

Photoredox Chemistry in Oxide Clusters. Photochromic and Redox Properties of Polyoxometalates in Connection with Analog Solid State Colloidal Systems

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Data on the electrochemical and photoredox chemistry of polyoxometalates of formula $H_4[SiW_{12}O_{40}]$ and $H_3[PMo_{12}O_{40}]$ are reported and analyzed in relation to those of related extended solids (WO_3 and colloidal WO_3 particles). These soluble multinuclear anions show reversible single-electron and multielectron reduction processes to yield blue mixed valent species. Similar reduced species can be obtained photochemically, with a concomitant oxidation of organic substrates. The reported photochromic behavior is similar to that of colloidal WO_3 particles. On the other hand, electrochemical potentials differ substantially from the flat band potential of WO_3 colloids. Finally, the title compounds are more stable and present the added advantage of having well-characterized monodisperse and controllable structures and tunable electrochemical properties.

Introduction

In recent years there has been a fast growing interest in the implications of the particle size of solid materials and specifically on the change in properties that take place in going from an extended solid system to quantum-sized, dimensionally confined analogs of it.^{1–4} Work on this topic has included both theoretical^{1,2} and experimental contributions.^{1,3–6} Among the latter, the studies on the photoluminescence of quantum-sized silicon have been the subject of recent controversy and probably constitute one of the most widely known examples of work in this field.^{5,6} There are, however, many other semiconducting materials that have been prepared in the colloidal state; cadmium chalcogenides¹ and semiconducting metal oxide colloids^{7–14} have been recently studied in relation to quantum-sized properties and photochemical and photocatalytic behavior, either as colloidal particles or as thin films.^{1,7–14}

Two reports on quantized WO_3 colloidal particles with sizes of ca. 450¹² and 20–50 Å¹³ have been published. These works describe the electrochemistry and photochemistry of these systems in relation to the bulk material, reporting their flat band potential¹² and describing electron transfer and storage capabilities of these colloids as well as their electrochromic and photochromic behaviors.^{12,13}

Polyoxometalates (isopoly- and heteropolyanions (HPAs)) are small oxide clusters whose size and solubility have caused them to be traditionally considered within the framework of molecular chemistry. They are indeed complex molecules with several metallic ions coordinated by shared oxide ions, thus forming a highly symmetrical ensemble reminiscent of metal oxides.¹⁵ The arrangement of the oxide ions can even be described in some cases as a fragment of a close-packed array. Atoms such as W, Mo, or V are the typical major components (addenda atoms) of these anionic molecules, which in the case of HPAs also contain other elements, like P, Si, or a transition element—in principle there are no restrictions on the nature of these so-called heteroatoms.¹⁵ Many heteropolyanions have been described and well characterized over the years, including their crystal (see Table S1 in the supporting information) and electronic structures. The number of addenda atoms in heteropolyanions is well defined for each species and varies typically

from 12 to 48 with a corresponding increase in their size from a diameter of 10 to ca. 25 Å, although larger clusters are known.¹⁶

Polyoxometalates present therefore a state of aggregation that makes them a natural link between the chemistry of bulk and colloidal, extended solids and the chemistry of monomeric molecules, the latter representing the ultimately “quantum-sized” systems.

On the other hand, heteropolyanions present very interesting electrochemical¹⁵ and electrochromic¹⁷ properties which are worth taking into account in comparison with those of related bulk or colloidal oxides.

First of all, the reversible reduction of many heteropolyanions to yield heteropoly-blues is a well-known process that has been thoroughly studied on many different anions.^{15,18,19} These reactions involve in principle one or two electrons, though higher degrees of reduction are possible. The molecular structure of these reduced heteropoly-blues is essentially the same as that of their parent oxidized species, with only minor variations in bond lengths and angles.^{20,21} Heteropoly-blues are class II mixed-valence systems^{15c} according to the classification of Robin and Day²² which implies a thermally activated delocalization of the added electrons among metal atoms in the molecule, but with a very small contribution from ground state delocalization.

The photochemistry of polyoxometalates has been studied and described only more recently. In this respect there are reports by several laboratories dealing with basic photochemical behavior of heteropolyanions^{23–26} and also with their photocatalytic reduction of water²⁷ and oxidation of organic substrates.^{28–35} A general mechanism for these photochemical reactions of polyoxotungstates has been proposed.²⁶

In this work we will specifically discuss the electrochemical and photochemical reductions of heteropolytungstate and heteropolymolybdate clusters of formula $[SiW_{12}O_{40}]^{4-}$ and $[PMo_{12}O_{40}]^{3-}$ (thereafter referred to as $[SiW_{12}]$ and $[PMo_{12}]$, respectively) in comparison with those of colloidal WO_3 particles. Both anions present the so-called Keggin structure, shown in Figure 1, which corresponds to the smallest¹⁶ heteropolyanions with 12 MO_6 octahedra ($M = Mo, W$) clustered around an AO_4 tetrahedron ($A = P, Si$) forming a closed array of 10 Å diameter.

