Preparation and Characterization of a Novel Layered Perovskite-Type Organic/Inorganic Hybrid Material Containing Silica Networks

Z. Y. Cheng,[†] B. X. Gao,[†] M. L. Pang,[‡] S. Y. Wang,[†] Y. C. Han,*[,†] and J. Lin*[,‡]

State Key Laboratory of Polymer Physics and Chemistry and Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

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Recently, much attention has been paid to the perovskite-type organic/inorganic materials due to their unique electronic, optical, and magnetic properties.[1−3] This kind of material, generally expressed by $(R-NH_3)_2MX_4$ or $(NH_3-R-NH_3)MX_4$ (where R = organic group; M=divalent metal; X = halogen), consists of an extended network of corner-sharing metal halide octahedra, alternating with a bilayer or monolayer organic moiety.[1] $R-NH_3^+$ is generally a primary amine cation with a long and narrow profile to fit the inorganic framework. The ammonium heads of the cations hydrogen/ionic bond to the halogens in the inorganic sheets and the organic tails extend into the van der Waals gap. Here, the inorganic framework plays an important role of template keeping the regular arrangement of the organic molecules. How to exploit the influence of inorganic template to obtain a new structure or properties of organic component is desired. An interesting example is solid-state polymerization within the organic layer of perovskite structures.[4] In this case, the monomers of organic components are integrated into the perovskite framework containing the unsaturated groups (such as diene or diyne) and can be transformed into the polymers by exposure to UV or γ irradiation.

Enlightened by this idea, we have thought of 3-aminopropyltrimethoxysilane $H_2N(CH_2)_3Si(OCH_3)_3$ (APS), a well-known coupling agent with extensive applications. This compound possesses a flexible aminopropyl head that can be used for anchoring the inorganic framework, and the tail trimethoxysilane can be used as a sol−gel precursor to form the Si−O networks by hydrolysis and condensation. As a result, it is expected that the APS will be a suitable precursor forming the perovskite-type organic/inorganic material with cross-linked Si−O networks. Therefore, in this communication, the precursors APS and $PbCl_2$ were employed as organic and inorganic components, respectively, to form the layered perovskite-type organic/inorganic material. Scheme 1 presents the synthetic procedures and the expected structure of the final product. This material was observed to show the exciton emission from the $PbCl_4^{2-}$ inorganic layers and a strong blue emission related to the silica networks.

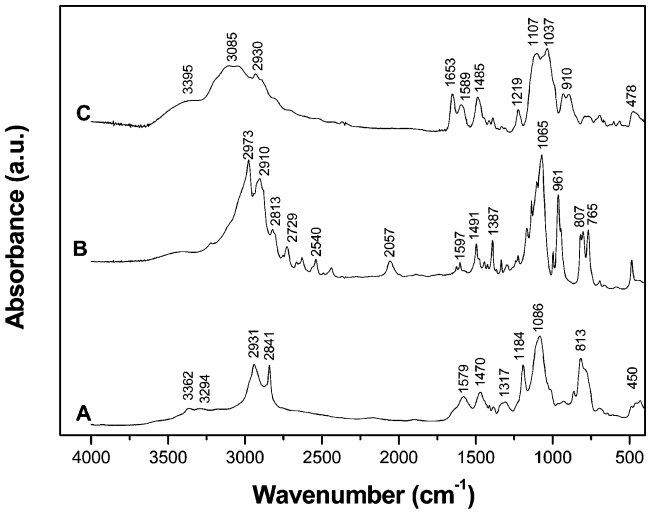

Figure 1. FT-IR spectra for 3-aminopropyltrimethoxysilane (APS, A, using liquid film on KBr crystal disk), amine salt of APS (APS·HCl, B, KBr pellet), and the layered perovskite with silica networks (APS·$PbCl_4$, C, KBr pellet).

