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It should not be forgotten that single shell nanotube samples contain tubes of not only different diameters but also different electronic properties. In any case, both semiconducting and metallic nanotubes will have high surface energies and, therefore, even if different their wetting properties will probably fall within the intervals reported here for γ_C and γ_{max}. When considering the capillarity of single shell tubes with very small inner diameter (< 1 nm), the fact that the inner and outer surfaces may have different energies owing to the asymmetry of the electronic densities[22] should be taken into account. To gain proper insight into such issues, it will be necessary to have samples with just one type of well-defined single shell nanotube, which are currently not available.

Experimental

Raw nanotubes were sonicated for 1 h in carbon disulfide (25 mL per 10 mg of nanotubes), filtered, and dried before wetting experiments. Pure samples were prepared by following the purification procedure described elsewhere [14]. The annealed nanotubes were first purified and then heated under vacuum (2×10^{-6} torr) at 100 °C for 10 min, followed by 15 min at 500 °C, and eventually the temperature was raised to 900 °C before natural cooling. The powders were ground in a mortar and divided in small quartz tubes containing 2–3 mg of nanotubes each. The samples were degassed under vacuum (5×10^{-6} torr) and heated for an hour (at 500 °C for the raw and annealed, 120 °C for the purified nanotubes) before being transferred under argon to a glove box. The chemical, (the purest quality available from Aldrich Chemical Company Inc., 99.95–99.99 %) to be melted was added on top of the packed nanotubes in an approximately 1:1 volume ratio. The quartz tube was then degassed for another hour at the same temperature as described earlier (or below the melting point of the chemical, depending on its nature) and sealed under vacuum ($2–5 \times 10^{-6}$ torr).

The sealed quartz tubes were heated from room temperature to 50 °C above the melting point of the tested compounds at about 1 °C/s and left at the final temperature for 1–4 h.

Received: April 24, 1998
Final version: June 29, 1998

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Low-Temperature Solution Route to Molybdenum Nitride**

By *Hsin-Tien Chiu*,* *Shiow-Huey Chuang*, *Gene-Hsiang Lee*, and *Shie-Ming Peng*

Transition metal nitrides are technologically important materials with many interesting properties.[1–3] Frequently, these materials are prepared at high temperatures by direct nitridation or chemical vapor deposition (CVD)[4] employing N_2 or NH_3 as the source of nitrogen atoms. Rapid solid-state synthesis, a highly exothermic self-propagating reaction, represents an alternative route.[5–9] Here, we wish to report the synthesis of molybdenum nitride powder,[10–12] an effective catalyst for hydro-desulfurization and hydro-denitrogenation of hydrocarbons,[13] via a sol-gel type of solution process, employing a mixture of Na_2MoO_4, $(Me_3Si)_2NH$, Me_3SiCl, and NEt_3 in refluxing DME (1,2-dimethoxyethane, boiling point 358 K). Although the growth of metal nitride thin films by CVD at 473 K has been reported,[14,15] this is the first time that a transition metal nitride has been prepared from solution at low temperature.

When Na_2MoO_4 was reacted with Me_3SiCl, $(Me_3Si)_2NH$ and NEt_3 in refluxing DME under N_2 or Ar atmosphere, a relatively air-stable black powder **1** precipitated, while a white solid, identified as Et_3NHCl, deposited on the inner surface of the condenser. $(Me_3Si)_2O$ was detected as the major by-product in the solution; no volatile Mo by-products were detected in the reaction mixture. The average particle size of **1** was determined to be 15–30 nm using

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[**] We thank the National Science Council of Taiwan, the Republic of China (NSC-85-2113-M-009-012) for support.