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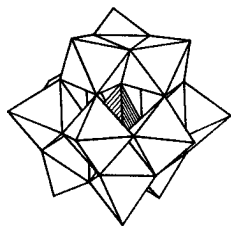


Figure 1. Structure of the multinuclear anions studied in this work. Both $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ and $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ present this so-called Keggin structure, with T_d symmetry. The inner tetrahedron (shaded) represents the Si or P atom surrounded by four oxygen atoms, and the octahedra represent W or Mo (addenda) atoms; the 12 octahedra form edge-sharing triads which are bridged to each other by corner sharing. The diameter of these polyoxometalates is 10 Å.

Experimental Section

Materials. Sodium tungstate was purchased from Baker Chemical Co. $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$ ($x = 29$) was purchased from Merck. The acid $\text{H}_4[\text{SiW}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$ ($x = 24$) was prepared according to well-established literature methods,³⁶ following modifications suggested in ref 37. Thus, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (100 g) was dissolved in 200 mL of distilled water. Six milliliters of sodium silicate solution (water glass: $\text{Na}_2\text{O} \cdot x\text{SiO}_2$, $x = 3-5$) was added, and the mixture was heated almost to boiling. Sixty milliliters of conc HCl were added dropwise, and the solution was left to stand for 18 h and then filtered to eliminate a gelatinous precipitate. To the filtrate, 40 mL of conc. HCl was added, and then the heteropolyanion was extracted with ethyl ether (70 mL). After the bottom layer, which contains a HPA-ether complex, was collected the other two layers were discarded. The HPA-ether solution was added to a mixture of 24 mL of conc. HCl and 76 mL of distilled water and extracted again with 20 mL of ether. The bottom layer was collected again and evaporated. The resulting solid was dissolved in a mixture of 24 mL of conc. HCl and 76 mL of H_2O , and the extraction was repeated. Finally, the HPA acid obtained was dried in an oven at 70 °C. The hydration state of each of the title compounds was determined by thermogravimetric analyses at 250 °C (Perkin-Elmer TGA7).

Measurements. Electrochemical measurements were carried out with an EG&G PAR 273A potentiostat/galvanostat, interfaced with a personal computer and controlled with the corresponding EG&G PAR 270 software. Cyclic voltammograms were obtained with a three-electrode setup (glassy carbon working electrode, Ag/AgCl (in saturated KCl) reference electrode, and Pt coil counter electrode). Scan rates were typically of 20 mV/s. For the electrochemical reductions carbon cloth was used as a working electrode. Photoreduction of the samples was carried out by irradiation with UV light from a Hg lamp (150 W) on solutions contained in quartz cuvettes. The reactions were followed by spectrophotometric measurements using a PE UV-visible λ array 3840 spectrophotometer between 300 and 900 nm. Additional absorption spectra were recorded on a CARY-5 UV-vis-near-IR spectrophotometer from 300 to 1500 nm. In all cases absorption spectra were recorded on argon-deaerated solutions, using as reference the corresponding solutions before reduction. Quartz cuvettes of 1 and 0.1 cm were used.

Results and Discussion

Photochemical and electrochemical reductions of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ and $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ in various solvents are presented. These reactions were followed spectrophotometrically and the results analyzed and compared with those obtained for WO_3 colloids.

Photoredox Chemistry of Polyoxometalates. Similar to what is found for WO_3 colloids, irradiation of heteropolytungstate solutions with UV light in the presence of oxidizable organic molecules yields dark blue solutions of the corresponding reduced species. Similar results are obtained for heteropoly-molybdates, included in this study for comparison. As reported previously for other polyoxoanions,²⁶ the results of this photoreduction reaction depend upon the solvent used, the organic additives present, etc. Our data on aqueous (HCl) and ethanol solutions of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ and $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ clearly manifest this tendency.

Figure 2a shows three representative spectra corresponding to the photoreduction process of $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ in ethanol. In addition to the shoulders observed at ca. 500 and 600 nm, the position of the maximum shifts with irradiation time from 730 to 760 nm. These spectra are very similar to those observed for $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ in ethanol (in this case with all maxima at 760 nm) (Figure 2b), in spite of the different chemical nature of these two anions. A solution of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ in aqueous HCl (0.12 M) plus formic acid (0.26 M) also gets reduced by irradiation with UV light, but the resulting spectrum presents a maximum clearly shifted to 855 nm with shoulders at 500 and 650 nm (Figure 2c). Furthermore, the ethanol solutions of both heteropolyanions were photoreduced much more quickly than the aqueous solution. Thus, after 30 min of irradiation under the conditions described in the experimental part, the former solutions had reached a saturation level of absorbance whereas the aqueous $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ solution was still very far from it.

