Electronic Supplementary Information

Experimental section

Materials: $Ni(NO_3)_2 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, $CO(NH_2)_2$, NH_4F and KOH were purchased from Aladdin Ltd. (Shanghai, China). Pt/C (10 wt% Pt) was provided by Alfa Aesar (China) Chemicals Co. Ltd. Ti mesh (TM) was purchased from Phychemi Hong Kong Company Limited. All chemicals were used as received. The water used throughout all experiments was purified through a Millipore system.

Synthesis of Ni-CeO_2/TM, Ni/TM and CeO_2/TM: $Ni(NO_3)_2 \cdot 6H_2O$ (0.82 g), $Ce(NO_3)_3 \cdot 6H_2O$ (0.61 g), NH_4F (0.30 g) and $CO(NH_2)_2$ (0.84 g) were dissolved in deionized water (40 mL) under continuous stirring. Then, the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave with a piece of TM (2 cm × 3 cm). The autoclave was sealed and maintained at 120 °C for 6 h. After the autoclave cooled down to room temperature, the sample was taken out and successively washed with deionized water and ethanol several times, and then dried at 60 °C under vacuum for 6 h. Subsequently, the sample was calcinated at 350 °C for 2 h to obtain NiO-CeO_2/TM. Finally, NiO-CeO_2/TM was placed in a porcelain boat and heated to 400 °C for 3 h in a tube furnace under H_2/Ar (v/v, 5%) flow with a heating speed of 2 ºC min^{-1}. After cooling down to room temperature, Ni-CeO_2/TM was obtained. The preparation of Ni/TM and CeO_2/TM was similar to the procedure described above, except no $Ce(NO_3)_3 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ for hydrothermal reaction, respectively.

Characterizations: X-ray powder diffraction (XRD) was conducted using a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM) images were taken with a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. High-resolution transmission electron microscopy (HRTEM) measurements were carried out a Hitachi H-8100 electron microscopy with an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) experiments were monitored with an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements: Electrochemical measurements were performed with a CHI660E potentiostat (CH Instruments, China) in a standard three-electrode configuration using Ni-CeO_2/TM as the working electrode, a graphite plate as counter electrode and an Hg/HgO electrode as reference electrode. Linear sweep voltammetry (LSV) with a scan rate of 2 mV s^{-1} was conducted in 1.0 M KOH. In all measurements, potentials were calibrated with respect to a reversible hydrogen electrode (RHE) scale based on the following formula: E (RHE) = [E (Hg/HgO) + (0.098 + 0.059 pH) $-iR$] V. R was determined through fitting of AC impedance data to a modified Randles circuit. The presented current density was referred to the geometrical area of TM (0.5 cm × 0.5 cm).

FE determination: FE was calculated by comparing the amount of the hydrogen generated at cathode with theoretically calculated gas. The experimentally evolved hydrogen was confirmed by gas chromatography (GC) analysis and quantified by monitoring the pressure change via a calibrated pressure sensor.

