

Supporting information

Inorganic Janus Nanosheets bearing two types of covalently bound organophosphonate groups via regioselective surface modification of $\text{K}_4\text{Nb}_6\text{O}_{17}\cdot 3\text{H}_2\text{O}$

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A. Details of the experiment

A-1 Material

K_2CO_3 (Tokyo Kasei Co.) and Nb_2O_5 (Wako Pure Chemical Ind. Co.) were used for preparation of $K_4Nb_6O_{17} \cdot 3H_2O$. Dimethyldioctadecylammonium chloride (Tokyo Kasei Ind.) and dodecylamine hydrochloride (Tokyo Kasei Ind.) were used as guest species for preparation of intermediates for surface modification. Octadecylphosphonic acid (ODPA) synthesized according to the method in the literature,^{1, 2)} and (3-carboxypropyl)phosphonic acid (CPPA, Wako Pure Chemical Ind.) were used for surface modification. Tetrahydrofuran (THF, Wako Pure Chemical Ind.), 2-butanone, (Kanto Chemical) and hydrochloric acid (Kanto Chemical) were used for surface modification. Only 2-butanone was dehydrated using a molecular sieve 4A before use. All other reagents were used as received without further purification.

A-2 Experimental Procedures

A-2-1. Preparation of $K_4Nb_6O_{17} \cdot 3H_2O$

$K_4Nb_6O_{17} \cdot 3H_2O$ was prepared by calcination of a mixture of K_2CO_3 (2.83 g) and Nb_2O_5 (7.43 g) at $1100^\circ C$ for 10 hours without intermittent grinding. The product was washed with water and dried in air.

A-2-2 Preparation of ODPA_NbO

$K_4Nb_6O_{17} \cdot 3H_2O$ (2.60 g) and dimethyldioctadecylammonium chloride (5.87g) ($K_4Nb_6O_{17} \cdot 3H_2O$ to dimethyldioctadecylammonium chloride molar ratio of 1 : 4) were reacted in water (200 mL) at $50^\circ C$ for 7 days to expand interlayer I. Fifty mg of the product was reacted with ODPA (0.048 g) ($K_4Nb_6O_{17} \cdot 3H_2O$ to ODPA molar ratio of 1 : 4) in 2-butanone (20 mL) at $150^\circ C$ for 7 days. The crude product, ODPA_NbO, was washed with THF and hydrochloric acid (pH = 3) and dried in air.

A-2-3 Preparation of ODPA_CPPA_NbO

ODPA_NbO (0.10 g) and dodecylamine hydrochloride (0.19g) (Nb_6O_{17} to dodecylamine hydrochloride molar ratio of 1 : 10) were reacted in water (10 mL) at $80^\circ C$ for 3 days to expand interlayer II. Subsequently, 50 mg of this product was reacted with CPPA (50 mg) (Nb_6O_{17} to dodecylamine hydrochloride molar ratio of 1 : 10) in 2-butanone (10 mL) at $80^\circ C$ for 3 days. The crude product was centrifuged and washed with THF twice, hydrochloric acid (pH = 3) twice and THF sequentially. The precipitate remaining after the last washing with THF was identified as ODPA_CPPA_NbO. The supernatant obtained during washing with THF was collected and dried on a glass substrate and called ODPA_CPPA_NbO_evaporation.

A-3 Analyses

Infrared (IR) adsorption spectra were recorded on a JASCO FT/IR-460 Plus spectrometer by the KBr disk method. Solid-state ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectroscopy performed with a JEOL JNM-ECX 400 spectrometer at 99.55 and 160.26 MHz, respectively. Solid-state ^{13}C NMR spectra were obtained with cross-polarization (CP) and magic angle spinning (MAS) techniques (pulse delay, 5 s;

