P.-S. Ho, *Synth. Commun.* **1996**, *26*, 3225; Y. Morisaki, T. Kondo, T. A. Mitsudo, *Organomet.* **1999**, *18*, 4742; Y. Matsushima, K. Onitsuka, T. Kondo, T. Mitsudo, S. Takahashi, *J. Am. Chem. Soc.* **2001**, *123*, 10405.

[8] D. J. Barnes, R. L. Chapman, R. S. Vagg, E. C. Watton, *J. Chem. Eng. Data* **1978**, *23*, 349; H. Adolfsson, C. Moberg, *Tetrahedron: Asymmetry* **1995**, *6*, 2023.

[9] B. M. Trost, M. Lautens, *J. Am. Chem. Soc.* **1987**, *109*, 1469.

[10] The results with ligands **14** and **15** mirror those in recent reports: A. V. Malkov, P. Spoor, V. Vinader, P. Kocovsky, *Tetrahedron Lett.* **2001**, *42*, 509–512.

[11] This conclusion contradicts those of Pfaltz and co-workers for related systems; see ref. [3f].

[12] M. D. Curtis, O. Eisenstein, *Organometallics* **1984**, *3*, 887.

Creation of a Unique Self-Supported Pattern of Radially Aligned Semiconductor Ag_2S Nanorods**

Qingyi Lu, Feng Gao, and Dongyuan Zhao*

Novel technologies based on nanoscale machines and devices will bring us a new world.[1] The key to realizing this nanotech world is to devise simple and efficient methods to create patterns of well-arranged nanocrystallites.[2] Recent research on metal and semiconductor nanostructures is expanding rapidly into the assembly of nanoparticles in two- (2D) and three-dimensional (3D) ordered superstructures.[3] A range of methods, including solvent evaporation of hydrophobic colloids,[4] molecular cross-linking in colloidal aggregates,[5] and biotemplate-directed synthesis,[6] have been reported, and they usually require the synthesis of initial nanoparticles with uniform size. One-dimensional (1D) nanostructures are of particular interest because of their potential in fundamental research and industrial applications.[7] The synthesis of nanorod arrays, especially the creation of aligned nanorods with novel patterns on surfaces, is considered to be a definitive step towards the fabrication of advanced electronic and opto-electronic nanodevices.[8] However, due to the anisotropic structure of nanorods, the oriented growth of nanorods on surfaces is difficult and usually requires solid templates, such as porous alumina,[9] polymer nanotubes,[10] and patterned catalysts,[11] to control the directional growth. Mostly substrates such as silicon wafers, Al_2O_3 membranes, and polycrystal glass plates are used to sustain nanorod growth.[12] The development of simple, mild, and effective methods for creating novel assemblies of 1D metal or semiconductor nanostructures on heterogeneous substrates, or even on self-generated homogeneous substrates, is of importance to nanotechnology and remains a key research challenge.

Here we demonstrate a room-temperature solution-growth method to synthesize of a self-supported pattern of radial semiconductor Ag_2S nanorod arrays with only $AgNO_3$, thiourea (Tu), and NaOH as the reagents. To the best of our knowledge, this is the first self-supported growth of Ag_2S nanorods. The reaction between $AgNO_3$ and Tu to form an unstable Ag-Tu complex has been well studied.[13] Our strategy is based on the experimental finding that basic conditions accelerate the decomposition of Tu.[14] We induce the reaction of $AgNO_3$ and Tu under basic conditions to control the decomposition rate of the complex and hence the nucleation and growth rates of crystalline Ag_2S. This synthetic process is very simple and mild, free of any templates (either membranes or surfactants), and provides a novel method for low-temperature homogeneous growth of 1D nanostructures and their simultaneous assembly into patterns.

The formation of the crystalline Ag_2S phase was established from X-ray diffraction (XRD) pattern (Figure 1). All peaks can be indexed to monoclinic Ag_2S with lattice constants comparable to the values of JCPDS card 14-72, and no impurities can be detected in this pattern, which indicates that crystalline Ag_2S is formed from solution at room temperature.

