While molecular water-oxidation catalysts are remarkably rapid, oxidative and hydrolytic processes in water can convert their active transition metals to colloidal metal oxides or hydroxides that, while quite reactive, are insoluble or susceptible to precipitation. In response, we propose using oxidatively-inert ligands to harness the metal oxides themselves. This approach is demonstrated by covalently attaching entirely inorganic oxo-donor ligands (polyoxometalates) to 3-nm hematite cores, giving soluble anionic structures, highly resistant to aggregation, yet thermodynamically stable to oxidation and hydrolysis. Using orthoperiodate (at pH 8), and no added photosensitizers, the hematite-core complex catalyzes visible-light driven water oxidation for seven days (7600 turnovers) with no decrease in activity, far exceeding the documented lifetimes of molecular catalysts under turnover conditions in water. As such, a fundamental limitation of molecular complexes is entirely bypassed by using coordination chemistry to harness a transition-metal oxide as the reactive center of an inherently stable, homogeneous water-oxidation catalyst.
A current challenge in the development of molecular water-oxidation catalysts is to overcome their inherent susceptibilities to oxidative or hydrolytic degradation under turnover conditions in water. Advances in the past decade have led to remarkably fast rates of $\text{O}_2$ formation, along with the parallel development of more stable catalysts, better able to withstand strongly oxidizing conditions in water. Nevertheless, organic ligands are susceptible to oxidation, which, combined with hydrolysis of their active transition-metal centers, often results in the formation of colloidal metal oxides. Entirely inorganic polyoxometalate (POM)-based water-oxidation catalysts, by contrast, are thermodynamically stable to oxidation, can utilize earth-abundant metals, and feature remarkably rapid rates. At the same time, molecular POM catalysts are stable to hydrolysis only under specific, albeit well-defined and by now, well-understood conditions, concerning variables such as pH and the nature and concentration of buffer. Fundamentally, however, their catalytically active transition metals are in equilibrium with trace concentrations in the aqueous solvent, which can lead to hydrolysis under non-optimal conditions. Hence, as advances in ligand design have led to impressively rapid rates and longer catalyst lifetimes under turnover conditions, catalyst stability nevertheless remains an ongoing topic of discussion and experiment.

One reason for this heightened level of concern is that colloidal metal oxides can be extremely active, such that considerable efforts are required to prove that the molecular catalyst, and not its products of decomposition in water, are the kinetically competent species in catalytic water oxidation. Given this situation, a compelling solution to catalyst stability might be to embrace the colloidal metal-oxide nanocrystals (NCs) themselves as thermodynamically stable water-oxidation catalysts. Apart from a few exceptions, however, colloidal metal oxides are either insoluble at most pH values in water, or rapidly aggregate and precipitate from water under turnover conditions. And, despite impressive advances in solvothermal syntheses of metal-oxide NCs, the requisite organic stabilizing ligands are not only susceptible to oxidation, but usually limit solubility in water and block access to the metal-oxide surface.

In this context, we recently discovered that heteropolytungstate cluster anions (POMs) could serve as covalently attached oxo-donor ligands for 6-nm anatase-$\text{TiO}_2$ NCs, giving water-soluble POM-complexed nanostructures. We now deploy Fe(III)-substituted $\alpha$-PW$_{11}$O$_{39}$$^-$ cluster anions as o xo-donor ligands for hematite (Fe$_2$O$_3$) cores, giving water-soluble catalysts, uniquely positioned between molecular iron-oxide clusters and colloidal hematite. The new catalyst features 3-nm hematite (Fe$_2$O$_3$) cores comprised of ca. 300 Fe atoms, sufficiently large to possess the visible-light semiconductor properties of hematite. Unlike colloidal hematite, however, covalent coordination of each Fe$_2$O$_3$ core by ca. 15 cluster anions renders the POM-complexed structure as a stable material in water, giving optically transparent solutions at pH values of 2.5 to 8. Moreover, fitted with entirely inorganic tungsten(VI)-oxide ligands, and formed in water at 220 °C, 1 is thermodynamically stable to both oxidative degradation and hydrolysis. As an inherently stable visible-light-activated water-oxidation catalyst, 1 is capable of continuous operation for 7 days under turnover conditions (corresponding to 7600 turnovers) with no decrease in activity.