  0935-9648/98/1712-1475 $ 17.50+.50/0

STEM (scanning transmission electron microscopy, Fig. 1a). ED (electron diffraction) (Fig. 1b) identifies overlapping diffraction signals, which are assigned to randomly dispersed microcrystals of a cubic-phase material with a = 4.2 Å and residual NaCl. The lattice parameter of a = 4.2 Å is close to that of γ-Mo_2N, 4.16 Å. Due to the small particle size of **1**, X-ray diffraction (XRD) only showed reflections of residual NaCl, the reason being that in general X-rays, with their wavelengths much longer than that of the electron beam, can only be used to show diffraction patterns of crystalline particles with sizes greater than 200 nm.[16] After **1** was thermally treated at 873 K for 1 h, broad XRD peaks corresponding to the γ-Mo_2N phase were observed. A high-resolution XPS (X-ray photoelectron spectroscopy) study of **1** showed signals corresponding to Mo($3d_{5/2}$), Mo($3d_{3/2}$), Mo($3p_{3/2}$), Mo($3p_{1/2}$), and N(1s) electrons at 228.2, 231.4, 394.1, 411.8, and 397.3 eV, respectively. The signals of C(1s) and O(1s) electrons were observed at 284.1 and 531.0 eV, respectively. They are assigned to by-products, which are yet to be fully separated. The N(1s) signal is characteristic for a metal nitride material. These data were compared with a commercial sample of Mo_2N, which showed corresponding elemental signals at 228.2, 231.3, 394.2, 411.7, and 397.2 eV. In Figure 2, high-resolution

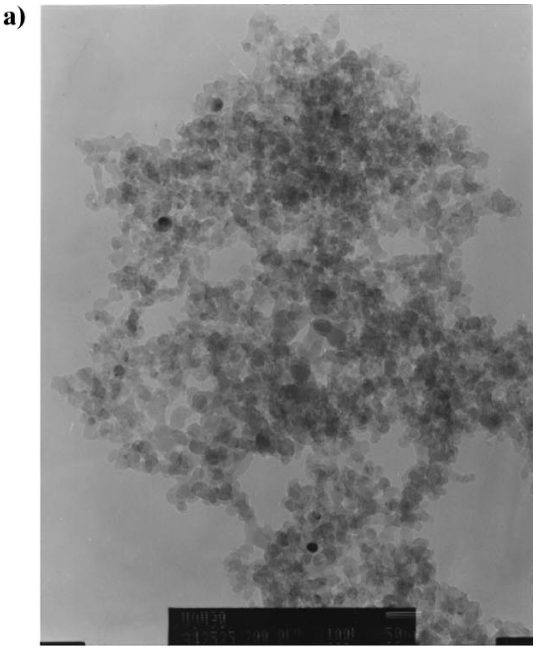

Fig. 1. a) STEM bright-field image and b) ED (L = 80 cm, λ = 0.0336 Å) of **1** (ultrasonically irradiated in ethanol).

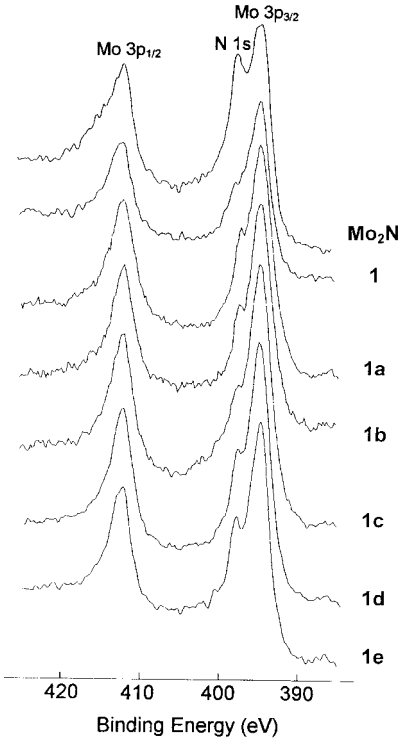

Fig. 2. High-resolution XPS signals of Mo($3p_{3/2}$), Mo($3p_{1/2}$), and N(1s) electrons of the powders (0.5 keV Ar^+ sputtering for 3 min).

spectra of Mo($3p_{3/2}$), Mo($3p_{1/2}$), and N(1s) electrons are shown for **1** and the reference sample, thus confirming that **1** contains molybdenum nitride. After NaCl was separated from **1** by dissolving the salt in water, the insoluble residue, **1a**, was collected and dried in vacuo at room temperature. XPS of **1a** indicates that the molybdenum and nitrogen signals (Fig. 2) differ little from those of **1**. Heating **1** in vacuum at 673 K, to remove traces of any volatile by-products, produced a black powder **1b**. As shown in Figure 2, the high-resolution XPS signals of **1b** show little difference either. In addition, XPS signals of NaCl were observed for **1b**. Neither **1a** nor **1b** showed C–H stretching signals in the IR spectra.