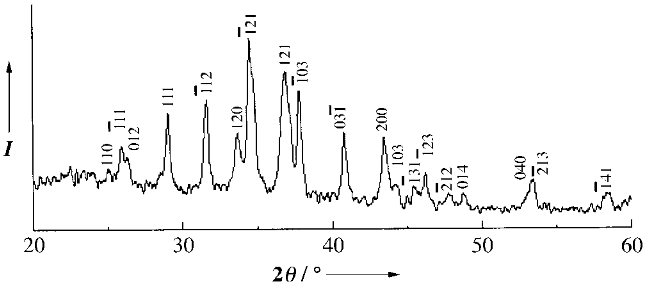

Figure 1. XRD pattern of the Ag_2S nanorod arrays.

The product morphology and chemical composition were determined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Figure 2 shows the unusual structure of radially aligned Ag_2S nanorods grown on a flakelike substance. The flakes usually have an irregular morphology with size up to dozens of micrometers, on which a large number of Ag_2S nanorods grow radially from one center. The nanorods have nonuniform diameters in the range of 50 to 200 nm and lengths of up to several micrometers. The Ag_2S nanorods at the radial center are slightly wider and longer than those at the edge. The EDS spectra (not shown) of the Ag_2S nanorods and flakes show strong silver and sulfur signals with Ag:S ratios of 2.00:1.03 and 2.04:1.00, respectively, which indicate stoichiometric relations between Ag and S in both the nanorods and the flakelike material. These results clearly indicate the formation of a distinctive radial pattern of aligned Ag_2S nanorods on self-provided Ag_2S flakes.

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[*] Prof. D. Zhao, Dr. Q. Lu, F. Gao
Molecular Catalysis and Innovative Materials Lab
Department of Chemistry
Fudan University
Shanghai 200433 (P.R. China)
Fax: (+86) 21-6564-1740
E-mail: dyzhao@fudan.edu.cn

[**] This work was supported by the National Natural Science Foundation of China (No. 20173012, 29925309, and 20101002), the Education Ministry of China, the Shanghai Science Foundation (0152nm029), the State Key Basic Research Program of PRC (2001CB610505) and the Chinese Post-doc Foundation.

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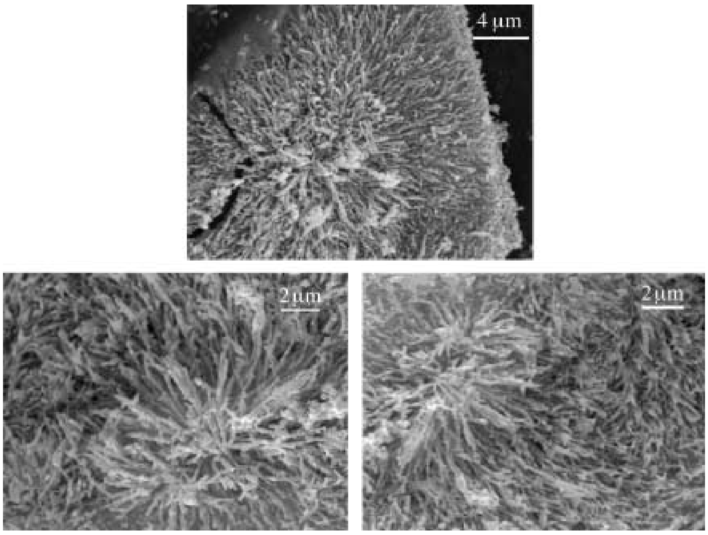


Figure 2. SEM images of the Ag_2S nanorod arrays.

