

Carbon nanotube Encapsulated Metal selenide Nanostructures for Efficient Electrocatalytic Oxygen Evolution Reaction

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Electrodeposition of RuO₂

Electrodeposition of RuO₂ on GC substrate was carried out from a mixture of RuCl₃ (0.452 g) and KCl (2.952 g) in 40 ml of 0.01M HCl by using cyclic voltammetry from 0.015 to 0.915 V (vs. Ag|AgCl) for 100 cycles at a scan rate of 50 mV s⁻¹. Finally heated at 200 °C for 3 h in presence of Air.

Materials

All the reagents were of analytical grade and were used as received. Nickel (II) bis(acetylacetonate) (C₁₀H₁₄NiO₄) and selenium shots (1–3 mm, amorphous, 99.999%) were obtained from Fisher Scientific. Selenium dioxide (SeO₂) and hydrazine hydrate (N₂H₄·H₂O) were purchased from Alfa Aesar and Acros Organics, respectively. MWCNTs (~1–5 μm in length, 20–25 nm in outer diameter) were purchased from Strem Chemicals Inc. and treated in 3 M HNO₃ solution at 80 °C for an hour before being used. Before usage, the Carbon cloth substrate was cleaned several times with acetone, ethanol, and distilled water.

Synthesis of NiSe₂@CNT

NiSe₂ nanoparticles wrapped with carbon nanotubes were synthesized via CVD reaction carried out in a horizontal tube furnace at 800 °C under a flow of N₂ as carrier gas (140 sccm). Graphite foils were used as the substrate for growth which was kept at the central zone of the horizontal furnace at 800 °C. The reaction unit was held in a continuous N₂ flow of 140 sccm with the help of a mass flow controller. Both the C₁₀H₁₄NiO₄ as well as the Se sublime at high temperatures and were strategically located in the reaction tube so that the temperature at the precursors expose above its temperature of sublimation when the central furnace region was at 800°C. Selenium shots were located at 400°C while the C₁₀H₁₄NiO₄ was held at 230°C. The C₁₀H₁₄NiO₄ and Se were originally maintained outside of the heating area by moving the ceramic liner toward the extreme left. The ceramic liner has been pulled to the right, until the central zone of the oven hit the reaction temperature (800°C) and C₁₀H₁₄NiO₄ and Se precursors exposed to 400°C and 250°C respectively. The reaction was performed for 30 minutes, and the furnace was cooled down at

5°C min⁻¹. After the reaction, a greyish deposition was observed on the graphite foil and further this deposition was confirmed by microscopy and structural characterization.

Characterization Technique

Without any further purification, the product was characterized by powder x-ray diffraction (PXRD) with Philips X-Pert using CuK α (1.5418 α) radiation. As the product formed a very thin layer on the graphite foil, the pxd was collected in thin-film geometry at grazing angles (GI mode and Göbel mirrors). The crystallinity of the as-synthesized samples were analyzed by powder X-ray diffraction (PXRD) using Philips X-Pert X-ray diffractometer (PANalytical, Almelo, The Netherlands) with CuK α source (1.5418 Å radiation). As synthesized NiSe₂@CNT characterized by Tecnai F20 in order to obtain high resolution TEM images (HRTEM). The morphology of the samples were examined by scanning electron microscope (SEM, Hitachi S4700) using an acceleration voltage of 15 kV and a working distance of 10 mm. The chemical composition of catalysts and the valence states of the elements were determined by X-ray photoelectron spectroscopy (XPS). The XPS was collected from pristine NiSe₂@CNT modified electrode without any surface sputtering. All XPS spectra were calibrated with the C 1s peak at 284.6 eV. The chemical composition was also analyzed before and after the OER stability studies. All XPS analyses were conducted without sputtering on the pristine catalyst surface. The Raman spectra of all synthesized samples were collected with LabRam ARAMIS (HORIBA Jobin-Yvon Raman spectrometer equipped with a CCD detector).

All electrochemical research was conducted with an IviumStat potentiostat. The electrochemical experiments were performed in three-electrode cell system with a graphite rod as the counter electrode, Saturated Calomel Electrode (SCE) as the reference electrode and the 0.015 mm thin NiSe₂ loaded graphite foil substrate or carbon cloth as working electrode.

