

Supporting Information

Novel Co-Ni-Graphene Composite Electrodes for Hydrogen Production

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Synthesis of graphene

Graphite flakes (1 g) were dispersed in 10 mL of EMIMBF₄ and ultrasonicated for 60 min (SONICS, 750 W, 30% amplitude). The resulting dispersion was mixed with 0.1 g of sodium tungstate and 4 mL of hydrogen peroxide and the mixture solution was ultrasonicated for 10 min. Then the mixture was refluxed in a high temperature microwave sintering furnace (2.45 GHz, 0-1.95 kW) at a power of 1200 W for 100 seconds. Under microwave irradiation, the precursors exfoliated rapidly, accompanied by sparks and violent fuming. After the microwave treatment, the suspension was ultrasonicated and centrifuged to remove the unreacted graphite. The graphene nanosheets dispersed in the centrifugate was filtered, washed repeatedly with distilled water and freeze dried for further use.

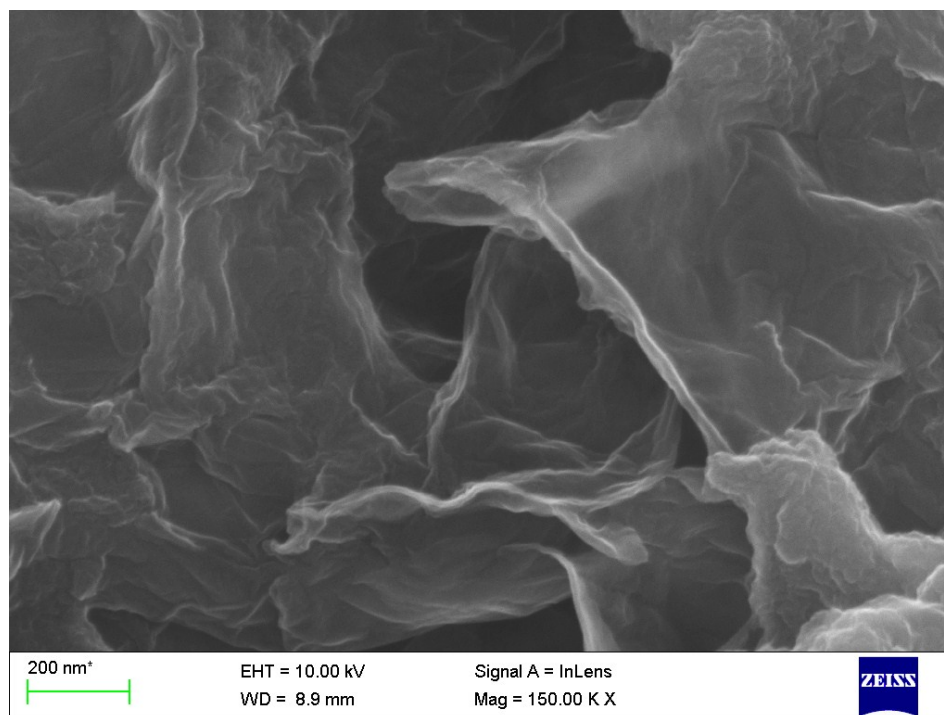
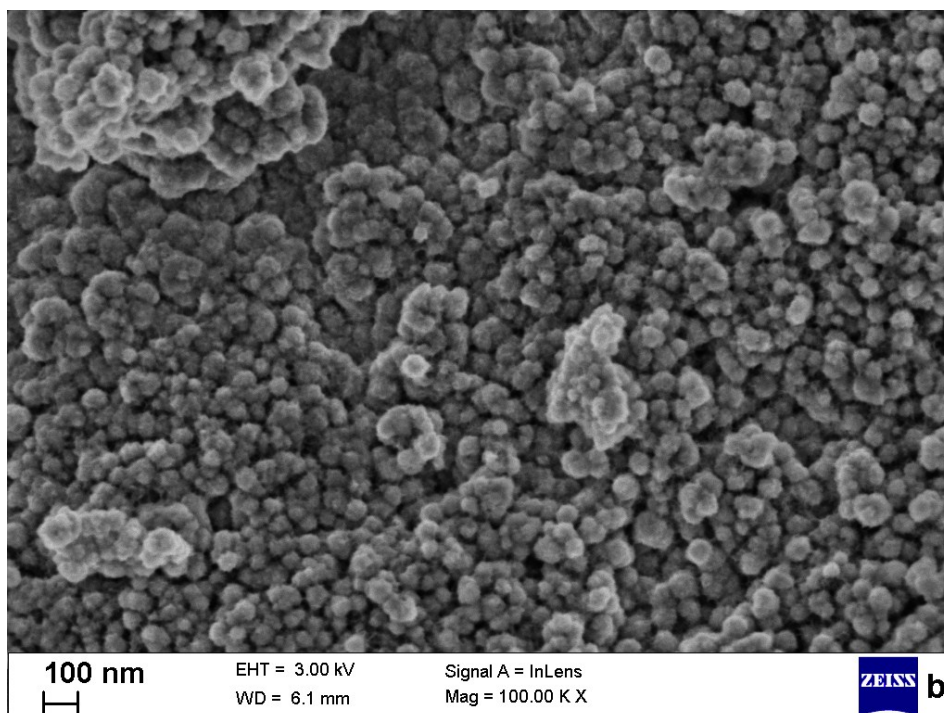
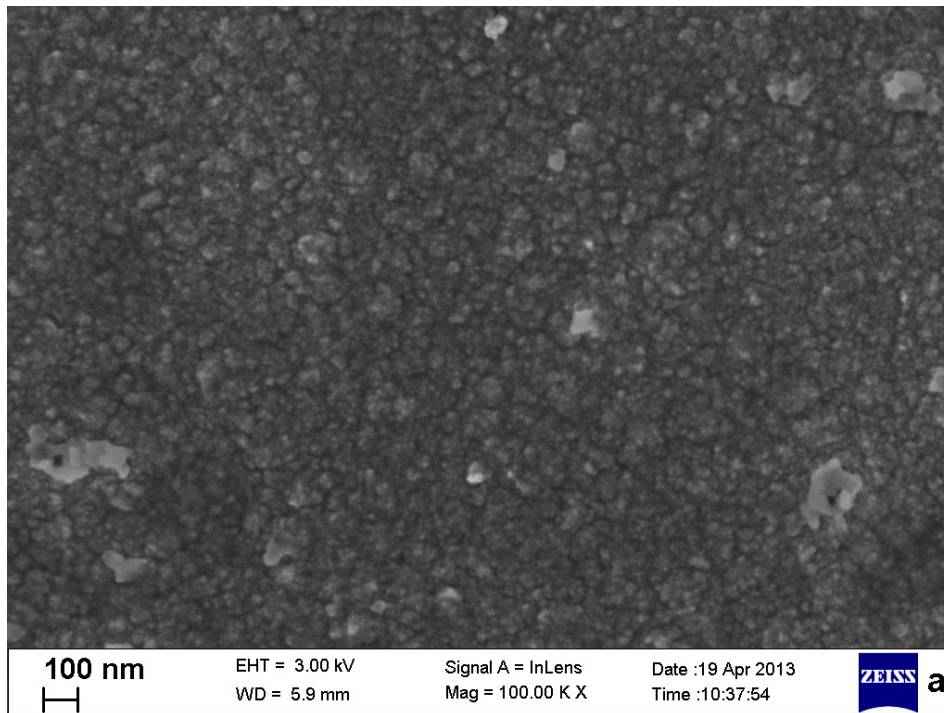


