Photocatalytic Reduction of Ag_2SO_4 by Dawson-Derived Sandwich Complex

Laurent Ruhlmann, Claire Costa-Coquelard, Sébastien Sorgues, Isabelle Lampre*

Summary: Photocatalytic reduction of $Ag^{I}_2SO_4$ from aqueous solutions is observed in the presence of Dawson-derived sandwich type polyoxometalates (POMs) $[M_4(P_2W_{15}O_{56})_2]^{16-}$, $M = Co^{2+}$, Ni^{2+} and Zn^{2+} as photocatalyst and an organic substrate (propan-2-ol) as sacrificial electron donor. The direct photochemical excitation of the Dawson-derived sandwich type polyoxometalates in the presence of propan-2-ol leads to its reduction. That first reduction step induces electron transfer to Ag^+ ions to give Ag^0 metal atoms which then form by aggregation colloidal metal nanoparticles stabilized by POM. In the case of $[Co_4(P_2W_{15}O_{56})_2]^{16-}$, TEM experiments reveal that the Ag_n particles obtained with a slight excess of Ag^+ are almost spherical with size in the range 20 – 50 nm. However, in a large excess of Ag^+, the obtained colloids are more oblate and assembled together to give larger aggregates.

Keywords: dawson; photocatalysis; polyoxometalates

Introduction

Metal recovery is a topic of great interest concerning metal pollution and resource conservation. Up to now, various methods have been established for the recovery of metals, involving chemical, thermal, radiolytic[1] and electrochemical[2] processes. Papaconstantinou and coll. have reported that photocatalytical processes using polyoxometalates (POMs) appeared as an alternating solution.[3–4] POMs are well-defined metal-oxygen (M-O) cluster anion having the ability to exchange several electrons whilst their structure remains intact. Recently, it was also shown that photochemically reduced $[SiW_{12}O_{40}]^{4-}$ or $[PW_{12}O_{40}]^{3-}$ Keggin anions as well as $[P_2Mo_{18}O_{62}]^{6-}$ Dawson anion in the presence of metal cation, such as Ag^+, $AuCl_4^-$, Pd^{2+} and $PtCl_6^{2-}$, lead to the formation of metal nanoparticles capped by the Keggin or Dawson anions. The photochemically reduced POM are produced by illumination in the O-M charge transfer band (near visible and UV region) in the presence of the electron donor. Indeed, the excited POMs are strong oxidants able to abstract electrons from organic compounds, for instance propan-2-ol. POM serve both as photocatalysts, reducing agents and play also a stabilizer role, since the obtained metal colloids are stable against aggregation.[4]

At natural pH, $[SiW_{12}O_{40}]^{4-}$, $[PW_{12}O_{40}]^{3-}$ Keggin anions as well as $[P_2Mo_{18}O_{62}]^{6-}$ Dawson anion exchange one-electron by redox process. It appears interesting to study the relationship between the number of exchanged electrons, the charge and the size of the polyoxometalate and the photocatalysis efficiency for the reduction of metal cations as well as the stabilization of nanoparticles and their sizes. The ability to modify the redox and chemical properties of Dawson-type heteropolyanions by replacing one or many elements, renders them particularly attractive for catalytic and electrocatalytic applications.[5–11]

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Within this context, we have undertaken a study using sandwich tungstophosphate Dawson type polyanions and we report here the photocatalytic reduction of Ag^+ in aqueous solutions in the presence of propan-2-ol using Dawson-derived sandwich type polyoxometalates $[M_4(P_2W_{15}O_{56})_2]^{16-}$ (abbreviated $\{M_4P_4W_{30}\}$) with $M = Co^{2+}$, Ni^{2+} or Zn^{2+} (Scheme 1). As the electrochemical behavior of those Dawson-derived sandwich type polyoxometalates exhibits three successive waves related to four-electron reactions,[12] they offer the possibility to increase the number of exchanged electrons and to study the influence of the metal M on the photocatalytic properties.