contact time, 1.5 s; spinning rate, 12 kHz), while solid-state ^{31}P NMR spectra were obtained with a MAS technique only (pulse delay, 30 s; spinning rate, 12 kHz). Hexamethylbenzene (17.4 ppm) and triphenylphosphine (-8.4 ppm) were used as external references for ^{13}C and ^{31}P NMR, respectively. Inductively coupled plasma emission spectrometry was performed with a Thermo Jarrell Ash ICAP-574 II instrument by the internal standard method after dissolution of the sample in a mixture of 4 mL of HNO_3 , 3 mL of HCl , and 1 mL of HF at 150°C overnight. The carbon, hydrogen, and nitrogen contents were determined by elemental analysis using a Perkin Elmer PE2400 II instrument. Transmission electron microscope (TEM) images were obtained using a JEM-1011 microscope operating at 100 kV. For the electron diffraction (ED) analysis, the incident electron beam was perpendicular to the lateral plane of the NSs. X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT-1000 diffractometer (Mn-filtered $\text{FeK}\alpha$ radiation), and a Rigaku SmartLab diffractometer with Mn-filtered $\text{FeK}\alpha$ radiation by the parallel-beam method.

B. IR spectra of of ODPA_NbO and ODPA_CPPA_NbO

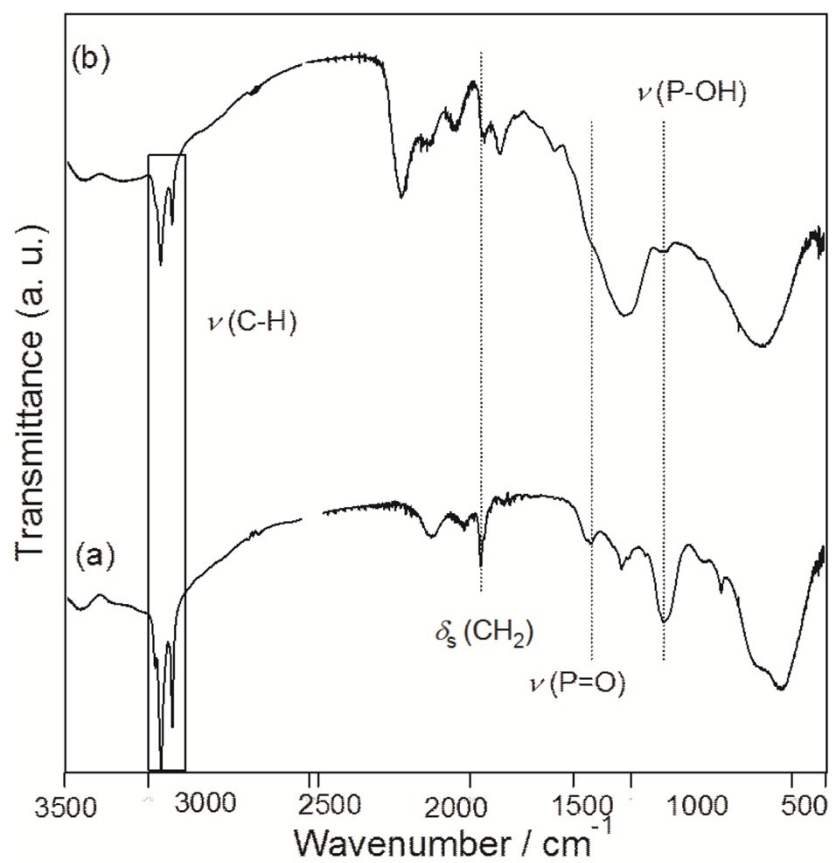


Figure S1 IR spectra of of ODPA_NbO and ODPA_CPPA_NbO

C. ^{13}C CP/MAS NMR of ODPA_NbO and ODPA_CPPA_NbO

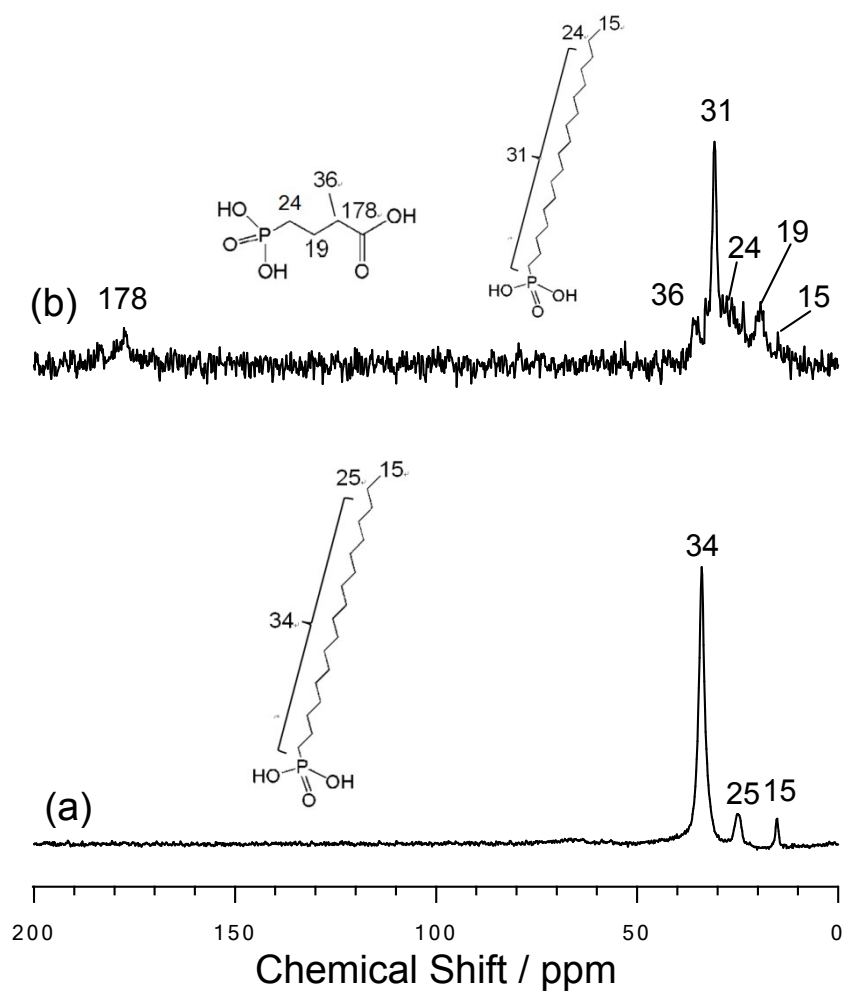


Figure S2 ^{13}C CP/MAS spectra of (a) ODPA_NbO and (b) ODPA_CPPA_NbO.

