



Polyoxometalates as photoelectrochemical models for quantum-sized colloidal semiconducting oxides

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Abstract

A comparative analysis is made of the photoredox, electrochemical and electron storage properties of polyoxotungstate and polyoxomolybdate clusters in comparison with those of colloidal WO_3 particles. Both species can harvest light and act as photocatalysts, but polyoxotungstates present a smaller size, wider gap, lower reduction potentials and greater tunability. Furthermore, WO_3 colloids are structurally ill-characterized and tend to coagulate whereas polyoxometalate structures are well characterized, controllable and stable in solution. These characteristics and the confinement of injected electrons in a zero-dimensional nanometre-sized polynuclear molecule make of polyoxometalates remarkable models for colloidal quantum-sized semiconducting oxides.

Keywords: Polyoxometalates; Tungstates (or tungsten); Molybdates (or molybdenum); Colloidal semiconductors; Photochromism; Photoreduction; Electron storage; Photoconversion; Quantum-dots

Materials: WO_3 ; $\text{H}_3[\text{SiW}_{12}\text{O}_{40}]$; $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$

1. Introduction

Polyoxometalates resemble discrete fragments of certain transition metal oxides [1]. Their well characterized crystal structures [1,2] reveal highly symmetrical polynuclear cluster arrangements, frequently anionic, that remind us of extended tungsten or molybdenum oxides but are zero-dimensional in nature and nanometric in size.

The similarities between polyoxometalates and oxides are not limited to topology and structure though. Despite their different dimensionality they share common features related to their redox chemistry [2,3], photochemistry [3] and photocatalytic properties [3–5]. The similarities are most striking when polyoxometalates are compared with colloidal

dispersions of nanometric-sized transition metal oxides [6].

Nanometric semiconducting particles are indeed the subject of many recent reports [7–13] that explore the implications of quantum confinement and try to exploit the features offered by wide-gap semiconductors, including oxides [11–13]. In this context there have been several reports on colloidal WO_3 particles of variable sizes, 450 Å [12] and 20 Å [13]. These works reported the photoredox properties of WO_3 colloids, their photochromism and electron storage capabilities [13], as well as their flat band potential [12] in relation to that of bulk WO_3 [14].

In their role as wide-gap semiconductors these colloids undergo electron–hole separation upon UV light irradiation; in the presence of suitable electron donors, D, the hole can be transferred and photooxidation of D to D^+ takes place (Fig. 1). Among the

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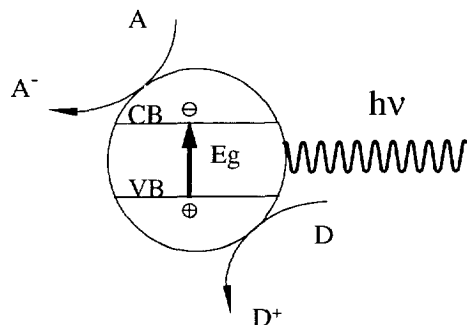


Fig. 1. Photoinduced charge transfer processes at a semiconducting particle. Absorption of a photon excites one electron from the valence band (VB) into the conduction band (CB). The hole produced can react with a suitable electron donor (D), leading to a net reduction of the semiconductor. In the presence of acceptors (A) the excited electron could be transferred.

most common hole scavengers there are many organic molecules, alcohols, carboxylic acids, etc. . . . The electron promoted to the conduction band (CB) upon photon absorption can be stored in the semiconducting particle in the absence of electron acceptors (A). Normally, lattice defects are invoked as the ideal electron-trapping features.

Polyoxometalates can also undergo photoreduction in the presence of a variety of electron donors [3] and are indeed used as photocatalysts [3–5], but their study has always been focused from a chemical point of view. It is very worthwhile to carry out a comparison of the behaviour and properties of these cluster models with those of colloidal semiconducting tungsten oxide in an attempt to bridge two fields that have advanced independently but are beginning to converge into some common ground. The anions described in this work are $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ and $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, the latter included for comparison; they will be denoted in the text as SiW12 and PMo12 respectively. Both present the well known Keggin structure [2,6].

