

Photoinduced Reaction at TiO₂ Particles. Photodeposition from Ni^{II} Solutions with Oxalate

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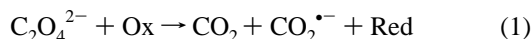
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In a photoinduced reaction, an intermediate produced by the reaction of a reductant R with photogenerated holes can promote a reduction reaction that is not observed in the absence of R. We illustrate this scheme by considering the reduction of Ni^{II} at TiO₂. In this case Ni^{II}, which is not deposited on illuminated TiO₂, can be reduced by the intermediate CO₂^{•-} produced from the anodic oxidation of oxalate ion (C₂O₄²⁻) at irradiated TiO₂ in water. Irradiation of an aqueous Ni^{II} solution containing 10 μg Ni/mL in the presence of TiO₂ particles led to 85% removal of the Ni from the solution. The mechanism of the reaction was probed by measurement of current-doubling effects for oxalate solutions at a single-crystal TiO₂ electrode.

Introduction

The photodeposition of metals on single crystal¹ and particulate TiO₂² occurs when an electron that has been excited into the conduction band (CB) is transferred to a metal ion in solution. For deposition of metal M to occur, the energy of the CB electron (defined in terms of the electrode potential vs NHE) must be more negative than the E° of the Mⁿ⁺/M couple as shown in Figure 1A. The energy of the CB of TiO₂, E_{CB}, depends on the pH and also on the crystalline form of TiO₂. For particles of anatase, at 25 °C, this ranges from about -0.29 V vs SCE at pH 0 to -1.12 V vs SCE at pH 14.³ Thus, only metal ions with relatively positive E° values, e.g., Pt, Cu, Pd, and Ag, are readily photodeposited in acidic or neutral solutions.^{2,4} For deposition of the less noble metals, e.g., Ni, a more energetic electron is needed. We show here that this can be attained by photooxidation of a species, e.g., oxalate ion, that undergoes a bond cleavage reaction to produce a more reducing intermediate capable of donating an electron to the metal ion as depicted in Figure 1B. We call this a *photoinduced* reaction.

This photoinduced reaction is closely related to parallel types of reactions carried out with chemical oxidants rather than light. For example, studies of oxalate ion oxidation (with oxidants (Ox) like Ru(bpy)₃³⁺ or Ce⁴⁺) have suggested that CO₂^{•-} is produced in reaction 1 through the production of emitting excited states:⁵



Photoinduced reactions at particles are also related to species that produce current doubling at semiconductor electrodes.^{6,7} Current doubling occurs when an intermediate (e.g., a free radical) produced by reaction with a photogenerated hole in the valence band is capable of injecting an electron into the CB as shown in Figure 1C. Indeed, this process may compete with the desired photoinduced reaction. However, it has also been demonstrated that the addition of an appropriate quencher that competes for the free radical electron can reduce the size of the current-doubling effect.⁸

For our initial studies we selected oxalate⁵ as the added reactant. Oxidation of this species leads to the cleavage of the

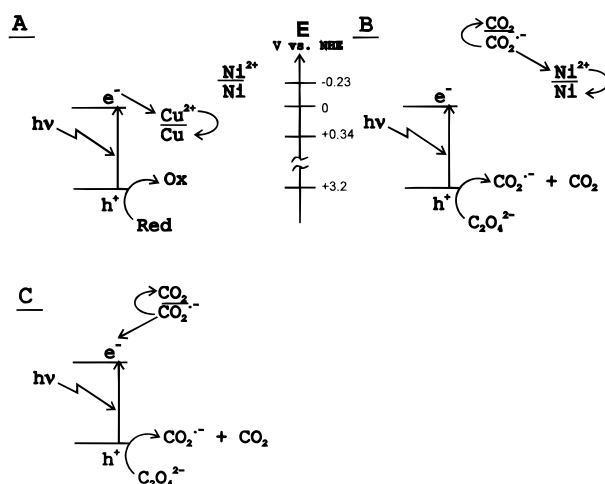
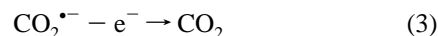
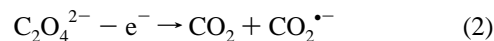


Figure 1. Relative energy diagram for the electron/hole pair generated in TiO₂ and the E° (vs NHE) of a variety of metal ions.

