Supporting information

Facilely solvothermal preparation of organic hybrid dysprosium selenidoantimonate for efficient oxygen evolution reaction

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General Remarks

All analytical grade chemicals were obtained commercially and used without further purification. The UV/Vis spectra were recorded at room temperature using a computer-controlled PE Lambda 900UV/Vis spectrometer equipped with an integrating sphere in the wavelength range of 250–800 nm. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr disks in the 4000–400 cm^{-1} range. Powder XRD patterns were collected on a D/MAX-3C diffractometer using graphite-mono-chromatized Cu–Kα radiation (λ = 1.54178 Å).The SEM measurements were performed on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. The solid-state UV/Vis spectra were measured at room temperature using an Agilent Cary 5000 UV/Vis spectrophotometer.

Crystal Structure Determination

Single crystal X-ray diffraction data for **SbSe-1** were recorded on a Rigaku Mercury CCD diffractometer using a ω−scan method with graphite monochromated Mo–Kα radiation (λ = 0.71073 Å) at 296(2) K to a maximum 2θ value (50.18 °). Absorption corrections were applied using the multi-scan technique. The structure of **SbSe-1** was solved by direct methods of SHELXS-9717 and refined by full-matrix least-squares techniques using the SHELXL-97 program. Non-hydrogen atoms were refined with anisotropic temperature parameters. The H atoms bonded to the C and N atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. The reference number of Cambridge Crystallographic Data Centre (CCDC) is 2285440. Technical details of data collections and refinement are summarized in Table S1.

Table S1 Crystallographic data for **SbSe-1**.

	SbSe-1
Chemical formula	$C_{12}H_{36}DyN_8SbSe_4$
Fw	892.59
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.2552(5)
b (Å)	13.4633(6)
c (Å)	19.6938(9)
β (deg)	92.7433(19)
V (Å^3)	2451.1(2)
Z	4
T (K)	296(2)
ρ_{calc}(g·cm^{-3})	2.419
F(000)	1668
Maximum 2θ (deg)	50.18
Reflections collected	22640
Unique reflections	4352
Reflections ($I>2\sigma(I)$)	3426
$R1$, $wR2$ [$I>2\sigma(I)$]	0.0292, 0.0458
$R1$, $wR2$ (all data)	0.0478, 0.0502
Goodness-of-fit on F^2	1.023

Computational method

The density of states (DOS) of **SbSe-1** was theoretically calculated by using the computer code CASTEP. [S1] The total energy is calculated with the density functional theory (DFT) using the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA).[S2] The following orbital electrons are treated as valence electrons: H $1s^1$, C $2s^22p^2$, N $2s^22p^3$, Se $4s^24p^4$, Sb $5s^25p^3$ and Dy $4f^{10}5s^25p^66s^2$. The number of plane waves included in the basis is determined by a cutoff energy of 280 eV, and the numerical integration of the Brillouin zone is performed using a Monkhorst–Pack k point sampling: 1 × 1 × 1. The Fermi level (E_F = 0 eV) was selected as the reference of the energy.

Electrochemical characterizations

The OER electro-catalytic activities of pure NF, AB/NF, **SbSe-1**/NF, Ni/NF, **SbSe-1**@AB/NF, **SbSe-1**@AB/Ni/NF, and Ni/**SbSe-1**@AB/NF electrodes were evaluated by using an electrochemical workstation (CHI 760E, China) with three-electrode system (different fabricated electrodes as working electrodes, Pt sheet as the auxiliary electrode, Ag/AgCl electrode as reference electrode) in the 1 M KH_2PO_4/K_2HPO_4 buffer solution (PBS, pH = 6.9) (30 mL). According to Nernst equation, the conversion of potential to Ag/AgCl ($E_{Ag/AgCl}$) and reversible hydrogen electrode (E_{RHE}) is as follows: $E_{RHE} = E_{Ag/AgCl} + E_{Ag/AgCl}$ (reference) + 0.0591 V × pH. Where E_{RHE} represents the converted potential versus RHE. At room temperature (25 °C), the value pair RHE of $E_{Ag/AgC1}$ (reference) is 0.197 V, and $E_{Ag/AgCl}$ is the obtained electric potential vs. Ag/AgCl. All potentials reported in our work are compared with RHE. The polarization curves were obtained by linear sweep voltammetry (LSV) in 1.0 M PBS at a scanning rate of 25 mV/s. And all the linear scan voltammetry (LSV) curves were iR compensated with a compensation level of 90 %. The Tafel plots of as-prepared catalysts were carried out from the corresponding LSV data using the following formula:

$$\eta = a + b \times \log j$$

where a, η, b and j represent the corresponding constant, potential, Tafel slope and current density, respectively.

Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 10^5 Hz to 10^{-2} Hz. The experimental data were fitted to the equivalent circuit diagram by ZSimpWin software, where R_s was the solution resistor, CPE was the constant phase element, and R_{ct} was the charge transfer resistor. Table S2 summarizes the series resistance (R_s) and charge-transfer resistance (R_{ct}) values of the materials, which were obtained by fitting the experimental data to the corresponding equivalent circuit model. The stability test was conducted at 1.49 V for 18 hours through I-t.

Cyclic voltammetry (CV) was acquired under the potential windows from 0.61 V to 0.71 V vs. RHE with different scan rates of 10, 20, 40, 60, 80, 100 mV/s. Furthermore, the double-layer capacitance (Cdl) is evaluated by the relationship between the capacitance current ($\Delta j = j_{anodic} - j_{cathodic}$) vs. potential sweep rate, and is considered to be proportional to the electrochemical active surface area (ECSA).The electrochemical active surface area (ECSA), which could be calculated by using the following equation:

$$\mathrm{ECSA} = \frac{C_{dl}}{C_s}$$

where C_s is the specific capacitance of the electrode in a neutral medium, its general value for a flat surface (1 cm^2) is in the range of 20~60 $\mu F/cm^2$, thus 40 $\mu F/cm^2$ for C_s is herein applied in 1 M PBS.

Table S2 The simulated series resistance (R_s) and charge transfer resistance (R_{ct}).

	$R_s(\Omega)$	$R_{ct}(\Omega)$
NF	2.62	38.39
AB/NF	2.66	34.92
SbSe-1/NF	2.63	30.63
Ni/NF	3.02	24.85
SbSe-1@AB/NF	2.43	15.58
SbSe-1@AB/Ni/NF	3.18	10.00
RuO_2/NF	2.52	7.58
Ni/SbSe-1@AB/NF	3.03	5.18

Calculate the number of active sites and conversion frequency (TOF) (Figure S8): CV curves were tested for samples from -0.2 V to 0.6 V vs. RHE in a phosphate buffer solution (pH = 6.9) at a scan rate at a scan rate of 100 mV/s to calculate the active site. The absolute components of the voltammetry charges (cathodic and anodic) can be obtained from the CV curves. The number of active sites can be obtained from the following equation:

$$n = \frac{Q}{4F}$$

Where Q is the number of voltammetric charges (C); F is the Faraday constant (96500 C mol^{-1}).

TOF can be estimated in the following:

$$TOF = \frac{1}{4} \cdot \frac{I}{nF}$$

Where I is the current (A) at different overpotentials under the OER polarization curve; $\frac{1}{4}$ is the factor means four electrons are needed to form one O_2 molecule.

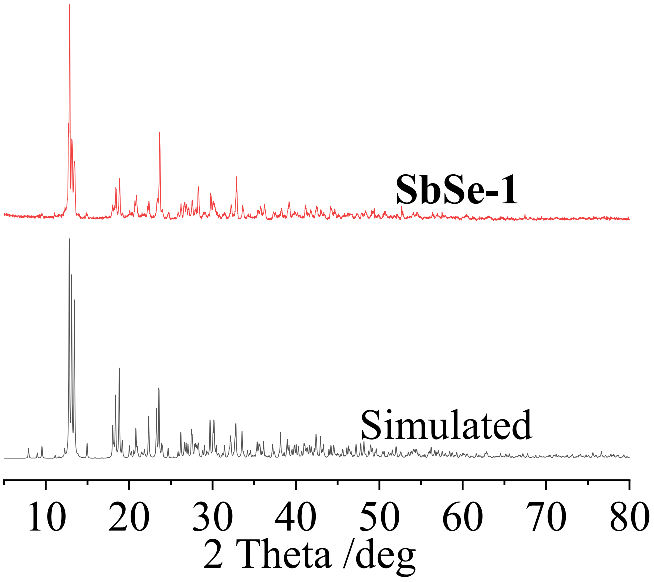

Fig. S1 Simulated, and experimental XRD patterns of **SbSe-1**.

