Hybridization with Ca$_2$Nb$_3$O$_5$ (CNO) nanosheets may be effective for immobilizing positively charged functional organic molecules on various inorganic materials. To prove this hypothesis, amphiphilic cyanine dyes have been spread on to the surface of a diluted CNO colloidal suspension. The dyes have formed Langmuir films with enlarged molecular areas due to the hybridization. The hybrid Langmuir films have been transferred on to solid substrates by means of the conventional vertical dipping method. Spectroscopic characterization of the obtained Langmuir-Blodgett films has suggested that organic-inorganic sandwiched structures are realized.

Key words: Organic-inorganic hybrid, metal-oxide nanosheet, cyanine dye, Langmuir-Blodgett technique

1. INTRODUCTION

Inorganic nanosheets are ultrathin (~1 nm thick) and large (~1 µm wide) ordered materials that are useful in constructing functional nanosystems [1,2]. Since most of the inorganic nanosheets are negatively charged, they can adsorb Langmuir films made of cationic surfactants spread on their aqueous colloidal suspensions [1].

Among the inorganic nanosheets, Ca$_2$Nb$_3$O$_5$ (CNO) nanosheets have been attracting special interests because a film of them deposited on a glass substrate works as an excellent seed layer in epitaxial growth of a Ca$_{0.6}$Sr$_{0.4}$TiO$_3$:Pr phosphor film [3]. The apparent photo-luminescence exhibited by the oxide film grown on CNO nanosheets reflected its good crystallinity unambiguously. To prepare the CNO seed layers efficiently, we intensively studied their adsorption behavior from their aqueous colloidal suspension to the gas-liquid interface with and without a Langmuir film of dioctadecyldimethylammonium (DOA) [4]. In brief, a quantitative analysis of the experimental results in the theoretical framework given by Langmuir indicated that the adsorption rate constant of the CNO nanosheets is increased by five times due to the presence of the DOA Langmuir film.

From another point of view, such hybridization can be utilized as a method for immobilizing functional organic molecules on various inorganic materials. By combining the Langmuir-Blodgett (LB) technique, furthermore, organic-inorganic sandwiched structures may be easily constructed. We have intended to prove this hypothesis by using positively charged cyanine dyes. Hence, we have prepared the hybrids of CNO nanosheets and amphiphilic cyanine dyes, NK2638 and NK2622 (Fig. 1), at the gas-liquid interface, and transferred the resultant hybrid Langmuir film on to solid substrates by means of the conventional vertical dipping method.

2. EXPERIMENTAL

A colloidal suspension of CNO nanosheets at a concentration of 2.0 g L$^{-1}$ was obtained by delaminating KCa$_2$Nb$_3$O$_{10}$ crystallites by successive cation exchanges with proton and tetrabuthylammonium through the procedure described in Ref. 3 and used as the “mother” suspension. This mother suspension was diluted to $4.0 \times 10^{-3}$ g L$^{-1}$ by adding pure water with a resistivity higher than $1.8 \times 10^7$ Ω cm provided by a Millipore Milli-Q system in order to be used as the subphase in the LB technique. No precipitation could be observed in the diluted suspensions. A Lauda Filmwaage apparatus was used as a Langmuir trough.

The cyanine dyes NK2638 and NK2622 were purchased from Hayashibara Co. Ltd. and used without further purification. They were dissolved into chloroform with a concentration of approx. $2 \times 10^{-3}$ mol L$^{-1}$ and $2 \times 10^{-4}$ L of each solution was spread on to the fresh surface of pure water or the diluted CNO suspension. The initial area of the surface was 690 cm$^2$, corresponding to a

![Fig. 1](image)

Fig. 1 Cyanine dyes used in this study.
molecular area of approximately 3 nm$^2$.

Pristine Si and CaF$_2$ plates were used as solid substrates. The ultraviolet (UV)-visible and infrared (IR) polarized transmission spectroscopic analyses were performed using Perkin-Elmer Lambda-900 and Spectrum-2000 spectrometers, respectively, with the angle of incidence set at 45°. Room temperature was controlled at 20°C throughout the experiments. (The subphase temperature was not independently controlled.)

