## Ni/NiO nanoparticles on phosphorous oxides /graphene hybrid for efficient electrocatalytic water splitting

Juan Wang<sup>a</sup>, YananXie<sup>a</sup>, Yuanyingyao<sup>a</sup>, Xing Huang<sup>b</sup>, Marc Willinger<sup>b</sup>, and Lidong Shao<sup>\*a</sup>

<sup>a</sup>Shanghai Key Laboratory of Materials Protection and Advanced

Materials in Electric Power, Shanghai University of Electric Power, 2103

Pingliang Road, Shanghai 200090, China.

E-mail address:lidong.shao@shiep.edu.cn

<sup>b</sup>Department of Inorganic Chemistry Fritz-Haber Institute of the Max

Planck Society Faradayweg 4-6, 14195 Berlin, Germany.

## **RHE** calibration



Figure S1 RHE calibration of reference electrode.

We used Hg/HgO electrode as the reference electrode in all measurements. It was calibrated with respect to reversible hydrogen electrode (RHE). The calibration was performed in the high purity hydrogen saturated electrolyte with a Pt wire as the working electrode. CVs were run at a scan rate of 1mV s<sup>-1</sup>, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions.



Figure S2. (a) XRD and (b) Raman profiles with a, b, c, d) corresponding to the samples of step 1-4 in Figure 1.



Figure S3. (a) XRD of Ni/NiO@HGP $_xO_y$  and Ni/NiO@HG. (b) is the magnification of (a).

## **Calculation of active sites**

The number of active sites are calculated from the cyclic voltammograms without faradic current in **Figure S4** at the rate of 200 mV s<sup>-1</sup> by integrating the current over the whole potential. Assuming a one electron redox process, this absolute charge was divided by two. The value was then divided by the Faraday constant to get the number of active sites of the catalysts. The total number of active sites for each catalyst can be calculated from cyclic voltammetry by integrating the current over the whole potential.

The number of active sites = Area under the curve / 2F

The calculated number of active sites for the electrode materials are,

n (Ni/NiO@HGPxOy) =  $1.0 \times 10^{-3}$ mol g<sup>-1</sup>

n (Ni/NiO@HG) =  $0.47 \times 10^{-3}$ mol g<sup>-1</sup>



**Figure S4** Cyclic voltammetry curves of (a) Ni/NiO@HG, and (b) Ni/NiO@HGP<sub>x</sub>O<sub>y</sub> in the range of 0.03-0.13 V vs. RHE. The scan rate is 40, 80, 120, 160 and 200, mV s<sup>-1</sup> for the curves from inside to outside.(c) The differences in current density ( $\Delta J$ ) plotted against scan rate fitted to a linear regression.



**Figure S5.** (a) Nyquist plots for Ni/NiO@HGP<sub>x</sub>O<sub>y</sub> and Ni/NiO@HG. (B) The lines were fitted by equivalent circuit.

**Table S1** Parameters obtained by fitting the Nyquist plots to theequivalent circuit model.

sample	R <sub>s</sub>	CPE <sub>1</sub>	$\mathbf{n}_1$	$R_1$	CPE <sub>dl</sub>	n <sub>dl</sub>	R <sub>ct</sub>	
	(Ω)	(FS <sup>n-1</sup> )		(Ω)	(FS <sup>n-1</sup> )		$(\Omega)$	
Ni/NiO@HGPxOy	30.36	0.01653	0.9999	51.3	0.005827	0.7809	83.37	
Ni/NiO@HG	31.62	0.00643	0.9743	112	0.002511	0.7132	349	