The reaction processes were monitored by a FT-IR spectrum of each product. (A), (B), and (C) of Figure 1 show the FT-IR spectra for APS (I), APS·HCl (II), and the perovskite superstructure of APS·$PbCl_4$ (III), respectively. In Figure 1A for APS, the weak peaks at 3362 and 3294 cm^{-1} are due to asymmetric/symmetric N−H stretching vibration of primary amine ($-NH_2$). The locations and their assignments for other absorption peaks are 2931 (ν_{as}, CH_2), 2841(ν_s, CH_2), 1579(δ, NH_2), 1470(δ, CH_2), 1184 (ν_{as}, Si−CH_2), 1086 (ν_{as}, Si−OCH_3), 813 (ν_s, Si−OCH_3), and 450 cm^{-1} (δ, Si−OCH_3) (where ν_{as} = asymmetric stretching, ν_s = symmetric stretching, δ = bending), respectively.[5−7] Some changes can be observed in the FT-IR spectrum after the reaction of APS with HCl (in absolute alcohol solution), as shown in Figure 1B. In Figure 1B for APS·HCl (II), owing to the formation of the amine salt in an anhydrous environment, the absorption of the νNH_2 (3362, 3294 cm^{-1}) and δNH_2 (1579 cm^{-1}) in Figure 1A almost disappeared. Instead, νNH_3^+ (near 3000 cm^{-1}, asymmetric/symmetric stretching vibration) as a broad band superimposed with C−H stretching bands and a series of overtones peaks from 2000 to 2900 cm^{-1} was observed.[6] Furthermore, a strong new peak is presented at 961 cm^{-1} due to the stretching vibration of Si−OH, which probably results from the replacement of $-OCH_3$ in APS by the −OH of EtOH.[5] Great changes occurred

* Authors to whom correspondence should be addressed. E-mail, jlin@ns.ciac.jl.cn; fax, 86-431-5698041; tel., 86-431-5262031 (Prof. J. Lin); e-mail, ychan@ns.ciac.jl.cn (Prof. Y. C. Han).
[†] State Key Laboratory of Polymer Physics and Chemistry.
[‡] Key Laboratory of Rare Earth Chemistry and Physics.

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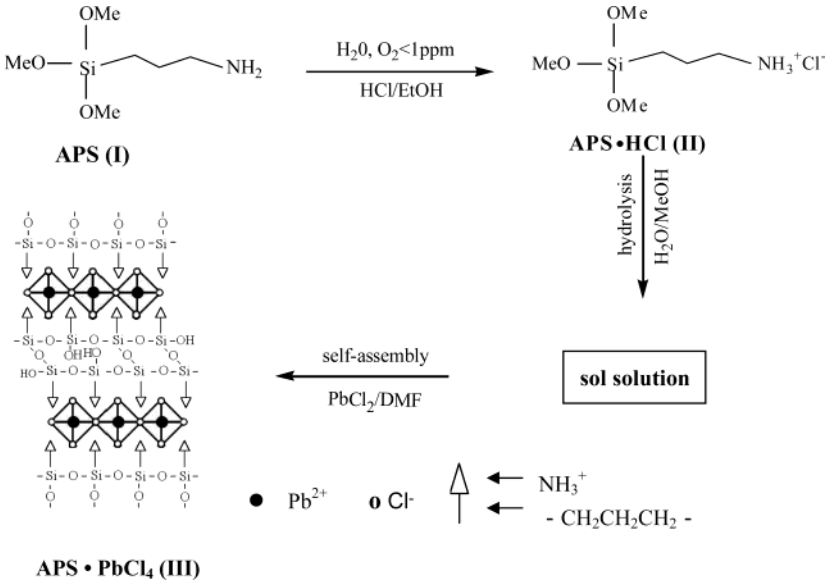
Scheme 1. Synthesis Procedures of the Layered Perovskite-Type APS·$PbCl_4$ Hybrid Material and Its Expected Structure



in the FT-IR spectrum of Figure 1C for APS·$PbCl_4$ (III) with respect to Figure 1B for APS·HCl (II). First, the peak around 3000 cm^{-1} of NH_3^+ headgroups in Figure 1B shifts to high energy (3085 cm^{-1}) and becomes broader in Figure 1C. This can be attributed to the different chemical environments of amine salt after self-assembling into the layered perovskite APS·$PbCl_4$ (III) compared with those in APS·HCl (II). In APS·$PbCl_4$ (III) the NH_3^+ headgroups align orderly and each NH_3^+ head is hydrogen-bonded to three halogens coordinated to Pb^{2+} in the inorganic framework,[8] while in APS·HCl (II) the NH_3^+ head is hydrogen and/or ionically bonded to free halogens. Second, the sharp peak of Si−OCH_3 (ν_{as} at 1065 cm^{-1}, Figure 1B) has been replaced by the broad and doublet peak at 1107 and 1037 cm^{-1} (ν_{as}, Si−O−Si, Figure 1C), which is characteristic of long-chain linear siloxanes and indicates the formation of Si−O−Si networks by the hydrolysis and condensation of APS.[9] Note that weak absorption peaks of the residual Si−OH groups at 3395 and 910 cm^{-1} and that of H_2O at 1653 cm^{-1} can still be observed in Figure 1C. Finally, it can be seen that the absorption peaks of −CH_2 (2930, 1485 cm^{-1}), Si−CH_2 (1219 cm^{-1}), and NH_2 (δ, 1589 cm^{-1}) still exist in Figure 1C for APS·$PbCl_4$ (III), indicating that −Si−CH_2−CH_2−CH_2−NH_2 chains remained in the material. This is consistent with the fact that no Si−C bond cleavage occurs during hydrolysis/condensation reactions.[10]

