SUPPORTING INFORMATION for:

Topotactic Transformations of Superstructures: From Thin Films to 2D Networks to Nested 2D Networks

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METHODS. *Synthesis*. Amorphous BiO_x films (50~200 nm) were deposited by RF reactive magnetron sputtering with gas flow ratios (Ar and O_2) of 20 and 5 sccm, respectively. β-Bi_2O_3 films were prepared by heating the amorphous BiO_x films at 500 °C for 2 h. BiOCl 2DONWs were obtained by dipping a β-Bi_2O_3 film in hydrochloric acid solution (0.24 M, actually the concentration can change from 0.01 to 1.00 M) for 0.5~10 min. For the synthesis of Bi_2S_3 N2DONWs, a β-Bi_2O_3 film was incubated at 60 °C for two days in pre-blended solution of hydrochloric acid (0.024 M) and TAA (0.045 M), BiOCl 2DONWs were formed very quickly to ensure its function as the sacrificial template for the formation of Bi_2S_3 N2DONWs.

Periodic BiOCl nanowalls were prepared as follows: a PMMA thin film was spin coated on a β-Bi_2O_3 film, and periodic hole arrays (diameter of 30 nm and pitch of 200 nm) in the PMMA film were fabricated by e-beam lithography. The specimen was then dipped in diluted hydrochloric acid solution (0.04 M), leading to the formation of periodic BiOCl nuclei. The PMMA film was then removed by washing in acetone so that the β-Bi_2O_3 film with periodic BiOCl nucleus arrays was naked. Finally the specimen was dipping in hydrochloric acid solution (0.04 M) again, and periodic BiOCl nanowall arrays were formed where with the preformed BiOCl nucleus arrays.

Preparation of TEM specimen. For obtaining a preferred specimen, a layer of photoresist (Shipley S1813) was spin-coated on a β-Bi_2O_3 film, and then a periodic pattern composed of squares was made by a standard UV photolithography process, thus partial the β-Bi_2O_3 film was covered by photoresist. After dipping it into hydrochloric acid solution (0.24 M), for some crystal domains, only the exposed area was turned to BiOCl 2DONW while the other part which was covered by photoresist remained β-Bi_2O_3 phase. A slice from the boundary of such a domain containing both β-Bi_2O_3 and BiOCl with the cross section rightly perpendicular to one set of

nanowalls (and parallel to the other set) was made using focused ion beam (FIB) milling, then welded to a Cu TEM grid and finally thinned to ~ 100 nm for TEM observation.

Characterization. Structure of the films was determined by XRD (Philips X' pert Pro) analysis. Reflected optical images of the films were taken by optical microscopy (Olympus BX-51), and we used SEM (Hitachi S-4800, 5~10 kV) and TEM (FEI Tecnai F20, 200 kV) to observe the morphology of the nanostructures. HRTEM and SAED operated in the FEI F20 TEM were used to characterize the crystal structure of the nanostructures.

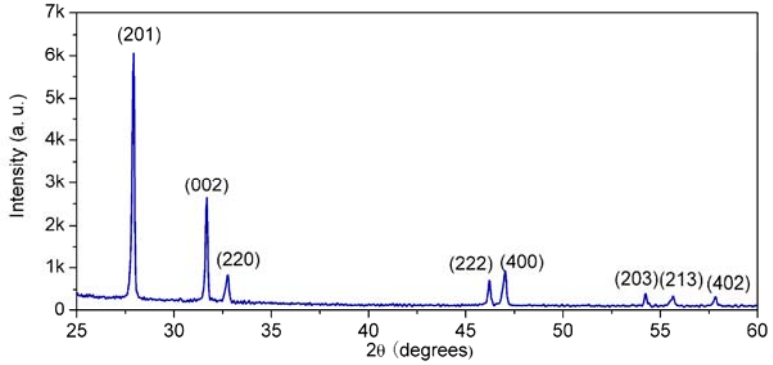

FIGURE S1. XRD pattern of a β-Bi_2O_3 film obtained by heating an amorphous BiO_x film (200 nm thick) at 500 °C for 3 h.

