# Electron transfer reactions and flat-band potentials of tungsten(VI) oxide colloids

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# Electron Transfer Reactions and Flat-Band Potentials of WO₃ Colloids

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Electron transfer reactions from different electron donors, such as $(CH_3)_2\dot{C}OH$, $\dot{C}OO^-$, $MV^+$, $Eu^{2+}$, and $H\dot{O}_2$ radicals, to $WO_3$ colloidal particles were studied by pulse radiolysis techniques. The optical properties of excess electrons in $WO_3$ colloids show an increase in absorption at wavelengths above 700 nm, which is consistent with free carrier absorption. The same absorption spectrum was also obtained after steady-state γ-irradiation and after illumination of $WO_3$ colloidal sols with visible light. Electrons injected into $WO_3$ colloids are stable in an argon atmosphere but disappear rapidly upon addition of $Fe^{3+}$, $O_2$, or $Fe(CN)_6^{3-}$. In the presence of $Cu^{2+}$ ions and PVA, the equilibrium $Cu^+ \rightleftarrows Cu^{2+} + (e^-)WO_3$ is established. The equilibrium concentration of excess electrons in the presence of $Cu^{2+}$ can be exploited to derive the flat-band potential of semiconductor colloids; the values are about 150 mV more negative than those for compact electrodes. The flat-band potential of $WO_3$ sols becomes slightly more negative with increasing radiation dose or intensity of light. These results are explained by the corresponding changes in the surface charge on the colloids.

## Introduction

In recent years numerous studies have been made on the use of semiconductor powders and colloids in various photoelectrosynthetic and photocatalytic reactions.[1] The semiconductor particles and colloids operate as miniature photoelectrodes, and information on their energy levels can be obtained by studying interfacial charge transfer reactions in microheterogeneous systems.

In the present work, electron transfer reactions involving electron donors ($M^{(n-1)+}$) and acceptors ($M^{n+}$) with $WO_3$ semiconductor colloids were studied:

$$M^{(n-1)+} + WO_{3\,coll} \rightleftarrows (e^-)WO_{3\,coll} + M^{n+} \qquad (1)$$
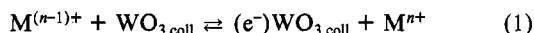
$WO_3$ has a band gap of 2.8 eV and its conduction band is at 0.55 to 0.8 V vs. NHE (at pH 0).[2] Previous work on the photoelectrochemistry of $WO_3$ demonstrated its photodecomposition resistance and ability to produce oxygen with $WO_3$ in particle form.[3,4]

A potential difference between the semiconductor colloidal particles and the solution can be produced by introduction of an appropriate redox couple in the solution. As shown in a previous study,[1p] the reduced donor, $M^{(n-1)+}$, can be generated by chemical

reactions that follow a radiolysis pulse, and electron transfer to the colloidal particles can be observed via kinetic spectrophotometry. In the present work various one-electron donors were used to inject electrons into $WO_3$ colloids, and the nature of electrons localized in the semiconductor was studied. In the presence of a suitable redox couple ($M^{(n-1)+}/M^{n+}$), the Fermi level of the semiconductor equilibrates in time with the redox potential of the couple. Under appropriate conditions, this potential can be identified with the flat-band potential of the semiconductor colloid.[1p] This equilibrium was also observed with electrons produced in colloidal particles by steady-state photolysis, and these results are compared with those determined in the dark by pulse radiolysis processes.

## Experimental Section

*Materials.* Sodium tungstate, sulfuric acid, and oxalic acid were purchased from Merck (A.R. Grade) and were used for preparation of the colloids. All other reagents were commercial products of the highest available purity. Triply distilled water was used throughout. Oxygen was removed by bubbling with argon.