D. ^{31}P MAS NMR of ODPA_NbO and ODPA_CPPA_NbO

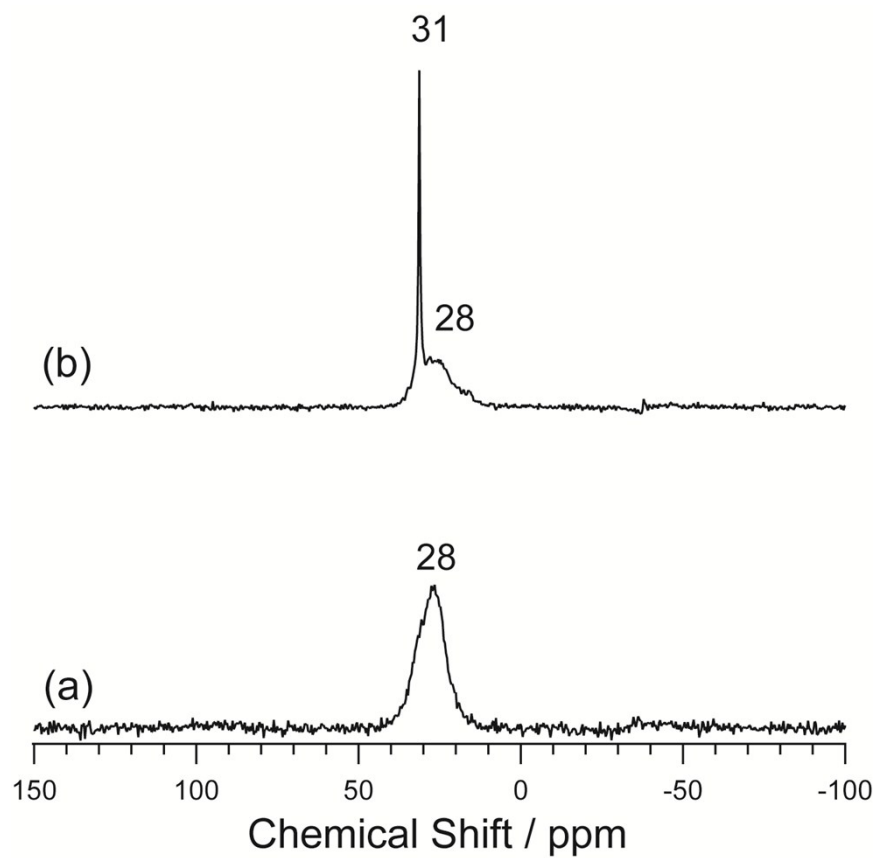


Figure S3 ^{31}P MAS NMR of ODPA_NbO and ODPA_CPPA_NbO

