Supporting Information

Wafer Scale Thin Film of Ultra-Small Sc_2O_3 Nanocrystals on 2D COF with High Rigidity

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Materials

5, 10, 15, 20-Tetrakis (4-aminophenyl) porphyrin (TAPP) was obtained from Sigma Aldrich. Terephthalaldehyde (TPA) was purchased from Macklin. Sodium dodecyl benzene sulfonate (SDBS) was obtained from Aladdin. Ytterbium (III) triflate ($Yb(OTf)_3$, 99%), Scandium(Ⅲ) triflate ($Sc(OTf)_3$, 99%) and Erbium(Ⅲ) triflate ($Er(OTf)_3$, 99%) were purchased from Sigma Aldrich. DMF (⩾99.9%) and n-penpane(99%) was purchased from Macklin. All the chemicals were used as received.

Synthesis of Sc_2O_3/COF

Two-dimensional Sc_2O_3/COF composite film was synthesized in a customized teflon reactor with the length of 8 cm, width of 4 cm and height of 4 cm in the outermost, and wall thickness is 5 mm. The reactor should be placed in a relatively stable place to reduce the influence on the reaction process. 5.6 mg TPA and 22 mg $Sc(OTf)_3$ were added in a solution of 2 ml DMF and 38 ml deionized water and ultrasonicated for 15 min until completely dissolved. $Sc(OTf)_3$ was used as catalyst[1] and DMF was added to increase the solubility of TPA[2]. Then 15 ml mixed solution was injected into the reactor forming a static air-water interface[3, 4]. Next, 40 µL SDBS (1 mg/mL in chloroform) was spread onto the interface. After the evaporation of solvent for 30 min[5], n-pentane was subsequently added to the surface (~5 ml). The TAPP was first dissolved in a mixture solvent of pyridine/methanol = 3:1 (v/v) to form a 0.1 mM solution[2]. And then 40 µl TAPP was injected into the Teflon reactor on the top of n-pentane phase by a syringe pump (LongerPump, LSP01-1A) at a rate of 10µl/min. After injection, the polymerization was allowed to stand for two hours and then can be transferred to silicon wafers or other substrates for characterization tests.

Synthesis of 2D Yb_2O_3/COF, 2D Yb_2O_3/ Sc_2O_3/COF and 2D Yb_2O_3/ Sc_2O_3/ Er_2O_3/COF

The synthesis method and conditions are the same as above, but the proportion of $Sc(OTf)_3$ is changed. The condition changed by the synthesized 2D Yb_2O_3/COF is 2.5 mM terephthalaldehyde (TPA) dimethylformamide (DMF)/water (v/v=1:19) solution with 0.5 mg/mL $Yb(OTf)_3$. The condition changed by the synthesized 2D Yb_2O_3/Sc_2O_3/COF is 2.5 mM terephthalaldehyde (TPA) dimethylformamide (DMF)/water (v/v=1:19) solution with 0.25 mg/mL $Yb(OTf)_3$ and 0.25 mg/mL $Sc(OTf)_3$. The condition changed by the synthesized 2D Yb_2O_3/Sc_2O_3/Er_2O_3/COF is 2.5 mM terephthalaldehyde (TPA) dimethylformamide (DMF)/water (v/v=1:19) solution with 0.17 mg/mL

$Yb(OTf)_3$, 0.17 mg/mL $Sc(OTf)_3$ and 0.17 mg/mL $Er(OTf)_3$. Other conditions for synthesis remain the same.

Characterizations

The Transmission electron microscope (TEM) images and the EDS analysis were recorded by a Tecnai G2 F20 U-TWIN transmission electron microscope (America). TEM samples were transferred to a copper grid with a lacy carbon film for testing. Atomic force microscope (AFM) was performed in air on a customized NTEGRA Aura/Spectra from NT-MDT with an SMENA head operated in contact mode. X-ray diffraction (XRD) and Raman samples were transferred to silicon wafers for testing, and the XRD data were tested at 5°/min in the range of 5° to 80° by Rigaku D/MAX-TTRIII (CBO) (Japan). The Raman spectra was measured by Renishaw inVia plus. In order to increase the signal of XPS data, the 2D polymer was transferred to the silicon chip repeatedly and then tested. The X-ray photoelectron spectroscopy (XPS) signals were collected by an ESCALAB250Xi (Thermo Fisher Scientific – CN).