Tungstic acid colloid was prepared by dissolving 3.7 g of $Na_2WO_4 \cdot 2H_2O$ in 100 cm³ of water and adding concentrated HCl drop by drop without stirring until the solution became acidic (pH ~4). A white, gelatinous precipitate formed and was washed several times by decantation at a low temperature (0–5 °C) in an argon atmosphere. The precipitate was then dissolved by gently warming in a concentrated solution of oxalic acid[5] (2.8 g in 20 cm³), and the solution then diluted to 200 cm³. The solution thus obtained is a transparent colloidal solution of white tungstic acid, which is the dihydrate, $WO_3 \cdot 2H_2O$. Oxalic acid was removed (<2 × 10⁻⁵ mol dm⁻³) from solution by dialysis; the sol was dialyzed against 0.1 mol dm⁻³ of $H_2SO_4$. The yellow colloid, $WO_3 \cdot H_2O$, was prepared from a solution which contained 2 cm³ of fresh white colloidal $WO_3 \cdot 2H_2O$, 2 cm³ of 1% poly(vinyl) alcohol (PVA), 2 cm³ of concentrated $H_2SO_4$ (96%), and 4 cm³ of water. After heating about 0.5 h at 50 °C, the solution turns yellow. This is due to the formation of the monohydrate, $WO_3 \cdot H_2O$, in 0.2% PVA; the colloid is stable in 3.5 mol dm⁻³ of $H_2SO_4$ for several days. It should be noted that the preparation of the yellow $WO_3$ colloid always requires fresh, white $WO_3$. Otherwise, the solution will not turn yellow and a white precipitate will appear at higher

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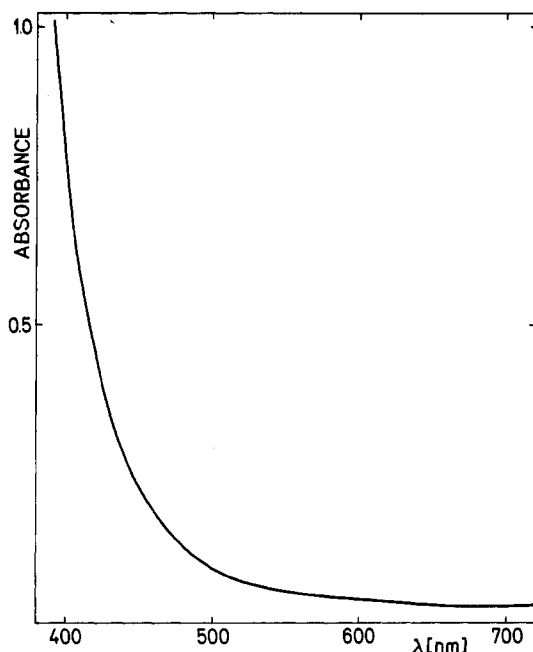
**Figure 1.** Absorption spectrum of the colloidal $WO_3$ (450-Å particle diameter, $2.2 \times 10^{-4}$ mol $dm^{-3}$ total concentration, 0.2% PVA) in a solution of 3.5 mol $dm^{-3}$ of $H_2SO_4$. Optical path length 1 cm.

$WO_3$ concentrations. The total concentration of $WO_3$ was in the range $2 \times 10^{-4}$ to $1.4 \times 10^{-2}$ mol $dm^{-3}$. Figure 1 shows the absorption spectrum of the yellow $WO_3$ colloid; this is the material that was used in the present study. The average particle diameter was estimated by electron microscopy at 450 Å. The molar concentrations of colloidal particles were calculated from the particle size and density and the molar concentration of $WO_3$.

*Apparatus.* Continuous production of the electron adduct of $WO_3$ was observed when the colloidal solution was illuminated with an Osram XBO 150-W xenon lamp. A 400-nm cutoff filter was placed in the beam to eliminate UV radiation. Each irradiation was carried out on a sample of argon-saturated solution of volume 3 $cm^3$. The light intensity was measured by potassium ferrioxalate actinometer to be $1.2 \times 10^{-6}$ einstein $min^{-1}$. Kinetic spectrometry was used to determine the absorbance of the electrons in $WO_3$ in time ranges less than 10 s. The spectrometer consisted of an Osram XBO 450-W xenon lamp, an Opton MM12 double monochromator, and an RCA 1P 8 photomultiplier tube coupled directly to a Tektronix 454 oscilloscope.

