Supporting Inforamtion

Dual Roles of sub-nanometer NiO in Alkaline Hydrogen Evolution

Reaction: Breaking Volmer Limitation and Optimizing d-Orbital

Electronic Configuration

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Experimental section

Reagents. All the chemicals used were commercial without any further purification. Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O; >99.0%, Sinopharm Chemical Reagent Co., Ltd.), 2-methyleimidazole (99.0%, Aladdin), methanol (99.5%, Sinopharm Chemical Reagent Co., Ltd.), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O; >99.0%, Sinopharm Chemical Reagent Co., Ltd.), ethanol (99.5%, Sinopharm Chemical Reagent Co., Ltd.), Hexachloroplatinum (IV) acid (H₂PtCl₆·6H₂O; >37.5%, Sinopharm Chemical Reagent Co., Ltd.), Pt/C (Johnson Matthey, 20%), sulfuric acid (95%, Sinopharm Chemical Reagent Co., Ltd.) and de-ionized water with the specific resistance of 18.25 MΩ·cm⁻¹ (obtained by reversed osmosis followed by ion-exchange and filtration).

Preparation of NPC. The NPC was prepared according to a reported method (with 20 mmol Zn(NO3)2·6H2O, 82.58 mmol 2-methyleimidazole). The prepared ZIF-8 was annealed at 1000°C for two hours under N2 atmosphere. Then the powder was denoted NPC.

Preparation of NiO/NPC. 0.172 mmol Ni(NO3)2·6H2O was dissolved in the 50ml ethanol with stirring, then the pre-prepared NPC (100 mg) was added to the solutions stirring for five hours, the samples were washed by ethanol, then annealed at 250°C for 0.5 hour in an air atmosphere. The prepared samples were denoted as NiO/NPC.

Preparation of Pt/NiO/NPC. The H2PtCl6·6H2O (0.005 mmol, 0.125 mmol, 0.276 mmol) mixed with NiO/NPC (50 mg) into ethanol stirring for five hours, the samples

were washed by ethanol, then annealed at 180°C for 1 hour in a H2/N2 atmosphere. The Pt loading was counted for 1.5, 3 and 6wt%. The prepared samples were denoted with 1.5%Pt/NiO/NPC, 3%Pt/NiO/NPC and 6%Pt/NiO/NPC, respectively.

Synthesis of PtNi/NPC and Pt/NPC. The H2PtCl6·6H2O (0.005 mmol) and Ni(NO3)2·6H2O (0.172 mmol); and single H2PtCl6·6H2O (0.005 mmol) were mixed in ethanol respectively, added pre-prepared NPC (50 mg) into those two solution stirring for five hours, the sample was washed by ethanol, then annealed at 180°C for 1h in a H2/N2 atmosphere. The Pt loading was counted as 1.5% and 1.7%. The prepared samples were recorded as 1.5%PtNi/NPC and 1.7%Pt/NPC.

Material characterization. Scanning electron microscopy (SEM) was performed on a SUPRA 55. Transmission electron microscopy (TEM) images and Wide-angle X-ray diffraction (XRD, D-MAX 2200 VPC) patterns. X-ray photoelectron spectroscopy (XPS) characterization was performed by a K-Alpha. Inductively coupled plasma mass spectrometer (ICP-MS) (iCAP7000, Thermo Fisher Scientific) was used to determine the Pt loading. The particle size distribution was determined by measuring more than 200 particles using a Nano Measurer.

Electrochemical methods. All the electrochemical measurements were conducted in a three-compartment cell at room temperature on an electrochemical workstation (CHI660E). The carbon rod and Ag/AgCl electrode (sat. KCl) were utilized as the counter and reference electrodes, respectively. The working electrode was as-prepared