Hydrothermal synthesis of nickel selenide

For the synthesis of Nickel selenide, firstly, 0.2M SeO₂ and 0.1M Ni(CH₃CO₂)₂·4H₂O were dissolved into 10 mL deionized water. After mixing for 30 min under vigorous stirring, N₂H₄·H₂O (2ml) was added to the mixture, and the mixture was stirred continuously for another 30 minutes. The final mixture was sealed and heated at 145 °C for 24 h in a 23 ml Teflon-lined stainless-steel autoclave. The autoclave was then allowed to cool down naturally. The final, black-colored product was then centrifuged and washed several times with a mixture of ethanol and deionized water. Finally, the product obtained was dried at 60°C in a vacuum oven.

Electrode preparation for hydrothermal synthesized NiSe₂ and MWCNT

To analyze the OER activity of hydrothermally synthesized NiSe₂ catalyst, a homogeneous catalyst ink was prepared by adding 2 mg of catalyst powder in 300 μL of ethanol mixed with Nafion (0.8 μL 5 wt %). For OER studies, this mixture was ultra-sonicated for about 1 h to prepare a homogeneous ink. 100 μL of the ink was drop casted onto carbon cloth (geometric area of 0.283cm²).

Turnover frequency (TOF)

Turnover frequency of the catalyst for OER can be calculated by using the equation below:

$$\text{TOF} = (J \times A) / (4 \times F \times n) \quad \text{Eq. S1}$$

Here, J is the current density in mAcm⁻² derived from the LSV curve, A is the area of the as prepared electrode in cm², factor 4 is the number of electrons per mole of O₂, F is the Faraday constant with a value of 96485 C mol⁻¹ and n is the number of moles of the electrocatalyst^{1,2}.

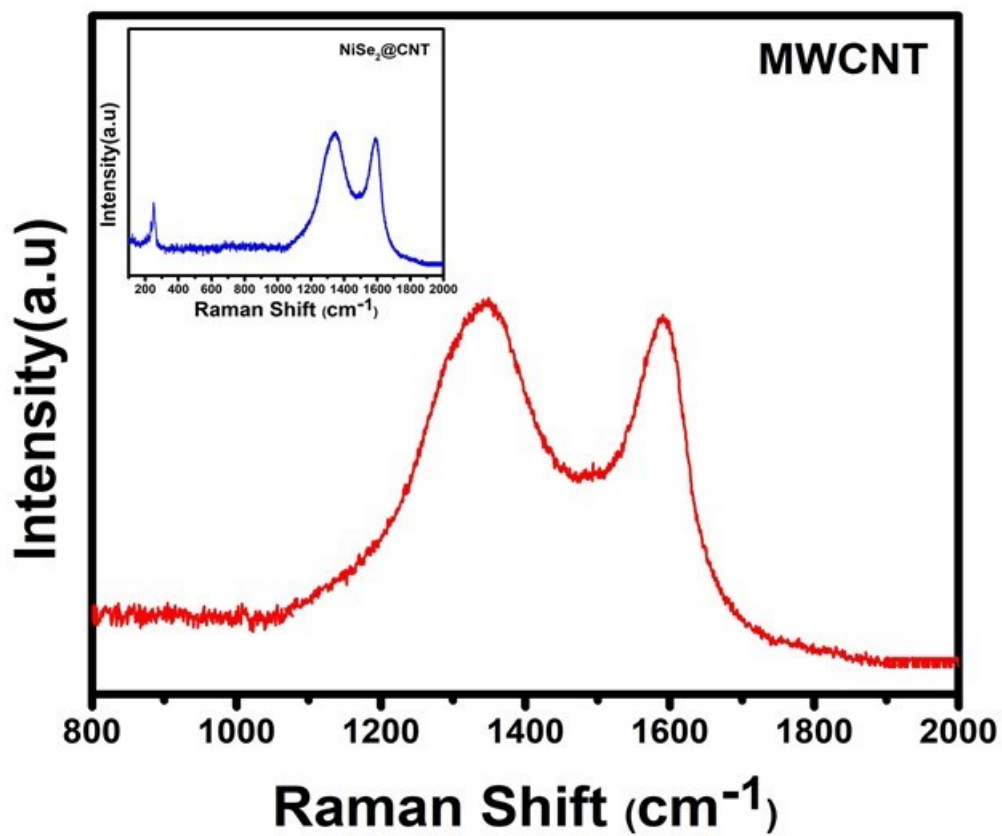


Figure S1. Raman Spectra of NiSe₂@CNT plotted from 800 to 2000 cm⁻¹ showing the MWCNT peaks. Inset shows the full range from 100 – 2000 cm⁻¹.