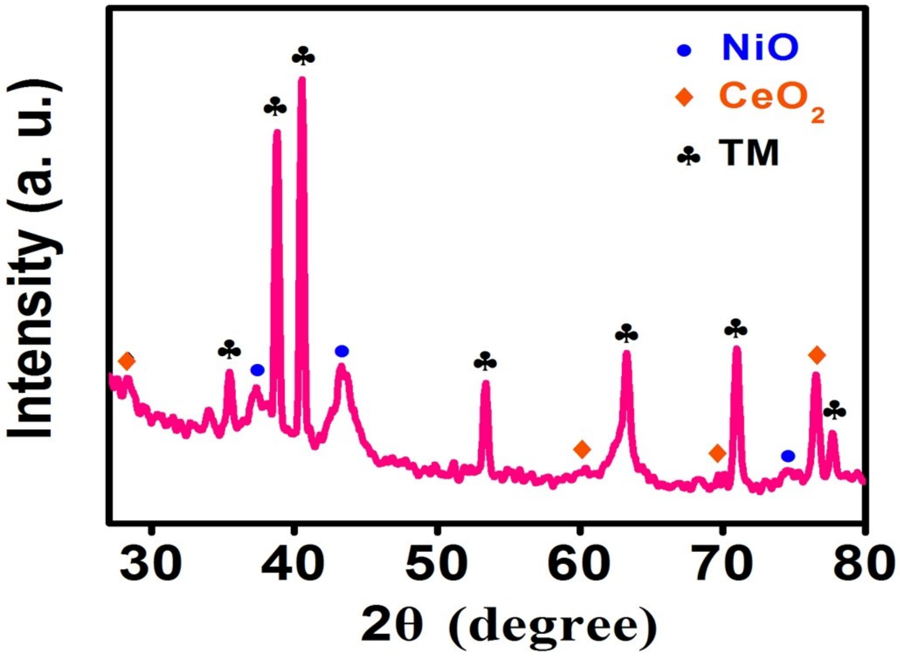

Fig. S1 XRD pattern of NiO-CeO_2/TM.

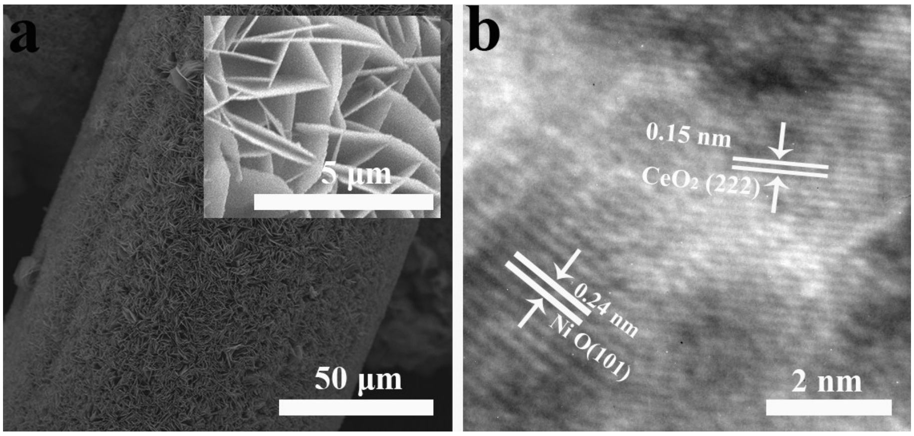

Fig. S2 (a) SEM and (b) HRTEM images of NiO-CeO$_2$/TM.

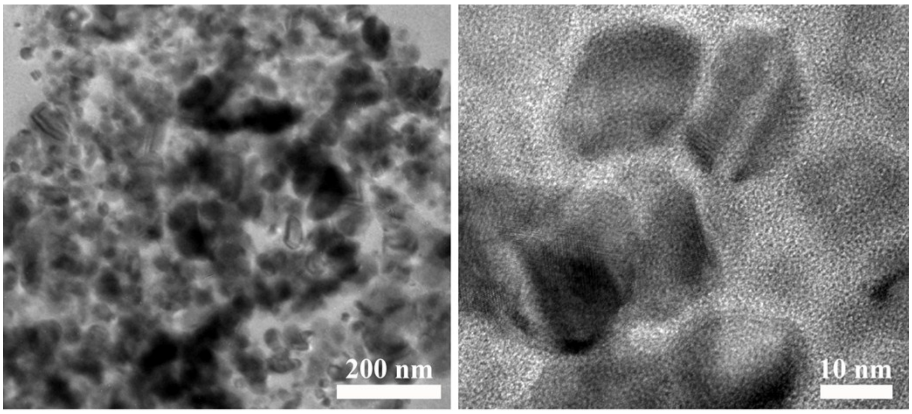

Fig. S3 TEM images of Ni-CeO_2/TM.

