Cathodic photoprocesses on titania films and in aqueous suspensions

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This paper is dedicated to Professor W.J. Albery. Although I met him only once when we were both participants in a NSF-UNESCO workshop in 1984, I have keenly followed his seminal contributions to our current state of knowledge on the transport and kinetics of photogenerated charge carriers in semiconductor electrodes and colloidal suspensions. His delightful book (with M.L. Hitchman) on ‘Ring-Disc Electrodes’ also left a profound impression on me during my formative years of grappling with the mysteries of electrochemical systems, as did his extensive studies on photogalvanic cells.

Abstract

The interaction and photocatalytic reactivity of 12 metal (or metalloid) ions: Mn²⁺, Zn²⁺, Cd²⁺, Ti⁴⁺, Ni²⁺, Pb²⁺, Cu²⁺, Se⁴⁺, Ag⁺, Hg²⁺, Cr⁶⁺, and Au³⁺, with UV-irradiated TiO₂ surfaces were compared. Two distinct groups were discerned, the first six ionic species showing essentially no or a very weak tendency to accept photogenerated electrons from TiO₂, and the last six, showing a strong tendency to undergo photocatalytic reduction. The selenium species were abnormal, both in their tendency toward strong adsorption on the TiO₂ surface in the dark, and in their very high photocatalytic reactivity. Chronopotentiometry measurements on TiO₂ films provided complementary data to those obtained from UV-irradiated titania suspensions. Collectively, the photocatalytic reactivity of the 12 species of interest here, could be correlated with the energy location of the corresponding redox couples in solution with respect to the TiO₂ conduction band-edge.

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1. Introduction

Anodic photoprocesses have been exceedingly well studied on titania electrode surfaces and in aqueous suspensions in recent years [1–3]. Much of the impetus for these studies undoubtedly stems from the fact that a wide range of organic substrates (many of them, environmental pollutants) can be oxidized by the photogenerated hydroxyl radicals or holes on titania surfaces. Contrastingly, the range of reducible substrates (especially inorganic species) that have been studied by TiO₂-based heterogeneous photocatalysis is significantly narrower [4,5]. The vast majority of such studies have focused on rather easily reducible substrates such as Cu(II) and other coinage or noble metal ions (see below).

In this paper, the TiO₂-assisted photoreduction of 12 different metal ions and metalloid species is examined in a collective and comparative fashion. In particular, we focus on their reactivity toward the photogenerated electrons in TiO₂ and how that is impacted by the relative disposition of the solution redox levels relative to the TiO₂ conduction band-edge. The proclivity of these ionic species to adsorb on the TiO₂ surface in the dark, is also compared.

While there is a substantial data base on many of the metal ion substrates considered in this study (Table 1), to our knowledge, the present study constitutes the first instance wherein reducible species on UV-irradiated TiO₂, have been examined from a collective perspective. A previous study from another laboratory [10] examined a series of eight metal (Ag, Au, Cd, Cr, Cu, Hg, Ni, Pt) ions in the presence of a variety of organic species. The
emphasize that this prior study [10] was on the synergism between the conjugate oxidation and reduction half-reactions constituting the overall photocatalytic process.

2. Experimental

All chemicals were at least of reagent grade and were used without further purification. The TiO$_2$ (Degussa, P-25) photocatalyst was predominantly anatase and had a specific surface area of $\sim$ 60 m$^2$ g$^{-1}$. Deionized water was used in all cases for making solutions or suspensions. The TiO$_2$ suspension dose was 2 g l$^{-1}$.

The initial metal ion concentration was 200 μM in all cases. Prior to UV-irradiation, the metal ion (and any additive, if used) loaded TiO$_2$ suspensions were equilibrated in the dark for $\sim$ 30 min. This was done to ensure that adsorption of either the metal (or metalloid) ion and/or any co-additive on the TiO$_2$ surface, would have essentially come to equilibrium during that timeframe. The difference between the initial concentration and the amount determined at the end of the equilibration period was taken as the amount adsorbed on the TiO$_2$ surface in the dark (see Table 4 below).

Procedures for aliquot withdrawal as well as spectro-photometric analyses of the metal ions have been given elsewhere [6,7,11,15,18,59,64]. Table 2 lists the analytical wavelengths and other relevant details associated with these analyses. The instrument is the same as that deployed in the earlier studies [6,7,11,15,18,59,64].

