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Photolysis of 4,4′-Dithiodipyridine Produces *cyclo*-Octasulfur Molecules: A Basis for Au/S$_8$ Microcrystalline Systems

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One of the more important issues in current nanoelectronics research is the shaping and directional control of nanowires.[1] A number of methods have been shown to be useful in this regard,[2−5] e.g., using biomolecules as templates,[6] followed by metallization with either gold[7] or silver;[8] conductive polymer formation, e.g., polymerization of polyaniline on the surface of a DNA molecule.[9,10] In principle, another method of forming nanowires with a predetermined configuration can be directional growth of nanocrystals, followed by metal deposition.

Here we present *cyclo*-octasulfur (S$_8$) as a starting molecule for the shape-controlled templating of a conductive core−shell nanosystem. S$_8$ is highly polymorphic and can form different crystal structures.[11] Three kinds of crystal structures are well-known: orthorhombic α-S$_8$ with space group *Fddd* is the most stable (a detailed description was presented by Abrahams[12] and verified later);[13,14] monoclinic β-S$_8$ arranged as needle-shaped, yellow crystals with space group $P2_1/c$ may be formed from orthorhombic α-S$_8$ at about 369 K, by slow cooling of molten sulfur, or by crystallization from organic solvents;[11,15] a second monoclinic form of S$_8$, γ-S$_8$ with space group $P2/c$, occurs as light-yellow, needlelike prismatic crystals and is also known to be stable.[11,16,17] Thus, by controlling the conditions of crystallization it is possible to produce shaped-controlled S$_8$ nanocrystals. On the other hand, to make them conductive, one can try to deposit gold on the surface of such nanocrystals. As has been widely shown, the interaction of gold with sulfur can result in well-ordered self-assembled films.[18,19] The nature of the gold−sulfur binding is chemisorption with directional covalent bond formation. However, studies of the sulfur/gold interaction have focused primarily on sulfur-containing self-assembled monolayer systems adsorbed on Au surfaces.

We have used photochemical degradation of 4,4′-dithiodipyridine (DTDP) to produce S$_8$ molecules. DTDP was dissolved in a pyridine/water mixture. Photolysis of DTDP in Py/H$_2$O solution at mol ratio 1:5−10:5−10 (DTDP/Py/H$_2$O) was performed by direct irradiation of the solution at room temperature in a UV-microreactor (5 mL volume; Sigma). A low-pressure, cold-cathode, mercury lamp (0.560 mW/cm^2) located in the center of the reactor was used for UV-irradiation. Time of irradiation did not exceed 3−5 min. During irradiation, the solution was purged gently with a flow of argon. The quartz tube between the UV-lamp and the solution was filled with triple-distilled water, which was continuously circulated (pump drive Heidolph PD 5001) to prevent heating of the solution. DTDP (Aldrithiol, Sigma) was used as is. The pyridine used was anhydrous 99.8% (Sigma). The water was triple distilled.

After short UV-irradiation the optical properties of the solution changed significantly. Absorption spectra were recorded on a Shimadzu UV-3101PC scanning spectrophotometer; excitation and emission spectra were measured on a Shimadzu RF-5301PC spectrofluorimeter. A new absorption band centered at 360 nm together with two emission bands at 524 and 652 nm appeared in the irradiated solution after photochemical transformation (data not shown). The solution prior to irradiation did not display these emission bands nor absorption at 360 nm. Both of those emissions were strongly polarized: the blue-green emission has a polarization coefficient of 0.3, as compared with 0.5 for the red emission. It is important to note that the optical property changes were observed only when DTDP was irradiated in a pyridine/water mixture. The same UV-irradiation of DTDP, either in water or in pyridine, did not cause changes in the optical properties, meaning that this photochemical reaction takes place only in the mixture of these solvents. The high catalytic activity of

