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

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Abstract

Co$_3$O$_4$ nanoparticles in the spinel crystalline structure are among the most promising catalyst for water oxidation reaction, displaying remarkable activity under electrochemical and light-assisted conditions. In the presence of Ru(bpy)$_2^{2+}$ as photosensitizer (bpy = 2,2’-bipyridine) and Na$_2$S$_2$O$_4$ 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 sites 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 solution buffer; (iii) borate promotes general base catalysis in the PCET of Co$_3$O$_4$ surface sites; (iv) inhibition of the PCET mechanism is observed at high buffer concentration, due to H$_3$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 pioneer studies by Harriman, cobalt oxide nanoparticles (NPs) have been recognized as very active WOCs, displaying low operating overpotential ($\eta = 0.30 - 0.40$ V), and residing close to the top of the Volcano plot for metal oxides, while promoting fast catalysis (turnover frequency (TOF) up to 3 s$^{-1}$ per surface catalytic site). 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)$_3^{3+}$ as oxidant, with quantum yield up to 0.07, with spectroscopic evidence of Co(III)-OH moieties as the active surface sites. Investigation of such light activated systems may lead to important mechanistic information on the catalyst evolution along the oxygenic cycle. In particular, we have recently reported that Co$_3$O$_4$ NPs, either without stabilizing ligands or capped with bisphosphonate alendronate pendant, suffer from a slow electron transfer (ET) to photogenerated Ru(bpy)$_3^{3+}$, occurring in a timescale of tens of milliseconds, resulting several orders of magnitude slower than ET observed with molecular Co complexes. Slow ET rates may compromise the performance of light activated systems, in particular when the catalyst is embedded in dye-sensitized photoelectrodes. In this work, we take advantage of laser flash photolysis studies to investigate the mechanistic origin of such photoinduced ET process involving surface sites on 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$_3$BO$_3$ coordination to surface sites.

Results and discussion

Co$_3$O$_4$ NPs with 5±1 nm size were synthesized as previously described, using the procedure by Niederberger et al; see characterization in the ESI (Fig. S1-S4T) and in reference 13. We examined by laser flash photolysis the ability of Co$_3$O$_4$ NPs (100 µM formal concentration) 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$_4$. 
in 0.004-0.4 M borate buffer at pH 8.0-9.5 (the concentration refers to the H$_3$BO$_3$/B(OH)$_4$ acid/base couple, pK$_a$ = 8.6$^{21}$), see eqs 1-4.$^{13}$

Ru(II)(bpy)$_2^{2+}$ + hν → *Ru(III)(bpy)$_2^{2+}$

(1)

*Ru(II)(bpy)$_2^{3+}$ + $S_2O_8^{2-}$ → Ru(III)(bpy)$_2^{3+}$ + $SO_4^{2-}$ + $SO_2^{2-}$

(2)

Ru(II)(bpy)$_2^{3+}$ + $SO_4^{2-}$ → Ru(III)(bpy)$_2^{3+}$ + $SO_2^{2-}$

(3)

Ru(III)(bpy)$_2^{3+}$ + Co$_3$O$_4$ → Ru(II)(bpy)$_2^{3+}$ + Co$_3$O$_4$(h$^+$)

(4)

Laser induced generation of Ru(III) (eqs 1-3) is associated to the initial negative $\Delta$OD at 450 nm (bleach of the absorbance, indicative of Ru(II)$\rightarrow$Ru(III) transformation) occurring in less than 10 $\mu$s.$^{16,21}$ subsequently, regeneration of Ru(II) and consequent increase of the $\Delta$OD (recovery of the bleach, see traces in Fig. 1), is indicative of reduction of Ru(III) to Ru(II) by Co$_3$O$_4$ NPs (eq. 4).$^{16,21}$

Concerning the nature of the sites involved in such ET to Ru(bpy)$_3^{3+}$, both tetrahedral Co(II) and octahedral Co(III) sites of the spinel Co$_3$O$_4$ structure could be considered.$^{4,25,26}$ different Co(III)-OH surface sites were envisaged based on time resolved rapid-scan infrared spectroscopy,$^7$ with fast catalytic sites being characterized by the presence of a second, neighbouring, dioxo bridged Co(III)-OH moiety (Fig. 2).$^7$ Moreover, Co$_3$O$_4$ NPs are also known to form amorphous cobaltate clusters at the surface, featuring dicobalt edge active sites (Fig. 2).$^{24,5}$