The chronopotentiometric (CP) measurements used TiO$_2$ films as the working electrodes. These films were made by dip-coating gold foils ($\sim$ 100 mm$^2$ area and 0.25 mm thickness, Alfa Aesar) in the Degussa P-25 TiO$_2$ suspensions (isopropanol containing 10 g l$^{-1}$ oxide dose) after carefully masking one side with cellophane tape. After the dip, the foil was baked in the oven for 10 min at $\sim$ 300 °C. The dip-bake sequence was repeated eight times after which, the final coated foil was baked for 17 h at $\sim$ 300 °C. The TiO$_2$ film thus built up on the Au surface had a thickness in the 0.5–1 μm range. A 100 ml quartz beaker, with the TiO$_2$/Au working electrode and a Ag/AgCl/satd. KCl reference electrode inserted in it, completed the cell for the CP experiments. Either 0.05 M Na$_2$SO$_4$ (or 0.05 M NaCl in the Pb(II) case for solubility reasons) was used as the supporting electrolyte for these measurements. The initial substrate concentration was 200 μM as in the experiments with TiO$_2$ suspensions described above.

The metal-laden electrolyte was equilibrated with the TiO$_2$ film surface in the dark for $\sim$ 60 min. Then the rest potential was recorded before film irradiation was initiated. A 75 W xenon arc lamp (Oriel) served as the light source for the CP measurements. The light source was 16 cm away from the TiO$_2$/Au working electrode surface, and the incident photon flux (as measured with an Oriel Model 70260 radiant power/energy meter) was 2.2 mW cm$^{-2}$. The potential changes with the light on were monitored on a Houston Instrument Model 2000 recorder. The time constant of this recorder was adequate for the slow, minute-scale temporal changes of interest here.

The UV photoreactor and the medium-pressure Hg lamp deployed for the suspension measurements have been described elsewhere [15,59,64]. The photon flux in this set-up was determined by ferrioxalate actinometry [72,73]. The relative photonic efficiency was determined by the method of Serpone and coworkers [74–77]. For this purpose, the photoreduction of Cu$^{2+}$ ions was chosen as the reference (see below).
In all the cases, the TiO$_2$ suspensions were purged with ultrapure N$_2$. A N$_2$ purge was also employed for the CP measurements. Therefore, in the data to be presented below, any effect of dissolved O$_2$ in the photocatalysis medium, can be discounted. All measurements below pertain to the laboratory ambient temperature.

3. Results and discussion

3.1. Interfacial energetics in the dark

Fig. 1 compares the relative disposition of the conduction and valence band-edges ($E_{CB}$ and $E_{VB}$, respectively) of TiO$_2$ with the redox levels for the 12 metal (or metalloid) species included in this study. The latter span a $\sim$ 2.5 V range from the very difficult to reduce (Mn$^{2+}$) to very easily reduced (Au$^{3+}$) species. Thermodynamically, those metal ions with standard reduction potentials more negative than the TiO$_2$ conduction band-edge ($Zn^{2+}$, Mn$^{2+}$) cannot be photo-reduced. It is known from our previous related studies [11] that significant band-edge movement (either due to Fermi level pinning or Moss–Burstein type effects) does not occur nor do photo-processes involving ‘hot’ electrons.

The other metal ion species that can be thermodynamically reduced by the photogenerated electrons in TiO$_2$ have redox levels that fall in the upper $\sim$ 60% of the energy band-gap in the oxide semiconductor with the most positive (Au$^{3+}$) being at $\sim$ 2.0 V more positive than the conduction band-edge. In the present discussion, also note that, as a first approximation, the standard reduction potentials are used as an indicator of the metal ion energy levels rather than the vacant ($D_{ox}$) levels of the redox couples [78]. In a relative sense, this would be valid provided that the reorganization energies [79] corresponding to the 12 redox couples of interest here, are comparable. The facts that the redox reactions involve multiple electrons in almost all these cases (Ti$^+$ and Ag$^+$ being the exceptions to this trend) and that the electrochemical processes are kinetically irreversible in many instances, have to be recognized as complicating factors when the experimental data trends are examined below. Finally, two ‘clusters’ of metal/metalloid species may be recognized in the compilation in Fig. 1, one group located at potentials negative of 0 V (vs. SHE) and the other, situated positive of this demarcation line. The Cu$^{2+}$/0 redox system constitutes a bridging link between these two groups.

