

Low-Temperature Synthesis of Transition Metal Nanoparticles from Metal Complexes and Organopolysilane Oligomers

Yu-Hsu Chang, Hsiao-Wan Wang, Ching-Wen Chiu, Der-Sun Cheng,
Ming-Yu Yen, and Hsin-Tien Chiu*

Department of Applied Chemistry, National Chiao Tung University,
Hsinchu, Taiwan, 30050, Republic of China

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Mo, W, and Cu nanoparticles (5–50 nm) are synthesized from reactions employing a metal complex, such as MoO_2Cl_2 (DME), MoCl_5 , WCl_6 , $(\text{CuO}^t\text{Bu})_4$, or CuCl_2 , and a organopolysilane oligomer $\text{Si}(\text{SiMe}_3)_4$ or $(\text{SiMe}_2)_6$ either in a hexane solution (343 K) or in a sealed tube (473–673 K). Oxo- and chlorophilicities of the silyl groups provide for an energetically favored reaction route to reduce the metal complexes. The reaction byproducts are removed easily either by evaporation or dissolution into hydrocarbon solvents. It is proposed that the homogeneous mixing of the reactants in vapor and solution phases allows the association and growth of molecules into small clusters, then into nanosized metal particles.

Introduction

Nanosized materials have attracted much technological and scientific attention due to their interesting size-dependent chemical and physical properties.^{1,2} Metal-based nanomaterials have been studied extensively because of their wide applications in catalysis, synthesis, electronics, magnetism, and optics.^{3–7} Various physical and chemical processes have been applied to synthesize nanosized particles.^{1,2} Examples of gas-phase processes include evaporation of metals,^{6,8,9} CVD (chemical vapor deposition),^{7,10} and reduction by alkali metals in gas phase.¹¹ In solution phase,^{12–25} many late transition

metal nanoparticles, due to their positive standard potentials, can be reduced by reacting mild reagents, such as sodium citrate, with metal complexes.^{12,13} Nanoparticles have reactive high surface areas and require proper stabilization and protection, usually by a layer of inert molecules bonding strongly to the surface atoms. For example, metallic copper nanoparticles can be formed in the cores of reverse micelles.^{26,27} On the other hand, syntheses of nanoparticles of early transition metals, due to their negative standard potentials, require strong reagents, such as sodium metal,²⁵ NaBET_3H ,^{15,16} or electrides^{5,19} to reduce the metal complexes. The early transition metals are more sensitive to oxidation. Preparation, separation and characterization of them in the nanometer dimension are usually more difficult. Here, we wish to report a new route to synthesize nanoparticles of transition metals, demonstrated by Mo, W, and Cu, under relatively mild conditions. The reaction employs air-stable organopolysilane oligomers, tetrakis(trimethylsilyl)silane, $\text{Si}(\text{SiMe}_3)_4$, and dodecamethylcyclohexasilane, $(\text{SiMe}_2)_6$ to reduce metal complexes of Mo, W, and Cu either in a hexane solution or in a solvent-free environment. The strategy is derived from an industrial W thin film deposition chemistry, the reduction of WF_6 by SiH_4 ,²⁸ which is a highly pyrophoric compound. The H atom and the SiMe_3 group are similar in many ways. Their

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Table 1. Summary of the Reactions between Metal Complexes and Organosilanes

metal complex	organosilane	reaction conditions ^a	reaction temp (K)	reaction time (h)	annealing temp (K)	annealing time (h)	metal product	particle size by TEM (nm)	crystal size by XRD ^e (nm)	yield (%)
MoO ₂ Cl ₂ (DME) ^b	(SiMe ₂) ₆	sealed tube	473	2	1273	6	Mo	20–50	20	75
MoCl ₅	Si(SiMe ₃) ₄	hexane solution	353	72	873	12	Mo	50		90
WCl ₆	Si(SiMe ₃) ₄	sealed tube	573	5 ^c	1273	6	W	15–50	30	70
WCl ₆	(SiMe ₂) ₆	hexane solution	353	72	1273	12	W	20–50	7	20
(CuO ^t Bu) ₄	Si(SiMe ₃) ₄	pyridine/ hexane solution	343	48	873	1	Cu	5–20 ^d	5	30
CuCl ₂	Si(SiMe ₃) ₄	sealed tube	573	2	1273	523	Cu		20	30