catalysts coated with a glassy carbon electrode. The electrolyte was N2 saturated 1 M KOH. The catalyst ink was prepared by blending the catalyst powder (2 mg) with 20 uL Nafion solution (5 wt%) and 980 uL of isopropanol in an ultrasonic bath. The catalyst ink was then pipetted onto the glassy carbon electrode surface (0.196 cm^{-2}) . The potentials in this work were converted to RHE according to $E(_{RHE}) = E(_{Ag/AgCl}) + 0.197 + 0.059 \cdot pH$. Before measurements, a steady CV of the working electrode was first obtained by cycling at 0.05-1.2 V (vs. RHE) at 50 mV·s⁻¹ in a N₂-saturated 1 M KOH solution. The hydrogen evolution reaction (HER) linear sweep voltammetry (LSV, 2 mV \cdot s⁻¹) was performed in a N₂-saturated 1 M KOH. Note that all the HER LSV tests were 98% iR-compensated. The accelerated durability test (ADT) was performed by sweeping electrode between -0.15-0.25 V at 100mV/s for 1000 cycles in a N₂-saturated 1 M KOH. The electrochemical impedance spectroscopy (EIS) was performed in a frequency range from 100 kHz to 0.1 Hz. The stability tests were carried out by repeating the potential scan at a sweep rate of 100 mV s⁻¹ with 1,000 CV cycles. The Tafel slopes were calculated by fitting to the Tafel equation: $\eta = b \cdot \log j + c$. The TOF values were calculated based on the Pt atom numbers

in each sample electrode according to the following equation: $TOF = \frac{I}{2F \cdot n}$, where I (in Amperes) is the current measured from LSV curves, F is the Faraday constant (96485.3, in C mol⁻¹) and n represents the atom number of Pt (in mol).

Density functional theory (DFT) calculation. All calculations are performed within the DFT framework, using the Vienna ab initio simulation package (VASP) that takes

spin polarization into account. We use the projected augmented wave (PAW) potentials to simulate the interaction between valence electrons and nuclei. In addition, Perdew-Burke-Ernzerh (PBE) and Generalized Gradient Approximation (GGA) using exchange correlation functions are used to study electron transfer and interrelationships. It is appropriate to select the kinetic energy cut-off point of plane wave expansion at 450 eV and the $3\times3\times1$ Monhorst-Pack k-point grid sampling of the first Brillouin zone. To determine the occupancy, we set the Gaussian dispersion width to 0.1 eV. The relaxation of the adsorption surface structure was calculated using a conjugate gradient algorithm. The unit lattice constant was 14.793 Å×14.772 Å×30.000 Å, and the maximum force and energy of unconstrained atoms were limited to 0.01 eV/Å and 1×10⁻⁶ eV, respectively. The electron iteration convergence value for self-consistent field (SCF) calculation was set to 1×10⁻⁶ eV.

Firstly, we used Pt/NiO, Pt/Fe₃O₄, Pt/Co₃O₄, Pt/MoO₃ and pure Pt clusters as the models, screening out the most promising metal oxide nanocluster for alkaline HER. Then, we used the models of Pt/NiO/NPC, PtNi/NPC, Pt/NPC and Pt/C to further study the function of NiO nanocluster under alkaline electrolyte. We chose the Pt atom on the top of model as the active site. The following two equations were used for adsorption energy and adsorption energy derived reaction Gibbs free energy, where n is the number of adsorbed protons, "surf" represents "surface", and where ΔE_{ZPE} is the zero-point energy difference between adsorbed hydrogen and that in gas phase, $\Delta S_H \tilde{=} -\frac{1}{2}S_{H_2}^0$,

entropy of H_2 gas at standard condition.

$$\Delta E_H = \frac{1}{n} (E(surf + nH) - E(surf) - \frac{n}{2} E(H_2))$$
(1)

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T \Delta S_H \tag{2}$$



Fig. S1 The detailed structures for hydrogen adsorption and desorption on the surface of

different models.



Fig. S2 PDOS plots of pure Pt.



Fig. S3 SEM images of NPC.



Fig. S4 (a-b) Bright-field TEM and HRTEM images of NiO/NPC, (c-d) HAADF-STEM

images of NiO/NPC.



Fig. S5 (a) LSV curves of Pt/NiO, Pt/Fe₃O₄, Pt/Co₃O₄, Pt/MoO₃ and Pt in 1.0 M KOH. (b)

The relationship between overpotential and d-band center.



Fig. S6 Bright-field TEM and HRTEM images of 1.5%PtNiO/NPC.