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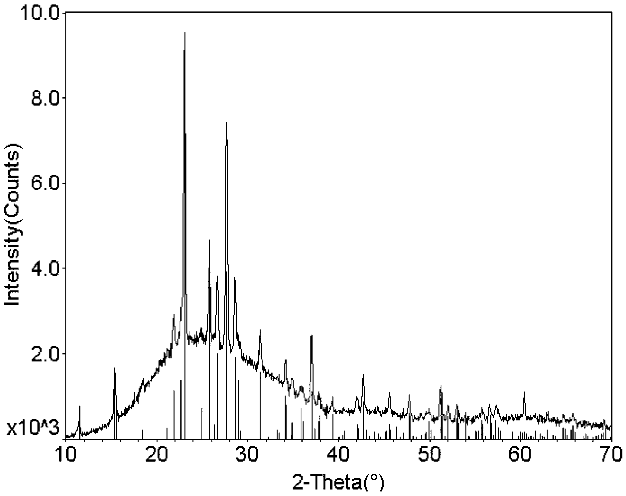

Figure 1. X-ray powder diffraction and PDF simulation for a thin layer of the photoinduced microcrystals and α-*cyclo*-octasulfur crystals, respectively.

pyridine in the excited state in the presence of water is, in our view, the reason for the photochemical reaction, since, although pyridine is a comparatively weak base with pK_a= 5.21 and hydrogen bond basicity pK_{HB}=1.86,[20] in the excited-state $S_2(\pi\pi^*)$ it converts to a strong base. According to semiempirical calculations the difference in proton affinity amounts to 12 kcal/mol between the ground and excited states.[21]

Almost immediately after irradiation small yellow crystals began growing in the slowly evaporating solution. After a few days, when further crystal growth could no longer be detected, the crystals were removed by filtration from the solution. In some few cases, prism-shaped crystals which were large enough to be successfully characterized by single-crystal X-ray diffraction measurements were obtained. These revealed two different forms of S_8 single crystals. One is α-orthorhombic S_8 (a = 1.0468 nm, b = 1.2866 nm, c = 2.4487 nm); and the other is γ-monoclinic, space group $P2/n$ (a = 0.81310 nm, b = 1.3046 nm, c = 0.8349 nm, β = 113.0°) with two independent half molecules in the asymmetric unit (CCDC registration code 228664). The monoclinic structure γ-S_8 was solved by Callacher and Pinkerton[17] and Watanabe.[16] The different crystal structures of S_8 can likely be explained by the changing Py/H_2O ratio during evaporation.[11]

In the case of the small yellow microcrystals, they were carefully cleaned and dispersed in water by using three cycles of centrifugation and ultrasonic cleaning (Hsiangtai and Branson 3210 units, respectively). X-ray powder diffraction measurements were performed on a thin layer of the microcrystals, using a D-Max/B powder diffractometer (Rigaku, Japan) affixed to an RU-200 rotating anode generator (Rigaku) operating at 7.5 kW. Step size and scanning rate were 0.05° and 1°/min, respectively. The data are presented in Figure 1. Fitting the X-ray powder diffraction pattern using the PDF database showed that the microcrystals were α-orthorhombic S_8. Figure 2 shows typical TEM images of these microcrystals. The sizes of the microcrystals were within the range of 50−200 nm. Fourier transform of the high-resolution TEM images of the microcrystals demonstrates that the d-spacing 0.386 nm is mainly observed which corresponds to the d-spacing (222) of α-S_8.

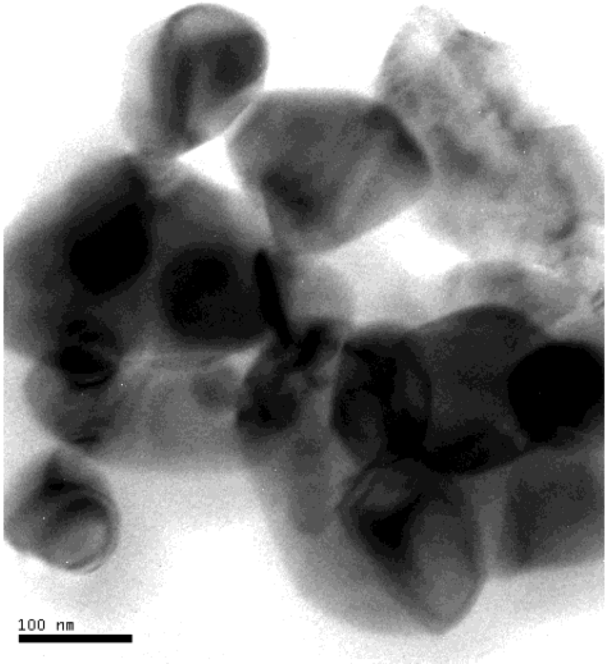

Figure 2. TEM image of *cyclo*-octasulfur microcrystals withdrawn from the irradiated solution.