**Results**

**Inorganic coordination complexes of hematite.** Complex 1 is prepared by converting micron-sized particles of $\gamma$-FeO(OH) to Fe$_2$O$_3$ (at 220 °C) in the presence of $\alpha$-PW$_{11}$O$_{39}$$^-$, after which, numerous Fe(III)-substituted anions, $\alpha$-PW$_{11}$O$_{39}$$^{\text{Fe(III)}}$$^4$$^-$$^-$, remain bound via bridging oxo linkages to 3-nm hematite cores (Fig. 1a and Supplementary Figures 1-7). The reaction gives an orange, optically transparent pH-7 solution of 1 (Fig. 1b, left inset). Dynamic light scattering (DLS) of the clear-orange solution reveals a number-weighted hydrodynamic radius of 1.9 nm (right inset to Fig. 1b). Cryogenic-TEM images of the same (vitrified) solution (right inset to Fig. 1b) reveal numerous freely diffusing particles with an average size of 2.8–3.0 nm, too small for resolution of their surface structures in cryo-TEM images (additional images in Supplementary Figure 8). (This limitation is consistent with extensive studies of POMs on gold nanoparticles, in which even well-ordered POM monolayers are not discernible on gold cores smaller than ca. 5 nm.)

The cores of 1 are single NCs of hematite (Fe$_2$O$_3$). High-resolution TEM images (Fig. 1c) reveal an inter-planar spacing of 2.69 Å, in agreement with the (104) crystal planes of hematite. Indexing of the well-defined rings found in electron diffraction of dry samples precisely matches hematite (Supplementary Figure 9a). And, the related dark-field images reveal individual 2.8 ± 0.5 nm (± denotes s.d.) diameter NCs (Supplementary Figure 10). The hematite structure was further confirmed by powder X-ray diffraction (XRD), for which the Debye–Scherrer equation gave a crystallite size of 3.5 ± 0.5 nm (Supplementary Figures 9b and 11).

**Isolation and stability to aggregation.** To isolate pure samples of 1, a clear-orange solution (inset to Fig. 1b) was made 2 M in NaCl. This gave a cloudy solution of salted-out 1, an orange-red solid isolated by centrifugation. Re-dissolution of 1 in pure water (10 mM) returned clear-orange solutions, even after multiple cycles of NaCl addition, centrifugation, and re-dissolution (Supplementary Figure 2). This solubility and remarkable stability to
aggregation differs dramatically from the properties of electrostatically stabilized colloids. Behaving more like a molecular macroanion, the hydrated Na\(^+\) salt of 1 can be stored indefinitely, and then readily dissolved in water. These findings provided the first indication that, as shown in Fig. 1a, heteropolytungstate cluster anions are covalently bound to the hematite cores.

**Cluster-anion ligands coordinated to hematite cores of 1.**

Energy-dispersive X-ray spectroscopic (EDX) analysis of \(\alpha-\text{Fe}_2\text{O}_3\), the tungsten atoms must reside at the hematite surface. The tungsten-based surface structures were characterized by electrospray ionization mass spectroscopy (ESI-MS). Mild HCl etching of 1 at pH 2 (6 h at 70 °C), gave a cloudy orange solution (Supplementary Figure 13). After removing an insoluble iron oxide by centrifugation, a pale-yellow powder precipitated upon addition of tetra-n-butylammonium \(\alpha-\text{Fe}_2\text{O}_3\) (suspension; gray squares) are positive at low pH values and negative at pH values above the isoelectric point near pH 5.5, as indicated by the dotted lines. By contrast, 1 (red diamonds) is soluble and negatively charged from pH 2.5 to 8. (Atomic connectivity of the cluster-anion ligands to the hematite surface is discussed below.)

provided further support for the presence of \([\alpha-\text{PW}_{11}\text{O}_{39}\text{Fe}^+\text{O}]\) anions at the hematite surface. While conceptually analogous to electrochemical studies of ferrocene-covered SiO\(_2\) nanoparticles\(^{33}\), to our knowledge, the observation of reversible redox chemistries of ligands bound to metal-oxide NCs in solution has few precedents in the literature\(^{25}\). It was made possible here by the abundance of cluster anions on the hematite surface, in combination with the water solubility imparted by their negative charges and numerous alkali-metal counter-cations. After adding LiClO\(_4\) (0.1 M), differential pulse voltammetry (DPV) revealed reversible redox processes consistent with the presence of the cluster anions identified by ESI-MS (DPV data for the independently prepared molecular cluster anions are provided in Supplementary Figure 15b).