AFM nanoindentation test calculation

In a simplified continuum mechanics model of the nanofilm, the relationship between the applied force at the center of the film and the resulting deformation of the suspended nanosheet can be calculated as following formula:

$$F = {\sigma_0}^{2D} \pi \delta + E^{2D} \frac{q^3}{R^2} \delta^3 \qquad (1)$$

where F is applied force, δ is the deflection at the center point, ${\sigma_0}^{2D}$ is the pretension in the film, R is the radius of the hole, and q is a dimensionless constant determined by Poisson's ratio v (q = 1/(1.05 − 0.15v − 0.16v^2)=1.01). Here, we do not have the exact value of v, but we take 0.3 as v from literature of similar COF system[6]. E^{2D} is the 2D Young's modulus and defined as E^{2D} = Et, with the Young's modulus E and the membrane thickness t. The strain energy density of the 2D Sc_2O_3/COF composite material is normalized by the area of the film rather than by the volume. For purposes of comparison to bulk materials and other materials, these quantities can be divided by the membrane thickness t[7, 8].

Supplemental Information Figures

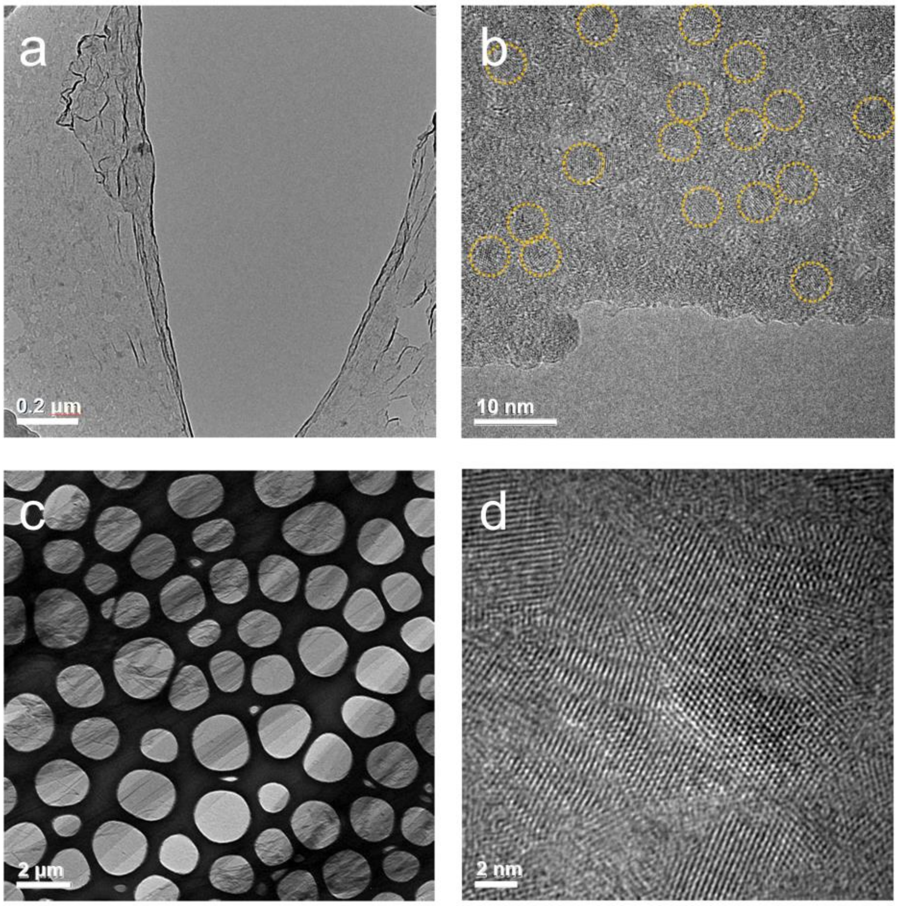

Figure S1 | (a-d) The TEM images of 2D Sc_2O_3/COF.

