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This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1557685> since 2016-03-14T16:24:51Z

Published version:

DOI:10.1002/anie.201501941

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Polyoxometalate Complexes of Anatase-TiO₂ Cores in Water

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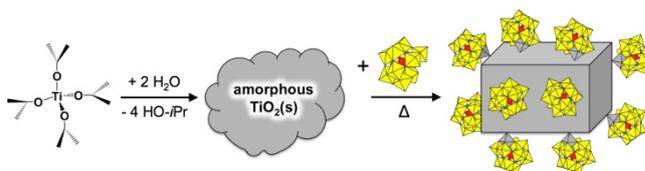
Abstract: Polyoxometalate (POM) cluster-anions here serve as covalently coordinated ligands for anatase-TiO₂ nanocrystals, giving isolable assemblies uniquely positioned between molecular macroanions and traditional colloidal nanoparticles. Na⁺ salts of the water-soluble polyanionic structures are obtained by reacting amorphous TiO₂ with the 1-nm lacunary ion, Na_(12-n)[α -XW₁₁O₃₉] (X = P⁵⁺), at 170 °C, after which, an average of 55 α -PW₁₁O₃₉⁷⁻ clusters are found as pentadentate ligands for Ti(IV) ions covalently linked to 6-nm single-crystal anatase cores. The attached POMs are reversible electron acceptors, and we show how their reduction potentials shift in a predictable fashion by changing the central heteroatom, X. Hence, just as POM cluster-anions control the reactivities of metal centers in molecular complexes, directly coordinated POM ligands with tunable redox potentials now provide new options for rationally controlling the reactions of semiconductor nanocrystals.

Polyoxometalates^[1] (POMs) serve as oxygen-donor ligands for mono-, di-, tri- and small-nuclearity oxide- and hydroxide-linked fragments of reactive transition (d-block) and main-group (p-block) metal ions, providing molecular complexes that catalyze a variety of oxidative and other processes. In many cases, catalytic activity emerges from the unique properties of the cluster-anions, often derivatives of plenary Keggin or Well-Dawson structures, that serve as ligands for the reactive metal centers. This is true as well for POM complexes of Ti(IV) ions,^[2] some of which catalyze photochemical reductions of CO₂ to methane,^[3] and selective oxidations by H₂O₂.^[4]

Structurally, a general feature of oxophilic Ti(IV) centers in molecular complexes is their natural tendency to form high-nuclearity oxide-bridged cores. Reported examples include POM complexes, such as [(α -Ti₃SiW₉O₃₇(OH)₃(TiO₃(OH)₂)₃)]¹⁷⁻^[2d] and [(α -1,2,3-P₂W₁₅Ti₃O₆₂)₄{ μ ₃-Ti(OH)₃}_4Cl]⁴⁵⁻,^[5] with cores of 10 and 16 Ti(IV)

atoms, respectively, while up to 34 Ti atoms^[6] are found in molecular titanium-oxide clusters capped by alkoxide and other^[2] organic anions. Notably, ligand-capped titanium-oxide clusters are fundamentally important *molecular models* for TiO₂ semiconductors.^[6-7]

We now report a conceptually new role for POM cluster-anions as covalently coordinated redox-active ligands in polyanionic “complexes” of *TiO₂-semiconductor nanocrystals themselves* (Scheme 1). Multiple lines of evidence from solid- and solution-state analytical methods unequivocally demonstrate that numerous Ti(IV)-substituted mono-defect Keggin-ion capping ligands, “[α -PW₁₁O₃₉Ti]-O⁻”, are covalently attached to ca. 6-nm anatase-TiO₂ cores (each comprised of 1800 ± 550 Ti atoms), resulting in isolable, water-soluble nanostructures, uniquely positioned between molecular macroanions^[2a-5] and more traditional—electrostatically stabilized—colloidal metal oxides.^[8] Moreover, the covalently attached POMs serve as tunable electron-acceptors at the surfaces of the anatase-semiconductor cores.^[7, 9]



Scheme 1. Direct coordination of Ti(IV)-substituted POM cluster-anions to anatase-TiO₂ cores. The reaction of amorphous TiO₂(s) with one-half an equivalent of the mono-defect Keggin anion, α -PW₁₁O₃₉⁷⁻ (**1**; yellow: W(VI)-centered polyhedra; red: P(V)-centered tetrahedra), gives a clear solution of 6-nm anatase-TiO₂ cores solubilized by covalently attached POM capping ligands, [α -PW₁₁O₃₉Ti]-O⁻ (far right; Ti(IV)-centered polyhedra are in grey).