We thus performed a control flash photolysis experiment with commercially available 30 nm size Co$_{70}$Fe$_{30}$O$_4$ NPs, having still spinel crystalline structure with tetrahedral Co(II) and octahedral Fe(III) sites. The silent trace observed (figure S5†) suggests that Co(II) are not reactive towards Ru(III) in this timescale,$^5$ and thus indicates that the Co(III) surface sites are the ones involved in the reduction of Ru(bpy)$_3^{3+}$.

Looking into more details at the kinetic traces in Fig. 1, the rate and the amount of the $\Delta$OD 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 $\Delta$OD recovery is first order in Ru(III) concentration and is thus expressed by eq. 5.

Rate = $-d$[Ru(III)]/dt = $k_{obs}$$\times$[Ru(III)]

(5)

In the present case, however, the traces were not accurately fitted with single-exponential decays, associated to eq. 5. Non-exponential kinetics were also 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.$^{27}$ Moreover, in the present case, this is also ascribed to a low recovery of the $\Delta$OD bleach in the instrumental timescale limit of ca 90 ms (see Fig. 1a), and to the impossibility of investigating the system under pure pseudo-

![Figure 1](image1.png)

**Figure 1.** Laser flash photolysis ($I_{exc} = 355$ nm) of 50 $\mu$M Ru(bpy)$_3^{3+}$ in the presence of 5 mM Na$_2$S$_2$O$_8$ and 100 $\mu$M Co$_3$O$_4$ NPs in: (a) 4-20 mM borate buffer, pH 8.0; (b) 4-30 mM borate buffer, pH 8.5; (c) 4-30 mM borate buffer, pH 8.9; and (d) 4-40 mM borate buffer, pH 9.5.

![Figure 2](image2.png)

**Figure 2.** Possible surface sites of Co$_3$O$_4$ NPs involved in ET to Ru(bpy)$_3^{3+}$.
first order conditions with respect to photogenerated Ru(III). Indeed, under optimized conditions, photogenerated Ru(III) ~2×10^{-8} M, while surface sites potentially involved in the PCET process with Ru(III) are ~2.5×10^{-5} M, being estimated as \( \frac{1}{3} \) of the total sites according to a formal concentration of CoOx NPs = 10^{-4} M.\textsuperscript{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 \( \Delta C \) in the experimental traces.\textsuperscript{4} The determined values of \( \tau \) and of \( k_{\text{obs}} \) in the different conditions are reported in table S1\textsuperscript{†}. 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 S1 and S2\textsuperscript{†}).

\[
k_{\text{obs}} = \frac{\ln(2)}{\tau}
\]

(6)

Under the different pH conditions employed, \( k_{\text{obs}} \) was observed to increase upon increasing the pH and the total buffer concentration (Fig. 3), and linear correlations with similar slopes were observed by plotting \( k_{\text{obs}} \) vs. the concentration of the B(OH)\(_4\) basic form of the buffer, and \([\text{buffer}]\) is the total buffer concentration (Fig. 3)\textsuperscript{28,29,30} These results suggest a general base catalysis behavior, with B(OH)\(_4\) assisting deprotonation of surface oxygen sites along a PCET process,\textsuperscript{31,32} as previously documented for the amorphous cobalt oxide (CoPi) under electrocatalytic conditions, where Co(III)-OH surface sites convert into Co(IV)=O\textsuperscript{33,34} This PCET transformation is also postulated as the primary event in the water oxidation cycle by CoOx NPs.\textsuperscript{3} The general base catalysis associated to the Co(III)-OH \( \rightarrow \) Co(IV)=O PCET is expected on the basis of the predicted large change in pK\(_a\) of the surface OH group upon oxidation of the cobalt centre. According to the libido rule,\textsuperscript{34} the pK\(_a\) of the acid/base couple (pK\(_a\)=8.6 for H\(_2\)BO\(_3\)/B(OH)\(_4\)) 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 \( k_b \) is the rate constant for the base assisted process and \( k_o \) represents the rate constant for the PCET under unbuffered conditions (i.e. with both water and OH\(^{-}\) acting as bases).