Analyzing these data, where the relative concentrations of Mo and N were determined from the XPS data by integrating the corresponding signals after curve fitting (with a commercial sample as a standard), we conclude that the black powder **1** contains nanosized molybdenum nitride

  0935-9648/98/1712-1476 $ 17.50+.50/0

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particles, MoN_x ($x = 0.4 \pm 0.1$). A balanced equation is proposed in Equation 1 to describe the overall reaction stoichiometry. The evolution of dinitrogen molecules has been proposed but has not yet been confirmed.

$$Na_2MoO_4 + 2(Me_3Si)_2NH + 4\ Me_3SiCl + 2\ NEt_3 \xrightarrow[\text{DME (reflux)}]{} NoN_x + 2\ NaCl + 4\ (Me_3Si)_2O + 2\ NEt_3HCl + (1 - 0.5x)\ N_2 \quad (1)$$

In order gain further insight into this reaction, we investigated the system by adding reagents sequentially, thus allowing reaction intermediates to be isolated. The observations are summarized in Scheme 1. Only Me_3SiCl showed an initial significant rate of reaction towards Na_2MoO_4 in DME. MoO_2Cl_2(DME), **2**, was isolated in high yield.[17] Reacting **2** with Me_3SiCl, $(Me_3Si)_2NH$, and NEt_3 in refluxing DME generated a black powder **1c**, characterized to be MoN_x by XPS (Fig. 2). Treatment of **2** with $(Me_3Si)_2NH$ yielded a pale yellow liquid, **3**, by distillation, which is yet to be fully characterized. Compound **3** gradually darkened, indicating further reaction at room temperature. A known dimeric nitrido complex $[N{\equiv}Mo(OSiMe_3)_3{\cdot}NH_3]_2$, **4**, crystallized from the mixture as a minor product.[18] Formation of $(Me_3Si)_2O$, $(Me_3Si)_2NH$ and a brown precipitate yet to be characterized were also observed. Addition of NEt_3 to **3** enhanced the apparent rate of formation of **4**. Addition of pyridine to **3** resulted in the isolation of another nitrido complex $N{\equiv}Mo(OSiMe_3)_3{\cdot}$py, **5**.[17] Reacting **3** with Me_3SiCl, $(Me_3Si)_2NH$, and NEt_3 in refluxing DME generated a black powder, **1d**, shown to be MoN_x by XPS (Fig. 2).

In an aprotic environment, $(Me_3Si)_2NLi$ was allowed to react with **2** in hexane to form a pale yellow liquid, formulated as a nitrido complex $N{\equiv}Mo(OSiMe_3)_2(N(SiMe_3)_2)$, **6**, in high yield. Contrary to the instability of **3** at room temperature, **6** showed little sign of decomposition. A pyridine adduct of **6**, $N{\equiv}Mo(OSiMe_3)_2(N(SiMe_3)_2){\cdot}$py, **7**, was crystallized in good yield from hexane. Compound **7** is a mononuclear five-coordinate complex with a distorted square pyramidal geometry about the metal center (Fig. 3).