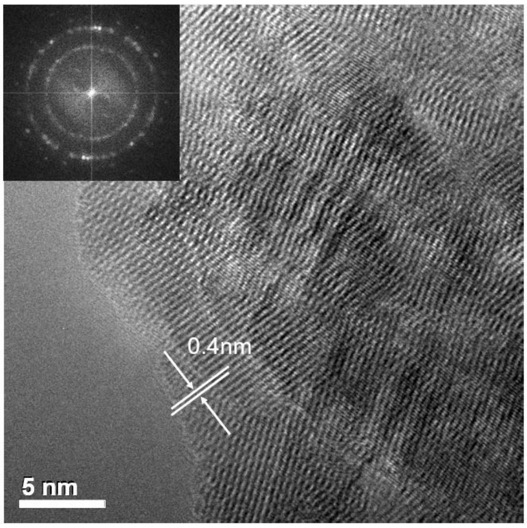

Figure S2 | TEM image of COF with minor Sc_2O_3. The inset is a SAED pattern.

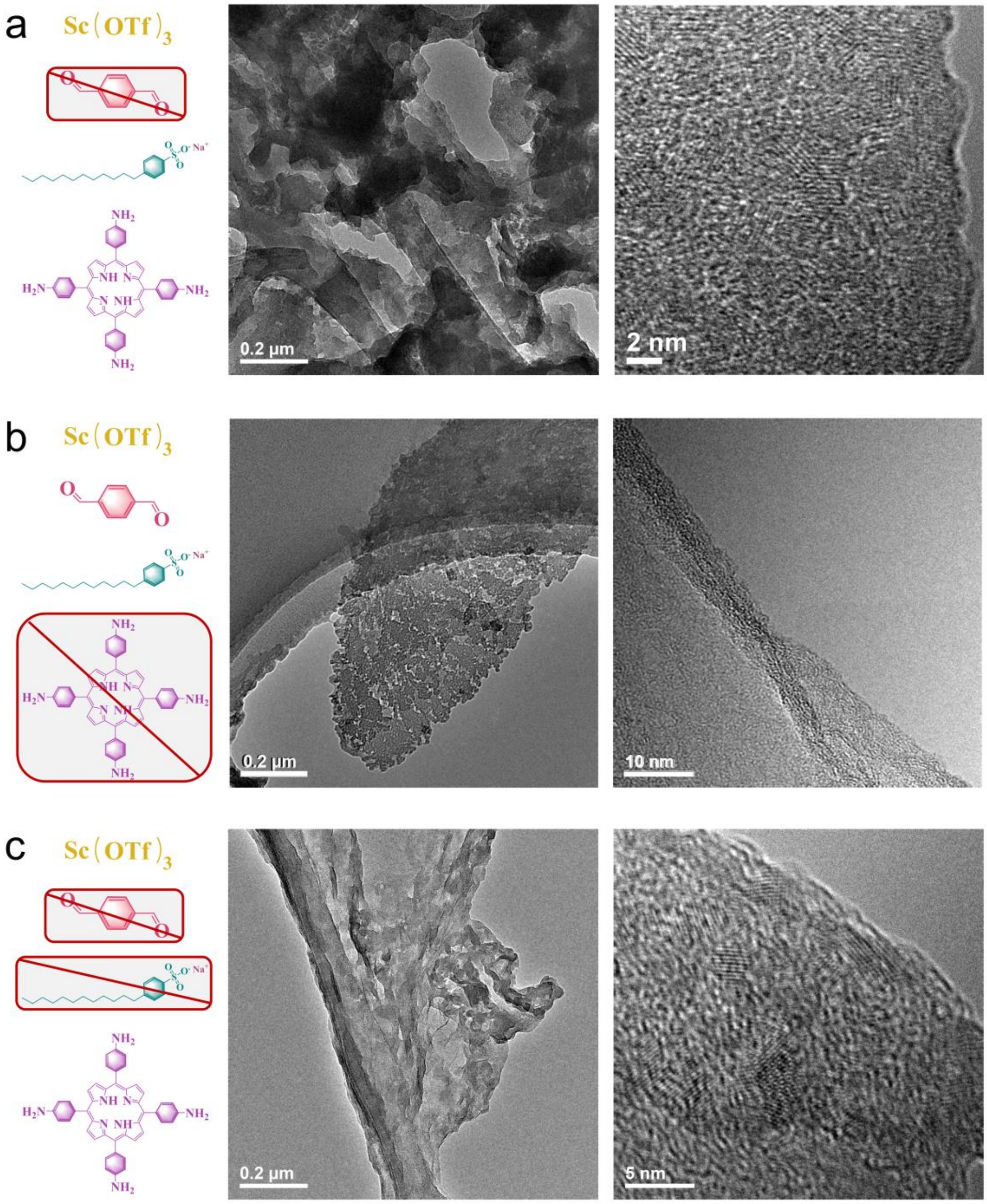

Figure S3 | Groping for synthetic conditions. TEM image with Sc, TPA, GO and SDBS as main raw materials, TEM image of synthetic materials (**a**) without TPA; (**b**) without TAPP; (**c**) without TPA and SDBS.