Fig. 1 High magnification FESEM image showing graphene nanosheets.

Surface and compositional characterization of Co-Ni alloy coatings

FESEM analysis

The FESEM images of Co-Ni alloy coatings deposited at 10, 20, 30 and 40 mA cm⁻² are shown in Fig. 2. It can be seen that the surface morphology of electroplated Co-Ni coating is greatly influenced by current density employed for coating. At low current density, the coating was smooth and non-porous as seen in Fig. 1a due to low wt. % of cobalt. But as the deposition current density is increased the surface roughness also increases (Fig. 1b and 1c). This may be due to the increased hydrogen evolution on cathode during deposition. In addition, with the increase in deposition current density, there's an increase in the rate of deposition. Hence large number of crystallite particles are formed. Agglomeration of these particles impart a coarse and rough surface on the coating increasing its specific surface area (Fig. 1d).



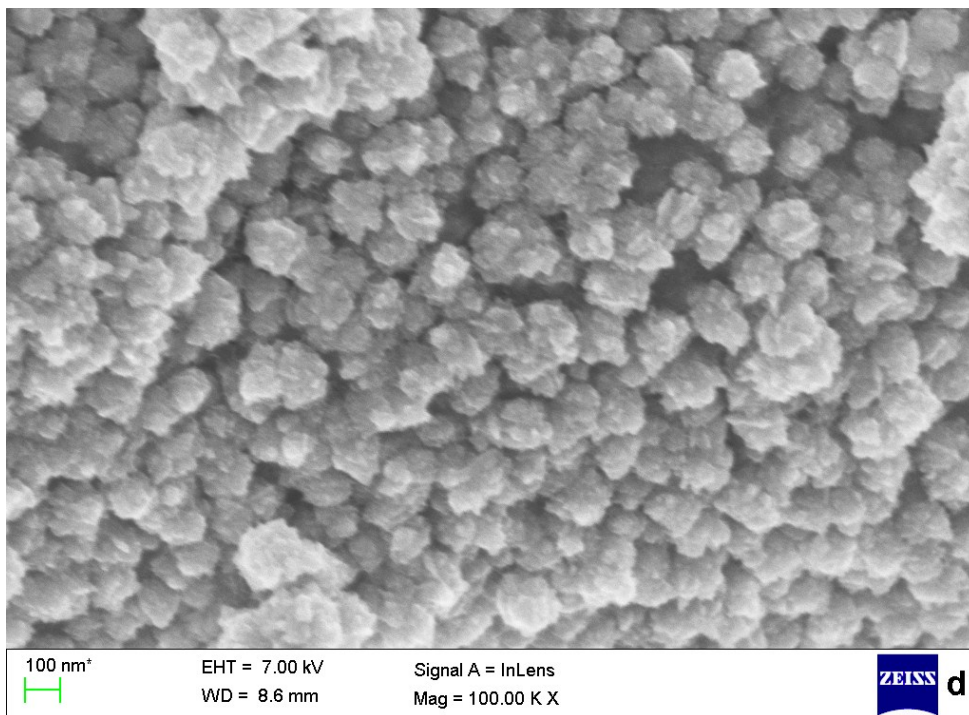
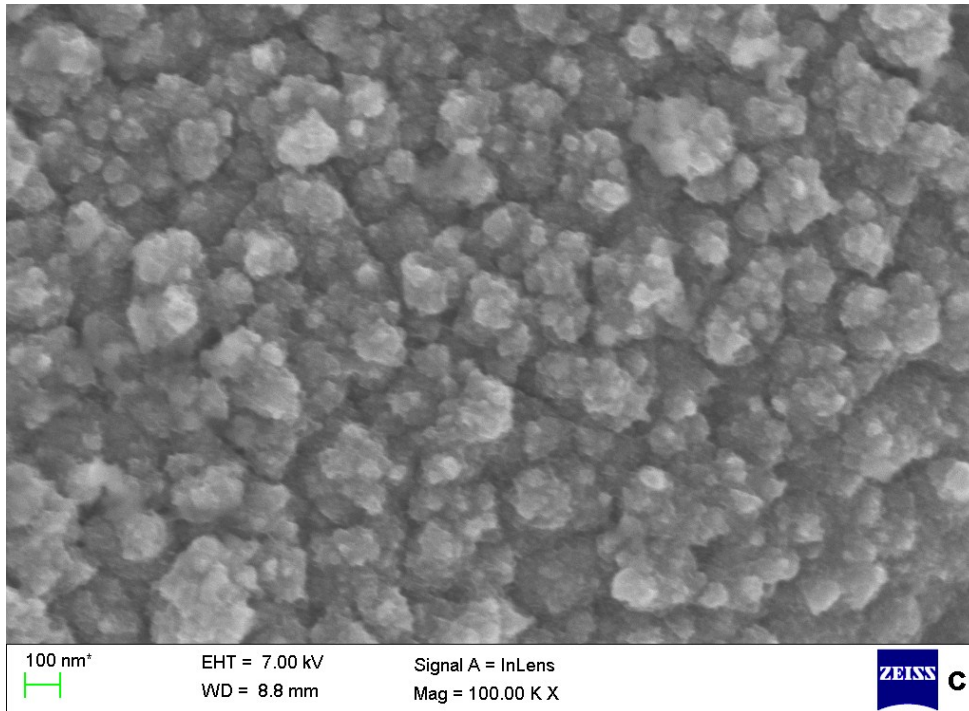


Fig. 2 Surface morphology of Co-Ni alloy coatings deposited at different current densities: a) 10 mA cm^{-2} , b) 20 mA cm^{-2} , c) 30 mA cm^{-2} and d) 40 mA cm^{-2} displaying different degree of surface roughness.

| Element | Weight% | Atomic% |
|---------|---------|---------|
| C | 10.95 | 37.59 |
| Co | 57.35 | 40.14 |
| Ni | 31.70 | 22.27 |
| Totals | 100.00 | 10.00 |

