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Proton coupled electron transfer from Co$_3$O$_4$ nanoparticles to photogenerated Ru(bpy)$_3$$^{3+}$: base catalysis and buffer effect

Giulia Alice Volpato,$^a$ Alessandro Bonetto,$^b$ Antonio Marcomini,$^b$ Pierre Mialane,$^c$ Marcella Bonchio,$^d$ Mirco Natali*$^a$ and Andrea Sartorel*$^a$

Co$_3$O$_4$ nanoparticles in the spinel crystalline structure are among the most promising catalysts for the water oxidation reaction, displaying remarkable activity under electrochemical and light-assisted conditions. In the presence of Ru(bpy)$_3$$^{3+}$ as photosensitizer (bpy = 2,2'-bipyridine) and Na$_2$S$_2$O$_8$ as electron acceptor, 5±1 nm size Co$_3$O$_4$ nanoparticles show a slow primary electron transfer (ET) to photogenerated Ru(III), occurring in a timescale of tens of milliseconds. We demonstrate herein that: (i) photo-oxidation of Co$_3$O$_4$ NPs by Ru(III) involves transformation of surface Co(III)-OH moieties to formal Co(IV)=O, along a proton-coupled electron-transfer (PCET) pathway; (ii) the rate of the process depends on pH, on the nature and concentration of the buffer; (iii) borate promotes general base catalysis of the PCET; (iv) inhibition of the PCET is observed at high buffer concentration, due to H$_2$BO$_3$ poisoning of the surface Co sites, resulting in depletion of the O$_2$ evolution activity.

Introduction

The development of efficient water oxidation catalysts (WOCS) has been the subject of intensive research in the last decade. Since the pioneering studies by Harriman,$^1$ cobalt oxide nanoparticles (NPs) have been recognized as very active WOCs, displaying low operating overpotentials ($\eta = 0.30 - 0.40 \text{ V}$)$^{2,3,4,5}$ and residing close to the top of the Volcano plot for metal oxides,$^6$ while promoting fast catalysis (turnover frequency (TOF) up to 3 s$^{-1}$ per surface catalytic site)$^{3,7}$

In addition, cobalt oxide NPs, in the Co$_3$O$_4$ cubic spinel crystalline structure, have been employed as WOCs in light activated sacrificial systems employing photogenerated Ru(bpy)$_3$$^{3+}$ oxidant.$^8,9,10,11,12$ with quantum yield up to 0.07,$^13$ and spectroscopic evidence of Co(III)-OH moieties as the active surface sites.$^7$ Investigation of such light-activated systems may lead to important mechanistic information on the catalyst evolution along the oxygenic cycle.$^{14-16}$ In particular, we have recently reported that Co$_3$O$_4$ NPs, either without stabilizing ligands or capped with bisphosphonate alendronate pendants, suffer from a slow electron transfer (ET) to photogenerated Ru(bpy)$_3$$^{3+}$, occurring in a timescale of tens of milliseconds,$^{13}$ resulting several orders of magnitude slower than ET observed with molecular Co complexes.$^{17-20,21}$ Slow ET rates may impact on the performance of light-activated systems, in particular when the catalyst is embedded in dye-sensitized photoelectrodes.$^{22,23}$ In this work, we take advantage of laser flash photolysis studies to investigate the mechanistic origin of such photoinduced ET process involving surface sites of Co$_3$O$_4$ NPs. Relevant observations are: i) the attribution of this process to a proton-coupled electron-transfer (PCET) involving oxidation of Co(III)-OH sites to Co(IV)=O, by comparison with CoFe$_2$O$_4$ spinel nanoparticles (30 nm size); ii) the impact of the solution buffer on the primary PCET event; iii) a general base catalysis effect of borate buffer along the PCET; iv) the inhibition of the PCET process and abatement of O$_2$ evolution activity at high buffer concentration, likely ascribable to H$_2$BO$_3$ coordination to surface sites.

