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Green Chemistry-Type One-Step Synthesis of Silver Nanostructures Based on Mo^{V}–Mo^{VI} Mixed-Valence Polyoxometalates

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Silver nanostructures display an array of unique optical, electrical, magnetic, and catalytic properties that depend on particle size and shape. As a consequence, synthesis and study of these structures remain the focus of strong interest.[1–5] For these purposes, a large variety of conditions and protocols were followed, including the traditional wet-chemical reduction in aqueous or organic media[3,5] with polyols, citrate, sodium borohydride, etc., as reducing agents in the presence of micelles or polymers, the latter acting in several examples both as reducing and capping agents. The main physical parameters include mere heating to temperatures largely exceeding 100 °C, photochemical,[6] or electrochemical[7] technologies. But the challenge remains as concerns the selection of fully "green chemistry-type" conditions with water, one of the best environmentally acceptable solvents, an ecofriendly reducing agent, and a nontoxic capping agent.

Recently, we reported a new synthesis method of metal nanoparticles (NPs) that complies with these criteria.[8,9] For efficient syntheses and stabilization of Pd and Pt NPs, reduced polyoxometalates (POMs) were used both as reducing and capping agents at room temperature in water. POMs are anionic structures constituted of early transition metal elements in their highest oxidation state, with an enormous structural variety combined with exciting properties in several domains.[10–13] UV irradiation of POMs was occasionally used for the synthesis of metal NPs in the presence of a sacrificial organic electron donor.[14–17] Recently, the metallic salt reduction based on V(IV) within POMs[8,18] has been extended to an association of V(IV) with POMs to generate silver ribbons and saws in acetonitrile.[19]

We now report on the one-step synthesis and stabilization of Ag nanostructures with two Mo^{V}–Mo^{VI} mixed-valence POMs in water at room temperature without any catalyst and selective etching agent. Both 0D and 1D nanostructures were observed, showing, for the first time, that POMs can also induce the synthesis of one-dimensional nanostructures in green chemistry conditions. 1D structure is known not to be the most favorable structure on the nanoscale.

The precursor salt was Ag_2SO_4. The two selected POMs were the same as those used previously for Pt and Pd NPs:[9] $(NH_4)_{10}[(Mo^{V})_4(Mo^{VI})_2O_{14}(O_3PCH_2PO_3)_2(HO_3PCH_2PO_3)_2]\cdot 15H_2O$ (**1**)[20] and $H_7[\beta\text{-}P(Mo^{V})_4(Mo^{VI})_8O_{40}]$ (**2**).[21] In a typical experiment, a mixture containing 1mM Ag_2SO_4 and 0.5 mM POM was assembled in water. The excess parameter is defined as γ = [metallic salt]/[POM].

Observations are first described with **1**. Several minutes after the mixing of the two reagents, the solution color turned from very light yellow to deep yellow, and even to brown for higher initial concentrations of the silver salt. The surface plasmon resonance (SPR) band appears around 400 nm, indicative of the formation of silver nanoparticles. The SPR peak location depends on the excess parameter γ as shown in Figure 1a. It is not affected by the initial concentrations of metallic salt and POM, provided γ is kept constant. Increasing γ induces a blue shift of the SPR. These observations indicate an influence for γ in the synthesis of Ag nanoparticles. Transmission electron microscopy (TEM) observations were performed with a JEOL 100CXII transmission electron microscope at an accelerating voltage of 100 kV. The sample drops were deposited and dried on a carbon-coated copper grid. A representative image is shown

