Supporting Online materials

Atomically-thin Non-layered Cobalt Oxide Porous Sheets for Highly Efficient Oxygen-evolving Electrocatalysts

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S1. Crystal structure of cubic Co_3O_4

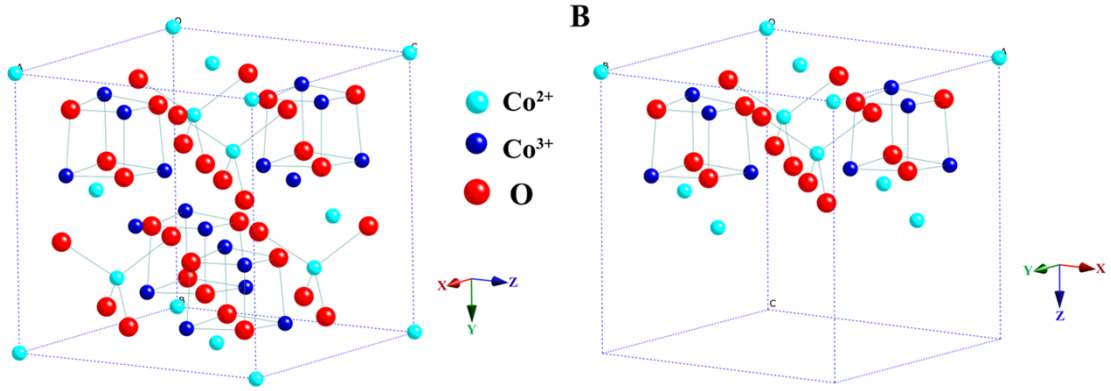

Figure S1. (A) Schematic unit cell of cubic Co_3O_4 (a=b=c=8.085 Å); (B) half a unit cell of cubic Co_3O_4 along the [001] direction.

S2. Characterizations of ultrathin CoO sheets

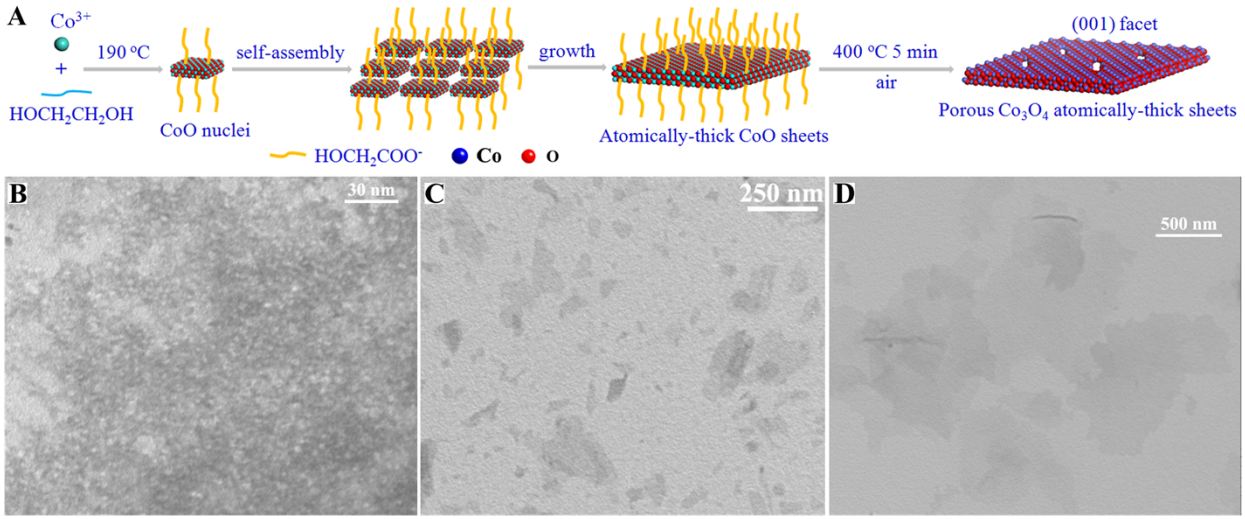

Figure S2. (A) Schematic illustration for the formation of clean and freestanding porous Co_3O_4 atomically-thin sheets, taking advantage of an intermediate precursor of atomically-thick CoO sheets. TEM images for the intermediate precursors obtained at 190 °C for (B) 1 h, (C) 4 h, (D) 48 h, respectively.