C–C bond to form CO₂ plus the strong reducing agent CO₂^{•-}:



The potential for the CO₂^{•-}/CO₂ couple has been reported as about -2.2 V vs SCE;^{5d} so CO₂^{•-} is capable of electron transfer to Ni^{II} and many other metal ions. Several publications have considered the photoelectrochemical oxidation of oxalic acid⁹ or oxalate,¹⁰ and we show here that although Ni^{II} is not directly reduced by irradiated TiO₂, the indirect reduction does proceed when oxalate is added to the solution. Other current-doubling agents (e.g., MeOH and EtOH) were also tested but were less effective for this reaction.

Experimental Section

Chemicals. Dimethylglyoxime (99+%, Aldrich, Milwaukee, WI), nickel sulfate hexahydrate (NiSO₄·6H₂O, 98%, Johnson Matthey, Ward Hill, MA), sodium oxalate (99.9%, J. T. Baker Inc., Phillipsburg, NJ), and titanium dioxide (TiO₂ [80% anatase, 20% rutile], Degussa P25, Teterboro, NJ) were used as received. Milli-Q water (Millipore Corp., Bedford, WA) was used for the aqueous photoelectrochemical experiments. Aqueous solu-

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tions of 5% sodium dimethylglyoximate were made by adding just enough sodium hydroxide to a dimethylglyoxime suspension to dissolve the solid.

Instrumentation. Current–potential curves were recorded on an RDE4 potentiostat (Pine Instruments Co., Grove City, PA) and a Hewlett-Packard 7045B *xy* recorder (Palo Alto, CA). A Christie Xenolite UF30KK illuminator (Christie Electric Corp., Los Angeles, CA) with a 2500 W xenon/mercury lamp operating at 1500 W was used for illumination in the single-crystal experiments. The light of the cell was filtered with a 0.5 M NiSO₄ solution in a quartz cell with a path length of 10 cm. The total intensity was determined with a Coherent Model 200 power meter. The light intensity for wavelengths below 390 nm at the cell was 5 mW/cm². UV–vis spectra were recorded on a Milton Roy Spectronic 3000 array spectrometer (Urbana, IL). Particle photocatalysis experiments utilized a Rayonet photochemical reactor (Model RPR-100) equipped with 16 mercury lamps at 350 nm (Southern New England Ultraviolet Co., Hamden, CT). For these experiments, solutions were contained in 3 cm diameter by 30 cm long quartz tubes where the incident light intensity was 9.2 mW/cm² on each tube surface.

Cells and Electrodes. A conventional three-electrode configuration was used for all single-crystal photoelectrochemical experiments. A 1 cm × 1 cm doped (by heating in a hydrogen atmosphere at 800 °C) single-crystal TiO₂ was polished on a felt pad (Buehler, Ltd., Lake Bluff, IL) with 0.05 μm alumina (Buehler, Ltd.) suspended in water. The polished crystal was mounted on a copper wire inserted in glass tubing and then encapsulated by TORR SEAL (Varian Associates, Lexington, MA). An ohmic contact between the TiO₂ semiconductor and the supporting copper wire was obtained by applying Ga–In eutectic. The resulting photoelectrode, with an effective surface area of 0.054 cm², was etched in 30% HF, rinsed with water, exposed to concentrated HNO₃ for 15 s, and then rinsed with water for about 1 min. The nitric acid treatment was repeated prior to each photoelectrochemical experiment. A 2 cm² Pt foil was used as the counter electrode, and the reference electrode was Ag/AgCl (3 M KCl).