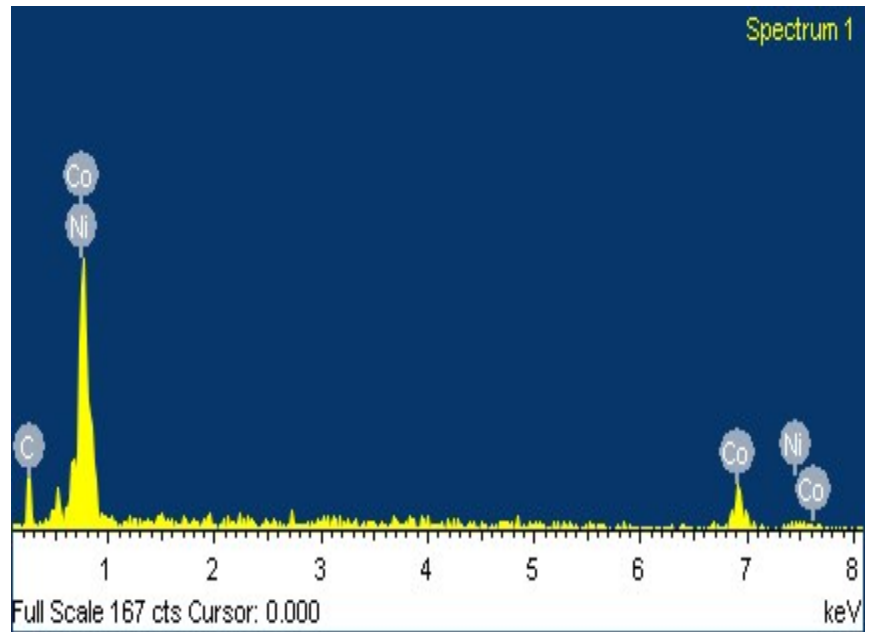


Fig. 3 Energy Dispersive X-ray (EDX) spectrum of Co-Ni-G composite electrode.

XPS analysis

The elemental composition of Co-Ni alloy and Co-Ni-G composite coatings are summarized in Table 1.

Table 1 Elemental composition of Co-Ni alloy and Co-Ni-G composite coatings from XPS analysis.

| | Co (at.%) | Ni (at.%) | C (at.%) | O (at.%) |
|----------------|--------------|--------------|-------------|-------------|
| Co-Ni | 12.6 | 7.28 | 33.77 | 46.35 |
| Co-Ni-G | 6.72 | 7.47 | 38.43 | 47.38 |

