Spin-Coating Preparation of Highly Ordered Photoluminescent Films of Layered PbI_2-Aminoalkyloxysilane Perovskites

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By utilising 3-aminopropyltrimethoxysilane (APTMOS) cations and PbI_2 as the organic and inorganic precursors, respectively, a spin-coated film of a layered perovskite-type organic/inorganic derivative of APTMOS-PbI_4 was prepared. The structure of APTMOS-PbI_4 was characterised by X-ray diffraction (XRD), UV/Vis absorption and infrared red spectroscopy (IR). The film showed green emission from the excitons of the inorganic layers and a weak blue emission related to the small amount of gel of adjacent APTMOS cations. Furthermore, the significant effect of the size of the inorganic framework on the cross-linking degree of APTMOS molecules is discussed.

Introduction

The self-organisation of molecules into highly ordered architectures with layered structures has attracted a wide range of scientific and practical interest. The perfect combination of the organic and inorganic components provides tremendous mechanical strength and toughness that is not possessed by a single phase alone. To date, the most frequently used method for the synthesis of 2D nanostructured hybrids is the sol-gel process, employing organic silane molecules in the presence of surfactants which are used as structure directors due to their amphiphilic nature in a selective solution.[1a−1g] On the other hand, the layered compounds can also be obtained by intercalating the guest molecules, generally organic species such as alkylammonium salts, into the interlayer spaces of a pre-existing inorganic layered structure.[2a−2c] Recently, layered polysiloxane containing alkylammonium groups has been prepared by the sol-gel reaction of 3-aminopropyltrimethoxysilane (APTMOS) with hydrochloric acid, without using any surfactants or long-chain alkyl groups in the monomers.[3] Similarly, we reported a simple method of preparing a layered nanocomposite containing a silica network by a perovskite-type self-organisation.[4] Lead(II) chloride was employed as the inorganic layer in this superlattice material and photoluminescence in the ultraviolet region was observed due to the nature of the low-dimensional structure. In order to further explore the feasibility of this method and obtain luminescence in the visible region, lead(II) iodide (with a smaller band-gap and a larger "footprint" of the inorganic framework) and APTMOS cations were used in this study. It was observed that these materials can also be self-organised into a perovskite-type layered structure which shows green luminescence arising from the inorganic semiconductor of the lead(II) iodide layers. The expected structure of PbI_2-based perovskite and the simulated structure of the APTMOS molecule are shown in Figure 1.

Results and Discussion

Synthesis and Film Preparation

At the beginning of the experiment for the preparation of APTMOS·HI, we tried to simply mix the APTMOS with PbI_2 in a dilute hydroiodic acid solution but we were unable to obtain the final product as expected. HI is a very strong acid and a nucleophile and APTMOS is very susceptible to hydrolysis and polycondensation in an acidic environment. The Si−O, C−O and Si−C bonds are broken upon nucleophilic attack by I^-. Thus, a rigorous procedure for removing water and a low temperature bath of diethyl ether/dry ice were applied in order to avoid the occurrence of the above reactions. In spite of these precautions, the acid-base reaction between the head of the amine group of APTMOS and HI was not be impeded at low temperature.

The molecular formula $[(CH_3O)_3Si-CH_2-CH_2-CH_2-NH_3]_2PbI_4$ (APTMOS-PbI_4 for short) was defined by the single layers of the <100> oriented perovskite sheets which

