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The self-assembly of a layered material: metal–alkanethiolate bilayers

F. Bensebaa, T.H. Ellis, E. Kruus, R. Voicu, and Y. Zhou

Abstract: Layered materials composed of metal–alkanethiolate units have been synthesized and characterized. The self-assembly occurs at the interface between a metal-ion-containing aqueous phase and an alkanethiol-containing organic phase. Key features of the structure have been determined from X-ray diffraction and infrared spectroscopy measurements. The highly ordered bilayers are characterized by tilted, all-*trans* alkyl chains. A new model for the in-plane structure has been presented, which is based on a hexagonal arrangement of metal atoms in the central plane.

Key words: self-assembly, alkanethiolates, layered materials, vibrational spectroscopy.

Résumé : On a synthétisé et caractérisé des matériaux en couches formés d'unités alcanethiolate de métal. L'autoassemblage se produit à l'interface entre une phase aqueuse contenant l'ion métallique et une phase organique contenant l'alkanethiol. On a déterminé les caractéristiques principales de la structure par diffraction des rayons X et par spectroscopie infrarouge. Les bicouches bien ordonnées sont caractérisées par des chaînes alkyles inclinées, complètement *trans*. On propose un nouveau modèle pour la structure dans le plan; elle est basée sur un arrangement hexagonal des atomes métalliques dans le plan central.

Mots clés : autoassemblage, matériaux en couche, spectroscopie de vibration.

[Traduit par la Rédaction]

Introduction

Alkanethiols ($\text{HS}(\text{CH}_2)_n\text{CH}_3$) are known to react and adsorb onto the clean surfaces of coinage metals, and to self-assemble into highly ordered monolayers (1, 2). These self-assembled monolayers (SAMs) provide a means of creating well-defined surface structures whose properties can be manipulated through substitutions to the initial alkanethiol molecules (3). A wide range of surface analysis techniques has been applied to the study of alkanethiolate SAMs, yielding a wealth of information.

Less well known than SAMs are layered materials composed of metal–alkanethiolate units (4–6). These are also materials that self-assemble in solution, forming a multibilayer structure that is illustrated in Fig. 1. Such materials can be viewed as SAMs having an infinite surface-to-volume ratio. As such, we have undertaken to study these materials as model systems for SAMs. Because it is a bulk material,

this greatly expands the range of measurement techniques available.

The goal of the present work is to describe the synthesis of these materials and the methods used to characterize their structure. Our preparation methods are a modification of those used for the preparation of short-chain silver–alkanethiolates (6), and we now have prepared copper–thiolate materials as well. Particular emphasis will be given to infrared spectroscopy measurements, where new information is revealed as a result of the enhanced signal from the bulk material.

Experimental section

The alkanethiols were purchased from Aldrich and used without further purification. All other reagents were acquired from general sources and used as received. Elemental analysis was performed on a Fisons Instruments model EA1108 analyser, and neutron activation analysis used the SLOW-POKE reactor at École Polytechnique de Montréal. The X-ray diffractometer is a Siemens D5000, using $\text{Co K}\alpha$ radiation. Infrared spectra were recorded on a Bomem MB 100 FTIR spectrometer in transmission mode using a DTGS detector. Several drops of the metal–alkanethiolate material suspended in toluene were dropcast onto a NaCl disk and dried in air. Typically, 20 scans were co-added, and the resolution was 1 cm^{-1} .

Results and discussion

The self-assembly process

The chemistry of the preparation procedure is elegant in its simplicity. The metal begins in the aqueous phase, in the

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Fig. 1. Cross-sectional view of the layered structure. Metal atoms: shaded circles; sulfur atoms: open circles; alkyl chains: rounded rectangles.

form of silver nitrate or cupric nitrate. The alkanethiol is dissolved in an organic solvent (toluene). When the two immiscible phases are brought into contact the metal–alkanethiolate material appears near the interface as a solid suspension in the organic phase. The reaction can take several hours to complete, and can be accelerated by mixing.