Procedures. Analysis of Ni^{II} was performed spectrophotometrically by complexation with dimethylglyoximate as previously described.¹¹ A stock solution of ~5% sodium dimethylglyoxime was prepared by dissolving 4.123 g of sodium dimethylglyoxime and 2.087 g of NaOH pellets in 94.4 mL of H₂O. For the Ni^{II} analysis, 4 mL of the slurry was removed at different times during photoirradiation and was filtered with 0.2 μm hydrophilic single-use filters (Cole-Parmer, Chicago, IL) to remove the TiO₂ particles. The filtered solution was placed in a 60 mL separatory funnel, and 1 mL of the stock sodium dimethylglyoxime solution was added. The mixture was shaken for 15 s followed by the addition of 5 drops of a 30% ammonia solution. After the mixture was shaken for another 15 s, 3 mL of spectroscopic grade CHCl₃ was added followed by shaking for 1 min. The CHCl₃ layer, which now contained the nickel glyoxime complex, was extracted and dried by adding 0.2 g Na₂SO₄. The light absorption of the nickel complex was followed from duplicate absorption peaks recorded at 329 and 375 nm measured on a Milton Roy Spectronic 3000 array spectrometer (Urbana, IL). All data reported are derived from the behavior of the 329 nm peak. A plot of absorbance vs Ni^{II} concentration (2–12 ppm) when complexed with dimethylglyoxime was linear (correlation coefficient of 0.999). Suspensions of the TiO₂ powders in the solvent were sonicated prior to irradiation experiments to break up and disperse the TiO₂ particles. The solutions in the photocatalytic experiments, which had a total volume of 135 mL, were purged with nitrogen during

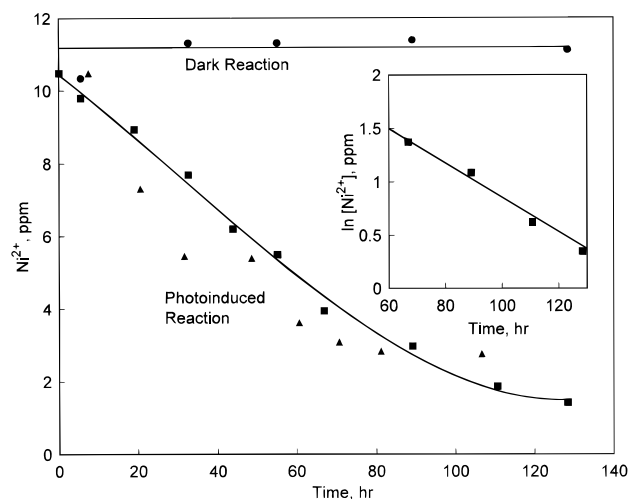


Figure 2. Aqueous Ni^{II} concentration vs time for an irradiated and a nonirradiated suspension of TiO₂ (1.0 g/L), Na₂SO₄ (0.1 M), sodium oxalate (approximately 0.05 M at 42 °C), and NiSO₄ (initially 10 ppm). Ni^{II} determined during a dark reaction (●), during a photoreaction (■), and during a photoreaction where the pH of the extracted solutions was adjusted to 2.5 prior to Ni^{II} analysis (▲). The initial pH was 7.3.

the experiments, and 5 mL aliquots were withdrawn periodically for analysis. The reaction was allowed to proceed at a steady temperature of 42 °C. The flow of nitrogen carried the evolving CO₂ gas, formed by reactions 2 and 3, into a trap of saturated Ba(OH)₂ solution in 1 M NaOH to form precipitated BaCO₃, which was weighed to determine the rate of CO₂ evolution.

In single-crystal TiO₂ experiments, where NiSO₄ was added to the electrolyte at high concentrations (1–250 mM NiSO₄), a 10 cm tubular quartz cuvette filled with 0.5 M NiSO₄ was used as a light filter. This filter decreased the variations of light intensity in the cell as a result of increasing NiSO₄ concentration and also filtered out IR radiation.