Experimental Part

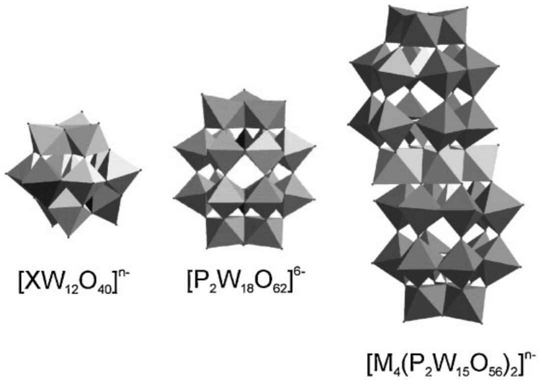
Most common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. Water was obtained by passing through a Milli-RO_4 unit and subsequently through a Millipore Q water purification set.

The Dawson-derived sandwich type polyoxometalates were prepared by published methods from $[P_2W_{18}O_{62}]^{6-}$. Indeed, $[P_2W_{18}O_{62}]^{6-}$ has the ability to be modified under hydrolysis/hydrolytic conditions into lacunar complexes containing one, three or more vacant sites.[13–15] The trivacant $[P_2W_{15}O_{56}]^{12-}$ can react with M^{2+} and yields to well known $[M_4(P_2W_{15}O_{56})_2]^{16-}$, $M = Co^{2+}$, Ni^{2+} or Zn^{2+}[12,16–27] where a sheet of four M^{2+} atoms are sandwiched between two $[P_2W_{15}O_{56}]^{12-}$ subunits (Scheme 1).

Irradiation was performed by a 300 W Xe arc lamp equipped with a water cell filter to absorb the near-IR radiation and a 305 nm cut-off filter in order to avoid direct photolysis of substrates. According to the supplier, the irradiance of the lamp from 320 nm to 790 nm was around 50 $mW.m^{-2}.nm^{-1}$. The samples consisted of 4 mL of aqueous Ag_2SO_4 solutions with propan-2-ol and POM catalyst contained in a spectrophotometer quartz cell of 1 cm path length. Deaerated solutions were obtained by bubbling with Argon (Ar-U, from Air liquide) before illumination. All the aqueous samples were at natural pH and all experiments were carried out at room temperature.

UV-vis absorption spectra were recorded with a single beam Hewlett-Packard HP 8453 diode array spectrophotometer operated at a resolution of 2 nm.

Transmission electronic microscopy (TEM) observations were performed with a JEOL 100 CXII TEM instrument operated at an accelerating voltage at 100 kV. Samples for TEM analysis were prepared



Scheme 1.
Polyhedral representation of the Keggin anion $[XW_{12}O_{40}]^{n-}$($X = Si$ or P), Dawson anion $[P_2W_{18}O_{62}]^{6-}$ and sandwich Dawson structure of $[M_4(P_2W_{15}O_{56})_2]^{16-}$ ($M = Co^{2+}$, Ni^{2+}, or Zn^{2+}).

by solution drops deposited and dried on carbon-coated copper TEM grids.

Results and Discussion

Figure 1A presents the optical absorption spectra of a deaerated aqueous solution containing only 8×10^{-6} mol.L^{-1} $\{Co_4P_4W_{30}\}$ and 0.13 mol.L^{-1} propan-2-ol before and after 32 hours illumination. Under UV light exposure for several hours, while the O-M charge transfer band of the POM below 320 nm decreases slightly, a new band around 570 nm appears and grows leading to a blue coloration of the solution. However, if the solution is put into contact with dioxygen, O_2, by opening the cell to air, the blue color disappears and the initial spectrum of the solution before illumination is recovered. Such evolution is characteristic of photolytic production of reduced POMs in deaerated solution containing POM and propan-2-ol. Similar results are obtained with $\{Ni_4P_4W_{30}\}$ and $\{Zn_4P_4W_{30}\}$ in the same experimental conditions.

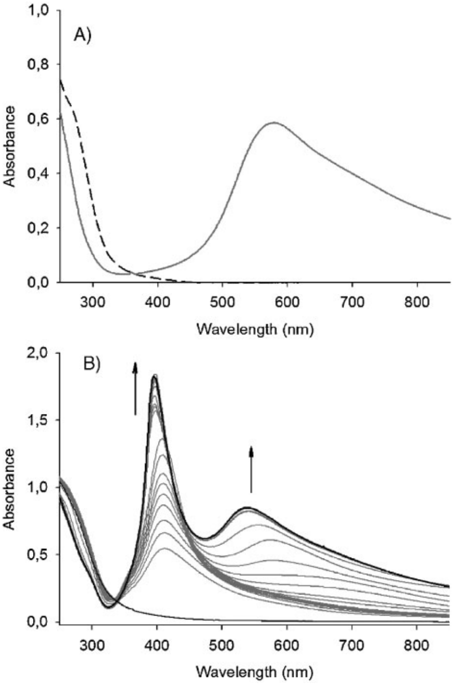


Figure 1.