2. Experimental

2.1. Materials

$\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ was purchased from Merck. The acid $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ was prepared as reported previously [6]. The synthetic procedure is also included

here to facilitate comparison with that of WO_3 colloids. Thus, $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$ (100 g) was dissolved in 200 ml distilled water. Six ml of sodium silicate solution (water glass: $\text{Na}_2\text{O} \times x \text{SiO}_2$, $x = 3-5$) was added and the mixture heated almost to boiling. Sixty ml 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 conc. HCl was added and then the heteropolyanion was extracted with ethyl ether (70 ml). After collecting the bottom layer, which contains a SiW12–ether complex, the other two layers were discarded. The SiW12–ether solution was added to a mixture of 24 ml conc. HCl and 76 ml 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 H_2O , and the extraction was repeated. Finally the SiW12 acid obtained was dried in an oven at 70°C .

2.2. 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. 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 lambda 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 contained in 1 cm quartz cuvettes and using as reference the corresponding solutions before reduction.

3. Results and discussion

3.1. Synthetic procedures

First of all, it is worthwhile considering the similarities and differences in the syntheses of WO_3 colloids and polyoxotungstates. Both are formed

during the acid condensation of the tungstate anion. Thus in both cases Na_2WO_4 and HCl are reacted (though in heteropolyanions such as SiW_{12} the heteroatom is introduced by dissolution of an additional reagent) and a 'tungstic acid' precipitate is formed. On the other hand, polyoxometalates are extracted from the filtrate whereas the colloids are formed by redissolving the precipitate, treating it with hot mild acids [12,13,15]. This is the key difference in the synthetic procedures: polyoxotungstates remain in solution as the fraction of smallest clusters; extraction and purification leads to the isolation of pure species that are in many cases easy to crystallize and have consequently been characterized structurally. WO_3 colloids, on the other hand, are formed by breaking the precipitate particles into smaller pieces by partial dissolution, a procedure that leads to polydisperse systems with larger particle size and makes difficult their crystallization and structural characterization.

3.2. Electronic spectra

The spectra of the parent (oxidized) polyoxometalates present no absorption in the near-IR region ($\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ solutions are colourless, 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) $\epsilon = 45\,000 \text{ M}(\text{SiW}_{12})^{-1} \text{ cm}^{-1}$ 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), $\epsilon = 77\,000 \text{ M}(\text{PMo}_{12})^{-1} \text{ cm}^{-1}$ 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 Fig. 2). These absorption bands are similar to those found for quantum-sized semiconductor colloids [10]. 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 [10]. 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].

3.3. Photochemical properties

The photoredox process and photochromic properties of polyoxotungstates and those of WO_3 colloids are similar. As has been reported for the colloids [12,13], SiW_{12} solutions containing suitable electron donors are reduced upon exposure to UV light and yield deep-blue species. This colour derives from the presence of an inter-valence charge transfer (IVCT) band in the near-IR region of the spectrum