E. ^{31}P MAS NMR of CPPA

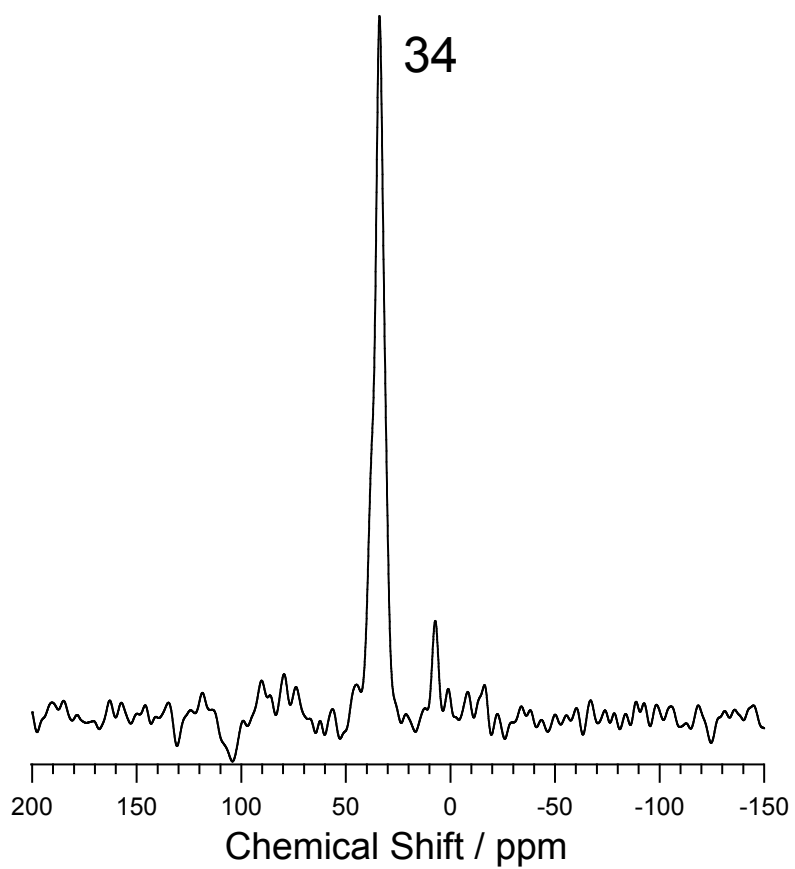
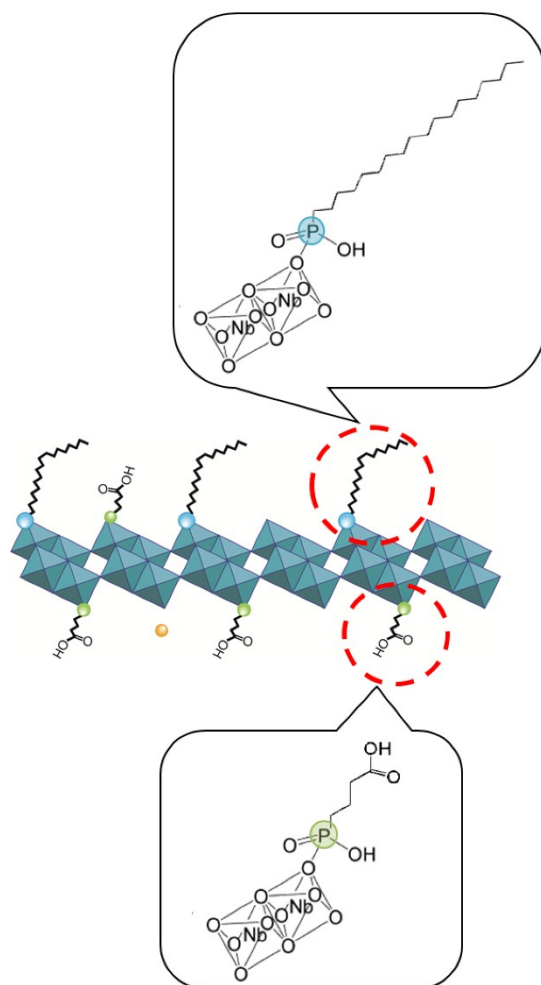