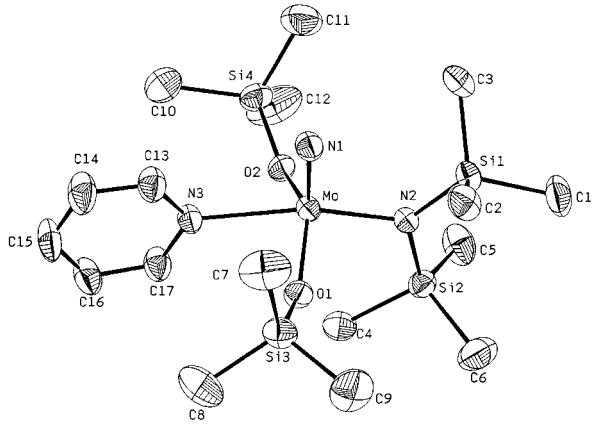
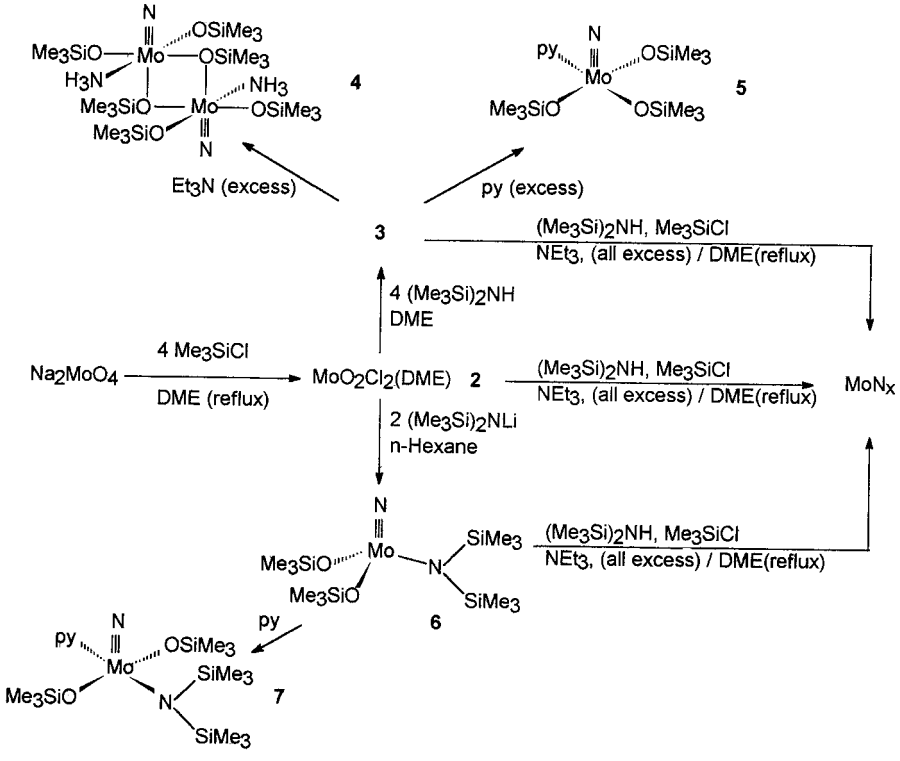


Fig. 3. ORTEP drawing of **7**, showing the numbering scheme for the non-hydrogen atoms. Selected bond distances (Å) and angles (°): Mo–N(1) = 1.640(3), Mo–N(2) = 1.973(3), Mo–N(3) = 2.334(3), Mo–O(1) = 1.921(3), Mo–O(2) = 1.924(2), N(1)–Mo–N(2) = 102.5(1), N(1)–Mo–N(3) = 92.0(1), N(2)–Mo–N(3) = 165.4(1), N(1)–Mo–O(1) = 106.6(1), N(1)–Mo–O(2) = 107.6(1), O(1)–Mo–O(2) = 139.1(1), O(1)–Mo–N(2) = 96.3(1), O(1)–Mo–N(3) = 77.7(1), O(2)–Mo–N(2) = 97.7(1), O(2)–Mo–N(3) = 79.2(1).



Scheme 1.

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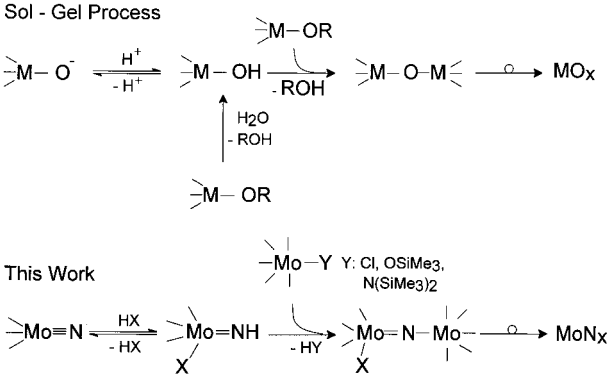
The Mo atom lies slightly above the basal plane while the nitrido ligand occupies the apical position. The N(1)–Mo distance is short, 1.640(3) Å. The overall geometry of **7** is closely related to those of **4**, **5**, and $[N\equiv MoCl_3(N(SiMe_3)_2)]^-$.[19] When **6** was reacted with Me_3SiCl, $(Me_3Si)_2NH$, and NEt_3 in refluxing DME a black powder **1e** resulted that was identified as MoN_x by XPS (Fig. 2).