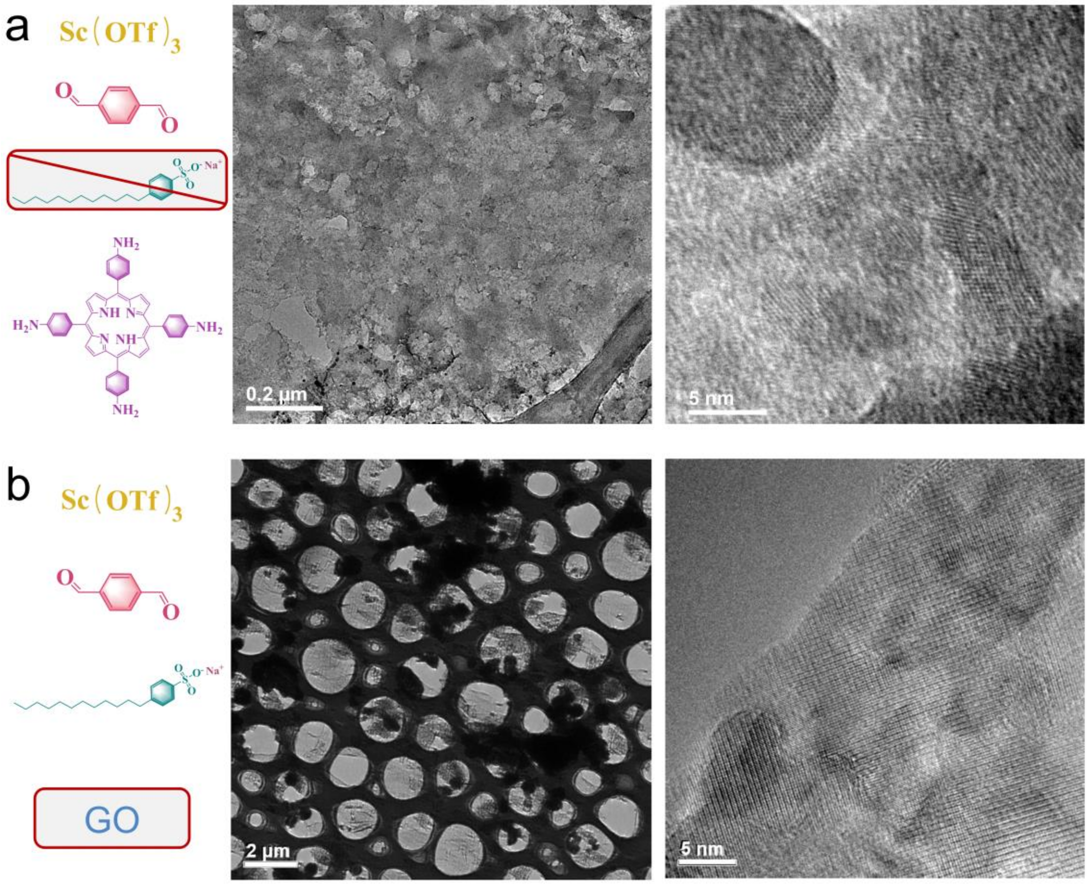

Figure S4 | Groping for synthetic conditions. TEM image with Sc, TPA, GO and SDBS as main raw materials, TEM image of synthetic materials (**a**) without SDBS; (**b**) replace TAPP with GO and include the other three ingredients.

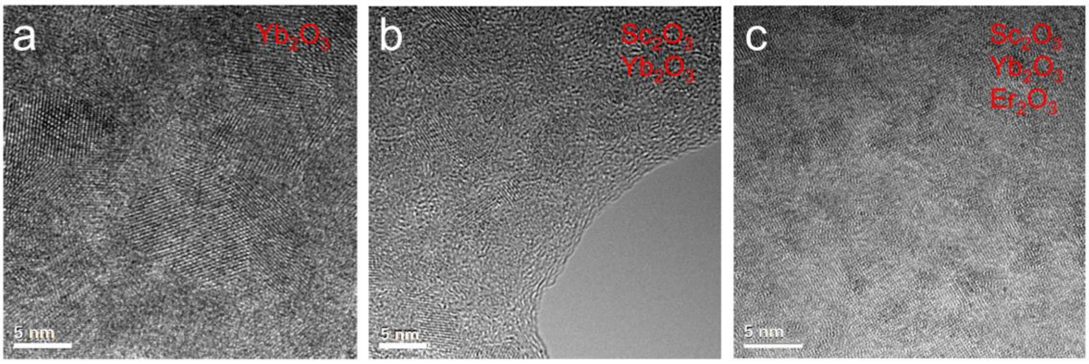