Figure S4 ^{31}P MAS NMR spectrum of CPPA

F. Schem of the estimated structure of the product



Scheme S1 Estimated structure of the product

G. XRD patterns of ODPA_NbO, ODPA_CPPA_NbO and ODPA_CPPA_NbO_evaporation.

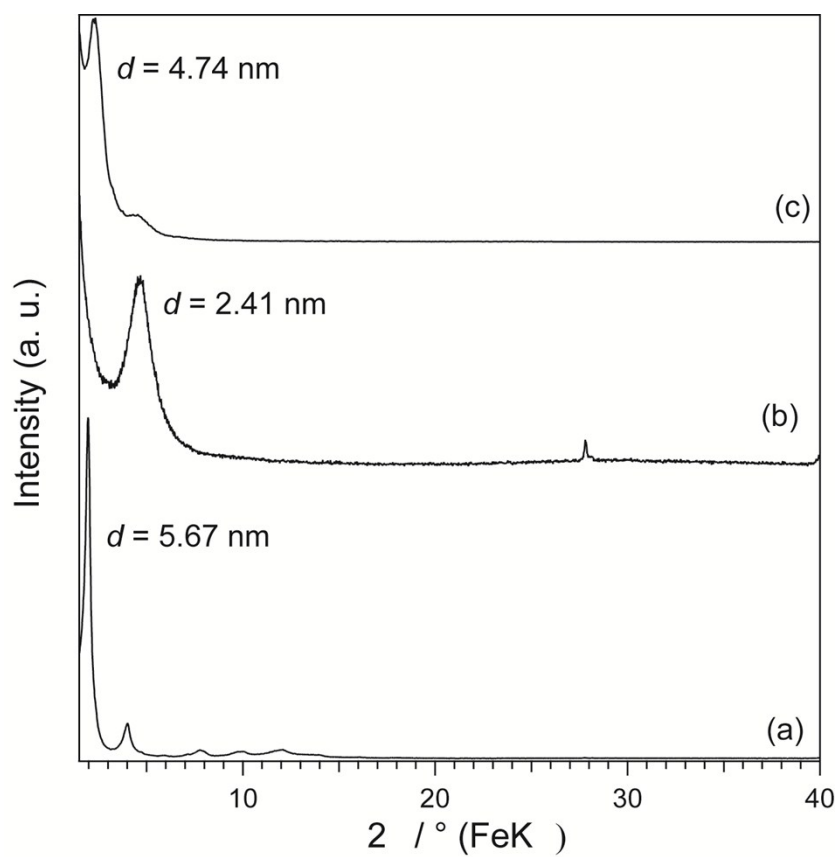


Figure S5 XRD patterns of (a)ODPA_NbO, (b)ODPA_CPPA_NbO and (c)ODPA_CPPA_NbO_evaporation.