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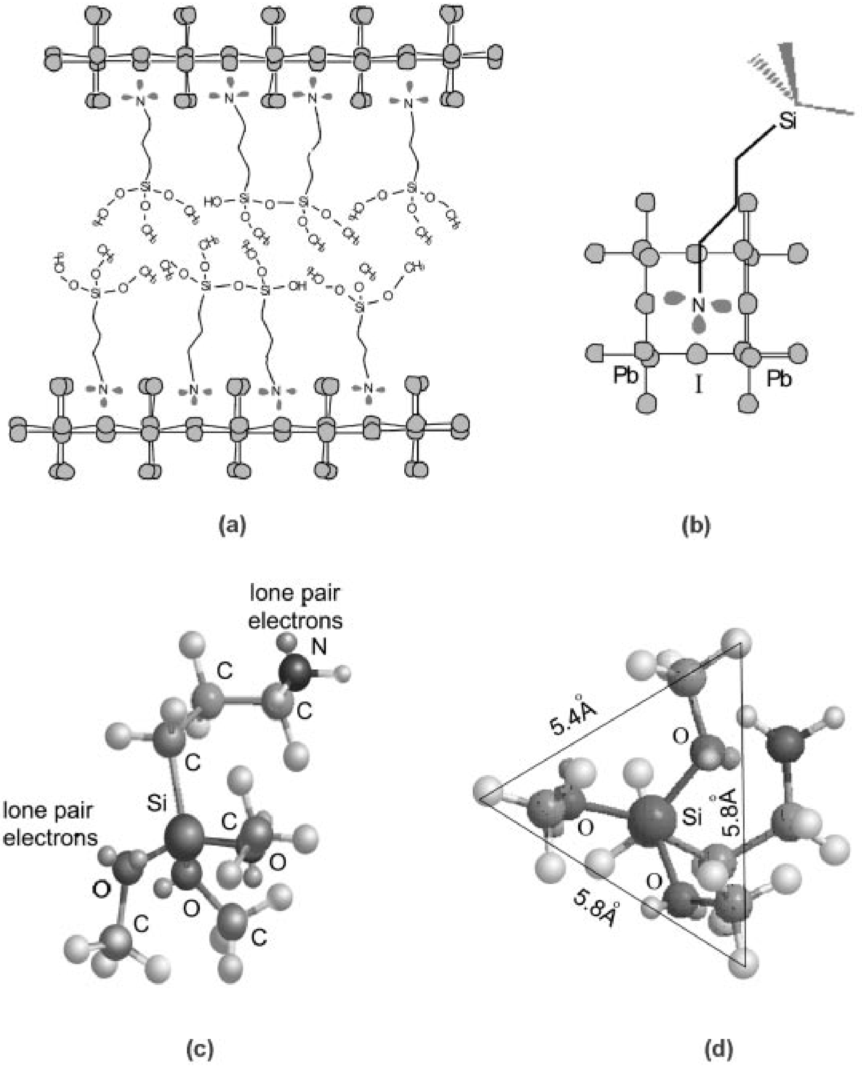

Figure 1. Schematic representation of the expected structure for APTMOS-PbI$_4$ perovskite and the simulated results of the dimensions of the APTMOS molecules; the APTMOS-PbI$_4$ layered superlattice consists of an extended framework of corner-sharing lead iodide octahedra alternating with a bilayer of APTMOS cations; (a) view parallel to the perovskite sheet of the APTMOS-PbI$_4$ structure, (b) view perpendicular to the perovskite sheet of the APTMOS-PbI$_4$ structure, (c) the profile of the APTMOS molecule, (d) the dimensions of the cross-section of the APTMOS molecule; the ball-and-stick model of the APTMOS molecule represents a favourable energy state

consist of corner-sharing metal halide octahedra, alternating with the ATMOS cation bilayers. Each octahedron has a Pb^{2+} cation in the centre and six I$^-$ units as coordination anions. The four bridging I$^-$ ions are shared by the two adjacent octahedra. Figure 1 (a and b) shows the model of the layered perovskite structure. From a view perpendicular to the perovskite sheets in the APTMOS-PbI$_4$ structures, each APTMOS cation is nominally located in a square defined by the four neighbouring Pb atoms and the Pb−I−Pb linkages can be regarded as the sides of the square (see b in Figure 1).[5] In contrast to the length of about 5.6 Å in Pb−Cl−Pb based structures,[6a] the PbI$_2$-based perovskite exhibits a larger framework of 6.4 Å for the Pb−I−Pb unit according to the single-crystal structure.[6b] The shape and relevant molecular dimensions of the APTMOS molecule are shown in parts c and d of Figure 1. These results were calculated using the MM2 force field with the Chem3D program (CambridgeSoft Corp.). The lengths of the sides of the silicon tetrahedra in an unhydrolysed APTMOS molecule are in a range of 5.4−5.8 Å. Thus, the PbI$_2$-based perovskites have enough space to accommodate the unhydrolysed APTMOS molecules in the self-assembly process. In contrast, in the preparation of the APTMOS-PbCl$_4$ perovskite, an intentional hydrolysis was applied before the film deposition for reducing the cross-sectional area of the APTMOS cations.[4]