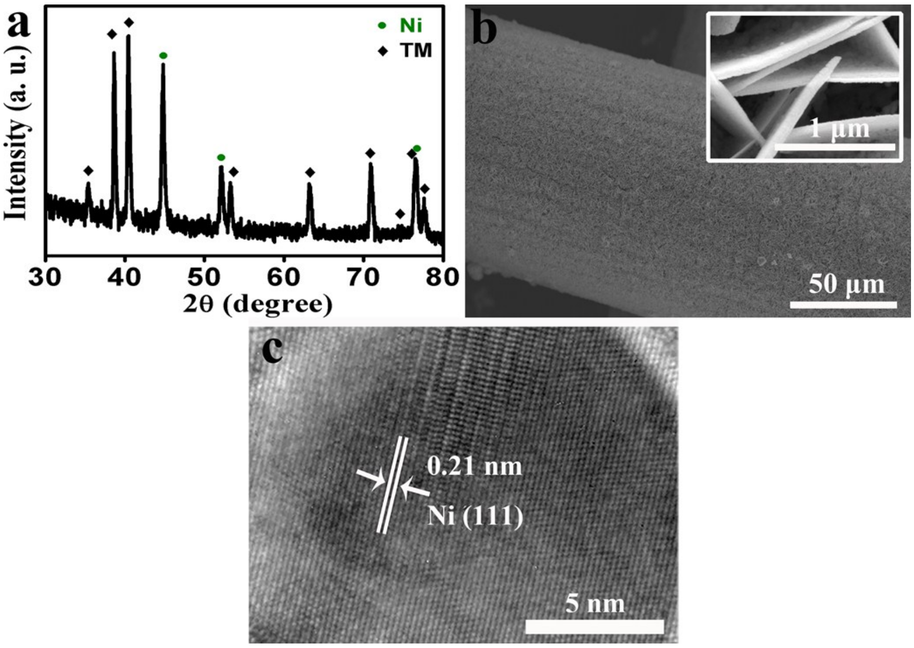

Fig. S4 (a) XRD pattern, (b) SEM and (c) HRTEM images of Ni/TM.

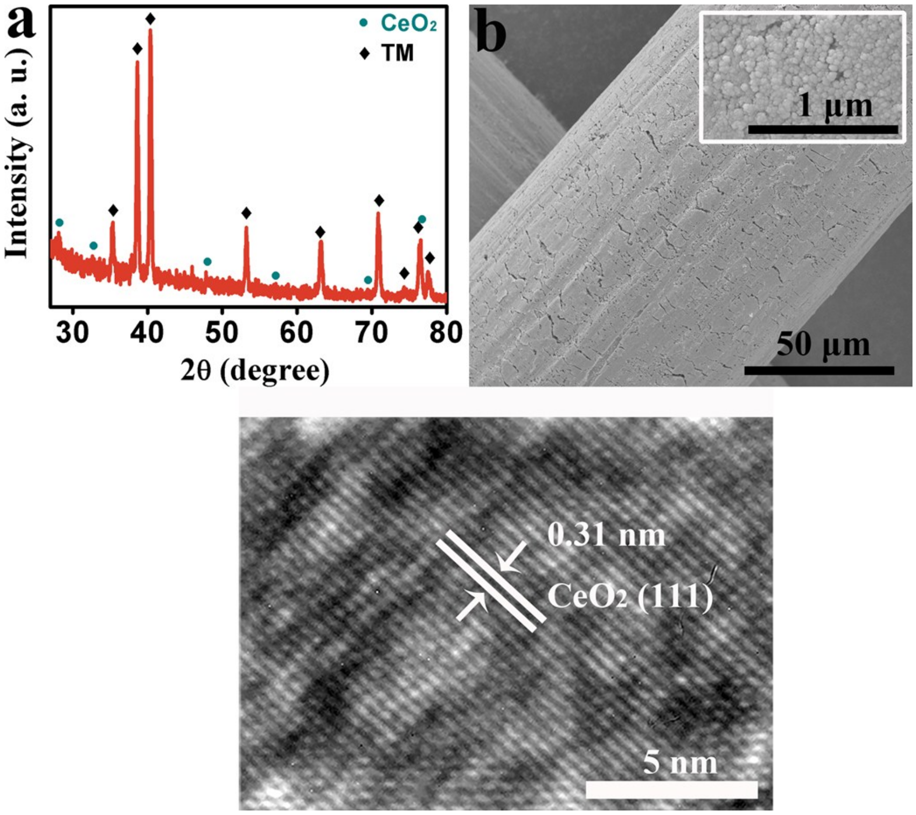

Fig. S5 (a) XRD pattern, (b) SEM and (c) HRTEM images of CeO_2/TM.