3. RESULTS AND DISCUSSION

3.1 F⁻–A isotherm and LB transfer

Surface pressure–molecular area isotherms observed for NK2622 and NK2638 spread upon pure water and the diluted CNO suspension are displayed in Fig. 2. Apparently, the molecular areas of the dyes on the CNO suspension are enlarged, when compared with those on pure water. Similar phenomenon was observed for dioctadecyl(dimethylammonium) when it was spread upon CNO suspensions and hybridized with CNO nanosheets [4].

Since Langmuir films of CNO nanosheets collapses under a surface pressure around 2.0 x 10$^{-2}$ N m$^{-1}$ [4], the cyanine dye-CNO nanosheet hybrid films have been transferred on to solid substrate at 1.6 x 10$^{-2}$ N m$^{-1}$. The conventional vertical dipping method has been adopted. The transfer ratios in the up- and downward processes have been estimated at nearly unity and zero, respectively, i.e., a nice Z-type deposition has been observed.

3.2 UV-visible absorption

UV-visible absorption of the cyanine dye-CNO nanosheet hybrids have been measured for monolayer samples deposited on CaF$_2$ substrates. Figure 3 shows the spectra recorded for the NK2638 case. These spectra have confirmed that cyanine dye molecules are contained in the present LB film. Similar result has been obtained for the NK2622 case.

In comparison to the solution spectrum, which is also displayed in Fig. 3, a red shift of 5 nm and an enhancement of the vibronic structure (seen around 410 nm) are noted. These may be caused by the difference in the electrostatic environment around the molecules between the solution and hybridized cases. In other words, no indication of aggregation has been detected.

The fact that the absorption recorded with $s$-polarization is larger than that with $p$-polarization reflects the molecular orientation in the LB film. Namely, the transition dipole moment, which is parallel to the long axis of the dye chromophore, is preferentially oriented along the substrate plane.

3.3 IR absorption

To prove that the present LB films contain not only dye molecules but also CNO nanosheets, IR transmission spectroscopy has been performed for multilayer samples (Fig. 4). In this connection, the absorption bands located at 956 and 791 cm$^{-1}$ attract our attention. The former and the latter are respectively assignable to the antisymmetric stretching modes of the outer and central NbO bonds in the O–Nb–O–Nb–O–Nb–O chain (Fig. 5) [5,6]. This Nb$_3$O$_4$ chain is the spine of the three interconnected NbO$_6$ octahedrons, which is the basic structural unit of CNO nanosheets [2]. Hence, the presence of CNO nanosheets in the LB films is proved. Detailed discussion concerning these assignments will be given in Appendix.

The bands seen at 2919, 2851 and 1468 cm$^{-1}$ originate from the alkyl group attached to the cyanine dye chromophores; the former two are the antisymmetric and symmetric CH$_2$ stretching modes, respectively, and the rest should be assigned to the CH$_2$ scissoring mode. Besides, the band detected at 1521 cm$^{-1}$ in the NK2638 case and those detected at 1550 and 1420 cm$^{-1}$ in the NK2622 case have been assigned to the central conjugating system of the dye chromophores. These assignments are based on the following discussion; elongation of the central conjugating system may cause splitting and red-shifting of its stretching mode. Thus, it is confirmed again that cyanine dye molecules are contained in the present LB film.

![Fig. 2](image2.png)

**Fig. 2** Surface pressure–molecular area isotherms of NK2638 and NK2622 observed upon pure water and a dilute CNO suspension recorded at 20°C.

![Fig. 3](image3.png)

**Fig. 3** UV-visible absorption spectra observed for the NK2638-CNO hybrid monolayer LB film with the angle of incidence set at 45°. Absorption spectrum observed for a dilute chloroform solution (2 x 10$^{-5}$ mol L$^{-1}$) of the dye is also indicated for comparison.
Furthermore, it should be emphasized that the NbO stretching modes at 956 and 791 cm\(^{-1}\) are distinct in the \(p\)-polarization spectra, but unnoticeable in the \(s\)-polarization spectra. This clearly indicates that the NbO chain axes are perfectly oriented along the direction normal to the substrate surface. That is to say, CNO nanosheets are flat against the substrate surface. (Note that the NbO chain axis is normal to the CNO nanosheet plane.)