Results and Discussion

Photocatalytic Induced Reduction of Ni^{II} on Particulate TiO₂. A series of experiments was undertaken to gauge the effectiveness of TiO₂ in the deposition of Ni. Figure 2 summarizes the results of a photoelectrochemical experiment on the reduction of Ni^{II} in the TiO₂/C₂O₄²⁻ system. This figure shows a steady decrease in the Ni^{II} concentration for an irradiated TiO₂ (1 g/L)/Na₂SO₄ (0.1 M)/oxalate (0.05 M)/Ni^{II} (10 ppm), initially pH 7.3, solution. The Ni^{II} concentration does not change when the same solution with TiO₂ is kept in the dark, showing that the removal of Ni^{II} is not simply by adsorption. Other control experiments are summarized in Table 1. These demonstrate that TiO₂, light, and oxalate are all required for Ni^{II} removal.

Since Ni^{II} complexes with oxalate, the concentration of free Ni²⁺ and the distribution of Ni^{II} among the various oxalato species depend upon the pH and oxalate concentration. The appropriate equilibrium constants for oxalic acid are $pK_{a1} = 1.271$ and $pK_{a2} = 4.272$, and the overall formation constants for the Ni^{II}–oxalate system are $\log k_1 = 5.3$, $\log k_2 = 7.64$, and $\log k_3 = 8.5$.¹² Thus, at a total oxalate concentration of 0.05 M and pH 1, 35% of the Ni^{II} is uncomplexed and 65% is in the form of the mono-oxalato species. At pH 7, the distribution is the following: free, 6.3×10^{-4} %; mono-, 6.3%; bis-, 69%; tris-, 25%. This complexation also causes the potential necessary for Ni^{II} reduction to become more negative. Thus, for 99% removal of Ni^{II} from a 10 ppm (1.7×10^{-4} M) solution, the thermodynamic potential required, taking $E^\circ(\text{Ni}^{2+}/\text{Ni}) = -0.23$

TABLE 1: Conditions for Removal of Ni^{II} by Irradiation of TiO₂ Suspension^a

coreactant	UV		Ni ^{II}	sets of experiments	% Ni ^{II} removed ^b
	illuminated	TiO ₂			
none		X	X	1	0
none	X		X	1	0
none	X	X	X	2	0
oxalate		X	X	5	0
oxalate	X	X	X	6	85
oxalate	X		X	2	0
formic acid	X	X	X	1	0
ethanol	X	X	X	1	2–5
butyraldehyde	X	X	X	1	0
tri- <i>n</i> -propylamine	X	X	X	1	0

^a Conditions: TiO₂ (1 g/L), Na₂C₂O₄ (0.3 M), Ni (10 ppm); irradiation with a Rayonet photochemical reactor (see Experimental Section); X indicates presence of component. ^b After 125 h irradiation (from Figure 2).

V vs NHE,¹³ would be -0.40 V for an uncomplexed ion, -0.41 V for 0.05 M oxalate (pH 1), and -0.55 V for 0.05 M oxalate (pH 7). Kinetic considerations would dictate a more negative potential. For example, Ni^{II} in 0.05 M (NH₄)₂C₂O₄ (pH 5–8) reduces at about -0.8 V vs NHE.¹⁴ However, the CO₂^{•-} intermediate generated from oxalate is a strong reductant, since the potential of the couple CO₂(aq)/CO₂^{•-}(aq) has been estimated as 1.84 V vs NHE.^{5c}

As shown in Figure 2, the Ni^{II} concentration decreases almost linearly with time for 60 h, characteristic of a zero-order reaction, and then falls off exponentially (inset). At the same time, the pH of the solution increases from the initial value of 7 to about 9. The pH increase, which is also seen during irradiation of slurries of TiO₂ in oxalate solutions in the absence of Ni^{II}, is caused by H⁺ reduction and is currently under investigation.¹⁵ Since the *pK_{sp}* for Ni(OH)₂ is about 10⁻¹⁵, the free Ni²⁺ is never sufficiently high to cause precipitation of the hydroxide. To ensure that colloidal Ni(OH)₂ was not being formed in the solution, in one run the aliquot for analysis was acidified to pH 2.5 (following filtration) to dissolve any precipitate. The results of this trial were close to those where acidification was not done. The overall reduction of a 10 ppm Ni^{II} solution under these conditions was relatively slow, and several days of irradiation were required to reduce the Ni^{II} concentration to 1.5 ppm. The quantum efficiency, moles of Ni removed per einstein of incident photons (350 nm), was about 1% (up to 60 h). Several coreactants other than oxalate, e.g., ethanol, formic acid, butyraldehyde, and tri-*n*-propylamine, were also tried. A small reduction of Ni^{II} concentration was found with EtOH upon TiO₂ irradiation, while the other species were ineffective.

