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Supplementary Material Available: Experimental data for compounds **3-5**, **8-12**, and **14-17** (25 pages). Ordering information is given on any current masthead page.

Determination of the Structural and the Electronic Properties of Surfaces Using Scanning Tunneling Microscopy Coupled with Chemical Modifications

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Scanning tunneling microscopy¹ (STM) is a new technique that can provide real-space atomic-resolution images of surfaces in vacuum,² air,³ and liquids.⁴ The ability to image surfaces in air and in liquids with high resolution suggests that it may be possible to probe the molecular details of interfacial reactions in situ by using STM.⁵ This technique should be particularly effective for probing surface reactivity because tunneling images contain both structural and electronic information (i.e., the two key factors that determine reactivity). However, few STM studies in air or in liquids have attempted to probe the contributions of these two important properties to observed images.^{6,7} In this communication we report a new approach to this problem that involves the use of well-defined charge-transfer intercalation reactions to perturb the electronic properties at the surface of the layered transition-metal material TaS₂.

TaS₂ consists of covalently bound S-Ta-S layers that are held together by weak Van der Waals (VdW) interactions between the sulfur planes of adjacent layers. The sulfur atoms are in a hexagonal close-packed (hcp) arrangement with the tantalum metal centers coordinated in either octahedral or trigonal prismatic holes, depending on the crystal polytype.⁸ Our studies focus on the octahedral form of this compound, 1T-TaS₂. Of particular importance to these structural-electronic investigations is the charge density wave (CDW) state in 1T-TaS₂.^{8,9} The CDW state is a temperature dependent periodic distortion of the lattice and the electron density within the S-Ta-S layers. The lattice distortions (ca. 0.1 Å) are smaller than the lateral resolution of the STM¹ (1-2 Å), but the periodic variation of the electron density (wavelength ~12 Å) is sufficiently large to be resolved. Hence

(1) (a) Binning, G.; Rohrer, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 606-614. (b) Hansma, P. K.; Tersoff, J. *J. Appl. Phys.* **1987**, *61*, R1-R23. (c) Quate, C. F. *Phys. Today* **1986**, *39*, 26-33. (d) Golovchenko, J. A. *Science (Washington, D.C.)* **1986**, *232*, 48-53.

(2) (a) Becker, R. S. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 4667-4670. (b) Tromp, R. M.; Hamers, R. J.; Demuth, J. E. *Science (Washington, D.C.)* **1986**, *234*, 304-309.

(3) Park, S.-I.; Quate, C. F. *Appl. Phys. Lett.* **1986**, *48*, 112-114.

(4) (a) Sonnenfeld, R.; Hansma, P. K. *Science (Washington, D.C.)* **1986**, *232*, 211-213. (b) Giambattista, B.; McNairy, W. W.; Slough, C. G.; Johnson, A.; Bell, L. D.; Coleman, R. V.; Schneir, J.; Sonnenfeld, R.; Drake, B.; Hansma, P. K. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 4671-4674. (c) Liu, H.-Y.; Fan, F.-R.; Lin, C. W.; Bard, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 3838-3839.

(5) (a) Lev, O.; Fan, F.-R.; Bard, A. J. *J. Electrochem. Soc.* **1988**, *135*, 783-784. (b) Foster, J. S.; Frommer, J. E.; Arnett, P. C. *Nature (London)* **1988**, *331*, 324-326. (c) Schneir, J.; Hansma, P. K. *Langmuir* **1987**, *3*, 1025-1027.

(6) Bryant, A.; Smith, D. P. E.; Binning, G.; Harrison, W. A.; Quate, C. F. *Appl. Phys. Lett.* **1986**, *49*, 936-938.

(7) Spectroscopic tunneling measurements have been used successfully in vacuum to study this problem but are difficult to carry out in air or in liquids.

(8) Wilson, J. A.; DiSalvo, F. J.; Mahajan, S. *Adv. Phys.* **1975**, *24*, 117-201.

(9) DiSalvo, F. J. In *Electron-Phonon Interactions and Phase Transitions*; Riste, T., Ed.; Plenum: New York, 1977; pp 107-136.