Surface coverage by the POM anions, based on a reasonable footprint of 1.9 nm\(^2\), places 15 POMs on the surface of an (idealized) spherical 3-nm-diameter hematite core (Supplementary Table 1). Such a structure would contain 165 W atoms and 279 Fe atoms, giving a relative atomic composition of 37% W and 63% Fe, nicely matching the %-atom values observed by EDX (Fig. 2a). The W to Fe ratio also gives ca. 18 \(\text{atom }\%\) \(\text{W}\) and 62 \(\text{atom }\%\) \(\text{Fe}\), nicely matching the %-atom values observed by EDX.

Not only is 1 remarkably stable to aggregation, it is soluble at pH values of 2.5–8. Over this wide pH range, its largely negative zeta potential values (\(\zeta = -35\) to \(-40 \text{ mV}\)) remain pH-invariant (Fig. 2d). By contrast, colloidal \(\alpha-\text{Fe}_2\text{O}_3\) precipitates at its isoelectric point (pH 5.5), at which \(\zeta = 0 \text{ mV}\). These findings...
represent three independent lines of evidence for strong coordination of the POM ligands to the α-Fe2O3 cores.

Given these inert linkages, metathesis of Na+ counter-cations (of the POMs) by n-R3N+ (R = hexyl or octyl) was used to render organic-solvent soluble. This cation-exchange procedure—typical of POM salts—gave optically transparent MeCN or MeOH solutions with no loss of POM ligands (Supplementary Figure 16), further evidence for their covalent attachment to the hematite cores.

It is extraordinarily difficult to precisely determine the atomic connectivities of molecules bound to colloidal NCs. However, the presence of a μ2-oxo linkage between Fe(III) ions in the known oxo-bridged dimer, [(α-PW11O39FeIII)2-μ2-O]10– (2)38, suggested that a similar linkage might bind oxo-donating [α-PW11O39FeIII]4−–O–ligands to Fe(III) atoms at the α-Fe2O3 surface. X-ray photoelectron spectroscopy (XPS) data for 1 revealed a 2.1 eV difference between W4f5/2 and W4f7/2 binding energies (Supplementary Figure 17). Notably, these W4f peaks are comparable with those of 2 (Supplementary Figures 18 and 19), consistent with the presence of Keggin-anion derived ligands connected to the surface of 1 via μ2-oxo linkages.

This was investigated in more detail by FTIR spectroscopy (Fig. 3). The IR-allowed vibrational modes of the central PO4 moieties within Keggin-derived structures are highly sensitive to changes in symmetry of the cluster anion. Removal of a single W4f7/2 and W4f5/2 binding energies (Supplementary Figure 17) .

The precise match between the PO4 bands of the bridged dimer, [(α-PW11O39FeIII)2-μ2-O]10− (2), and of monomeric POMs with aqua and hydroxo ligands, FeIII(OH2)3 and FeIII(OH)2 (Fig. 3, c and d).

The precise match between the PO4 bands of the POM ligands on 1 (1090 and 1051 cm–1; Fig. 3a) with the corresponding PO4 bands of 2 (1090 and 1050 cm–1; Fig. 3b), is consistent with μ2-oxo linkages between the POM ligands and the hematite cores. Combined with the EDX data in Fig. 2a, this reasonable atomic connectivity suggests structures of the form, [(α-PW11O39FeIII)-μ2-O]-15−(α-Fe3O4)250, in which 15 POMs are bound to cores comprised of ca. 150 Fe2O3 units.

This covalent attachment of POM cluster anions is fundamentally distinct from the use of POMs to electrostatically stabilize colloidal metal-oxide NCs. Notably, in a series of seminal papers, Murray37, Milleron and Helms38, and Talapin39 used NOBF4, Me3OBF4, and Ph3CBF4, respectively, to replace organic protecting ligands on metal-oxide NCs by electrostatically associated BF4− anions in polar organic solvents.39 Milleron41,42 and Talapin39 then replaced the weakly bound BF4− anions by hexaniobate and other POMs, respectively, giving clear solutions of NCs electrostatically stabilized by the POM anions. Having removed the more tightly bound organic ligands, Milleron used hexaniobate-stabilized Sn-doped In2O3 (ITO) NCs as building blocks for tunable nanocrystal-in-glass composites.41,42 While Talapin showed that films prepared by depositing POM-stabilized Fe2O3 on ITO electrodes were more effective electrocatalysts for water oxidation than analogous ones prepared from organic-ligand protected NCs.39

In the present work, the covalent attachment of POM ligands to the hematite cores of 1 gives substitutionally inert structures that occupy a unique position at the interface between molecular iron-oxide clusters and electrostatically stabilized colloidal iron-oxide NCs. We now show that, when used as a soluble photocatalyst for visible-light driven water oxidation, 1 is inherently stable under turnover conditions in water.