Figure S5 | TEM images of (**a**) 2D Yb_2O_3/COF; (**b**) 2D Yb_2O_3/Sc_2O_3/COF; and (**c**) 2D Yb_2O_3/Sc_2O_3/Er_2O_3/COF were synthesized by the same method.

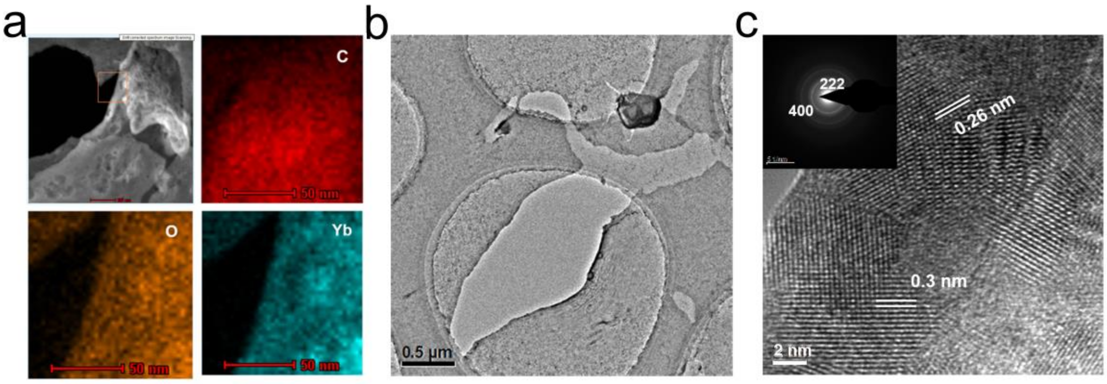

Figure S6 | (**a**) TEM mapping image of 2D Yb_2O_3/COF. (**b,c**) TEM images of 2D Yb_2O_3/COF. The insert in **c** is a SAED pattern of the 2D Yb_2O_3/COF.