Fig. S7 (a-b) Bright-field TEM and HRTEM images of 3%Pt/NiO/NPC, (c-d) HAADF-

STEM images of 3%Pt/NiO/NPC.



Fig. S8 (a-b) Bright-field TEM and HRTEM images of 6%Pt/NiO/NPC, (c-d) HAADF-

STEM images of 6%Pt/NiO/NPC.



Fig. S9 TOFs of Pt/NiO/NPC and commercial 20%Pt/C.



Fig. S10 (a) XRD patterns of Pt/NiO/NPC, PtNi/NPC, Pt/NPC and NiO/NPC. (b) Pt 4f XPS spectra comparison of Pt/NPC, PtNi/NPC and Pt/NiO/NPC. (c) Ni 2p XPS spectra comparison of NiO/NPC, PtNi/NPC and Pt/NiO/NPC.



Fig. S11 (a) Overpotential at 10 mV/cm⁻². (b) Tafel curves.



Fig. S12 (a) TOFs of 1.5%Pt/NiO/NPC, 1.5%PtNi/NPC, 1.7%Pt/NPC, NiO/NPC and commercial 20%Pt/C. (b) Corresponding TOF values at the overpotential of 50 mV vs.

RHE.

Samples	Free energy / eV
Pt/NiO	0.394
Pt/Fe ₃ O ₄	-1.016
Pt/Co ₃ O ₄	-0.301
Pt/MoO ₃	-1.056
Pt	0.803

Table S1. The Gibbs free energy of water splitting of different models.

Table S2. The Gibbs free energy of intermediate state (H *) generations of different

mo	de	ls.

Samples	Free energy / eV
Pt/NiO	-0.092
Pt/Fe ₃ O ₄	-0.133
Pt/Co ₃ O ₄	-0.204
Pt/MoO ₃	-0.266
Pt	-1.216

 Table S3. ICP-OES of Pt and Ni mass percentage of different catalysts.

Samples	Pt	Ni
NiO/NPC	/	3.6
1.7%Pt/NPC	1.7	/
1.5%PtNi/NPC	1.5	3.2
1.5%Pt/NiO/NPC	1.5	3.4
3%Pt/NiO/NPC	3	3.5
6%Pt/NiO/NPC	6	3.5

Table S4. Nanocluster size statistics for Pt/NiO/NPC.

Samples	Average nanocluster size (nm)	Range (nm)
1.5%Pt/NiO/NPC	0.84	0.5-1.1
3%Pt/NiO/NPC	1.27	1.1-1.9
6%Pt/NiO/NPC	2.34	1.8-3.0
1.7%Pt/NPC	0.92	0.7-1.3
1.5%Pt/NiO/NPC after 1000 cycles CV	0.87	0.5-1.1

Samples	Pt ⁰ 4f _{7/2}	Pt ²⁺ 4f _{7/2}	Pt ⁰ 4f _{5/2}	Pt ²⁺ 4f _{5/2}
1.7%Pt/NPC	71.08	72.05	74.42	75.39
1.5%PtNi/NPC	71.20	72.17	74.54	75.51
1.5%Pt/NiO/NPC	71.45	72.42	74.79	75.76
3%Pt/NiO/NPC	71.31	72.28	74.65	75.62
6%Pt/NiO/NPC	71.21	72.18	74.55	75.52

 Table S5. XPS spectra of different catalysts with Pt 4f.

Table S6. XPS spectra of different catalysts with Ni 2p.

Samples	Ni ²⁺ 2p _{3/2}	
NiO/NPC	855.35	
1.5%PtNi/NPC	855.26	
1.5%Pt/NiO/NPC	854.10	
3%Pt/NiO/NPC	854.39	
6%Pt/NiO/NPC	855.15	

Table S7. Comparison of the HER activity of the catalysts obtained in this work and