Infrared Spectroscopy

The FT-IR spectra of APTMOS (a), APTMOS·HI (b) and the perovskite structure of APTMOS-PbI$_4$ (c) are given in Figure 2. In Figure 2 (see a), for APTMOS, the weak peaks at 3376 and 3298 cm^{-1} are due to asymmetric/symmetric N−H stretching vibrations of primary amine (−NH$_2$) groups. The locations and assignments of the other absorption peaks are 2938 (ν_{as}, CH_2), 2832 (ν_s, CH_2), 1576 (δ, NH_2), 1469 (δ, CH_2), 1190 (ν_{as}, $Si-CH_2$), 1085 (ν_{as}, $Si-OCH_3$), 815 (ν_s, $Si-OCH_3$) and 450 cm^{-1}(δ, $Si-OCH_3$) (where ν_{as} stands for asymmetric stretching, ν_s for symmetric stretching, and δ for bending).[7a–7c] After treatment with dry HI gas, as shown in part b of Figure 2, the N–H stretching at 3298 and 3376 cm^{-1} disappeared. Instead, a broad band centred at 2900 cm^{-1} and a series of overtone peaks from 2000 to 2705 cm^{-1} were observed which are typical characteristics of organic amine salts. The weak absorptions at 3450 and 920 cm^{-1} due to silanols of hydrolysed APTMOS molecules could be observed, despite a rigorous procedure for removing water and the application of a low temperature during the preparation of the amine salt. Other than the absorption of the silanols at 3430 cm^{-1} becoming more strong, there were no great differences between the FT-IR spectrum of APTMOS-PbI_4 (see c in Figure 2) and that of APTMOS·HI (b in Figure 2). Note that the asymmetric stretching mode at 1085 cm^{-1} and the symmetric stretching mode at 817 cm^{-1} corresponding to the $Si-OCH_3$ group also remained as shown in Figure 2 (see c), indicating that a large amount of unhydrolysed APTMOS cations remained in the perovskite structure. The Si–O–Si bond also gives at least one very intense band in the 1100–1000 cm^{-1} region due to the asymmetric stretching mode. Thus, the mode corresponding to Si–O–Si or Si–O–C appearing in this region cannot be easily distinguished. As for the short open-chain alkylpolysiloxanes or small cyclic polysiolxanes, the asymmetric stretching of Si–O–Si shows a characteristic single band at 1000–1100 cm^{-1}.[1b] With progressively longer linear alkylpolysiloxanes or larger cyclic polysiloxanes, the band in this region splits into two or more overlapping components and becomes broader.[8a–8b] Base on this fact, the appearance of only a singlet absorption band at 1079 cm^{-1} for APTMOS-PbI_4 perovskite is consistent with the formation of a mixture which is composed largely of $Si-OCH_3$ functionalities, silanol groups and perhaps a small amount of short-chain polysiloxanes/small cyclic polysiloxanes. In contrast to the FT-IR spectrum of APTMOS-$PbCl_4$, where the Si–O–Si asymmetric stretching band is characteristic of long-chain linear siloxanes with two broad doublet peaks at 1107 and 1037 cm^{-1},[4] the APTMOS cations in the APTMOS-PbI_4 perovskite have less cross-linking because only one band is present in this region. This can be attributed to the fact that the space provided by the PbI_2-based framework is too large for the perpendicular APTMOS cations to form long Si–O–Si chains. The films of APTMOS-PbI_4 have poor stability compared with the APTMOS-$PbCl_4$ films and traditional organic/inorganic perovskites such as $(C_4H_9NH_3)_2PbI_4$. The APTMOS-PbI_4 films usually decomposed in air over several days and became colourless. The instability of the APTMOS-PbI_4 films may be ascribed to the large spaces in the PbI_2-based framework and the strong propensity for polycondensation between the adjacent APTMOS cations confined in the perovskite structure. These factors cause the layered perovskite structure to eventually collapse.

