# Evidence for the role of organic layers in photoconductivity of organic/inorganic hybrid nanosheets as prepared by Langmuir–Blodgett methods†

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**By measuring the photoconductivity of hybrid LB films of exfoliative layered niobate and octadecylamine, it was evidenced that the film underwent a transition from an insulator to a photosemiconductor during photo-modification treatment by UV light, which was rationalized in terms of the direct contact of inorganic nanosheets achieved by the elimination of organic layers.**

Layered perovskite-type oxides are a unique class of materials exhibiting novel physical properties such as semiconductivity,[1] superconductivity,[2] ferroelectricity[3] and photocatalytic activity.[4] The exfoliation of these layered perovskites promises a novel possibility to utilize a nanosheet-shaped layered metal oxide as a composite in an organized film.[5,6] We have recently developed a method to prepare a single layered film of inorganic nanosheets by hybridizing with organic monolayers. According to this method, the monolayer of an organic amphiphile is formed onto a subphase of an aqueous dispersion of layered oxide. Hybridization proceeds at an air–water interface between a floating monolayer and exfoliated inorganic nanosheets in a subphase.[7,8] Since an organic part is an inevitable component for this method, there is an urgent need to clarify the role of the organic layer in the functionality of a prepared film. This communication reports the effect of photo-modification treatment by UV light on the electric properties of a deposited hybrid LB film.

$KSr_2Nb_3O_{10}$ (K-type) was synthesized by reacting a solid mixture of $K_2CO_3$, $SrCO_3$ and $Nb_2O_5$ at 1150 °C for 24 hours.[9] A K-type powder was acidified to form a powder of $HSr_2Nb_3O_{10}$ (H-type) by being refluxed in 6 M HCl at 60 °C for 16 hours.[10] The obtained H-type powder was mixed with tetramethylamine (TMA) in an autoclave at 60 °C for 72 hours, being transformed into a powder of $(CH_3)_3NH^+Sr_2Nb_3O_{10}^-$ (TMA-type). The TMA-type sample was exfoliated in pure water by being stirred for more than one week. An aqueous dispersion of a TMA-type powder thus prepared was stable for several months.

A $\pi$–$A$ isotherm curve was measured when a 9 : 1 (v/v) chloroform/methanol solution of octadecylammonium hydrochloride ($ODAH^+Cl^-$) ($4.05 \times 10^{-4}$ mol dm$^{-3}$) was spread onto an aqueous dispersion of TMA-type niobate (0.512 g dm$^{-3}$). After 30 minutes, the surface was compressed at a rate of 10 cm$^2$ min$^{-1}$. Surface pressure started off at 0.3 nm$^2$ molecule$^{-1}$ until the film collapsed at 45 nm$^2$ molecule$^{-1}$. A floating film was repeatedly deposited onto a hydrophilic glass plate (15 mm × 8 mm) as a Y-type film at a surface pressure of 20 mN m$^{-1}$ by the perpendicular dipping method.

Aluminium was evaporated as an electrode onto 10- and 5-layered LB films and the electrical properties of a film sample (2 mm (electrode spacing) × 8 mm (width)) were measured with a LC meter (Hioki 3532-50, Japan). AC impedance measurements were operated at a constant voltage of 1.0 V in the frequency range from 2 MHz down to 50 Hz. The measurements were carried out under vacuum conditions (<0.1 Torr). For photo-modification, a film was irradiated directly with a 150 W Xe lamp (Hamamatsu Photonics, Japan) at the intensity of *ca.* $2.1 \times 10^{18}$ quanta cm$^{-2}$ s$^{-1}$. For the photoconductivity measurements, the same film was illuminated with the same Xe lamp through an interference filter (280 nm) and a 10 cm quartz cell containing pure water at an intensity of $2.0 \times 10^{16}$ quanta cm$^{-2}$ s$^{-1}$. Under this set-up, the temperature rise of a sample film was found to be ~5 °C. Before the electrical measurements, the film was pre-irradiated by 280 nm light for 30 minutes until a stable value was obtained (denoted as pretreatment).