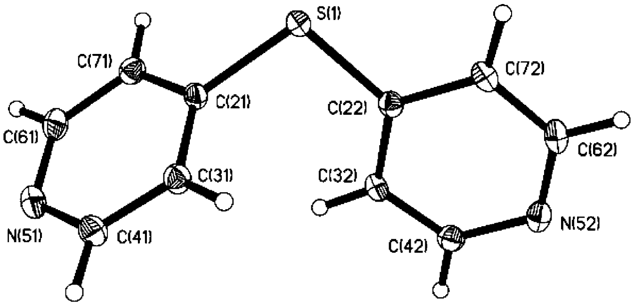

Figure 3. ORTEP drawing of $(C5H4N)_2S$ (50% probability).

After removal of S_8 crystals from the solution, it was subjected to further slow evaporation, till dryness. A second type of pale yellow prism-shaped crystal formed. These crystals were also characterized by single-crystal X-ray diffraction measurements. We succeeded in obtaining for the first time (to our knowledge) the crystal structure of 4,4′-thiodipyridine crystals. The ORTEP drawing of the 4,4′-thiodipyridine molecule in the crystal is shown in Figure 3, (CCDC registration code 228665).

On the basis of the crystallographic data, our explanation of the photoreaction is as follows. UV irradiation of disulfides caused homolytic C−S and S−S bond breaking.[22,23] The initial stage of the mechanism of the photochemical reaction involved formation of radicals of 4-pyridyl, 4-thiopyridyl, 4-dithiopyridyl, and sulfur (see Scheme 1). Recombination of these radicals led to the formation of 4,4′-thiodipyridyne and *cyclo*-octasulfur

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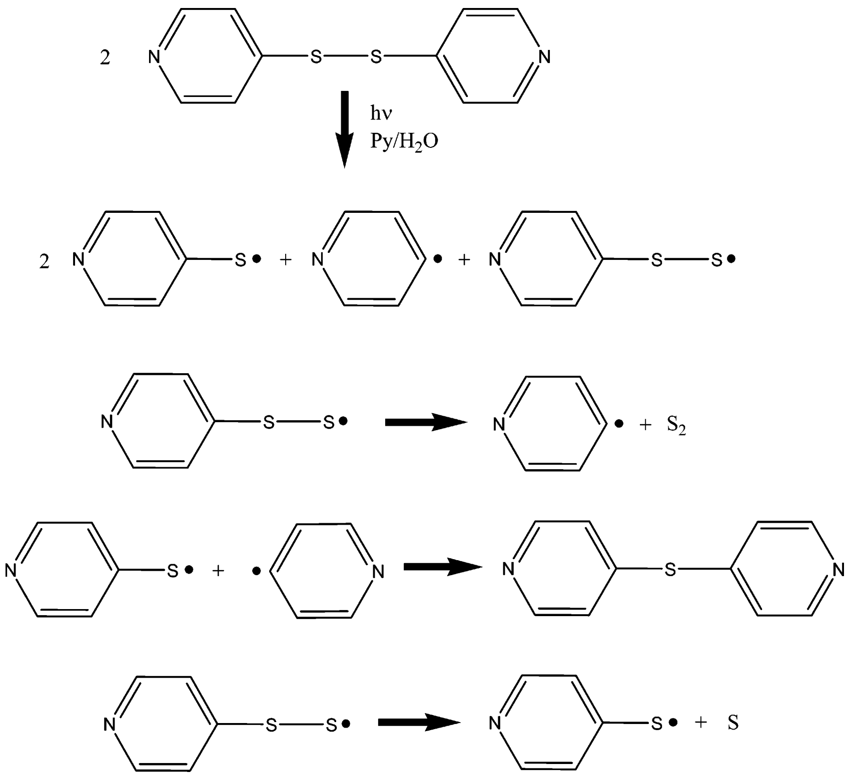
Scheme 1. Mechanism of the Photolysis of 4,4′-Dithiodipyridine in Pyridine/Water Mixture



S_8. Judging from the NMR data (not shown) some 4,4′-dipyridine was also formed due to recombination of the two 4-pyridyl radicals. Unfortunately, we were unable to isolate 4,4′-dipyridine owing to the small amount present.

