A nickel containing polyoxometalate water oxidation catalyst

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Fig. S1 Infrared spectrum of K_{10}H_{2}[Ni_{5}(OH)_{6}(OH_{2})_{3}(Si_{2}W_{18}O_{66})]•34H_{2}O (KH-1).
**Fig. S2** Thermogravimetric analysis of KH-1. The weight loss observed (10.3%) is attributed to waters of hydration and corresponds to 34 water molecules.

**Fig. S3** UV-vis spectra of 40-fold diluted solution of 1 mM [Ru(bpy)$_3$]$_2^{2+}$ and 5.0 mM Na$_2$S$_2$O$_8$ in 80 mM borate buffer before the photodriven catalytic water oxidation reaction (black curve) and after this reaction (after irradiation) in the absence (blue curve) and presence (red curve) of 2 µM KH-1.
**Fig. S4** UV-visible spectrum of 6 mM KH-I in 80 mM pH 8 sodium borate buffer.
**Fig. S5** Kinetic traces of the local maxima of KH-1 in the UV-visible spectrum of 6 mM KH-1 in 80 mM pH 8 sodium borate buffer, showing no change in the spectrum upon aging the solution overnight.

**Fig. S6** Particle size distribution measured by DLS in a solution of 0.5 µM KH-1, 1 mM [Ru(bpy)$_3$]Cl$_2$ and 5 mM Na$_2$S$_2$O$_8$ in 80 mM pH 8.0 sodium borate buffer.
**Fig. S7** Particle size distribution measured by DLS in a solution of 2 µM KH-1, 1 mM [Ru(bpy)$_3$]Cl$_2$ and 5 mM Na$_2$S$_2$O$_8$ in 80 mM pH 8.0 sodium borate buffer before (red dotted line) and after (black solid line) photoirradiation for 11 min (455 nm LED light, 17 mW).
**Fig. S8** Infrared spectra of KH-1. Black: spectrum of the freshly prepared and purified KH-1. Red: precipitate obtained from mixing [Ru(bpy)_3]^{2+} and KH-1 solutions (the peaks are a simple superposition of the spectra of each compound). Blue: precipitate isolated from a post reaction solution. The spectra before and after water oxidation (irradiation for 100 minutes, TON ca. 40) show no changes indicative of structural rearrangement or metal oxide formation.
**Fig. S9** Infrared spectra of KH-1 and nickel hydroxide. Black: spectrum of KH-1. Red: KH-1 doped with ~10% nickel hydroxide. Blue: nickel hydroxide, highlighting the characteristic peaks at 525 cm\(^{-1}\) and 3640 cm\(^{-1}\) that would be visible if KH-1 decomposes to nickel hydroxide particles under catalytic conditions.
Fig. S10 Fast-mixing O₂ yield vs. KH-1 concentration in the dark water oxidation reactions measured with a FOXY-R probe using sacrificial oxidant [Ru(bpy)₃]³⁺. Each point represents the average of three consecutive shots, with error bars showing the range of measured values. Conditions: 1 mM [Ru(bpy)₃]³⁺, 80 mM sodium borate buffer at pH 8.0.

Fig. S11 Kinetics of [Ru(bpy)₃]³⁺ self-decomposition (black) and catalytic reduction with 1 µM (purple), 2 µM (red), 3 µM (orange), 4 µM (blue), 5 µM (green) KH-1. Conditions: 1.0 mM [Ru(bpy)₃]³⁺, 80 mM sodium borate buffer with initial pH 8.0, in the dark.
**Fig. S12** Notation of atoms in the calculated structure of KH-1.