Electronic Supplementary Information

Experimental section

Materials: $NaBH_4$ was bought from Tianjing Fuchen Chemical Reagent Factory. $Ni(NO_3)_2 \cdot 6H_2O$, $Na_2S \cdot 9H_2O$ and Ethanol was obtained from Beijing Chemical Corporation. Urea was purchased from Xilong Chemical Reagent Co., Ltd (Guangdong, China). Se powder was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. All chemicals were used as received without further purification. The water used throughout all experiments was deionized water purified through a Millipore system. Ni foil was purchased from Hongshan District, Wuhan Instrument Surgical Instruments business and ultrasonically cleaned in dilute HCl solution, water and absolute ethanol sequentially.

Preparation of NiSe/Ni: In a typical experiment, NaHSe solution was prepared by adding 0.75 mmol Se powder into 1.5 mL deionized water containing 1.71 mmol $NaBH_4$ with vigorous stirring. Subsequently, the clear NaHSe solution was transferred into 40 mL Teflon-lined stainless steel autoclave containing 30 mL methanol, then a piece of pretreated Ni foil (1.5×2.5 cm^2) was immersed in the above solution. The autoclave was sealed and maintained at 140 ºC for 12 h. After the autoclave cooled down to room temperature, the reacted Ni foil was taken from the solution, rinsed with distilled water several times, and dried in vacuum at 60 ºC for 4 h. The mass loading of NiSe nanowire arrays on Ni foil was calculated to be 1.2 mg cm^{-2}.

Preparation of Ni_3S_2/Ni and NiO/Ni: In a typical synthesis, $Ni(NO_3)_2 \cdot 6H_2O$ (1.25 mmol) and urea (2.5 mmol) were dissolved in distilled water (35 mL) and stirred to form a clear solution. Subsequently, the pretreated Ni foil (2 cm × 4 cm) was immersed into the above solution in a Teflon-lined stainless-steel autoclave (50 mL) and maintained at 100 ºC for 15 h. The thin film on the substrate were taken out and cleaned by sonication in ethanol and distilled water. Then the precursor was treated in a hydrothermal environment with sodium sulfide. In brief, 25 mM $Na_2S \cdot 9H_2O$ was dissolved in 35 mL of deionized water, and then the precursor and solution were transferred into a 50 mL Teflon-lined stainless steel autoclave, then heated to 120°C for 8 h. The Ni_3S_2 nanowires on Ni foil (Ni_3S_2/Ni) were obtained, washed with ethanol and deionized water, and dried at 60°C for 5 h. For contrast, NiO nanowires on Ni foil (NiO/Ni) have been synthesized by annealing the as-prepared precursor in argon atmosphere at 300 ºC for 3 h in a tube furnace. The mass loading of Ni_3S_2 and NiO was determined to be 2.05 and 1.44 mg cm^{-2}, respectively.

Characterizations: Powder X-ray diffraction (XRD) data were acquired on a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). Scanning electron microscopy (SEM) measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements: The Electrochemical measurements are performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai). The performance for methanol electro-catalytic oxidation was tested by cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). All the measurements were carried out in a conventional three-electrode system containing NiSe/Ni as the working electrode, a graphite plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. All tests were carried out at room temperature.

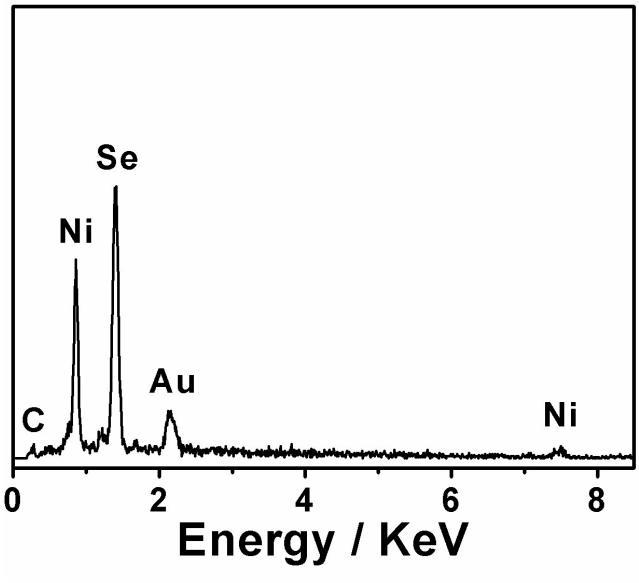

Fig. S1 EDX spectrum of the NiSe/Ni electrode.