From these saturation levels we estimate the nominal absorption coefficients (at 760 nm) for ethanol solutions to be 10 000 $\text{M}(\text{SiW}_{12})^{-1} \text{cm}^{-1}$ and 15 000 $\text{M}(\text{PMo}_{12})^{-1} \text{cm}^{-1}$, or expressed per mole of metal atom, 800 $\text{M}(\text{W})^{-1} \text{cm}^{-1}$ and 1300 $\text{M}(\text{Mo})^{-1} \text{cm}^{-1}$ for $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ and $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$, respectively.

Concerning the reoxidation processes, all these reduced species are unstable toward oxidation in air, the aqueous $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ being the most unstable. A spectrum corresponding to a partially reoxidized sample (still blue-colored) of irradiated $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ in ethanol is shown in Figure 2d. Further exposure to air leads to a colorless species identical to the parent anion.

The spectra of the parent title compounds present no absorption band in the near-IR region ($\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ solutions are colorless; those of $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ are yellow). On the other hand, they present characteristic strong absorption bands in the UV-vis region (max at 263 nm (4.7 eV) $\epsilon = 47\,000 \text{ M}(\text{SiW}_{12})^{-1} \text{cm}^{-1}$ for a solution of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$, $1.07 \times 10^{-5} \text{ M}$ in 0.001 M HCl; max at 220 nm (5.6 eV), $\epsilon = 78\,000 \text{ M}(\text{PMo}_{12})^{-1} \text{cm}^{-1}$ for a solution of $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$, $0.91 \times 10^{-5} \text{ M}$ in 0.001 M HCl.) (See Figure S1 in the supporting information). These absorption bands are similar to those found for quantum-sized semiconductor colloids.^{1d} The electronic excitations of the title polyoxometalates appear at high energies due to their very reduced size, in good agreement with the general inverse dependence of energy gap with size.^{1d} Unfortunately, a direct comparison with WO_3 colloids is not possible since no clear bands were observed in that case for spectra recorded just down to 300 nm.¹³

Electrochemical Potentials of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ and $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$. Effect of pH and Solvent. Cyclic voltammograms of the title compounds were obtained in order to determine their electrochemical potentials both in ethanol and aqueous (HCl) solvents. The results are shown in Figure 3 and summarized in Table 1, which show the many partial reduction processes these compounds suffer, including single-electron and multi-

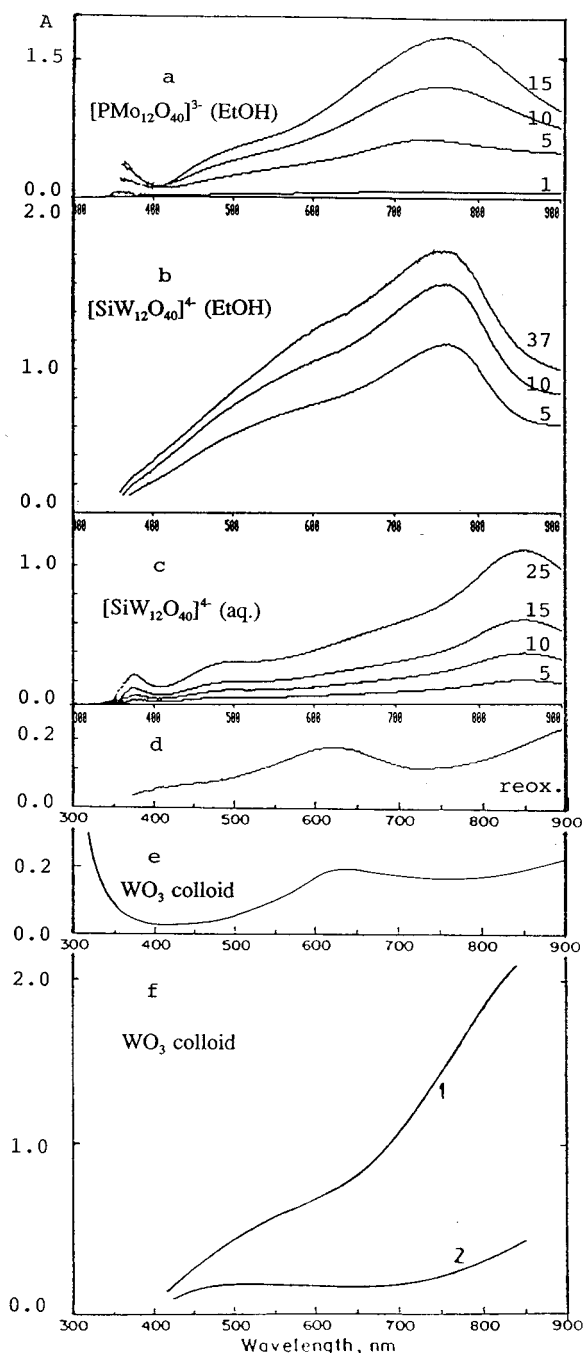
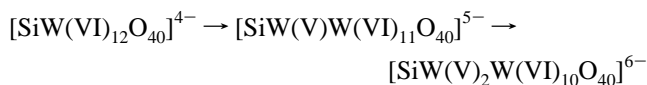