Pulse radiolysis employed a Febetron 707 (Field Emission Corporation) electron accelerator with a pulse duration of 20 ns, the operating conditions being similar to those described previously.[6] The total light path through the cell was 5.1 cm. The absorbed doses were in the range of 5–130 Gy per pulse, measured by using a potassium ferrocyanide dosimeter[7] and taking $\epsilon_{420}$- $[Fe(CN)_6{}^{3-}]$ as 1000 $mol^{-1}$ $dm^3$ $cm^{-1}$ and $G[Fe(CN)_6{}^{3-}] = 5.6$.

Steady-state irradiation was performed with a $^{60}Co$ source. The absorbed doses were in the range of 50–1000 Gy and the dose rate was 50 Gy $min^{-1}$. The measurements were made at 20 ± 1 °C.

## Results and Discussion

*Nature of Injected Electrons.* The optical properties of excess electrons in semiconductors provide information on their character. The absorption spectrum of the electron adduct of $WO_3$ was observed (see Figure 2) in the presence of 0.1 mol $dm^{-3}$ propanol-2, where $(CH_3)_2\dot{C}OH$ radicals are formed which inject electrons into the colloid. The $(CH_3)_2\dot{C}OH$ radicals have a large negative redox potential for electron donation, $E[(CH_3)_2CO/(CH_3)_2\dot{C}O^-\cdot H^+]$
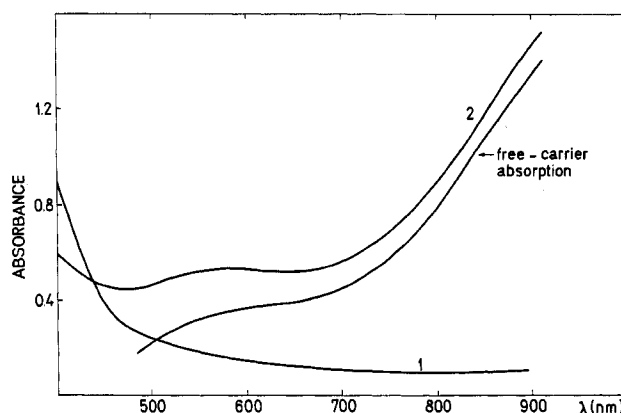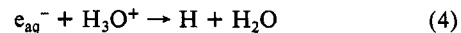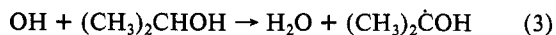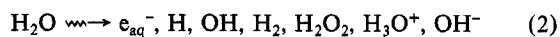


**Figure 2.** Absorption spectra obtained after $\gamma$-irradiation of a colloidal $WO_3$–PVA solution in the presence of 0.1 mmol $dm^{-3}$ of propanol-2 and 3.5 mol $dm^{-3}$ of $H_2SO_4$. Curve 1 before and curve 2 after $\gamma$-irradiation (200 Gy). After subtraction of these two spectra, free carrier absorption spectra was obtained.

$= -1.23$ $V^8$ (vs. NHE), and they can react with the sols according to

$$H_2O \rightsquigarrow e_{aq}{}^-, H, OH, H_2, H_2O_2, H_3O^+, OH^- \qquad (2)$$

