CHEMISTRY OF MATERIALS

VOLUME 12, NUMBER 9 SEPTEMBER 2000

Communications

Self-assembly of Tiled Perovskite Monolayer and Multilayer Thin Films

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Received May 17, 2000
Revised Manuscript Received July 30, 2000

Layer-by-layer chemical adsorption is a convenient way to make thin films of materials with specific stacking sequences.[1] These complex superstructures are not easily attained in bulk materials, and in some cases they have interesting optical[2] and electronic[3] properties. One of the outstanding challenges in this area is to devise synthetic methods that give well-ordered monolayer and multilayer thin films from inorganic precursors with specific electronic, magnetic, optical, catalytic, and other properties. Toward this goal, perovskite compounds, which are well-known as ferroelectrics,[4]

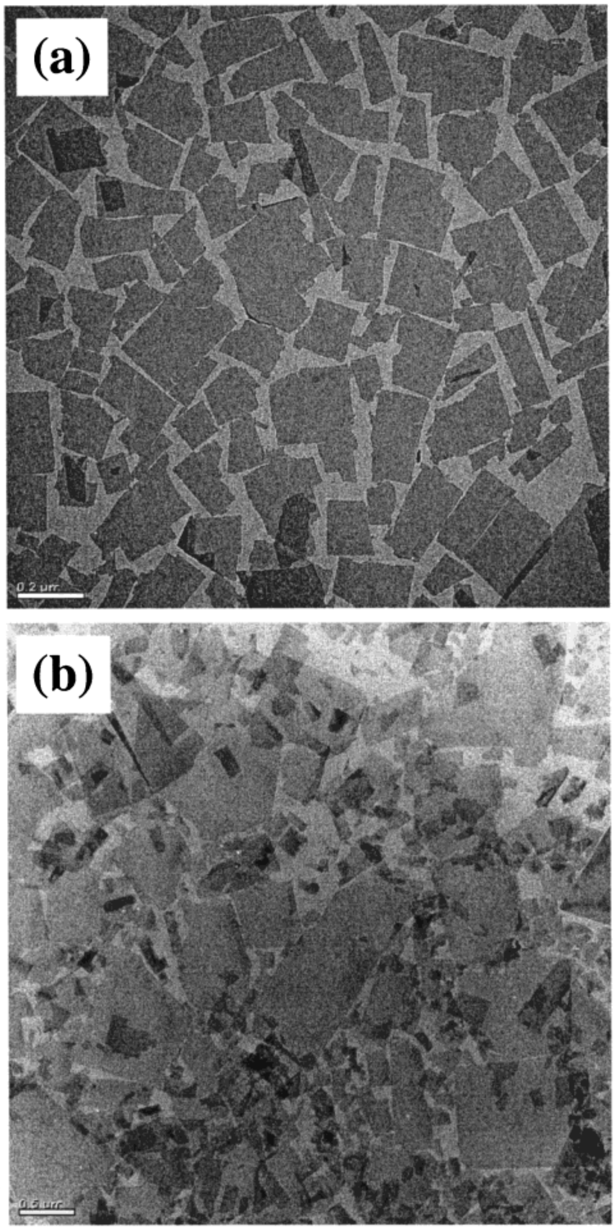

Figure 1. TEM micrographs of (a) $TBA_xH_{1-x}Ca_2Nb_3O_{10}$ and (b) $TBA_xH_{1-x}Sr_2Nb_3O_{10}$ sheets. The scale bar is 200 nm in (a) and 500 nm in (b).