\[
k_{\text{obs}} = k_o + k_b[B]
\]

(7)

According to eqs 7, \( k_o \) and \( k_b \) rate constants can be determined from the fitting of the data in Fig. 3 (see table 1). \( k_b \) values obtained under different pH conditions fall in an appreciably narrow range of 6.3-8.5×10\(^{-7}\) M\(^{-1}\)s\(^{-1}\) (table 1). Experiments conducted in deuterated medium (figure S6\textsuperscript{†}) show a \( k_b \) value of 4.9±1.0×10\(^{-7}\) 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.\textsuperscript{35} Values comprised between 1.6 and 2.7 were observed for substituted pyridines assisted PCET from Mn-oxides.\textsuperscript{36}

Concerning \( k_o \), its value is pH dependent, as expected due to separate contributions of H\(_2\)O and OH\(^{-}\) acting as base (eq. 8), see Fig. S7\textsuperscript{†}; from a linear fitting of \( k_o \) vs [OH\(^{-}\)], values of \( k_{H,0} = 1.7 \) s\(^{-1}\) and \( k_{OH} = 5.5 \times 10^{5} \) M\(^{-1}\)s\(^{-1}\) can be estimated (Fig. S7\textsuperscript{†}).

\[
k_o = k_{H,0} + k_{OH}[OH^{-}]
\]

(8)

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**Figure 3.** Plot of \( k_{\text{obs}} \) vs. [Base], where Base is B(OH)\(_4\), and the concentrations are given by [Base]=f\(_b\)×[buffer], where f\(_b\) is the fraction of the basic form of the buffer in solution, and [buffer] is the total buffer concentration;\textsuperscript{37} pK\(_a\) for the H\(_2\)BO\(_3\)/B(OH)\(_4\) couple = 8.6. For \( k_{\text{obs}} \) values at pH 8 the error bars are smaller than the circles and are thus not visible in the graph (for related data see Table S1 in the ESI).
The error bars are smaller than the borate buffer at pH 9.5; Bottom: plot of $k_{\text{obs}}$ associated linear fittings (see fig. 3).

Figure 4. Top: laser flash photolysis ($\lambda_{\text{exc}} = 355$ nm) of 50 $\mu$M Ru(bpy)$_3^{2+}$ in the presence of 5 mM Na$_2$S$_2$O$_8$ and 100 $\mu$M Co$_3$O$_4$ NPs in 0.04 - 0.4 M borate buffer at pH 9.5; Bottom: plot of $k_{\text{obs}}$ vs borate buffer concentration, under the different pH conditions investigated. For $k_{\text{obs}}$ values at pH 8 the error bars are smaller than the circles and are not visible (for related data see Table S1 in the ESI).

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 (Fig. 4a; see Fig. S10† in ESI for traces at pH values 8.0 – 8.9). The most evident feature associated to these traces is that the recovery of the bleach is not anymore complete in such timescale and progressively decreases upon increasing buffer concentration (Fig. 4a). A detrimental effect of highly concentrated buffer in the PCET process, may be ascribed to surface coordination of borate species to the Co(III) sites, by replacing OH ligands, thus hampering the possibility to access the PCET event. Plotting the derived $k_{\text{obs}}$ values vs. total buffer concentration (Fig. 4b) shows a clear borate inhibition effect; this phenomenon is more evident under acidic conditions, where the abatement of the $k_{\text{obs}}$ values occurs at lower buffer concentration (Fig. 4b). This indicates that coordinatively unsaturated H$_2$BO$_3$ rather than saturated B(OH)$_4^-$ is responsible for the Co$_3$O$_4$ NPs poisoning, in agreement with previous observation by Ullman et al. dealing with water oxidation electrocatalysis by

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**Table 1.** Kinetic rate constants for PCET from Co$_3$O$_4$ NPs to Ru(III)(bpy)$_3^{2+}$ determined by flash photolysis experiments. Errors are given from the associated linear fittings (see fig. 3).