The results of the impedance measurements are shown as Cole–Cole plots in Fig. 1. The fresh films behaved as insulators in the dark (plots with filled diamonds). Before photo-modification, the impedance plot was shaped like part of a large semi-circle even under the illumination of 280 nm light (plots (a)). When the 10-layered film was illuminated with a Xe lamp for 0.5–4.5 hours with no filter (photo-modification), the radius of the semi-circle became smaller as shown by plots (b)–(f). After more than 4.5 hours of photo-modification, the plots stayed constant (plots (f)–(g)). The 5-layered film also showed a similar pattern, though the impedance plot was unchanged after 30 minutes irradition (photo-modification). The effects of photo-modification were analyzed in terms of an equivalent circuit of one of resistance ($R$) and one of capacitance ($C$) in parallel. As a result, the $R$ component decreased from 600 to 65 MΩ (10-layered film) and to 175 MΩ (5-layered film) with the $C$ component nearly constant at 2.0 ± 0.2 pF. The DC photoconductivity was measured when the AC photoconductivity was constant. The Ohmic current was obtained in the 0–10 voltage region, giving resistivities of 69 MΩ and 125 MΩ for the 10- and 5-layered films, respectively. The values coincided well with the $R$ component in the AC measurements.

In order to clarify the structural change of the film during photo-modification, the IR absorption spectra were measured as a

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† Electronic supplementary information (ESI) available: AFM images, results of DC and GCMS measurements. See http://www.rsc.org/suppdata/cc/b4/b419064e/

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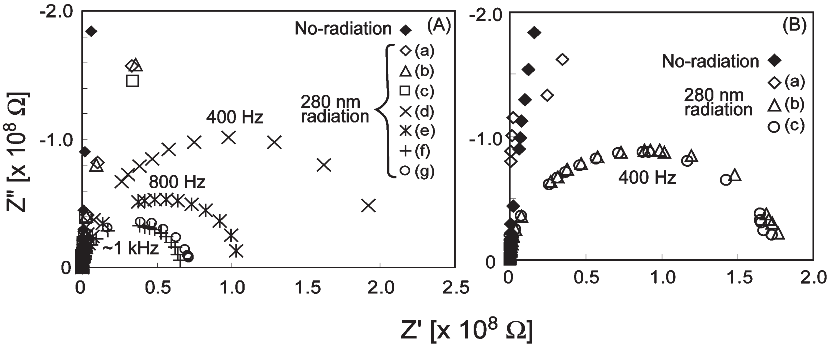

**Fig. 1** Cole–Cole plots of the impedance measurements on 10-layered (A) and 5-layered (B) LB films: (◆) in the dark; (a) under the illumination of 280 nm light before photo-modification; (b)–(g) under the illumination of 280 nm light after the photo-modification with a Xe lamp for 0.5, 1.5, 2.5, 3.5, 4.5 and 8.5 hours, respectively.

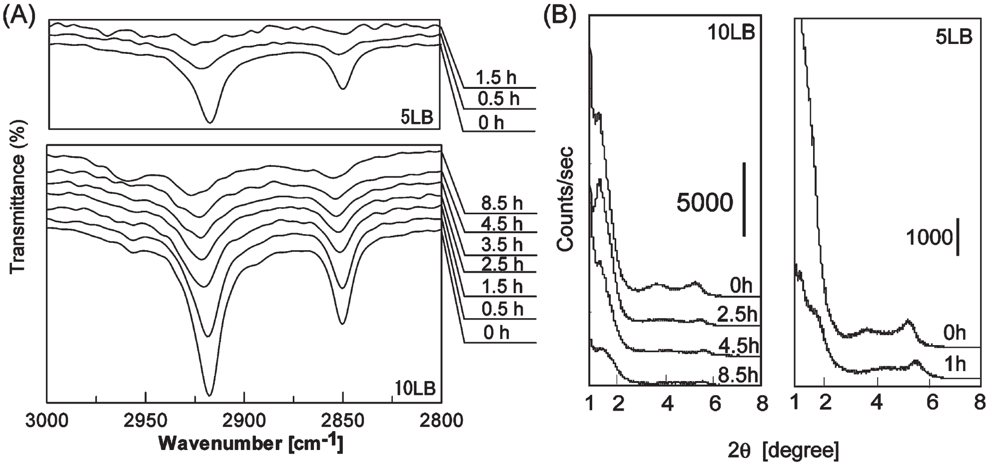

**Fig. 2** **(A)** Infrared absorption spectra for the 10- and 5-layered LB films, showing the reduction of peaks at 2923 and 2852 cm$^{-1}$. **(B)** XRD patterns for the 10- and 5-layered LB films by varying the photo-modification time.

function of photo-modification time (Fig. 2(A)). The peaks at 2923 and 2853 cm$^{-1}$ (the symmetric and antisymmetric –$CH_2$– stretching vibration bands, respectively,[8]) decreased on increasing illumination time. The eliminated gases were trapped at 77 K when *ca.* 5 mg of ODAH$^+$-exchanged niobate was photo-modified for 8 hours. The compositions of the trapped gas were analyzed with a GCMS insrument. As a result, the main components were found to be $H_2O$, $CO_2$, $C_4H_8O$ and $C_6H_{14}$. Thus it was concluded that ODAH$^+$ was decomposed under the photocatalytic activity by niobate layers. After the decomposition of ODAH$^+$, protons were assumed to be present as counter cations.[11] No such change of the IR spectrum was observed during the 30 minutes irradiation of 280 nm light (pretreatment), implying that monochromatization of the incident light made the light intensity so low as to cause no photodecomposition of the organic layer.