**Catalytic water oxidation.** The activity of 1 as a visible-light water-oxidation catalyst was explored by irradiating pH-8 solutions of 1 with visible light (150 W Xe lamp, cutoff λ ≥ 420 nm, Supplementary Figures 21 and 22). Four oxidants were evaluated: Ce(IV), Ag+-, S2O82−, and periodiate (IO4−). Ce(IV) was not suitable as it is only stable at pH values below 1, at which hematite itself dissolves. Although Ag+ is soluble at neutral pH values, these large cations form strong ion pairs with the negatively charged POM ligands, leading to precipitation at desired Ag+ concentrations. By contrast, 1 is soluble in 20 mM solutions of the anionic oxidants. For S2O82− and IO4−, 1025 and 6330 μmol O2 per gram of α-Fe2O3 in 1, respectively, were produced in 8-h reactions (Table 1, entries 1 and 2; Supplementary Figure 23).

Although written as IO4−, a recent report shows43 that its dominant form in water is actually orthoperiodate, H3IO6, which behaves as a polyprotic acid, with pKa1, pKa2, and pKa3 values of ca. 1, 7.5, and 11, respectively. For simplicity, entries in Table 1 refer to added periodate (IO4−).

The greater reactivity of IO4− relative to S2O82− (Table 1) is not unique to visible-light driven reactions of 1. Notably, IO4− is also more effective than S2O82− in trapping photoexcited electrons from visible-light irradiated WO344, Ru(bpy)32+, and Fe(bpy)32+. Specifically, visible-light driven electron transfer (ET) from Ru (bpy)32+ to IO4− is twice as fast as the corresponding reduction of S2O82−, and for Fe(bpy)32+, visible-light driven ET to IO4− is two orders of magnitude faster than ET to S2O82−.45

Support for periodate acting as a two-electron acceptor. For the reaction in entry 2, two equivalents of IO4− are reduced to IO3−.
for each equivalent of evolved O₂ (Supplementary Figure 24), consistent with IO₄⁻ acting as a 2-e⁻ oxidant. Moreover, all three components (IO₄⁻, 1, and visible light) are required for O₂ formation (entries 3–5), and the quantum yield (3.9%) is typical of water oxidation by hematite nanocrystals (Supplementary Table 2). At the same time, when using IO₄⁻, decomposition or oxo-transfer reactions 46, that could generate O₂ without removing four electrons from water, must be ruled out 47,48. This required numerous control experiments (see Supplementary Figure 25 and Table 3), necessitated by the fact that the oxide ligands of periodate equilibrate rapidly with water, precluding the use of ¹⁸O-labeling to definitively prove that the oxygen atoms in evolved O₂ originate from H₂O 49. The results of the control experiments performed are fully consistent with the clean two-electron reduction of IO₄⁻ to IO₃⁻.

In brief, photochemical decomposition of IO₄⁻ (capable of generating O₂) occurs only under UV irradiation 46. When irradiated with visible light (λ ≥ 420 nm), no decomposition of IO₄⁻ was observed, and no O₂ was detected (Table 1; entry 4). Secondly, oxo-transfer mechanisms (noted above) invariably involve thermal (dark) reactions of molecular Fe, Ru, and Ir complexes 46–48,53. By contrast, dark reactions of IO₄⁻ with 1 gave no O₂ (entry 5), while the dark reaction of IO₄⁻ with [(α-PW₁₁O₃₉Fe₂)O]¹⁰⁻ (2) gave only traces of O₂ (entry 6). The same reaction in visible light (entry 7) also gave traces of O₂, probably due to the dark reaction. These findings definitively rule out catalysis by the [α-PW₁₁O₃₉FeIII]³⁻–O⁻ ligands bound via oxo linkages to the α-Fe₂O₃ surface, including via oxo transfer from periodate to the POM-complexed Fe(III) atoms. In addition, no O₂ is produced in dark reactions of IO₄⁻ with γ-Fe(O)OH 43 or α-Fe₂O₃, and no O₂ was detected when IO₄⁻ was reacted under visible light with partially hydroxylated Fe³⁺ (entry 8).