When titanium tetraisopropoxide (TTIP; 8 mM) is added at room temperature to one-half an equivalent of aqueous Na₇[α -PW₁₁O₃₉] (Na₇ **1**; 4mM, pH 6), rapid hydrolysis of the TTIP gives a cloudy solution containing micron-sized particles of amorphous TiO₂(s) (Figure 1a). The pH remains unchanged,^[10] as does the ³¹P-NMR spectrum of **1** (Figure 1b). After 18 hours at 170 °C, however, a clear pH6.5 solution of nano-sized particles is obtained (Figure 1c), and α -PTiW₁₁O₄₀⁵⁻ (**2**),^[4d, 4e, 11] a by product of the reaction, is the only POM observed by ³¹P NMR spectroscopy (Figure 1d).

The nano-sized TiO₂-based particles differ dramatically from traditional examples of electrostatically stabilized colloidal TiO₂. They are indefinitely stable in water over a wide range of pH values (from 2 to 8), giving optically clear solutions in the complete absence of added organic ligands.^[12] Even more remarkable is that—like molecular macroanions—they are *uniquely resistant to aggregation*: after isolation as solids, they can be stored as *water-soluble* sodium salts.

Isolation and purification were carried out as follows. First, isopropanol and inorganic byproducts (including **2**) were partially removed from the clear reaction mixture (10 mL) by extensive dialysis against pure water. The dialyzed reaction mixture was then made 2 M in NaCl, giving a cloudy solution from which a hydrated white solid was obtained by centrifugation. When 10 mL of pure water were added, the white solid readily dissolved, giving—once again—a clear solution. The precipitation / redissolution cycle was carried out *four times*,

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[**] IAW thanks the Israel Science Foundation (ISF; 190/13), the ISF & Planning and Budgeting Committee-CORE Program (152/11), and the Adelis Foundation.

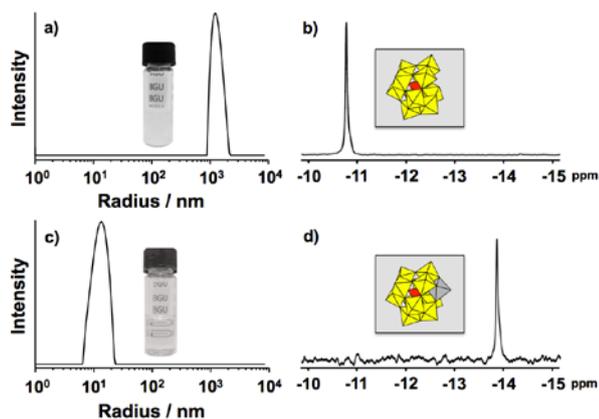
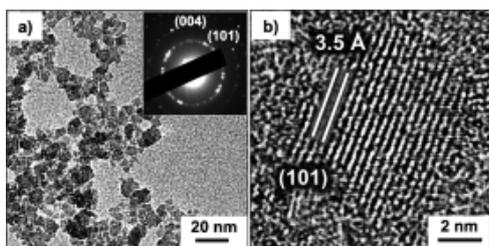


Figure 1. Dynamic light scattering (DLS) data and ^{31}P NMR spectra before and after reaction of amorphous $\text{TiO}_2(\text{s})$ with $\text{Na}_7[\alpha\text{-PW}_{11}\text{O}_{39}]$ (Na_7 **1**). Room-temperature hydrolysis of TTIP (8 mM), in the presence of **1** (4 mM), gives micron-sized particles of $\text{TiO}_2(\text{s})$, (a) and inset, and no change in the ^{31}P NMR spectrum of **1** (-10.8 ppm; b). Heating for 18 hours at 170 °C gives a clear solution of nano-scale particles, (c) and inset, and $[\alpha\text{-PTiW}_{11}\text{O}_{40}]^{5-}$ (**2**) is the only POM observed by ^{31}P NMR spectroscopy (-13.8 ppm; d); the full ^{31}P NMR



spectrum and a balanced equation are provided as Supporting Information.