Fig. 2(B) shows the XRD measurements on 10- and 5-layered films under CuKα radiation through a Ni filter. Three peaks were observed at $2\theta = 1.31$, 3.83 and 5.4°, though the first peak was not observed on the 5-layered film. Supposing that the peak at $2\theta = 1.31°$ corresponded to the basal reflection (001), the thickness of a unit layer was estimated to be 6.73 nm. Since the present film was deposited as a Y-type film, the unit layer was thought to consist of one ODAH$^+$ double molecular layer sandwiched by two niobate layers. The thickness of a niobate layer and the molecular length of ODAH$^+$ are reported to be 1.23 nm and ~2.4 nm,[12] respectively. Thus when ODAH$^+$ molecules were inclined by 33 degrees from the normal direction, the unit layer of the film was estimated to have the thickness of ~6.7 nm, which was nearly equal to the observed value. The other two peaks possibly corresponded to (003) and (004) reflections with the disappearance of the (002) reflection. All three peaks decreased during photo-modification with a slight shift towards larger $2\theta$ (Fig. 2(B)). Thus the layer-by-layer structure of the film collapsed with a loss of the ODAH$^+$ layer.

The surface structure was observed with an atomic force microscope (AFM; Nanoscope IIIa, DI) before and after the photo-modifcation treatment. Fig. 3 shows the AFM image of a surface of the single layered LB film after 4.5 hours photo-modification. Plate-like sheets were observed on the substrate. The thickness of a sheet with a flat surface was estimated to be 1–3 nm, which was possibly composed of either one or two niobate nanosheets and interlayered oxionium ions (~0.3 nm).[10] The surfaces of some sheets were characterized by the presence of the bright domains (*e.g.* the region of arrow 1 in Fig. 3). The height of such a domain was estimated to be 2–3 nm, which was consistent with the length of ODAH$^+$ (~2.4 nm).[12] Similar features were

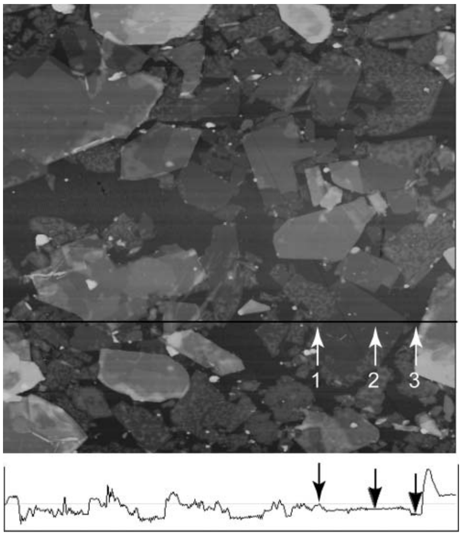

**Fig. 3** An AFM image (10 μm × 10 μm) of a single layered LB film of niobate after Xe lamp modification (4.5 hours). The vertical distance between the 2 and 3 arrowed positions was estimated to be 1.88 nm. It corresponded to the thickness of a niobate layer.

previously observed for a hybrid film of ODAH$^+$ and a clay.[13] It was ascribed to the self-aggregated domains of adsorbed ODAH$^+$. A quantity of the ODAH$^+$ aggregated regions on a niobate surface was found to decrease as a result of the photo-modification treatment. In correspondence to this, the bare flat region of the surface (as indiacted by arrow 2 in Fig. 3) increased remarkably. These observations were consistent with a view that ODAH$^+$ molecules were removed during the photo-modification

Combining the above data, it was concluded that the partial elimination of organic moieties by photo-modification changed the film from an insulator into a photosemiconductor. Most probably the organic part behaved as a barrier to electric conduction between the nanosheets. The elimination of such a part resulted in the direct junction of nanosheets allowing the carrier to flow through the film. This is an initial observation on the role of an organic part on the function of an organic/inorganic nanosheet, *i.e.* the patterning of conductive and non-conductive parts in a film.

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## Notes and references

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