The interfacial energetics in Fig. 1 were compared at a ‘reference’ pH of 7. However, as Table 3 illustrates, the initial pH of the metal (metalloid) ion-laden solutions were on the acidic side to a varying extent, with the Au and Se cases being significantly so, on account of either the acidic nature of the HAuCl$_4$ salt or hydrolysis of the dissolved SeO$_2$, respectively. No attempts were made to buffer the solutions because of complications anticipated with the addition of the buffer agents to the photocatalysis medium either from adsorption, from photocatalytic activity of the buffer agents themselves.

<table>
<thead>
<tr>
<th>Species</th>
<th>Initial pH</th>
<th>After equilibration</th>
<th>After photocatalysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>5.27</td>
<td>5.45</td>
<td>4.91</td>
</tr>
<tr>
<td>Se$^{4+}$</td>
<td>4.45</td>
<td>5.35</td>
<td>5.68</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>6.21</td>
<td>5.67</td>
<td>5.02</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>5.83</td>
<td>5.89</td>
<td>4.07</td>
</tr>
<tr>
<td>Cr$^{6+}$</td>
<td>5.64</td>
<td>6.14</td>
<td>9.60</td>
</tr>
<tr>
<td>Au$^{3+}$</td>
<td>3.57</td>
<td>3.58</td>
<td>3.36</td>
</tr>
</tbody>
</table>

a Nominal uncertainty: $\pm 0.01$.

b For 30 min with 2 g l$^{-1}$ TiO$_2$ and N$_2$ purge on.

c Reaction times varied from 10 min (Ag$^+$, Au$^{3+}$), 30 min (Cu$^{2+}$, Se$^{4+}$, Hg$^{2+}$) to 60 min (Cr$^{6+}$) so that the substrate conversion was complete.

![Fig. 1](https://example.com/fig1.png) Relative disposition of the conduction and valence band-edges in TiO$_2$ and the redox energy levels for the 12 species of interest to this study. Note the discontinuity in the potential scale at $\sim$ 1.6 V (vs. SHE).
or both. The medium pH established after TiO₂ addition and the 30 min purge (Table 3) reflect the competing influences of ion interactions with the TiO₂ surface and equilibration of the hydroxylated TiO₂ surface with the aqueous solutions. We shall discuss the pH changes after photocatalysis (the fourth column in Table 3) later but for now, it is worth noting that only two of the redox potentials in Fig. 1 are pH-dependent (the Se⁴⁺ and Cr⁶⁺ cases, see below). The TiO₂ band-edges themselves have a Nernstian pH dependence of −59 mV per pH unit [1].

3.2. Dark adsorption of metal/metalloid ions on the TiO₂ surface

Table 4 compares the tendency of ten of these species to be adsorbed on the Degussa P-25 TiO₂ surface in the dark (see Section 2 for how this tendency was quantified). Se(IV) exhibits by far the greatest proclivity and Mn(II), the least, in terms of adsorption, relative to the other species, and the adsorbed amounts in these two cases differ by an order of magnitude in both directions from the other ‘median’ cases. It must be noted in this regard that both the medium pH as well as the presence of co-additives (e.g. formate, oxalate) can exert a drastic influence on substrate adsorption, and we have described these effects elsewhere for many of the species considered in Table 4 [80,81]. The remaining two species, Ni²⁺ and Au³⁺, not specifically considered in Table 4 have been examined, in terms of their adsorption proclivity on the TiO₂ surface, both by us [15] and by others [66] respectively, but under rather different conditions than those employed in this study. Thus, ~10–25% of the initial Ni²⁺ added, was adsorbed on the TiO₂ surface at pH 7 in the dark from more concentrated solutions (2–10 mM) [15]. The dark adsorption of gold chlorocomplexes was reported to be strongly pH dependent with the adsorption peaking at ~3.5 [66], which is very close to the pH in this study (Table 3).