These results are consistent with the indirect reduction of Ni^{II} by CO₂^{•-} formed from the oxidation of C₂O₄²⁻ by the strongly oxidizing holes of irradiated TiO₂. Presumably, Ni^{II} is reduced to a Ni^I species, which in turn is reduced to Ni⁰ either by an additional CO₂^{•-}, a conduction band electron, or disproportionation of Ni^I to form Ni^{II} and Ni⁰. To maintain steady-state reactions at irradiated TiO₂, the conduction band electron must be removed by reduction of a solution species. Potential oxidants in the deaerated solution include water or proton and Ni^I. Four mass-spectroscopy experiments of the gas above the irradiated solutions withdrawn at different times showed the presence of small amounts of hydrogen. Hydrogen generation has also been found during irradiation of TiO₂ slurries of oxalate in the absence of Ni^{II}. To determine whether the TiO₂ particles were being charged by electrons, with a shift of the Fermi level toward more negative potentials and a decrease in the oxalate oxidation efficiency, the previously described gravimetric

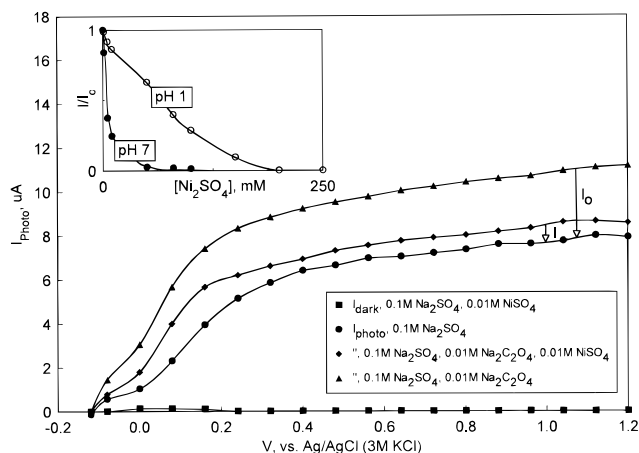


Figure 3. TiO₂ current-potential measurements: (■) I_{dark} with 0.1 M Na₂SO₄, 0.01 M NiSO₄; (▲) I_{photo} with 0.1 M Na₂SO₄, 0.01 M Na₂C₂O₄; (◆) 0.1 M Na₂SO₄, 0.01 M Na₂C₂O₄, 0.08 M NiSO₄; (●) 0.1 M Na₂SO₄. The decrease in the oxalate-induced current-doubling effect on TiO₂ upon addition of Ni^{II} is demonstrated. The effect of Ni^{II} on the EtOH-induced current-doubling effect is smaller than that of oxalate. The inset shows the decreasing trend of I_{photo} upon addition of NiSO₄.

analyses with Ba(OH)₂ were repeated. In this case, saturated solutions of Ba(OH)₂ were replaced daily, and the accumulated BaCO₃ precipitate collected over a 24 h period was weighed. A steady BaCO₃ formation of about 16 mg/day was detected, indicating that TiO₂ particle charging, if taking place at all, did not cause a large shift in the particle energy levels. Quantitatively, the number of moles of BaCO₃ obtained during the experiment is a factor of about 10 higher than the number of moles of Ni^{II} being reduced so that most of the CO₂^{•-} was not utilized for the reduction of Ni^{II}.

When the easily reducible species Fe³⁺ was added to the reaction mixture, no pH change or removal of Ni²⁺ was observed. In this case, Fe³⁺ competes for electrons in the TiO₂ and from CO₂^{•-}.