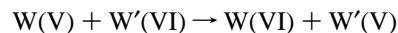
Figure 2. Absorption spectra of argon-deaerated solutions of polyoxometalates and WO_3 colloids. (a) Spectra showing the photoreduction process of an ethanolic solution of $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ (1.8×10^{-4} M (formula weight 1825)) after 1, 5, 10, and 15 min irradiation. (b) The same process for $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ in ethanol (1.9×10^{-4} M (formula weight 2878.28)). (c) The same process for an aqueous 4.2×10^{-3} M solution of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$, 0.26 M formic acid, 0.12 M HCl. In all cases the numbers on each curve indicate the time of irradiation in minutes, and the corresponding unreduced solutions were used as references. (d) The same solution used in b but subject to partial reoxidation by air (the solution was still pale blue). (e) Spectrum of deaerated aqueous WO_3 colloidal suspension (20–50 Å particle size), 0.16 M in oxalic acid. The spectrum corresponds to a sample irradiated for 6 min, after which time the intensity of the band at 630 nm seemed to get stabilized (from ref 13). (f) Absorption spectra of WO_3 colloids (450 Å particle size) 1.1×10^{-2} M (solvent: poly(vinyl alcohol)/ $\text{H}_2\text{SO}_4/\text{HCOOH}$ in water). (1) 1.1×10^{-2} M irradiated in Ar-saturated solution. (2) 3.1×10^{-3} M irradiated solution after 90 min of equilibration with air (from ref 12).

electron processes. Among them, the most relevant for comparison with photochemical results are the first and second

reduction potentials (one electron each) which correspond to the following reactions:



These reactions are reversible and lead to the formation of deep blue colored species that are easily reoxidized in air, as discussed below. The blue color results from the presence of strong absorption bands in the near-IR region which have been assigned to intervalence charge transfer processes.^{15c} These processes correspond to thermally activated delocalization of the added electrons among the different metal nuclei, i.e. to the following continued transfer process:



Contrary to other multielectron processes taking place at more negative potentials, the potentials of the first two reduction processes indicated in the scheme above are independent of pH (see Figure S2 and S3 in the supporting information). In aqueous 0.1 M HCl, the reduction potentials obtained are $E_r(1) = -0.252(5)$ V and $E_r(2) = -0.509(10)$ V, respectively (values at the maximum of the reduction wave). These values were obtained as the average of potentials measured at eight different pH values within the range $0.8 < \text{pH} < 2.8$, each measured vs a Ag/AgCl reference electrode. The corresponding values of $E_{1/2}$ ($(E_{\text{red}} + E_{\text{ox}})/2$) for each of these two initial redox processes are $E_{1/2}(1) = -0.214(2)$ V and $E_{1/2}(2) = -0.473(7)$ V (averaged as above between $0.835 < \text{pH} < 2.78$).

On the other hand, the next reduction process involves two electrons and is pH dependent, with a variation rate of ca. -0.09 V per pH unit. A linear regression of $E_{1/2}$ values in the range $0.835 < \text{pH} < 2.78$ results in the following dependence: $E_{1/2}(3)$ (V) = $-0.585 - 0.084 \text{ pH}$ (see Figure S3).

The acid $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ presents a qualitatively similar behavior: a pH-independent single-electron initial process followed by more pH-dependent multielectron processes. Quantitatively though, its behavior is quite different, with reduction potentials $E_r(1) = +0.414$ V and $E_r(2) = +0.274$ V (vs Ag/AgCl) (corresponding to potentials $E_{1/2}(1) = 0.45(1)$ V and $E_{1/2}(2) = 0.30(1)$ V) and a linear dependence of $E(3)$ as $E_{1/2}(3)$ (V) = $0.224 - 0.069 \text{ pH}$ (see Figure S4 in the supporting information). In all cases these values are much more positive than those found for SiW_{12} . This behavior is reasonable in view of the lower charge of the PMo_{12} anion.