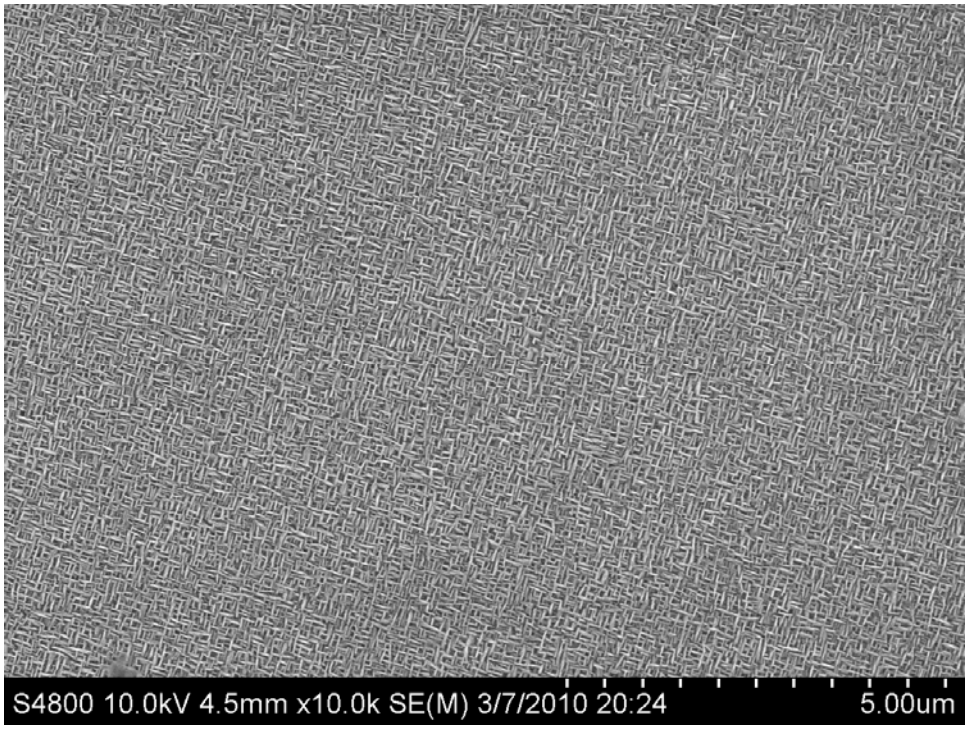

FIGURE S2. SEM image of a vertical BiOCl 2DONW on micron scale.

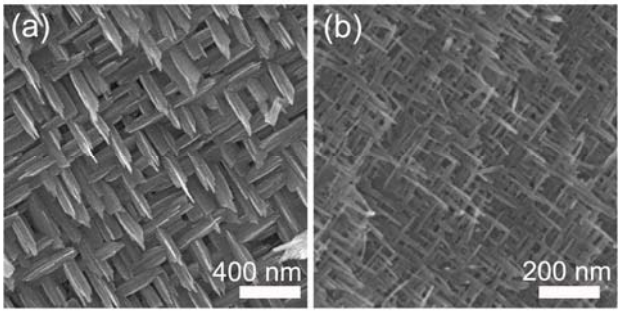

FIGURE S3. Bi_2S_3 networks evolved from tiled BiOCl nanowalls by reacting in preblended solution of TAA and HCl with different concentrations of HCl: (a) 0.05 M TAA +0.10 M HCl; (b) 0.05 M TAA +0.02 M HCl.

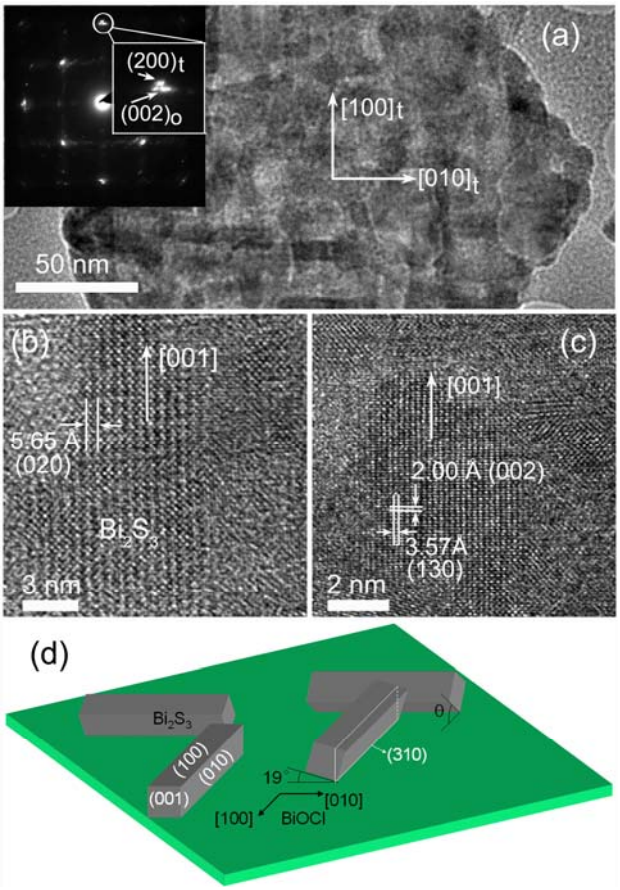

FIGURE S4. (a) TEM image of a heterostructured BiOCl-Bi_2S_3 plate, in which only a part of BiOCl has transformed to Bi_2S_3 nanorods or nuclei. The inset is a corresponding SAED pattern ('t' represents tetragonal BiOCl while "o" represents orthorhombic Bi_2S_3) indicates the lattice matching of Bi_2S_3 and BiOCl with $(002)_{Bi2S3}||(200)_{BiOCl}$. (b) and (c) HRTEM images of two Bi_2S_3 nuclei, although both of their [001] directions are parallel to the [100] direction of the BiOCl precursor, they are actually not in the same crystal orientation but with a lattice rotation of ~ 19° around the *c*-axis. (d) Schematic illustration of Bi_2S_3 nanorods grown on BiOCl, the angle 'θ' implies that the nanorods grow without a definite epitaxial relationship with the BiOCl precursor.