^a Sealed tubes are under low pressure. ^b DME, 1,2-dimethoxyethane. ^c In minutes. ^d Before annealing. ^e After annealing.

electronegativities are close and they are closely related according to the isolobal analogy.²⁹ In many reactions, HX and Me₃SiX (X: halogens) compounds perform equally well in preparing halogenated compounds. Thus, the SiMe₃ group can be viewed as a “pseudohydrogen” and consequently, Si(SiMe₃)₄ as a “much-safer SiH₄”. By analogy, (SiMe₂)₆, a known source of :SiMe₂, can be regarded as a “much-safer :SiH₂ hexamer”. CVD of W using silylene as the reductant is also known.³⁰

Experimental Section

General Procedures. All chemicals and solvents were manipulated under dry and oxygen-free environments. MoCl₅ (99.6%), WCl₆ (99.9%), and CuCl₂ (98%) were purchased from Strem and used without further purification. MoO₂Cl₂(DME) (DME: 1,2-dimethoxyethane), (CuO^tBu)₄, Si(SiMe₃)₄, and (SiMe₂)₆ were synthesized using published procedures.^{21,31–33} As summarized in Table 1, excess amount of the organosilanes were allowed to react with the transition metal complexes either directly in a Pyrex tube sealed under vacuum³⁴ at 473–673 K or in a refluxing hexane solution. Syntheses of Mo and Cu powders in a sealed Pyrex tube and in a solution, respectively, are given below as the examples. The byproducts were removed under vacuum or by dissolving in hexane and separated apart from the metal nanoparticles by filtration.

The as-prepared samples were annealed at higher temperatures to increase their air stability and crystallinity.

Sealed-Tube Synthesis of Mo. MoO₂Cl₂(DME) (0.20 g, 0.69 mmol) was mixed and pulverized with (SiMe₂)₆ (0.96 g, 2.8 mmol) in a Pyrex tube, with enough space allowing the reactants to vaporize. The tube was sealed under vacuum and heated to 473 K for 2 h. After cooled to room temperature, formation of a black powder was observed. The black solid, spread over the inner surface of the container, was collected and washed by *n*-hexane to remove byproducts. The isolated yield was 0.050 g (75% yield based on Mo).

Solution Synthesis of Cu. [Cu(O^tBu)₄] (1.0 g, 2.1 mmol), Si(SiMe₃)₄ (2.4 g, 7.5 mmol), and excess of pyridine (10 mL, 120 mmol) were allowed to react in hexane (50 mL) at 343 K

for 48 h. Dark brown powders were formed and isolated. After they were washed by hexane (10 mL) three times, the powders were annealed at 473 K under vacuum for 1 h. 0.16 g of Cu was isolated (65% yield based on Cu).

Instrumentation. XRD (X-ray diffraction) studies were carried out using a MAC MXP-3 diffractometer with Cu K α radiation. TEM (transmission electron microscopy) and ED (electron diffraction) data collection were accomplished on a JEOL JEM-2000FX and a JEOL JEM-2010 operating at 200 keV. The XPS (X-ray photoelectron spectroscopy) measurements were carried out using a Perkin-Elmer PHI-1600 spectrometer with Mg K α (1253.6 eV) radiation. The sample powders were pressed on an indium foil and the In 3d_{5/2} electron (443.8 eV) was used as the reference. The data were recorded after the samples were sputtered by Ar⁺ ions (5 kV, 25 mA). The volatile products were collected and analyzed by a Varian Unity-300 NMR (nuclear magnetic resonance) spectrometer and a Vacuum Generator Trio-2000 GC-MS (gas chromatography–mass spectrometry) instrument.

Results and Discussion

As summarized in Table 1, excess amount of organosilanes were allowed to react with transition metal complexes of Mo, W, and Cu directly in a tube sealed under vacuum at 473–673 K or in a refluxing hexane solution. The byproducts were removed by sublimation. Also, they were separated from the solids by dissolving into organic solvents and removed by filtration. The as-prepared samples might be annealed at higher temperatures to increase their air stability and crystallinity. Volatile products were collected and identified by using NMR and GC-MS. Several examples are described below.

