Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting Information(SI):

Well-Dispersed Ultrasmall VC Nanoparticles Embedded in N-doped Carbon Nanotube as Highly Efficient Electrocatalysts for Hydrogen Evolution Reaction

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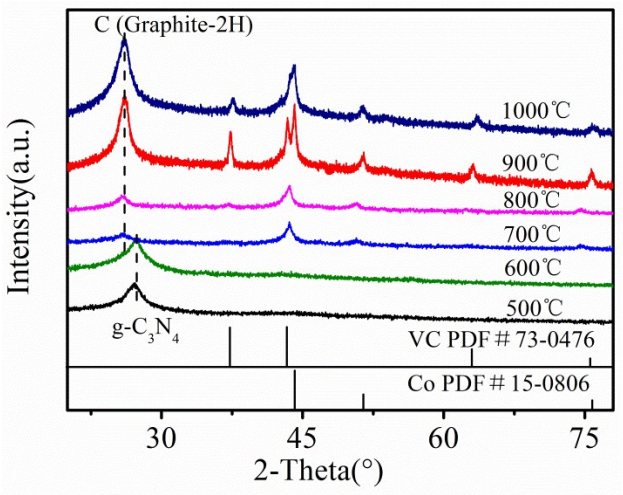

Fig. S1. XRD patterns of samples carbonized in different temperatures.

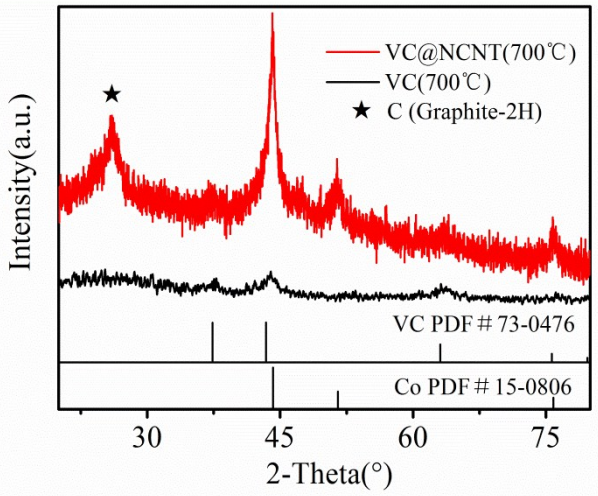

Fig. S2. XRD patterns of VC@NCNT (700℃) and VC nanoparticles.

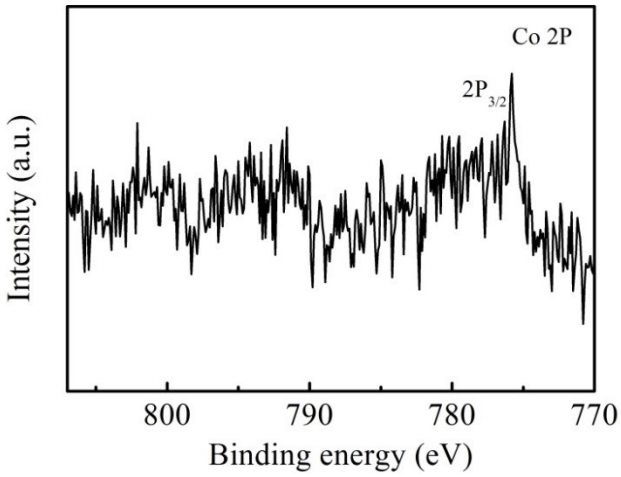

Fig. S3. High-resolution Co 2p XPS spectra for the VC@NCNT.

Table S1. Surface elements contents of samples carbonized in different temperatures obtained by XPS.

Catalyst	C 1s	O 1s	V 2p	N 1s
700℃	84.04 %	7.98%	0.65%	5.29%
800℃	86.17%	7.76%	1.09%	3.32%
900℃	90.15%	5.89%	0.59%	3.17%
1000℃	87.61%	6.51%	0.81%	3.11%