<table>
<thead>
<tr>
<th>pH</th>
<th>$k_0$ s$^{-1}$</th>
<th>$k_B$/10$^3$, 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±0.7</td>
</tr>
<tr>
<td>8.6$^{(a)}$</td>
<td>3.4±1.0</td>
<td>4.9±1.0</td>
</tr>
</tbody>
</table>

$^{(a)}$In deuterated solvent; pHD was calculated according to the equation pH$D = 0.929 \times$ pH + 0.42, where pH is the pH measured with a pH-meter.$^{36,37}$

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$_3$PO$_4$/HPO$_4^{2-}$ couple), where $k_B = 1.7\pm0.2 \times 10^3$ M$^{-1}$s$^{-1}$ and $2.2\pm0.6 \times 10^3$ M$^{-1}$s$^{-1}$ at pH = 8.0 and 8.9, respectively, while $k_0 = 1.9\pm0.5$ s$^{-1}$ and $5.8\pm1.8$ s$^{-1}$ at pH = 8.0 and 8.9, respectively (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$_3^-$ ($pK_a = 7.7$) and therefore to the reduced ability of bicarbonate to assist the PCET on Co$_3$O$_4$ (a $k_B \approx 9\times10^4$ M$^{-1}$s$^{-1}$ can be roughly determined from the kinetic treatment of the associated flash photolysis traces, Fig. S9†). It is worth noting that the $k_B$ values employing different bases do not follow a clear trend as a function of the $pK_a$ values; this can be possibly explained by a specific, coordinating effect of the solution buffering species to the cobalt oxide surface.

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**Figure 4.** Top: laser flash photolysis ($\lambda_{\text{exc}} = 355$ nm) of 50 $\mu$M Ru(bpy)$_3^{2+}$ in the presence of 5 mM Na$_2$S$_2$O$_8$ and 100 $\mu$M Co$_3$O$_4$ NPs in 0.04 - 0.4 M borate buffer at pH 9.5; Bottom: plot of $k_{\text{obs}}$ vs borate buffer concentration, under the different pH conditions investigated. For $k_{\text{obs}}$ values at pH 8 the error bars are smaller than the circles and are not visible (for related data see Table S1 in the ESI).
amorphous cobalt oxide films, where \( \text{H}_2\text{BO}_3 \) coordination leads to inhibition of water oxidation electrocatalysis. Consistently, an abatement of oxygen evolution performance by CoO NPs within the photoactivated Ru(bpy)_3^2+/S\(_2\)O\(_8^2^-\) system 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 the initial rate \( R_0 \) (7.6±0.2, 5.5±0.2 and 3.0±0.7 x10^3 \( \mu \text{mol(O}_2\text{)s}^{-1} \) at 0.08, 0.2 and 0.4 M borate, respectively) and of the total amount of evolved \( \text{O}_2 \) (26.0±0.4 \( \mu \text{mol}, \ 17.0±1.0 \mu \text{mol} \) and 7.8±0.6 \( \mu \text{mol} \) at 0.08, 0.2 and 0.4 M borate, respectively; these values correspond to 70±1, 46±2 and 20±2 yield based on the amount of Na\(_2\)S\(_2\)O\(_4\)).

![Graph showing oxygen evolution kinetics with 1 mM Ru(bpy)_3^2+ in the presence of 5 mM Na\(_2\)S\(_2\)O\(_4\) and 165 \( \mu \text{M} \) CoO NPs at pH 8 in 80-400 mM borate buffer (light blue and blue traces). Experiments were conducted in triplicates in 15 ml total volume, irradiation with white LED light.](image)

### Conclusions

The primary electron transfer from CoO NPs (5±1 nm diameter) to photogenerated Ru(bpy)_3^2+ has been investigated by laser flash photolysis, being the first event in photo-assisted water oxidation. The process involves a proton coupled oxidation of surface Co(III)-OH sites to Co(IV)=O and occurs through general base catalysis by borate (\( k_b = 6.3-8.3\times10^2 \ M^{-1}s^{-1} \); KIE = 1.4±0.3) buffer. Higher borate buffer concentrations were shown to inhibit the PCET process, likely due to coordination of \( \text{H}_2\text{BO}_3 \) to surface sites; consistently, this is associated to an abatement of oxygen evolving activity within the photoactivated cycle. This is a further confirmation of the importance of specific buffer/solvent conditions that have a definite impact on the surface reactivity of metal-oxide NPs. Therefore, benchmarking of water oxidation catalysis should take into consideration that favourable mechanistic pathways can originate from a tailored reaction environment.