$$OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2\dot{C}OH \qquad (3)$$

$$e_{aq}{}^- + H_3O^+ \rightarrow H + H_2O \qquad (4)$$

$$H + (CH_3)_2CHOH \rightarrow H_2 + (CH_3)_2\dot{C}OH \qquad (5)$$

$$2(CH_3)_2\dot{C}OH \rightarrow product \qquad (6)$$

$$(CH_3)_2\dot{C}OH + WO_{3\,coll} \rightarrow (e^-)WO_{3\,coll} + (CH_3)_2CO + H^+ \qquad (7)$$
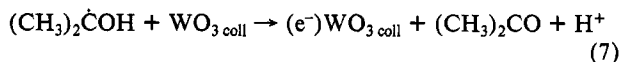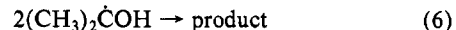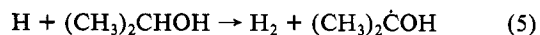
$(e^-)WO_{3\,coll}$ is a long-lived intermediate since the same absorption spectrum (Figure 2) was obtained both after pulse radiolysis and after steady-state $\gamma$-irradiation. Figure 2 (curve 2) shows a broad absorption that increases rapidly with increasing wavelengths above 700 nm; this absorption also increases with increased electron concentration in the $WO_3$ colloid. This type of spectrum is consistent with free carrier absorption.[9] However, it should be noted that strong absorption for wavelengths above 700 nm in $WO_3$ can also be obtained through the formation of hydrogen tungsten bronze ($H_xWO_3$).[10] This process involves double injection of protons and electrons into $WO_3$:

$$xe^- + xH^+ + WO_3 \rightleftarrows H_xWO_3 \qquad (8)$$
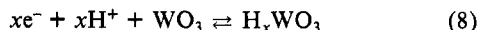
and occurs at a standard redox potential of $-0.29$ V (vs. NHE).[11] If $x$ becomes greater than about 0.5, then free carrier absorption develops.[10]

We suggest that the long wavelength absorption in the $WO_3$ colloids develops from free carrier absorption produced by direct electron injection into, and subsequent reduction of, $WO_3$ to form $WO_{3-x}$. This conclusion is based on the fact that the conduction band edge of the $WO_3$ colloid is much more positive (+0.3 to 0.5 V vs. NHE) than the $E°$ for reaction 8. Thus, electrons available from the radical donors produced by pulse radiolysis will be preferentially injected into the conduction band of $WO_3$ and have insufficient negative potential to drive reaction 8. Likewise, electrons photogenerated in $WO_3$ will also have insufficient negative potential to form the hydrogen tungsten bronze. However, additional experiments are required to unequivocally establish the absence of hydrogen tungsten bronze formation.

Beside $(CH_3)_2\dot{C}OH$, other electron donors such as $\dot{C}OOH$, $Eu^{2+}$, and methylviologen monocation can also inject electrons into $WO_3$; all these electron donors have strong negative redox

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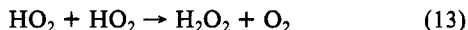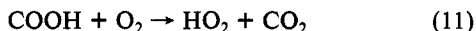(7) J. Rabani and M. S. Matheson, *J. Phys. Chem.*, **70**, 761 (1966).

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**TABLE I: Electron Transfer Reactions**

| reactions | redox potential, V | rate constant,[a] $dm^3 \ mol^{-1} \ s^{-1}$ |
|---|---|---|
| $(CH_3)_2\dot{C}OH + WO_3$ | $E[(CH_3)_2CO/(CH_3)_2\dot{C}O^-\cdot H^+] = -1.2$[b] | $\sim 2 \times 10^{11}$[c] |
| $MV^+ + WO_3$ | $E(MV^{2+}/MV^+) = -0.443$ | $2.2 \times 10^{11}$ |
| $Eu^{2+} + WO_3$ | $E(Eu^{3+}/Eu^{2+}) = -0.44$ | $4.5 \times 10^{10}$ |
| $HO_2 + WO_3$ | $E(O_2 \cdot H^+/HO_2) = -0.037$ | $4 \times 10^7$[d] |
| $(e^-)WO_3 + O_2$ | $E(2H^+ \cdot O_2/H_2O_2) = 0.65$ | $<2 \times 10^1$ |
| $(e^-)WO_3 + Fe(CN)_6^{3-}$ | $E[Fe(CN)_6^{3-}/Fe(CN)_6^{4-}] = 0.38$ | fast |
| $(e^-)WO_3 + Fe^{3+}$ | $E(Fe^{3+}/Fe^{2+}) = 0.79$ | fast |