The product was further characterized by high-resolution transmission electron microscopy (TEM), accompanied by EDS and selected-area electron diffraction (SAED). Figure 3a shows a typical TEM image of the product. The diameters of the nanorods are in the range of 30 to 120 nm, slightly less than those determined by SEM. This may be due to the Au cladding sprayed on the sample for SEM observation, which makes the diameters determined from SEM images slightly larger than the true sizes.[15] The high-resolution TEM image of an individual Ag_2S nanorod (inset in Figure 3a) clearly shows that the nanorod is highly crystalline and has a preferred growth direction. The calculated interplanar distance is 2.4 Å for the ($\bar{1}03$) face, consistent with that previously reported.[16] The ($\bar{1}03$) face is parallel to the long axis of the rod, that is, the preferred growth direction is [010]. Figures 3b and c show the SAED pattern and EDS spectrum, respectively, of an individual nanorod. The diffraction spots, indexed in Figure 3b, further suggest that the nanorod has a [010] growth direction. Figures 3d and e show a typical SAED pattern and an EDS spectrum, resectively, of a single flake; they indicate that the flakelike material is polycrystalline Ag_2S. The Cu and Cr signals are attributed to Cu grids for TEM observation. The powder XRD pattern (Figure 1) does not show any distinguishing diffraction peaks, which may be due to the fact that this pattern was measured on the randomly oriented polycrystalline flakes with radial nanorods. The TEM results are consistent with those obtained from SEM observations and further confirm the formation of the unique self-supported pattern of radially aligned Ag_2S nanorods.

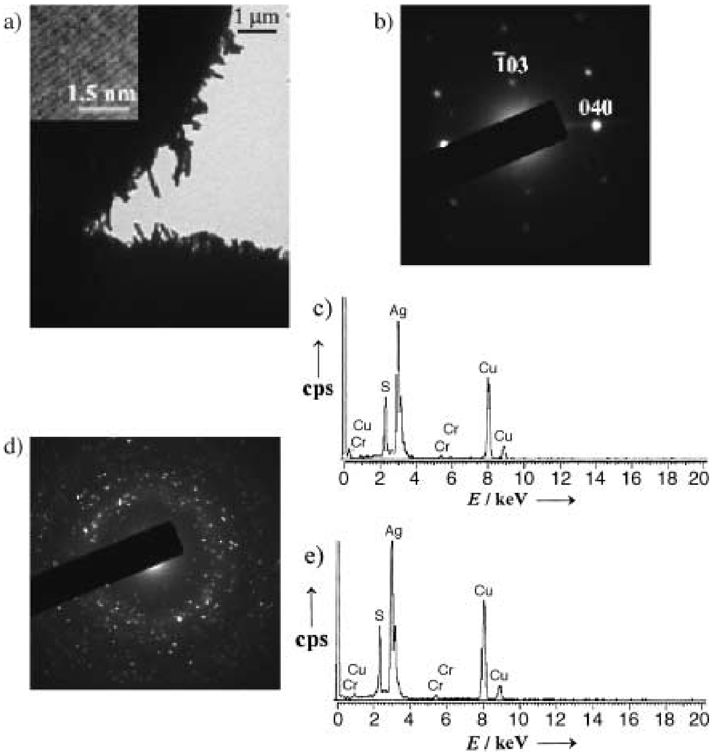


Figure 3. a) TEM image of the Ag_2S nanorod arrays. The inset is a high-resolution TEM image of a nanorod. b) SAED pattern obtained from a nanorod. c) EDS spectrum obtained from a nanorod. d) SAED pattern obtained from a flake. e) EDS spectrum obtained from a flake.

The addition of an appropriate amount of NaOH is undoubtedly vital in the formation of the unique pattern. In our experiments, 0.75–1.15 mL of 2 M NaOH solution led to formation of the self-supported pattern of radial Ag_2S nanorod arrays; otherwise, no nanorod arrays were observed. The reaction without NaOH resulted in the formation of Ag_2S microrods due to the strong coordinating ability of Tu. At low concentrations of NaOH (0.50 mL), the decomposition and nucleation rates are very slow, and the gradual transference and aggregation of the substance lead to the formation of flakelike Ag_2S. At high concentrations of NaOH (1.95 mL), decomposition of the Ag-Tu complex is so fast that much Ag_2S nucleates immediately after the two solutions are mixed, and homogeneous Ag_2S nanoparticles are formed.