The reaction to form the silver–alkanethiolate material can be written as follows:

(The product will be abbreviated as AgSC($n + 1$)). The exchange between the proton from the alkanethiol and the silver ion is confirmed by an analysis of the aqueous phase after the completion of the reaction: the pH of this phase is greatly diminished and no silver can be detected via precipitation with Cl^- .

The two phases are then separated, the organic phase is washed several times with water, and the suspension is collected by centrifuging. The resulting powder is washed several times with toluene and centrifuged again to purify. Analyses by elemental and neutron activation analysis (Table 1) confirm that the stoichiometry is exactly 1:1 (metal-to-alkanethiolate).

The following is an example of the synthetic conditions of AgSC12: 0.2 mL $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ (~0.84 mmol) in 15 mL toluene was added to 0.10 g AgNO_3 (~0.59 mmol) in 30 mL H_2O with stirring. After 1 h, the aqueous phase is clear and the measured pH is 1.5. The precipitate in the organic phase was washed three times with 50 mL H_2O , then three times with 50 mL toluene, then vacuum dried.

Table 1. Measured and calculated composition (%) of AgC12 and CuC12.

	C	H	S	Metal
Silver	46.7 ^a	8.2 ^a	10.4 ^a	36 ^b
	46.6 ^c	8.1 ^c	10.4 ^c	34.9 ^c
Copper	54.4 ^a	9.7 ^a	12.4 ^a	—
	54.4 ^c	9.5 ^c	12.1 ^c	24.0 ^c

^aElemental analysis measurements, $\pm 0.2\%$.

^bNeutron activation measurement, $\pm 2\%$.

^cCalculated based on a 1:1 stoichiometry.

In the case of the copper–thiolate material, the reaction is slightly more complex. Since the starting material is in the Cu(II) oxidation state, it must be reduced during the reaction. Elemental analysis (Table 1) proves that the final product has a 1:1 metal-to-thiolate stoichiometry. Our copper–thiolate material is probably similar to a precipitate that was synthesized as part of a study of multilayer films on copper (7), although the structure of that material was not determined. In that work it was suggested that copper may be reduced when two thiols react to form a disulfide. It is also possible that nitrate groups can be oxidized and liberated as gaseous products during the reaction. The overall reaction tends to be slower for copper, compared to silver, perhaps because of this extra complexity.

Both silver and copper thiolate materials have been synthesized using a variety of chain lengths. The resulting AgSC7–AgSC18 powders are pale yellow in colour. Shorter chains routinely produce bright yellow powders. Natan and co-workers have made an extensive study of butane thiolate (6), and found that powders of either colour can be produced by varying the synthesis conditions. They have labeled these materials *trans* and *gauche*, since the bright yellow *gauche* material has been found to contain *gauche* conformational defects in the alkyl chain. It was previously demonstrated that the yellow colour correlates to a trigonal sulfur-to-metal coordination, in contrast to a digonal coordination for white compounds (8). Finally, our copper material has a pale green colour (CuSC8, CuSC12, and CuSC18 have been studied to date).

Both silver and copper materials often have the form of small, flat sheets (flakes). The largest size flakes are seen in the copper material, sometimes being several millimeters long and wide. It has also been observed that both materials can turn black, either as a result of heating or aging. Curiously, no significant change in composition or structure has been detected that correlates to this alteration.

The structure

Powder X-ray diffraction (XRD) measurements of both the Ag and Cu materials are dominated by lines that can be indexed to the interlayer spacing of the two-dimensional layered structure illustrated in Fig. 1, as shown in Fig. 2. It is worth noting that there is a complete absence of lines corresponding to the bulk (three-dimensional) metal structure. We have observed the latter in measurements of thiolate-capped metal nanoparticles, which were also produced using chemical synthesis (9, 10). Clearly, the procedures used in the present work result in a very different material.