[a] Particle concentrations were in the range $5 \times 10^{-10}–3.5 \times 10^{-8}$ mol $dm^{-3}$, diameter size 450 Å. [b] Taken from ref 8. [c] Competition with radical recombination $k[(CH_3)_2\dot{C}OH + (CH_3)_2\dot{C}OH] = 1 \times 10^9 \ dm^3 \ mol^{-1} \ s^{-1}$ (ref 14) was taken into account (50–100 Gy). [d] Competition with radical recombination $k(HO_2 + HO_2) = 8.6 \times 10^5 \ dm^3 \ mol^{-1} \ s^{-1}$ (ref 15) was taken into account (10–120 Gy).
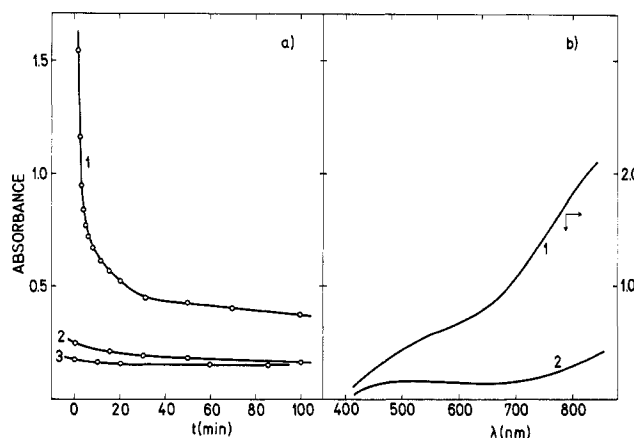
potentials ($<-0.4$ V vs. NHE). Since in $\gamma$-radiolysis the steady-state concentration of $(CH_3)_2\dot{C}OH$ radicals is very low ($10^{-9}$ mol $dm^{-3}$), there is no competition between reactions 6 and 7, and only reaction 7 takes place. The optical absorption of electrons accumulated in WO₃ colloids increased linearly with absorbed doses. These experiments were used to calculate the molar absorptivity of electrons in WO₃; the value was found to be $\epsilon_{800} = 5600 \pm 500 \ mol^{-1} \ dm^{-3} \ cm^{-1}$. Approximately the same value was also obtained when $Eu^{2+}$ or methylviologen monocation were used as electron donors in pulse radiolysis experiments for small absorbed doses ($<20$ Gy).

It is to be noted that $HO_2$, which has a redox potential $E°(H^+ \cdot O_2/HO_2) = -0.037$ V,[12] can also transfer electrons to WO₃ colloids. In aerated solutions in the presence of formic acid, only $HO_2$ radicals are formed and they can react with WO₃ colloids according to

$$OH + HCOOH \rightarrow COOH + H_2O \quad (9)$$

$$H + O_2 \rightarrow HO_2 \quad (10)$$

$$COOH + O_2 \rightarrow HO_2 + CO_2 \quad (11)$$

$$HO_2 \rightleftarrows O_2^- + H^+ \quad pK = 4.8 \quad (12)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (13)$$