reducing the amount of free $\alpha\text{-PTiW}_{11}\text{O}_{40}^{5-}$ (**2**) to less than 10 picoM (based on a dilution factor of 1×10^8). The final white solid *readily dissolved in water*, with the number-weighted average radius having increased by only 0.5 nm (by DLS; Figure S2), and no change in zeta potential (particle charge), which remained constant at -50 mV.

The TiO_2 cores were characterized by transmission electron microscopy (TEM), and electron and powder X-ray diffraction (XRD). TEM images of dried samples (Figures 2a) revealed an average particle size of 6.9 ± 1.4 nm (based on measurements of 50 particles). Although not morphologically homogeneous, many particles appear to be approximately rectangular prismatic in shape (see Figure S3 for more images). Electron diffraction of the particles (inset) featured well-defined rings—indicative of crystalline structure—which, when indexed, gave a precise match for anatase.^{[13][14]}

Figure 2. Characterization of anatase- TiO_2 nanocrystals "cores". a) TEM image of the purified nanoparticles (dried); inset: selected-area electron diffraction pattern of the particles. b). HRTEM image of a single anatase core with fringes corresponding to (101) planes of Ti atoms

Debye-Scherrer^[15] analysis of XRD data (Figure S3) gave an anatase-crystallite size of 6.1 ± 0.2 nm, statistically identical to the average particle size obtained from TEM images. This correspondence between *crystallite* size (from XRD) and *particle* size (from TEM) shows that, on average, each metal-oxide core is a single nanocrystal of anatase TiO_2 . Finally, high-resolution TEM (HRTEM) images of the nanocrystals (NCs) revealed exposed facets with atomic fringes separated by distances matching the d-spacing of the (101) planes of anatase (Figure 2d).^[13c]

Next, capping ligands on the surfaces of the anatase NCs were observed by cryogenic-TEM (cryo-TEM) and high-angle annular dark field (HAADF) imaging. Cryo-TEM images (Figure 2e)^[16] revealed numerous ca. 1-nm diameter clusters at the surfaces of the anatase cores (see Figure SG for additional images). To our knowledge, *this is the first reported image of capping ligands on a soluble metal-oxide nanocrystal*. The 1-nm clusters were further analyzed by HAADF imaging of a dried sample (panel f), which again revealed numerous ca. 1-nm objects, now appearing as white objects on a darker background. Consistent with heavier elements giving rise to brighter regions in HAADF images, data from energy-dispersive X-ray (EDX) spectroscopy (0.4-nm² spot-analysis) showed the 1-nm objects to be tungsten based (Figure S5).

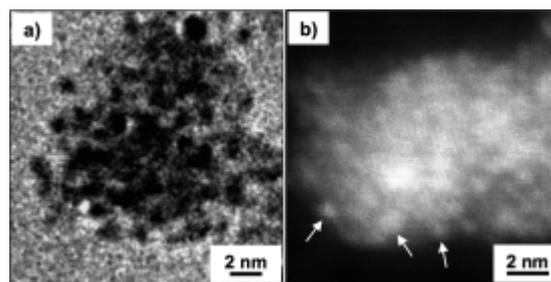


Figure 3. Tungsten-based capping ligands on individual anatase- TiO_2 cores. a) Cryo-TEM image of numerous ca. 1 nm clusters (dark objects) on the surface of an anatase NC (for comparison, images of anatase with no surface-attached clusters are provided in Figure S4). b) High angle annular dark field (HAADF) image of the ca. 1 nm clusters on an anatase NC. EDX data (Figure S5) show that the numerous bright-white spots (three of which are indicated by yellow arrows) are tungsten based, while the grey areas are mostly titanium.

