Supporting Information

Coexistence of Magnetic Order and Ferroelectricity at 2D Nanosheet Interfaces

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**Experimental Procedure**

**Synthesis of nanosheets.** Oxide nanosheets (Ti_{0.8}Co_{0.2}O_2, Ca_2Nb_3O_{10}) were prepared by delaminating layered compounds according to previously described procedures\(^9,10\). The starting materials (K_{0.8}Ti_{1.6}Co_{0.4}O_4, KCa_2Nb_3O_{10}), which were prepared by a solid-state reaction, were converted into protonic forms (H_{0.8}Ti_{1.6}Co_{0.4}O_4·nH_2O, HCa_2Nb_3O_{10}·1.5H_2O) in 1 M HCl and 5M HNO_3 solutions. Colloidal suspensions of Ti_{0.8}Co_{0.2}O_2, Ca_2Nb_3O_{10} nanosheets were then synthesized by delaminating these protonic oxides with aqueous solution of TBAOH.

**Film fabrication.** The superlattice films were fabricated onto various substrates such as Si, glass and SrRuO_3 using the LB deposition process\(^12\). For electric characterization, we used an atomically flat conducting SrRuO_3 substrate, consisting of a 50-nm-thick (001)-oriented epitaxial SrRuO_3 film grown on a (001) SrTiO_3 single crystal. Prior to film deposition, the SrRuO_3 substrate (1×1 cm\(^2\)) was photochemically cleaned using UV light irradiation in ozone. In the cases of Si and quartz glass, the substrates were cleaned by chemical treatment in a bath of 1/1 CH_3OH/HCl and then concentrated H_2SO_4 for 30 min each. The colloidal suspension of nanosheets was diluted with ultrapure water and was placed in the LB trough at a regulated temperature of 25 ± 0.5°C. During LB deposition, the packing density of the nanosheets was controlled by the surface pressure at the air–water interface. The highly condensed phase appeared at the surface pressure of 15 and 10 mN m\(^{-1}\) for Ca_2Nb_3O_{10} and Ti_{0.8}Co_{0.2}O_2, and the resulting monolayer films were characterized by neat-tilting arrangements of nanosheets without considerable gaps and overlaps. The procedure for the LB transfer involving two different nanosheets was repeated an appropriate number of times to fabricate a superlattice assembly. After each LB deposition cycle, the film was dried at 110 °C for 20 min, and exposed to UV white light from an Xe lamp (1 mW cm\(^{-2}\)) for 10 min. The as-grown film samples were irradiated by UV light for 48 h in order to totally decompose the TBA\(^+\) ions used in the exfoliation process.

**Characterization.** The film quality was characterized by AFM, XRD, HRTEM, UV-visible spectroscopy and hard X-ray photoelectron spectroscopy (HX-PES). The surface morphology of the nanosheet films was measured using an SII nanotechnology E-sweep AFM with a Si tip cantilever (14 N m\(^{-1}\)). Out-of-plane XRD data were collected by a Rigaku RINT 2200 powder diffractometer using monochromatized Cu K\(\alpha\) radiation (\(\lambda =0.15405\) nm). In-plan XRD (\(\lambda =0.11971\) nm) data were performed at the BL-6C in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-PF). HRTEM images were taken using a Hitachi H-9000.
microscope operating at 200 kV. The superlattice buildup process was monitored by a UV-visible spectrophotometer (Hitachi U-4100). HX-PES was carried out at BL 15XU of SPring-8.