A) UV-visible absorption spectra of a deaerated aqueous solution at pH 6.5 containing propan-2-ol (0.13 mol.L^{-1}) and $Na_{16}[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]$ (8×10^{-6} mol.L^{-1}) before (- - -) and after 32 hours of illumination (—). B) UV-visible absorption spectra of a deaerated aqueous solution at pH 6.5 containing propan-2-ol (0.13 mol.L^{-1}), $Na_{16}[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]$ (8×10^{-6} mol.L^{-1}) and Ag_2SO_4 (6.4×10^{-5} mol.L^{-1}) as a function of illumination time till 8 hours.

As the first redox couple of the studied Dawson-derived type polyoxometalates $\{M_4P_4W_{30}\}$ ($M = Co^{2+}$, Ni^{2+} or Zn^{2+}) is related to a four-electron reaction process,[12] the mechanism should involve the photochemical oxidation of propan-2-ol by the excited POM and the concomitant formation of the reduced POM($4e^-$) according to reactions 1–2:

$$[M_4(P_2W_{15}O_{56})_2]^{16-} + 2(CH_3)_2CHOH \xrightarrow{hv} [M_4(P_2W_{15}O_{56})_2]^{20-} + 2(CH_3)_2CO + 4H^+ \tag{1}$$

$$[M_4(P_2W_{15}O_{56})_2]^{16-} + 4(CH_3)_2CHOH \xrightarrow{hv} [M_4(P_2W_{15}O_{56})_2]^{20-} + 4(CH_3)_2C^{\bullet}OH + 4H^+ \tag{2}$$

or with an intermediate POM($2e^-$) formation step (reactions 3–4):

$$[M_4(P_2W_{15}O_{56})_2]^{16-} + 2(CH_3)_2CHOH \xrightarrow{hv} [M_4(P_2W_{15}O_{56})_2]^{18-} + 2(CH_3)_2C^{\bullet}OH + 2H^+ \tag{3}$$

$$[M_4(P_2W_{15}O_{56})_2]^{18-} + 2(CH_3)_2C^{\bullet}OH \xrightarrow{hv} [M_4(P_2W_{15}O_{56})_2]^{20-} + 2(CH_3)_2CO + 2H^+ \tag{4}$$

Figure 1B presents the optical absorption spectra of a deaerated aqueous solution containing 8×10^{-6} mol.L^{-1} $\{Co_4P_4W_{30}\}$, 0.13 mol.L^{-1} propan-2-ol and 6.4×10^{-5} mol.L^{-1} Ag_2SO_4 as a function illumination time. In the presence of Ag^+ cations, as the illumination time increases, first the well-know plasmon absorption band of silver clusters around 400 nm is observed indicating that the Ag^+ cations are reduced and that metal atoms coalesce to form clusters stabilized by POMs. Then, the absorption band of the reduced POM appears around 550 nm.

After 200 min, no change of the UV-vis spectra is noticed which indicates the end of the reaction and the total reduction of Ag^+ into Ag_n clusters. As the reduced POM hardly absorbs at 395 nm, position of the plasmon band maximum, we can estimate the molar extinction coefficient per Ag^0 atom at 395 nm to be 14300 $dm^3.mol^{-1}.cm^{-1}$. This value is close to those usually reported for small silver clusters in solution.[28–29]

When opening the cell to air, the absorption band around 550 nm disappears quickly showing the complete oxidation of the reduced POM, while the plasmon band at 395 nm decreases slightly and shift to 402 nm indicating a weak oxidation of the smallest clusters but the presence of stable silver nanoparticles.