Further study by ^{29}Si solid-state NMR for APS·$PbCl_4$ (III) confirms the cross-linking of silicon atoms in this material, as shown in Figure 2. In this figure two intense signals at −69 and −61 ppm and a weak one at −51 ppm appeared, which are assigned to $SiC(OSi)_3$ (T^3), $SiC(OH)(OSi)_2$ (T^2), and $SiC(OH)_2(OSi)$ (T^1) substructures, respectively.[11,12] The integrated intensity ratio of T^3:T^2:T^1 is about 52:46:2. It is indicative of a highly condensed siloxane network with an average of one uncondensed OH group per two silicon atoms in APS·$PbCl_4$ (III).[11] These results are consistent with those observed in the FT-IR spectra (Figure 1). The organosiloxane with any alkyl group attached to the Si atom longer than a methyl group is incapable of fully cross-linking because the hydrogens on the second carbon sterically prevent cross-linking of one of the functional groups of the Si atom.[12] This is probably why there are substantial residual Si−OH groups in APS·$PbCl_4$ (III).

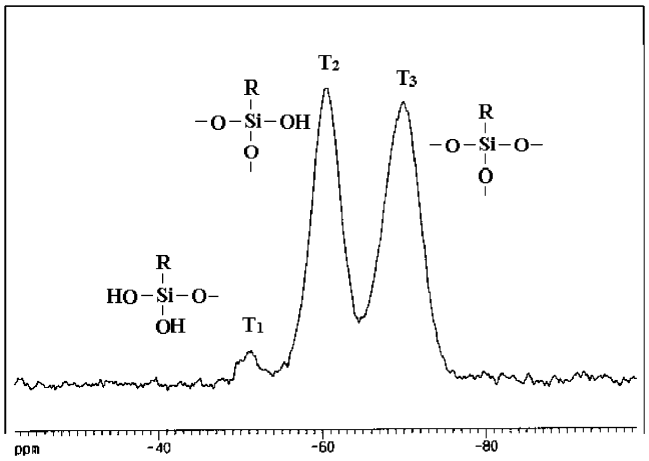


Figure 2. ^{29}Si solid-state CP/MAS NMR spectra of the layered perovskite containing the silica networks (APS·$PbCl_4$, spinning rate at 4.0 kHz, contacting time of 5 ms and relaxation delay of 3 s performed on the Bruker AV 400-MHz spectrometer).

The formation of layered perovskite-type organic/inorganic material for APS·$PbCl_4$ (III) can be confirmed by the X-ray diffraction (XRD) and UV/vis absorption and photoluminescence (PL) emission spectra. Figure 3 shows the XRD profile of APS·$PbCl_4$ (III) film dip-

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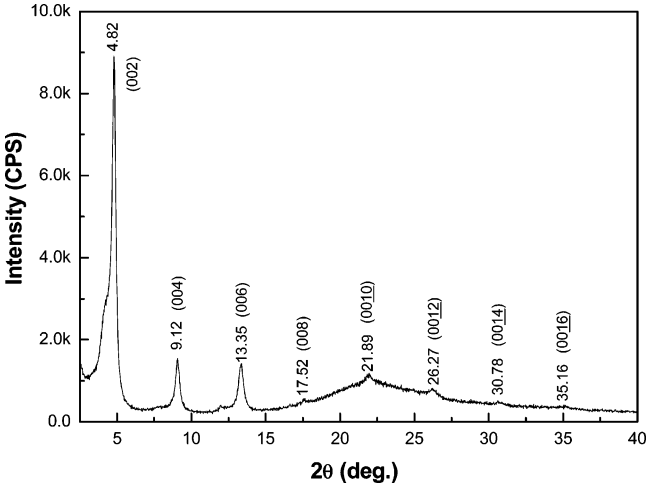

