

Ni/NiO Heterostructures Encapsulated in Oxygen Doped Graphene as  
Multifunctional Electrocatalysts for HER, UOR and HMF Oxidation Reaction

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**This file includes:**

Electrochemical test of Urea and HMF oxidation  
Fig. S1- S6  
Table S1

### **Electrochemical oxidation of urea or HMF**

The electrocatalytic activities Ni@C and Ni@C-250 for OER, UOR, and overall water splitting were studied using three electrodes (for OER/UOR and HER) and a two-electrode system (for overall water splitting and urea electrolysis). The 1 cm<sup>2</sup> area of CP deposited with Ni@C or Ni@C-250 were used directly as working electrodes. A graphite rod and Hg/HgO were used as counter and reference electrodes, respectively. Freshly prepared aqueous 1.0 M KOH and 1.0 M KOH containing 0.5 M urea solutions were used separately as electrolytes for water electrolysis and urea electrolysis, respectively. The two electrodes system was tested with Ni@C-250 deposited CF with anode and cathode electrode.

### **HPLC analysis of oxidation products of HMF**

In addition, the electrochemical oxidation of HMF was measured in the same system with 1M KOH solution with 50 mM HMF as electrolyte. To analyse the products quantitatively and calculate the corresponding Faradaic efficiencies, the electrochemical oxidation of HMF was also conducted at a constant potential of 1.45V vs. RHE in three electrode system. During and after the reaction, 10  $\mu$ L of the solution was periodically taken from the anode compartment and diluted with 490  $\mu$ L water, which was then analyzed by high-performance liquid chromatography (HPLC) (Waters) using a UV detector set at 280 nm and a C18 column. Sulfuric acid (5 mM) and Acetonitrile (10/90, vol/vol) was used as the mobile phase with a flow rate of 1 mL min<sup>-1</sup>.

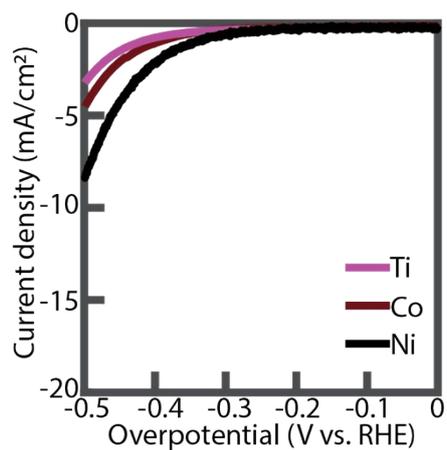


Fig. S1. polarization plots of various metals encapsulated by graphene in 1M KOH. The loading amount is 0.35mg/cm<sup>2</sup>

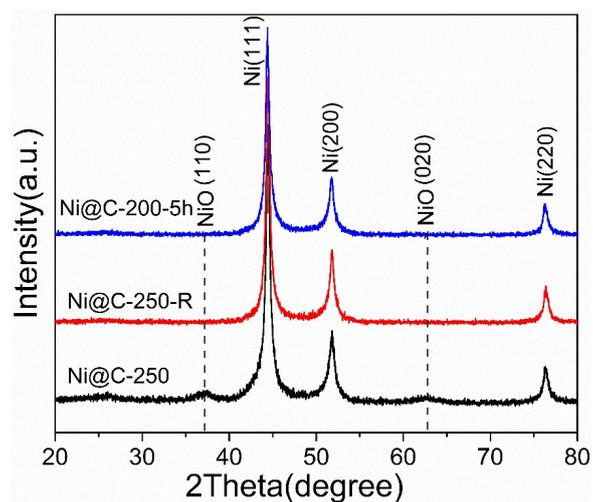


Fig. S2 XRD patterns of Ni@C-250, Ni@C-250-R and Ni@C-200-5h.

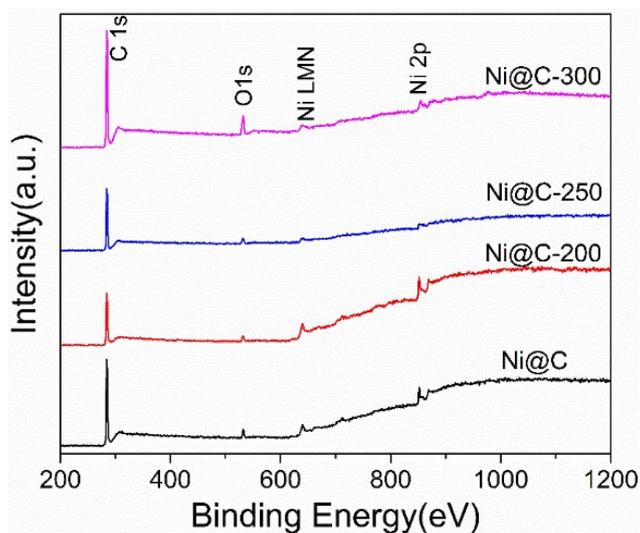


Fig. S3 (a) XPS survey spectra of Ni@C, Ni@C-200, Ni@C-250 and Ni@C-300.