The TEM micrographs (Figure 2) confirm the formation of the silver particles upon illumination of deaerated aqueous solution containing propan-2-ol, $\{Co_4P_4W_{30}\}$ and Ag^+. The silver nanoparticles produced are almost spherical with sizes in the range 20 to 50 nm. The obtained particles were stable against aggregation, what may be attributed to the stabilizing role of POM. Indeed, the colloidal solution contains no other potential stabilizing agent but POM. Moreover, the volume of $\{Co_4P_4W_{30}\}$ (with a length of ca 20 Å and the width of ca 10 Å) and its (16-) negative charge could account for the prevention of agglomeration of the metal particles, as for other POM.[30]

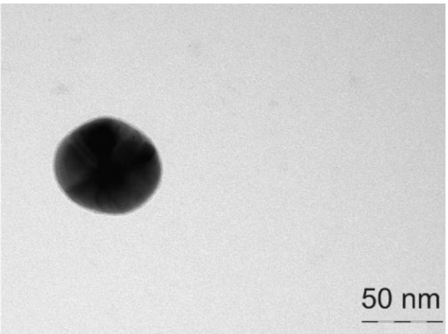


Figure 2.
TEM micrograph of Ag nanoparticles formed upon illumination of deaerated aqueous solution containing $Na_{16}[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]$ (8×10^{-6} mol.L^{-1}), propan-2-ol (0.13 mol.L^{-1}) and Ag_2SO_4 (6.4×10^{-5} mol.L^{-1}).

Figure 3 illustrates the effect of Ag^+ concentration on the formed silver nanoparticles. When silver ions are in large excess (100 equivalents) compared to $\{Co_4P_4W_{30}\}$, illumination of deaerated solution containing propan-2-ol, $\{Co_4P_4W_{30}\}$ and Ag^+ give large nanoparticles with sizes between 20 and 80 nm. The TEM micrographs show that the Ag_n particles obtained in large excess of Ag^+ are more oblate compared to the spherical particles obtained in less concentrated solutions (Figure 2) and are assembled together to give larger agglomerates. A zoom on the TEM images provide a direct evidence of the crystalline structures of the silver particles. Changes of direction of the "lamellae" structures are observed at junctions of silver particles confirming agglomeration. Similar behavior with gold nanorods has already been reported by Gai et al. [31]

In the case of the Dawson-derived sandwich type polyoxometalates $\{Ni_4P_4W_{30}\}$ and $\{Zn_4P_4W_{30}\}$, the spectral evolution under illumination of deaerated aqueous solutions containing 8×10^{-6} mol.L^{-1} POM, 0.13 mol.L^{-1} propan-2-ol and 6.4×10^{-5} mol.L^{-1} Ag_2SO_4 resembles that previously described for $\{Co_4P_4W_{30}\}$ with the same experimental conditions (Figure 1B). However, for $\{Ni_4P_4W_{30}\}$ and $\{Zn_4P_4W_{30}\}$, the absorption plasmon band of the formed silver aggregates peaks appears at 393 nm and is more symmetric compared to that obtained for $\{Co_4P_4W_{30}\}$ suggesting smaller particles with a more homogeneous size distribution. That is corroborated by the fact that those particles are not stable when the cell is opened to air, in contrast to the case of $\{Co_4P_4W_{30}\}$.

Nevertheless, for larger amount of Ag^+ ions (100 equivalents), the produced particles become larger and stable when put in the presence of O_2, but no agglomerate is observed. Indeed, TEM micrographs reveal that, in those concentration conditions, the silver nanoparticles formed using

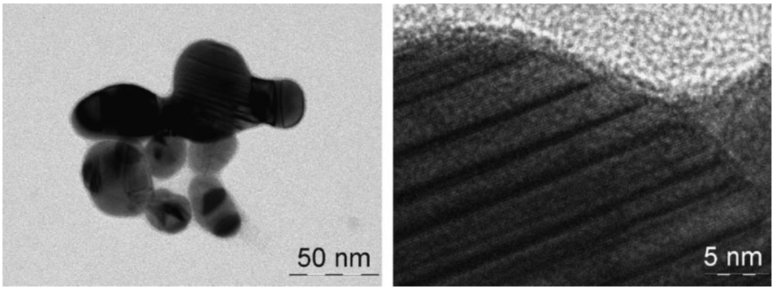


Figure 3.
TEM micrographs of Ag nanoparticles obtained from illumination of deaerated aqueous solution containing $Na_{16}[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]$ (8×10^{-6} mol.L^{-1}) propan-2-ol (0.13 mol.L^{-1}) and Ag_2SO_4 (4×10^{-4} mol.L^{-1}).