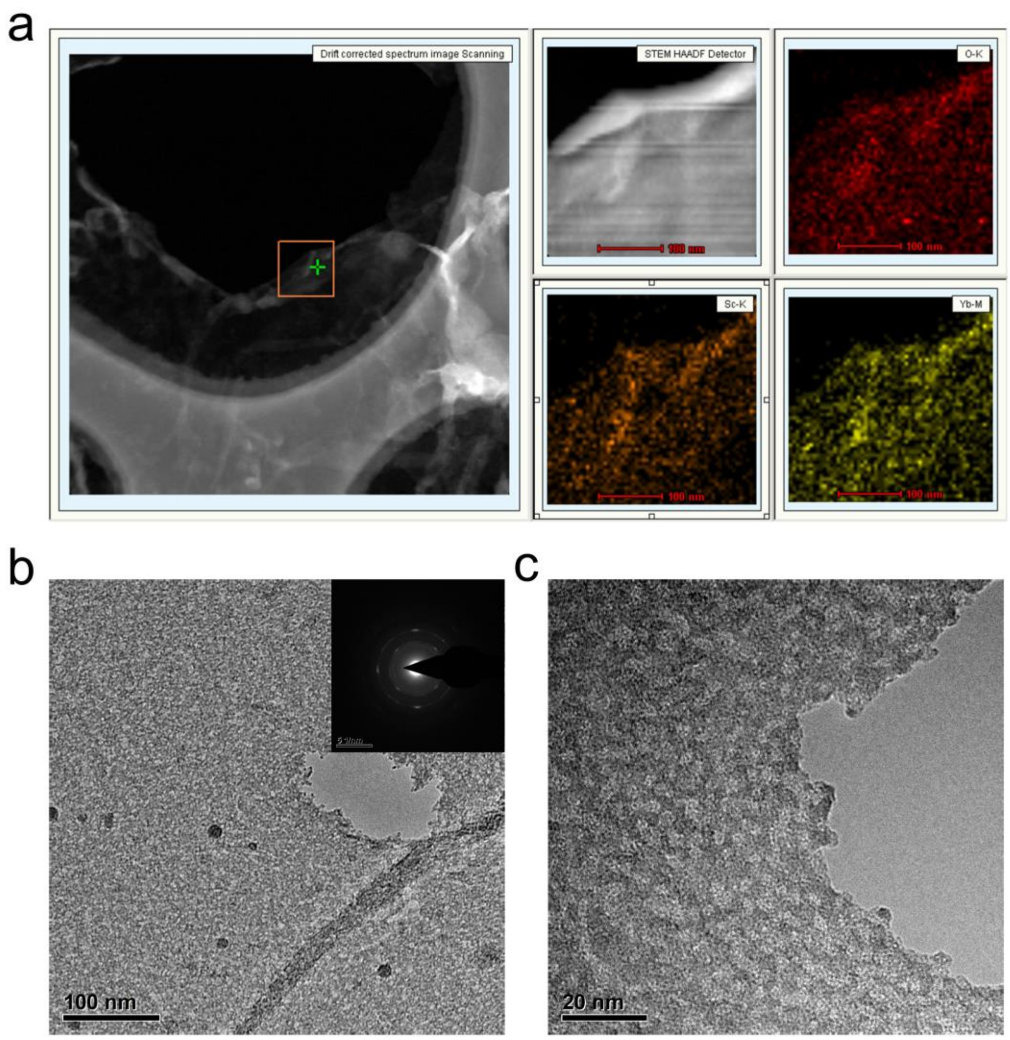

Figure S7 | (**a**) TEM mapping image of 2D Yb_2O_3/Sc_2O_3/COF. (**b,c**) TEM images of 2D Yb_2O_3/Sc_2O_3. The insert in **c** is a SAED pattern of the 2D Yb_2O_3/Sc_2O_3/COF.

