Supporting information

Two dimensional Oxygen-Vacancy-Rich Co₃O₄ Nanosheets with Excellent Supercapacitor Performances

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1. Method

1.1 Synthesis of Cobalt hydroxides precursor.

In a typical synthesis, 5 mmol $Co(NO_3)_2$ •6H₂O and 20 mmol urea are dissolved in 15 mL deionized water and 105 mL ethylene glycol to form homogenous solution under stirring. Then the mixture is stirred at 80°C for 12 h in a three-necked flask to undergo a hydrolysis reaction. By the time the reaction completes, the green precipitates are collected by centrifugation and rinsed several times with abundant amount of deionized water and ethanol. Then, the solid products are dried in a vacuum oven at 60°C for 12 h.

1.2 Preparation of OVR-Co₃O₄ NSs and H200-Co₃O₄ NSs.

In a typical preparation of OVR-Co₃O₄ NSs, the as-prepared precursors are calcined in air at 300°C for 2 h, the calcined products are denoted as Co₃O₄ NSs. Then 0.1 g pristine Co₃O₄ NSs are immersed in 100 mL 1.0 M NaBH₄ solution for 1 h at room temperature. After reduction, the black samples are filtered, thoroughly washed with deionized water and ethanol for several times and dried in a vacuum oven at 60°C for 12 h. The H200-Co₃O₄ NSs are synthesized by reducing the Co₃O₄ NSs in 5 vol % H₂ in N₂ atmosphere at 200°C for 2 h according to the Temperature-programmed desorption of hydrogen (H₂-TPR) results in Figure S5.¹

2. Characterizations

The morphology of the as-prepared materials is characterized by field emission scanning electron microscopy (FESEM, Hitachi, S-4800), transmission electron microscopy (TEM, JEOL, JEM-1101) and high-resolution transmission electron microscopy(HRTEM, JEOL, JEM-2100). X-Ray diffraction (Bruker D8 Advance A25, Co K α radiation of 1.7902 Å) is used to examine the structure of the sample. Nitrogen adsorption/desorption isotherms at liquid nitrogen temperature is conducted on an ASAP 3020 instrument. X-ray photoelectron spectroscopy (XPS) is obtained on a PHI 5000 VersaProbe with an Al K α excitation source. Temperature-programmed desorption of hydrogen (H₂-TPR) is performed on Tianjin XQ TP-5080 chemisorption instrument. The electrical conductivity is measured by a four-wire method using a source measure unit (SMU, Keithley 6430), as described in detail in other published paper.²

3. Electrochemical Measurements

The electrochemical properties of pristine-Co₃O₄ NSs, H200-Co₃O₄ NSs, and OVR-Co₃O₄NSs are investigated in a three-electrode configuration with a Pt counterelectrode and an Hg/HgO reference electrode in 6.0 M KOH solution at a potential sweep window of 0~0.55 V. The working electrode is fabricated by mixing active materials, acetylene black and polytetrafluoroethylene (PTFE) in a weight ratio of 8:1:1 with several drops of ethanol. The slurry is coated on the single surface of nickel foams with a size of 1 cm × 1 cm and dried in vacuum at 80°C for 12h. Then, the nickel foams with Co₃O₄ are pressed under 10 MPa to obtain working electrodes with the thickness of 0.11 mm. The mass loading of active material is about 1.6 mg cm⁻². The electrochemical AC impedance measurements are carried out to assess the electrical properties at an open circuit voltage with frequency from 0.01 Hz to 100 kHz and an amplitude of 5 mV. All the electrochemical tests are carried out on the electrochemical working station (CHI660E, Shanghai, China).

The specific capacitance of the supercapacitor can be calculated by galvanostatic discharge-charge (GCD) test as following equation:

$$C_m = \frac{I}{m} \times \frac{\Delta t}{\Delta V}$$

Where C_m is the specific capacitance of the capacitor (F g⁻¹); *I* is the current of the charge/discharge process; Δt is the discharging time period in seconds for the

potential change ΔV , in volts; *m* is the mass load of the active material. All the electrochemical measurements are carried out at room temperature.

The specific capacitance of the supercapacitor also can be calculated from cyclic voltammogram (CV) test as following equation:

$$C_m = \frac{i}{m} \times \frac{dV}{dt}$$

Where C_m is the specific capacitance of the capacitor (F g⁻¹); *i* is the average current in the capacitive potential region, dV/dt the scan rate, and *m* is the mass loading of the active material.

4. Supporting Figures



Figure S1. TEM images of (a) precursors, (b) pristine- Co_3O_4 , (c) H200- Co_3O_4 and (d) OVR- Co_3O_4 NSs.



Figure S2. (a-c) Cyclic voltammograms curves of pristine- Co_3O_4 , H200- Co_3O_4 and OVR- Co_3O_4 NSs at various scan rates of 5, 10, 20, 50 and 100 mV s⁻¹. (d-f) Galvanostatic charge and discharge voltage profiles of pristine- Co_3O_4 , H200- Co_3O_4 and OVR- Co_3O_4 NSs at various current densities of 1 A g⁻¹, 2 A g⁻¹, 4 A g⁻¹, 8 A g⁻¹, 16 A g⁻¹ and 32 A g⁻¹.



Figure S3. The volumetric capacitance of OVR-Co₃O₄ NSs and comparison with those of the cobalt oxide/sulfide-based electrodes in previous reports.



Figure S4. Plots of specific capacitance as a function of scan rate of pristine- Co_3O_4 , H200- Co_3O_4 and OVR- Co_3O_4 NSs.



Figure S5. H₂-TPR profile of pristine-Co₃O₄ NSs.

References

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