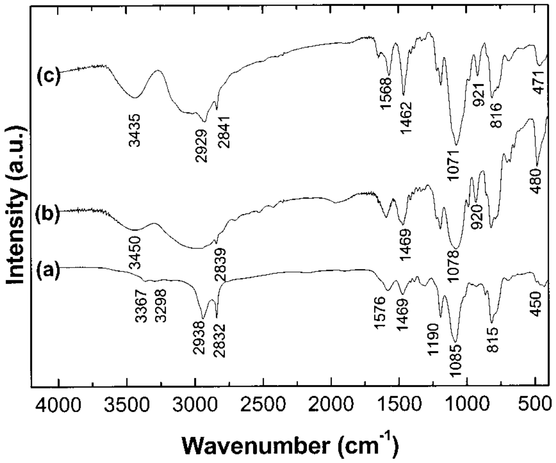

Figure 2. FT-IR spectra for 3-aminopropyltrimethoxysilane (APTMOS, a: using liquid film on KBr crystal disk), the amine salt of APTMOS (APTMOS·HI, b: KBr pellet) and the layered perovskite with a silica network (APTMOS-PbI_4, c: KBr pellet)

XRD

X-ray diffraction (XRD) is the most useful tool for the structural characterisation of a crystalline material. From the XRD pattern (Figure 3) of an APTMOS-PbI_4 film spin-coated on a fused silica plate, only 00*l* diffraction peaks were detected due to the extremely high degree of preferential orientation arising from the manner in which the sample was mounted. The 00*l* reflections can be counted as corresponding to $l = 1, 2, 3...$ or $l = 2, 4, 6...$ and we chose the latter based on previous literature for the layered perovskite-type organic/inorganic $(C_4H_9NH_3)_2PbI_4$ structure.[6b] The observation of these multiple order diffraction peaks supports the formation of a PbI_2-based perovskite structure in the films and the alternating layers stack perpendicularly to the substrate surface. The 00*l* reflections correspond to an extended network of corner-sharing metal halide octahedra with an interlayer distance of 1.91 nm separating the inorganic sheets. According to the structural properties of the general hybrid perovskites, the interlayer space decreases from Pb–Cl to Pb–Br and to Pb–I.[9] This can be attributed to the larger space provided by the inorganic frame and the alkyl chains can tilt or interdigitate. Compared with the APTMOS-$PbCl_4$ perovskite structure which has an interlayer space of 1.83 nm,[4] a small increase of 0.08 nm in APTMOS-PbI_4 was observed by XRD, rather than a decrease. This abnormal increase may be due to the unhydrolysed APTMOS molecules which have a longer chain and a larger silane tail which hinders the APTMOS molecules from tilting/interdigitation.

UV/Vis Absorption Spectroscopy

A simple way to confirm the formation of the layered perovskite structure is using UV/Vis absorption spectroscopy since exciton absorption can be observed at room temperature due to the quantum confinement effect.[10a–10c] Figure 4 shows the UV/Vis absorption spectrum of

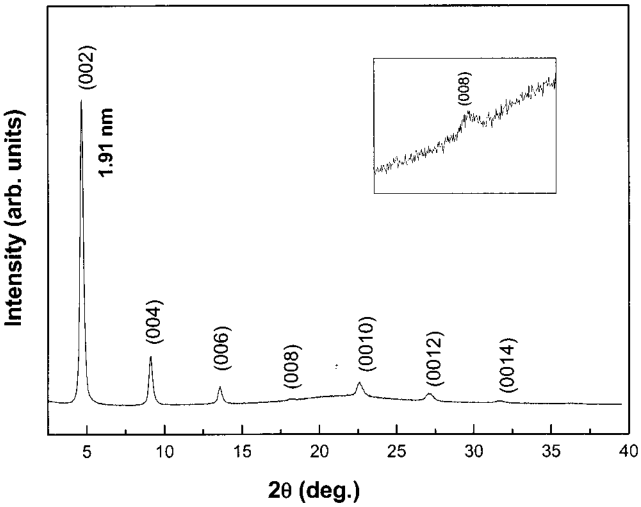

Figure 3. X-ray diffraction profiles for a spin-coated film of APTMOS-PbI$_4$ on a quartz plate; the inset is an enlarged figure for clarity