**Electrical characterization.** Electrical measurements were carried out by forming Au/(nanosheet)$_n$/SrRuO$_3$ nanocapacitors. Au top-electrodes with a thickness of 30 nm were deposited by an electron beam evaporation (Sanyu, SVC-700). The capacitance and dielectric loss were measured using a precision impedance analyzer (Agilent Technologies 4294A) in the range of 100 Hz – 10 MHz. Ferroelectric ($P$-$E$) curves were collected using a precision ferroelectric tester (Radient Premier II). Magnetic measurements were performed using a magnetic properties measurement system (Quantum Design MPMS). All of the curves shown in this letter are corrected to eliminate the diamagnetic background of the substrate. The ME effects were characterized by a dynamic ME coupling measurement setup.$^{S1,2}$ An ac source (Keithley 6221) was used to supply the constant amplitude ac current to the solenoid to generate a 5 Oe ac magnetic field $h(f)$ with the frequency from dc to 100 kHz. A lock-in amplifier is employed to detect the induced ME voltage $V(f)$ across the sample thickness ($d$) with the same frequency of the ac current source. The background voltage noise due to the Faraday’s Law has been successfully reduced to a very small level (below several microvolts) by a careful design of the voltage detecting circuit with twisting and electric field shielding. The high signal-to-noise ratio can guarantee the accuracy of our measurements. The ac magnetic field was applied parallel to the direction of the induced ME voltage, i.e., in a longitudinal mode. The linear ME coefficient $\alpha$ is defined as $\alpha = \frac{\delta E}{\delta H} = \frac{V_0(f)}{h_0(f)} \times \frac{1}{d}$.


Figure S1. AFM images for monolayer films of Ti$_{0.8}$Co$_{0.2}$O$_2$ and Ca$_2$Nb$_3$O$_{10}$ nanosheets on a Si substrate. Selected nanosheets are outlined for clarity.

Figure S2. UV-visible absorption spectra for the superlattice assemblies. (a) (Ti$_{0.8}$Co$_{0.2}$O$_2$)$_3$/(Ca$_2$Nb$_3$O$_{10}$)$_2$/(Ti$_{0.8}$Co$_{0.2}$O$_2$)$_3$, (b) Ca$_2$Nb$_3$O$_{10}$/[(Ti$_{0.8}$Co$_{0.2}$O$_2$)$_2$/Ca$_2$Nb$_3$O$_{10}$]$_3$. (c) UV-visible absorption spectra for monolayer films of Ti$_{0.8}$Co$_{0.2}$O$_2$ and Ca$_2$Nb$_3$O$_{10}$ and superlattice film of Ti$_{0.8}$Co$_{0.2}$O$_2$/Ca$_2$Nb$_3$O$_{10}$. 
Figure S3. In-plane XRD patterns for (a) the superlattice film of $(Ti_{0.8}Co_{0.2}O_2/Ca_2Nb_3O_{10})_4/Ti_{0.8}Co_{0.2}O_2$ and (b, c) monolayer films of $Ti_{0.8}Co_{0.2}O_2$ and $Ca_2Nb_3O_{10}$ on a quartz glass substrate. (d) Out-of-plane XRD patterns for superlattice films with different stacking orders.
**Figure S4.** Polarization ($P - E$) property for the 10-layered film of Ca$_2$Nb$_3$O$_{10}$ nanosheets. $P - E$ measurements were performed on SrRuO$_3$. All the measurements were made at 300 K.

**Figure S5.** Conducting AFM images for the monolayer and bilayer LB films of Ca$_2$Nb$_3$O$_{10}$ nanosheets on a SrRuO$_3$ substrate.
Figure S6. Magnetic-modulation on the dielectric constant ($\varepsilon_r$) for (a) (Ti$_{0.8}$Co$_{0.2}$O$_2$/Ca$_2$Nb$_3$O$_{10}$)$_4$/Ti$_{0.8}$Co$_{0.2}$O$_2$, (b) (Ti$_{0.8}$Co$_{0.2}$O$_2$)$_3$/(Ca$_2$Nb$_3$O$_{10}$)$_2$/(Ti$_{0.8}$Co$_{0.2}$O$_2$)$_3$, (c) Ca$_2$Nb$_3$O$_{10}$/[(Ti$_{0.8}$Co$_{0.2}$O$_2$)$_2$/Ca$_2$Nb$_3$O$_{10}$]$_3$ on a SrRuO$_3$ substrate. The measurements were made at 300 K. Note that no modulation was observed in (a) and (b).
Figure S7. (a) Ti 2p, (b) Co 2p, and (c) Nb 3d core level HX-PES spectra for the superlattice film of (Ti$_{0.8}$Co$_{0.2}$O$_2$/Ca$_2$Nb$_3$O$_{10}$)$_4$/Ti$_{0.8}$Co$_{0.2}$O$_2$ on a SrRuO$_3$ substrate.