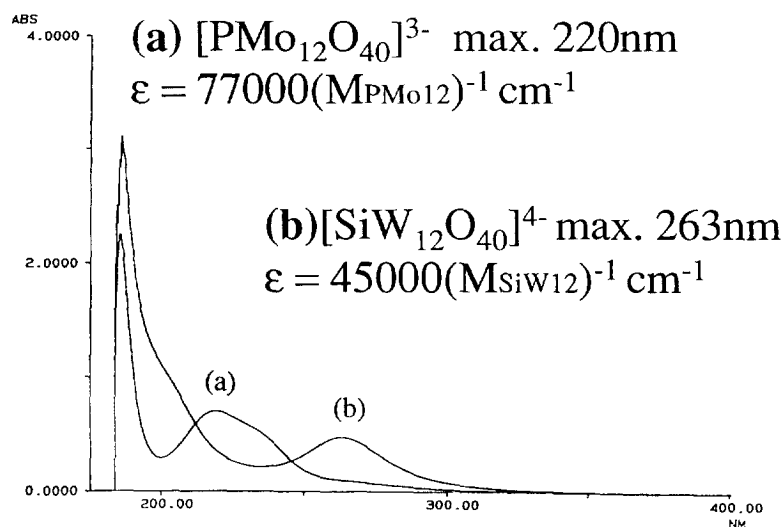


Fig. 2. Electronic spectra of aqueous polyoxometalate solutions in their initial oxidized state. (a) $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ $0.91 \times 10^{-5} \text{ M}$ (max. 220 nm, $\epsilon = 77\,000 (\text{M}_{\text{PMo}_{12}})^{-1} \text{ cm}^{-1}$). (Shoulder at 235 nm). (b) $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ $1.07 \times 10^{-5} \text{ M}$ (max. 263 nm, $\epsilon = 45\,000 (\text{M}_{\text{SiW}_{12}})^{-1} \text{ cm}^{-1}$). 1 cm quartz cuvettes were used. No other absorption bands were detected down to 1500 nm.

that extends its tail to the long-wavelength part of the visible region. Examples of these bands are shown in Fig. 3 and resemble those found for photoreduced WO_3 colloids [12,13]. Fig. 3 also serves to illustrate the solvent-dependent nature of these bands. Solvent dependence has also been reported for the spectra of oxide colloids and it has been associated with surface interactions with the corresponding solvent. Also similarly to WO_3 colloids, SiW12 can store the injected electrons for long periods, as long as no electron acceptors are present (i.e. in the absence of air). Exposure to air oxidizes the blue species regenerating the cluster in its original form.

The nature of the injected electrons is another

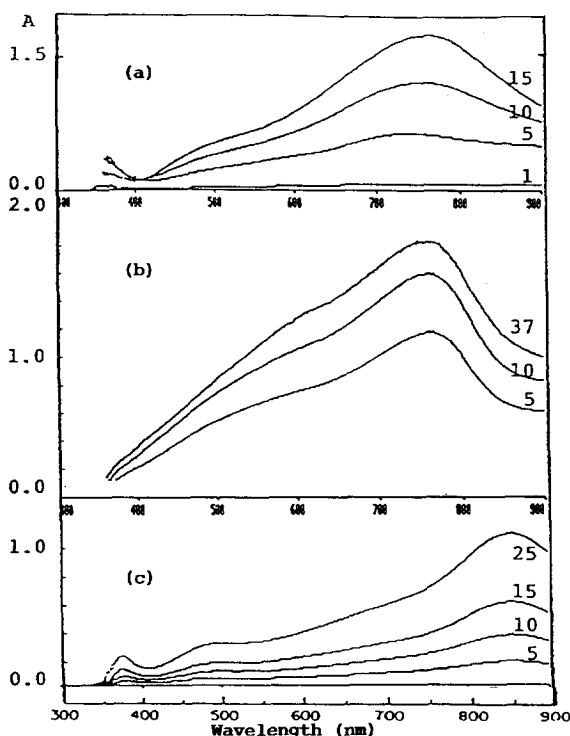


Fig. 3. Photochromic properties. Absorption spectra of argon-deaerated solutions of polyoxometalates. (a) Spectra showing the photoreduction process of an ethanolic solution of $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ (1.8×10^{-4} M (formula weight 1825) after 1, 5, 10 and 15 min. irradiation. (b) 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 $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$, 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.

matter for comparison. In semiconductors these electrons are considered to be localized at defects and move through the lattice by means of a hopping mechanism, thus explaining the thermally activated conduction opposed to a metallic behaviour. In quantum-sized clusters such as polyoxotungstates bulk conductivity is out of consideration since the inter-cluster electron transfer barrier is high. Nevertheless, in the blue reduced species there is a well-characterized intra-cluster delocalization of the injected electrons [2]. This is not a ground-state delocalization but rather a thermally activated one, as for the semiconducting particles. It must be emphasized though that in SiW12 all twelve W atoms are chemically equivalent due to the high symmetry of the cluster. Therefore, localization of the injected electrons at defects cannot be invoked in this case. It could be supposed that the temporal residence of the electron on a particular tungsten atom would lead to a local deformation of the structure around that nucleus, but this deformation would be associated to the inter-metallic electron transfer itself. A polaron-like description of the process could therefore be most adequate, taking the polyoxotungstate cluster as a model compound for a semiconducting WO_3 particle.