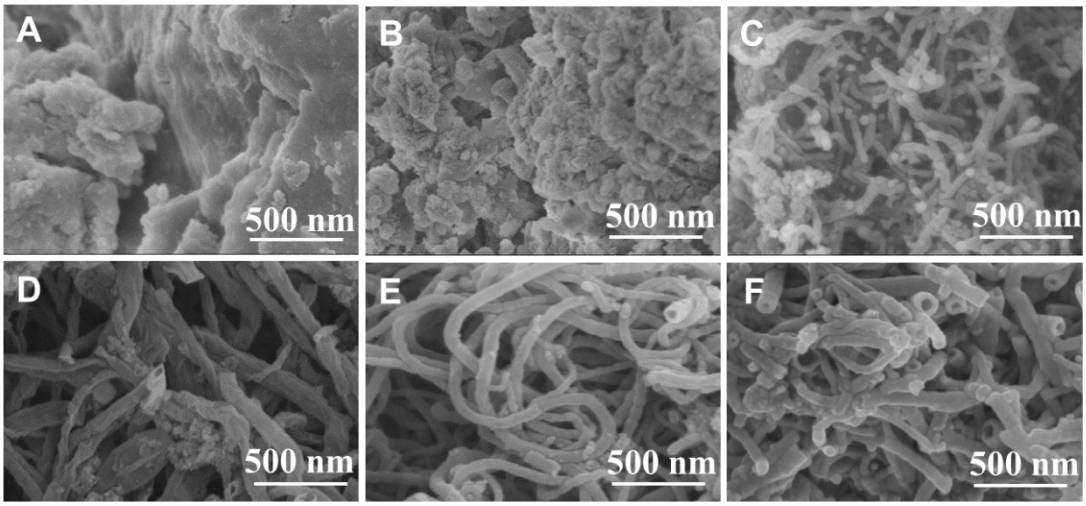

Fig. S4. SEM images of samples carbonized in different temperatures: (A) 500℃; (B) 600℃; (C) 700℃; (D) 800℃; (E) 900℃; (F) 1000℃.

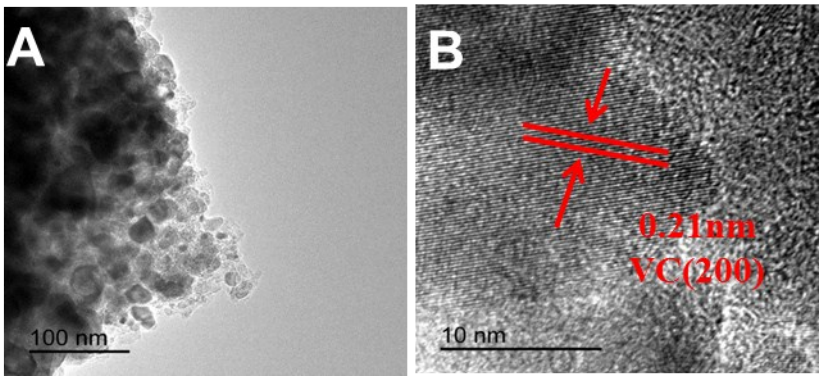

Fig. S5. (A) TEM images, (B) HRTEM images of VC.

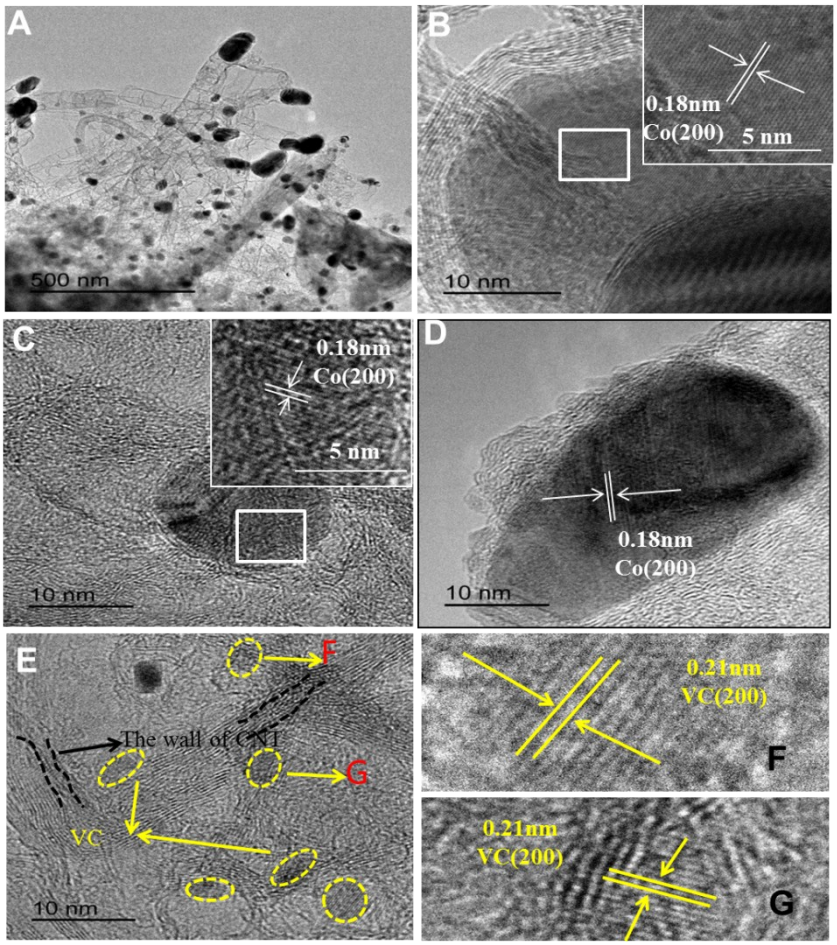

Fig. S6. (A-G) TEM images, HRTEM images of VC@NCNT.

