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Supplementary Materials for

PtNi alloy nanoparticles grown in situ on nitrogen doped carbon for efficient oxygen reduction reaction

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Contents:

Materials and methods

Synthesis of NC nanoparticles: Two types of nitrogen doped carbon (NC) were prepared by hydrothermal and thermal annealing methods, respectively. Typically, 120 mg carbon (XC-72R), 280 mg urea, 20 mL ethanol and 20 mL deionized water were well mixed by 1 h ultrasonication. The solution was autoclave treated at 180°C for 14 h. After centrifugation with ethanol, the product was labeled as NC(H). In another typical synthesis method, 120 mg carbon (XC-72R), 280 mg urea and 10 mL ethanol were stirring in the oil bath at 80°C for 30 min. After centrifugation and drying in vacuum experimental box, the solids were annealed for 5 h in Ar atmosphere at 650°C with a ramp rate of 10°C/min. The obtained product was labeled as NC(T).

Synthesis of PtNi NPs: 13 mL $H_2PtCl_6{\cdot}6H_2O$ in ethanol (1.5 mg_{Pt}/mL), 25 mg $Ni(acca)_2{\cdot}4H_2O$, 80 mg CTAC and 40 mL OAM were added into the solution and stirred magnetically for 6 h. The homogeneous solution was transferred into a 100 mL Teflon-lined autoclave and heated at 180 °C for 14 h. After cooling down to room temperature, the resultant was collected by centrifugation with an ethanol/acetone mixture (volume ratio of 3/1) for three times and etched in nitric acid (HNO_3, 0.5 M) to remove Ni from active site and obtain PtNi NPs.

Synthesis of PtNi/NC[H] NPs: The above synthesized PtNi NPs were further supported on the NC(H) synthesized by hydrothermal mixing, which performed more active for ORR than NC(T). In a typical process, 40 mg NC(H) and 10 mg PtNi NPs were dispersed in 40 mL OAM. The homogeneous black solution was mixed in cyclohexane under stirring for 12 h and dried at oven at 50 °C. The product was labeled as PtNi/NC[H]. The resultant product was fully grinded and annealed for 4 h in Ar atmosphere at 350°C.The product was labeled as PtNi/NC[H]-350.

Figures

Figure S1

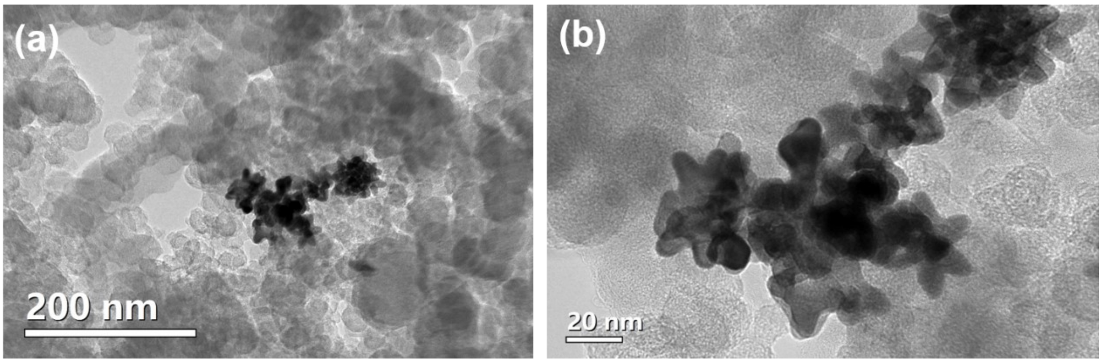

Figure S1. TEM images of PtNi/NC[H]-350 synthesized by a two-step hydrothermal method.