Figure 3. X-ray diffraction pattern for a dip-coated film of APS·$PbCl_4$ on silica glass substrate.

coated on silica glass substrate. Diffraction peaks at 2θ = 4.82, 9.12, 13.35, 17.52, 21.89, 26.27, 30.78, 35.16° are detected, which are equally spaced by about 4.33°, respectively. These peaks correspond to the reflections of (00l, l = 2, 4, 6...) for the perovskite sheets, as observed previously for the layered perovskite-type organic/inorganic $(C_4H_9NH_3)_2PbX_4$ (X= Cl, Br, I) films.[1] This indicates that the film was highly ordered and oriented along the *c*-axis; that is, the alternating layers stack perpendicularly to the substrate surface, with an interlayer distance (between two separating $PbCl_4^{2-}$ layers) of 1.83 nm (calculated by the Bragg equation, $d = \lambda/2 \sin \theta$). One dip-coated film has an average thickness of 315 nm (determined by carefully scraping some of the material off the substrate with a razor blade and then measuring the height difference between the substrate and the surface of the film by AFM topographical imaging), so it is estimated that about 170 $PbCl_4^{2-}$ layers were included. Note that the broad band from $2\theta = 15°$ to $2\theta = 30°$ in the XRD profile of Figure 3 is from the silica glass substrate.

Figure 4A shows the UV/vis absorption spectrum for the above APS·$PbCl_4$ film on silica glass substrate. It can be seen that two strong absorption peaks at 256 and 332 nm are present in the absorption spectrum, which is very similar to the previously reported other perovskite-type organic/inorganic films containing $PbCl_4^{2-}$ component, such as $(C_4H_9NH_3)_2PbCl_4$[1] and $(C_{10}H_{21}NH_3)_2PbCl_4$.[13] The absorption at 332 nm is a typical absorption of exciton rising from the 2D $PbCl_4^{2-}$-based organic/inorganic perovskite structure. Upon excitation into the absorption band at 256 nm, a sharp exciton emission at 336 nm is observed, as shown in Figure 4B. The very small Stokes shift (4 nm) between the UV−vis absorption and PL emission spectra as well as the narrow bandwidth of the peaks are characteristic of exciton. The appearance of the sharp exciton absorption and emission denotes that a layered perovskite structure was formed in APS·$PbCl_4$ film on a silica glass substrate. The exciton luminescence originates from the electronic transitions within the inorganic pervoskite layer.[14] It is assumed that the lowest exciton state arises

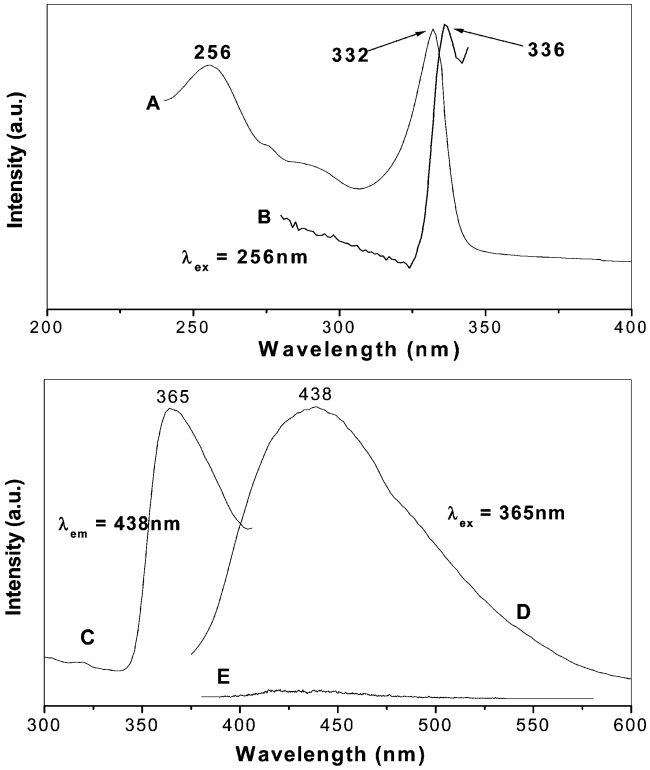

Figure 4. The UV/vis absorption (A), photoluminescence emission (B, λ_{ex} = 256 nm; D, λ_{ex} = 365 nm), and excitation (C, λ_{em} = 438 nm) spectra for APS·$PbCl_4$ film on silica glass substrate. The emission spectrum of blank silica glass substrate is shown as a reference (E, λ_{ex} = 365 nm).

from the excitations between the valence band consisting of a mixture of Pb(6s) and Cl(3p) states and the conduction band derives mainly from the Pb(6p) states.[15] Owing to the low-dimensional semiconductor nature, the exciton which has a large binding energy and high oscillator strength can be observed even at room temperature.