The large abundance of tungsten-based clusters made it possible to obtain a definitive vibrational spectrum of these "capping" ligands (Figure 3a). After correcting the background for absorbance by anatase (Figure S1), the solid-state FTIR spectrum of the purified material (red curve in Figure 3a) was strikingly similar to that of $\alpha\text{-PTiW}_{11}\text{O}_{40}^{5-}$ (**2**, black curve in Figure 3a), both featuring two P-O stretching bands, at 1066 and 1085 cm^{-1} , diagnostic for derivatives of the mono-defect ion, $\alpha\text{-PW}_{11}\text{O}_{39}^{7-}$ (**1**), whose central PO_4 units possess local C_{3v} symmetry. The 20 cm^{-1} separation between these two bands is much smaller, however, than the ca. 40 cm^{-1} separation observed for **1** (1085 and 1041 cm^{-1}), and unambiguously signifies "in-pocket" occupancy of the defect site by a metal cation, i.e., M^{n+} in $[\alpha\text{-PM}^{n+}\text{W}_{11}\text{O}_{39}]^{(7-m)-}$.^[12] In the

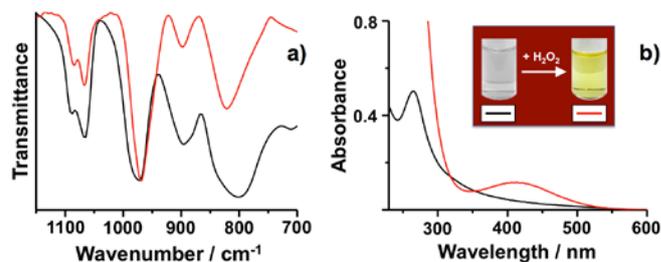


Figure 4. Spectroscopic characterization of the heteropolytungstate capping ligands. a) FTIR spectra of (red curve): the heteropolytungstate-capped anatase (corrected for absorbance by TiO_2), and (black curve): pure $\text{Na}_5[\alpha\text{-PTiW}_{11}\text{O}_{40}]$ (Na_5 **2**). b) After mildly etching the anatase NCs with HCl, and then adjusting the pH to 1.5, the UV-vis spectrum was consistent with the presence of **2** (supported by ESI MS data; see the text), which upon addition of H_2O_2 was converted to the peroxy complex, $[\alpha\text{-PTi}(\text{O}_2)\text{W}_{11}\text{O}_{39}]^{5-}$ (**3**, red curve). Inset to b): Colorless and yellow solutions before and after reaction with H_2O_2 (concentrated for better visualization).

present case, M^{m+} can only be Ti(IV). The terminal W=O stretch (at 970 cm^{-1}) is also characteristic of M^{m+} -substituted ions; in the parent ion, **1**, this band occurs at a much lower energy (950 cm^{-1}). Particularly striking is that in both spectra, the band at 1066 cm^{-1} is more intense than is the one at 1085 cm^{-1} , a “signature” characteristic of **2**.

The P(V) heteroatom was quantified by X-ray photoelectron spectroscopy (XPS), which analyzes the particle surfaces to a depth of several nm. It gave integrated signal intensities for P (2p) and W (4d) in an atomic ratio of 1 P per 12 ± 2 W, statistically identical to the 1:11 ratio in **2**.^[18] The presence of P(V) was further confirmed by solid-state ^{31}P NMR spectroscopy (for the complete solid-state NMR analysis, see the supporting information and Figure S7).

The POM capping ligand was independently identified by electrospray ionization mass spectroscopy (ESI-MS). For this, room temperature “etching” of the TiO_2 surfaces by HCl (4 M) gave a cloudy dispersion, which was removed by centrifugation. After adjusting the pH of the supernatant solution to 1.5,^[11] ESI-MS revealed **2** (Figure S8). The UV-vis spectrum of the pH-1.5 solution was also consistent with the presence of **2** (Figure 4b, black curve), and reaction of this solution with H_2O_2 gave the expected peroxo complex, $\alpha\text{-PTi}(\text{O}_2)\text{W}_{11}\text{O}_{39}^{5-}$ (**3**),^[19] indicated by a pale-yellow color and an absorbance maximum at ca. 400 nm (Figure 4b, red curve and inset). Control experiments showed the new band was not due to reaction of H_2O_2 with small amounts of Ti(IV)^[20] dissolved during etching by HCl.