$$HO_2 + WO_{3 \ coll} \rightarrow (e^-)WO_{3 \ coll} + H^+ + O_2 \quad (14)$$

The $(e^-)WO_{3 \ coll}$ product formed in reaction 14 was observed after completion of reactions 9–14 by following the absorption at 800 nm. Under pulse radiolysis experimental conditions, the $HO_2$ concentrations formed in reactions 9–11 were in the range of $3 \times 10^{-6}–6 \times 10^{-5}$ mol $dm^{-3}$; WO₃ particle concentrations of $3 \times 10^{-8}$ mol $dm^{-3}$ were used. For calulation of $k_{14}$ (rate constant for forward reaction of reaction 14) the equation given by Jayson et al.[13] was used, and the value $k_{14} = (4 \pm 1) \times 10^7 \ mol^{-1} \ dm^3 \ s^{-1}$ was obtained. Reaction 14 is slower than predicted for a diffusion-controlled reaction. The rate constants for electron injection into WO₃ by various donors are given in Table I.
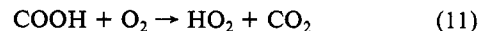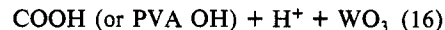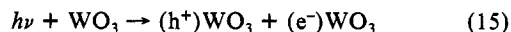
WO₃ sols with free electrons $[(e^-)WO_3]$ can be stored in argon-saturated solution and used subsequently to reduce ions with more positive standard redox potentials than the flat-band potential of the WO₃ colloid. Thus, the absorption of $(e^-)WO_3$ at 800 nm disappears immediately in the presence of $Fe^{3+}$ or $Fe(CN)_6^{3-}$ and after a few minutes upon admission of air. $Cu^{2+}$ ions are only partially reduced with electrons from WO₃, and equilibrium is established (in the presence of PVA). This effect is used to
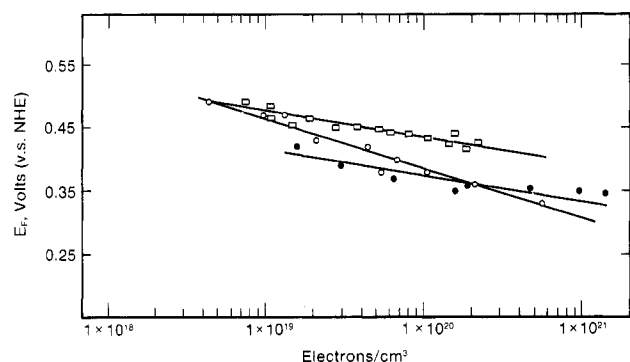
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**Figure 3.** (a) Absorbance at 800 nm as a function of time after admission of air to an irradiated solution of WO₃–PVA ($3.1 \times 10^{-3}$ mol $dm^{-3}$ total concentration, 0.2% PVA) in the presence of 3.5 mol $dm^{-3}$ of $H_2SO_4$ and 0.1 mol $dm^{-3}$ of HCOOH. Solutions were illuminated with light ($>400$ nm): (1) $6.5 \times 10^{-4}$ einsteins in argon-saturated solution; (2) $6.7 \times 10^{-5}$ einsteins in argon-saturated solution; (3) $6.7 \times 10^{-5}$ einsteins in air-equilibrated solution. (b) Absorption spectra of electrons obtained in solution of WO₃–PVA in the presence of 3.5 mol $dm^{-3}$ of $H_2SO_4$ and 0.2 mol $dm^{-3}$ HCOOH equilibrated with air: (1) $1.1 \times 10^{-2}$ mol $dm^{-3}$ of WO₃ total concentration, 0.2% PVA, illuminated with $8 \times 10^{-4}$ einsteins in argon-saturated solution; (2) $3.1 \times 10^{-3}$ mol $dm^{-3}$ WO₃ total concentration, 0.2% PVA, solution illuminated with $6.7 \times 10^{-5}$ einsteins after 90 min of equilibration with air.

determine the flat-band potential of WO₃ colloids (see below).

The same absorption spectrum as shown in Figure 2 was obtained for electrons in WO₃ produced by steady-state photolysis experiments. In these experiments, photogenerated holes were scavenged by formic acid. The following scheme explains the production of free carriers in WO₃ during the photolysis experiments:

$$h\nu + WO_3 \rightarrow (h^+)WO_3 + (e^-)WO_3 \quad (15)$$

$$(h^+)WO_3 + HCOOH \ (or \ PVA) \rightarrow$$
$$COOH \ (or \ PVA \ OH) + H^+ + WO_3 \quad (16)$$

$$COOH + O_2 \rightarrow HO_2 + CO_2 \quad (11)$$

$$HO_2 + WO_{3 \ coll} \rightarrow (e^-)WO_{3 \ coll} + H^+ + O_2 \quad (14)$$

*Effect of Oxygen.* Electrons were accumulated in WO₃ upon the continuous illumination of WO₃ colloidal sols which were equilibrated with air. There was little difference in the initial rate of electron accumulation between aerated and argon-saturated sols. For longer times of irradiation ($>75$ min), a lower steady-state concentration of electrons was established in the presence of oxygen.