Comparing this observation with the experiment employing **3** to form molybdenum nitride, little difference exists except that **6** was first prepared in an aprotic medium and then exposed to a protic medium. Therefore, we propose protonation of **6** to be an essential step. This step probably converts the nitrido ligand to an imido ligand,[20] then, through condensation reaction steps, into MoN_x. For **3**, in the presence of a base such as pyridine or NEt_3, deprotonation occurs and the nitrido complexes **4** and **5** are generated. In Scheme 2, a generalized Mo–N–Mo polymeriza-



Scheme 2.

tion route is proposed to account for the formation of the molybdenum nitride. Intermolecular condensation reaction, removal of a molecule HY from Mo=NH and Y–Mo results in a Mo–N–Mo linkage. This step is comparable to the M–O–M formation pathway proposed for sol-gel routes to metal oxide materials.[21] The proposed Mo≡N and Mo=NH species resemble the $M–O^-$ and M–OH species in a regular sol-gel process. Analogous reactions are known for Mo–O–Mo and W–N–W connectivity formations.[20,22] Repeating the condensation step polymerizes the monomeric MoN-containing units, such as imido and nitrido intermediates, into clusters of oligomers. Ladder structures found for $[(^tBuCH_2)_2TaN]_5$ and $W_4N_4(NPh_2)_6(OBu)_2$ may be viewed as models to represent the initial stages of the oligomerization.[23,24] Further polymerization causes these oligomers to coagulate into nanosized molybdenum nitride powders.

In order to extend the chemistry to include other metals, we attempted to prepare tungsten nitride powder by reacting Na_2WO_4 with Me_3SiCl, $(Me_3Si)_2NH$, and NEt_3 in refluxing DME. The reaction did not proceed probably due to the high W–O bond strength. However, reacting a mixture of WCl_6, $(Me_3Si)_2NH$, and NEt_3 in refluxing DME produced a black precipitate. Preliminary characterization of this black powder by XPS indicated the presence of tungsten nitride with some residual chloride.[25]

In summary, we have demonstrated a low-temperature solution route to molybdenum nitride by reacting a mixture of Na_2MoO_4, Me_3SiCl, $(Me_3Si)_2NH$, and NEt_3 in refluxing DME. From the molecular complexes observed in this study, the process shows parallels to the sol-gel processing of metal oxide materials in many ways. This study extends the already versatile chemistry of interconversions among various metal–nitrogen containing complexes by showing an excellent correlation between molybdenum nitrido complexes and molybdenum nitride. Further investigations to extend our understanding of the reaction are in progress.

Experimental

All chemicals and solvents were manipulated under dry and oxygen-free N_2 atmosphere. Reactions carried out under Ar atmosphere showed same result.

*Compound **1***: To Na_2MoO_4 (2.0 g, 9.7 mmol) suspended in DME (100 mL), NEt_3 (5.5 mL, 40 mmol), $(Me_3Si)_2NH$ (4.1 mL, 19 mmol), and Me_3SiCl (11.1 mL, 87.5 mmol) were added sequentially. The mixture gradually darkened within 1 h, after which it was refluxed for 12 h. During this time, a white solid deposited on the inner surface the condenser. An air-stable black precipitate was collected from the reaction mixture.

*Compound **1a***: After **1** was washed with H_2O, the insoluble black precipitate was collected and dried under vacuum.

*Compound **1b***: **1** was heated at 673 K under vacuum for 1 h. The black solid was collected.