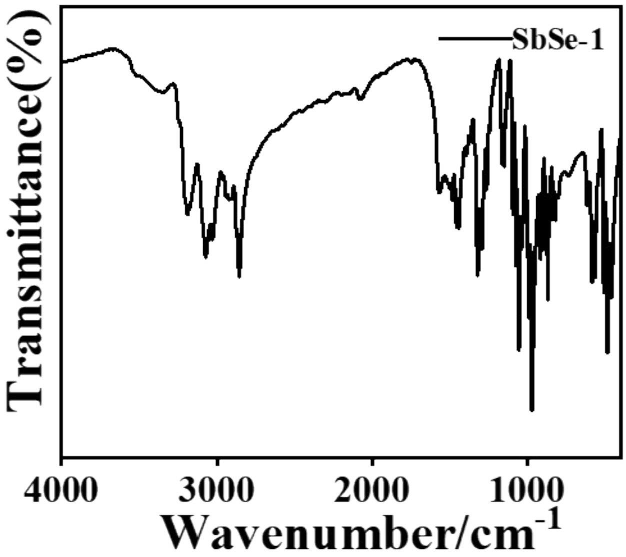

Fig. S2 IR spectrum of **SbSe-1**.

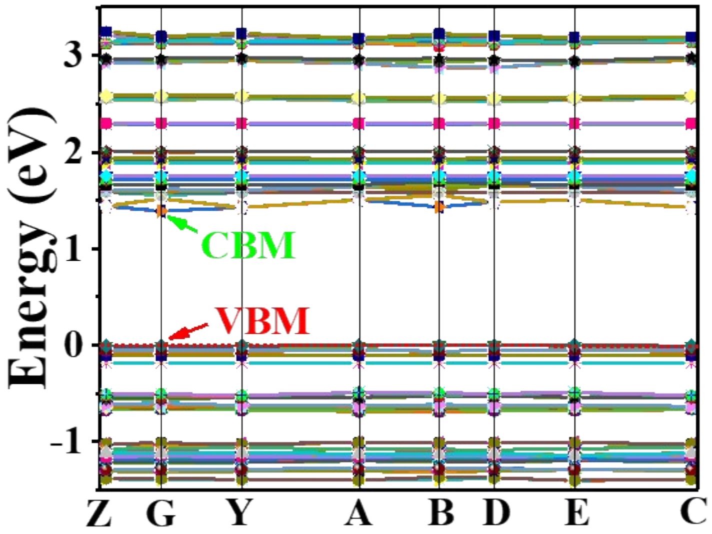

Fig. S3 Band structure of **SbSe-1.**

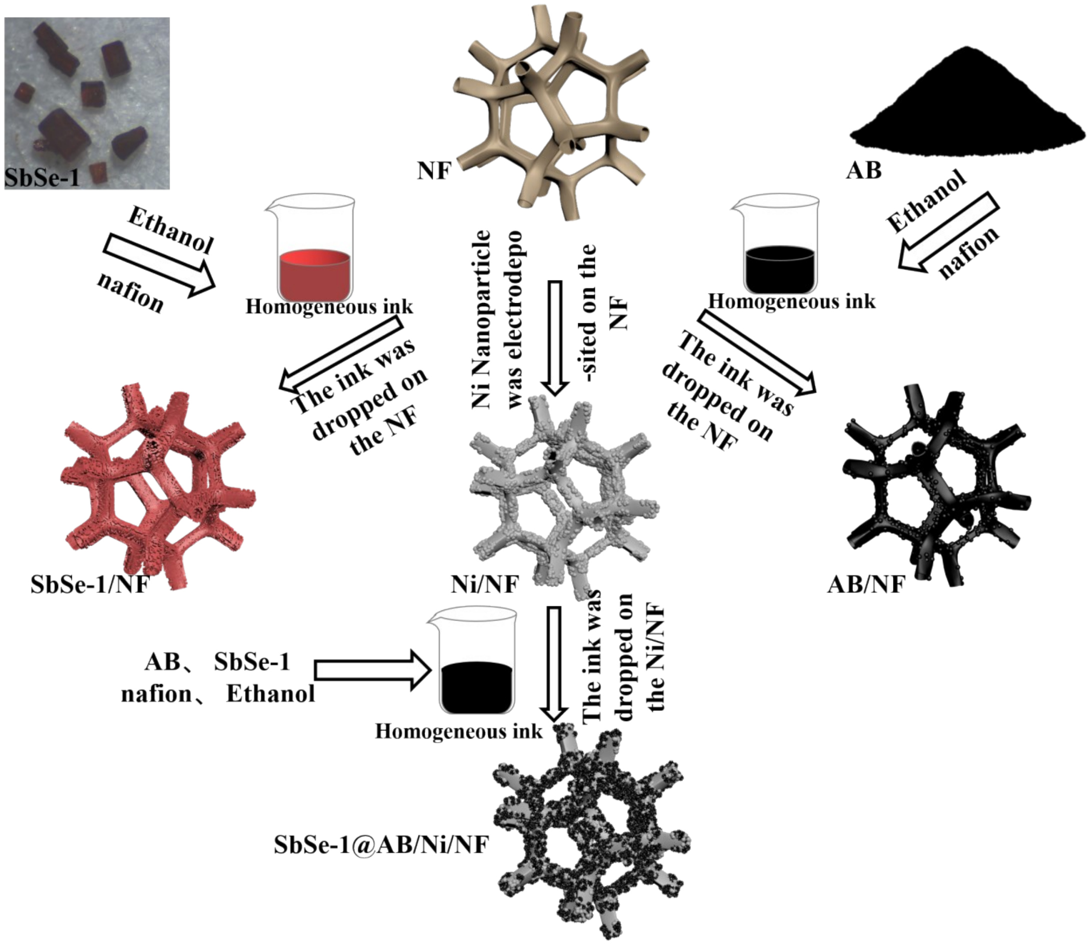