Extensive coverage of the anatase surfaces by Ti(IV)-substituted Keggin ions closely related to **2** was supported by *wide-area* EDX analysis of the bulk material, which gave an atom-percent composition of $25 (\pm 3) \% \text{ W}$ to $75 (\pm 3) \% \text{ Ti}$ (Figure S9). Notably, these values correspond to the percentages obtained by simple calculation. If each cluster anion is allocated a reasonable^[21] 1.8 nm^2 “footprint” on the anatase surface, an average of 55 ± 10 undecapentate-based clusters (605 ± 110 W atoms) are present on each ca. 6-nm (1800 ± 550 Ti-atom) anatase core (Table S1). The zeta potential of the NCs, -50 mV , assigns a net charge of $15e$ for each assembly,^[22] such that, like POM monolayers on gold nanoparticles,^[23] most of the (hydrated) Na^+ counterions must be lie between the closely separated cluster anions.

Although closely related to $[\alpha\text{-PTi}^{\text{IV}}\text{W}_{11}\text{O}_{40}]^{5-}$ (**2**), the POM capping ligands (heretofore designated **2'**), are directly coordinated to the anatase NCs. This was supported by five lines of evidence: 1) No aggregation of the NCs was observed by DLS after 14 days of dialysis against pure water.^[24] Hence, unlike traditional colloids with electrostatically associated stabilizing ions, *the 2' cluster-anions are not labile*. 2) After repeated cycles of precipitation (in 2 M NaCl), centrifugation and redissolution, the isolated NCs readily dissolved in pure water to give clear solutions. This is in stark contrast to the insoluble solids obtained when traditional colloids are similarly treated. 3) Upon drying, the POM ligands remain tightly bound to the TiO_2 NCs, giving HAADF images of intact structures (Figure 3b), closely resembling those imaged in their vitrified “solution state” by cryo-TEM (Figure 3a). 4) The repeated NaCl treatments had no effect on the net charges of the nanoparticles: zeta potential values remained unchanged (-50 mV). 5) The solubility of the NCs in water increased twenty-fold – from 5 to 100 nM Ti – when the Na^+ counter cations were replaced by Li^+ , while , 6) replacement of Na^+ by organic counter cations, ($n\text{-Bu}_4\text{N}^+$ and $n\text{-Octyl}_4\text{N}^+$) gave organic-solvent soluble analogs (Figure S10).^[25] 7) In a final definitive experiment, *no anion-exchange was observed* when **2'**-capped anatase NCs were reacted with $[\alpha\text{-AlW}_{12}\text{O}_{40}]^{3-}$ (1 mM; ca. 600 times the concentration of anatase NCs, and 10 times that of surface-bound **2'** ligands; Figure S11).^[26] None of these findings is compatible with electrostatic association of POMs to the anatase NCs; *they can only be understood as the result of a unique situation in which 2' capping ligands are directly coordinated (covalently attached) to the anatase surface*.

This conclusion goes hand-in-hand with partial consumption of amorphous $\text{TiO}_2(\text{s})$ by **1** during synthesis (Scheme 1), and with the tendency for Ti(IV) ions to form stable oxo-bridged structures. Namely, at $170\text{ }^\circ\text{C}$, **1** initially consumes $\text{TiO}_2(\text{s})$ by serving as a pentadentate ligand for the titanyl ion, $\text{Ti}=\text{O}^{2+}$, giving freely solvated **2** (Figure 1d). At completion of the reaction, however, numerous POM-ligated Ti(IV) atoms must remain coordinated to the anatase surface. Consistent with this, the “Ti=O” ligand in **2** readily forms $\mu\text{-O}$ linkages to other Ti(IV) ions as, for example,^[11] in $[(\alpha\text{-PW}_{11}\text{O}_{39}\text{Ti})_2\text{-}\mu_2\text{-O}]^{8-}$. Based on this — and by analogy to alkoxide- (RO^-) ligands on molecular TiO_2 clusters^[6]—1-nm “[$\alpha\text{-PW}_{11}\text{O}_{39}\text{Ti}$]-O” capping groups might be coordinated to the anatase surface via $[\alpha\text{-PW}_{11}\text{O}_{39}\text{Ti}]\text{-}\mu_2\text{-O}^-$ linkages to single Ti atoms (upper right in panel Figure 5a), or via $[\alpha\text{-PW}_{11}\text{O}_{39}\text{Ti}]\text{-}\mu_3\text{-O}^-$ linkages to *two* Ti atoms (left in panel a). Further studies will address this issue, which might only be resolved by single-crystal X-ray diffraction of *molecular* analogs with smaller TiO_2 cores.^[22]

