

Facile synthesis of silver nano/micro-ribbons or saws assisted by polyoxomolybdate as mediator agent and vanadium(IV) as reducing agent†

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Original and effective syntheses of crystalline silver wires and saw bundles, using reduced Keggin polyoxomolybdovanadate (POM) as mediator and reducing agent, were performed in acetonitrile at room temperature; several parameters influencing the final silver 1D-structures, with micrometric length and nanometric thickness, were varied: the nature of the POM, silver salts, vanadium(IV) source and the mild conditions.

In the last ten years, nanometre-sized architectures of metals, semiconductors and metallic oxides have received great interest in materials science.¹ One-dimensional (1D) nanostructures such as nanotubes and nanowires have attracted special attention due to their unique physical properties and their potential applications in different nanodevices.² At the frontier of these nanoscale materials, a new family of 1D nanostructures has emerged, namely nanobelts, nanoribbons and nanosaws.³ While such nanostructures have been realized with semiconductors (CdSe, CdS and ZnS),^{4–6} oxides (SnO₂ and Ga₂O₃)^{7,8} and metals (Sn, Ni, Au and Ag),^{9–12} their controlled synthesis remains an actual challenge. Significant efforts are currently being devoted to the development of the 1D silver metal subgroup because of its numerous properties and applications (electronic, photonic, sensing, catalysis and optics).¹³ A tremendous number of papers have recently dealt with the synthesis of silver nanostructures with various well-defined shapes^{14–17} (rods,^{12,18} prisms,¹⁹ cubes²⁰ and wires²¹) while only a few papers have described the formation of Ag-nanoribbons.²² Silver nanowires were generally synthesized using various templates.^{23–26} For example, Zhan *et al.* used a helical organic superstructure for the formation of silver nanohelices.¹³ Parallel to this domain, Keggin polyoxometalate derivatives (POMs) are anionic oxoclusters with a high nucleophilic character and with a large topological and electronic versatility.²⁷ Keggin POMs have the general formula [XM₁₂O₄₀]^{(8–n)-}, where X is a heteroatom such as Si or P and M is W, Mo or V. The metal M is usually in its highest oxidation state (+VI for Mo and W) but mixed Keggin structures (M = Mo/W, Mo/V or W/V) with mixed valences (+VI/+V or +VI/+IV) have been described.²⁴ These metallic

oxoclusters have found a variety of applications in many areas such as catalysis, electro- and photo-chromism, and medicine.²⁸ Such a variety of applications can be explained considering that POMs display a combination of valuable properties. Keggin anion derivatives have been recently used in nanomaterials science^{29–33} playing the role of reducing agent and/or stabilizing and functionalizing agent.^{26–30} The stabilization of metal nanoparticles was achieved through covalent²⁶ or electrostatic interactions.²⁸ In the literature, two main strategies have been described to reduce metallic salts using reduced POMs: in the first strategy, POMs such as [PMo₁₂O₄₀]³⁻ or [SiW₁₂O₄₀]⁴⁻ were activated by photo-reduction processes while in the second strategy, the POM was chemically reduced to yield ZnH₅[PV^{IV}₂Mo₁₀O₄₀] as active species.³³

In our laboratory, we are interested in the development of new catalysts for selective oxidation of alkanes by silver(I) salts of [PV^V₂Mo^{VI}₁₀O₄₀]⁵⁻ in solution.³⁴ We are also interested in the elaboration of multifunctional metallic nanocomposites based on inorganic systems such as polyoxothiometalates.³⁵ In this paper, we describe a mild process for the facile synthesis of crystalline silver ribbons and saws with polyoxomolybdovanadates (POMs) as mediators and reducing agents, in acetonitrile. We also show the influence of various synthesis parameters on the final 1D-Ag structure. Three types of POMs that differ in the location and the number of vanadium centres have been studied: H(VO)[PMo₁₂O₄₀] (denoted *VOPMo*₁₂) containing one vanadyl counter-cation, [N(Bu)₄]₅[PMo₁₁VO₄₀] (denoted *PMo*₁₁*V*) in which the vanadium(IV) centre is part of the Keggin structure, and a mixture of the lacunary Keggin ion Na₃[H₆PMo₉O₃₄] (denoted *PMo*₉) with three equivalents of vanadyl acetylacetonate in order to form *in situ* the vanadium trisubstituted Keggin anion.