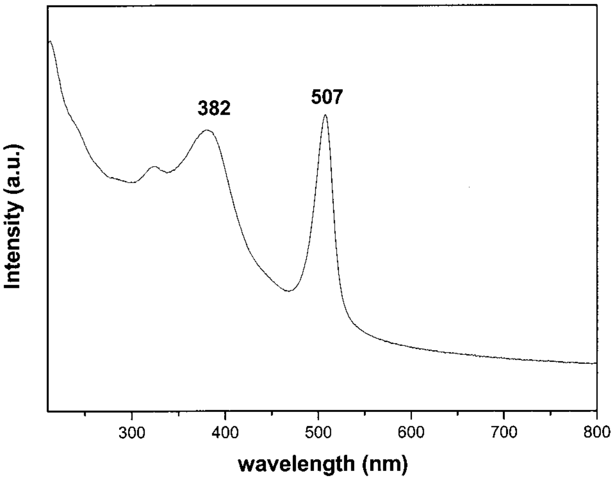

Figure 4. UV/Vis absorption spectrum for an APTMOS-PbI$_4$ spin-coated film on a quartz plate

APTMOS-PbI$_4$ films on a fused silica plate. Two strong absorption bands at 382 and 507 nm can be observed. The former is due to the band-gap absorption of the PbI$_2$-based perovskite structure with one layer of inorganic sheets. Generally, the top of the valence-band of this class of material consists primarily of a mixture of I (5P$_{xy}$), Pb (6s) and I (5P$_z$), whereas the bottom of the conduction-band consists primarily of the Pb (6P$_{xy}$) state.[10] Note that a strong and sharp absorption peak at 507 nm is present which is similar to the previously reported PbI$_2$-based perovskite structure with a single-layer inorganic sheet.[6b] This suggests that the extended 2D PbI$_4{}^{2-}$ frameworks are sandwiched on both sides by the APTMOS cations with alkyl chains which have a much lower dielectric constant compared with the inorganic component. The two dimensionality of the layered structure combined with the dielectric confinement effect enables the formation of a stable exciton with a large binding energy in the PbI$_4{}^{2-}$ semiconductor layer. As a result, the feature of the sharp absorption of excitons can be observed even at room temperature. This generally cannot be observed in bulk PbI$_2$. This is also the reason that the colour of the APTMOS-PbI$_4$ films is somewhat different from PbI$_2$. The difference in colour can be simply used to judge the formation of a layered perovskite structure in the spin-coating procedure.

Photoluminescence

From the photoluminescence spectra (Figure 5), a dominant emission of an exciton state at 518 nm was observed. In contrast to the PbCl$_2$-based perovskite, the band-gap of PbI$_2$-based perovskite is reduced and the luminescence absorption red-shifted from the ultraviolet to the visible region.[6b] As a result, the green luminescence could be seen when the spin-coated APTMOS-PbI$_4$ films were exposed to a hand-held UV lamp at room temperature. The photoluminescent properties of the PbCl$_2$-based layered perovskite structure incorporated with APTMOS cations have the features of a weak emission in the ultraviolet region originating from the exciton state and a strong blue emission at 440 nm which corresponds to the highly condensed siloxane network of the tails of the APTMOS cations.[4] Interestingly in Figure 5 one can see, apart from the strong emission of the exciton at 518 nm, that there is a strong background emission between 425 and 600 nm with a maximum at 456 nm. This should come from the organic component and is related to the photoluminescence of the sol-gel derived silica gel of the APTMOS cations.[8a,11a–11c] The weak intensity can be attributed to the reduced cross-linking between the APTMOS cations in the APTMOS-PbI$_4$ film. This result is consistent with the FT-IR spectrum (see c in Figure 2) which only demonstrates the existence of short Si–O–Si chains (one peak at 1071 cm^{-1}). Note that the shoulder emission analogues were generally observed at higher wavelengths in the previously reported organic-inorganic perovskites and were explained as being due to degradation or the presence of impurities.[6b,12]

Formation of the Perovskite Structure

We propose that the formation of the layered APTMOS-PbI$_4$ superlattice occurs mainly by an organic/inorganic perovskite-type self-organisation.[9] Such behaviour is different from that of long-chain amphiphiles because there are no strong interactions between the short alkyl chains of the APTMOS cations. The main driving force is the propensity of metal halides to format the extended corner-sharing networks of MX$_6$ octahedra. The ammonium "heads" of the organic cations interact with the halogens of the inorganic sheets in an ionic or hydrogen bonding manner and then hydrolysis and condensation may occur between some adjacent APTMOS molecules, leading to an alternating layered structure. Thus, the inorganic framework plays an important templating role for the APTMOS cations. In ad-

