Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Water oxidation by manganese oxides formed from tetranuclear precursor complexes: The influence of phosphate on structure and activity

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O_2 evolution experiments

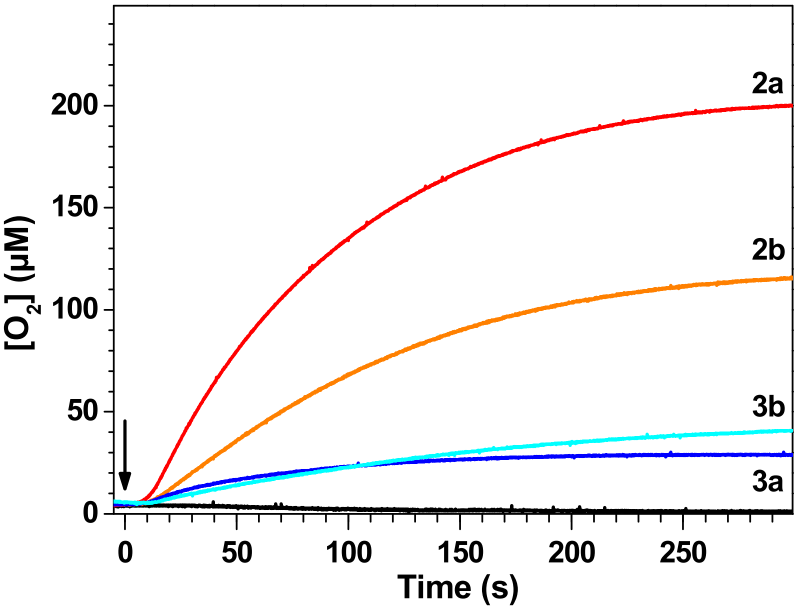

Figure S1. Oxygen evolution traces showing the light-driven water oxidation catalyzed by **2a** (red, [Mn] ~80 μM), **2b** (orange, [Mn] ~80 μM), **3a** (blue, [Mn] ~100 μM), **3b** (cyan, [Mn] ~100 μM) or with no catalyst (black) with $[Ru(bpy)_3]^{2+}$ (1 mM) as photosensitizer and $S_2O_8^{2-}$ (10 mM) as electron acceptor in 50 mM phosphate buffer (pH 7). The arrow indicates the start of the illumination.

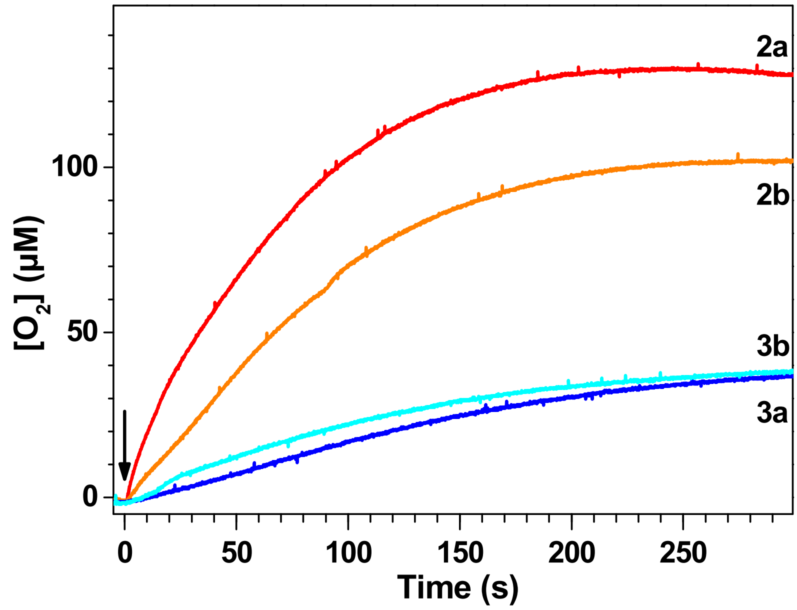

Figure S2. Oxygen evolution measurements using $[Ru(bpy)_3]^{3+}$ (20 mM) as the oxidant and **2a** (red, [Mn] ~80 μM), **2b** (orange, [Mn] ~80 μM), **3a** (blue, [Mn] ~100 μM), and **3b** (cyan, [Mn] ~100 μM) as catalysts. The experiments were performed in 50 mM phosphate buffer (pH 7). The arrow indicates the addition of the oxidant.