Catalyst	Overpotential at	Tafel slope	Mass activity	Ref.
1 5%Pt/NiO/NPC	25.2	22.5	<u> </u>	This work
3%Pt/NiO/NPC	37.9	35.2	5 33	This work
6 %Pt/NiO/NPC	48 7	<i>4</i> 9 2	1 93	This work
Dt./HMCS	46.7	49.2	3.23	1 ¹
Pt@mh 3D MYana	31	40.1	12.04	1 22
$Pt/Ni(HCO_{1})$	J1 45	+1 52	12.94	2 33
$\frac{1}{2} \frac{1}{1} \frac{1}$	43	32 20	1.//	<u> </u>
$\mathbf{P}_{t} = \mathbf{N}_{t} \left(\mathbf{N} \right)$	13	29 27	5.2	4 55
rt-INI ASS	27.7	21 567	5.2	5-
$N_{15}P_4$ -Ku	123	JO. /	-	$\frac{0^{\circ}}{7^{7}}$
$\begin{array}{c} \text{CO-P I} \\ \text{N: } W \text{ COO} \end{array}$	1/5	84 52	-	/'
N1-W-000	59	52	-	8° 09
$MOS_2(a)N1O$	406	43	-	9 ⁹
$L_{1_X}N_1O/N_1$	36	50	-	1010

other high-performance HER catalysts.

Table S8. The EIS fitting parameters from equivalent circuits of Pt/NiO/NPC and

Samples	R_s/Ω	R_{ct}/Ω
1.5%PtCo/NPC	5.02	15.1
3%PtCo/NPC	5.04	20.7
6%PtCo/NPC	5.07	25.7
20%Pt/C	5.04	63.0

commercial 20%Pt/C.

Table S9. The Gibbs free energy of intermediate state (H *) generations of different

models.

Samples	Free energy / eV
Pt/NiO/NPC	-0.082
PtNi/NPC	-0.417
Pt/NPC	-0.121
Pt/C	-0.133
NiO/NPC	-0.181

 Table S10. The Gibbs free energy of water splitting of different models.

Samples	Free energy / eV
Pt/NiO/NPC	0.294
PtNi/NPC	-0.859
Pt/NPC	0.720
Pt/C	1.325
NiO/NPC	-0.901

References

- 1. X. K. Wan, H. B. Wu, B. Y. Guan, D. Luan and X. W. D. Lou, Adv. Mater., 2020, 32, 1901349.
- L. Xiu, W. Pei, S. Zhou, Z. Wang, P. Yang, J. Zhao and J. Qiu, *Adv. Funct. Mater.*, 2020, 30, 1910028.
- M. Lao, K. Rui, G. Zhao, P. Cui, X. Zheng, S. X. Dou and W. Sun, *Angew. Chem., Int. Ed.*, 2019, 58, 5432-5437.
- 4. Y. Xie, J. Cai, Y. Wu, Y. Zang, X. Zheng, J. Ye, P. Cui, S. Niu, Y. Liu, J. Zhu, X. Liu, G. Wang and Y. Qian, *Adv. Mater.*, 2019, **31**, 1807780.
- Z. Zhang, G. Liu, X. Cui, B. Chen, Y. Zhu, Y. Gong, F. Saleem, S. Xi, Y. Du, A. Borgna, Z. Lai, Q. Zhang, B. Li, Y. Zong, Y. Han, L. Gu and H. Zhang, *Adv. Mater.*, 2018, **30**, 1801741.
- Q. He, D. Tian, H. Jiang, D. Cao, S. Wei, D. Liu, P. Song, Y. Lin and L. Song, *Adv. Mater.*, 2020, 32, 1906972.
- A. Sumboja, T. An, H. Y. Goh, M. Lubke, D. P. Howard, Y. Xu, A. D. Handoko, Y. Zong and Z. Liu, ACS Appl. Mater. Interfaces, 2018, 10, 15673-15680.
- 8. Y. K. Li, G. Zhang, H. Huang, W. T. Lu, F. F. Cao and Z. G. Shao, *Small*, 2020, 16, 2005184.
- 9. Z. H. Ibupoto, A. Tahira, P. Tang, X. Liu, J. R. Morante, M. Fahlman, J. Arbiol, M. Vagin and A. Vomiero, *Adv. Funct. Mater.*, 2019, **29**, 1807562.
- K. Lu, Y. Liu, F. Lin, I. A. Cordova, S. Gao, B. Li, B. Peng, H. Xu, J. Kaelin, D. Coliz, C. Wang, Y. Shao and Y. Cheng, *J. Am. Chem. Soc.*, 2020, 142, 12613-12619.