From a mixture of MoO₂Cl₂(DME) and (SiMe₂)₆, heated at 473–673 K in a sealed tube under low pressure for 2–3 h, the black powders were synthesized and isolated. A representative TEM image, shown in Figure 1a, demonstrates that the particles prepared at 473 K are about 20–40 nm. The ED pattern did not show clear reflections, suggesting an amorphous nature. The TEM and ED images (Figure 1b) indicate that an annealed particle (1273 K) is less than 50 nm and cubic with an estimated lattice parameter $a = 0.32$ nm. The

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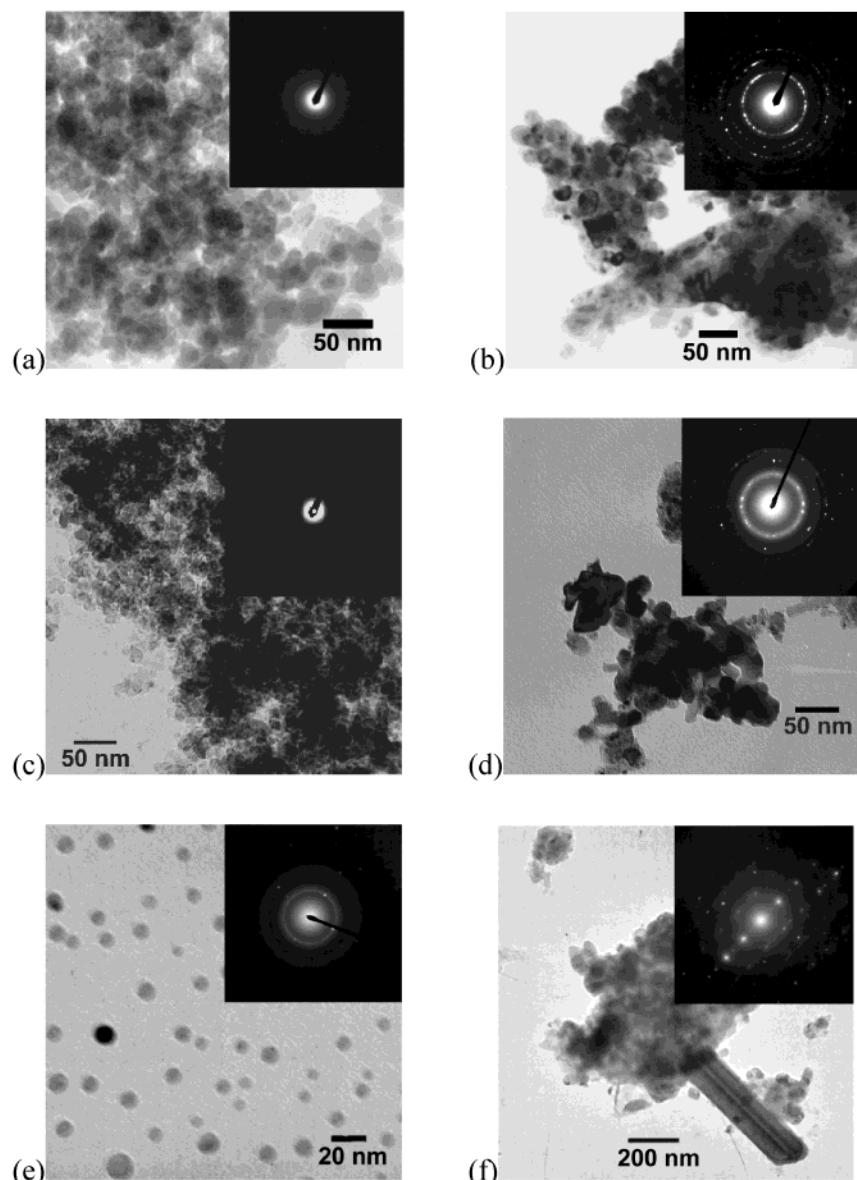


Figure 1. TEM and ED images of (a) Mo nanoparticles prepared at 473 K and (b) annealed at 1273 K. (c) W nanoparticles prepared at 573 K and (d) annealed at 873 K. (e) Cu nanoparticles prepared at 343 K and (f) annealed at 523 K.