To confirm that ET to IO₄⁻ does not generate O₂, periodate was stoichiometrically reduced to IO₃⁻ by two equivalents of the 1-e⁻ donor, [α-AIVIIIW₁₅O₄₉]₁⁰⁻–. No O₂ was detected (Supplementary Figure 26a). To model the trapping of photoexcited electrons from 1, [Ru(bpy)₃]²⁺ was reacted with IO₄⁻. While no reaction occurred in the dark, visible-light (λ ≥ 420 nm) promoted the 2-e⁻ reduction of IO₄⁻ to IO₃⁻. Again, no O₂ was detected (Supplementary Figure 26b).

Finally, direct evidence that water is required for O₂ formation was obtained by reacting organic-solvent-soluble forms of 1 and IO₄⁻ in dry and wet MeCN (entries 9 and 10; see Supplementary Figure 27) 51. Although less definitive than isotope labeling, the results show that H₂O is necessary for O₂ formation, consistent with H₂O as the source of O₂ in pure water.

### Table 1: Visible-light driven water oxidation by 1

| Entry | Oxidantb | Catalyst | Lightc | Solvent       | O₂ (μmol g⁻¹)      |
|-------|----------|----------|--------|---------------|-------------------|
| 1     | S₂O₃⁻²   | 1        | Visible| H₂O           | 1025              |
| 2     | IO₄⁻     | 1        | Visible| H₂O₂O        | 6300              |
| 3     | None     | 1        | Visible| H₂O           | 0                 |
| 4     | IO₄⁻     | None     | Visible| H₂O           | 0                 |
| 5     | IO₄⁻     | 1        | Dark   | H₂O₂O        | 0                 |
| 6     | IO₄⁻     | [(α-PW₁₁O₃₉Fe₂)O]¹⁰⁻ (2) | Visible| Dark | H₂O₂O | 60 ± 20 |
| 7     | IO₄⁻     | [(α-PW₁₁O₃₉Fe₂)O]¹⁰⁻ (2) | Visible| Dark | H₂O₂O | 60 ± 20 |
| 8     | IO₄⁻     | 1        | Visible| H₂O           | 0                 |
| 9     | IO₄⁻     | 1        | Visible| Dry MeCN      | 0                 |
| 10    | IO₄⁻     | 1        | Visible| 1:1 H₂O:MeCN  | 1640              |

*a All reactions were carried out at pH 8 for 8 h (40 ± 1°C)
*b Oxidant concentrations were 20 mM
*c Light source was a 150 W Xe lamp with a λ ≥ 420-nm cutoff filter
*d Values reported are per gram of the α-Fe₂O₃ cores, or of the catalysts listed in column three
*e These two control experiments (entries 6 and 7) rule out oxygen evolution by reaction of periodate with the Fe(III) atoms complexed within the hematite-bound POM ligands. They were carried out at pH 5 to ensure integrity of the molecular dimer, 2. In 8 h at pH 5, 1 gave 3200 μmol O₂ g⁻¹
*f After air oxidation of FeSO₄ at pH 5 and 8

### Rate optimization and stability under turnover conditions.

Unlike most polyoxometalate-based water-oxidation catalysts, 1 is stable in water over a wide range of pH values, from 2.5 to 8. And, in contrast to colloidal hematite that precipitates from solution at its isoelectric point (i.e., at pH 5.5), 1 is soluble over this entire pH range (see Fig. 2d). Hence, unlike most purely molecular or traditional colloidal catalysts, the activity of 1 can be investigated over a wide range of pH values. The results (Fig. 4a) reveal an approximate doubling of rate from pH values of 5 to 8. At pH 8, the rate of O₂ formation is 800 ± 50 μmol g⁻¹ h⁻¹ (at λ ≥ 420 nm using a 150 W Xe lamp), somewhat exceeding the fastest reported rates for visible-light driven water oxidation by colloidal α-Fe₂O₃ (see Supplementary Table 4 for reported values and related light sources).