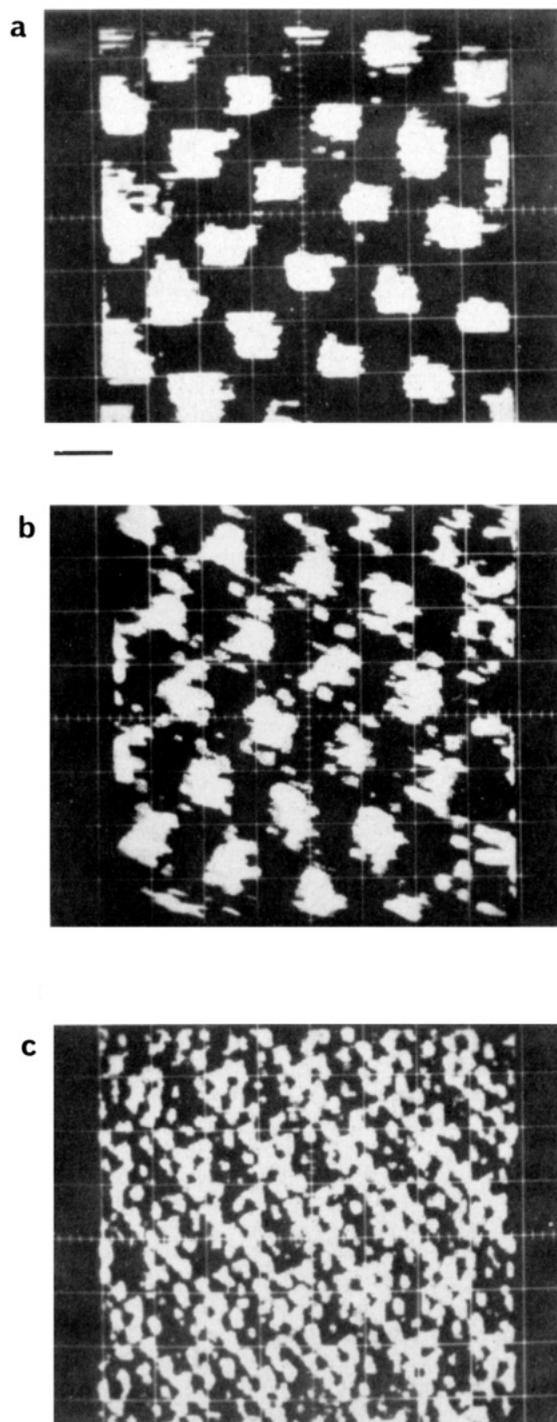
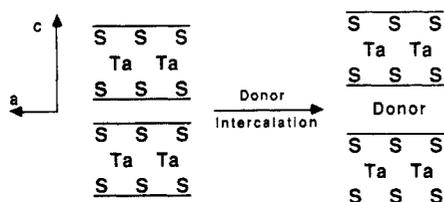


Figure 1. Top-view images of the (a) TaS₂, (b) TaS₂-¹/₄EDA, and (c) Li-TaS₂ samples recorded with the following STM parameters: (i) tunneling current = 1.8 nA, (ii) sample-tip bias voltage = 6 mV, and (iii) horizontal and vertical scan frequencies of 31 and 0.12 Hz, respectively. The horizontal and vertical distance scale, black line = 10 Å, is the same for the three images. The white spots correspond to peaks in the tunneling conductivity.

a key question to address is how does the CDW affect observed tunneling images? At temperatures ≤ 77 K the CDW state dominates the tunneling images of 1T-TaS₂ because the majority of the conduction electrons have condensed into this state.¹⁰ Our studies have been carried out at room temperature where there are significantly more free carriers⁹ and hence as with normal

(10) (a) Coleman, R. V.; McNairy, W. W.; Slough, C. G.; Hansma, P. K.; Drake, B. *Surf. Sci.* **1987**, *181*, 112-118. (b) Slough, C. G.; McNairy, W. W.; Coleman, R. V.; Drake, B.; Hansma, P. K. *Phys. Rev. B* **1986**, *34*, 994-1005. (c) Coleman, R. V.; Drake, B.; Hansma, P. K.; Slough, G. *Phys. Rev. Lett.* **1985**, *55*, 394-397.

Scheme I



metallic materials it may be possible to image the surface sulfur atoms.