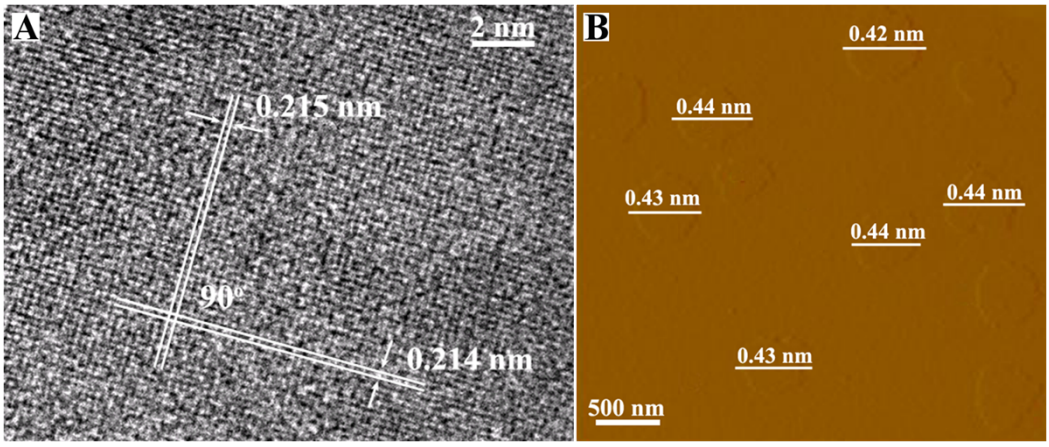

Figure S3. Characterizations for the atomically-thick CoO sheets obtained at 190 °C for 48 h: (A) HRTEM image and (B) AFM image, inset denotes their thickness.

As shown by the TEM image in Fig. S2D, the finally obtained CoO exhibited graphene-like morphology with a size of ~500 nm. The XRD pattern and XPS spectra in fig. S4 demonstrated the formation of cubic CoO, while the HRTEM image in Fig. S3A showed their [001] orientation. In addition, atomic force microscopy (AFM) in Fig. S3B revealed their average thickness of ca. 0.44 nm, which corresponded to the thickness of a unit cell along the [001] direction.

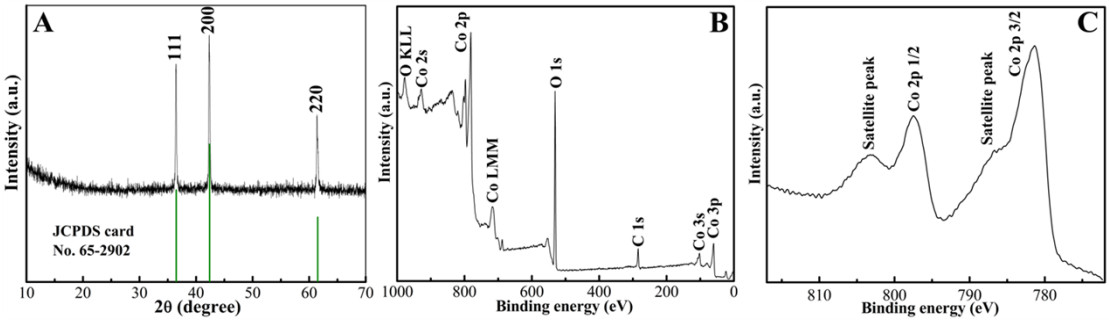

Figure S4. (A) XRD and (B, C) XPS spectra for the as-obtained atomically-thick CoO sheets obtained at 190 °C for 48 h.