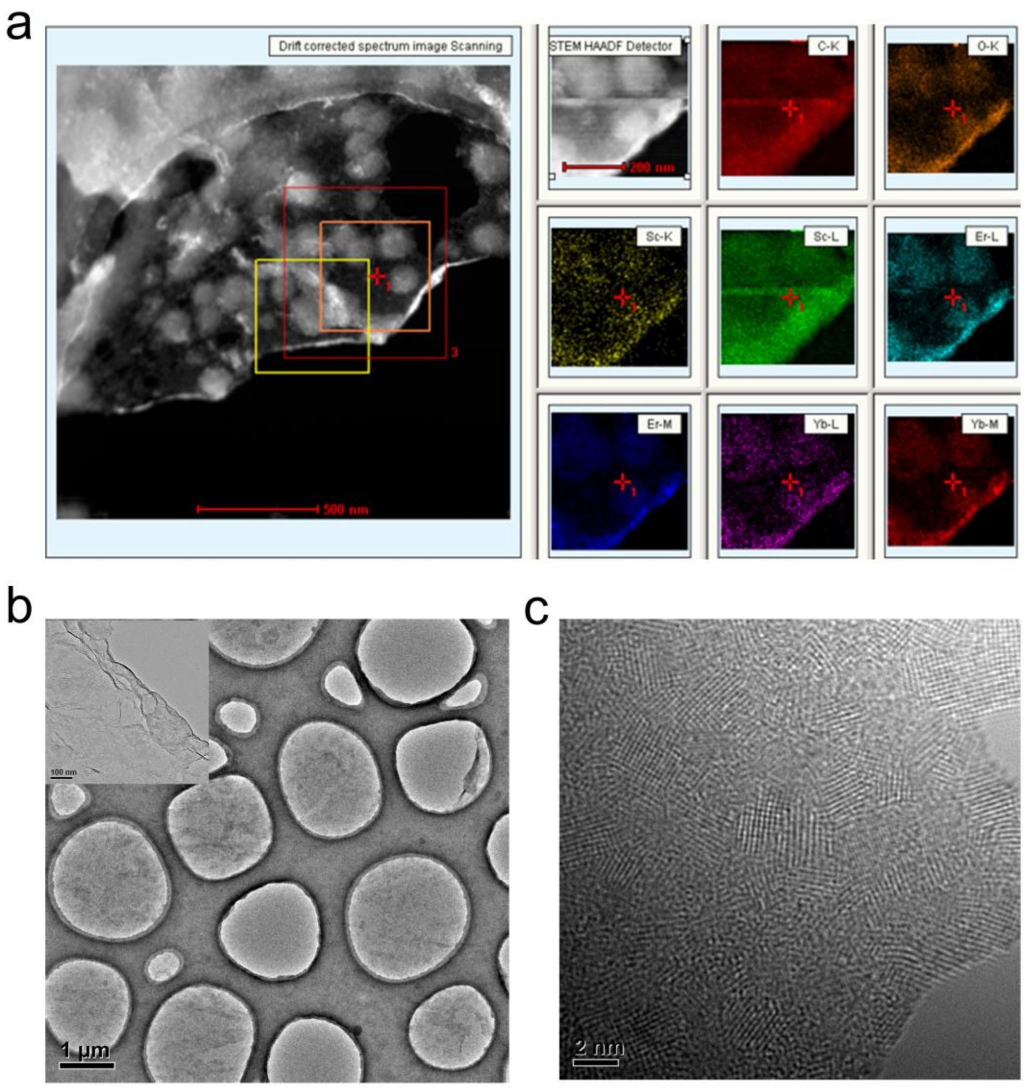

Figure S8 | (a) TEM mapping image of 2D $Yb_2O_3/Sc_2O_3/Er_2O_3$/COF. (**b,c**) TEM images of 2D $Yb_2O_3/Sc_2O_3/Er_2O_3$/COF.