H. TEM image of exfoliated ODPA_CPPA_NbO and corresponded ED pattern.

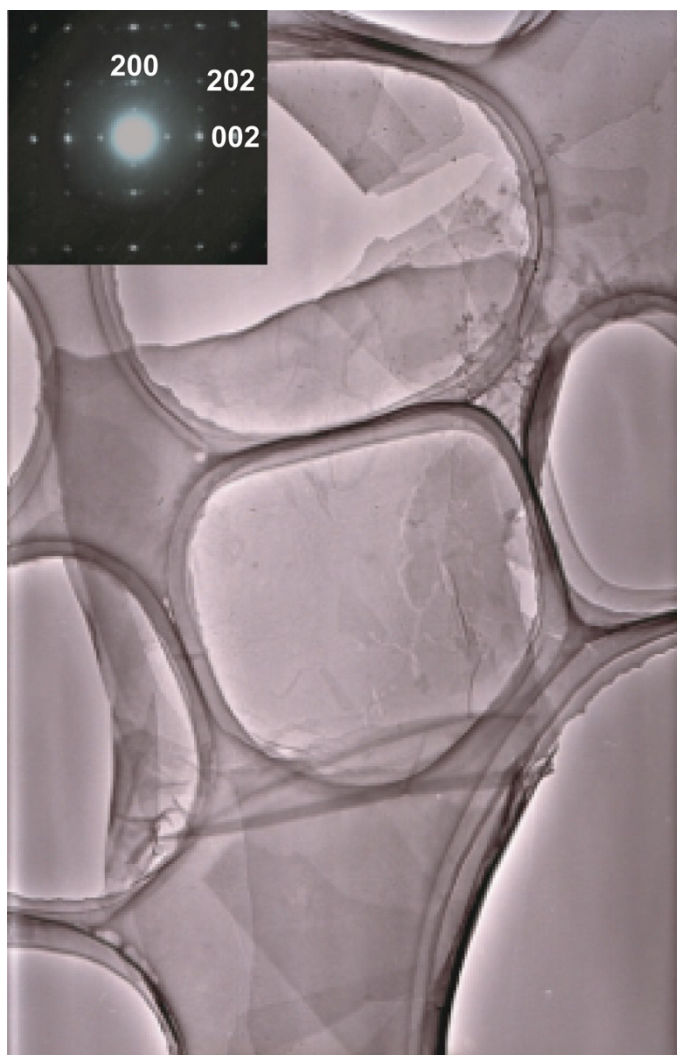


Figure S6 TEM image of exfoliated ODPA_CPPA_NbO. The inset shows the corresponding ED pattern.

I. Preparation of a Janus nanosheets sample for AFM observation

Topographic and phase images were simultaneously recorded using an Agilent 5500 AFM/SPM machine in acoustic AC mode under ambient conditions and in air. An ordinary commercial silicon cantilever was used as an AFM tip (e.g., a RTESP-300 from Bruker; resonance frequency ≈ 300 kHz, and spring constant ≈ 40 N/m).

In order to avoid aggregation, isolated nanosheet samples were intentionally prepared by rapid drying using a spin-coating method. The rapid drying resulted in a nanosheet immobilized with both faces by kinetically nonselective adsorption. In addition, the abundance ratio of the “**yellow-red**” face was roughly twice as high as that of the “**yellow-green**” face in Figure 2, probably indicating an affinity of the “**yellow-green**” face for the silicon substrate.

The co-existence of the two surfaces of the Janus nanosheets on a substrate indicates that no specific adsorption of the nanosheets on the substrate occurred under the preparation conditions we applied. In fact, when the sample solution was cast and dried slowly, re-aggregation of the dispersed nanosheets occurred.

J. Reference

- 1) J. T. Woodward, A. Ulman and D. K. Schwartz, *Langmuir*, **12**, 3626-3629 (1996).
- 2) B. Y. Kim, E. L. Ratcliff, N. R. Armstrong, T. Kowalewski and J. Pyun, *Langmuir*, **26**, 2083-2092 (2010).