Current-Doubling Studies at a Single-Crystal TiO₂ Electrode. Further evidence for the reaction of the intermediate from oxalate oxidation (presumably CO₂^{•-}) with Ni^{II} can be obtained from studies of the photocurrent at a single-crystal TiO₂ electrode. Current doubling on TiO₂ via oxalate, EtOH, and formic acid has been reported previously.^{6–8} The basic idea is that the production of the intermediate can be estimated by the additional photocurrent found in the presence of a current-doubling agent compared to that found in the presence of a one-equivalent (noncurrent-doubling) reductant. The decrease in this additional photocurrent in the presence of Ni^{II} is a measure of the reduction of this species by the intermediate. The photocurrent-potential (*i*-*E*) response for a single crystal of TiO₂ in 0.1 M Na₂SO₄, pH 7, with the addition of different species is shown in Figure 3. In 0.1 M Na₂SO₄, the photocurrent is governed by the oxidation of water or hydroxide ion and is limited by the incident light flux. The addition of oxalate or EtOH as current-doubling agents causes an increase in the current because highly reducing intermediates can inject electrons into the conduction band. Introducing oxalate into a TiO₂/photoelectrochemical cell results in a current increase by as much as 50%, while EtOH produces about a 30% increase. When Ni^{II} is introduced, the doubled current is decreased (Figure 3) because the intermediate CO₂^{•-} can reduce Ni^{II} in competition with electron injection into the TiO₂. Note that the decrease in current is much smaller for EtOH than it is for oxalate. A similar effect is seen at pH 1 (0.1 M H₂SO₄). The decrease in

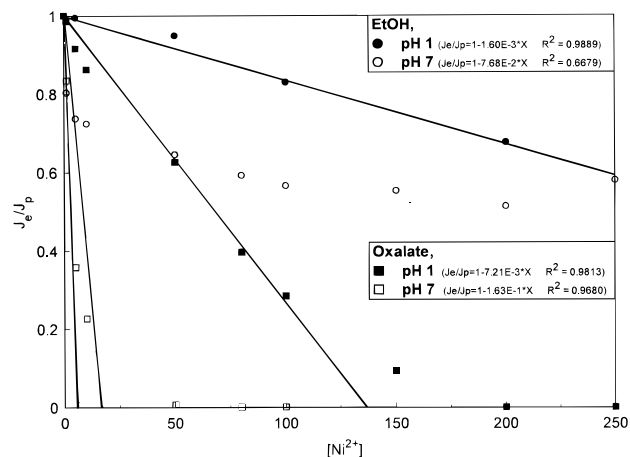


Figure 4. Ratio of electron to hole current J_e/J_p vs $[\text{Ni}^{\text{II}}]$ in solution. Data were fit following the procedure in ref 8b. The electrolyte initially contained 0.01 M $\text{Na}_2\text{C}_2\text{O}_4$ at either pH 1 (0.1 M H_2SO_4) or pH 7 (0.1 M Na_2SO_4).

photocurrent on addition of Ni^{II} at this pH is more gradual than at pH 7 (Figure 3, inset).

To ensure that the observed decrease upon addition of Ni^{II} was not caused by adsorption of the light by the solution, Ni^{II} was added to the solution in the absence of a current-doubling agent. No decrease in the photocurrent was seen. Similarly, changing the NiSO_4 concentration in the light filter from 0.5 to 0.1 M did not affect the photocurrent.

As shown previously,^{6,8} if the photocurrent density with a one-equivalent reductant is J_p and the additional contribution to the overall current density J by electron injection by the intermediate ($\text{CO}_2^{\bullet-}$) into the conduction band is J_e , then

$$J = J_p + J_e \quad (4)$$

When no other competitive processes take place, other than oxidation of the current-doubling agent and electron injection by the intermediate, $J_e = J_p$ (i.e., actual current doubling). Usually, the observed current increase is smaller because competitive oxidation of one-equivalent reductants by holes in the valence band and competitive reactions of the intermediates with oxidants in solution occur. Thus, with oxalate, when another reaction of the intermediate $\text{CO}_2^{\bullet-}$ takes place, J_e decreases, and the observed photocurrent is smaller. This occurs when Ni^{II} is added to the oxalate-containing medium. The inset of Figure 3 shows how the overall photocurrent decreases as a function of Ni^{II} concentration at pH = 1 and 7.