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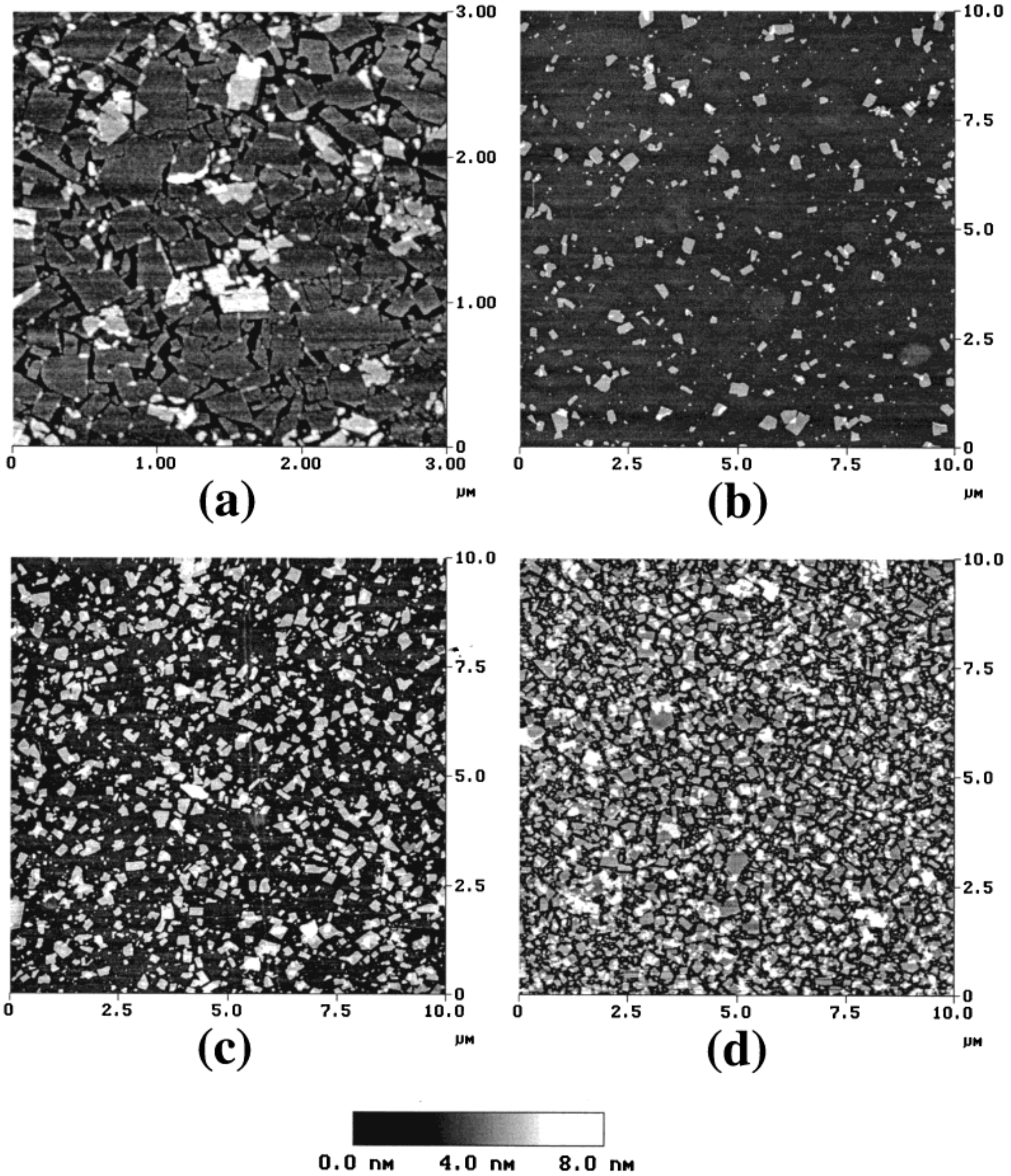

Figure 2. AFM images of TBA$_x$H$_{1-x}$Ca$_2$Nb$_3$O$_{10}$ monolayers. In (a), pH 8.4 sheets were adsorbed for 20 min near 40 °C. Sheets at pH 8.75 were adsorbed at 27 °C for (b) 20 s, (c) 1.5 min, and (d) 20 min.

superconductors,[5] magnetoresistors,[6] and superconductors,[7] are interesting building blocks for layered assemblies.

Protonated members of the Dion−Jacobson series of layered perovskites[8] are well-known to react with Brønsted bases. This reaction can lead to delamination of the solid into colloidal sheets if the base contains a large alkylammonium cation.[9] The colloidal sheets can be reassembled layer by layer on a cationic substrate,[10] but the resulting thin films suffer from incomplete coverage and significant overlap of sheets. There is a narrow pH range in which high-quality tiled monolayers of HTiNbO$_5$[10] and α-Zr(HPO$_4$)$_2$·H$_2$O[11] can be grown on an ionizable polycation such as poly(allylamine hydrochloride) (PAH), but pH control alone is insufficient to induce surface tiling in the perovskite systems. By using the pH-independent polycation poly(diallyldimethylammonium chloride) (PDDA) instead of PAH, we eliminated the influence of pH on the substrate charge density and focused on adsorption time, temperature, and pH (for controlling the negative charge on the sheets). We report here that when the temperature and pH are controlled during the adsorption process, high-quality tiled monolayers of perovskite sheets form over a wide range of other conditions. This robust layer-by-layer assembly method can be applied to a variety of

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Dion−Jacobson precursors to synthesize multilayer thin film heterostructures.