Figure S2

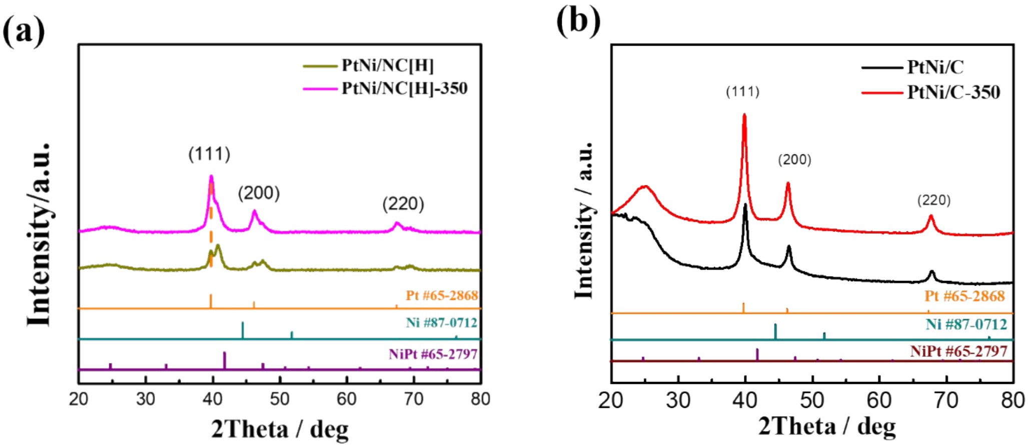

Figure S2. (a) XRD patterns of PtNi/NC[H] and PtNi/NC[H]-350 synthesized by a two-step hydrothermal method. (b) XRD patterns of PtNi/C and PtNi/C-350 synthesized without urea by a one-pot method.

Figure S3

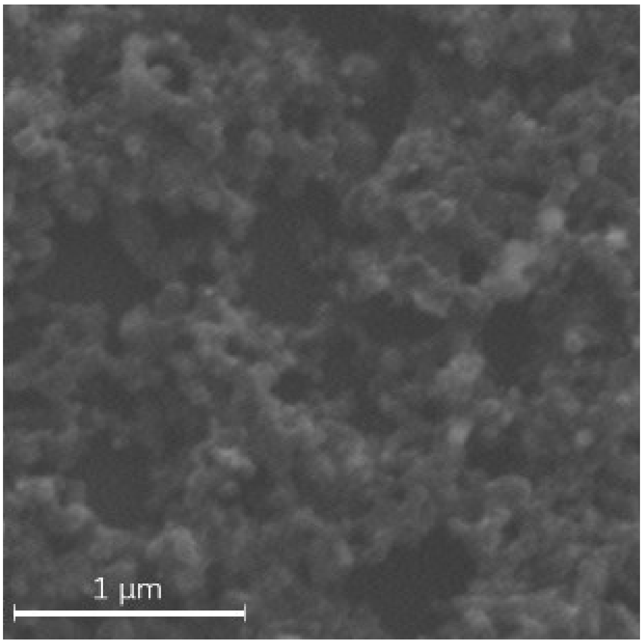

Figure S3. SEM images of PtNi/NC-350 after etching process.

Figure S4

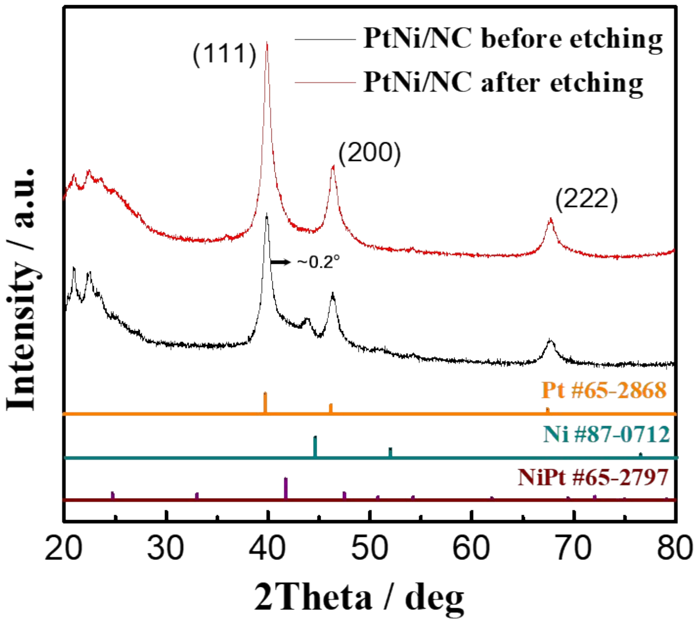

Figure S4. XRD patterns of PtNi/NC before and after HNO_3 etching.