Table 4

<table>
<thead>
<tr>
<th>Ionic species</th>
<th>[M⁺⁺]ads/μM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn²⁺</td>
<td>5.60</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>32.6</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>11.1</td>
</tr>
<tr>
<td>Ti²⁺</td>
<td>20.0</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>86.3</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>51.3</td>
</tr>
<tr>
<td>Se⁴⁺</td>
<td>158</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>59.8</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>14.1</td>
</tr>
<tr>
<td>Cr₂O₇²⁻</td>
<td>38.5</td>
</tr>
</tbody>
</table>

Fig. 2. Photocatalytic conversion of five inert species. The lines are least-squares fits and are mainly shown as a guide to the data points. The initial concentration of the metal ion in each case was 200 μM. The concentrations at time zero reflect the amount adsorbed on the TiO₂ surface (refer to text and Table 4).

Fig. 3. As in Fig. 3 but for the reactive species. The lines are least-squares fits.

3.3. Photocatalytic reactivity of the various metall metalloid species toward the photogenerated electrons in TiO₂

Figs. 2 and 3 contain the relevant data, once again for ten species. The comparative behavior of Ni²⁺ and Au³⁺ is deferred to a later juncture in this discussion. Clearly, the two substrate clusters identified in the preceding section manifest very different photocatalytic behavior: those with standard reduction potentials negative of 0 V (vs. SHE) being inert (Fig. 2) and the other group, comprising of species with rather positive standard reduction potentials, being reactive (Fig. 3). However, close examination of the ‘inert’ group in Fig. 2, does reveal subtle variations in reactivity with Ti¹⁺
and Pb\(^{2+}\) showing a slight but measurable tendency toward photoreduction. Referring back to Fig. 1, note that both these species do ‘lie below’ the TiO\(_2\) conduction band-edge.

More drastic reactivity variations are seen within the ‘reactive’ group in Fig. 3. Interestingly, four of the five species here exhibit the same zero-order kinetics trend (constant rate), and even Cr(VI) falls in that category in the initial photoreaction time span (less than 10 min). The rate thereafter slows down abruptly in this case for reasons discussed by us elsewhere [64]. Specifically, Cr(VI) is anomalous relative to the other cases discussed in that its reduction requires a hefty dose of protons in the interfacial zone. At a pH \(\sim 6\) (Table 3), this reaction zone is rapidly starved of protons (see below) resulting in a progressive diminution of the conversion rate [64].

Characteristic photoreaction half-times \((t_{1/2})\) are plotted versus the standard reduction potential \((E^\circ)\) for five of the ‘reactive’ cases in Fig. 4 (c.f. Fig. 3). A rough correlation between the two parameters translates to a generally faster reaction rate with a more positive redox potential (with respect to the TiO\(_2\) conduction band-edge), or equivalently to a greater thermodynamic driving force for the photodriven electron-transfer process. The abnormally low \(t_{1/2}\) value in the Se(IV) case in Fig. 4 is probably related to its significantly higher adsorption on the TiO\(_2\) surface (Table 4), and the fact that the photoreduction proceeds beyond the elemental \((\text{Se}^0)\) state (see below). The Ag\(^+\) case is also an outlier in the correlation in Fig. 4 in that its \(t_{1/2}\) value is lower than expected. Referring to Table 4, it is seen that the adsorption affinity of this ion to the TiO\(_2\) surface, exceeds that of the other two reactive species \((\text{Hg}^{2+} \text{ and Cr}^{6+})\) with more positive redox potentials. (While the adsorption of Cu\(^{2+}\) and Ag\(^+\) is roughly comparable (Table 4), the former has a much more negative standard reduction potential, see Fig. 1).

Turning to the two cases not specifically considered in Figs. 2 and 3, namely Ni\(^{2+}\) and Au\(^{3+}\), we see that the \(t_{1/2}\) value for the reactive Au\(^{3+}\) species (taken from Ref. [66]) does fall in line with the other species in the correlation plot in Fig. 4. The nickel case has been studied previously in our laboratory (albeit under conditions somewhat different from those employed here) [15]. Its photocatalytic reactivity is comparable to Pb\(^{2+}\), and thus Ni\(^{2+}\) must be included in the photocatalytically ‘inert’ group, of the two groups discussed earlier in Fig. 1. On the other hand, another metal ion species not considered here, but extensively studied previously [1–5], namely Pt\(^{4+}\), falls in the photocatalytically reactive category with its rather positive redox potential (0.7175 V vs. SHE).