value is close to that of Mo, $a = 0.31472$ nm.³⁵ The XRD pattern (Figure 2a) of the annealed product showed reflections at $2\theta = 40.5$, 58.6, and 73.7 degrees, corresponding to the Mo (110), (200), and (211) reflections, respectively.³⁵ For the as-prepared sample (473 K), the XPS showed that the surface contained Mo (35%), Cl (8%), Si (14%), O (22%), and C (22%) atoms. In Figure 3a, high-resolution signals of Mo 3d_{3/2} and Mo 3d_{5/2} electrons are observed at 231.2 and 228.0 eV, respectively, close to the values of the Mo metal.³⁶ Since the XPS is a surface study technique, the observations suggest that the as-prepared powder contains nanosized amorphous particles, each with a Mo metal core and a layer of surface atoms of Cl, Si, O, and C. These elements may be part of the residual ligands on the

metal surface. The possible surface fragments include $-\text{OSiMe}_3$, $-\text{OSiMe}_2\text{O}-$, polymeric organosilicon species, and $-\text{Cl}$. Although the nanoparticles were synthesized and purified under an oxygen-free environment, they were exposed to air before being inserted into the XPS instrument. The step may be responsible for the oxidation of the surface also. The major byproducts were identified to be DME, Me_3SiCl , $\text{O}(\text{SiMe}_3)_2$, and $(\text{Me}_2\text{SiO})_3$. Other volatile byproducts, such as linear permethylsiloxanes and silanols, were also detected in low quantities.

A TEM image of W nanoparticles, produced from a reaction employing WCl_6 and $\text{Si}(\text{SiMe}_3)_4$ in a sealed tube at 573 K for 5 min, is shown in Figure 1c. The particles are amorphous, as suggested by ED, and less than 30 nm. The XPS survey showed the presence of W (35%), Cl (7%), Si (5%), O (48%), and C (5%) atoms on the surface. The high-resolution XPS signals (Figure 3b) of W 4f_{5/2} and W 4f_{7/2} electrons were observed at 33.7 and 31.6 eV, respectively, for the as-prepared sample. The

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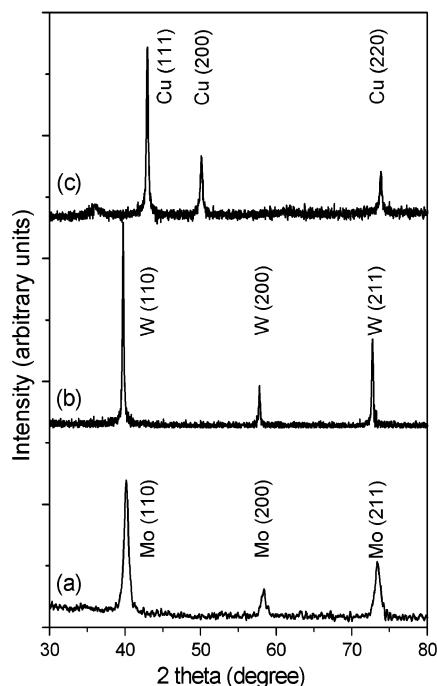


Figure 2. XRD patterns of (a) Mo nanoparticles annealed at 1273 K, (b) W nanoparticles annealed at 1273 K, and (c) Cu nanoparticles annealed at 523 K.

values are close to those of W metal.³⁶ The XPS data suggest that the as-prepared powder contains W particles with oxidized shells. While the source of the surface oxygen atoms in the Mo sample mentioned above may come from the siloxo groups formed by the silylation of the oxo ligands, the surface oxygen atoms in this case have a different origin. The W precursor, WCl_6 , without oxo ligands, may form W particles with extensive surface chloride ligands. Then, the surface was oxidized upon exposed to the air before the sample was transferred into the instrument. After being annealed at 873 K, the sample shows a TEM image in Figure 1d. The lattice parameter $a = 0.31$ nm was estimated from the ED pattern. The value is close to that of W, $a = 0.3164$ nm.³⁷ The product was annealed at 1273 K and showed XRD signals (Figure 2b) corresponding to the reflections of W.³⁷ The major byproduct was Me_3SiCl . Some Me_2SiCl_2 and SiCl_4 were also detected, indicating that a methyl-chloro exchange process was in operation among the silyl groups.