As it could be expected, the cyclic voltammograms of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ and $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ in ethanol differ substantially from those obtained in aqueous HCl. Figure 3 presents cyclic voltammograms for SiW_{12} and PMo_{12} in aqueous (HCl) and ethanol solutions. In general the peaks appear less resolved in the latter case, and, for instance, the two one-electron processes detected in aqueous solvents cannot be resolved in ethanol. Nevertheless, we have observed a slow evolution of the cyclic voltammogram of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ over time, leading to a better separation of the different reduction waves.

Spectroscopic Studies on the Electrochemical Reduction of Polyoxometalates. Previous to each reduction experiment, the electrochemical behavior of the corresponding species in a particular solvent was characterized by means of cyclic voltammograms. Several redox processes were detected corresponding to successive reduction processes as described above (see Figure 3). A solution of 2.2×10^{-3} M $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ in 0.93 M aqueous HCl was cathodically reduced at -0.55 V vs Ag/AgCl. After 90 min, the initially colorless solution had turned deep blue. The spectrum of the reduced species and their reoxidation

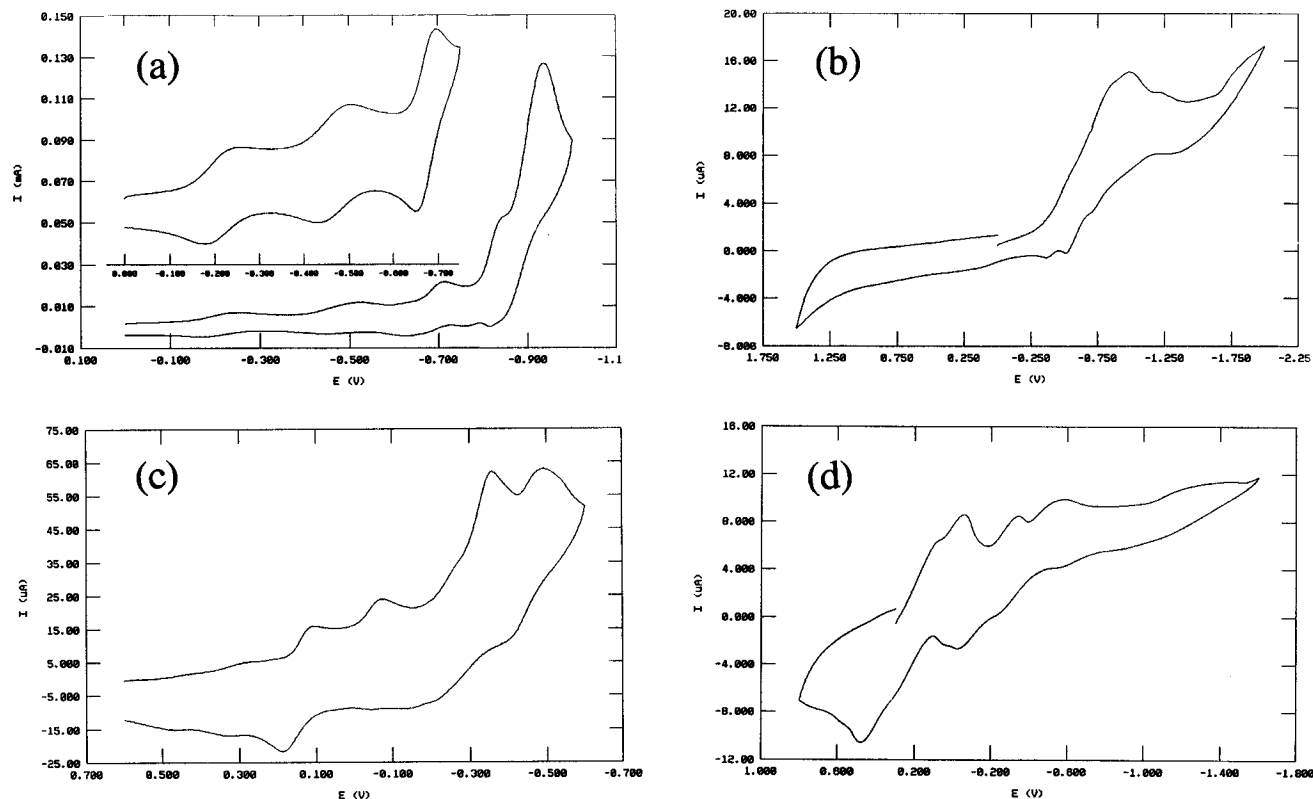


Figure 3. Cyclic voltammograms of the title compounds in aqueous (HCl) and ethanol solvents. In all cases the working electrode was glassy carbon, the reference electrode was Ag/AgCl, and the counter electrode was Pt coil; scan rate 20 mV/s. (a) $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$, 1.07×10^{-3} M in 0.1 M aqueous HCl, 0.175 M LiCl (pH = 1.3). The inset shows a CV run on the same sample between 0.0 and -0.75 V. (b) Freshly prepared $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$, 1.043×10^{-3} M in ethanol. (c) $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$, 0.91×10^{-3} M in 0.1 M aqueous HCl (pH = 1.18). (d) $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$, 0.90×10^{-3} M in ethanol. All solvents were deaerated with Ar.