Finally, it is pertinent to point out that the vertical displacement of the various conversion profiles in Figs. 2 and 3 (at time zero) is related to the corresponding adsorption affinity of the ionic substrate toward the TiO\(_2\) surface (see Table 4 above).

### 3.4. Relative photonic efficiencies for the photocatalytic reduction of metallaloid species

To provide a relative ordering of the photocatalytic reactivity, the initial (< 10 min) rate of reduction of the various metal ions was compared against copper as a reference under identical experimental conditions (same initial concentration, same reactor, same incident photon flux, etc). This ratio of the initial reaction rate can be viewed as a relative photonic efficiency for the photocatalytic process of interest [74–77].

Tables 5 and 6 contain our results on the 11 metal ion substrates included in this study. Selenium was not included in this compilation because of the associated complications alluded to earlier and elaborated in the next section. Copper was chosen as the reference substrate because it forms the bridging link between the inert substrates and the reactive ones (see above and Fig. 1). The data in both these tabulations were acquired under identical experimental conditions (see Section 2) and under an incident photon flux (as determined by ferrioxalate actinometry) of \(2.28 \times 10^{-2}\) mol min\(^{-1}\). The group in Table 5 contains five of the reactive species and Pb\(^{2+}\) (the most reactive among the inert substrates, Fig. 2). As with the correlation presented earlier in Fig. 4, the trend in the relative photonic efficiency parallels that established earlier in Figs. 3 and 4 with the exception of Ag\(^+\) which shows a high value for this parameter (recall that this substrate also showed an anomalously low value for \(t_{1/2}\), Fig. 4).

The corresponding group in Table 6 contains the photocatalytically inert candidates. To provoke a measurable photoconversion in these cases (c.f. Fig. 2), a co-

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Fig. 4. Correlation of the photocatalytic reaction half-lives \((t_{1/2})\) for the six reactive species. The \(t_{1/2}\) value for the Au\(^{3+}\) case was taken from Ref. [66] and the other five values were culled from the data in Fig. 3.
additive, namely formate, was also added to the medium. From companion studies in our laboratory [7] and elsewhere [14,17,42,82], we know that initial photooxidation of formate generates highly reducing free radicals which in turn, can reduce the various Mn/C27 (M = metal) species. Interestingly, Pb2+/C27 exhibits the highest relative photonic efficiency in this instance and Mn2+/C27 along with Zn2+/C27 show rather low values for this parameter. Equally intriguingly, the ordering of these six substrates in Table 6 is roughly in line with the location of their corresponding standard reduction potentials (Fig. 1), Ni2+/C27 being the lone exception with an anomalously low value for the relative photonic efficiency. All other things being equal, the relative ordering of the values for this parameter in Table 6, must somehow reflect the thermodynamic driving force for the reaction between the formate radical (with $E^\circ = -1.81$ V vs. SHE, Ref. [83]) and the various metal ion species with progressively more positive values for $E^\circ$ (Fig. 1). In this regard, the factors underlying the anomalously low reaction cross-section in the Ni2+/C27 system are currently not known although complexation effects [14] could play a role here. Another complicating factor in correlations such as those in Fig. 4 and Tables 5 and 6 (as pointed out by a reviewer) is the fact that the various metal-ion containing solutions may have a variable UV light-screening action.

### 3.5. Chronopotentiometry data

Figs. 5–7 contain the CP data grouped into the photocatalytically inert species with either negligible or very small (but measurable, Fig. 2) photocatalytic reactivities (Fig. 5) (Ti+/C27, Pb2+/C27, Zn2+/C27), two (Cu2+/C27, Cr3+/C27) photocatalytically reactive cases (Fig. 6), and the anomalous Se4+/C27 case (Fig. 7). In each of these figures, the control CP run, involving the supporting electrolyte and no intentionally added electron acceptor, is also shown for comparison. The profiles for Mn2+/C27 and Cd2+/C27 are omitted from Fig. 5 for the sake of clarity. The CP profiles for the Na2SO4 and NaCl supporting electrolytes (see Section 2) were virtually indistinguishable; therefore, only the former is shown in Figs. 5–7. All potentials in this section are quoted with respect to the Ag/AgCl reference electrode unless otherwise mentioned.

