of the initial dark loss of SO_3^{2-} discussed above that occurred with CdS. The reason for the different catalytic behavior of the two CdS samples is not known. However, significantly different photon efficiencies have been noted for CdS[15] depending
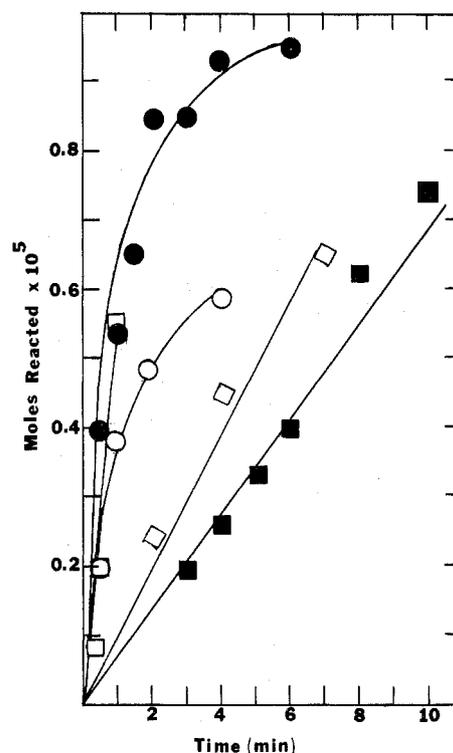
Figure 3. Number of mol of SO_3^{2-} that reacted in 10 mL of 1 mM Na_2SO_3 (also 10 mM acetic acid) following illumination with 450-W xenon lamp while bubbling O_2. Solution also contained (●) 0.1 g of Fe_2O_3 powder, (□) 0.1 g of ZnO powder, (○) 0.1 g of CdS powder prepared in this lab, (◇) 0.1 g of CdS powder, commercial, (■) 0.1 g of anatase TiO_2 powder.

upon the method of preparation.

The quantum efficiency for SO_3^{2-} removal with the TiO_2 can be estimated by the same method as that used with CN^{2-} to be about 0.16. The quantum efficiency of ZnO on the basis of the TiO_2 results is greater than 1. Polarographic analysis of the solutions following illumination in the presence of SO_3^{2-} showed no reduction wave for H_2O_2 for any of the semiconductors. The likely fate of any H_2O_2 would be the reaction of SO_3^{2-}.

Discussion

The mechanism for the photocatalytic oxidation of compounds by oxygen at semiconductors has been discussed.[3] Irradiation of a semiconductor with band gap light results in creation of holes in the semiconductor valence band by excitation of an electron to the conduction band. The valence band hole is scavenged by solution species before electron–hole recombination can occur within the semiconductor. Electroneutrality within the semiconductor is maintained by reduction of dissolved oxygen or other solution species by the conduction band electron. The process is repeated until the solution oxygen or reducing agents are exhausted.

Thus the process for removal of CN^- can be represented as follows:

$$(TiO_2) + 2h\nu \rightarrow (TiO_2) + 2p^+ + 2e^- \tag{1}$$

$$CN^- + 2OH^- + 2p^+ \rightarrow OCN^- + H_2O \tag{2}$$

$$O_2 + 2e^- + 2H_2O \rightarrow H_2O_2 + 2OH^- \tag{3a}$$

or

$$^1/_2O_2 + 2e^- + H_2O \rightarrow 2OH^- \tag{3b}$$
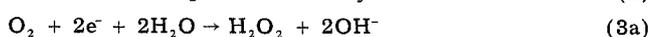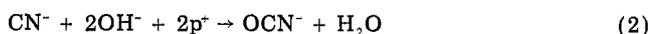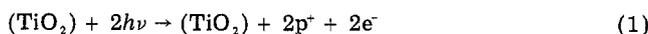
The rate of the photocatalysis is determined by several factors. Among these are the competitive rates of recombination of photogenerated electron–hole pairs within