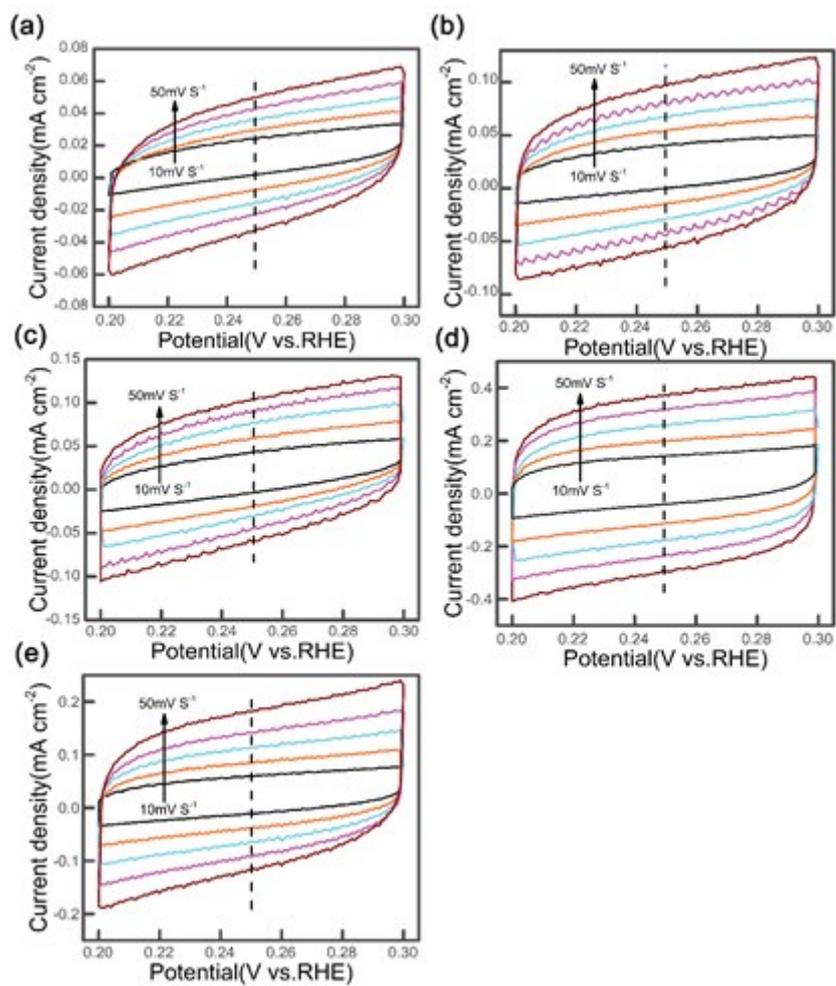


Fig S4. Fig. S4 Cyclic voltammograms of (a) unoxidized Ni@C, (b) Ni@C-150, (c) Ni@C-200, (d) Ni@C-250, Ni@C-300.

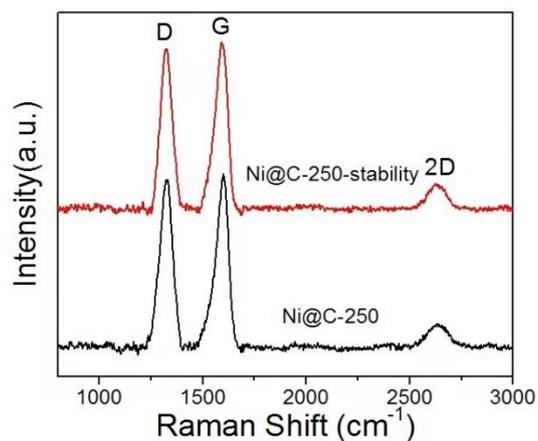


Fig. S5. Raman spectrum of Ni@C-250 before and after stability test. There is no change in the Raman spectrum after stability test, indicating the sample is stable during the test.

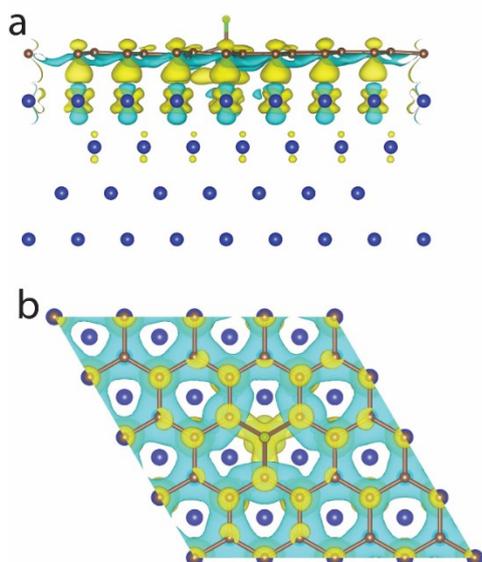


Fig S6 (a) Top view and (b) side view of the differential charge density of Ni@C system (atoms with purple, brown, and orange colors represent Ni, O and C atoms, respectively, charge transfer with light blue and yellow colors represent charge loss and charge accumulation).

Table S1 Comparison of HER activity of Ni-based catalysis in alkaline electrolyte.

	Current density (mA cm <sup>-2</sup> )	Overpotential (mV)	ref
Ni@NC	10	205	1
NiCu@C	10	94	2
Ni@graphene	10	240	3
Ni/NiO	10	120	4
Ni <sub>0.9</sub> Fe <sub>0.1</sub> /NC	10	231	5
NiS <sub>2</sub> /MoS <sub>2</sub>	10	204	6
Ni-NiO@3DHPG	10	310	7
Ni-GCS	10	205	8
Ni nanosheets	10	173	9
V-Ni/CP	10	178	10
NiO/Ni@C-O	10	89	This work

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