The α-orthorhombic S_8 microcrystals, dispersed in water, were covered with gold, using the spontaneous gold–sulfur interaction which follows the addition of hydrogen tetrachloroaurate (III) trihydrate (Sigma, 5×10^{-5} mol/L). The solution was kept at room temperature at least .5 h, and then the resulting microcrystals were precipitated by centrifugation and stored in water. Figure 4 presents the high-resolution TEM images of gold-covered S_8 microcrystals. Fourier transforms of selected regions of the high-resolution TEM images revealed the *d*-spacings 0.235 and 0.204 nm which correspond to the (111) (with intensity $I = 100$) and (200) (with intensity $I = 52$) reflections of Au, respectively, thereby confirming the formation of crystallized gold on the microcrystalline surfaces. Crystallized gold nanolayers had domain structures (sizes of domains were within the range 7–20 nm); and the thickness of nanolayers was about 5 nm (Figure 4).

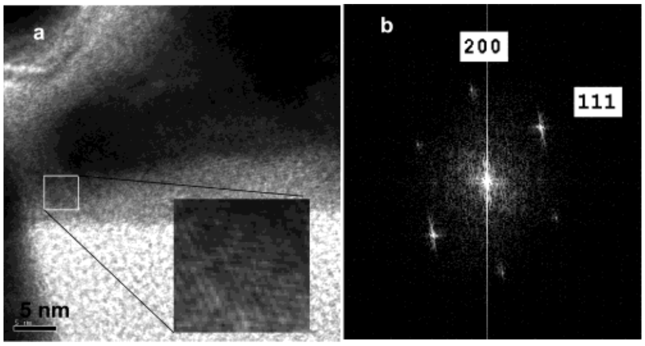


Figure 4. (a) High-resolution TEM image of Au/S_8 core–shell microcrystal system; and (b) Fourier transform image of the designated area in (a). The observed diffraction peaks correspond to 0.235 nm (111) and 0.204 nm (200) of crystalline gold.

We studied the conductivity of the Au/S_8 core–shell microcrystal systems using conducting probe atomic force microscopy (Nanoscope Dimension 3100 scanning probe microscope with Nanoscope IV controller).[24] Under an applied bias of 20 V, a current of 120 pA was registered (the range of the available current: 70 fA to 120 pA). In comparison, for S_8 microcrystals without gold deposition no current was raised under applied bias. We therefore conclude that deposition of gold crystal nanolayers on S_8 leads to the appearance of the conductive properties of such core–shell systems.

Currently, the optimal conditions of gold deposition and crystallization of needle-shaped monoclinic γ-S_8 nanocrystals are under investigation.

To summarize, we demonstrated that α-orthorhombic S_8 microcrystals can serve as a template for the crystallization of gold nanolayers. Photoinduced DTDP degradation in pyridine/water solution provides a simple means for producing S_8 molecules. We propose that UV-irradiation of DTDP in Py/H_2O solution produces 4-pyridyl, 4-thiopyridyl, 4-dithiopyridyl radicals, and sulfur. The radicals interact with each other with the formation of 4,4′-thiodipyridine and *cyclo*-octasulfur molecules. The identification of these molecules has been verified by X-ray crystallography. Single crystals formed from 4,4′-thiodipyridine, which has not been previously isolated in crystalline form, and *cyclo*-octasulfur molecules have been observed. The α-orthorhombic S_8 microcrystals, dispersed in water, were covered

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with gold, using the spontaneous gold−sulfur interaction which follows the addition of hydrogen tetrachloroaurate (III) trihydrate. Au/S_8 microcrystal systems exhibited conductive properties, as demonstrated by conducting probe atomic force microscope measurements. The polymorphism of S_8 can be useful for the shape-controlled design of gold nanolayer templates.

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Supporting Information Available: Crystallographic information files for DTDP, S_8, and 4,4′-thiodipyridine crystals (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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