TABLE 1: Values for the Successive Reduction Waves Observed for the Title Compounds in Different Solvents^a

	$E_r(1)$	$E_r(2)$	$E_r(3)$	$E_r(4)$	$E_r(5)$		
$\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ aq HCl (pH = 1.28)	-0.245	-0.525	-0.712	-0.850 ^b	-0.936		
$\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ EtOH		-0.465 ^b	-0.720	-0.858	-1.294		
$\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ aq HCl (pH = 1.30)	0.420 ^b	0.276 ^b	0.102	-0.078	-0.282 ^b	-0.356	-0.516
$\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ EtOH		0.350 ^b	0.080 ^b	-0.058		-0.340	-0.586

^a Values correspond to the maximum of each reduction wave and are given in Volts vs Ag/AgCl reference electrode. ^b Shoulder.

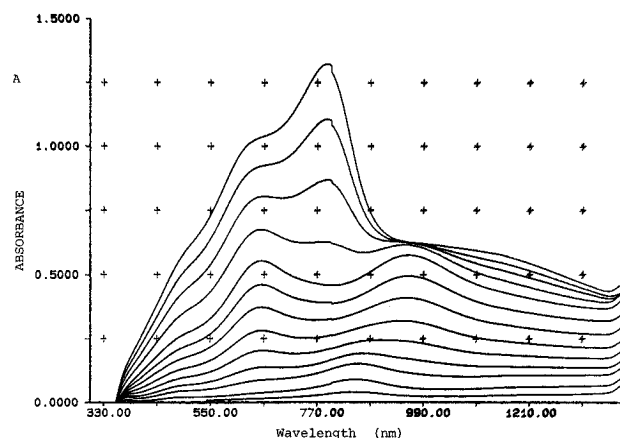


Figure 4. Absorption spectra of an argon-deaerated solution of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$, 2.2×10^{-3} M in 0.93 M aqueous HCl electrochemically reduced at -0.55 V vs Ag/AgCl for 90 min (top spectrum); the same solution before reduction was used as the reference. The descending series of spectra show several stages of the process of reoxidation suffered upon exposure to the air. Quartz cuvettes (0.1 cm) were used for these measurements.

products is shown in Figure 4. Initially, a two-electron reduced species is obtained (with possible contamination of a four-electron product associated to the maximum at 790 nm).

Gradual oxidation of the solution by air leads to the transient obtention of a one-electron reduced species with a shoulder at 500 nm and maxima at 654 and 960 nm ($\epsilon = 2000 \text{ M}(\text{SiW}_{12})^{-1} \text{ cm}^{-1}$). These absorption peaks in turn decrease in intensity and eventually “coalesce” into a new maximum at 850 nm (ϵ of the order of $700 \text{ M}(\text{SiW}_{12})^{-1} \text{ cm}^{-1}$) with shoulders at 500 and 650 nm. This final spectrum, corresponding to a reduction level of a fraction of an electron per SiW_{12} unit is the one more closely matching the spectra obtained during the initial stages of photoreduction in aqueous HCl described above.³⁸ This similarity points out to the same nature of the reduced species in both experiments (in the same aqueous HCl medium).

Concerning the nature of photoreduced and electrochemically reduced species, we can conclude that they are the same, provided the same concentration of electrons is injected into the solids. This is shown here for the case of polyoxotungstates and is equally likely for WO_3 colloids. The different mechanisms of the photochemical and electrochemical reductions of semiconductors are well established; electrochemical reduction injects electrons directly into the conduction band of the solid (LUMO for molecules), whereas the photochemical process yields an electron–hole separation that can evolve in different ways. The presence of hole scavengers (oxidizable molecules) commonly used in the present and other studies leads to the

isolation of electrons in the solid. Thus, the end result of both processes would essentially be the same.

On the other hand, the reduced compounds present spectra sensitive to the solvent used. This sensitivity to solvent has also been observed for amorphous and crystalline films of bulk WO_3 , where the adsorption of solvent molecules onto the surface of the semiconductor has been proposed to account for the different enhancement of light absorption induced on this oxide by several alcohols.³⁹ In this sense the molecular species could be considered as ultimately dispersed oxides clusters with all WO_6 groups on the surface, i.e. on the solid-liquid interphase.

