Supporting Information

Ni-reduced graphene oxide composite cathodes with new hierarchical morphologies for electrocatalytic hydrogen generation in alkaline media

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1. Synthesis of graphene oxide (GO)

GO was prepared from natural graphite powder using a modified Hummers method.[1] 1.5 g KNO_3 was dissolved in a beaker containing 50 mL of 98% H_2SO_4 placed in an ice-water bath below 5 °C. Then, 1 g graphite powder was added into the mixture with stirring. After 10 min, 8 g $KMnO_4$ was slowly added to the mixture and was stirred for another 6 h in a water bath at 35 °C. After that, 200 mL of water was slowly added into the solution over a period of 15 min. Subsequently, the temperature of the mixture was heated to 80 °C and kept for 30 min before cooling down naturally. Finally, 200 mL of water and 20 mL of 30wt % H_2O_2 were added into the mixture to stop the reaction. The diluted mixture was washed in succession five times with 20 mL of water and 30 mL of 37wt % HCl. Then, the mixture was washed with

water several times until pH > 6 by centrifugation to remove the unreacted graphite, the last one time with alcohol by ultrasonication for 2 h. Finally, the resulting mixture was vacuum-dried at 40 °C for further use.

2. Characterization of graphene oxide (GO)

The morphology of the prepared GO is characterized by TEM and the image is shown in Fig. S1(a). The GO exhibits a typical wrinkled sheet-like feature with the size about 3-4 μm. The inset XRD pattern of GO shows only one diffraction peak at 9.74° corresponding to an increased layer distance of 0.91 nm according to the Bragg's law, which is ascribe to the introduction of oxygen functional groups as well as water molecules in the interlayer of GO sheets.[2, 3] AFM was performed to investigate the thickness of the prepared GO sheets, the image and the measured result are shown in Fig. S1(b) and (c) respectively. It can be seen clearly from Fig. S1(c) that the thickness of GO sheets is ca. 1.0 nm, indicating single layer GO sheets were obtained. Fig. S1(d) presents the FT-IR spectrum of the prepared GO. The spectrum exhibits a number of adsorption peaks assigned to the functional groups appear in GO, corresponding to the stretching vibrations of O-H from hydroxyls and trapped water molecules (3430 cm^{-1}), C=O from carbonyl or carboxyl groups (1720 cm^{-1}), C=C from sp^2 graphite ring (1634 cm^{-1}), O-H from phenol (1380 cm^{-1}), C-OH (1228 cm^{-1}) and C-O from carboxyl (1045 cm^{-1}) respectively.[4, 5]