the semiconductor and the scavenging of holes and electrons by oxygen and reducing agents such as CN^- and SO_3^{2-}.[1] Electron–hole recombination will depend on the degree of band bending within the semiconductor and the presence of any electron and hole traps at the particle surface and the space-charge region. Since the degree of band bending is expected to be less in the individual particles of a powder than can be induced in a semiconductor electrode, the separation of electrons and holes should be less efficient in the powder and recombination should play a more important role than in a semiconductor electrode. Accordingly, the quantum efficiencies should be considerably less than the near unity efficiencies seen with electrodes held at sufficiently positive potentials.[2a,11,16] The presence of surface states at energies within the band gap region can either decrease or increase the lifetime of electrons and holes depending upon whether these energy levels function as efficient recombination centers or as surface traps which prolong the life of a hole and an electron. The difference in photocatalytic activity between the anatase and rutile forms of TiO_2 was in part explained by possible trapping of electrons in the anatase form at the surface where they can more easily react with oxygen.[4] The existence of these levels seem well established by electroluminescence and other experiments.[17]

If H_2O_2 is produced and can react with a reductant in solution, more efficient removal of the reductant will be observed. Thus, for example, for the photocatalyzed oxidation of SO_3^{2-} at ZnO two modes of SO_3^{2-} removal are possible: direct oxidation of sulfite at the illuminated part of the particle and reaction of SO_3^{2-} with H_2O_2 produced by reduction of O_2 in the dark reaction. The overall reaction scheme (without implying mechanistic details) is

$$(ZnO) + 2h\nu \rightarrow (ZnO) + 2p^+ + 2e^- \quad (4)$$

$$SO_3^{2-} + 2p^+ + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad (5)$$

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \quad (6)$$

$$H_2O_2 + SO_3^{2-} \rightarrow SO_4^{2-} + H_2O \quad (7)$$

$$\overline{2h\nu + 2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-}} \quad (8)$$
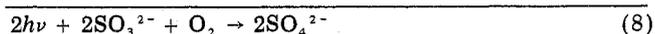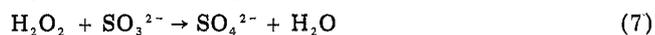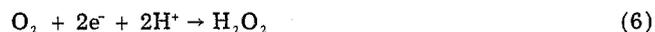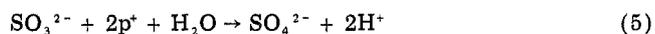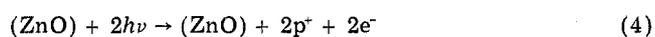
This could explain the anomalously high quantum efficiency (calculated by assuming only oxidation by holes was the cause of SO_3^{2-} removal) observed with ZnO.

The photocatalytic behavior displayed by semiconductors could be of technological significance. Thus processes related to those observed here may be responsible for the degradation and "chalking" observed in TiO_2- and ZnO-based paints.[18] The addition of the proper semiconductor powder to a waste stream could be used to purify it of selected impurities by using solar energy ir-

radiation. Similarly, the same type of processes could be used for synthetic purposes. Of the semiconductors investigated here, TiO_2 is the most satisfactory from the standpoint of its chemical and photochemical stability under a wide variety of conditions. The biggest disadvantage of TiO_2 is that it absorbs such a small fraction of the solar spectrum. However, even with its low absorbance and low absolute quantum efficiency (0.06 for CN^-), TiO_2 may be worth considering in industrial processes. We have previously mentioned the common industrial methods for removing cyanide from industrial waste streams and the high capital and operating costs of these methods.[4] One method gaining some popularity is oxidation of CN^- in an electrochemical reactor.[19] If one assumes a typical reactor is capable of processing 81 000 mol of CN^- (7.8 tons of NaCN) per year, the same amount of cyanide could be processed by a TiO_2 solar reactor 85 m on a side and 3 cm deep containing sufficient TiO_2 to just cover the bottom of the reactor, assuming the rate of cyanide oxidation determined in Figure 2 as an average.

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