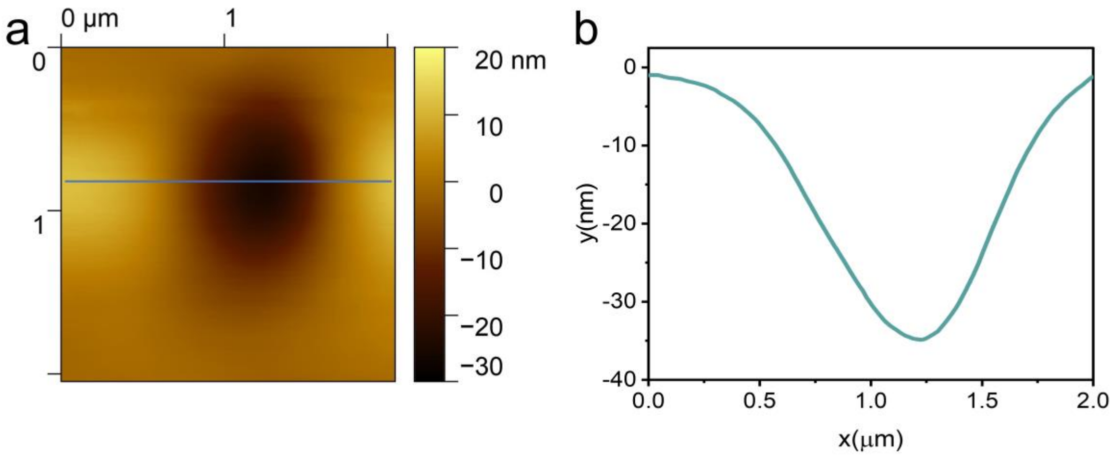

Figure S9 | (**a**) AFM images of the 2D Sc_2O_3/COF film transferred to porous silicon wafer. (**b**) The depth chart of **a**.

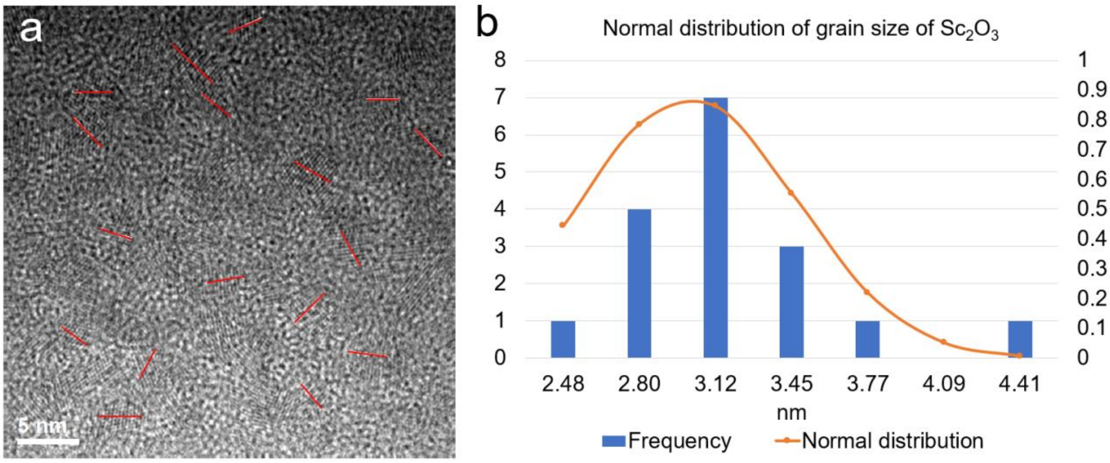

Figure S10 | (**a**) The TEM image of 2D Sc_2O_3/COF, the red line represents the Sc_2O_3 grains involved in size statistics. (**b**) The statistical graph and normal distribution curve of grain size of Sc_2O_3 corresponding to **a**.

Supplemental Information Tables

Supplementary Table 1 | Young's modulus obtained by 2D Sc_2O_3/COF、2D Yb_2O_3/COF、and 2D Er_2O_3/COF nanoindentation test.

Sample	Young's modulus/GPa				Average
	1	2	3	4	
2D Sc_2O_3/COF	89.7	85.3	88.4	92.9	89.1
2D Yb_2O_3/COF	63.4	60.8	62.7	64.2	62.8
2D Er_2O_3/COF	47.6	43.1	49.5	42.9	45.8

References

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