The change in pH from 5 to 8 spans the isoelectric point of hematite (near pH 5.5; Fig. 2d). As such, the increase in rate may correlate with deprotonation of water molecules bound to the hematite surface, to give more reactive (negatively charged) hydroxide ligands, in combination with the more favorable, pH-dependent Gibbs free energy for water oxidation itself. For periodate to trap photoexcited electrons, it must diffuse to within a close proximity to the α-Fe₂O₃ surface. The cluster-anion ligated surface of 1, including [H₃IVIIO₆]²⁻ (orthoperiodate—the dominant periodate species present at pH 8—drawn to scale), and Na⁺ counter-cations (without their hydration shells), is illustrated in Fig. 4b, with iron atoms at the hematite surface shown with the terminal hydroxide ligands that dominate at pH 8. Orthoperiodate is smaller than hydrated Na⁺ cations; 54 the radius of six coordinate I(VII) is 0.67 Å, compared to 1.16 Å for Na(I) in the aquo complexes, [Na(H₂O)₉]⁺, likely located between the negatively charged POM ligands. As such, [H₃IVIIO₆]²⁻ anions, and/or hydrogen-bonded ion pairs such as [(H₂O)₅NaOH₂–O₂I(O)(OH)₃], should easily approach Fe³⁺–OH moieties at the hematite surface.

The rate of visible-light driven water oxidation by 1 is enhanced by the relatively small size of the hematite cores, which is critically important 28 due to the short, 2–4 nm, hole-diffusion length 25 of α-Fe₂O₃. This leads to a quantum yield of 3.9%, closely matching values reported for optimized reactions of similarly sized colloidal hematite 28,56.
confirmed by operando infra-red spectroscopy to be an intermediate in photoelectrochemical water oxidation on hematite films. The subsequent one-electron oxidation of FeIV=O by the reactive I(VI) radical (in a dark reaction) would give a species abbreviated as [Fe=O]+ (C), whose precise electronic structure is unknown. Computational results argue that distances between adjacent Fe atoms at the hematite surface are too large to give stable peroxide-bridged di-iron intermediates, FeIII-OO-FeII60. At the same time, the first and third-order dependence of hole formation reported by Durran and Song, support O–O formation both at a single Fe atom, and at larger hole densities and/or highly basic pH values, via coupling between adjacent surface-trapped holes. For solutions of 1 at pH 8, O–O formation is more likely to occur at a single Fe atom, giving the iron(III)-hydroperoxide intermediate, FeIII-OOH (D). Dioxygen is then generated by two-electron oxidation of Fe(III)-bound hydroperoxide ligand, resulting in E, which reacts rapidly with water to give A.

Throughout four consecutive 8-h reactions (a total of approximately 1400 turnovers per equivalent of 1 over 32 h), the turnover frequency (TOF) remained constant (44 ± 1 h−1) and the solutions remained optically transparent. After each 8-h reaction, the catalyst was quantitatively isolated by salting out with NaCl (2 M) and centrifugation, followed by re-dissolution in water. And, while acknowledging that the initial rate of O2 formation by 5-nm colloidal α-Fe2O3 (no POM ligands) was ca. 320 µmol g−1 h−1, but decreased dramatically within a few hours due to aggregation processes typical of colloidal metal oxides in water, the present TON is more than seven times that reported for the most stable, water-soluble Fe-based catalysts, its relatively small (ca. 20 Å) α-Fe2O3 center is...
nevertheless large enough to retain the photochemical properties of bulk hematite. It is from this perspective that I can be viewed as a soluble complex of a reactive metal-oxide core.

Discussion

Oxidatively inert heteropolytungstate cluster anions serve as coordinately saturated oxo-donor ligands for 3-nm hematite (α-Fe₂O₃) cores, giving anionic complexes soluble in water over a wide range of pH values (from 2.5 to 8), and that catalyze visible-light driven water oxidation with no need for added photosensitizers. Like molecular macroanions, I is highly resistant to aggregation processes that typically lead to the precipitation of electrostatically stabilized hematite and other colloidal metal oxides. And, formed by reaction with entirely inorganic tungsten-oxide-based ligands at 220 °C in water, I is inherently (thermodynamically) stable to the oxidative and hydrolytic processes that can limit the active lifetimes of molecular water-oxidation catalysts. As such, I can continuously catalyze water oxidation for 7 days (1 week) with no detectable decrease in activity. Moreover, the method used to prepare I is not limited to iron oxide, but can be modified according to the pH-controlled aqueous speciation chemistries of numerous other transition-metal ions. As such, the coherent coordination of oxidatively inert polyoxometalate ligands to metal-oxide nanocrystal cores represents a conceptually new and general approach to the design of inherently stable water-oxidation catalysts.