$KCa_2Nb_3O_{10}$, $KSr_2Nb_3O_{10}$, $RbCaLaNb_2TiO_{10}$, and $RbLaNb_2O_7$ were synthesized by conventional solid-state reactions and were proton-exchanged in 2 M HNO_3. The protonated phases were exfoliated by reaction for several days with a 20-fold molar excess of tetra-(*n*-butyl)ammonium hydroxide (TBA^+OH^-). A transmission electron microscope[12] (TEM) image of sheets of $TBA_xH_{1-x}Ca_2Nb_3O_{10}$ ($x \approx 0.15-0.20$ for all of the exfoliated Dion−Jacobson phases, as determined by CHN analysis[13]) is shown in Figure 1a. The $TBA_xH_{1-x}Ca_2Nb_3O_{10}$ sheets have average lateral dimensions of 100−400 nm, although smaller and larger sheets are also seen. $TBA_xH_{1-x}Sr_2Nb_3O_{10}$, $TBA_xH_{1-x}CaLaNb_2TiO_{10}$, and $TBA_xH_{1-x}LaNb_2O_7$ sheets appeared similar, although these compounds tended to produce larger sheets with a larger polydispersity (Figure 1b). Layer spacings, from X-ray diffraction data of the protonated compounds, agree well with ellipsometric thickness data and AFM height scans obtained after monolayer adsorption. This confirms that the adsorbed sheets, which appear to have low and uniform contrast in the TEM micrographs, are indeed unilamellar.

The colloidal suspensions were allowed to settle for at least 2 h (to allow the largest sheets and any unexfoliated material to settle to the bottom) and then were diluted by a factor of 10 and adjusted to the standard pH of 8.75[10] using 0.01 M HCl. A Si(100) substrate, sonicated for 15 min in piranha solution (1:4 H_2O_2:H_2SO_4) to expose a clean SiO_2 surface, was derivatized in 20 mM PDDA for 5 min. After thorough rinsing, the substrate was placed in a preheated suspension of sheets for 20 min without stirring. The adsorption temperatures, kept constant to within ±2 °C, spanned the range from 20 to 45 °C. Adsorption temperatures below 25 °C gave partial coverage and overlap of sheets. However, at temperatures between 25 and 40 °C, the sheets completely and uniformly tiled the surface. An AFM image of a typical Si/SiO_2/PDDA/$TBA_xH_{1-x}Ca_2Nb_3O_{10}$ surface is shown in Figure 2d.[14] At higher temperatures (>40 °C), the sheets tend either to restack on the silicon substrate as a thick film or to aggregate and precipitate from the colloidal suspension.

The added thermal energy provided by heating the sample during adsorption allows the strongest attractive interactions (anionic sheets−cationic polymer) to dominate. This same idea is the key to successful thin film growth using other molecular techniques such as atomic layer epitaxy.[15] While the sheets tile to best cover the surface, there are uniform lateral gaps that are presumably due to the electrostatic repulsion between the negatively charged sheets. By lowering the pH to 8.4 (which decreases the negative charge on the sheets) and increasing the temperature to near 40 °C (to overcome some of the anionic repulsion), the densely tiled surface shown in Figure 2a can be obtained. In this case, the lower charge density allows the sheets to come into closer proximity. Higher pH values (8.6−9.4) cause more sheet−sheet repulsion and result in tiling like that shown in Figure 2d.