Electrochemical characterization of Co-Ni alloy coatings

Hydrogen evolution reaction

Cyclic voltammetry study

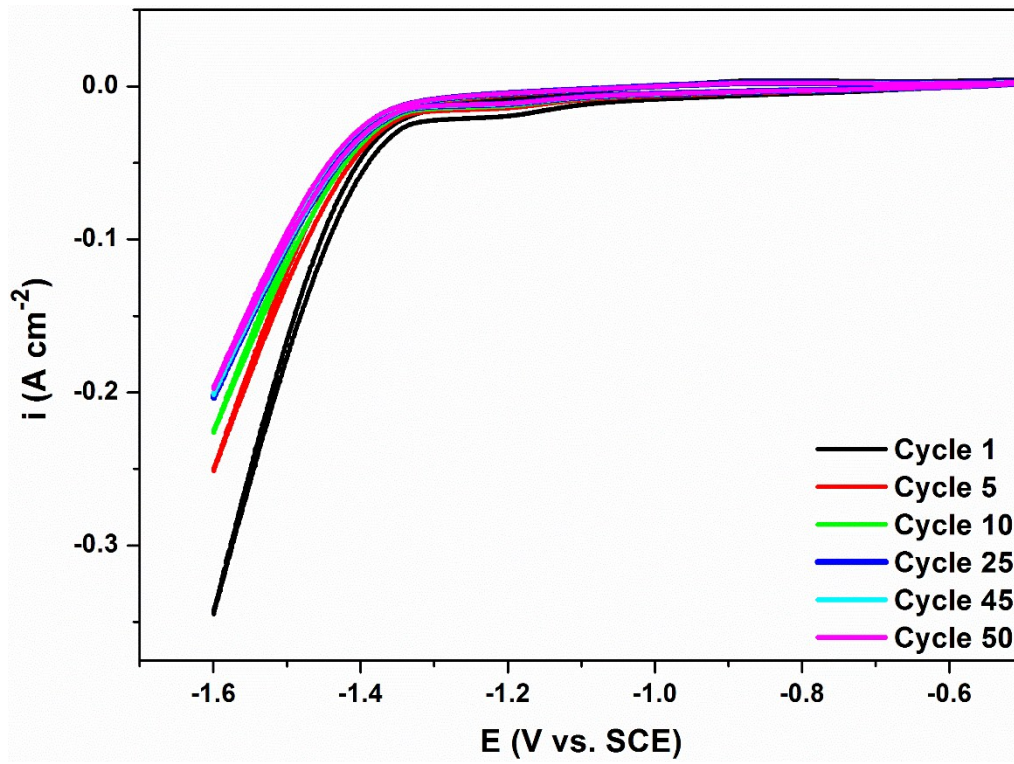


Fig. 4 CV curves for HER on Co-Ni coating developed at 40 mA cm^{-2} in 6 M KOH showing an increase in i_{pc} with the number of cycles and stabilization after 25th cycle.

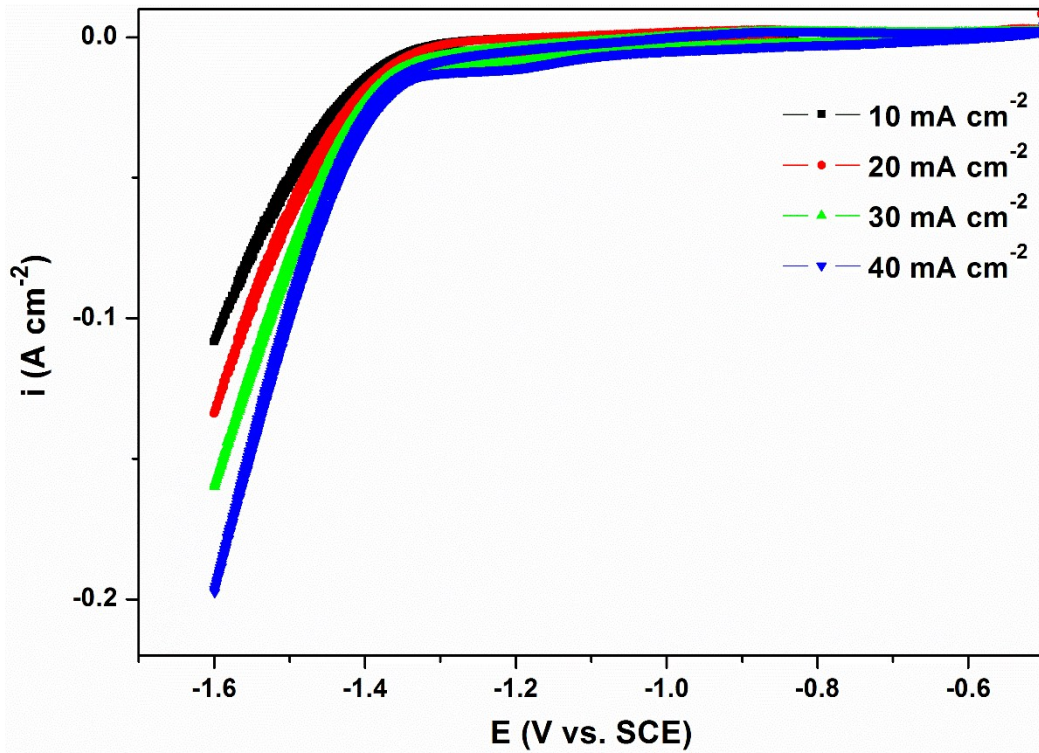


Fig. 5 CV curves showing the peak current density (i_{pc}) attained at the end of 50th cycle on Co-Ni alloy coatings deposited on copper substrate at different current densities.

Table 2

Electrocatalytic parameters for HER on Co-Ni alloy deposited at

| | i (mA cm ⁻²) | i_{pc} at -1.6 V (A cm ⁻²) | Onset potential of H ₂ evolution (V vs. SCE) | Volume of H ₂ evolved in 300 s (cm ³) |
|--|-------------------------------|---|---|---|
| different current densities from optimal Co-Ni bath. | 10 | -0.10 | -1.38 | 4.1 |
| | 20 | -0.13 | -1.35 | 4.5 |
| | 30 | -0.16 | -1.31 | 5.6 |
| | 40 | -0.20 | -1.29 | 7.0 |

different current densities from optimal Co-Ni bath.