Fig. S4 The formation process of the Ni/NF, AB/NF, **SbSe-1**/NF, **SbSe-1**@AB/NF and **SbSe-1**@AB/Ni/NF composite electrodes.

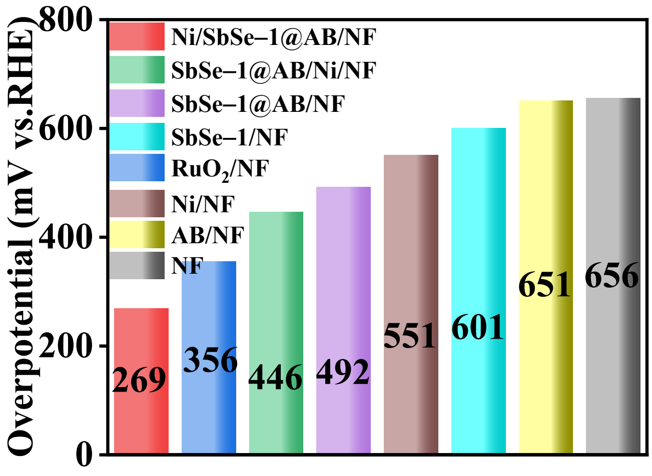

Fig. S5 Overpotentials of the different electrodes at 10 mA/cm^2.