Nanoparticles of Cu were isolated by reacting $(\text{CuO}^t\text{Bu})_4$ with $\text{Si}(\text{SiMe}_3)_4$ in hexane in the presence of excess pyridine at 343 K for 48 h. The TEM image in Figure 1e shows that the size is 5–20 nm. The ED indicates a face-centered-cubic (fcc) ring pattern with $a = 0.37$ nm, close to the lattice parameter of Cu, 0.3615 nm.³⁸ After annealed at 523 K for 1 h, the spherical particle size enlarged, as shown in Figure 1f, probably through a melting–recrystallization process. The lowering of melting point of nanosized metal particles is well-known.¹ Formation of trace amount of large rod-shaped Cu crystals was also observed. In Figure 1f, a 120 nm by

500 nm Cu rod is shown. The origin of this phenomenon is not clear. There are many reports about producing metal wires/rods under the assistance of surfactants.^{39,40} We speculate that some of the reaction byproducts may play functions similar to the surfactants in the reported cases. For samples annealed at 523 K, the XRD pattern in Figure 2c showed 2 θ of Cu (111), (200), and (220) reflections at 43.3, 50.4, and 74.1°, respectively.³⁸ The XPS survey of the as-prepared nanoparticles indicated that Cu was the major component (78%) on the surface. In addition, traces amount of Si (5%), C (5%), and O (12%) were observed. Based on the elemental composition, the heteroatom surface layer appears to be thinner than the layers on the Mo and the W nanoparticles. Being a late transition metal, Cu has a positive standard potential and is more difficult to be oxidized. The high-resolution spectrum (Figure 3c) shows signals at 932.6 and 952.4 eV, corresponding to the binding energies of metallic Cu 2p_{3/2} and Cu 2p_{1/2} electrons, respectively.³⁶ The presence of pyridine in the reaction is important. Without it, the reduction of $(\text{CuO}^t\text{Bu})_4$ did not take place at 343 K. Pyridine probably assisted the dissociation of $(\text{CuO}^t\text{Bu})_4$. This would generate more space around the Cu–O bond, allowing the silane molecules to react. An example of a related dimeric compound, $(^t\text{BuOCuPPPh}_3)_2$, is known.³¹ Analyses of the reaction byproducts by GC-Mass and NMR revealed the presence of $\text{Me}_3\text{SiO}^t\text{Bu}$ as the major byproduct. Traces of other volatiles, such as $\text{Me}_2\text{C}=\text{CH}_2$, $^t\text{BuOH}$, $(\text{Me}_3\text{Si})_2\text{O}$, and $(\text{Me}_2\text{SiO})_4$ were detected also. The observation suggests that the reaction pathways were complex. The activation of the alkoxide ligand and the redistribution of the methyl groups among the silyl ligands were probably in operation.

Based on the analyses of the byproducts described above, it is suggested that the organosilyl groups, such as $-\text{SiMe}_3$ and $-\text{SiMe}_2-$, actively assisted the removal of the chloro, alkoxy and oxo ligands from the metal complexes. This is due to the strong oxo- and chlorophilicities of the Si center. Removal of the ligands also proceeded with the reduction of the metal centers, generating a strong tendency to form small polynuclear cluster compounds with M–M bonds.⁴¹ When the ligands were further removed, the clusters were reduced to their metallic state and associated into nanoparticles. Residual ligands on the surface of the nanoparticles probably formed a thin protective layer so that the composition and the bonding of the metal inside were stabilized. Otherwise, the surface was oxidized after being exposed to the air.

Conclusions

In this study, we employed $\text{Si}(\text{SiMe}_3)_4$ and $(\text{SiMe}_2)_6$ to reduce $\text{MoO}_2\text{Cl}_2(\text{DME})$, MoCl_5 , WCl_6 , $(\text{CuO}^t\text{Bu})_4$, and CuCl_2 , into nanoparticles of Mo, W, and Cu, respectively, at low temperatures. The reactions, both carried