All imaging studies were carried out by using a modified commercial instrument (Digital Instruments, Santa Barbara, CA) and platinum-iridium tips; the STM was operated in the constant current mode.¹ Images were recorded in real-time on an analogue storage oscilloscope (without digital processing) and then photographed. Single crystals of 1T-TaS₂¹¹ were cleaved along the VdW bonded planes to yield atomically flat surfaces that are suitable for STM imaging. A typical example of a room temperature tunneling image for 1T-TaS₂ is shown in Figure 1a. In this top-view image the white spots, corresponding to peaks in the tunneling conductivity, form a hexagonal array with a peak spacing of $11.6 \pm 0.2 \text{ \AA}$. These peaks correspond to the expected periodic variation in electron density of the CDW state.^{9,10} Notably, the hcp surface sulfur plane, which has a sulfur-sulfur spacing of 3.35 \AA , is not observed in this image, clearly demonstrating the importance of the electronic properties for this material.

To better understand the importance of this electronic contribution to the observed images we have taken advantage of the fact that a variety of electron donor compounds, such as amines and alkali metals, can be intercalated between the weakly bonded sulfur planes of TaS₂ (Scheme I).¹² The driving force for these intercalation reactions is believed to be a charge transfer to the tantalum d-band.¹³ We have investigated both the ethylenediamine (EDA) and lithium intercalation complexes of 1T-TaS₂. Diffraction studies¹³ of these complexes have shown that the only major structural change that occurs following intercalation is an expansion along the crystallographic *c*-axis.

The moderately air-stable EDA intercalation complex of 1T-TaS₂, TaS₂-¹/₄EDA, and the air-sensitive Li complex, Li-TaS₂, were prepared by using published procedures.^{13,14} A top view of the EDA complex recorded at the same resolution as TaS₂ is shown in Figure 1b. Although the CDW peaks are also prominent in this image (large white spots with a $11.5 \pm 0.2 \text{ \AA}$ separation), smaller peaks are visible around the CDW maxima. The spacing between these peaks, $3.3 \pm 0.2 \text{ \AA}$, agrees closely with the S-S spacing;⁸ we assign these satellite peaks to the surface sulfur atoms. A reasonable explanation of these results is that by increasing the carrier concentration via the charge-transfer reaction,¹³ the metallic character of the material is enhanced.¹⁵ In support of this conclusion we find that the STM images of Li-TaS₂ show more atomic structure than TaS₂-¹/₄EDA.¹⁶ Clusters of peaks with

a peak-peak separation of 3.3 \AA , the expected S-S spacing, can be clearly distinguished in Figure 1c; the spacing between these clusters is $10.5 \pm 0.2 \text{ \AA}$. These observations are consistent with the greater charge transfer in the Li system ($\approx 1e^-/\text{Li}$ is donated)^{13b} versus the EDA intercalation complex.¹⁷ The 10.2 \AA periodicity in the clusters of atomically resolved peaks suggests that the CDW is still present in Li-TaS₂; the reduction in the CDW wavelength is also consistent with electron donation to the Ta d-band. Studies designed to obtain a more quantitative understanding of these effect of charge transfer on the images of TaS₂ are currently in progress.

In summary, we have shown for the first time that it is possible to delineate the electronic and structural contributions to STM images by utilizing charge-transfer intercalation reactions which systematically perturb a materials electronic properties. We believe that our approach and other well-defined chemical strategies will be useful in general for probing the structural and the electronic information contained in tunneling images. Studies such as these will be crucial for developing STM as a useful tool to probe the local molecular details of surface reactivity in situ.

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(17) A quantitative value for the degree of charge transfer in TaS₂-¹/₄EDA is not known; however, in the related NbS₂-¹/₂pyridine system $0.2 e^-/\text{nitrogen}$ was reported to be transferred: Ehrenfreund, E.; Gossard, A. C.; Gamble, F. R. *Phys. Rev. B* 1972, 5, 1708.