3.4. Electrochemical properties

Electrochemical properties of polyoxometalates are well known [2]. As an example Fig. 4 shows a cyclic voltammogram (CV) of an acidic solution of SiW12 in water. The first two waves correspond to single electron processes and are pH-independent, whereas the third wave corresponds to a pH-dependent redox process involving two electrons.

The flat-band potential of WO_3 colloids has been reported [12] to be in the range 0.35–0.50 volts vs. the normal hydrogen electrode (NHE), slightly varying as a function of the concentration of electrons injected [12]. These values have been reported to be ca. 150 mV more negative than those for compact WO_3 electrodes [14], due to the more negative surface charge of the colloids [12]. If we compare the first redox potential of SiW12 (-0.017 V vs. NHE) with the flat-band potential of the colloids, we obtain an even more negative value for the polyoxotungstate, in good agreement with its smaller size

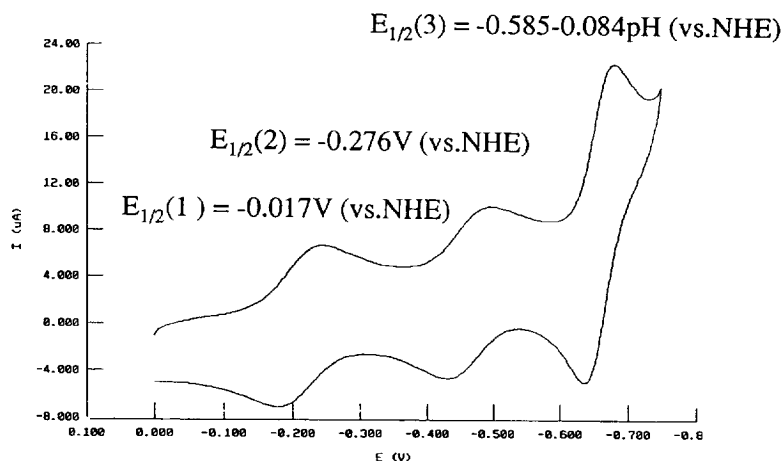


Fig. 4. Cyclic voltammogram of $H_4[SiW_{12}O_{40}]$ 1.07×10^{-3} M in aq. HCl 0.1 M, LiCl 0.175 M (pH = 0.8). Glassy carbon working electrode, reference electrode Ag/AgCl and counterelectrode Pt coil; scan rate 20 mV/s. The first two redox processes are pH-independent in the range studied ($0.8 < \text{pH} < 3.0$). The values given correspond to averages over that pH range.

and higher electron density per volume (see Fig. 5). Indeed we can consider that in the case of polyoxometalates with the Keggin structure [2] such as SiW12 and PMo12, all twelve MO_6 polyhedra are at the surface of the cluster, in contact with the electrolyte and supporting all the negative charge; thus representing the ultimately dispersed oxide particle. Polyoxotungstates are therefore more difficult to reduce than WO_3 colloids and consequently would lead to stronger reducing species upon electron injection.