Fig. 2. XRD patterns of the CuSC12 and AgSC12 layered materials. Lines indexed to the interlayer spacing ($0k0$) are labeled. The line assigned to the in-plane structure is indicated by an asterisk.

The interlayer spacings of the Ag and Cu materials determined in this way are 35.0 ± 0.2 Å and 35.6 ± 0.2 Å, respectively. These distances are not consistent with the smaller copper radius, which could make the central layer smaller. Figure 1 indicates that the alkyl chains can be tilted with respect to the direction normal to the central plane of metal atoms. It is therefore likely that the two materials have a different chain tilt angle. A preliminary analysis of the data, for all measured chain lengths, indicates that the tilt angles with respect to the surface normal are $12 \pm 3^\circ$ and $10 \pm 3^\circ$ for Ag and Cu, respectively. It is not possible at present to determine whether the tilted chains adopt the herringbone structure shown in Fig. 1, or some other combination of positive and negative tilt angles.

The tilt angle of the silver layered materials compares well to the value of $13 \pm 2^\circ$ obtained by Laibinis et al. (2) for alkanethiolate SAMs on silver surfaces. Their angles were determined from a detailed modeling of the infrared spectra. For comparison, it is generally accepted that alkanethiolate SAMs on gold surfaces are more tilted, with values ranging from 26° to 34° , as determined by IR (2) and XRD (11) measurements. It is often speculated that tilting is driven by the optimization of van der Waals interactions between alkyl chains, due to the mismatch between the metal surface lattice and the close-packed spacing in bulk alkanes. However, it is worth noting that both Ag(111) and Au(111) have virtually identical lattice constants. While SAMs on Au(111) form a commensurate $\sqrt{3} \times \sqrt{3}$ structure, it is now known that SAMs on Ag(111) are in fact incommensurate with the underlying silver lattice (12–14). The measured overlayer lattice constant is 4.4–4.8 Å, as compared to 5.0 Å on Au(111). This would explain the smaller tilt angle observed for SAMs on Ag(111). Further, the driving forces for this incommensurate structure of these SAMs is undoubtedly related to the assembly mechanism of the layered material.

Fig. 3. Top view of the central plane. Metal atoms: shaded circles; sulfur atoms: open circles; alkyl chains: not shown. The row-to-row spacing is shown.

We can now add to this discussion the tilt angle of $\sim 11^\circ$ determined for the copper layered material. Since copper is significantly smaller than both silver and gold, it is logical to expect that the alkyl chains would be packed closer together, and there would be less of a tendency to tilt. Other factors will certainly play a role as well, such as the inherent metal–sulfur–carbon bond angle, and fine details of the alkyl chain packing.

Previous studies of silver layered materials were not able to determine the in-plane structure from XRD measurements (4, 6). A new proposal for the in-plane structure is shown in Fig. 3. It features a plane of metal atoms that adopt a hexagonal structure. By placing sulfur atoms in the digonal (two-fold bridging) sites shown, they template a close-packed arrangement of the attached alkyl chains (which are not shown in this view). This is the main feature that separates this model from previous models (4, 6). A close examination of Fig. 3 shows that digonal bonded sulfur atoms appear both above and below the plane, which results in the formation of long rows composed of covalently bonded metal–sulfur units. These rows run horizontally in the drawing. The digonal bonding of the S atoms is confirmed by the pale yellow colour of the Ag material (8). Other structural features remain to be determined, such as the possible buckling of metal atoms in the central plane.

We have observed a number of XRD lines, both sharp and broad, that do not shift when the chain length is varied. They probably originate from the in-plane structure. For example, there is sharp peak at 4.55 ± 0.03 Å and 4.47 ± 0.04 Å for the Ag and Cu materials, respectively (see Fig. 2). This is much less than the difference in the size of the metal atoms (Ag is 13% larger than Cu), and indicates that chain packing plays a significant role in determining the in-plane lattice distances. The slightly smaller size of the Cu lattice is also consistent with the observed smaller tilt angle.