Results and discussion

Co$_3$O$_4$ NPs with 5±1 nm size were synthesized as previously described,$^{13}$ using the procedure by Niederberger et al.$^{12}$ see characterization in the ESI (Fig. S1-S4†) and in reference 13. We examined by laser flash photolysis the ability of Co$_3$O$_4$ NPs (100 µM formal concentration)$^{13}$ in giving ET to Ru(bpy)$_3$$^{3+}$, photogenerated in few ns upon laser excitation of 50 µM Ru(bpy)$_3$$^{2+}$ in the presence of 5 mM Na$_2$S$_2$O$_8$ in 0.004-0.4 M borate buffer at pH 8.0-9.5 (the concentration refers to the H$_2$BO$_3$/B(OH)$_2$ acid/base couple, pK$_a$ = 8.6$^{24}$), see eqs 1-4.$^{13}$

$$\text{Ru(II)(bpy)}_3^{2+} + h\nu \rightarrow \text{*Ru(II)(bpy)}_3^{2+}$$

(1)
The laser-induced generation of Ru(III) (eqs 1-3) is associated to the prompt formation of a negative ΔOD at 450 nm (bleaching of the MLCT ground-state absorption, indicative of Ru(II)→Ru(III) transformation by photoinduced oxidative quenching with persulfate) and occurs within ca 10 μs.\(^\text{16,21}\) The progressive increase of the ΔOD\(^\text{450}\) (bleach recovery, see traces in Fig. 1) is then representative of the occurrence of the reduction of Ru(III) to Ru(II) by CoO\(_2\) NPs (eq 4).\(^\text{16,21}\)

\[\text{Ru(II)(bpy)}^2+ + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Ru(III)(bpy)}^3+ + \text{SO}_4^{2-} + \text{SO}_2\text{O}_4^{2-} \quad (2)\]

\[\text{Ru(II)(bpy)}^2+ + \text{SO}_4^{2-} \rightarrow \text{Ru(III)(bpy)}^3+ + \text{SO}_2\text{O}_4^{2-} \quad (3)\]

\[\text{Ru(III)(bpy)}^3+ + \text{CoO}_4 \rightarrow \text{Ru(II)(bpy)}^2+ + \text{CoO}_4\text{(h}^+) \quad (4)\]

Looking into more details at the kinetic traces in Fig. 1, the rate and the amount of the ΔOD\(^\text{450}\) recovery in a timescale of ca 90 ms were found to be dependent on the pH and on the concentration of the buffer. Typically, the rate of the ΔOD\(^\text{450}\) recovery is first order in Ru(III) concentration and is thus expressed by eq. 5.

\[\text{Rate} = -d[\text{Ru(III)}]/dt = k_{\text{obs}}[\text{Ru(III)}] \quad (5)\]

In the present case, however, the traces were not accurately fitted with single-exponential decays associated to eq. 5. Non-exponential kinetics were observed for photoinduced proton-coupled electron-transfer (PCET) involving ZnO nanocrystals, and were attributed to the presence of different type of subsurface and surface sites.\(^\text{27}\) Moreover, in the present case, difficulties in fitting the traces are also due to a low recovery of the ΔOD\(^\text{450}\) bleach in the instrumental timescale limit of ca 90 ms (see Fig. 1a), and to the impossibility of investigating the system under pure pseudo-first order conditions with respect to photogenerated Ru(III).\(^\text{7}\) Indeed, under optimized conditions, photogenerated Ru(III) concentration is \(\sim2\times10^{-5}\) M, while surface sites potentially involved in the PCET process are \(\sim2.5\times10^{-5}\) M, being estimated as \(\%\) of the total formal concentration of CoO\(_2\) NPs \(=10^{-3}\) M.\(^\text{13}\) We thus estimated the kinetic constant \(k_{\text{obs}}\) of the process from the reciprocal of the Ru(III) lifetime according to eq. 6, where \(\tau\) is experimentally determined at half recovery of the ΔOD\(^\text{450}\) in the experimental traces.\(^\text{7}\) The determined values of \(\tau\) and of \(k_{\text{obs}}\) in the different conditions are reported in table S\(1^\text{1}\). For the sake of comparison, we have also included the \(\tau\) and \(k_{\text{obs}}\) values derived from single or multi-exponential fitting of the traces, that lead to a good match with the values determined as described above (see Table S\(1^\text{1}\) and S\(2^\text{1}\)).