The structure-directing agent (Tu) is also important for controlling the decomposition of the Ag-Tu complex, and therefore the growth of Ag_2S nanorods. In our experiments, a slight increase in the amount of Tu did not seriously affect the formation of the nanorod arrays, but did lead to a slight decrease in diameter. The reaction temperature is another factor that affects diameter and length. Increasing the reaction temperature from 20 to 40 °C increased the average diameter of the Ag_2S nanorods and decreased the length.

In summary, a simple and mild solution-growth method, free of any templates and substrates, creates a unique self-supported pattern of radial semiconductor Ag_2S nanorod arrays at room temperature, and may provide a new method for directed growth of nanorods and related materials.

Experimental Section

In a typical procedure for the synthesis of self-supported, radially aligned Ag_2S nanorods, 0.95 mL of 2 M NaOH solution was mixed with 10 mL of 0.26 M Tu solution with stirring. Then the mixed solution was slowly added to 5 mL of 0.39 M $AgNO_3$ solution, and the mixture was kept at room temperature for several days. The resulting black precipitate was collected by filtration, washed several times with distilled water and absolute alcohol, and dried at room temperature.

Received: November 27, 2001
Revised: March 4, 2002 [Z18286]

[1] a) S. K. Haram, B. M. Quinn, A. J. Bard, *J. Am. Chem. Soc.* **2001**, *123*, 8860; b) T. Trindade, P. O'Brein, N. L. Pickett, *Chem. Mater.* **2001**, *13*, 3843; c) C. Feldmann, H. O. Jungk, *Angew. Chem.* **2001**, *113*, 372; *Angew. Chem. Int. Ed.* **2001**, *40*, 359; d) H. Yu, P. C. Gibbons, K. F. Kelton, W. E. Bubro, *J. Am. Chem. Soc.* **2001**, *123*, 9198.

[2] a) M. P. Pileni, *J. Phys. Chem. B* **2001**, *105*, 3358; b) C. B. Murray, C. R. Kagan, M. G. Bawendi, *Science* **1995**, *270*, 1335; c) S. He, J. Yao, P. Jiang, D. Shi, H. Zhang, S. Xie, S. Pang, H. Gao, *Langmuir* **2001**, *17*, 1571; d) J. Lergand, A. T. Ngo, C. Petit, M. P. Pileni, *Adv. Mater.* **2001**, *13*, 58; e) M. A. Firestone, D. E. Williams, S. Seifert, R. Csencsits, *Nano Lett.* **2001**, *1*, 129; f) K. Soulantica, A. Maisonnat, M. C. Fromen, M. J. Casanove, P. Lecante, B. Chaudret, *Angew. Chem.* **2001**, *113*, 462; *Angew. Chem. Int. Ed.* **2001**, *40*, 448.

[3] a) T. Yonezawa, S. Onoue, N. Kimizuka, *Adv. Mater.* **2001**, *13*, 140; b) B. A. Korgel, S. Fullam, S. Connolly, D. Fitzmaurice, *J. Phys. Chem. B* **1998**, *102*, 8379; c) R. Maoz, E. Frydman, S. R. Cohen, J. Sagiv, *Adv. Mater.* **2000**, *12*, 424; d) Z. Y. Pan, X. J. Liu, S. Y. Zhang, G. J. Shen, L. G. Zhang, Z. H. Lu, J. Z. Liu, *J. Phys. Chem. B* **1997**, *101*, 9703; e) T. Vossmeyer, E. DeIonno, J. R. Heath, *Angew. Chem.* **1997**, *109*, 1123; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1080.