The recorded anisotropy in the intensity of the bands assigned to the central conjugating system of the dye chromophore indicates that the long axes of the chromophores preferentially lie in the film plane, being consistent with the anisotropy in the electronic absorption band (Fig. 3). In addition, the anisotropy observed for the bands from the alkyl group suggests that the long axes of dye chromophores lie along the nanosheet plane in both of the NK2638 and NK2622 cases.

4. CONCLUSION
To prove that hybridization of positively charged functional organic molecules and CNO nanosheets can be utilized for immobilization of the former, amphiphilic cyanine dyes have been spread on to the surface of a diluted CNO colloidal suspension. Formation of hybrid Langmuir films has been observed and they have been transferred on to solid substrates by means of the LB technique. Polarized IR transmission spectroscopy has confirmed that both of the inorganic and organic materials are contained in the resultant LB films. Moreover, it has been suggested that organic-inorganic sandwiched structures flat against the substrates are realized, though further experiments including X-ray diffraction measurements are required to clarify the structure.

REFERENCES

APPENDIX
Lu et al. [5] unambiguously showed that the stretching mode of the terminating Nb–O bond in a polyoxoanion NbW\(_3\)O\(_{19}\)\(^{3-}\) is observed at 915 cm\(^{-1}\) and in its dimer (NbW\(_3\)O\(_{18}\))O\(^4-\) the stretching mode of the bridging Nb–O–Nb is observed at 692 cm\(^{-1}\). In our case, however, the stretching vibrations of all the bonds in the O–Nb–O–Nb–O–Nb–O chain may be strongly correlated with one another. In fact, assuming that the all bonds in this chain have the same spring constant, the energy ratio of the highest and the

\[\text{O–Nb–O–Nb–O–Nb–O} \]
second highest antisymmetric modes reaches 1.39, being unacceptably larger than 956/791 (the present experimental data). In addition, it is not obvious whether introduction of double bonds decreases this energy ratio. Therefore, we have evaluated the effect of double bonds on the ratio.

Let us start the simplest case, where the spring constants of all bonds are the same (=k). Writing the mass of O and Nb atoms \( m \) and \( M \), respectively, and the displacement of the \( i \)-th atom \( x_i \), the kinetic energy of the system \( T \) is given by

\[
T = \frac{1}{2} \sum_{i=1}^{7} \dot{X}_i^2 ,
\]

(A1)

where \( X_i = \frac{\sqrt{m} x_i}{\sqrt{M} x_i} \) (for odd \( i \)) and \( \dot{X} \) represents the time derivative of \( X \). The elastic energy \( U \) is given by

\[
U = \frac{k}{2m} XVX ,
\]

(A2)

where \( X \) is a vector consisting of \( X_i \) and \( V \) is a matrix of

\[
\begin{pmatrix}
1 & -\mu & -\mu & 2\mu^2 & -\mu & -\mu & 2\mu^2 & -\mu \\
-\mu & 2 & -\mu & 2\mu^2 & -\mu & 2 & -\mu & 2\mu^2 & -\mu & -\mu & 1
\end{pmatrix} .
\]

(A3)

Here, \( \mu = \sqrt{m/M} \).

Generalized displacement \( Q_j \) is defined as

\[
Q_j = c_j X ,
\]

(A4)

where \( c_j \) is the \( j \)-th unit eigenvector of \( V \). By using \( Q_j \) and \( V \)'s eigenvalue \( \lambda_j \) corresponding to \( c_j \), eqs. (A1) and (A2) can be rewritten as

\[
T = \frac{1}{2} \sum_{j=1}^{7} \dot{Q}_j^2 ,
\]

(A1')

and

\[
U = \frac{k}{2m} \sum_{j=1}^{7} \lambda_j Q_j^2 .
\]

(A2')

Considering the conservation of energy (\( T + U = \text{const.} \)), the angular frequencies of the stretching modes are obtained as

\[
\omega_j = \sqrt{\lambda_j/m} .
\]