\[k_{\text{obs}} = \ln(2)/\tau \quad (6)\]

\(k_{\text{obs}}\) was observed to increase upon increasing both the pH and the total buffer concentration (Fig. 3). At each pH investigated, linear correlations were observed by plotting \(k_{\text{obs}}\) vs. the concentration of the B(OH)_\text{4}^- base in solution, with the latter given by [Base] = \(f_B\times[\text{buffer}]\), where \(f_B\) is the fraction of the B(OH)_\text{4}^- basic form of the buffer, and [buffer] is the total buffer concentration (Fig. 3).\(^\text{28,29,30}\) These results suggest a general base catalysis by B(OH)_\text{4}^-, assisting deprotonation of surface oxygen sites along a PCET process.\(^\text{31,32}\) A similar observation was previously documented for the amorphous cobalt oxide (CoPi) under electrocatalytic conditions, where Co(III)-OH surface sites convert into Co(IV)=O.\(^\text{15,18}\) Importantly, this PCET transformation is also postulated as the primary event in the water oxidation cycle by CoO\(_2\) NPs.\(^\text{7}\) The general base catalysis associated to the Co(III)-OH → Co(IV)=O PCET is expected on the basis of the predicted change in pK\(_a\) of the surface OH group upon oxidation of the cobalt centre. According to the libido rule,\(^\text{24}\) the pK\(_a\) of the acid/base couple (pK\(_{a}\)=8.6 for H\(_2\)BO\(_3^{-}/\text{B(OH)}^\text{3-}\)) has to be intermediate between the pK\(_a\) of Co(III)-OH and Co(IV)-OH groups. The general kinetic law for the PCET can thus be expressed according to eq. 7, where \(k_0\) is
the rate-constant for the base assisted process and \( k_b \) (eq 8) represents the rate constant for the PCET under unbuffered conditions (i.e., with both water and OH\(^-\) acting as base).

\[
\begin{align*}
  k_{obs} &= k_0 + k_b[B] \\
  k_0 &= k_{H_2O} + k_{OH^-}[OH^-]
\end{align*}
\]

(7) (8)

According to eq 7, the rate constants \( k_0 \) and \( k_b \) can be determined from the fitting of the data in Fig. 3 (see table 1). As expected, \( k_b \) values obtained under different pH conditions fall in an appreciably narrow range of 6.3-8.5 × 10\(^{-2}\) M\(^{-1}\) s\(^{-1}\) (table 1). Importantly, experiments conducted in deuterated medium (figure S6†) show a lower \( k_b \) value of 4.9 ± 1.0 × 10\(^{-2}\) M\(^{-1}\) s\(^{-1}\), corresponding to a kinetic isotope effect, KIE = \( k_b(H)/k_b(D) \) = 1.4 ± 0.3. The small isotope effect is indicative of a low modification of the overlap integrals of the donor-acceptor states along the proton transfer coordinate by replacing H with D.\(^{35}\) Interestingly, values comprised between 1.6 and 2.7 were observed for PCET involving Mn-oxides assisted by substituted pyridines.\(^{36}\)

Concerning \( k_0 \), its value is pH dependent, as expected due to separate contributions of H\(_2\)O and OH\(^-\) acting as base (eq. 8). From a linear fitting of \( k_0 \) vs [OH\(^-\)], values of \( k_{H_2O} = 1.7 \pm 0.1 \) s\(^{-1}\) and \( k_{OH} = 5.5 \times 10^{-2} \) M\(^{-1}\) s\(^{-1}\) can be estimated (Fig. S7†).