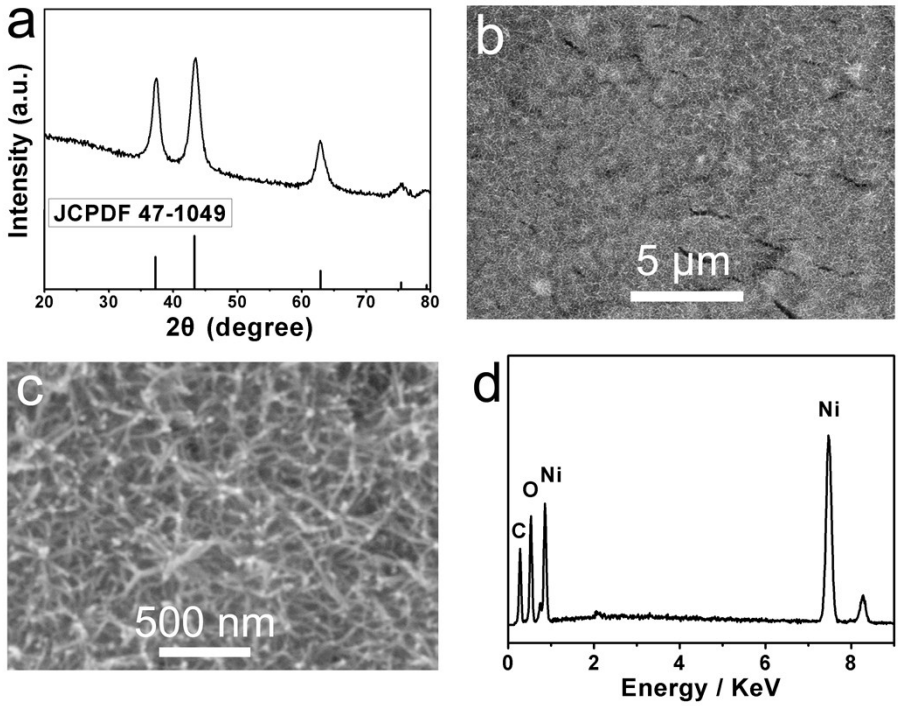

Fig. S2 (a) XRD pattern of NiO scratched down from Ni foil. (b, c) SEM images and (d) EDX spectrum of NiO/Ni.

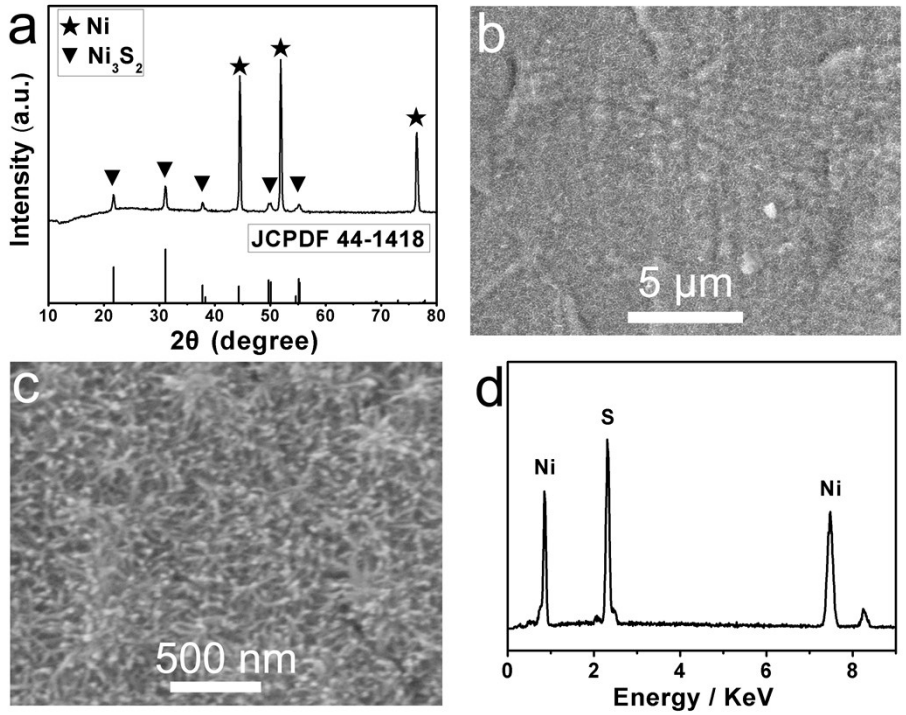

Fig. S3 (a) XRD pattern of Ni_3S_2/Ni. (b, c) SEM images and (d) EDX spectrum of Ni_3S_2/Ni.

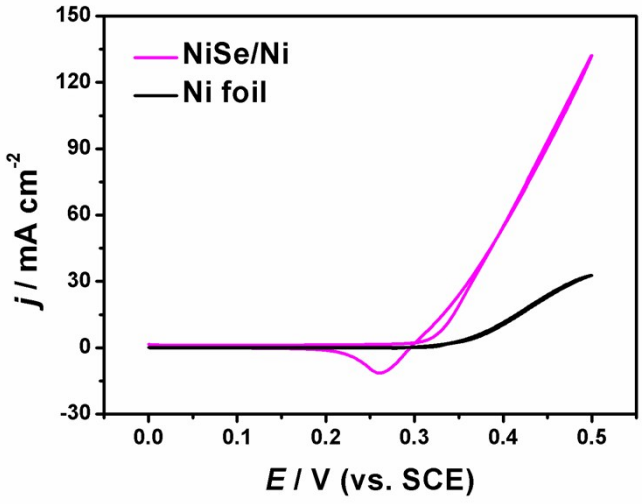

Fig. S4 CVs of NiSe/Ni and bare Ni foil in 1 M KOH with 0.5 M methanol at a scan rate of 10 mV s^{-1}.

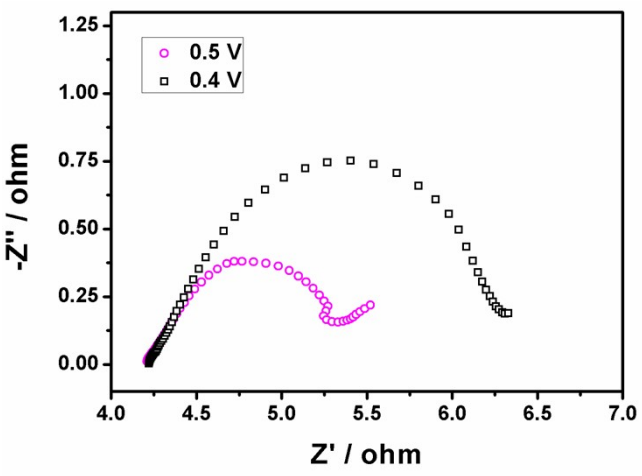

Fig. S5 EIS plots of NiSe/Ni electrode in 1 M KOH with 0.5 M methanol at 0.4 V and 0.5 V.