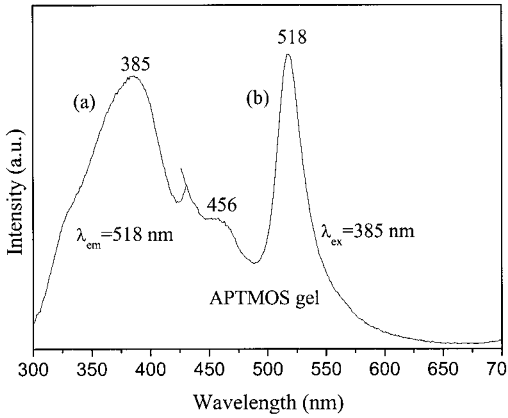

Figure 5. Photoluminescence excitation (a) and emission (b) spectra for an APTMOS-PbI_4 film on a quartz substrate

dition, the H-bonds between silanols have the effect of forming a tail-to-tail arrangement of the APTMOS cations.[13]

Conclusions

In this study, the spin-coating method was successfully used to prepare highly ordered perovskite-type films with a layered structure in which the lead iodide inorganic layer was sandwiched by the APTMOS cations. The films show strong green luminescence arising from the excitons of the inorganic semiconductor lead iodide layers and the weak blue emission relates to the hydrolysed APTMOS cations. The large framework provided by the inorganic layer impedes the APTMOS cations from forming a network with a high degree of cross-linking. This kind of self-organising system offers a potential method for the preparation of nano- and mesoporous silica films after the lead iodide template has been removed.

Experimental Section

Syntheses: The starting materials used in the synthesis were PbI_2 (99.999%, Aldrich) and 3-aminopropyltrimethoxysilane (>97%, Aldrich). HI gas was obtained by dropwise addition of water into a Schlenk tube containing an iodine-red phosphorus mixture. The liberated HI gas was dried using a $CaCl_2/P_2O_5$ mixture packed into the drying towers and collected by condensing into a liquid nitrogen trap. APTMOS (10 mL) was dissolved in absolute diethyl ether (150 mL, refined by heating to reflux for 12 h over sodium) and the solution was maintained at −78 °C in an acetone/dry-ice bath. The trap containing the solid hydrogen iodide was then removed from the liquid nitrogen and dipped into a bath with a K_2CO_3/ice mixture (−30 °C) to release the HI gas slowly. The small steam of HI gas was directed to flow into the APTMOS/diethyl ether solution, resulting in the formation of an APTMOS salt (APTMOS·HI, white precipitate). Note that the excess noxious HI gas was collected in a vacuum desiccator containing sodium hydroxide. The powder of APTMOS·HI was obtained after removal of the diethyl ether by evaporation in a vacuum at room temperature. The final APTMOS·HI powder was stored in an evacuated desiccator using $P_2O_5/CaCl_2$ as the desiccant at −25 °C.

Film Preparation: Dimethylformamide (DMF) was dried over calcium hydride for two days with stirring and was then distilled under reduced pressure. PbI_2 and APTMOS·HI (1:2 molar ratio) were dissolved in the dry DMF to form a clear solution (2.5 wt%). The solution was spin-coated on fused silica plates at 700 rpm for 3s and then 1500 rpm for 45s at room temperature in air. After drying at 70 °C under vacuum for 6 h, continuous and crack-free films of the PbI_2-based layered perovskite $[(CH_3O)_3Si-CH_2-CH_2-CH_2-NH_3]_2PbI_4$ were obtained. A small amount of APTMOS-PbI_4 powder was scraped off the substrates for FT-IR measurements.

Characterisations: The FT-IR spectra were recorded on a Bio-rad FTS 135 spectrometer with a nominal resolution of 4 cm^{-1}. The X-ray diffraction (XRD) of film samples was examined on a Rigaku-Dmax 2500 diffractometer using Cu-K_α radiation (λ = 0.15405 nm). The UV/Vis absorption spectrum was measured on a TU-1901 spectrophotometer. The photoluminescence excitation and emission spectra were recorded on a Hitachi F-4500 spectrofluorimeter equipped with a 150-w xenon lamp as the excitation source.

Acknowledgments

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