![Figure 3. Plot of \( k_{obs} \) vs. [Base], where Base is B(OH)\(_4\)\(^-\), and the concentrations are given by [Base]=[buffer], where \( f_b \) is the fraction of the basic form of the buffer in solution, and [buffer] is the total buffer concentration;\(^{37}\) \( pK_a \) for the H\(_3\)BO\(_3\)/B(OH)\(_4\)\(^-\) couple = 8.6. For \( k_{obs} \) values at pH 8 the error bars are smaller than the circles and are thus not visible in the graph (see Table S1 in the ESI).](image)

**Table 1.** Kinetic rate constants for PCET from Co\(_3\)O\(_4\) NPs to Ru(III)(bpy),\(^{38}\) determined by flash photolysis experiments. Errors are given from the associated linear fittings (see fig. 4).

<table>
<thead>
<tr>
<th>pH</th>
<th>( k_{H_2O} ) s(^{-1})</th>
<th>( k_{OH^-} ) × 10(^{-2}) M(^{-1}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>2.3 ± 0.2</td>
<td>6.3 ± 0.9</td>
</tr>
<tr>
<td>8.5</td>
<td>2.6 ± 0.2</td>
<td>6.3 ± 0.5</td>
</tr>
<tr>
<td>8.9</td>
<td>8.8 ± 0.5</td>
<td>8.5 ± 1.2</td>
</tr>
<tr>
<td>9.5</td>
<td>15.9 ± 1.1</td>
<td>7.0 ± 0.3</td>
</tr>
<tr>
<td>8.6(^{37})†</td>
<td>3.4 ± 1.0</td>
<td>4.9 ± 1.0</td>
</tr>
</tbody>
</table>

\(^{37}\)In deuterated solvent; \( pD \) was calculated according to the equation \( pD = 0.929pH_{\text{deut}} + 0.42 \), where \( pH_{\text{deut}} \) is the measured pH of the deuterated solution, with a pH-meter calibrated with non-deuterated standard buffers.\(^{38}\)

The general base catalysis in photoinduced PCET from Co\(_3\)O\(_4\) NPs to Ru(III) is observed also employing phosphate buffer (\( pK_a \) = 7.2 for H\(_2\)PO\(_4\)/HPO\(_4^{2-}\) couple), where \( k_0 = 1.7\pm 0.2 \times 10^{-2} \) M\(^{-1}\) s\(^{-1}\) and 2.2 ± 0.6 × 10\(^{-3}\) M\(^{-1}\) s\(^{-1}\) with \( k_b = 1.9\pm 0.5 \) s\(^{-1}\) and 5.8 ± 1.8 s\(^{-1}\) were determined at pH = 8.0 and 8.9, respectively (see ESI, Fig. S8†). As a third probe, flash photolysis experiments in bicarbonate buffer, pH 8, show almost silent traces at 5-100 mM buffer concentrations (Fig. S9†). This evidence can be attributed to the lower basicity of HCO\(_3^-\) (\( pK_a = 6.3 \)) and therefore to the reduced ability of bicarbonate to assist the PCET on Co\(_3\)O\(_4\) (a \( k_b \approx 90 \) M\(^{-1}\) s\(^{-1}\) can be roughly determined from the kinetic treatment of the associated flash photolysis traces, Fig. S9†). However, it is worth noting that the \( k_b \) values attained employing different bases do not follow a clear trend as a function of the \( pK_a \). This can be possibly explained by a specific, coordinating effect of the solution buffering species on the cobalt oxide surface.