Figure S5

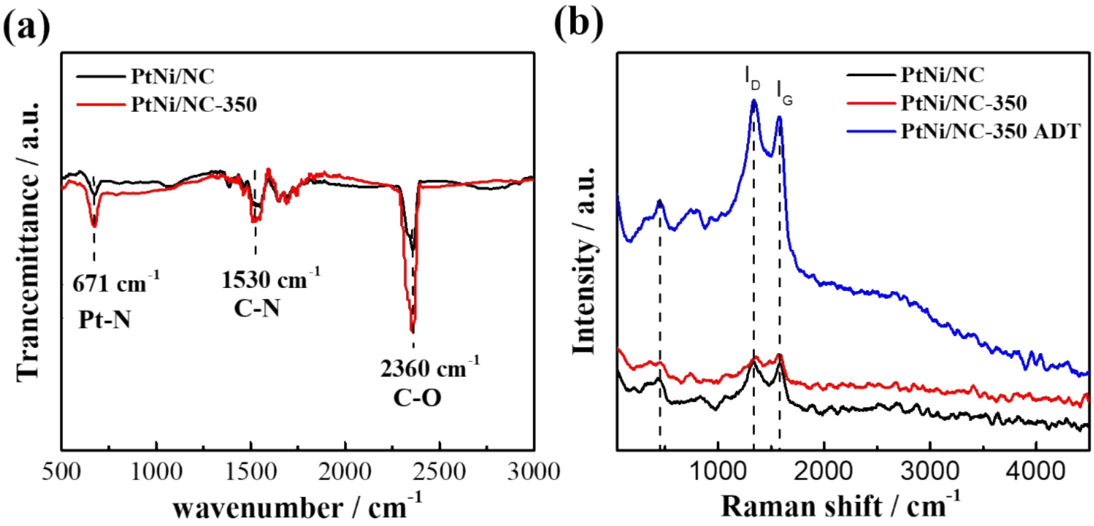

Figure S5. (a) FTIR and (b) Raman spectra of PtNi/NC and PtNi/NC-350.

Figure S6

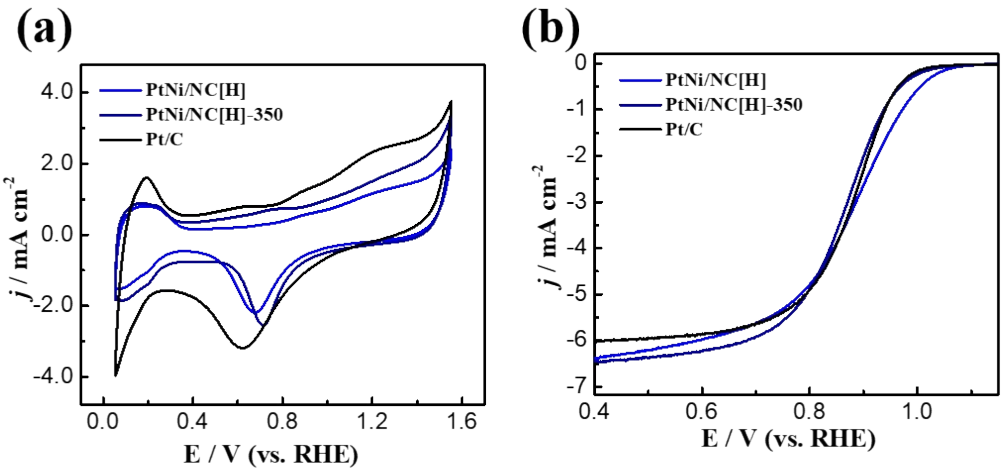

Figure S6. The ORR permormance of PtNi/NC[H] before and after annealing treatment and commercial Pt/C. (a) Cyclic voltammograms (CVs) in N_2-saturated 0.1 M $HClO_4$ electrolyte at 50 mV/s. (b) Linear sweep voltammetries (LSVs) in O_2-saturated electrolyte at 5 mV/s.