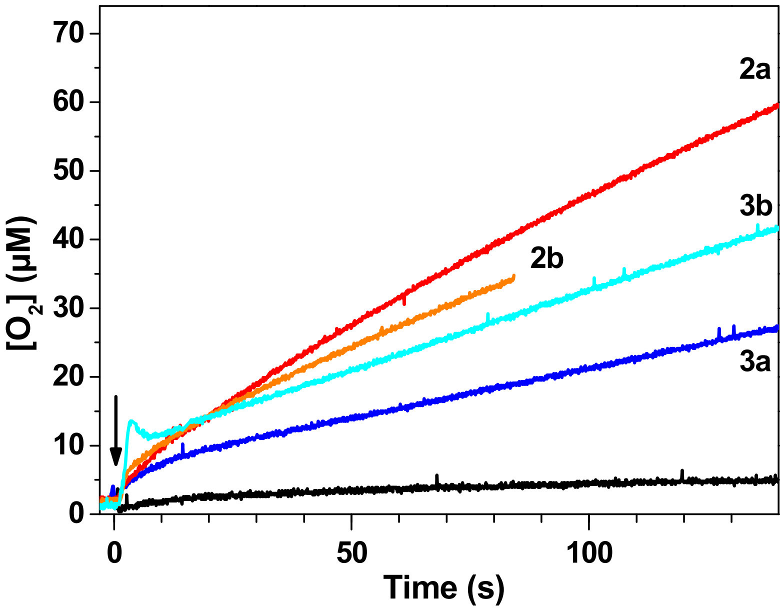

Figure S3. Oxygen evolution measurements using cerium(IV) (0.25 M) as the oxidant and **2a** (red, [Mn] ~80 µM), **2b** (orange, [Mn] ~80 µM), **3a** (blue, [Mn] ~100 µM), and **3b** (cyan, [Mn] ~100 µM) as catalysts, or without catalyst (black). The oxygen evolution rate was measured after ca 5 s to avoid influence from an artifact caused by the addition of cerium(IV), especially visible for **3b**. The experiments were performed in 50 mM phosphate buffer (pH 7). The arrow indicates the addition of the oxidant.

XAS measurements.

X-ray absorption spectroscopy at the *K*-edge of manganese was performed at the KMC-1 beamline at the BESSY synchrotron (Helmholtz-Zentrum Berlin, Germany) at 20 K in a liquid-helium cryostat as described elsewhere.[1] Spectra were recorded in absorption mode using ionization chamber (Oxford-Danfysik) or in fluorescence mode using a 7-element ultra-low energy resolving Ge detector (Canberra). The spectra collected in fluorescence mode were corrected for the small (less than 5% of the normalized edge jump) saturation effect. The correction was done using the rationale described in the following.

The intensity of the X-rays passing through the sample is described Eq. (1):

$$I(E) = I_0 \cdot e^{-\mu(E)x_{eff}}, \qquad (1)$$

where I_0 is the intensity of the beam in front of the sample and I is the attenuated intensity of the beam after passing through the sample with an effective thickness described by x_{eff} . The μ-parameter is the energy-dependent absorption coefficient (in cm^{-1}); its value depends on the types of atoms and the density of the material. Equation 1 implies that the X-rays absorbed by the sample (I_{abs}) are given by Eq. (2).

$$I_{abs}(E) = I_0 - I = I_0 \cdot \left(1 - e^{-\mu(E)x_{eff}}\right) \qquad (2)$$

In the following, we consider only the absorption at the *K*-edge of the element of interest. The experimentally detected K_α fluorescence is, to a good approximation, proportional to the absorbed X-rays. Thus,

$$F_{exp}(E) \approx c_{exp} \cdot \left(1 - e^{-\mu(E)x_{eff}}\right), \qquad (3)$$

where c_{exp} is energy-independent. Its value is determined by the spectroscopic properties of the sample (e.g. K_α-fluorescence yield) and the properties of the experimental set-up.

We simulated the measured fluorescence signal, $F_{sim}(E)$ (after normalization to unity edge-jump) using the normalized absorption spectrum, $Abs(E)$ (as calculated from experimentally determined values, $Abs = -ln(I/I_0)$) according to Eq. (4).

$$F_{sim}(E) = b \cdot \left(1 - e^{-Abs(E)\cdot a}\right) \qquad (4)$$

The parameters a and b were determined using the Levenberg-Marquardt algorithm to minimize the sum of the squared differences between the experimentally obtained and the simulated fluorescence signal. Knowing the parameters a and b, the corrected fluorescence (F_{corr}) is calculated according to Eq. (5):

$$F_{corr}(E) = -\frac{1}{a} \cdot ln\left(1 - F_{exp}(E)/b\right), \qquad (5)$$

where $F_{exp}(E)$ is the experimentally detected fluorescence signal.