The general synthesis procedure comprised mixing silver salts with POMs/vanadium(IV) systems. A precipitate rapidly formed which was removed from the green solution. The filtrate was allowed to stay undisturbed for 2–3 days. During this time, the colour changed from green to orange corresponding to the combined effects of the oxidation of V(IV) to V(V) and the presence of a suspension of bright silver 1D-nano- and micro-structures. Two preliminary experiments were realized in order to identify the roles of both the vanadium(IV) and the POMs. The first synthesis was realized without any vanadium(IV) while keeping constant all the other parameters. In these conditions, no reduction of the silver salts was observed. In the second experiment, vanadium(IV) was introduced as the acetylacetonate salt, the source of Mo being ammonium heptamolybdate; in this experiment the reduction of

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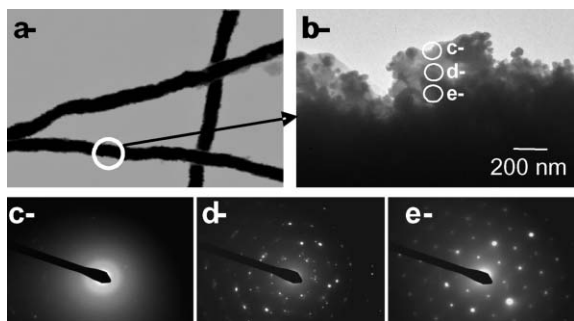


Fig. 1 a- Overview of silver ribbons observed by SEM. b- Selected area observed by TEM. Electron diffraction (SAED) patterns taken from an individual silver ribbon observed in Fig. 1a: c- in the weak contrast zone, d- closer to the surface with apparent nanoparticles and e- in the dark zone.

Ag(I) was observed together with the instantaneous formation of a precipitate, without any evidence of silver nano- or micro-structure in the filtrate even after several days. Both experiments illustrated that vanadium(IV) was indeed the reducing agent but they also demonstrated the major role of the POMs as structuring agents to generate the silver 1D nano- or micro-structures. A simple photochemical process without POM was also ruled out since these blank experiments were performed at ambient conditions without light protection.

In the first system, the Keggin anion $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, with vanadyl counter-cation $[\text{V}^{\text{IV}}\text{O}(\text{H}_2\text{O})_5]^{2+}$, was reacted with six molar equivalents of silver(I) acetate. After reaction and washing (see experimental section $\{\text{VOPMo}_{12}\}\text{-}\{\text{AgOAc}\}$), metallic 1D-microstructures were visible to the naked eye. SEM analysis revealed 1D-microribbons with a width of about $4\ \mu\text{m}$ with an irregular surface covered with a thin skin (Fig. 1). TEM analysis confirmed the irregularity of the surface and the presence of a less dense phase surrounding the ribbons (Fig. 1b). EDX analyses showed the presence of silver (atomic percentage 96%), molybdenum (atomic percentage 3.6%) and traces of vanadium and phosphorus.

In the second system, namely $[\text{N}(\text{Bu})_4][\text{PMo}_{11}\text{V}^{\text{IV}}\text{O}_{40}]$, vanadium(IV) was introduced as part of the POM structure and not as a free counter-cation. TEM analysis revealed the formation of ribbons by coalescence of NPs. Several fibrous structures containing metallic NPs and POMs were observed (Fig. S1).³⁶ While the reducing properties of V(IV) were indeed modified depending on its location, as a counter-cation or as part of the Keggin structure, no noticeable modification of the final structure was observed with VOPMo_{12} and PMo_{11}V . This second system was also used to study the influence of the nature of the silver salt on the final 1D-structures. Ag(I) was introduced either as acetate or as carbonate salt without real modification of 1D-structures.

In the third system, the proportion of vanadyl per POM was increased by preliminary reaction between the trilacunary $[\text{H}_6\text{PMo}_9\text{O}_{34}]^{3-}$ anion³⁷ and three equivalents of $\text{V}^{\text{IV}}\text{O}(\text{acac})_2$. *In situ* formation of a saturated Keggin anion with three vanadium(IV) was expected (Fig. S2) before addition of silver acetate and all other synthesis parameters were kept identical with the previous systems. Only ribbons were obtained, with length and width similar to those observed in the two previous systems. EDX cartography (Ag, Mo, V) showed the presence of POM on the

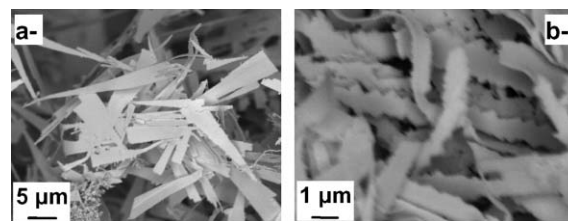


Fig. 2 SEM images of a- nanosaws obtained from $[\text{PMo}_9\text{O}_{34}]^{9-}$ and addition of three equivalents of $\text{V}^{\text{IV}}\text{O}(\text{acac})_2$ (crystallization in the dark) and b- nanoribbons with saws on both sides of the ribbons, obtained with an excess of silver salts.

silver 1D-structure (Fig. S3).³⁶ Crystallization of these systems in the dark modified noticeably their morphologies as in this case only saws were observed (Fig. 2a). With an excess of silver acetate, bundles of ribbons with saws on both sides of the ribbons were obtained (Fig. 2b). If crystallization was realized at $4\ ^\circ\text{C}$, only silver nanoparticles (NPs) were obtained, with a diameter between 3 and 12 nm (Fig. 3). This last experiment showed the crucial role of the temperature on the formation of these 1D-nanostructures.