Figure S7

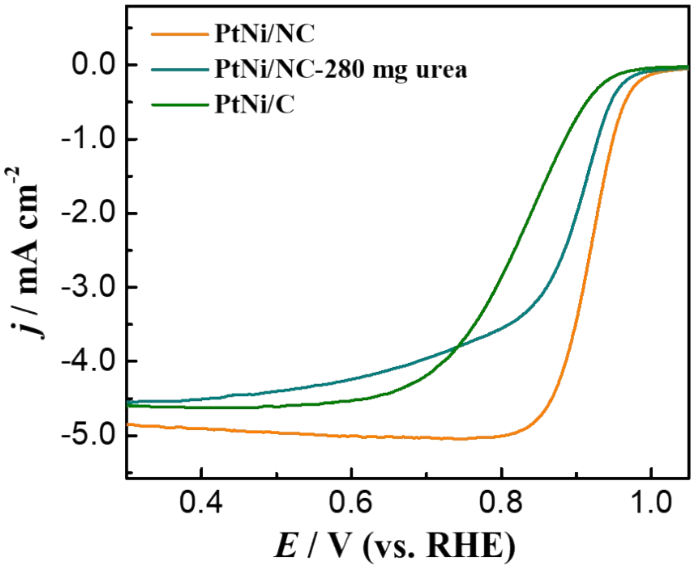

Figure S7. Linear sweep voltammetry (LSV) curves for differnt samples in O_2-saturated electrolyte at 5 mV/s

Figure S8

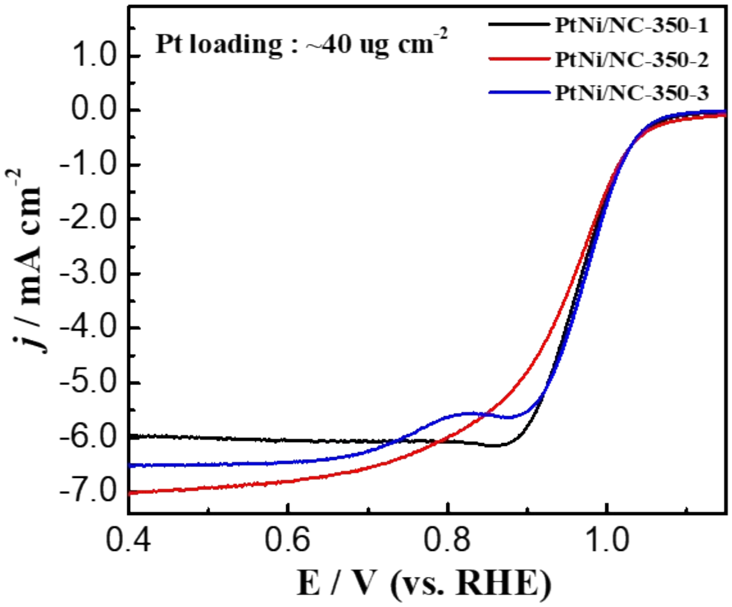

Fig. S8 PtNi/NC reproducible tests of ORR polarization for PtNi/NC-350 with ~ 40 μg·cm^{-2} Pt loading.

Figure S9

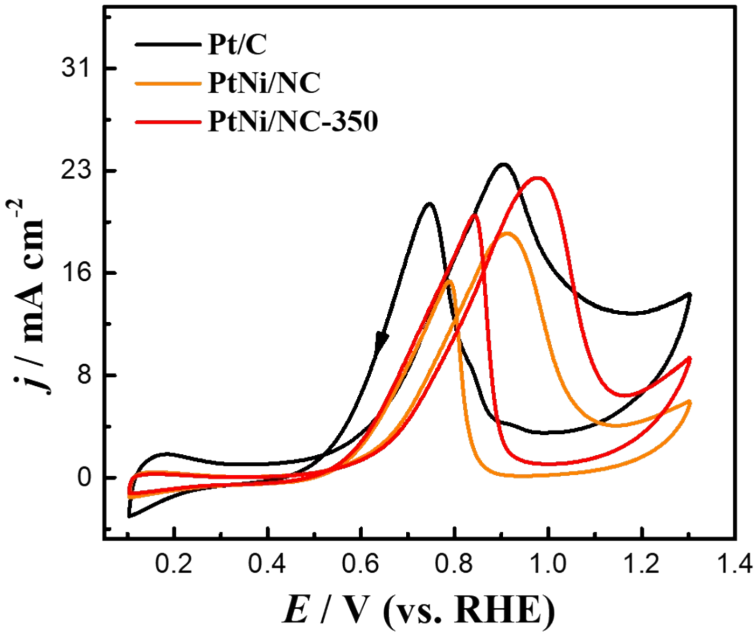

Figure S9. Cyclic voltammograms (CVs) curves of the prepated samples in 0.1 M $HClO_4$ and 1 M CH_3OH electrolyte at 50 mV/s.