Comparative Analysis of WO_3 Colloids and Polyoxotungstate Photoredox Properties. We note that the spectra of electrochemically reduced WO_3 colloids reported by Kamat et al.¹³ are qualitatively similar to the spectra of both photo-reduced and electrochemically reduced [SiW12], with a strong absorption band between 700 and 900 nm. The same is true for both electrochemically and photochemically reduced thin WO_3 films prepared from the same quantum-sized colloidal particles.¹⁴ On the other hand, the spectrum reported by the same authors for the photolyzed WO_3 dispersed colloids¹³ (shown in Figure 2e) lacks such a strong band and resembles more closely the features of the spectrum obtained for the partially reoxidized [SiW12] compound, both with a maximum at 600–650 nm. A similar behavior upon exposure of WO_3 colloids to air was reported by Nozik et al.,¹² where a strong absorption band with maximum above 800 nm, observed only for the more intensely irradiated samples, got drastically reduced for air-equilibrated solutions (see Figure 2f). Since Kamat et al. used deaerated solutions in the reported experiment, we can only speculate that a possible reason for the absence of this typical band could be the short irradiation times used (up to 6–8 min) leading to an only partially reduced species.

The absorption coefficients of photogenerated electrons in WO_3 colloids are an interesting parameter for comparison with polyoxotungstates, but its evaluation is not trivial. On the one hand, values of $\epsilon = 5600 \pm 500 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ have been reported¹² for electrons in WO_3 from γ -radiolysis experiments with WO_3 colloids. On the other hand, “effective” values of ϵ deduced from saturation plots of UV-irradiated samples are lower.

Despite the overall qualitative similarities between their photochemical properties analyzed above, the values of their absorption coefficients could represent a difference in the optical properties of photoreduced colloidal WO_3 and those of polyoxotungstates. This is first indicated by the very different concentrations used to study the reduced solutions in each case. In the case of polyoxoanions, we must use very dilute concentrations of $\sim 10^{-4} \text{ M}$ (SiW12) (ca. 10^{-3} M in tungsten) in order to record spectra with reasonably low absorbance; as indicated above, this results in absorption coefficients of the order of $10\,000 \text{ M}(\text{SiW12})^{-1} \text{ cm}^{-1}$, i.e. $800 \text{ M}(\text{W})^{-1} \text{ cm}^{-1}$ at 750 nm, as for other two-electron reduced species reported in the literature.^{15c,19} On the other hand, the spectra of WO_3 colloids with sizes of 20–50 Å, comparable to the polyoxometalates, are recorded for much more concentrated solutions (0.4 M in tungsten).¹³ A reliable estimate of absorption coefficients in these colloidal systems is certainly difficult, and no coefficient was reported for these quantum-sized colloids; nevertheless, the very high concentrations used prompted us to calculate a rough estimate of an effective value for the colloidal systems on the basis of the published plots showing a saturation of the absorption by aqueous suspensions,¹³ resulting in size-dependent values ranging from 10 to 20 M (per W atom)⁻¹ cm⁻¹ at 630 nm. Similar nominal values obtained from our saturation

plots on [SiW12] (ethanol) are $800 \text{ M}(\text{W})^{-1} \text{ cm}^{-1}$ (at 760 nm) and $600 \text{ M}(\text{W})^{-1} \text{ cm}^{-1}$ (at 600 nm). In the case of our aqueous solution, no saturation was apparent after 30 min of irradiation, but, at that time, the absorption coefficients were already $27 \text{ M}(\text{W})^{-1} \text{ cm}^{-1}$ (at 855 nm) and $12 \text{ M}(\text{W})^{-1} \text{ cm}^{-1}$ (at 650 nm), that is, comparable in magnitude to those of the colloids and still growing.

Therefore, our work shows that polyoxotungstate anions present photochromic properties at least comparable to quantum-sized WO_3 particles of comparable size in the same solvent, with even larger absorption coefficients. Of course this is not to say that the redox chemistries of both kinds of systems are identical; their different electrochemical properties will be compared and discussed in the following section.

Electrochemical Potentials of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ and $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ in Relation to the Flat Band Potential of WO_3 Colloids. The flat band potential of WO_3 colloids has been shown to depend on the number of electrons injected per volume of sample; the values obtained depend as well on the method used for its determination.¹² The values obtained range from 0.35 to 0.45 V vs the normal hydrogen electrode (NHE).¹² From the data given above the two first reduction waves of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ in aqueous acidic solutions appear at maximum wave values of $E_r(1) = -0.055 \text{ V}$ and $E_r(2) = -0.312 \text{ V}$ (vs NHE)⁴⁰ with half-wave potentials of $E_{1/2}(1) = -0.017 \text{ V}$ and $E_{1/2}(2) = -0.276 \text{ V}$. In ethanol the first reduction wave would be even more negative ($E_r(1) = -0.27 \text{ V}$ vs NHE at maximum wave), but the overlapping makes more difficult a precise characterization.