Binding energies [eV]. **1a**: Mo($3d_{5/2}$), 228.4; Mo($3d_{3/2}$), 231.5; Mo($3p_{3/2}$), 394.4; Mo($3p_{1/2}$), 411.9; N(1s), 397.0. **1b**: Mo($3d_{5/2}$), 228.0; Mo($3d_{3/2}$), 231.3; Mo($3p_{3/2}$), 394.4; Mo($3p_{1/2}$), 411.9; N(1s), 397.0. Based on the intensities of C(1s) and O(1s) signals, both elements are judged to be insignificant components. **1c**: Mo($3d_{5/2}$), 228.3; Mo($3d_{3/2}$), 231.5; Mo($3p_{3/2}$), 394.4; Mo($3p_{1/2}$), 411.6; N(1s), 397.1. **1d**: Mo($3d_{5/2}$), 228.2; Mo($3d_{3/2}$), 231.4; Mo($3p_{3/2}$), 394.3; Mo($3p_{1/2}$), 411.6; N(1s), 397.2. **1e**: Mo($3d_{5/2}$), 228.4; Mo($3d_{3/2}$), 231.6; Mo($3p_{3/2}$), 394.4; Mo($3p_{1/2}$), 411.8; N(1s), 397.3.

*Compound **3***: To **2** (5.0 g, 17 mmol) in hexane (100 mL), $(Me_3Si)_2NH$ (14.6 mL, 69.2 mmol) was added. After work up, a yellow liquid was isolated (3.1 g, 40 % yield based on Mo). Initially, the liquid was formulated to be $(Me_3SiN=)_2Mo(OSiMe_3)_2$ based on NMR spectroscopy evidence [26]. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.11 (s, OSiMe_3), 0.20 (s, NSiMe_3). Although the two signals appeared to correspond to an equal number of hydrogen atoms, accurate integrations were difficult to obtain due to the broadening of the signal at 0.11 ppm. Contrary to the literature description of $(Me_3SiN=)_2Mo(OSiMe_3)_2$, **3** showed sign of decomposition and gradually darkened at room temperature. We speculate that a minor proton-containing molecule coexisted because regardless how carefully we prepared **3**, stretchings of O–H (3779, 3730, 3640, 3570 cm^{-1}) and N–H (3404, 3357, 3241, 3161 cm^{-1}) were observed in the IR spectra. The mass spectrometry (MS) data suggest that ions of three different complexes coexisted when **3** was evaporated into the spectrometer. MS (EI = 12 eV, direct inlet, ^{98}Mo): m/z = 379 ($MoNO_3Si_3C_9H_{27}^+$), 450 ($MoN_2O_2Si_4C_{12}H_{36}^+$), 526 ($MoN_2O_3Si_5C_{15}H_{46}^+$ – Me + 1). The assignments are m/z = 379, $N\equiv Mo(OSiMe_3)_3$; m/z = 450, $(Me_3SiN=)_2Mo(OSiMe_3)_2$; m/z = 526, a fragment of $(Me_3SiN=)Mo(NHSiMe_3)(OSiMe_3)_3$. Thus, we speculate that when freshly prepared, **3** was a mixture of $(Me_3SiN=)_2Mo(OSiMe_3)_2$, a major product, and Me_3SiOH, a minor by-product. Upon standing at room temperature, Me_3SiOH reacted with $(Me_3SiN=)_2Mo(OSiMe_3)_2$ through several addition–elimination and silyl group migration steps. **3** thus became a mixture of molybdenum complexes, including a nitrido complex later isolated as **4** and **5**.

*Compound **6***: To **2** (1.51 g, 5.20 mmol) stirred vigorously in hexane (50 mL), $LiN(SiMe_3)_2$ (1.74 g, 10.4 mmol) was added. The mixture was stirred for 2 h. After work-up, **6** was isolated as a yellow liquid (2.0 g, 85 % yield based on Mo). ^1H NMR (300 MHz, toluene-d_8, –20 °C): δ 0.25 (s, 9H, NSi_aMe_3), 0.33 (s, 18H, $OSiMe_3$), 0.54 (s, 9H, NSi_bMe_3); ^{13}C NMR (75 MHz, toluene-d_8, –20 °C): δ 1.8 ($OSiMe_3$), 2.7 (NSi_aMe_3), 5.0 (NSi_bMe_3). MS (EI, ^{98}Mo): m/z = 450 (M^+).