Figure S10

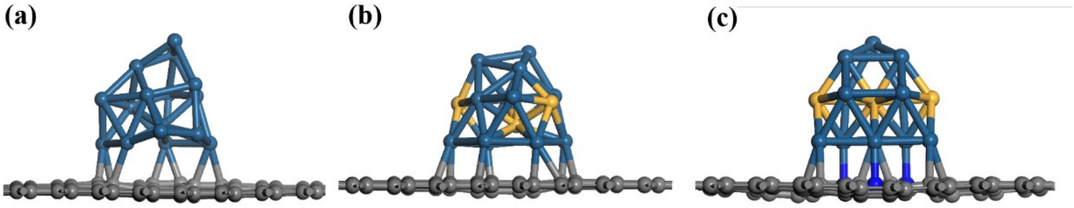

Figure S10. Optimized Models of Pt/C, Pt_4Ni/C and Pt_4Ni/NC. Color mode: gray blue: Pt; yellow: Ni; light blue: N; gray: C. The bond of Pt-Left Ni (Same site for Pt in Pt/C) in average calculated as 2.68, 2.48, 2.52 Å for Pt/C, PtNi/C and PtNi/NC. The bond of Pt-right Ni (Same site for Pt in Pt/C) in average calculated as 2.57, 2.46 and 2.54 Å for Pt/C, PtNi/C and PtNi/NC, in consistent with the experimentally synthesized catalysts.

Figure S11

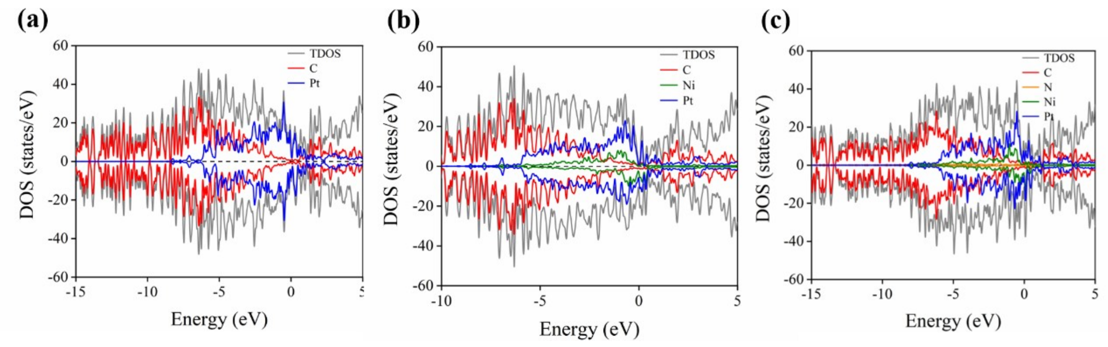

Figure S11. The total density of states and partial density of Pt, C, Ni, N states of Pt/C, PtNi/C and PtNi/NC.

Table S1. The atomic ratio of Pt, Ni and N element in PtNi/NC and PtNi/NC-350 obtained by XPS and ICP-OES profiles, respectively.

Samples	**XPS**			**ICP**		
	Pt (at%)	**Ni (at%)**	**N (at%)**	**Pt (wt%)**	**Ni (wt%)**	**Pt/Ni atom ratio**
PtNi/NC without acid treatment	/	/	/	8.217	4.457	1:2
PtNi/NC	0.44	0.26	1.37	8.678	0.680	4:1
PtNi/NC-350	0.55	0.30	0.87	/	/	

Table S2. PtNi/NC-350 reproducible tests of mass activity (MA) with ~ 40 μg cm^{-2} Pt loading.

	PtNi-350-1	**PtNi-350-2**	**PtNi-350-3**	Average value of MA	Standard deviation of MA
$J_{0.9V}$ (mA·cm^{-2})	5.52	4.9	5.8	/	/
MA (A·mg_{Pt}^{-1})	0.84	0.6	1.05	0.83	0.18

Table S3. d band center calculation of Pt/C,PtNi/C and PtNi/NC.

	d-band-Center (UP) (eV)	d-band-Center (DOWN) (eV)	d-band-Center (Average) (eV)
Pt/C	-2.0287	-1.9741	-2.0014
PtNi/C	-2.0171	-1.734	-1.8757
PtNi/NC	-2.0615	-1.8181	-1.9399