The extracted spectrum was weighted by k^3 and simulated in *k*-space (E_0 = 6547 eV). All EXAFS simulations were performed using in-house software (SimX3) after calculation of the phase functions with the FEFF program[2, 3] (version 8.4, self-consistent field option activated). Atomic coordinates of the FEFF input files were generated for several reasonable structural models; the EXAFS phase functions did not depend strongly on the details of the used model. An amplitude reduction factor S_0^2 of 0.7 was used. The data range used in the simulation was 20–820 eV (1.85–14.61 Å^{-1}). The EXAFS simulation was optimized by a minimization of the error sum obtained by summation of the squared deviations between measured and simulated values (least-squares fit). The fit was performed using the Levenberg-Marquardt method with numerical derivatives. The error ranges of the fit parameters were estimated from the covariance matrix of the fit, and indicate the 68 % confidence intervals of the corresponding fit parameters. The fit error was calculated as in ref. 4.

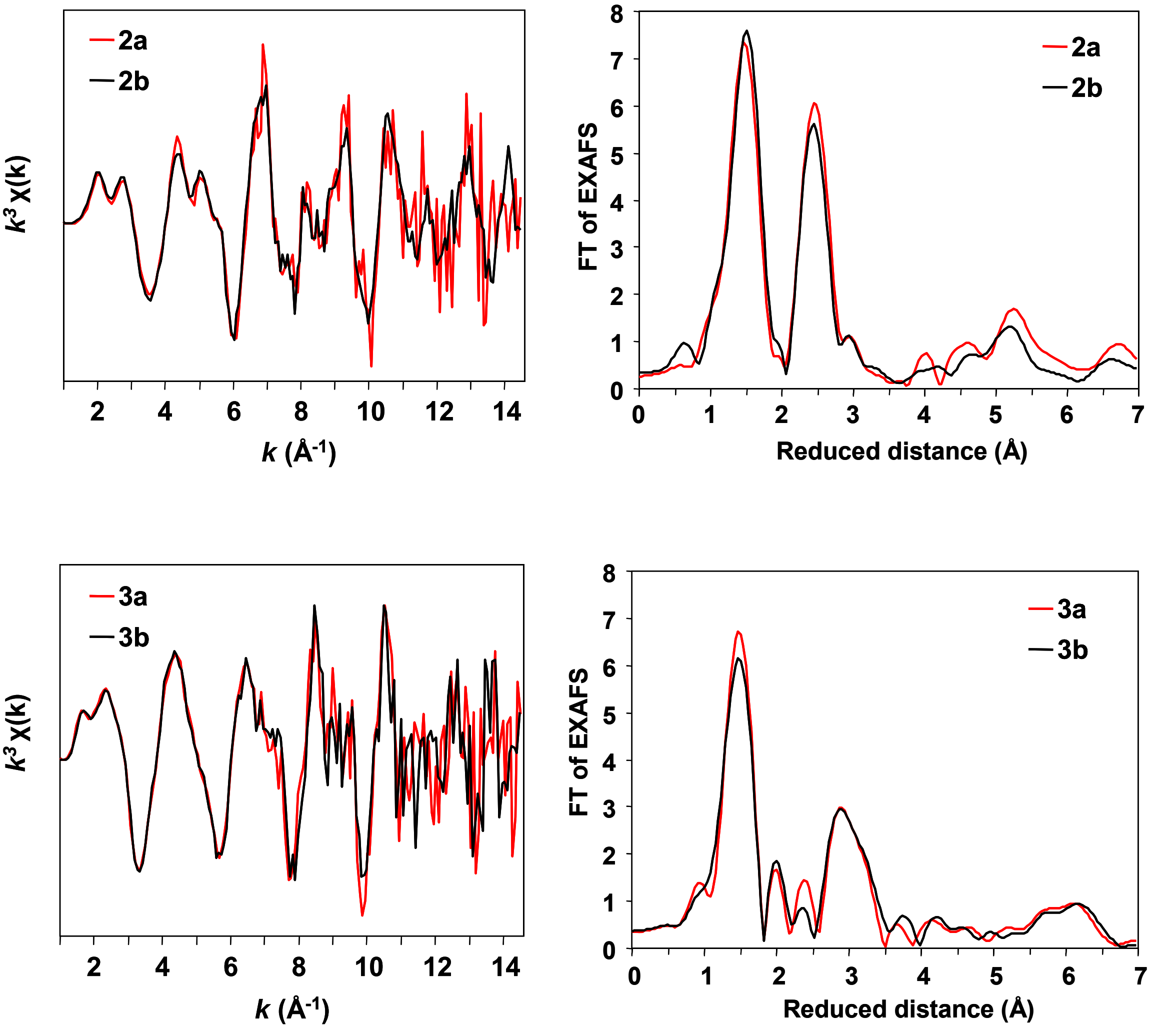

Figure S4. Comparison between the experimental EXAFS spectra of the manganese precipitates obtained from **1a** and **1b** compounds without phosphate (top) and with phosphate (bottom).

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