Vibrational spectroscopy

Previous studies of alkyl chain systems have shown that many spectral features are highly sensitive to the chain conformational order. Figure 4 shows transmission IR spectra of the AgSC12 and CuSC12 materials. It is first evident that there are a large number of sharp, well-resolved peaks. This is different from IR measurements on monolayers,

Fig. 4. Transmission FTIR spectra of the CuSC12 and AgSC12 layered materials. Peak positions and assignments are given in Table 2.

where signal levels are too low to permit detailed observation of the low-wavenumber region (2, 15). The spectra are also more detailed than those reported for thiolate capped nanoparticles (9, 10).

The degree of order can be better quantified by a detailed analysis of the peaks, whose positions are summarized in Table 2. The CH_2 stretching peaks, which can be measured with sensitivity in all alkyl chain systems, are known to shift to lower frequency with increasing conformational order. In general, antisymmetric (d^-) peaks at $2918\text{--}2920\text{ cm}^{-1}$ and below are typical of ordered solid systems, where all-*trans* chain conformations predominate. In liquid (disordered) systems, the peaks tend to be above 2920 cm^{-1} , indicating large percentages of *gauche* conformational defects in the chains (16–18). As seen in Table 2, the layered materials are clearly characterized by all-*trans* chain conformations. For all the chain lengths studied, values of $2915\text{--}2917\text{ cm}^{-1}$ and $2917\text{--}2920\text{ cm}^{-1}$ have been found for Ag and Cu, respectively. By comparison, well-ordered monolayers (2) on gold surfaces and thiolate-capped gold nanoparticles (9, 10) are typically characterized by d^- peak values of $2918\text{--}2920\text{ cm}^{-1}$. (In all

Table 2. Peak positions (in cm^{-1}) and assignments for AgSC12 and CuSC12 layered materials. The nomenclature conforms to refs. 2 and 21.

Assignment	AgSC12		CuSC12	
r_a^-	2958	sh	2960	sh
r_b^-	2953	s	2954	s
FR	2934	m	2939	m
d^-	2916	vs	2918	vs
FR	2895	sh	2890	sh
r^+	2872	m	2873	m
d^+	2847	vs	2849	vs
δ	1469	vs	1470	vs
δ_s	1423	s	1424	s
U	1377	m	1376	m
	1356	m		
W_7	1339	w		
W_6	1318	w	1319	vw
W_5	1293	s	1293	s
W_4	1267	s	1266	s
W_3	1240	s	1238	s
W_2	1212	s	1210	s
W_1	1186	s	1184	s
R_2	1127	vw	1130	s
R_3	1081	w	1082	vw
R_n	1067	s	1068	s
P_{11}	1028	m	1028	m
P_{10}	983	w	981	w
P_9	932	m	930	m
β	891	w	890	w
P_8	879	vw	877	w
P_7	828	m	825	m
P_6	784	vw	783	w
P_5	753	s	751	s
P_4	734	w		
P_3	724	sh		
P_1	720	vs	718	vs

cases, the higher wavenumbers are systematically observed to occur with shorter chain lengths.) It can therefore be concluded that the layered materials are the most highly ordered (in terms of chain conformational order) of all the thiolate self-assembled systems. This is probably because in other systems the metal lattice is constrained by sub-surface metal atoms, whereas there will be more flexibility in the single layer of metal atoms in the layered materials, producing less strain in the alkyl chain structure.

A preliminary temperature-dependent study indicates that this order remains right up to the disordering transition, at about 402 K for AgSC12 and 416 K for CuSC12. This would be in contrast to temperature-dependent studies of SAMs on gold (12, 19, 20) and thiolate-capped gold nanoparticles (10), where a more continuous shift as a function of temperature is observed. Perhaps more importantly, the disordering of those systems occurred at a much lower temperature (at or below 350 K).