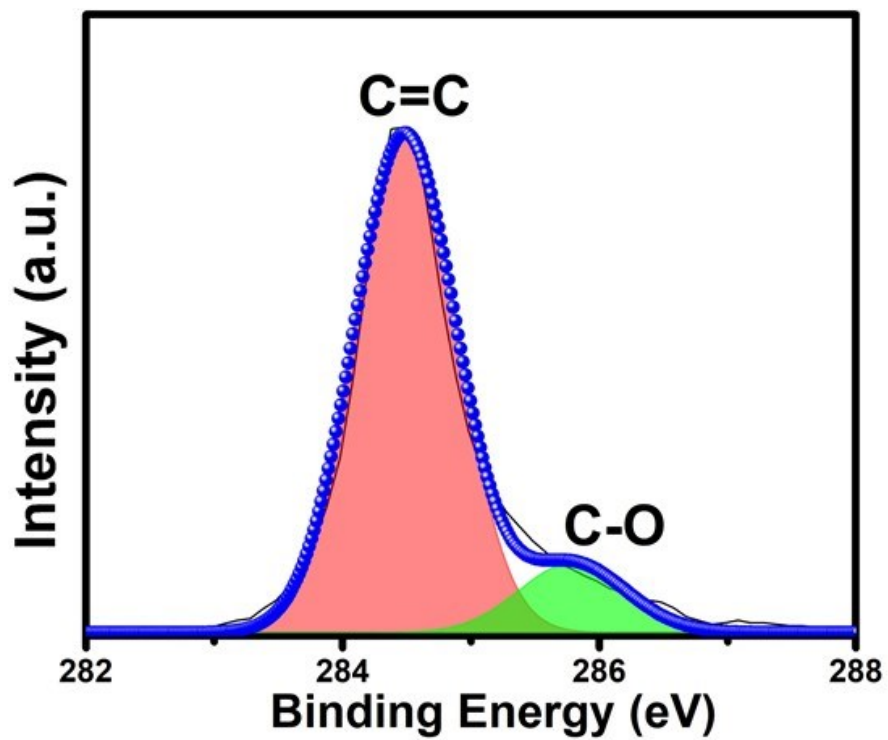


Figure S2. High resolution XPS spectra of NiSe₂@CNT showing C1s peaks.

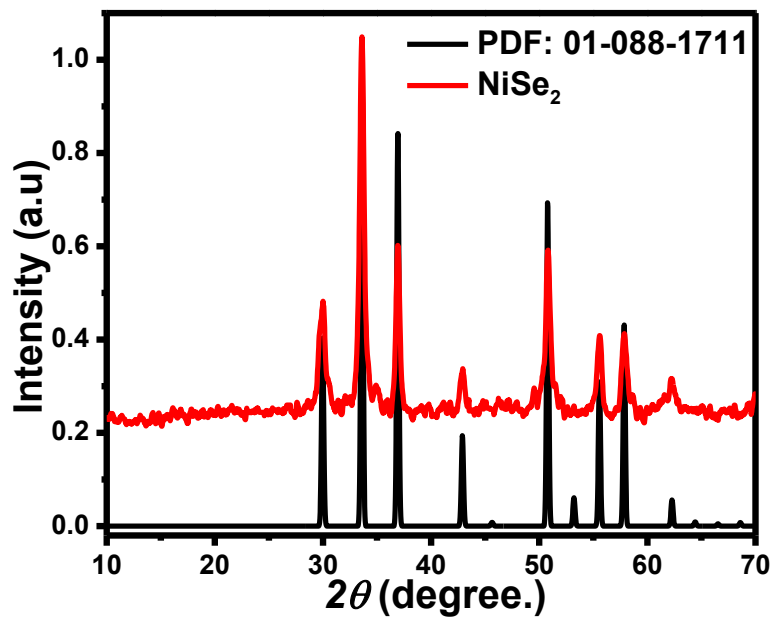


Figure S3. PXRD pattern of hydrothermally synthesized NiSe₂.