The rest potentials in the dark span a ~ 300 mV range in the various cases (Figs. 5 and 6), with Cr6+/C27 being the most positive and Pb2+/C27 being the most negative. In the absence of any additive to the suspension, the rest potential of the TiO2 film is ~ 230 mV. This value, of course, depends on the medium pH as elaborated.
Elsewhere [84]. For the inert cases, the rest potentials fall within a narrower, 150 mV span. These variations in the rest potential, presumably reflect subtle ion–film interaction processes within the double-layer region, and are not directly germane to the focus of the present study.

When the excitation light source is turned on, the TiO$_2$ film potential becomes negative in all the cases in Figs. 5–7, regardless of the presence/absence of any substrate and the photocatalytic reactivity of the latter. This potential excursion and its negative polarity reflect the population of the TiO$_2$ conduction band with photogenerated electrons [85]. The subsequent behavior over the next couple of minutes is what is most germane to this study: i.e. the pattern thereafter is sensitive to whether an electron acceptor is present and its photocatalytic reactivity. Let us consider the baseline TiO$_2$ | electrolyte interface first (i.e. one containing no reducible substrate).

Upon photoexcitation, the TiO$_2$ film potential moves ~550 mV negative of its rest value in the dark. Thereafter, there is an abrupt polarity shift followed by a slow relaxation, and a gradual positive shift over the next ~5 min before the final potential attains a plateau value of ~−100 mV. We assign the positive shift and the relaxation to carrier trapping at the film | solution interface. This appears to be a surprisingly slow process which presumably reflects the fact that the film is mesoporous and the electrolyte can permeate its porous network [86]. Mass transport limitations are not likely to be a major contributor here because of stirring of the electrolyte by the inert gas purge. A more detailed account of this CP behavior along with numerical simulations will be published elsewhere [84].

Turning now to the influence of substrates on the CP behavior, we can begin with the inert or mildly reactive ones first (Fig. 5). No appreciable perturbation of the CP profile (from the control case with no added substrate) is seen and the rest→negative→positive→plateau potential progression is essentially preserved.

In the presence of mildly reactive substrates (Fig. 5), the negative excursion is much less when the light is initially turned on, and the upturn occurs at ~100 mV. The final potential plateau attained in the Ti$^{2+}$ and Pb$^{2+}$ cases is essentially identical, although the progression to it is rather different in shape. Note that the plateau potential is positive of the control case and even more so, relative to the inert substrates (c.f. Ti$^{2+}$ and Zn$^{2+}$ profiles in Fig. 5).

The reactive substrates manifest a more drastic perturbation of the basic CP profile in that the initial negative excursion is quenched to varying degrees, Cr$^{6+}$ much more so than in the case of Cu$^{2+}$ (Fig. 6). The final plateau potential is appreciably more positive than the cases discussed earlier, and is now ~100 mV for Cu$^{2+}$ and ~350 mV for Cr$^{3+}$. In the case of Cr$^{6+}$, the negative potential ‘spike’ (and the subsequent upturn) is not seen but instead, the CP profile manifests a smoother progression to the final plateau potential.

Finally, the temporal potential profile of the TiO$_2$ film in contact with Se$^{4+}$ is compared with the control case elsewhere [84]. For the inert cases, the rest potentials fall within a narrower, 150 mV span. These variations in the rest potential, presumably reflect subtle ion–film interaction processes within the double-layer region, and are not directly germane to the focus of the present study.
in Fig. 7. Contrasting with all the examples presented earlier in Figs. 5 and 6, the plateau potential in the Se⁴⁺ case is considerably more negative ( ~ −300 mV), and the upturn after the initial negative excursion, is now barely discernible. Indeed, Cr⁶⁺ and Se⁴⁺ represent limiting examples of cases with the most positive and most negative plateau potentials respectively. The plateau potential presumably is defined by the potential at which the quasi-Fermi level within the irradiated titania phase is ‘pinned’ at steady-state. This is obviously influenced by the depolarization effect of the electron acceptor added to the suspension. In the absence of this ‘depolarizer’, the quasi-Fermi level will reflect the trap state location at the surface where the photogenerated electrons undergo recombination with the holes.