As shown in Fig. S4A, all the X-ray diffraction peaks could be readily indexed to the cubic CoO, corresponding to JCPDS No. 65-2902. X-ray photoelectron spectroscopy in Fig. S4B-C depicts that the Co 2p core spectrum has binding energies at 781.4 eV (2p3/2) and 797.5 eV (2p1/2) with two satellites located at 786.9 eV and 803.3 eV, which is characteristic of a CoO phase.[1,2]

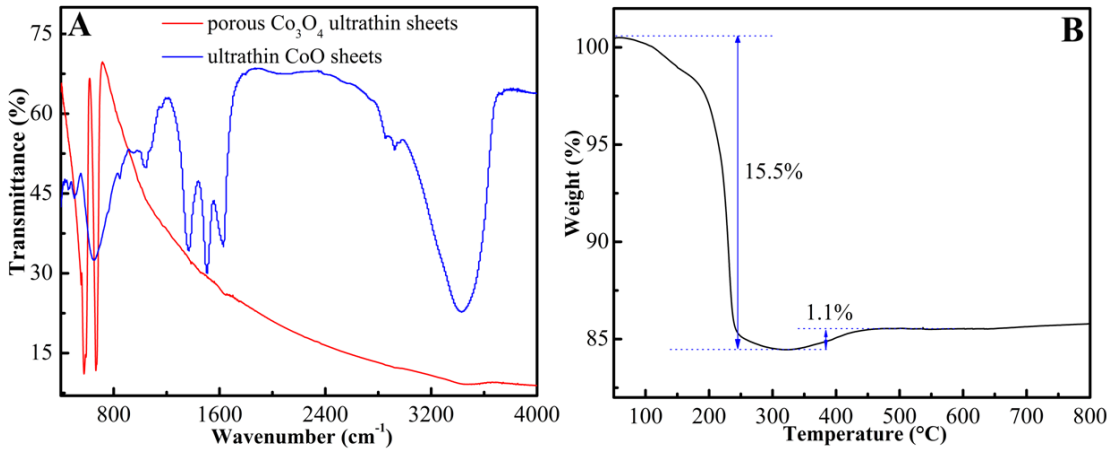

Figure S5. (A) FTIR spectra for the as-obtained porous Co_3O_4 ultrathin sheets and ultrathin CoO sheets; (B) TG analysis for the as-obtained ultrathin CoO sheets.

As shown in Fig. S5A, the peaks between 1600 cm^{-1} and 1400 cm^{-1} correspond to the COO^- stretch, while the peaks at 2952 cm^{-1} and 2851 cm^{-1} could be assigned to the antisymmetric and symmetric methylene strectches ($\upsilon_{as}(CH_2)$, $\upsilon_s(CH_2)$). Also, the peak at 1030 cm^{-1} could be attributed to the υ(C-O) stretch. The above results demonstrates the presence of $HOCH_2COO^-$, which comes from the partial oxidation of the $HOCH_2CH_2OH$ solvent.[3] Meanwhile, the corresponding TG analysis in Fig. S5B showed a loss decrease between 30 °C and 200 °C, which could be ascribed to the release of physically adsorbed water.[4,5] In addition, there was a dramatic decrease at the temperature range between 200 °C

and 325 °C, which corresponded to the loss of combustion or decomposition of $HOCH_2COO^-$. Moreover, there was a mass increase between 325 °C and 450 °C, corresponding to oxidation of CoO into Co_3O_4. Note that the mass increase of 1.1% was smaller than that of the oxidation process, which could be ascribed to the fact that the mass loss of $HOCH_2COO^-$ offseted the mass increase in the oxidation process from CoO to Co_3O_4.