A second measure of order is the observation of peaks that belong to the wagging (W_x) and rocking–twisting progressions (P_x), located in the $1180\text{--}1350\text{ cm}^{-1}$ and $715\text{--}1030\text{ cm}^{-1}$ ranges, respectively. These progressions result from the coupling

of n identical methylene oscillators (21). They have been observed in the spectra of solid alkanes (21) and lipid bilayers (18), and they were previously used as order parameters (18). They have not been previously observed for thiolate monolayers, but they were observed, less well resolved, with thiolate-capped nanoparticles (9). Because the peaks are so clearly resolved in the present case, it has been possible to assign each individual peak. As seen in Table 2, both silver and copper layered materials have virtually identical peak values, indicating a similar chain conformation in both cases. Clearly, the different tilt angles do not affect the chain conformation. Once again, preliminary temperature-dependent studies indicate that a high degree of order remains right up to the phase transition that occurs above 400 K.

The peak that is labeled as δ_s in Table 2 is assigned as the CH_2 bending mode arising from the carbon atom that is bonded to S, and it is observed between 1421 and 1425 cm^{-1} . This was previously suggested by Murray and co-workers (9) based on measurements of thiolate-capped gold nanoparticles, where it is observed at 1414–1423 cm^{-1} . There is no obvious correlation to the nature of the metal atom, the tilt of the chain, or the length of the chain.

Because the spectra are composed of well-resolved peaks on a flat background, it is possible to comment on the absence of small peaks that are known to be associated with conformational defects. It has been established that peaks at 1338 cm^{-1} , 1368/1308 cm^{-1} , and 1344 cm^{-1} can be assigned to double *gauche*, internal kink, and end-*gauche* defects, respectively (22). These peaks are systematically absent from spectra of layered materials, for all chain lengths, both Ag and Cu. In contrast, some end-*gauche* defects were observed on thiolate-capped nanoparticles, where domain sizes are much smaller, and where there may be less end-to-end packing.

Information about conformational defects can also be obtained from C–C stretching peaks. In solid alkanes, these peaks form the progression labeled as R_x . The evolution of these peaks as a function of the chain length of these peaks is less systematic than the W_x and P_x series, but we have tentatively assigned three peaks in both AgSC12 and CuSC12 to this series. A detailed Raman study of this region exists for solid alkanethiols and thiolate monolayers (23). In the case of the former, three peaks are systematically observed at values close to those shown in Table 1, and all three are assigned to the *trans* conformation. One issue yet to be resolved is the fact that the peak at 1068 cm^{-1} is consistently the most intense peak in this series, and it is not clear why. Secondly, the peak at 1131 cm^{-1} is anomalously intense in the CuSC12 material, compared to all others. It is perhaps worth noting that the CuSC12 material is slightly less conformationally ordered than the AgSC12 material, as judged by peak positions and shapes.

Taking all of the above observations together, it is clear that the self-assembly process of the layered materials allows the alkyl chains to adopt an all-*trans* configuration. This will allow for the full optimization of the attractive interactions between the chains. Further, the organization of the thiolate groups appears to create a stabilization of the entire structure. In addition to the preliminary temperature-dependent studies, it should be mentioned that the short-chain materials that have been synthesized are also highly ordered. For example, the AgSC7 material has a d^* wavenumber at

2917 cm^{-1} , and 12 peaks assigned to progressions are clearly resolved. At room temperature, bulk alkanes and lipid bilayers of similar chain length are disordered. A similar stabilization of the alkyl chains occurs in other thiolate systems. Although some authors have suggested that short-chain systems are disordered at room temperature, there are now clear indications that it is indeed possible to have ordered thiolate monolayers and thiolate-capped nanoparticles with very short chains (9, 24). Combined with results from the layered materials, one can now say that self-assembled alkanethiolate systems have an inherent stabilization, with the layered materials being the most stable.