In aerated solutions electrons reduce $O_2$ to $H_2O$; no $H_2O_2$ was found, after filtration of the colloid, by the iodide method for $H_2O_2$ detection.[16] If air is admitted to an irradiated WO₃ sol, the absorption of $(e^-)WO_3$ at 800 nm decreases, and after 20 min reaches an approximately constant value (Figure 3a). This absorption decrease in the presence of oxygen depends upon the concentration of electrons initially present in the WO₃ colloids. It can be seen from Figure 3a that WO₃ with a relatively small concentration of electrons (corresponding to an absorbance of 0.1 to 0.4 at 800 nm) only shows a slight change in absorbance with $O_2$, and it does not depend on whether the electrons are accumulated in argon or in air-saturated sols. However, WO₃ with larger concentrations of electrons shows a fast initial decrease in absorbance.

*Determination of Flat-Band Potentials.* It has been previously shown[1p] that the equilibration of the Fermi level (i.e., electrochemical potential) of a semiconductor colloid with the redox

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**Figure 4.** Flat-band potential as a function of electrons accumulated in $WO_3$ colloids: (O) pulse radiolysis experiments, solutions of $1 \times 10^{-3}$ mol $dm^{-3}$ of $CuSO_4$, (2.9–9.4) $\times 10^{-3}$ mol $dm^{-3}$ of $WO_3$, 0.2% PVA, 3.5 mol $dm^{-3}$ of $H_2SO_4$, 0.1 mol $dm^{-3}$ of propanol-2, absorbed doses 10–550 Gy; (●) solutions of (0.9–1.4) $\times 10^{-4}$ mol $dm^{-3}$ of $WO_3$, 0.2% PVA, 3.5 mol $dm^{-3}$ of $H_2SO_4$, and 0.1 mol $dm^{-3}$ of propanol-2 were $\gamma$-irradiated (50–1500 Gy) and then $1 \times 10^{-3}$ mol $dm^{-3}$ of $CuSO_4$ was added under argon atmosphere; (□) steady-state photoilluminated solutions of $1 \times 10^{-3}$ mol $dm^{-3}$ of $CuSO_4$, $3.1 \times 10^{-3}$ mol $dm^{-3}$ of $WO_3$, 0.2% PVA, 3.5 mol $dm^{-3}$ of $H_2SO_4$, and 0.1 mol $dm^{-3}$ of HCOOH ($5 \times 10^{-6}$–$3 \times 10^{-4}$ einsteins).

potential of a redox couple in solution can be used to determine the flat-band potential of the semiconductor colloid. In the present study, the $Cu^{2+}/Cu^+$ redox couple was used to determine the flat-band potential of $WO_3$:

$$e^-(WO_3) + Cu^{2+} \rightleftarrows Cu^+ \qquad (17)$$
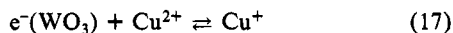
In simple aqueous solutions, $Cu^+$ is not stable and $Cu^{2+}$ is reduced to $Cu^0$. However, we find that in 0.2% poly(vinyl) alcohol (PVA) solutions, the $Cu^{2+}/Cu^+$ couple is stabilized and nearly reversible. Cyclic voltammograms show two waves that are rather well separated, corresponding to $Cu^{2+}/Cu^+$ and $Cu^+/Cu^0$ redox processes. From the cyclic voltammograms, the standard redox potential for $Cu^{2+}/Cu^+$ was determined to be +0.29 V (vs. NHE). Thus, at equilibrium with the $WO_3$ colloid:

$$E_F = E_{fb} = 0.29 + 0.059 \log [Cu^{2+}]/[Cu^+] \qquad (18)$$

The usual $E^0$ for $Cu^{2+}/Cu^+$ is +0.153 V (vs. NHE). The more positive $E^0$ values measured in PVA solution reflect effects of complexation by the polymer.