The anomalous CP behavior in the presence of Se⁴⁺ can be rationalized on the basis of recent observations from another laboratory [34]. These authors observed that selenate ions are reduced to hydrogen selenide via amorphous selenium in UV-irradiated titania suspensions. The reaction:

\[
\text{Se} + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{Se}
\]  

has an associated standard reduction potential of −0.4 V (vs. SHE). Referring to Fig. 1, we see that the corresponding energy level would fall below the TiO₂ conduction band-edge. Indeed the final plateau potential in Fig. 7 falls in the regime where this reaction can become important. The interfacial formation of Se²⁻ species would also explain our earlier observation of a progressive reduction in the amount of Cd²⁺ ions when dosed into a suspension containing Se-modified TiO₂ particles [33]. That is, the ‘reduction’ of Cd²⁺ is induced by the generation of CdSe:

\[
\text{Cd}^{2+} + \text{Se}^{2-} \xrightarrow{hv} \text{CdSe}
\]  

It is tempting to attribute the extreme photocatalytic reactivity of Se⁴⁺ species (note that a net transfer of 6e⁻ would be required to generate Se²⁻ species) to its strong affinity for the TiO₂ surface (see Table 4). In retrospect, the anomalous location of Se⁴⁺ in the correlation presented earlier in Fig. 4 can also be readily accommodated within the framework of the CP data.

3.6. Conjugate reaction effects

At steady-state, the cathodic photocorss on the TiO₂ particle surfaces must be balanced by their anodic conjugate reaction counterparts [87]. Clearly, the oxidation reaction components in these cases involve the photogenerated holes in TiO₂. While not directly probed in detail in this study, the observed pH changes after photocatalysis (Table 3) do afford useful clues on these conjugate processes as well as on any consumption of protons by the cathodic reaction counterparts themselves. Thus, in every photocatalytically active case in this study except Se⁴⁺ and Cr⁶⁺, there is a measurable and consistent downward shift in the medium pH after photocatalysis (Table 3) signaling that protons are released in the overall photocatalytic process. Clearly, these protons must originate from the anodic conjugate reaction involving the photooxygenation of either the TiO₂ surface hydroxyl groups or water itself.

On the other hand, the net pH increase observed in the Se⁴⁺ and Cr⁶⁺ cases (Table 3) must imply that the pH decrease (proton liberation) from the anodic conjugate process is largely offset by the consumption of protons in the cathodic reaction counterparts:

\[
\text{SeO}_3^{2-} + 6\text{H}^+ + 4e^- \rightarrow \text{Se} + 3\text{H}_2\text{O} \quad (3)
\]

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad (4)
\]

The relative magnitudes of the pH change in the two cases (i.e. chromium manifesting a much larger change, Table 3) are consistent with the stoichiometry of the two cathodic reactions in Eqs. (3) and (4), respectively.

4. Concluding remarks

Reasonably well-defined trends have been unearthed in this study on the interaction and photocatalytic reactivity of 12 metal (or metalloid) ions with UV-irradiated TiO₂ surfaces. These species can be divided into two groups: one containing Mn²⁺, Zn²⁺, Cd²⁺, Ti⁴⁺, Ni²⁺, and Pb²⁺, which are photocatalytically inert and another, comprised of Cu²⁺, Se⁴⁺, Ag⁺, Hg²⁺, Cr⁶⁺, and Au³⁺, which are photocatalytically reactive. It would appear from the data presented above that the most reactive species (Se⁴⁺) are also the most strongly adsorbing on the TiO₂ surface (c.f. Table 4 and Fig. 4). It is tempting to attribute the similarly high photocatalytic reactivity of Ag⁺ ions to its strong tendency toward adsorption on the TiO₂ surface. In all cases, there is a broad trend toward higher photocatalytic reactivity (i.e. a stronger electron accepting tendency) with a more positive standard reduction potential of the corresponding metal ion, with respect to the TiO₂ conduction band-edge.

The good correlations and trends observed here are encouraging considering that possible complications from complexation and speciation effects (involving the variousionic species in solution) have been ignored in this study. Future efforts will focus on an examination of such higher-order effects as well as those induced by chemical modification of the titania surface.
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References

[84] W. Sun, K. Rajeshwar, to be published.