Self-assembled thin films from lamellar metal disulfides and organic polymers

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The intercalation/exfoliation reactions of MoS2 and SnS2 yield lamellar colloids, which may be grown layer-by-layer on cationic surfaces by alternate adsorption of cationic clusters or polymers.

Over the past several years, self-assembly has become increasingly useful as a simple and inexpensive method for making functional thin films. While much of this work has focused on organic monolayers, inorganic surface heterostructures are also interesting because of the structural, magnetic, electrochemical and other properties associated with inorganic compounds. Unfortunately, to date, the building blocks of these thin films have been electronic insulators: clays, metal phosphates and lamellar oxides. Here, we report the successful extension of this technique to lamellar chalcogenides, which in bulk form are semiconductors, semimetals, and metals. These materials have been used previously to prepare interesting bulk compounds. Unfortunately, to date, the building blocks of these thin films have been electronic insulators: clays, metal phosphates and lamellar oxides. Here, we report the successful extension of this technique to lamellar chalcogenides, which in bulk form are semiconductors, semimetals, and metals. These materials have been used previously to prepare interesting bulk nanocomposites.

Lamellar metal disulfides (MoS2, SnS2) were reductively intercalated by reaction with excess Bu4Li in hexane, then added to water to make exfoliated suspensions that were approximately 5 mass% MS2. As prepared, these suspensions were basic, but upon dilution to 1 mass%, the pH decreased to 8–9. Attempts to lower the pH further resulted in flocculation. These 1% suspensions were stable for periods of days (orange–brown SnS2) to weeks (brown–black MoS2), and transmission electron microscopy (Fig. 1) revealed intact single- and multiple-sheet aggregates ranging in lateral dimensions from ca. 20–500 nm.

Growth of the metal disulfide films was initiated by first priming polished silicon wafers with a cationic monolayer. This was accomplished by hydroxylating the surface, by 30 min sonication in piranha solution (4:1 conc. H2SO4–30% H2O2), and then adsorbing a monolayer of aluminium Keggin ions [Al13O4(OH)24(H2O)12]7+. (5 min adsorption from an 80 °C aqueous solution of the chloride salt), or poly(allylamine hydrochloride), PAH (15 min adsorption from a 0.01 M aqueous solution at pH 8 and ambient temperature). Both surface priming procedures create a high charge density surface, which binds the anionic MS2 sheets. The first monolayer of MS2 sheets was adsorbed by immersing the primed silicon into the appropriate colloidal suspension for 15 min, and rinsing with water. These MS2 monolayers tile the surface incompletely, as shown in tapping-mode atomic force microscopy (AFM) images, Fig. 2. The adsorption process appears to select relatively small sheets from the broad distribution of sizes present in the colloid (Fig. 1). Surface coverage was estimated at about 75% for MoS2 on the Al-Keggin-primed surface, and about 50% on the PAH-primed surface. While it was not possible to resolve the lattice structure of the MS2 sheets, AFM line scans over the terraces of sheets showed mean roughness of the order of 1–2 Å, consistent with exposure of the basal planes. The step height from the primed substrate to the top of the sheets was typically 13–15 Å, which corresponds roughly to the thickness of a single layer of MoS2 sheets (6 Å) plus a layer of hydrated Li+ cations.

Multilayer films were grown by sequentially adsorbing the MS2 colloids and polymeric PAH cations in 15 min cycles, with intermediate washing steps. The layer growth was monitored by ellipsometry, transmission UV–VIS spectroscopy (using quartz substrates), and AFM. The observed change in average layer thickness per adsorption cycle, Fig. 3, was consistently 14.8(3) Å per layer pair for MoS2/PAH and 23.8(3) Å for SnS2/PAH. UV–VIS spectra confirmed the regular stepwise growth of film thickness. In the case of MoS2, the layer pair thickness is approximately that expected for a monolayer of PAH plus a single sheet of MoS2, whereas for SnS2 it is apparent that more than one monolayer is deposited in each adsorption cycle. Consistent with this observation, TEM studies of the SnS2 colloid show that it is not completely exfoliated. For both MoS2 and SnS2, the layer pair thickness was quite insensitive to the adsorption time, up to several hours. This observation is consistent with the model of electrostatic self-assembly as a self-limiting process in which film growth ceases once the layer charge is inverted by adsorption of poly-anions or -cations.

In contrast to the more regularly tiled surfaces observed with zirconium phosphate/polymer multilayers, AFM images of the MoS2 multilayer films reveal a 'spongy' morphology, in which sheets and polymer appear randomly oriented. The rms roughness of a four layer pair film of MoS2/PAH was 16 Å on the PAH-anchored substrate, and 8 Å on the Al-Keggin derivatized surface. This is consistent with the model proposed by Kleinfeld and Ferguson for multilayer growth on islands, which eventually coalesce into smoother films. The more densely tiled first monolayer that grows on the Keggin-primed surface yields a smoother film after a few layers are grown. XPS analysis of Si–SiOx–Al Keggin–(MoS2–PAH)x–MoS2 (n = 0, 3; Table 1) films confirms that the sheets are intact and cover the surface relatively well after deposition of four layers. In the monolayer spectra, the surface coverage is low and the XPS spectrum is dominated by adventitious carbon and signals from the Si/SiO2 substrate. Both Mo and S are present in the film, but their ratio cannot be determined accurately because of counting errors. With multilayer films, the Si, Al and O signals from the buried substrate and primer layer are attenuated relative to Mo and S, which are present in the expected 1:2 ratio.

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The basal plane surface of MS₂ colloids is relatively non-polar, relative to previously studied clay, metal oxide and metal phosphate lamellar colloids. MoS₂ and SnS₂ exfoliated colloids can be re-stacked by neutral polymers, such as poly(ethylene oxide), PEO. Accordingly, the cationic PAH polymer was replaced by a solution of neutral PEO, and multilayer films were grown by the same method. The film growth, monitored by ellipsometry and UV–VIS spectroscopy, is regular and the trend is similar to that found with PAH, 15 Å per layer pair with MoS₂ and 35 Å per layer pair with SnS₂. Apparently, PEO complexes the Li⁺ ions that charge-compensate the colloid sheets, much as it does in the bulk intercalation compounds. This interaction is sufficiently strong to persistently bind sequentially adsorbed layers.

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Notes and References

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