Gomes et al.⁸ have suggested that the variation of J_e upon addition of an oxidant Y follows the relation

$$J_e/J_p = 1 - \gamma[\text{Y}] \quad (5)$$

where $[\text{Y}]$ is the concentration of Y (here, Ni^{II}) and γ is an empirical parameter related to the rate constant for the reaction between the intermediate and Y (i.e., $\text{CO}_2^{\bullet-}$ and Ni^{II}). The intercept is taken as 1, although in a current-doubling experiment, J_e/J_p in the absence of Y is usually smaller than 1. Such a plot for the system under consideration is shown in Figure 4. The slope of the linear portion of the plot yields $\gamma = 7.21 \text{ M}^{-1}$ for oxalate and $\gamma = 1.61 \text{ M}^{-1}$ for EtOH at pH 1 and 77 M^{-1} and 163 M^{-1} at pH 7. These numbers represent the effectiveness of Ni^{II} in oxidizing the intermediate vs electron injection into the CB. By comparison of these findings to previous results,⁸ the reaction of $\text{CO}_2^{\bullet-}$ with Ni^{II} at pH 1 is about 3 orders of magnitude slower than that found for the quenching of the intermediate of MeOH or EtOH photooxidation at single-crystal

ZnO by $\text{Cu}(\text{NH}_3)_4^{2+}$. Thus, Ni^{II} is not very effective at oxidizing $\text{CO}_2^{\bullet-}$. However, the EtOH intermediate, which was efficiently oxidized by $\text{Cu}(\text{NH}_3)_4^{2+}$, is even less effective in the reduction of Ni^{II} compared to oxalate by about a factor of 7.

The single-crystal experiments showed that EtOH, formic acid, and butyraldehyde produced current-doubling effects and almost certainly yielded intermediates with potentials high enough to reduce Ni^{II} , yet only the oxalate intermediate reduced Ni^{II} at a rate to compete effectively with electron injection into the conduction band, and the rate with oxalate is much larger at pH 7 than at pH 1. A possible explanation for this behavior lies in the adsorption of the intermediates on the TiO_2 surface. At pH 7, the TiO_2 has a negative surface charge (since its isoelectric point is around pH 5) and the $\text{CO}_2^{\bullet-}$ is also negatively charged, decreasing the extent of adsorption of intermediate. At pH 1, the TiO_2 has a positive surface charge and the intermediate is protonated (HCO_2^{\bullet}) ($\text{p}K_a[\text{HCO}_2/\text{CO}_2^{\bullet-}] = 1.4$).¹⁶ Similarly, the intermediate in EtOH oxidation is uncharged. The uncharged intermediates may be adsorbed more readily on the TiO_2 and hence react more slowly with Ni^{II} .

Conclusions

An electrochemical oxidation–reduction scheme with $\text{C}_2\text{O}_4^{2-}$ as a coreactant has been used to reduce Ni^{II} indirectly via the strongly reducing intermediate $\text{CO}_2^{\bullet-}$. Although direct photoelectrochemical reduction of Ni^{II} at TiO_2 does not occur, the indirect reduction of Ni^{II} takes place when irradiated TiO_2 is used to oxidize $\text{C}_2\text{O}_4^{2-}$ to $\text{CO}_2^{\bullet-}$. Although the efficiency of the reaction of photogenerated $\text{CO}_2^{\bullet-}$ with Ni^{II} is low, removal of Ni from solutions containing ppm levels by irradiation in the presence of particulate TiO_2 and oxalate is possible. Coreactants, including butyraldehyde, EtOH, and formic acid, were also studied. The radical intermediates for these species, even though strong enough to reduce Ni^{II} , did not do so at significant rates. Current-doubling experiments at single-crystal TiO_2 electrodes in the absence and presence of Ni^{II} also provided evidence for the proposed reaction scheme.

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