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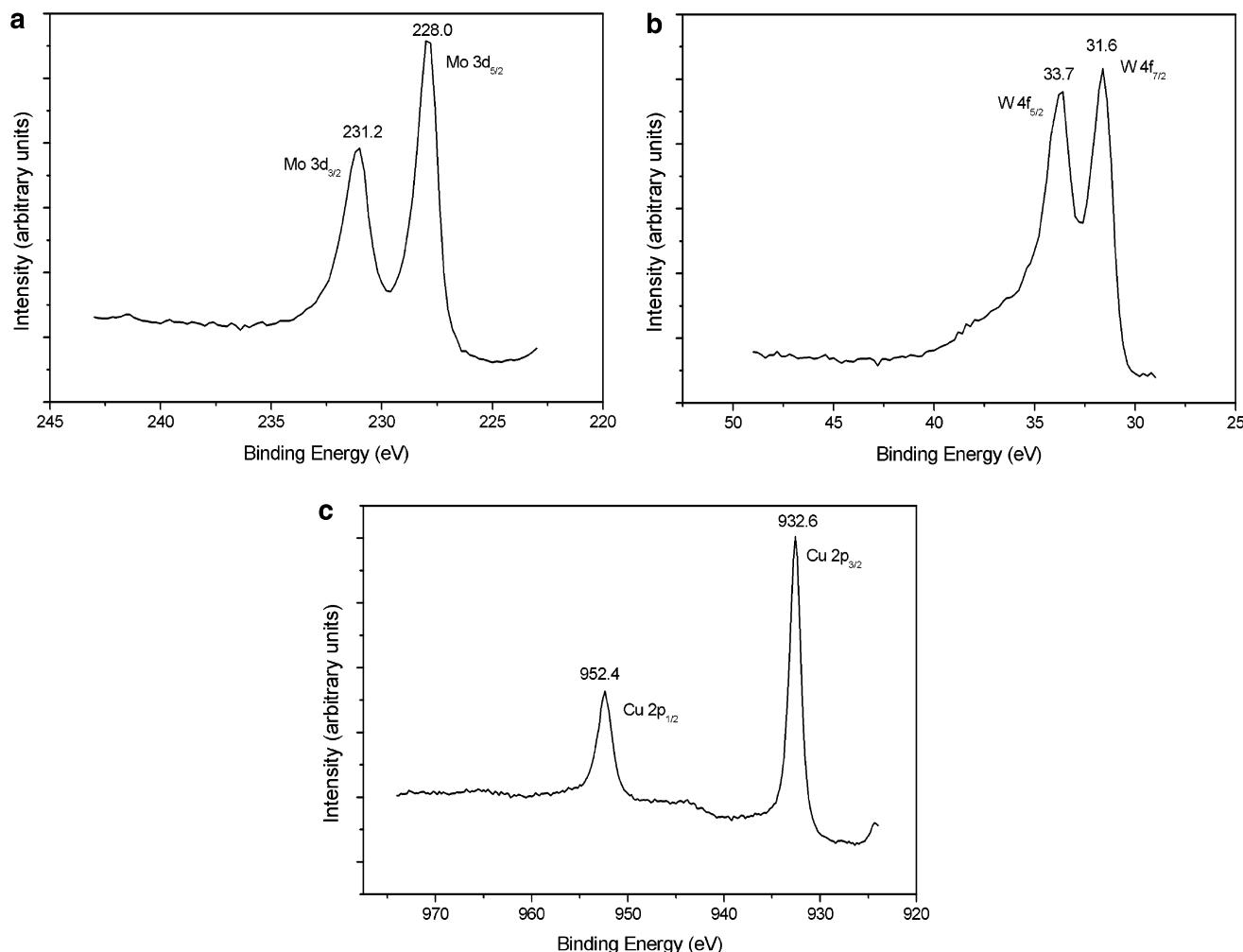


Figure 3. High-resolution XPS signals of (a) Mo 3d_{5/2} and Mo 3d_{3/2} electrons of nanoparticles prepared at 473 K, (b) W 4f_{5/2} and W 4f_{7/2} electrons of nanoparticles prepared at 573 K, and (c) Cu 2p_{3/2} and Cu 2p_{1/2} electrons of nanoparticles prepared at 343 K.

out in the solution and the low-pressure sealed tube, allow homogeneous mixing of the reactants at the molecular level. Moreover, the byproducts are easily separated from the nanoparticles by dissolving into organic solvents or by sublimation. We expect that by employing this new molecular route, many other transition metal nanoparticles can be synthesized successfully.

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Supporting Information Available: XPS, XRD, and TEM data of nanoparticles of Mo, W and Cu (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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