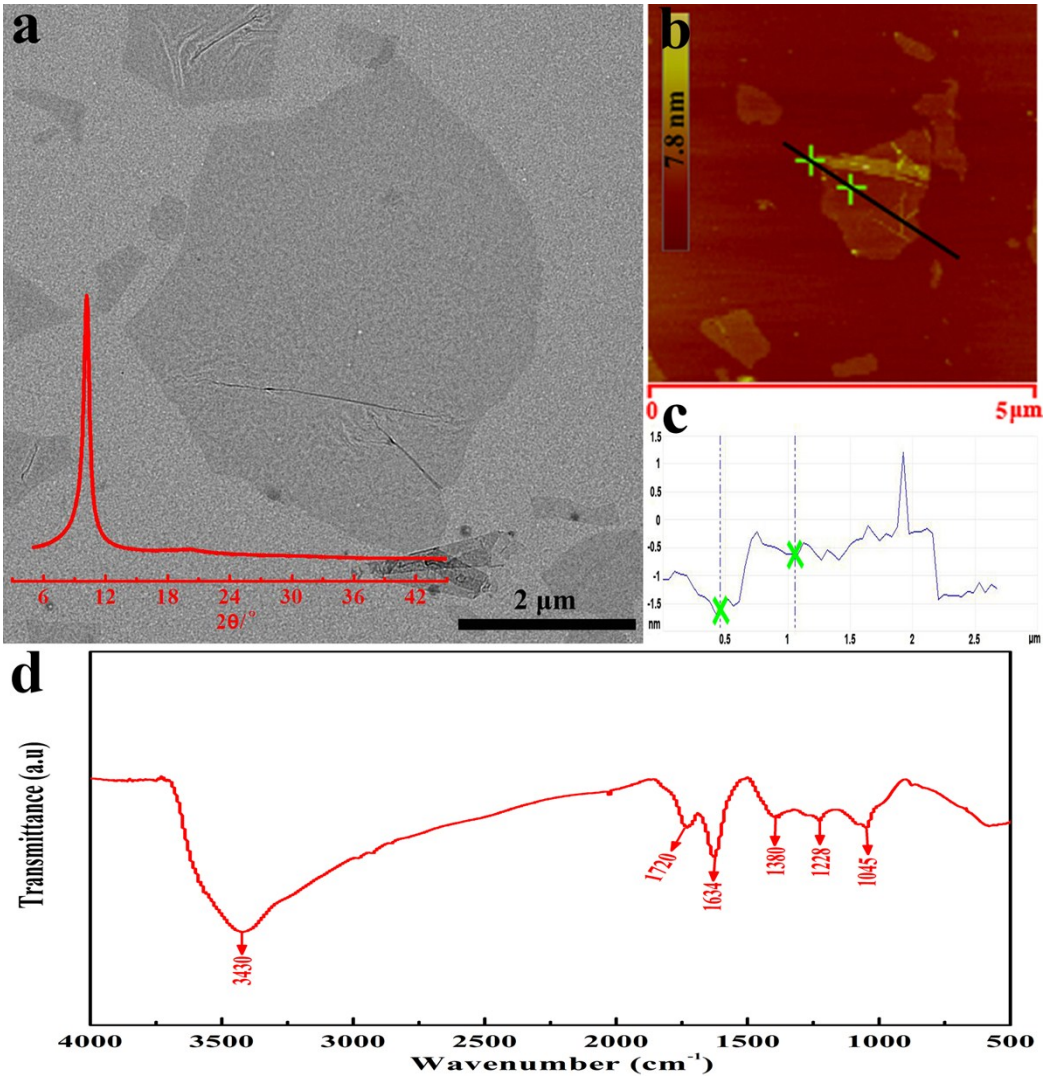

Figure S1. (a) TEM image of the prepared GO. (b) AFM image of the prepared GO. (c) AFM result of the thickness for the prepared GO. (d) FT-IR spectrum of the prepared GO.

Table S1. HER electrochemical parameters for some Ni-based electrocatalysts.

Catalyst	Method	Electrolyte	T (°C)	j_0 (mA cm^{-2})	b (mV dec^{-1})	Ref.#
Ni-rGO[a]	electrodeposition	1M NaOH	25	0.741	120	This paper
Ni-CeO_2	electrodeposition	1M NaOH	25	0.338	147	6
Ni-CNT	electrodeposition	1M NaOH	25	0.824	135	7
Ni-Graphene	electrodeposition	0.1M KOH	25	1.430	348	8
Ni-P-WO_3	electroless plating	32% NaOH	30	6.943×10^{-5}	108	9
$Ni_{71}Mo_{10}B_{19}$	melt spinning	1M KOH	25	0.0162	120	10
Fe-Ni-Graphene	electrodeposition	6M NaOH	25	0.133	125	11
NiMn	electrodeposition	30% NaOH	25	0.600	130	12
$Ni_{60}Fe_{30}Cr_{10}$	ball milling	1M NaOH	25	0.134	102	13
nanocrystalline Ni	magnetron sputtering	1M NaOH	25	0.307	173	14
Ni-P+Fe_2O_3-TiO_2	electroless plating	32% NaOH	30	6.02×10^{-6}	121	15
rGO-Ni foam	electrophoretic	1M KOH	22	1.04	130	16

[a] Electrodeposited under supergravity field (N= 3000 rpm).

Table S2. Electrical equivalent circuit parameters obtained by fitting EIS data.

GO concentration (g L^{-1})	N value (rpm)	R_s (Ω cm^{-2})	R_{ct} (Ω cm^{-2})	R_p (Ω cm^{-2})	Q ($m\Omega^{-1}$ s^n cm^{-2})
0	3000	3.17	475.9	1083	0.481
0.1	3000	3.08	9.86	3.28	14.91
0.4	3000	3.05	6.48	2.65	24.31
0.7	normal	2.88	37.39	8.49	5.028
0.7	2500	2.83	12.82	4.00	13.31
0.7	2750	2.98	9.21	3.19	19.69
0.7	3000	2.89	5.47	1.48	40.09
0.7	3250	2.98	6.66	3.15	20.85
0.7	3500	3.06	8.59	2.60	18.98
1.0	3000	2.95	6.08	1.73	20.94
1.5	3000	3.03	6.95	2.90	18.22

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