S3. Characterizations of porous Co_3O_4 ultrathin sheets

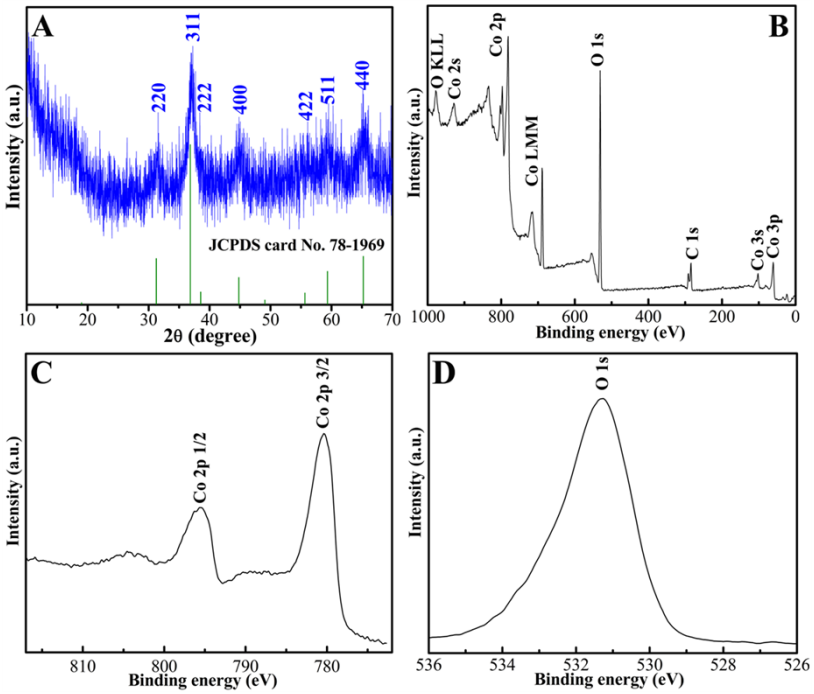

Figure S6. (A) XRD pattern for the collected powder sample accumulated by the as-obtained porous atomically-thin sheets; (B-D) XPS survey spectra for the porous Co_3O_4 ultrathin sheets.

As shown in Fig. S6A, all the X-ray diffraction peaks could be readily indexed to the spinel phase of Co_3O_4 with cubic structure, corresponding to JCPDS No. 78-1969. X-ray photoelectron spectroscopy in Fig. S6B-D shows that the obtained products consist of element Co and O, while no evident impurities such as nitrogen are detected. Fig. S6C depicts that the Co 2p core spectrum of the sample, which appears as a spin-orbit doublet at 780.1 eV (2p3/2) and 795.2 eV (2p1/2) with a spin-energy separation of 15.1 eV, which is characteristic of a Co_3O_4 phase.[6,7] The core level centered at 531.3 eV (Fig. S5D) corresponds to the oxygen species in the Co_3O_4 phase.[6]