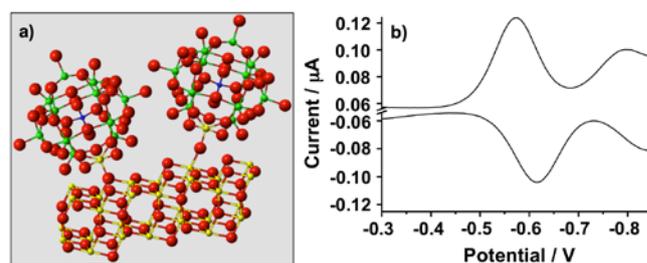


Figure 5. Coordination modes and redox chemistry of POM capping ligands on anatase nanocrystals. a) By analogy to alkoxide ligands on molecular TiO_2 clusters, **2'** is shown bound via $\mu_2\text{-O}$ or $\mu_3\text{-O}$ linkages to a facet perpendicular to (101) planes of anatase (O: red, Ti: yellow, W: green). b) Forward and reverse differential pulse voltammograms (versus Ag/AgCl, 3M NaCl) of **2'**-capping ligands on anatase nanocrystals in 0.2 M aqueous LiClO_4 .

Meanwhile, unlike simple alkoxide capping ligands, **2'** is redox active, serving as a well behaved electron acceptor.^[28] This was demonstrated using a $1.7\text{ }\mu\text{M}$ solution of **2'**-capped anatase NCs in 200 mM LiClO_4 (Figure 5b and S12). Differential pulse voltammetry (DPV; a technique much more sensitive than cyclic voltammetry) gave definitive cathodic currents with maxima at ca. -565 and -790 mV , followed by corresponding anodic currents, indicating that the capping ligands are cleanly reduced and re-oxidized on the anatase surface.^[29]

Finally, the redox properties of the POM capping ligands can be rationally tuned. This was demonstrated by reacting amorphous $\text{TiO}_2(\text{s})$ with $\alpha\text{-SiW}_{11}\text{O}_{39}^{8-}$ (K^+ salt) thus increasing the negative charge of the resulting capping ligands by one unit (characterization data are provided in Figure S13). Consistent with established correlations between anion charge and reduction potential,^[30] the first cathodic wave was shifted by ca. 175 mV in the negative direction (Figure S13, panel f).^[31]

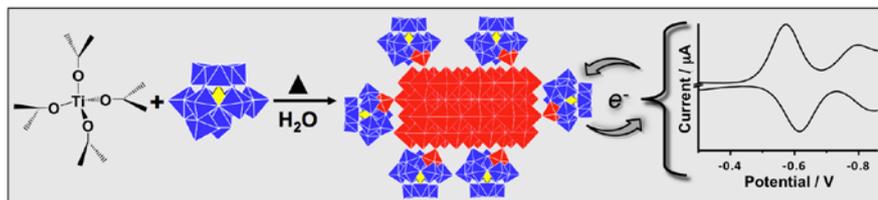
In summary, direct coordination of numerous polyoxometalate cluster-anions to the surfaces of anatase- TiO_2 nanocrystals gives stable “macroanion”-like assemblies, which can be isolated as their alkali-metal-cation or $n\text{-R}_4\text{N}^+$ salts, and subsequently re-dissolved in water or organic solvents. And, just as traditional ligands control catalytically active *metal centers* in *molecular* complexes, the tunable redox chemistry of covalently-attached POM capping ligands provides new options for rationally modifying the reactions of metal-oxide semiconductor cores.^[32] More generally, the covalent attachment of redox-active POM capping ligands to nanocrystals of titanium and other transition-metal oxides promises access to a new family of catalytic assemblies uniquely situated at the interface between molecular macroanions and traditional colloidal nanoparticles.