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Compound **7**: To **6** (2.0 g, 4.4 mmol) in hexane (50 mL), pyridine (py) (1.5 mL, 19 mmol) was added. After stirring for 18 h, the solvent was removed, producing a yellow solid. Recrystallization from hexane yielded yellow crystals (1.5 g, 64 % based on Mo). ^{1}H NMR (300 MHz, toluene-d_8, –10 °C): δ 0.14 (s, 18H, OSiMe_3), 0.43 (s, 9H, NSi_aMe_3), 0.67 (s, 9H, NSi_bMe_3), 6.42 (t, 2H, −NCHC*H*CH), 6.79 (t, 1H, −NCHCHC*H*), 8.44 (d, 2H, −NC*H*CHCH); ^{13}C NMR (75 MHz, toluene-d_8, –10 °C): δ 2.0 (OSiMe_3), 2.9 (NSi_aMe_3), 5.4 (NSi_bMe_3), 124.8 (−NCH*C*HCH), 137.7 (−NCHCH*C*H), 150.7 (−N*C*HCHCH). MS (EI, ^{98}Mo): m/z = 379 (M^+ – py). Crystal parameters of **7** at 298 K: space group $P\bar{1}$, a = 10.499(1), b = 10.974(3), c = 13.001(3) Å, α = 83.03(2)°, β = 81.49(2)°, γ = 80.31(2)°, V = 1453.1(5) Å^3, Z = 2, D_c = 1.206 g/cm^3, R_f = 0.036, R_w = 0.034.

Received: April 20, 1998
Final version: June 30, 1998

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A Novel Pathway to PbSe Nanowires at Room Temperature**

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Recently, one-dimensional (1D) structures with nanometer diameter, such as nanowires (nanorods) and nanotubes, have attracted considerable attention due to their special properties.[1–13] Compared with micrometer-diameter whiskers, they are expected to have remarkable mechanical properties, including electrical, optical, and magnetic properties that are in principle tunable by varying the diameter and chirality.[14,15] These new nanoscale materials have potential applications in both mesoscopic research and development of nanodevices. Previous work in this field focused on carbon nanowires and nanotubes, which were the by-product of fullerene research.[16] Conventionally, carbon nanowires or nanotubes can be grown in an arc discharge at a temperature of 3000 K,[17,18] by thermal deposition of hydrocarbons,[19] or vapor–liquid–solid (VLS) growth.[3,4,12] Comparatively little research has been carried out on other 1D materials and nearly all the previous methods of preparing nanowires or nanotubes require extreme conditions. Therefore, one of the important goals of materials scientists is to prepare nanoscale materials under milder conditions. Here we report a novel route to PbSe nanowires: $PbCl_2$, Se, and KBH_4 were kept in a sealed flask at room temperature for 4 h using ethylenediamine as the solvent. The study on PbSe is meaningful because it could be widely used for IR sensors,[20] solar cells, infrared detectors,[21] chemical sensors,[22] and so on. To our knowledge, the method here is the mildest route so far to produce nanowires and it is reasonable to assume that other nanoscale materials can be obtained by a similar process except that so far only the reactant $PbCl_2$ has been substituted by other MCl_n compounds.

In a standard experimental procedure, an appropriate amount of Se powder, $PbCl_2$, and KBH_4 were placed in a flask, which was filled with ethylenediamine up to 90 % of its volume. The flask was then sealed and maintained at about 10 °C for 4 h. The precipitate was filtered and washed with distilled water, the black product was collected, and, finally, dried in vacuum at about 10 °C for 12 h.

X-ray powder diffraction (XRD) was used to characterize the product. It was collected on a Rigaku D/max γA ro-

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[**] This work is supported by the Chinese National Natural Science Fund and National Nanometer Materials Climbing Program.

  0935-9648/98/1712-1479 $ 17.50+.50/0