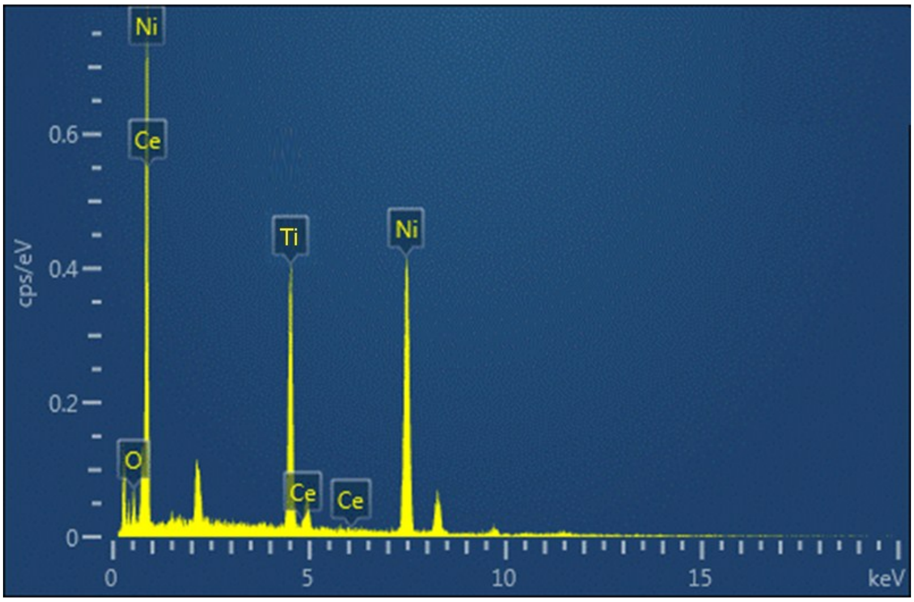

Fig. S6 EDX spectrum of Ni-CeO_2/TM.

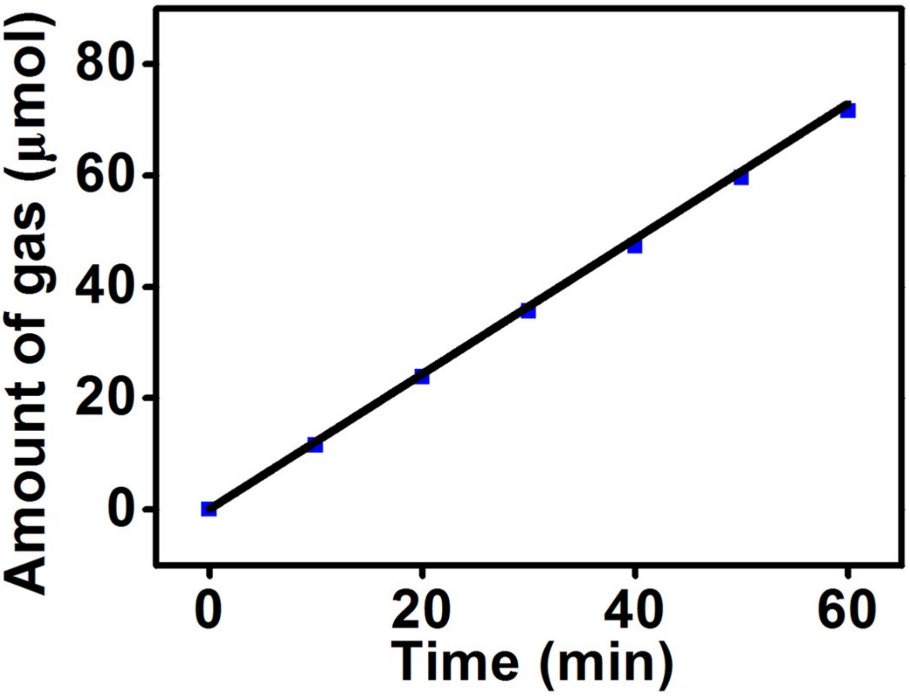

Fig. S7 The measured H_2 quantity (blue) compared with theoretically calculated H_2 (black) quantity vs. time for Ni-CeO_2/TM.

Table S1. Comparison of Ni-CeO_2/TM and other Ni-based catalysts for HER performance in alkaline medium.