Keywords: Polyoxometalates • Synthesis (inorg.) • Titanium • Nanostructures • Electron Transfer

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- [22] The calculation was done as shown in ref. [21c].
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- [24] The pH was nearly identical to the isoelectric point of anatase (pH 6.7), at which its colloids typically precipitate from water: X.-Q. Chen, W.-H. Shen, *Chem. Eng. Technol.* 2008, 31, 1277-1281. In the present case, however, the solution remained optically clear.
- [25] After adding (n-Bu)₄NBr to precipitate the 2'-capped NCs from water, the resultant white solid readily dissolved in MeOH, giving a clear solution (see Figure S10 for DLS and TEM data). Analogous n-Octyl₄N⁺ salts dissolved in toluene, CH₂Cl₂, MeCN and THF.
- [26] After 3 h at room temperature, the NCs were removed by precipitation (via NaCl addition and centrifugation), and the supernatant solution was concentrated from 10 to 3 mL and treated with H₂O₂. If the 2' cluster-anions were electrostatically associated with the NCs, anions exchange with the relatively large concentration of [α-AlW₁₂O₄₀]⁵⁻ would have caused extensive release of 2' to the bulk solution. However, no titanium-peroxo complexes, 3, were detected by UV-vis spectroscopy (Figure S11). Notably, exchange of only ~5% of the POM ligands, 2', would have given rise to a detectable absorbance band at 400 nm.
- [27] The situation is similar to that of alkanethiolate-protected Au nanoparticles (RS-Au NPs): Many years, and thousands of published articles, after discovery of the RS-Au NPs themselves, the "staple" motif of RS-binding was determined from molecular Au₂₅(SR)₁₈ and Au₁₀₂(SR)₄₄ clusters; see, respectively: a) M. W. Heaven, A. Dass, P. S. White, K. M. Holt, R. W. Murray, *J. Am. Chem. Soc.* 2008, 130, 3754-3755; b) P. D. Jadzinsky, G. Calero, C. J. Ackerson, D. A. Bushnell, R. D. Kornberg, *Science* 2007, 318, 430-433.
- [28] Functionalized organic ligands are now being investigated as *electron-donating* sensitizers for molecular TiO₂ clusters; see ref. [7].
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- [31] For comparison, the first one-electron reduction potential of α-SiW₁₂O₄₀ 4- is ca. 190 mV more negative than that of α-PW₁₂O₄₀ 3-.
- [32] For example, the POM ligand has a profound affect on photocatalytic activity for a well known reaction: Under UV irradiation (150 W Xe lamp) in 10 vol-% MeOH in water, H₂ evolution proceeded at 900 mmols g⁻¹ h⁻¹ for [α-SiW₁₁O₃₉Ti]-O⁻ capped NCs (per g TiO₂), and increased to 1600 mmols g⁻¹ h⁻¹ for the 2'-capped NCs. Furthermore, these rates are an order of magnitude larger than the values of 78 and 138 mmols g⁻¹ h⁻¹ obtained under identical conditions for commercial anatase and pure 2, respectively, revealing dramatically enhanced reactivity upon covalent attachment of the POMs to the TiO₂-NC cores.

Entry for the Table of Contents

COMMUNICATION



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Polyoxometalate Complexes of Anatase-TiO₂ Cores in Water

Redox-active ligands for TiO₂: Polyoxometalate electron acceptors serve as covalently coordinated inorganic ligands for individual anatase-TiO₂ nanocrystals in water, giving isolable assemblies uniquely positioned between molecular macroanions and traditional colloidal nanoparticles. The directly coordinated POM ligands possess tunable redox potentials, providing a new option for rationally controlling the reactions of a semiconductor nanocrystal.