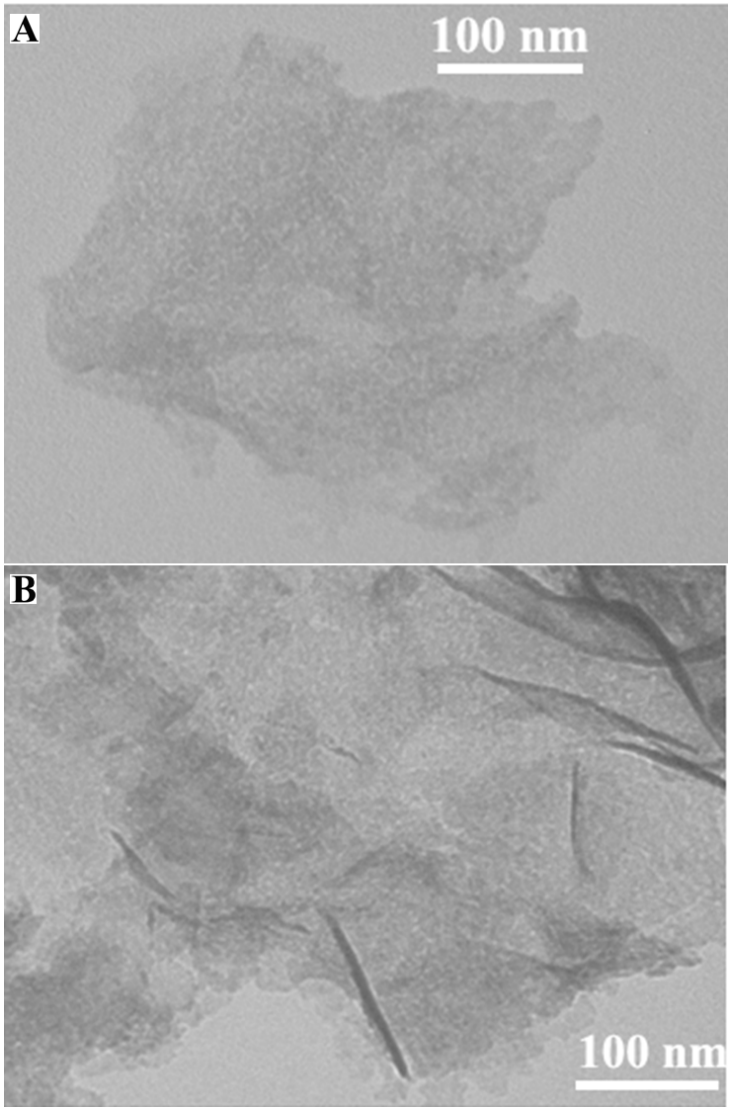

Figure S7. (A, B) TEM images for porous Co_3O_4 ultrathin sheets; note that one can clearly see that there are lots of pores on the surface of the as-obtained porous Co_3O_4 ultrathin sheets.

S4. Characterizations of bulk Co_3O_4

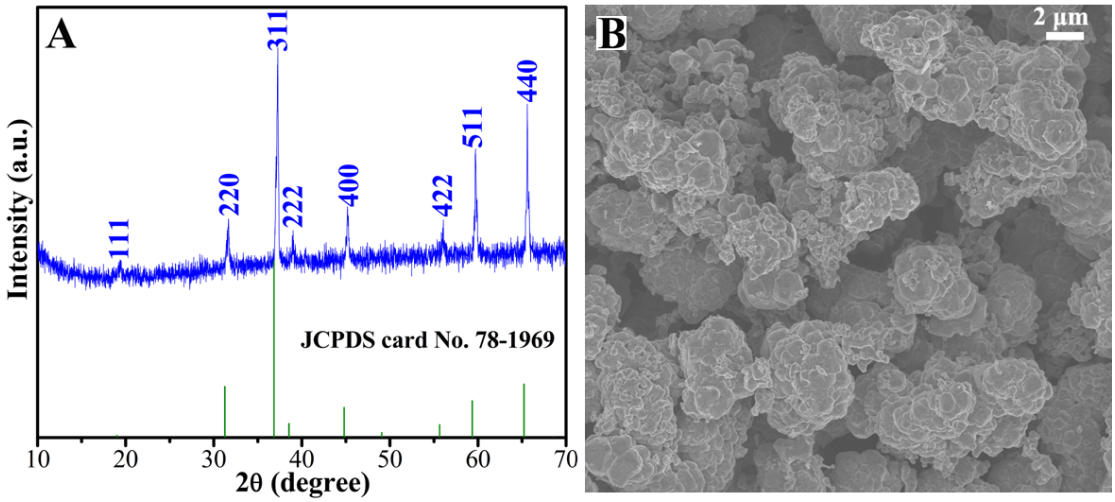

Figure S8. (A) SEM image and (B-D) XRD pattern for bulk Co_3O_4.

References

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