(A5)

Since only antisymmetric modes are IR active, the specific equation to be solved becomes

\[
\begin{bmatrix}
\lambda - 1 & \mu & \mu & \lambda - 2\mu^2 & \mu & \lambda - 2\mu^2 & 2\mu & \lambda - 2\mu^2 \\
\mu & \lambda - 2\mu^2 & \mu & \lambda - 2\mu^2 & \mu & \lambda - 2\mu^2 & 2\mu & \lambda - 2\mu^2 \\
\mu & \lambda - 2\mu^2 & \mu & \lambda - 2\mu^2 & \mu & \lambda - 2\mu^2 & 2\mu & \lambda - 2\mu^2 \\
\mu & \lambda - 2\mu^2 & \mu & \lambda - 2\mu^2 & \mu & \lambda - 2\mu^2 & 2\mu & \lambda - 2\mu^2 \\
\lambda - p & \mu & \mu & \lambda - (p + q)\mu^2 & q\mu & q\mu & \lambda - (1 + q)\mu & 2\mu & \lambda - 2\mu^2 \\
\mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & 2\mu & \lambda - 2\mu^2 \\
\mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & 2\mu & \lambda - 2\mu^2 \\
\mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & 2\mu & \lambda - 2\mu^2
\end{bmatrix} = 0 .
\]

(A6)

One of the solutions of this equation is zero, corresponding to the translation of the whole chain, so that the equation is cubic in actual. Replacing \( m \) and \( M \) by the real values (15.99 and 92.91), the ratio of the largest and second largest eigenvalues is evaluated at 1.93.

To take into account the modification of the bond strength due to the chemical status (Fig. 5), we rewrite the spring constants of the outer and intermediate Nb–O bonds to \( pk \) and \( qk \), respectively, while keeping that of the central Nb–O bond at \( k \). Consequently, the specific equation is given by

\[
\begin{bmatrix}
\lambda - p & \mu & \mu & \lambda - (p + q)\mu^2 & q\mu & q\mu & \lambda - (1 + q)\mu & 2\mu & \lambda - 2\mu^2 \\
\mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & 2\mu & \lambda - 2\mu^2 \\
\mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & 2\mu & \lambda - 2\mu^2 \\
\mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & 2\mu & \lambda - 2\mu^2 \\
\lambda - p & \mu & \mu & \lambda - (p + q)\mu^2 & q\mu & q\mu & \lambda - (1 + q)\mu & 2\mu & \lambda - 2\mu^2 \\
\mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & 2\mu & \lambda - 2\mu^2 \\
\mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & 2\mu & \lambda - 2\mu^2 \\
\mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & \mu & \lambda - (p + q)\mu^2 & 2\mu & \lambda - 2\mu^2
\end{bmatrix} = 0 ,
\]

(A7)

or, more simply,

\[
\lambda^3 - \frac{3}{2} + 2\mu^2 + (p + q)\mu^2 + (p + q)\mu^2 (\frac{1}{2})^{2} + \frac{p + q(1 + 2\mu^2)}{(p + q)\mu^2 (\frac{1}{2})^{2}} \lambda^3 - \frac{p + q(1 + 2\mu^2)}{(p + q)\mu^2 (\frac{1}{2})^{2}} \lambda^2 - \frac{p + q(1 + 2\mu^2)}{(p + q)\mu^2 (\frac{1}{2})^{2}} \lambda = 0 .
\]

The relationship between \( p \) and \( q \) is unclear, but the simplest assumption is \( p + q = 2 \). With this assumption, resonance of double- and non-bonding states in the Nb–O–Nb–O–Nb–O chain markedly reduces the energy ratio of \( \omega_1/\omega_2 \) as demonstrated in Fig. A-1. On the other hand, it has been shown that this ratio is not significantly reduced by Nb–O–Nb bridges between the chains, which increase \( V_{22} \), \( V_{44} \), and \( V_{66} \) in eq (A3) in the lowest-order approximation. Thus, our assignments of the Nb–O modes shown in Fig. 5 are fairly rationalized.

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