The electrochemical reduction potential of the title polyoxotungstate presents, therefore, values that are substantially more negative than those found for the flat band potential of WO_3 colloids. In turn, the latter were found to be ca. 150 mV more negative than those for compact bulk WO_3 electrodes. This general trend is in good agreement with the well-known shift of flat band potentials toward more negative values as the negative surface charge increases.¹² In these sense, polyoxotungstates represent the ultimately dispersed state of WO_3 ; there is no “bulk”, just 12 WO_6 octahedra all of which are at the interface with the solvent and with a charge of -4 (in its original unreduced salt form) distributed among them.

The lower reduction potential values of the title polyoxotungstate make it more difficult to reduce from a thermodynamic point of view. Nevertheless, the photochromic behavior of the polyoxotungstate and WO_3 colloids are comparable because the UV-vis light range is wide enough to induce photoexcitation in both cases. On the other hand, the stronger reducing character of the photoreduced polytungstate as compared with the photoreduced WO_3 colloid makes the former a candidate for performing redox reactions that are not possible for the colloids. Thus, the negative potential of the tungstate makes feasible the reduction of protons to yield H_2 . This process has indeed been observed in some cases as reported earlier.²⁶

Finally, another important difference concerning the electrochemical properties of both kinds of systems is related to the change in electrochemical potentials as the number of electrons accumulated in each system increases: In the case of WO_3 colloids this change is relatively small, and the flat band potential changes from ca. 0.45 to ca. 0.35 V (vs NHE) upon an increase of 2 orders of magnitude in the number of electrons accumulated. On the other hand, the polyoxotungstate suffers a change in potential from -0.017 V for the first electron reduction to -0.276 V (vs NHE) for the second electron reduction. That is, just doubling the number of electrons accumulated in a given volume results in a decrease of 0.25 V

in the potential This must be due to the larger ratio e^-/W atom reached in the polyoxotungstate redox reactions or, equivalently, to an increased surface charge effect. This large effect of charge on potentials can be profitably used in order to tune the electrochemical properties of polytungstates. An illustrative example of this is given by the substantial decrease in the reduction potentials of a series of clusters of formula $[XW_{12}O_{40}]^{n-}$ in going from $X = P$ ($n = 3$) to Si ($n = 4$) to Fe ($n = 5$).²⁶

From Molecules to Solids. As it has been advanced in the Introduction, both colloidal WO_3 particles and polyoxotungstates constitute intermediate systems bridging the gap between isolated tungstate ions and bulk WO_3 . Whereas colloidal particles have their starting point in extended solids, polyoxometalates originate from a molecular approach. Nevertheless, both systems share common features of great significance, like the aggregation of multiple tungsten centers that can lead to mixed valence systems with thermally activated delocalization and the fact that this aggregation is spatially limited so as to prevent a truly extended nature (bandlike) of their electronic structure.

Furthermore, from a chemical point of view, colloidal WO_3 and molecular polyoxotungstates are synthesized by very closely related methods, since both systems are products of the acid condensation of the tungstate anion and differ mainly on the degree of aggregation of WO_6 units. On the other hand, polyoxotungstates are very well-characterized, truly monodisperse clusters with structures precisely known, whereas very little is known about the actual structure of WO_3 colloidal particles. The assumption of these colloids having the structure of $WO_3 \cdot 2H_2O$ ¹³ completely neglects the fact that in particles of 20–50 Å a very significant portion of the solid is at the surface thus probably presenting a distorted (maybe curved?) structural arrangement, similar to what is found for the limiting molecular case in $[SiW_{12}]$ (Figure 1).

In addition to the structure, the particle size and the dispersity of oxide colloids are also difficult to control, in spite of their great importance in determining their physical properties. This difficulty is notorious when comparing the particle sizes of colloids prepared by two different groups^{12,13} following the same standard method, with minor modifications.⁴¹ While electron microscopy examinations gave average diameters of 450 Å in one case, in the other the same analytical method showed diameters from 20 to 50 Å.⁴² Thus, we want to note the need for a better structural characterization of colloidal WO_3 particles and the necessity of a better control of particle size and monodispersity as a first step in controlling their properties.

On the other hand, we want to point out how the monodisperse character and well-characterized molecular and electronic structures of polyoxometalates make them ultimately controllable analogs of what is known in physics as quantum dots.

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Supporting Information Available: Crystal structure and reduction potentials (5 pages). Ordering information is given on any current masthead page.

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