[4] a) P. C. Ohara, J. R. Heath, W. M. Gelbart, *Angew. Chem.* **1997**, *109*, 1119; *Angew. Chem. Int. Ed. Engl.* **1996**, *36*, 1078; b) X. M. Liu, H. M. Jaeger, C. M. Sorensen, K. J. Klabunde, *J. Phys. Chem. B* **2001**, *105*, 3353; c) Z. L. Wang, Z. Dai, S. Sun, *Adv. Mater.* **2000**, *12*, 1944.

[5] R. P. Andres, J. D. Bielefeld, J. I. Henderson, D. B. Janes, V. R. Kolagunta, C. P. Kubiak, W. J. Mahoney, R. G. Osifchin, *Science* **1996**, *273*, 1690.

[6] I. Willner, F. Patolsky, J. Wasserman, *Angew. Chem.* **2001**, *113*, 1913; *Angew. Chem. Int. Ed.* **2001**, *40*, 1861.

[7] a) D. Xu, Y. Xu, D. Chen, G. Guo, L. Gui, Y. Tang, *Adv. Mater.* **2000**, *12*, 520; b) Z. L. Wang, *Adv. Mater.* **2000**, *12*, 1295; c) A. M. Morales, C. M. Lieber, *Science* **1998**, *279*, 208; d) J. H. Song, B. Messer, Y. Wu, H. Kind, P. Yang, *J. Am. Chem. Soc.* **2001**, *123*, 9714; e) Z. Zhang, D. Gekhtman, M. S. Dresselhaus, J. Y. Ying, *Chem. Mater.* **1999**, *11*, 1659; f) C. C. Chen, C. Y. Chao, Z. H. Lang, *Chem. Mater.* **2000**, *12*, 1519; g) N. R. Hana, L. Gearheart, C. J. Murphy, *J. Phys. Chem. B* **2001**, *105*, 4065.

[8] a) L. Vayssieres, N. Beermann, S. E. Lindquist, A. Hagfeldt, *Chem. Mater.* **2001**, *13*, 233; b) Z. Zhang, G. Ramanath, P. M. Ajavan, D. Goldberg, Y. Bando, *Adv. Mater.* **2001**, *13*, 197; c) X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, A. P. Alivisatos, *Nature* **2000**, *404*, 59; d) A. Hatzor, P. S. Weiss, *Science* **2001**, *291*, 1019; e) Z. L. Wang, R. P. Gao, J. L. Gole, J. D. Stout, *Adv. Mater.* **2000**, *12*, 1938; f) M. Li, H. Schnablegger, S. Mann, *Nature* **1999**, *402*, 393; g) J. K. N. Mbindyo, B. D. Reiss, B. R. Martin, C. D. Keating, M. J. Natan, T. E. Mallouk, *Adv. Mater.* **2001**, *13*, 249.

[9] a) H. Masuda, T. Yanagishita, K. Yasui, K. Nishio, I. Yagi, T. N. Rao, A. Fujishima, *Adv. Mater.* **2001**, *13*, 247; b) D. Routkevitch, T. Bigioni, M. Moskovits, J. M. Xu, *J. Phys. Chem.* **1996**, *100*, 14037.

[10] H. Cao, Z. Xu, H. Sang, D. Sheng, C. Tie, *Adv. Mater.* **2001**, *13*, 121.

[11] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science* **2001**, *292*, 1897.

[12] a) L. T. Canham, *Appl. Phys. Lett.* **1990**, *57*, 1046; b) L. Vayssieres, N. Beermann, S. E. Lindquist, A. Hagfeldt, *Chem. Mater.* **2001**, *13*, 233; c) Z. Zhang, G. Ramanath, P. M. Ajavan, D. Goldberg, Y. Bando, *Adv. Mater.* **2001**, *13*, 197; d) J. K. N. Mbindyo, B. D. Reiss, B. R. Martin, C. D. Keating, M. J. Natan, T. E. Mallouk, *Adv. Mater.* **2001**, *13*, 249.

[13] X. Zhong, W. Xiao, Q. Yuan, R. Lou, S. Xu, Q. Xu, Y. Tian, S. Liu, Y. Lu, W. Wang, S. Liu, Z. Ji, *A Series of Inorganic Chemistry Books (No. 6)*, 1st ed., Kexue Press, Beijing, **1995**.