Catalyst	***j* (mA cm^{-2})**	***η* (mV)**	**Electrolyte**	**Ref.**
Ni-CeO_2/TM	10	67	1.0 M KOH	This work
NiO/Ni-CNT	10	80	1.0 M KOH	1
Ni-MoC_x/C (HC800)	10	123	1.0 M KOH	2
Ni/ceria-rGO (1,3)	10	208	1.0 M KOH	3
Ni/ceria-rGO (1,1)		111		
Ni/ceria-rGO (3,1)		485		
Ni/ceria		588		
Ni/rGO		289		
Ni-Mo_2C-R	10	~130	1.0 M KOH	4
NF-NiS_2-A	10	67	1.0 M KOH	5
Ni-Mo_2C/C	10	91	1.0 M KOH	6

MoS2@Ni/CC

MF Ni-Mo$_2$C/CMF Ni-Mo$_2$				

C/CMF Ni-Mo$_2$C/CMF Ni-Mo				

2 C/C MF MoS_2@Ni/CC				
Ni_2P/Ni/NF	10	98	1.0 M KOH	7
$Ni(OH)_2$@Ni/CC	10	68	1.0 M KOH	8
Ni/Ni_3S_2/CC	10	95	1.0 M KOH	9
Ni@$Ni(OH)_2$/Pd/rGO	10	76	1.0 M KOH	10
Ni-NiO/N-rGO/NF	10	140	1.0 M KOH	11
Ni/CeO_2-CNT	10	91	1.0 M KOH	12
Ni-Mn_3O_4/NF	10	91	1.0 M KOH	13
Ni/NiP	10	130	1.0 M KOH	14
Ni/NiS		230		

References

1 M. Gong, W. Zhou, M.-C. Tsai, J. Zhou, M. Guan, M.-C. Lin, B. Zhang, Y. Hu, D.-Y. Wang, J. Yang, S. J. Pennycook, B.-J. Hwang and H. Dai, *Nat. Commun.*, 2014, **5,** 4695.

2 X. Xu, F. Nosheen and X. Wang, *Chem. Mater.*, 2016, **28**, 6313–6320.

3 M. Zhiani and S. Kamali, *J. Mater. Chem. A*, 2017, **5**, 8108–8116.

4 P. Xiao, Y. Yan, X. Ge, Z. Liu, J.-Y. Wang and X. Wang, *Appl. Catal. B*, 2014, **154–155**, 232–237.

5 Q. Ma, C. Hu, K. Liu, S.-F. Hung, D. Ou, H. M. Chen, G. Fu and N. Zheng, *Nano Energy*, 2017, **41**, 148–153.

6 Z. Xing, X. Yang, A. M. Asiri and X. Sun, *ACS Appl. Mater. Interfaces*, 2016, **8**, 14521–14526.

7 B. You, N. Jiang, M. Sheng, M. W. Bhushan and Y. Sun, *ACS Catal.*, 2016, **6**, 714–721.

8 Z. Xing, L. Gan, J. Wang and X. Yang, *J. Mater. Chem. A*, 2017, **5**, 7744–7748.

9 Y. An, B. Huang, Z. Wang, X. Long, Y. Qiu, J. Hu, D. Zhou, H. Lin and S. Yang, *Dalton Trans.*, 2017, **46**, 10700–10706.

10 Z. Deng, J. Wang, Y. Nie and Z. Wei, *J. Power Sources*, 2017, **352**, 26–33.

11 X. Liu, W. Liu, M. Ko, M. Park, M. G. Kim, P. Oh, S. Chae, S. Park, A. Casimir, G. Wu and J. Cho, *Adv. Funct. Mater.*, 2015, **25**, 5799–5808.

12 Z. Weng, W. Liu, L.-C. Yin, R. Fang, M. Li, E. I. Altman, Q. Fan, F. Li, H.-M. Cheng, and H. Wang, *Nano Lett.*, 2015, **15**, 7704–7710.

13 X. Li, P. F. Liu, L. Zhang, M. Y. Zu, Y. X. Yang and H. G. Yang, *Chem. Commun.*, 2016, **52**, 10566–10569.

14 G.-F. Chen, T. Y. Ma, Z.-Q. Liu, N. Li, Y.-Z. Su, K. Davey and S.-Z. Qiao, *Adv. Funct. Mater.,* 2016, **26**, 3314–3323.