Apart from the characteristic exciton emission at 336 nm from the $PbCl_4^{2-}$ inorganic layers, the above perovskite-type organic/inorganic material also shows a strong blue emission in the visible region, as shown in Figure 4D. The emission spectrum extends from 350 to 600 nm with a maximum at 438 nm, and the corresponding excitation spectrum has a maximum at 365 nm (Figure 4C). Under the excitation of 365-nm irradiation, the blank silica glass substrates also show a very weak emission in the blue region (Figure 4E), but its intensity is about 50 times weaker than that from the film sample. So the strong blue luminescence (438 nm) can be excluded from the silica glass substrate. It must be related to the silica networks of the perovskite-type APS·$PbCl_4$ because the excitation and emission spectra are rather similar to those of the sol−gel-derived (organically modified) silica gels reported by others[16−19] and one of us.[20] The origin of the luminescence in sol−

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gel-derived silica gels has not been well understood yet. Several possible mechanisms, such as defect mechanism,[16] carbon impurity mechanism,[17] and most recently the cluster mechanism,[19] have been proposed to explain the luminescence phenomena in the silica gels (or organically modified silica gels).

Accordingly, it can be concluded that a layered perovskite-type organic/inorganic material containing silica networks intercalated in the inorganic sheet of $PbCl_4^{2-}$ has formed in the APS·$PbCl_4$(III) system, whose composition unit can be expressed as $[H_3N(CH_2)_3Si-O-Si(CH_2)_3NH_3]PbCl_4$. Owing to the existence of a large amount of $SiC(OSi)_3$ (T^3, see Figure 2) units in APS·$PbCl_4$(III), it can be reasonably assumed that there is cross-linking between adjacent layers of APS organic cations in addition to cross-linking within a layer, as shown in Scheme 1.

The self-organization into an ordered structure in the APS·$PbCl_4$(III) system may result from a range of interactions among molecular components. First, in addition to the ammonium "heads" hydrogen/ionic interacting with the halogens of the inorganic sheets, here the formation of the Si−O−Si networks brings the molecular units close to each other and has an effect on directing the layered structure formed. Second, it is important to take into account the interaction of H-bonds between silanols in the self-assembling process.[21] This weak interaction of silanols between the interface is favorable for forming a tail-to-tail arrangement, which is similar to the van der Waals gap between the bilayer organic R groups in the general organic−inorganic perovskite. Finally, due to the smaller cross-sectional area or lower steric hindrance, the partially hydrolyzed APS·HCl with a tail of silanols is favorable for self-organization compared with the unhydrolyzed APS·HCl.[8]

Experimental Details. Dry HCl gas was dissolved in absolute C_2H_5OH to form a 0.19 M solution. The powder of the compound APS·HCl (II) (in Scheme 1) was obtained by dropping APS into the above HCl/C_2H_5OH solution (molar ratio APS:HCl = 0.8:1) in a drybox (where the concentration of H_2O and O_2 is less than 1 ppm) with stirring, and then evaporating off the solvent and excess HCl at a reduced pressure at room temperature. The obtained APS·HCl (II) powder was dissolved in CH_3OH to form a 1 wt % solution. Then a small amount of H_2O (molar ratio H_2O:Si = 1:20) was added to the APS·HCl/CH_3OH solution and stirred for 5 h for the partial hydrolysis of APS. After removal of the CH_3OH by vacuum evaporation, a certain amount of DMF (*N*,*N*-dimethylformamide) containing 1 wt % $PbCl_2$ was introduced immediately in the resulted residue (molar ratio APS·HCl:$PbCl_2$ = 1:2) under stirring to form a transparent solution, which was used for the film deposition. A piece of thoroughly cleaned silica glass was dipped into the above solution and withdrawn at a rate of 0.5 cm/s^{-1} or the solution was simply dropped onto the surface of the silica glass substrate. After curing at 70 °C for 48 h, a final film of APS·$PbCl_4$ (III) in Scheme 1 was obtained.

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