Furthermore, it is interesting to note the effect of increasing the number of injected electrons on the redox potentials of colloids and polyoxotungstate. This effect is relatively small for the colloids as can

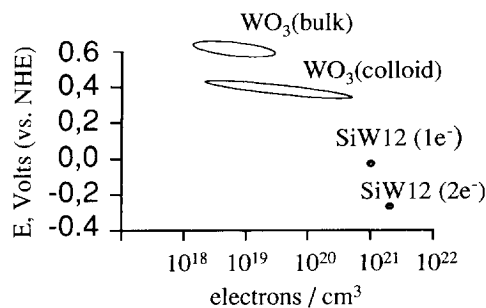


Fig. 5. Schematic diagram showing the effect of particle size on the flat band redox potentials of WO_3 and polyoxotungstates. Values for the oxide were taken from Ref. [12].

be seen in Fig. 5; this is probably due in part to the low concentrations of injected electrons attained (10^{19} – 10^{21}) [12] but also to the relatively large size of the colloidal particles (450 Å). On the other hand, injecting a second electron on SiW12 ($+1e^-$) results in a redox potential of $E_{1/2}(2) = -0.276$ V vs. NHE (as compared with the first potential of $E_{1/2}(1) = -0.017$ V vs. NHE). We see how the smaller size of polyoxometalates results then in a higher concentration of added electrons and consequently in a stronger dependence of the redox potentials on the number of injected electrons. Thus, compared with WO_3 colloids, polyoxometalates are subject to a greater tunability of their redox properties, especially since a wise substitution of the heteroatom (Si) can lead to different overall charges and therefore to different reduction potentials [2].

As a matter of fact, the potentials of the related phosphomolybdate anion PMo12 also exemplify this tunability. PMo12 has a charge of -3 (as opposed to -4 for SiW12) which is consistent with its more positive values of reduction potentials ($E_{1/2}(1) = +0.647$ V and $E_{1/2}(2) = +0.497$ V vs. NHE) [6].

Taking into account the relative sizes, absorption spectra and redox potentials of WO_3 (bulk and colloidal), SiW12 and PMo12 we can make a qualitative band/MO (molecular orbitals) scheme for comparison of the different systems (Fig. 6). The scheme shows the progressive widening of the band

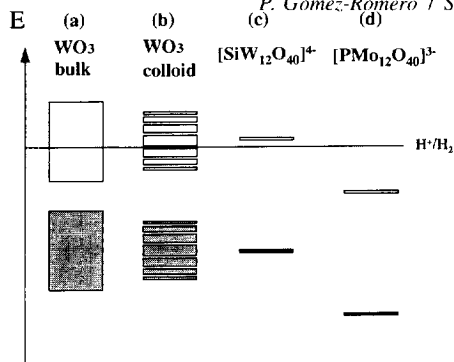


Fig. 6. Schematic band structure diagram of polyoxometalates and WO_3 (bulk and colloid). The horizontal line represents the normal hydrogen electrode reference potential.

gap as the size of the tungsten oxide particles decrease, reaching a maximum for SiW_{12} . Reduction potentials get correspondingly more negative along this series. On the other hand, PMo_{12} presents a wider gap (absorption at higher energies) but a more positive reduction potential. It is important to notice that the reduction in size when working with the polyoxotungstate (SiW_{12}) leads to a qualitative difference in redox properties: the potential of its reduced species to reduce water to hydrogen from a thermodynamic point of view; such reaction is not possible with WO_3 .

Finally the accompanying Table 1 could serve to summarize conclusions on the comparative chemistries of WO_3 colloids and polyoxotungstates. To the

Table 1
Comparative analysis

Polyoxotungstates	WO_3 colloids
<ul style="list-style-type: none"> • photoreducible • e-storage • 10 Å diameter • monodisperse • reproducible synthesis • controlled composition • well-known structure • stable in solution • lower potentials • more tunability 	<ul style="list-style-type: none"> • photoreducible • e-storage • 20–450 nm • polydisperse • uncontrolled parameters with unknown effect – pH • unknown structure • less stable (ageing, coagulation)

lower reduction potentials and greater tunability associated to their smaller size, polyoxotungstates add a well known structure stable over time. This together with their photoredox behaviour makes them very interesting models for related quantum-sized semiconducting oxides.

Acknowledgements

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