$\{Ni_4P_4W_{30}\}$ and $\{Zn_4P_4W_{30}\}$ are much smaller and more spherical compared to those obtained with $\{Co_4P_4W_{30}\}$, as their size does not exceed 30 nm. Those results give evidence that the Dawson-derived sandwich type polyoxometalates $\{M_4P_4W_{30}\}$ ($M = Co^{2+}$, Ni^{2+} and Zn^{2+}) exhibit a photocatalytic activity toward the reduction of Ag^+ ions in the presence of propan-2-ol. However, the thermodynamics of the involved species are not favorable as the redox potentials of the ($[M_4(P_2W_{15}O_{56})_2]^{16-}/[M_4(P_2W_{15}O_{56})_2]^{20-}$) and ($Ag^+/Ag^0$) couples are ~ -0.5 V and -1.8 V *vs.* NHE, respectively. Consequently, we may suggest two explanations for the reduction of Ag^+ ions. On the one hand, we invoke the possible formation of a complex between the Ag^+ cations and the POM anions, leading to a change in the redox potentials.

On the other hand, the reduction process can be initiated by the alcohol radical produced upon the photoreduction of the POM, the mechanism involving a complexation step as proposed in radiolysis experiments[32] according to reactions 5–6.

$$(CH_3)_2C^\bullet OH + Ag^+ \rightarrow [Ag(CH_3)_2C^\bullet O]^+ + H^\bullet \quad (5)$$

$$[Ag(CH_3)_2C^\bullet O]^+ + Ag^+ \rightarrow Ag_2^+ + (CH_3)_2CO + H^+ \quad (6)$$

Association and coalescence reactions of the Ag^+ ions and initial silver clusters (reactions 7–9) lead then to the formation of silver particles.

$$Ag^0 + Ag^+ \rightarrow Ag_2^+ \quad (7)$$

$$2Ag_2^+ \rightarrow Ag_4^{2+} \quad (8)$$

$$Ag_m^{x+} + Ag_p^{y+} + \rightarrow Ag_{(m+p)}^{(x+y)^+} \quad (9)$$

Furthermore, as the redox potential of the silver clusters, $E^0(Agn+/Ag_n)$ increases with the nuclearity n,[33] for clusters of nuclearity superior to 4, the direct reduction of the $Agn+$ clusters by the reduced POM(4-) or the alcohol radical $(CH_3)_2C^\cdot OH$ become thermodynamically favorable.

Conclusion

The photocatalytic reduction of $Ag^I{}_2SO_4$ in deaerated aqueous solutions is observed in the presence of Dawson-derived type polyoxometalates $\{M_4P_4W_{30}\}$ ($M = Co^{2+}$, Ni^{2+} and Zn^{2+}) as photocatalyst and an organic substrate (propan-2-ol) as sacrificial electron donor. The direct photochemical excitation of the POM in the presence of propan-2-ol leads to its reduction. That photoreduction step induces electron transfer to Ag^+ ions to give Ag^0 metal atoms which form Ag_n colloidal metal nanoparticles stabilized by POM.

In the case of $\{Co_4P_4W_{30}\}$, a slight excess of Ag^+ compared to POM leads to almost spherical particles stable against aggregation because of stabilizing role of POM, whereas with large excess of Ag^+, the obtained particles are more oblate and assembled together to give large agglomerates. In contrast, for $\{Ni_4P_4W_{30}\}$ and $\{Zn_4P_4W_{30}\}$, with a slight excess of Ag^+, the particles formed in deaerated aqueous solutions are small and not stable when the cell is open to air, while with a large excess of Ag^+, the particles are larger and stable in air conditions but no agglomerate is observed.

So, the central metal M of the POM seems to have an influence on the size and stability of the formed particles. Experiments with other $\{M_4P_4W_{30}\}$ are in progress to study that effect. Moreover, preliminary results with aerated solutions have showed that photocatalysis can also be effective under air conditions, what is promising for application purposes and is also under investigation.

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