A Novel Chiral Route to Substituted Tetrahydrofurans. Total Synthesis of (+)-Verrucosidin and Formal Synthesis of (-)-Citreoivridin

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Verrucosidin (1), a potent neurotoxin isolated from the fungus *Penicillium verrucosum* var. *cyclopium* by Burka and co-workers,¹ has been assigned structure 1 on the basis of the chemical, spectroscopic, X-ray crystallographic, and synthetic studies.^{2,3} Verrucosidin (1) is structurally related to citreoivridin (2),^{4,5} asteltoxin,⁶ and aurovertin B⁷ which are potent inhibitors of mitochondrial ATPase activity.^{4,8} The combination of their characteristic molecular architectures and their potent biological activities has stimulated significant synthetic efforts.^{9,10} We wish

(11) Single crystal samples of 1T-TaS₂ were provided by Prof. F. J. DiSalvo and P. E. Rauch of Cornell University.

(12) Gamble, F. R.; Osiecki, J. H.; Cais, M.; Pisharody, R.; DiSalvo, F. J.; Geballe, T. H. *Science (Washington, D.C.)* 1971, 174, 493-497.

(13) (a) Meyer, S. F.; Howard, R. E.; Stewart, G. R.; Acrivos, J. V.; Geballe, T. H. *J. Chem. Phys.* 1975, 62, 4411-4419. (b) Murphy, D. W.; DiSalvo, F. J.; Hull, G. W.; Waszczak, J. V. *Inorg. Chem.* 1976, 15, 17-21. (c) Beal, A. R.; Liang, W. Y. *Phil. Mag.* 1973, 27, 1397-1416.

(14) The TaS₂-¹/₄EDA and Li-TaS₂ samples were prepared by reaction of single crystals of 1T-TaS₂ with EDA (140 °C) and BuLi (45 °C), respectively, in sealed tubes for 2-3 days. TaS₂-¹/₄EDA was imaged in air immediately after cleaving a crystal; greater stability was obtained by covering the freshly cleaved surface with an inert oil.^{5c} The air-sensitive Li-TaS₂ samples were handled at all times in a Ar-filled glovebox; surfaces were cleaved and either imaged under Ar or oil. Images were recorded over many areas of several independent samples with different STM tips for both the EDA and Li systems; Figure 1 (parts b and c) is representative of these recorded data.

(15) If 1T-TaS₂ had a normal metallic electronic structure, only the hcp surface sulfur atoms would be visible in the tunneling images.

(16) It is unlikely that this atomic structure is due to direct observation of the lithium because it is disordered at room temperature (F. DiSalvo, personal communication).

(1) Wilson, B. J.; Byerly, C. S.; Burka, L. T. *J. Am. Vet. Med. Assoc.* 1981, 179, 480. Burka, L. T.; Ganguli, M.; Wilson, B. J. *J. Chem. Soc., Chem. Commun.* 1983, 544.

(2) Ganguli, M.; Burka, L. T.; Harris, T. M. *J. Org. Chem.* 1984, 49, 3762. (3) Nishiyama, S.; Shizuri, Y.; Shigemori, H.; Yamamura, S. *Tetrahedron Lett.* 1986, 27, 723.

(4) Hirata, Y.; Goto, T.; Sakabe, N. *Tetrahedron Lett.* 1964, 1825. Hirata, Y.; Sakabe, N.; Goto, T. *Tetrahedron* 1977, 33, 3077.

(5) Yamamura and co-workers have isolated more than 10 metabolites of *Penicillium citreoivridin* B. related to citreoivridin, see: Nishiyama, S.; Shizuri, Y.; Toshima, H.; Ozaki, M.; Yamamura, S.; Kawai, K.; Kawai, N.; Furukawa, H. *Chem. Lett.* 1987, 515 and earlier papers.

(6) Kruger, G. J.; Steyn, P. S.; Vleggaar, R.; Rabie, C. J. *J. Chem. Soc., Chem. Commun.* 1979, 441.

(7) Mulheirn, L. J.; Beechey, R. B.; Leworthy, D. P.; Osselton, M. D. *J. Chem. Soc., Chem. Commun.* 1974, 874. Steyn, P. S.; Vleggaar, R.; Wessels, P. L. *J. Chem. Soc., Chem. Commun.* 1979, 1041.

(8) Vleggaar, R. *Pure Appl. Chem.* 1986, 58, 239. Frank, B.; Gehrken, H. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 461.