### Experimental

#### Instrumentation and procedures.

Nanosecond transient measurements were performed with a custom laser spectrometer comprised of a Continuum Surelite II Nd:YAG laser (FWHM 6–8 ns) with frequency doubled (532 nm, 330 ml), or tripled (355 nm, 160 ml), option, an Applied Photophysics xenon light source including a mod. 720 150 W lamp housing, a mod. 620 power controlled lamp supply and a mod. 03-102 arc lamp pulser. Laser excitation was provided at 90° with respect to the white light probe beam. Light transmitted by the sample was focused onto the entrance slit of a 300 mm focal length Acton SpectraPro 2300i triple grating, flat field, double exit monochromator equipped with a photomultiplier detector (Hamamatsu R3896) and a Princeton Instruments PIMAX II gated intensified CCD camera, using a RB Gen II intensifier, a ST133 controller and a PTG pulser. Signals from the photomultiplier (kinetic traces) were processed by means of a TeledyneLeCroy 604Zi (400 MHz, 20 GS/s) digital oscilloscope.

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 \( \text{O}_2 \). 15 mL of aqueous buffer were inserted 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\(^{-2}\)).

Inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed by double channel Universal Cell (sp-ICP-MS NexION 350X, Perkin Elmer). For the quantification of Ruthenium, isotope \(^{103}\)Ru was selected because more abundant and the absence of PD in the samples. In order to remove the polyatomic interference in the mass \(^{59}\)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 \( \mu \text{g L}^{-1} \) to 50 \( \mu \text{g L}^{-1} \) for Ruthenium and 5 points over the concentration range 0.1 to 5 \( \mu \text{g L}^{-1} \) for Co).
range 50 µg L⁻¹ to 5000 µg L⁻¹ for Cobalt. Yttrium at 5 µg L⁻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 are 1.79 ng L⁻¹ and 0.66 ng L⁻¹ for Ruthenium and Cobalt respectively. The background concentration signal BEC (providing the actual magnitude of noise) detected was respectively 0.001 ng L⁻¹ and 0.003 ng L⁻¹ for Cobalt and Ruthenium.

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.

**Synthesis of Co₃O₄:**

Co₃O₄ nanoparticles were prepared by dissolving cobalt(II) acetate in benzyl alcohol and heating the solution at reflux (T = 165 °C) after adding NH₃ 25%. After cooling to room temperature, the Co₃O₄ NPs were washed via centrifugation–redispersion cycles with ethanol. ICP-MS: Co 75.1% (calc. for Co₃O₄ 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⁻¹): 658, 555 (Co-O).

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

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### Notes and references

§ Generation of octahedral Co(III) sites in an amorphous phase was also observed to occur upon oxidative corrosion of cobalt oxide NPs with cerium ammonium nitrate, and was reported to activate the surface towards electrochemical water oxidation, see ref. 40.

 §§ The apparent inertia of Co(II) sites towards oxidation to Co(III) could be associated to the expected reorganization energy due to changes of coordination geometry (tetrahedral to octahedral) and of spin state (high spin to low spin) associated to Co(II)→Co(III) transition.

 † Utilization of higher formal [Co₃O₄] concentrations leads to inefficient Ru(III) photoproduction and unreliable kinetic determination due to fluctuation of the analysis beam caused by the increasing scattering phenomena. An appreciable first-order dependence on the formal Co₃O₄ concentration of the 450-nm bleach recovery was, however, previously found for Co₃O₄ NP concentration in the order of 10⁻⁴ M, see reference 13.

 ♦ Due to the limited time-window of our instrumental setup, at pH 8.0 and 8.5 the bleach recovery cannot be completely determined. In order to attain kinetic information, the experimental traces were fitted with linear functions, used to determine the r.

 ♠ The Co(IV)=O state is often described with a partial Co(III)-O- character, see ref. 7.