![Figure 4. Top: laser flash photolysis (\( \lambda_{exc} = 355 \) nm) of 50 μM Ru(bpy)_3\(^{2+}\) in the presence of 5 mM Na\(_2\)S\(_2\)O\(_4\) and 100 mM Co\(_3\)O\(_4\) NPs in 0.04 - 0.4 M borate buffer at pH 9.5; Bottom: plot of \( k_{obs} \) vs borate buffer concentration, under the different pH conditions investigated. For \( k_{obs} \) values at pH 8 the error bars are smaller than the circles and are not visible (see Table S1 in the ESI).](image)

Importantly, a secondary effect on the PCET kinetics is observed at higher borate buffer concentration, see as a representative case the range 0.04-0.4 M at pH 9.5 in Figure 4a (see Fig. S10† in ESI for traces at pH values between 8.0-8.9). The most evident feature associated to these traces is that both the rate and amount of bleach recovery progressively decrease upon increasing buffer concentration (Fig. 4). The detrimental effect of highly concentrated buffer on the PCET process may be ascribed to coordination of borate species to both the rate and amount of bleach recovery progressively decrease upon increasing buffer concentration (Fig. 4). The detrimental effect of highly concentrated buffer on the PCET process may be ascribed to coordination of borate species to surface Co(III) sites by replacing OH ligands,\(^{39}\) thus hampering the possibility to access the PCET event. The plot of the derived \( k_{obs} \) values vs. total buffer concentration (Fig. 4b) shows indeed a clear inhibition effect by borate. This

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The primary electron transfer from Co\textsubscript{3}O\textsubscript{4} NPs to photogenerated Ru(bpy)\textsubscript{3}\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} catalystic cycle was observed by increasing the concentration of borate buffer from 0.08 to 0.4 M at pH 8 (Fig. 5). This is associated to a drop of both the initial rate \textit{R}\textsubscript{o} \textit{(7.6±0.2, 5.5±0.2,} and \textit{3.0±0.7} \times 10\textsuperscript{-3} \text{µmol(O}_{2}\textsubscript{)s}\textsuperscript{-1} at 0.08, 0.2, and 0.4 M borate, respectively\textit{)} and the total amount of evolved O\textsubscript{2} \textit{(26.0±0.4} \text{µmol, 17.0±1.0} \text{µmol, and 7.8±0.6} \text{µmol} at 0.08, 0.2, and 0.4 M borate, respectively. These values correspond to 70±1, 46±2, and 20±2 chemical yield (CY) based on the amount of Na\textsubscript{3}S\textsubscript{2}O\textsubscript{6}.

Conclusions

The primary electron transfer from Co\textsubscript{3}O\textsubscript{4} NPs (5±1 nm diameter) to photogenerated Ru(bpy)\textsubscript{3}\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} catalytic cycle was observed by increasing the concentration of borate buffer from 0.08 to 0.4 M at pH 8 (Fig. 5). This is associated to a drop of both the initial rate \textit{R}\textsubscript{o} \textit{(7.6±0.2, 5.5±0.2,} and \textit{3.0±0.7} \times 10\textsuperscript{-3} \text{µmol(O}_{2}\textsubscript{)s}\textsuperscript{-1} at 0.08, 0.2, and 0.4 M borate, respectively\textit{)} and the total amount of evolved O\textsubscript{2} \textit{(26.0±0.4} \text{µmol, 17.0±1.0} \text{µmol, and 7.8±0.6} \text{µmol} at 0.08, 0.2, and 0.4 M borate, respectively. These values correspond to 70±1, 46±2, and 20±2 chemical yield (CY) based on the amount of Na\textsubscript{3}S\textsubscript{2}O\textsubscript{6}. Where Co\textsubscript{3}O\textsubscript{4} NPs were more evident at lower pH, where the abatement of the \textit{k}_{\text{obs}} values occurs at lower buffer concentration (Fig. 4b). This indicates that coordinatively unsaturated H\textsubscript{2}BO\textsubscript{4}\textsuperscript{-}, rather than saturated B(OH)\textsubscript{4}\textsuperscript{-}, is most likely responsible for the poisoning of the Co\textsubscript{3}O\textsubscript{4} surface sites. This is in agreement with previous observations by Ullman et al. dealing with water oxidation electrocatalysis by amorphous cobalt oxide films,\textsuperscript{24} where H\textsubscript{2}BO\textsubscript{4}\textsuperscript{-} coordination led to inhibition of the water oxidation electrocatalysis.