Conclusions

Layered materials composed of silver and copper thiolates have been synthesized and analyzed. They form a highly ordered bilayer structure, characterized by tilted, all-*trans* alkyl chains. A new model for the in-plane structure has been presented that is based on a hexagonal arrangement of metal atoms in the central plane. These systems lend themselves to detailed analysis by a large number of techniques, which makes them an excellent model system for other metal-thiolate materials.

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References

1. R.G. Nuzzo and D.L. Allara. *J. Am. Chem. Soc.* **105**, 4481 (1983).
2. P.E. Laibinis, G.M. Whitesides, D.L. Allara, Y.-T. Tao, A.N. Parikh, and R.G. Nuzzo. *J. Am. Chem. Soc.* **113**, 7152 (1991).
3. A. Ulman. *Chem. Rev.* **96**, 1533 (1996).
4. I.G. Dance, K.J. Fisher, R.M. Herath Banda, and M.L. Scudder. *Inorg. Chem.* **30**, 183 (1991).
5. M.J. Baena, P. Espinet, M.C. Lequerica, and A.M. Levelut. *J. Am. Chem. Soc.* **114**, 4182 (1992).
6. H.G. Fijolek, J.R. Grohal, J.L. Sample, and M.J. Natan. *Inorg. Chem.* **36**, 622 (1997).
7. H. Kellor, P. Simak, W. Schrepp, and J. Dembowski. *Thin Solid Films*, **244**, 799 (1994).
8. I.G. Dance, L.J. Fitzpatrick, A.D. Rae, and M.L. Scudder. *Inorg. Chem.* **22**, 3785 (1983).
9. M.J. Hosterler, J.J. Stokes, and R.W. Murray. *Langmuir*, **12**, 3604 (1996).
10. A. Badia, S. Singh, L. Demers, L. Cuccia, R.G. Brown, and R.B. Lennox. *Chem. Eur. J.* **2**, 359 (1996).
11. P. Fenter, P. Eisenberger, P. Burrows, S.R. Forrest, and K.S. Liang. *Physica B (Amsterdam)*: **221**, 145 (1996).
12. P. Fenter, P. Eisenberger, N. Camillone III, S. Bernasek, G. Scoles, T.A. Ramanarayanan, and K.S. Liang. *Langmuir*, **7**, 2013 (1991).
13. R. Heinz and J.P. Rabe. *Langmuir*, **11**, 506 (1995).
14. A. Dhirani, M.A. Hines, A.J. Fisher, O. Ismail, and P. Guyot-Sionnest. *Langmuir*, **11**, 2609 (1995).
15. R.G. Nuzzo, E.M. Korenic, and L.H. Dubois. *J. Chem. Phys.* **93**, 767 (1990).

16. R.G. Snyder, H.L. Strauss, and C.A. Elliger. *J. Phys. Chem.* **86**, 5145 (1982).
17. D.G. Cameron, H.L. Casal, and H.H. Mantsch. *Biochemistry*, **19**, 3665 (1980).
18. L. Senak, D. Moore, and R. Mendelsohn. *J. Phys. Chem.* **96**, 2749 (1992).
19. L.H. Dubois, B. Zegarski, and R.G. Nuzzo. *J. Electron Spectrosc. Relat. Phenom.* **54/55**, 1143 (1990).
20. F. Bensebaa, T.H. Ellis, A. Badia, and R.B. Lennox. *J. Vac. Sci. Technol. A*: **13**, 1331 (1995).
21. R.G. Snyder and J.H. Schachtschneider. *Spectrochim. Acta*, **19**, 85 (1963).
22. R.G. Snyder. *J. Chem. Phys.* **47**, 1316 (1967).
23. M.A. Bryant and J.E. Pemberton. *J. Am. Chem. Soc.* **113**, 8284 (1991).
24. K.D. Truong and P.A. Rowntree. *J. Phys. Chem.* **100**, 19917 (1996).