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(1) Chen, S.; Carroll, D.L. *Nano. Lett.* **2002**, *2*, 1003–1007.
(2) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, M.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353–389.
(3) Tao, A.; Sinsermsuksakul, P.; Yang, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 4597–4601.
(4) Wiley, B. J.; Chen, Y.; McLellan, J.; Xiong, Y.; Li, Z.-Y.; Ginger, D.; Xia, Y. *Nano. Lett.* **2007**, *7*, 1032–1036.
(5) Wiley, B.; Sun, Y.; Mayers, B.; Xia, Y. *Chem.—Eur. J.* **2005**, *11*, 454–463.
(6) Maillard, M.; Huang, P.; Brus, L. *Nano Lett.* **2003**, *3*, 1611–1615.
(7) Cui, S.; Liu, Y.; Yang, Z.; Wie, X. *Mater. Des.* **2007**, *28*, 722–725.
(8) Keita, B.; Mbomekalle, I. M.; Nadjo, L.; Haut, C. *Electrochem. Commun.* **2004**, *6*, 978–983.
(9) Keita, B.; Zhang, G.; Dolbecq, A.; Mialane, P.; Sécheresse, F.; Miserque, F.; Nadjo, L. *J. Phys. Chem. C* **2007**, *111*, 8145–8148.
(10) Hill, C. L. (Guest Ed.). *Chem. Rev.* **1998**, *98*, 1–389.
(11) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.
(12) Hill, C. L. Polyoxometalates: Reactivity. In *Comprehensive Coordination Chemistry II: Transition Metal Groups 3–6*; Wedd, A. G., Ed.; Elsevier Science: New York, 2004; Vol. 4, Chapter 4.11, pp 679–759.
(13) Keita, B.; Nadjo, L. *Electrochemistry of Polyoxometalates, Encyclopedia of Electrochemistry*; Bard, A. J., Stratmann, M., Eds.; Wiley-VCH: Weinheim, Germany, 2006; Vol. 7, pp 607–700.
(14) Troupis, A.; Hiskia, A.; Papaconstantinou, E. *Angew. Chem., Int. Ed.* **2002**, *41*, 1911–1914.
(15) Mandal, S.; Selvakannan, P. R.; Pasricha, R.; Sastry, M. *J. Am. Chem. Soc.* **2003**, *125*, 8440–8441.
(16) Yang, L.; Shen, Y.; Xie, A.; Zhang, B. *J. Phys. Chem. C* **2007**, *111*, 5300–5308.
(17) Mandal, S.; Das, A.; Srivastava, R.; Sastry, M. *Langmuir* **2005**, *21*, 2408–2413.
(18) Maayan, G.; Neumann, R. *Chem. Commun.* **2005**, 4595–4597.
(19) Marchal-Roch, C.; Mayer, C. R.; Michel, A.; Dumas, E.; Liu, F.-X.; Sécheresse, F. *Chem. Commun.* **2007**, DOI 10.1039/b704774f.
(20) Dolbecq, A.; Lisnard, L.; Mialane, P.; Marrot, J.; Bénard, M.; Rohmer, M. M.; Sécheresse, F. *Inorg. Chem.* **2006**, *45*, 5898–5910.
(21) Ishikawa, E.; Yamase, T. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 641–649.

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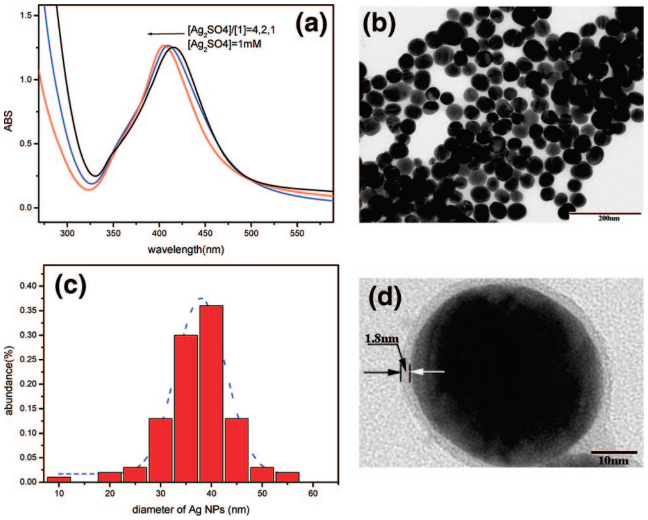

Figure 1. (a) SPR spectra of Ag nanoparticles obtained from different molar ratios, (b) a representative TEM image of Ag nanoparticles obtained from the mixture with $\gamma = 4$, (c) size histogram of Ag nanoparticles of about 200 NPs counted from TEM image showing the distribution of Ag NPs, and (d) a magnified Ag nanoparticle.

in Figure 1b, obtained from the mixture with $\gamma = 4$. The nanoparticles are spherically shaped and quasi-monodisperse (standard deviation < 10%) with a diameter around 38 ± 5 nm, in agreement with the histogram of about 200 NPs counted from the TEM image (Figure 1c). We found that the size of the NPs can simply be tuned by the molar ratio between the salt and **1**. Increasing γ, the average diameter of Ag NPs decreased to about 30 nm (picture not shown), in agreement with the blue shift of SPR peaks. The obtained colloidal solution is very stable and does not show any precipitate after more than half a year without adding any organic stabilizer, an indication that the POM serves both as a reductant and efficient stabilizer. TEM observations suggest an Ag@POM core–shell structure for the NPs. With a higher magnification than in Figure 1b of the same sample, a thin layer with ~2 nm thickness is clearly observed in Figure 1d. To the best of our knowledge, this is the first example of observation of such kind of Ag@POM core–shell structure. Synthesis of Ag^0 NPs by **1** is corroborated by XPS analysis (see the Supporting Information, Figure 1 SI).