Overall, the results presented herein further confirm the favourable mechanistic pathways can also originate from a tailored choice of the reaction environment.

Experimental

Instrumentation and procedures

Figure 5. Oxygen evolution kinetics with 1 mM Ru(bpy)\textsubscript{3}\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} in the presence of 5 mM Na\textsubscript{3}S\textsubscript{2}O\textsubscript{6} and 165 mM formal concentration of Co\textsubscript{3}O\textsubscript{4} NPs at pH 8 in 80-400 mM borate buffer. Experiments were conducted in triplicates in 15 mL total volume, irradiation was performed using a white LED light (power density 3.8 mWcm\textsuperscript{-2}).}

Light driven catalytic tests for water oxidation were conducted in a home-made glass reactor, equipped with a FOXY oxygen selective probe from Ocean Optics inserted in the headspace, for real time monitoring of evolved O\textsubscript{2}. 15 mL of aqueous buffer were injected in the reactor, which was then closed and purged under dark atmosphere with nitrogen for 30 minutes: after purging, the solution was allowed to equilibrate in the dark for 10 minutes and then illuminated with a white LED spotlight (power density 3.8 mWcm\textsuperscript{-2}). Inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed by double channel Universal Cell (sp-ICP-MS NexION 350X, Perkin Elmer). In order to remove the polyatomic interference in the mass 59\textsuperscript{Co} (CaO), the analysis was performed in KED mode as He as carrier gas. Samples were quantified by external calibration method using a multi-point curve (6 points over the concentration range 0.1 µg L\textsuperscript{-1} to 5000 µg L\textsuperscript{-1} for Ruthenium and 5 points over the concentration range 50 µg L\textsuperscript{-1} to 50 µg L\textsuperscript{-1} for Cobalt. Yttrium at 5 µg L\textsuperscript{-1} was used as internal standard. Potential contamination from the laboratory was controlled by adding at least one reagent blank during the digestion session. The limit of detection (LOD) were calculated for each sample set as the average of blanks + 3 standard deviation (SD) and is 0.66 ng L\textsuperscript{-1} for Cobalt. The background concentration signal BEC (providing the actual magnitude of noise) detected for Cobalt was 0.001 ng L\textsuperscript{-1}.

Microwave digestion of the samples were performed by using a Discover SP-D oven (CEM Corporation); each sample was added to Discover SP-D 35 mL vessel and a total of 4 mL of ultra-pure aqua regia was added. The digestion parameters are ramp time: 5 minutes, hold time: 2 minutes, digestion time: 170°C. Afterwards, the samples were allowed to cool down for 30 minutes at room temperature and properly diluted with MilliQ water.

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Synthesis of CoOx.\textsuperscript{12,13} CoOx nanoparticles were prepared by dissolving cobalt(II) acetate in benzyl alcohol and heating the solution at reflux (T = 165 °C) after adding NH\textsubscript{3} 25%. After cooling to room temperature, the CoOx NPs were washed via centrifugation–redispersion cycles with ethanol. ICP-MS: Co 75.1% (calc. for CoOx 73.4%). Zeta potential analysis (1 mg/mL suspended in water) indicates a positive value of 16 mV of the apparent potential. ATR-IR: ν (cm\textsuperscript{-1}): 658, 555 (Co-O).

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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Flash photolysis studies indicate general base catalysis by borate in photoinduced proton-coupled electron transfer from Co$_3$O$_4$ nanoparticles to Ru(III)(bpy)$_3^{3+}$.