[14] X. Jiang, Y. Xie, J. Lu, W. He, L. Zhu, Y. Qian, *J. Mater. Chem.* **2000**, *10*, 2193.

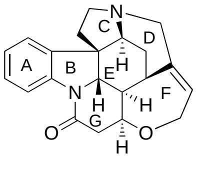
[15] C. H. Liang, G. W. Meng, G. Z. Wang, L. D. Zhang, *Chem. Mater.* **2001**, *13*, 2150.

[16] M. C. Brelle, J. Z. Zhang, L. Nguyen, R. K. Mehra, *J. Phys. Chem. A* **1999**, *103*, 10194.

Total Synthesis of (−)-Strychnine

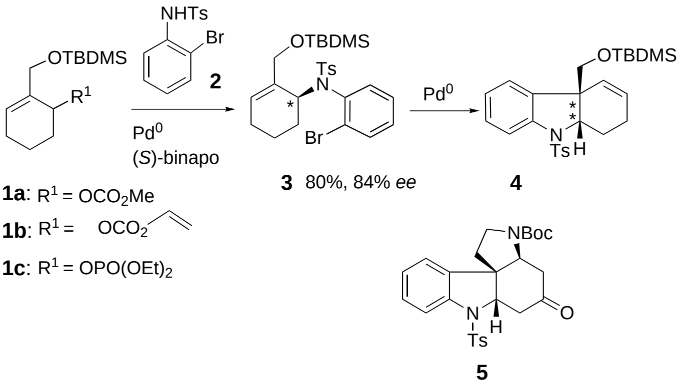
Masato Nakanishi and Miwako Mori*

(−)-Strychnine (**A**),[1] the most famous of the *Strychnos* alkaloids, has seven rings and six stereogenic centers in the molecule and is one of the most complex natural products of its size. Although Woodward et al. succeeded in the total synthesis of (−)-strychnine in 1954,[2] there were no reports of its total synthesis for 40 years. In 1992, Magnus et al. reported the total synthesis of strychnine,[3] and then Overman and coworkers succeeded in the first asymmetric total synthesis of (−)- and (+)-strychnine in 1993.[4] Since then, several groups have reported the total synthesis of (−)- or (±)-strychnine.[5, 6] Very recently, Vollhardt and coworkers completed the total synthesis of (±)-strychnine by using an ingenious cobalt-catalyzed [2+2+2] cycloaddition as a key step.[7]



A

We recently reported a novel method for synthesizing indole derivative **4** by means of palladium-catalyzed cyclization of 2-bromoaniline **3**. The aniline derivative **3** was obtained from cyclohexenol **1** and aniline **2** by using palladium-catalyzed asymmetric allylic substitution (Scheme 1).[8] (−)-Dehydrotubifolin and (−)-tubifolin were synthesized from tetracyclic ketone **5**, which was formed from **10** (Scheme 3; cf. **4**).



Scheme 1. Palladium-catalyzed asymmetric allylic substitution. Ts = toluene-4-sulfonyl, TBDMS = *tert*-butyldimethylsilyl, binapo = (*S*)-2,2′-bis(diphenylphosphanoxy)-1,1′-binapthyl, Boc = *tert*-butoxycarbonyl.

These results prompted us to synthesize (−)-strychnine, as tetracyclic ketone **5** is considered to be a very important intermediate in the syntheses of *Strychnos* indole alkaloids. Our retrosynthetic analysis of (−)-strychnine is shown in Scheme 2. The method for the construction of the G ring is

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[*] Prof. M. Mori, M. Nakanishi
Graduate School of Pharmaceutical Sciences, Hokkaido University
Sapporo 060-0812 (Japan)
Fax: (+81) 11-706-4982
E-mail: mori@pharm.hokudai.ac.jp

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1433-7851/02/4111-1934 $ 20.00+.50/0