For experiments with compound **2**, it is worth reminding that a target in great demand in NPs research is the fabrication of 1D nanostructures, both for fundamental study and applications.[2,22] Ingredients to achieve this goal in wet chemical environment include a weak reductant, a high temperature, and an appropriate capping agent such as polyvinylpyrrolidone (PVP) to control the nanowire growth. Previous NP synthesis with **1** and **2**[9] has indicated that **2** is a softer reductant than **1**, a feature from which different behaviors in Ag nanostructures synthesis can be expected.

With compound **2**, the reduction process is relatively slow and the observed structures strongly depend on the aging time of the mixture. In less than 4 h of aging, irregularly shaped Ag NPs are observed, some of them clearly showing a pentagonal symmetry (see the Supporting Information, Figure 2 SI). After 4 h, short Ag nanowires were observed combined with many irregular Ag NPs (see the Supporting Information, Figure 3 SI). TEM analysis of a sample taken directly from the reaction mixture after 6 h of aging shows (Figure 2a) that more than 95% of the image represents long nanowires, with an average diameter of ~40 nm and a length of several tens of micrometers. The aspect ratio of the nanowires ranges from 300 to more than 1000. A large scale image of these nanowires with their length exceeding largely 100 μm is shown in the Supporting Information, Figure 4 SI. Figure 2b shows a magnified picture of the nanowires, in which a core–shell structure of Ag nanowires is clearly suggested as also admitted in the case of synthesis in the presence of a large concentration of PVP.[5] The initial shell thickness of about 4 nm can be significantly decreased by thoroughly washing the sample with water (more than 5 times). Following this washing, the shell thickness decreases to only about 1 nm, as shown in the Supporting Information, Figure 5 SI, just matching the molecular dimension of **2.**[21] Further washing could not destroy the shell, indicating a very strong interaction between **2** and Ag nanowires. It can be concluded that the POM might form a stable monolayer on the surface of the nanowires. The electronic diffraction (ED) of the nanowires, shown in the inset of Figure 2b, demonstrates their high crystallinity. From the ED analysis, the reflection assignments agree well with the previously reported results for nanowires.[2,22] Observation of nanocrystals with pentagonal symmetry suggests[22] that nanowires grow along the ⟨111⟩ direction (see the Supporting Information, Figure 2 SI). About 20% of nanowires show a highly twisted helical structure (Figure 2b). Figure 2c gives a magnified image of a twisted helical nanowire. Work is in progress to explain the existence of these few "twisted" nanowires. The X-ray diffraction pattern (Figure 2d) recorded from a dry powder of Ag nanowires fixed on adhesive double sided tape clearly shows the (111), (200), and (220) Bragg reflections of face-centered cubic (fcc) of silver with intensity ratios in good agreement with a preferential growing of nanowires along the ⟨111⟩ direction.[23] In previous reports on the wet chemical method,[20,21] PVP, used as the shape controller, is known to

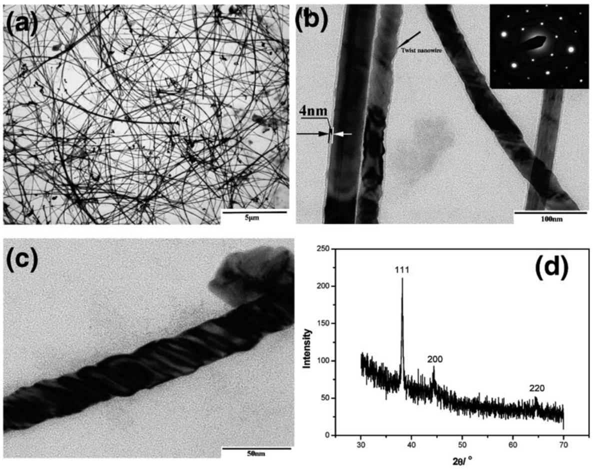

Figure 2. (a) TEM image of as-obtained Ag nanowires directly taken from the reaction mixture, (b) magnified nanowires, (c) magnified twisted helical nanowire, and (d) XRD pattern of Ag nanowires fixed on an adhesive double-sided tape.