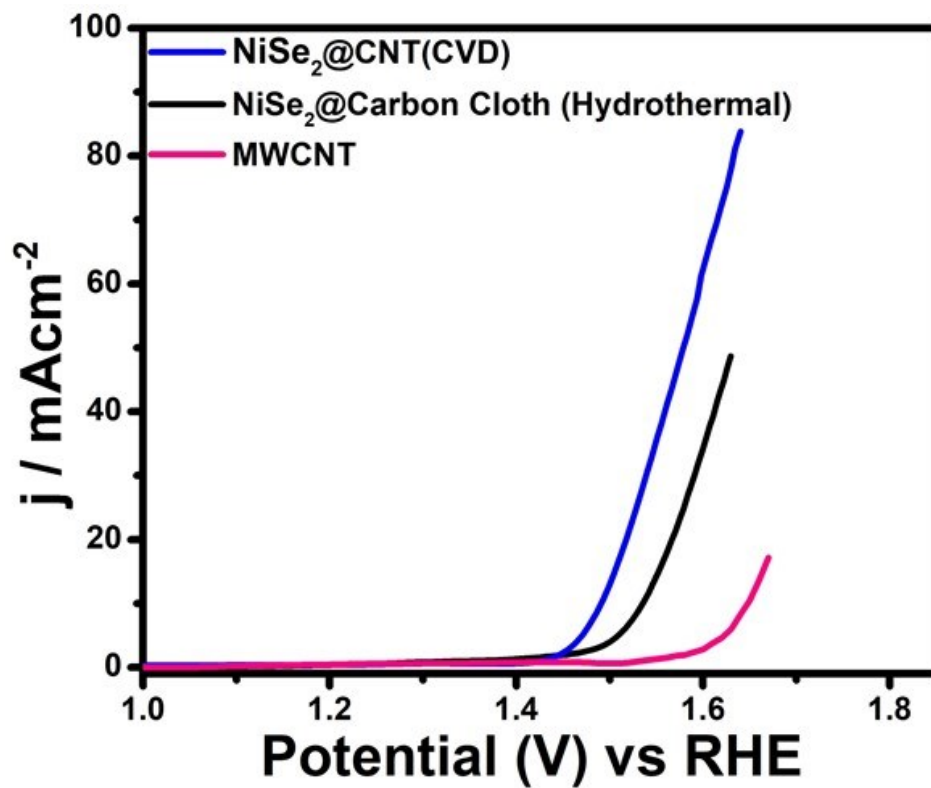


Figure S4. LSV plots of the as-prepared MWCNT, hydrothermally synthesized NiSe₂ and CVD synthesized NiSe₂@CNT on carbon cloth electrode in 1 M KOH solution measured with a scan rate of 10 mV s⁻¹.

Table S1. Comparison of electrocatalytic parameters of Nickel selenide catalysts towards OER

OER Catalysts	Electrolytes	η @ 10 mA cm ⁻² (mV vs RHE)	Tafel slope mV dec ⁻¹	Reference
NiSe₂@CNT	1 M KOH	260	82.54	Our Work
NiSe ₂	1 M KOH	250	38	³
Ni _{0.85} Se	1 M KOH	302	62	⁴
Ni _{0.85} Se/RGO	1M KOH	320 @30 mA cm ⁻²	91	⁵
NiSe/NF	1M KOH	270@20 mA cm ⁻²	64	⁶
CNT@NiSe/SS	1.0 M KOH	267	-	⁷
Ni ₃ Se ₂ /NF	1.0 M KOH	279@20 mA cm ⁻²	-	⁸
Ni ₃ Se ₂	1.0 M KOH	320@100 mA cm ⁻²	60	⁹
Ni ₃ Se ₂	1.0 M KOH	605@60 mA cm ⁻²	174	¹⁰
Ni ₃ Se ₂	1.0 M KOH	353@100 mA cm ⁻²	-	¹¹
NiSe ₂	1.0 M KOH	290	77.1	¹²
NiSe ₂ /NiO _x	1.0 M KOH	295	53.4	¹³
Ni ₃ Se ₂	1.0 M KOH	315@100 mA cm ⁻²	40.2	¹⁴
NiSe ₂	1.0 M KOH	266	65.3	¹³
Ni ₃ Se ₂	0.3 M KOH	290	97.2	¹⁵

Table S2. Equivalent Circuit Parameters Obtained from Fitting of EIS Experimental Data

Parameter	NiSe ₂ @MWCNT	Graphite Foil@800°C
R_s/Ω	8.2	12.5
R_{ct}/Ω	209	416
CPE _{catalyst} /F	0.85	1.6

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