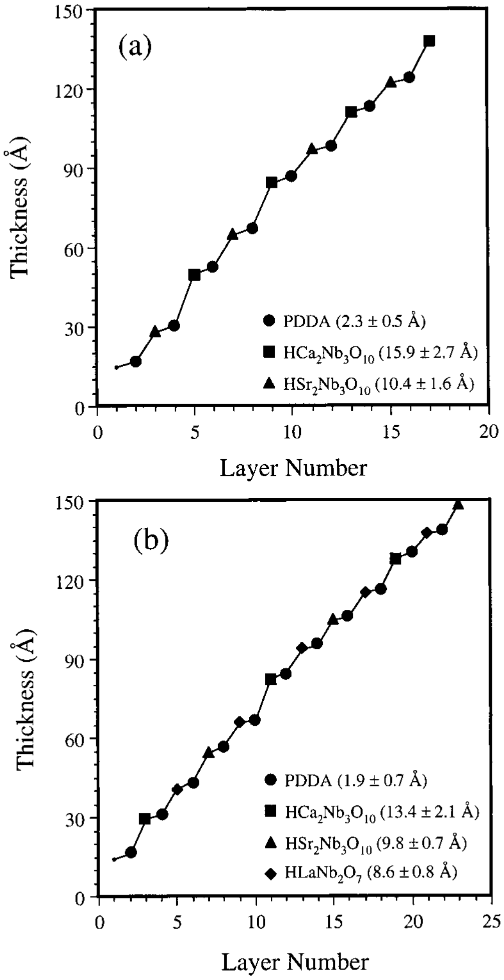

Figure 3. Ellipsometric film thickness plots for (a) ($HSr_2Nb_3O_{10}$/PDDA/$HCa_2Nb_3O_{10}$/PDDA)$_n$ and (b) ($HCa_2Nb_3O_{10}$/PDDA/$HLaNb_2O_7$/PDDA/ $HSr_2Nb_3O_{10}$/PDDA/$HLaNb_2O_7$/PDDA)$_n$ multilayer sequences.

When the pH is fixed at 8.75 and the temperature at 27 °C, the kinetic snapshots shown in Figure 2b−d were obtained. After 20 s, only a few percent of the surface is covered by sheets, as shown in Figure 2b. After 1.5 min (Figure 2c), the surface is more densely covered, but coverage is still incomplete. Beyond 10 min, full surface coverage is obtained (Figure 2d). Unlike systems such as $HTiNbO_5$[10] and α-$Zr(HPO_4)_2 \cdot H_2O$,[11] in which an intermediate pH provides moderate surface charge that supports reversible adsorption, the data in Figure 2 are more consistent with a mechanism that involves irreversible adsorption of sheets to the surface. Over time, more and more sheets adhere to bare areas of the cationic substrate, and the added thermal energy disfavors overlapping. As for similar systems based on electrostatic assembly,[1] the film thickness is self-limiting to a single monolayer because adsorption ends when all of the positive charge is compensated by negative charge.

Because dense monolayers can easily be made with a variety of Dion−Jacobson phases, it is possible for the

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(12) TEM images were obtained using a JEOL 1200EXII microscope at 80 kV at the Electron Microscope Facility for the Life Sciences in the Biotechnology Institute at the Pennsylvania State University. The colloids were imaged on Formvar-coated Cu grids.

(13) Elemental analysis for C, H, and N were performed by Atlantic Microlabs, Inc., Norcross, GA.

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first time to prepare multilayer heterostructures with perovskite-block stacking sequences that are inaccessible in bulk compounds. By sequentially adsorbing PDDA and heated suspensions of $TBA_xH_{1-x}Ca_2Nb_3O_{10}$ and $TBA_xH_{1-x}Sr_2Nb_3O_{10}$ sheets, we synthesized a PDDA polymer intercalation compound of $HA_2Nb_3O_{10}$ (A = Ca, Sr) that has perovskite-block A-site cations ordered in successive triple layers. The ellipsometric thickness data are shown in Figure 3a. The sequence represented by ellipsometry data in Figure 3b, containing alternating $HCa_2Nb_3O_{10}$/$HLaNb_2O_7$/ $HSr_2Nb_3O_{10}$/$HLaNb_2O_7$ layers (interleaved with PDDA), is an intergrowth of the $n = 2$ Dion−Jacobson phase $HLaNb_2O_7$ and the $n = 3$ phase $HA_2Nb_3O_{10}$, with the A-site cations ordered in their respective layers. The thicknesses of the layers of the thin-film intercalation compounds as determined by ellipsometry are consistent with their crystallographic thicknesses and the density of surface tiling, within experimental error.

This work presents a robust technique for preparing high-quality tiled monolayer and multilayer thin films of intercalation compounds that are based on the Dion−Jacobson series of layered perovskites. Using this technique, it may be possible to improve the quality of thin films derived from other lamellar solids, including MoS_2,[16] graphite oxide,[17] layered double hydroxides,[18] and the Ruddlesden−Popper series of layered perovskites.[19] It may also be possible to apply to the thin films the topochemical reactions that convert layered perovskites into three-dimensional defective[20] and nondefective[21] phases. By adapting the optimized procedure presented here, one could assemble many new thin films and thin film heterostructures that are of sufficient quality to exhibit enhanced properties because the properties of perovskite materials (e.g., ferroelectricity,[4] superconductivity,[5] magnetoresistance,[6] and photocatalysis[7]) depend sensitively on composition and structure.

Acknowledgment. This work was supported by the National Science Foundation Grant CHE-9529202. Instrumentation for AFM experiments was provided by National Science Foundation Grant CHE-9626326. This material is based upon work supported under a National Science Foundation Graduate Fellowship.

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