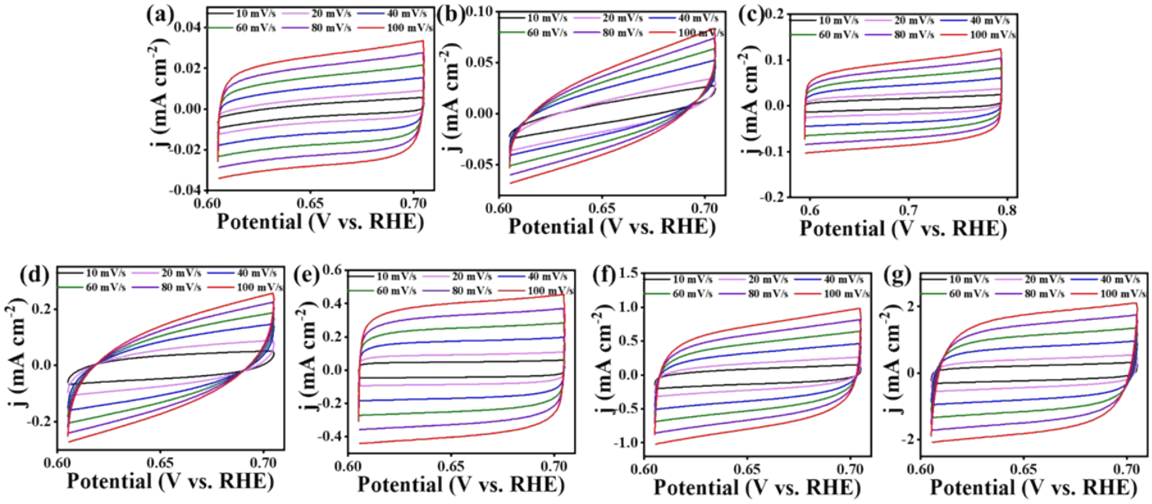

Fig. S6 CV curves of NF (a), AB/NF (b), **SbSe-1**/NF (c), Ni/NF (d), **SnSe-1**@AB/NF(e), **SnSe-1**@AB/Ni/NF(f), Ni/ **SbSe-1**@AB/NF (g) at 10-100 mV/s scan rates.

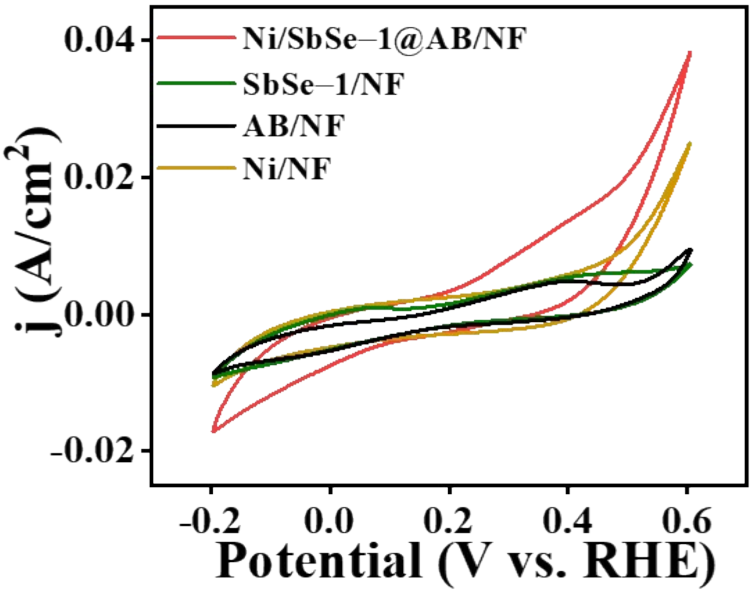

Fig. S7 Cyclic voltammograms of the samples in phosphate buffer (pH = 6.9) with a scan rate of 100 mV·s^{-1}.

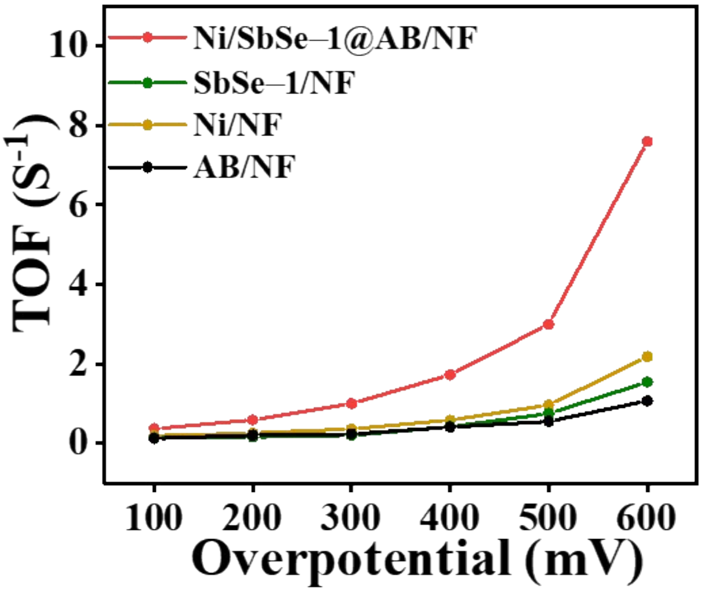

Fig. S8 Calculated O_2 TOF for AB/NF, **SbSe-1**/NF, Ni/NF and Ni/**SbSe-1**@AB/NF.

References

(s1) (a) M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne, *J. Phys.: Condens. Matter*, 2002, **14**, 2717; (b) V. Milman, B. Winkler, J. A. White, C. J. Pickard, M. C. Payne, E. V. Akhmatskaya and R. H. Nobes, Int. *J. Quantum Chem*. 2000, **77**, 895.

(s2) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett*. 1996, **77**, 3865.