The 1D-structures have been characterized by powder XRD, EDX and SAED analyses. TEM and SEM images of silver ribbons obtained using VOPMo_{12} are shown in Fig. 1. SAED analyses were performed on the different regions from the surface to the inner part of the ribbon (Fig. 1c-e). No diffraction spot was observed on the thin skin coating the ribbons (weak contrast region, Fig. 1c). According to EDX analyses, it can be postulated that the skin is made of amorphous POM probably as silver(I) salts. In the SAED pattern (Fig. 1d) of the region close to the nanoribbons, characterized by the presence of darker particles, the spots were attributed to the superimposition of crystallographic domains of different silver nanoparticles. Finally, the darkest region is characteristic of well-crystallized silver ribbons (Fig. 1e). It can be suggested that metallic silver microribbons are formed by merging small metallic aggregates covered by slightly soluble silver salts of POM.

The driving force for the formation of metallic nanostructures is the reduction of Ag(I) by the presence of V(IV) in solution, as counter-cation of POM or as part of the Keggin structure. The presence of POMs is a critical parameter to form 1D-structures considering that it was not possible to isolate 1D-structures without POM. It is well-known that Keggin anions generate 1D-, 2D- and 3D-assemblies with silver(I) salts.^{34,38} In our systems, such initial assemblies must be generated in acetonitrile and the presence of the reducing agent V(IV) close to Ag(I) probably induces the mild reduction of Ag(I) to form silver nanoclusters. Such particles

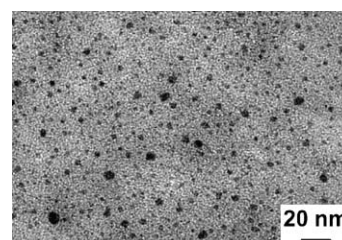
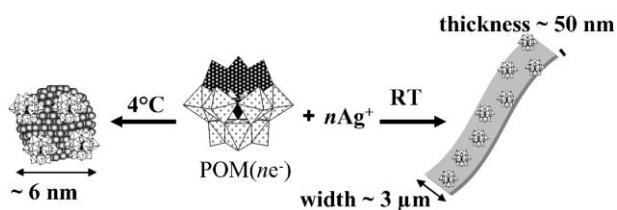


Fig. 3 TEM image of Ag-NPs obtained at $4\ ^\circ\text{C}$ from $[\text{PMo}_9\text{O}_{34}]^{9-}$ and addition of three equivalents of $\text{V}^{\text{IV}}\text{O}(\text{acac})_2$.



Scheme 1 Schematic representation of the formation of Ag-NPs or Ag-1D-structures coated with POM. POM(nc⁻) stands for POM/V(IV) systems.

can be in strong interaction with POMs as already observed by Neumann *et al.*³³ The presence of POMs deposited on the metallic surface confirms its role of mediator agent. In acetonitrile at ambient temperature, preferential adsorption of POMs on some crystalline faces of the silver particles can generate a preferential crystallization direction for their merging in 1D-structures. The aggregation process is temperature dependent since the growth of 1D-structures is quenched at 4 °C (Scheme 1). Several trends can be inferred from our first experiments. At micrometric scale, the variation of the reducing properties of V(IV), depending on its location as part of the structure or as counter-cation, doesn't seem to have a critical influence on the final morphology of the first and second systems. In the same way, it seems that the charge of the POM and the Ag/V ratio are not crucial parameters for the final 1D-structure, while increasing the Ag/POM ratio seems to favour the formation of saws. Further experiments are currently underway in order to study the exact role of the various parameters on the formation kinetics and on the final morphology of these silver structures.

The mild reduction process described in this paper is very interesting as it generates silver 1D-structures with micrometric length and nanometric thickness functionalized by POMs. Such systems provide the opportunity to combine the electronic properties of silver 1D-structures and POMs, especially by using POMs displaying electrochromic or photochromic properties. In addition, nanosaw structures with sharp corners, coated by POMs, are a perfectly adapted active substrate for SERS detection.

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