The concentration of the $Cu^+$ ions used in the determination of the flat-band potential (eq 18) was calculated from the decrease of the electron concentration in the $WO_3$ colloids caused by the presence of $Cu^{2+}$ ions.

The flat-band potentials were determined via experiments that used three different methods of electron generation in the semiconductor colloid. First, pulse radiolysis was performed with $Cu^{2+}$ present, and the absorption of $WO_3$ at 800 nm ($\epsilon_{800} = 5600$ $dm^3$ $mol^{-1}$ $cm^{-1}$) was followed as the electron transfer process proceeded to equilibrium (eq 17). Second, the electrons were first accumulated in the semiconductor colloid by $\gamma$-irradiation followed by radical oxidation, $Cu^{2+}$ ions were then added in an argon atmosphere, and the change of optical absorption in $WO_3$ was then observed. Finally, absorption at 800 nm was measured in illuminated (>400 nm) colloidal solutions with and without the presence of $Cu^{2+}$ ions. For the same type of experiments the standard deviation of the determined flat-band potentials was less

than 5%; the results for the three types of experiments are shown in Figure 4.

Figure 4 presents the dependence of $E_{fb}$ as a function of electron concentration in the $WO_3$ colloids as calculated from absorption spectra with $\epsilon_{800} = 5600$ $mol^{-1}$ $dm^{-3}$ $cm^{-1}$. The different electron concentrations were obtained by changing the absorbed radiation dose from 5 to 500 Gy or the absorbed light intensity from $5 \times 10^{-6}$ to $3 \times 10^{-4}$ einsteins, and also changing the particle concentration. As seen in Figure 4, the flat-band potential measured by using photogenerated electrons in $WO_3$ is slightly more positive than that determined in the dark from radiation/chemical processes for generating the electrons in $WO_3$. This indicates that the concentration of negative charge on the particle surface is less in the light experiments compared to the dark experiments. This is expected for n-type semiconductors if oxidation of surface species by photogenerated holes occurs, and/or the recombination rate of surface electrons is increased by the photogeneration of holes.

The values of $E_{fb}$ in Figure 4 are about 150 mV more negative than those for compact electrodes[2] and only show about 15 mV change per decade change in electron concentration; this suggests an effect of surface charge. It is well-known in photoelectrochemistry that adsorbed negative surface charge shifts $E_{fb}$ to negative values.[17] Higher concentrations of electrons injected into the colloid will change the relative amount of negative surface charge on $WO_3$ and shift $E_{fb}$ accordingly. The higher levels of adsorbed surface charge could also interfere with the usual protonic/oxide equilibrium at the surface. However, additional work is required to unequivocally assign these effects to differences in adsorbed surface charge.

## Conclusion

Yellow transparent colloidal $WO_3$ stabilized with PVA was prepared in acid solution and was stable in 3.5 M $H_2SO_4$ for several days. Absorption spectroscopy was used to study the nature of electrons injected into the semiconductor colloid. Various electron donors with redox potential more negative than −0.2 V inject electrons into $WO_3$ sols. The absorption spectrum of the accumulated electrons shows increased absorption for wavelengths above 700 nm; this is consistent with free carrier absorption.

Flat-band potentials determined in the dark upon equilibration of the $Cu^{2+}/Cu^+$ redox couple with the semiconductor colloids show an effect of surface charge. The flat-band potential of $WO_3$ colloids is about 150 mV more negative than that for compact electrodes. This difference is attributed to the negative surface charge on the colloids. However, electrons accumulated in $WO_3$ colloids are not sufficiently negative to cause proton reduction and tungsten bronze formation.

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