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(22) Chen, J.; Wiley, B. J.; Xia, Y. *Langmuir* **2007**, *23*, 4120–4129.

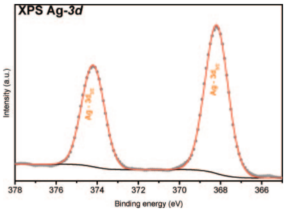
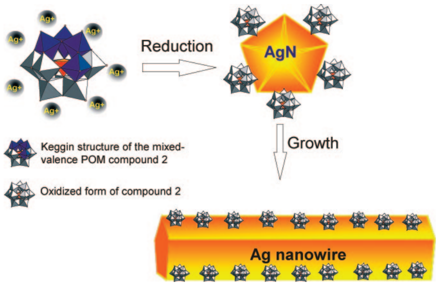


Figure 3. Deconvolution of the silver core 3d level XPS spectrum.

Scheme 1. Schematic Picture of the Process of the Formation of Ag Nanowires



strongly interact with (100) facets of Ag nanoparticles, thus favoring their growing into nanowires along the ⟨111⟩ direction. In complete analogy with these observations, the results obtained in the present work suggest that **2** interacts in the same way with Ag nanoparticles. A schematic picture of the formation of the Ag nanowires is proposed in Scheme 1.

XPS analysis corroborates the preceding results. Identical XPS analysis results were obtained for Ag nanoparticles and Ag nanowires and are illustrated here for nanowires. In Figure 3, the $3d_{3/2}$ and $3d_{5/2}$ contributions of Ag are cleanly observed. With the charge effect corrected by fixing the photoelectric peak 1s of carbon at 285.0 eV, the $3d_{5/2}$ level is located at 368.2 ± 0.3 eV and the $3d_{3/2}$ level at 374.2 ± 0.3 eV. These values indicate unambiguously that silver is present only in the metallic form.[24] The Ag $3d_{5/2}$ levels for AgO and Ag_2O are expected around 367.2 and 367.7 eV, respectively, and are not observed, a feature that rules out any important oxidation of silver nanoparticles.

For both nanoparticles and nanowires, the presence of molybdenum was detected by XPS, despite the thorough washing of the samples. This observation supports the hypothesis that the polyoxometalate serves both as a reductant and as a capping layer, in agreement with the propensity, particularly of Mo-based POMs, to self-assemble on metal and other solid surfaces.[9,25] The ratio between the attached Mo-based POM to NP might vary both with the metal and the starting POM. In the case of the present Ag nanowires, a semi-quantitative analysis of the sample, with the respective surface areas of the peaks corrected by the appropriate Scofield sensitivity factors, gives an atomic percentage of 21.7% for Mo and 78.3% for Ag. It is worth noting that Mo(VI) and a smaller amount of Mo(V) are simultaneously detected in the shell.

In summary, we have reported the one-step, room-temperature synthesis in water of well-shaped Ag (0D and 1D) nanostructures without any catalyst and selective etching agent. Both the shape and the size of nanoparticles can be tuned by using different POMs and different molar ratios. The POMs serve as reductant, stabilizer, and shape controller. Ag@POM core–shell structure could be observed. Future work will systematically explore all these features. Such Ag–POM composite nanostructures are expected to have favorable photo-, electronic, analytical, and catalytic properties.

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Supporting Information Available: XPS experimental conditions, XPS of silver nanopariticles, complementary TEM images of the nanoparticles and nanowires (PDF). This materials is available free of charge via the Internet at http://pubs.acs.org.

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(23) Gou, L.; Chipara, M.; Zaleski, J. M. *Chem. Mater.* **2007**, *19*, 1755–1760.

(24) *Handbook of X-ray Photoelectron Spectroscopy*; Chastain, J., King, R. C., Eds.; Physical Electronics: Eden Prairie, MN, 1995.

(25) Klemperer, W. G.; Wall, C. G. *Chem. Rev.* **1998**, *98*, 297–306.