Methods

Preparation of I. Iron(II) sulfate (FeSO₄·7H₂O, 16.7 mg, 0.06 mmol) was dissolved into 8 mL of deionized water, and stirred for 1 hour, giving a pale-yellow solution. Freshly prepared 0.2 N KOH (2.2 equiv, 700 μL) was then added dropwise with vigorous stirring, resulting in the formation of an orange-red pH 7.0 suspension of partially amorphous γ-Fe(OH)₃. After 20 h of vigorous stirring at room temperature, 750 μL of 40 mM Na₃[α-PW₁₁O₃9] (0.03 mmol) was added dropwise, and 550 μL of deionized water was added to reach a final volume of 10 mL, and stirred for 1 h at room temperature, giving an orange pH 6.7 suspension. The suspension (6 mM Fe(III) and 3 mM Na₃[α-PW₁₁O₃9]), was then heated for 24 h at 220 °C in a 23-ml Teflon-lined 316 stainless-steel reaction vessel, to give a clear orange-red, pH 6.5 solution of I. Details of isolation and purification are provided as Supplementary Materials and Methods.

Visible-light driven water oxidation. Photochemical O₂ production was carried out in a gas-tight quartz cuvette connected to an upper bulb with a headspace volume of 16 mL. Carefully weighed samples of I were dissolved in 2.7 mL of water along with sodium periodate (NaIO₄; 12.8 mg in 0.1 mL of water) to give a final NaIO₄ concentration of 20 mM. The addition of NaIO₄ led to a drop in pH from 6.5 to 5, and either 0.2 N KOH or 0.2 N HCl solutions were used to adjust the pH to desired values (see Fig. 4a). The headspace within the cuvette was evacuated and filled with 6.5 to 5, and either 0.2 N KOH or 0.2 N HCl solutions were used to adjust the pH to desired values (see Fig. 4a). The headspace within the cuvette was evacuated and filled with NaIO₄ (135 mg in 0.1 mL of water) to give a final NaIO₄ concentration of 20 mM. The addition of NaIO₄ led to a drop in pH from 6.5 to 5, and either 0.2 N KOH or 0.2 N HCl solutions were used to adjust the pH to desired values (see Fig. 4a). The headspace within the cuvette was evacuated and filled with NaIO₄ (135 mg in 0.1 mL of water) to give a final NaIO₄ concentration of 20 mM. The addition of NaIO₄ led to a drop in pH from 6.5 to 5, and either 0.2 N KOH or 0.2 N HCl solutions were used to adjust the pH to desired values (see Fig. 4a).

Water oxidation for 7 days under turnover conditions. A solution of I (5.4 μM) and NaIO₄ (20 mM) in 3 mL of water at pH 8 (adjusted using 0.2 N KOH) was degassed as described above and irradiated with visible light (λ > 420 nm) for 1 day, during which, amounts of O₂ in the headspace were quantified at regular intervals (see Fig. 4d). After 1 day, 6.4 mg of solid NaIO₄ dissolved in 0.1 mL of water was added to the solution (an additional 10 mM concentration of IO₄⁻) and the reaction continued for a second day. After day 2, I was quantitatively separated from accumulated iodate (IO₃⁻; ca. 5.5 mM) by making the solution 0.5 M in NaCl and isolating the salted-out catalyst by centrifugation. (A control experiment later carried out after recharging the supramolecular solution with periodate, followed by irradiation, showed no activity (i.e., no O₂ in 8 h). This demonstrated that possibly unidentified soluble components were not responsible for the catalysis.) The pellet of I isolated after day 2 was then dissolved in 3 mL of water containing freshly added periodate (20 mM), adjusted to pH 8, degassed, and irradiated for day 3. (Similar separations of I from accumulated IO₄⁻ were repeated after days 4 and 6.) After days 3 and 5, additional 10 mM concentrations of IO₄⁻ were added. Turnover numbers were calculated based on the moles of O₂ produced per mole of I.

Data availability

All data generated or analyzed during this study are included in this published article (and its supplementary information files).

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