Table S2 Comparison of charge transfer resistance (R_{ct}) values of all samples

Catalyst	R_{ct} (Ω/cm^2) Acid medium (η=259 mV)	R_{ct} (Ω/cm^2) Alkaline medium (η=213 mV)
VC@NCNT	22	138.8
Co-NRCNTs	153.8	434.8
VC	1522	1201

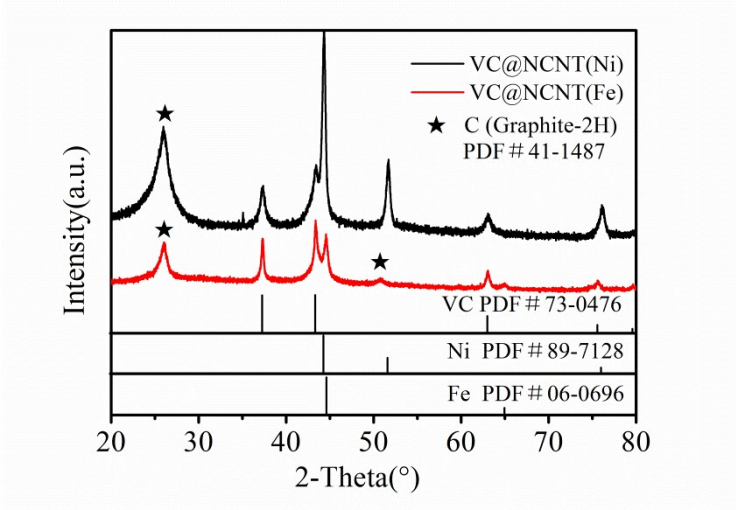

Fig. S7. XRD patterns of VC@NCNT (Ni) and VC@NCNT (Fe).

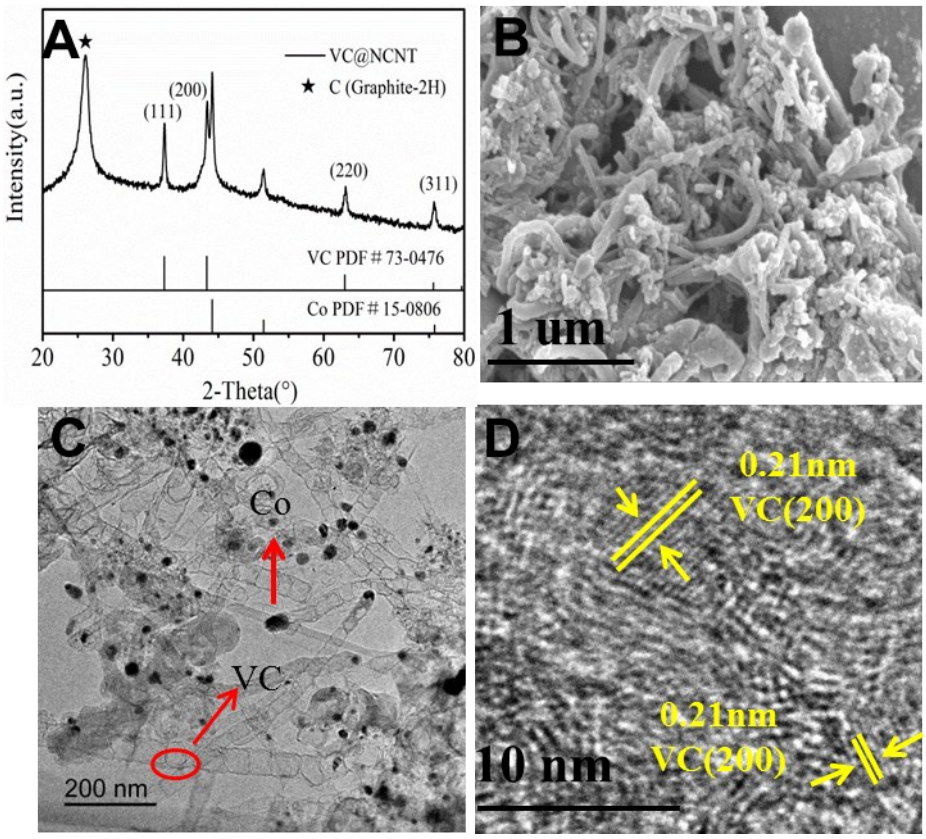

Fig. S8. (A-D): XRD, SEM, TEM and HRTEM images of VC@NCNT after the stability test of *i-t* curve for 100 h at pH 14.

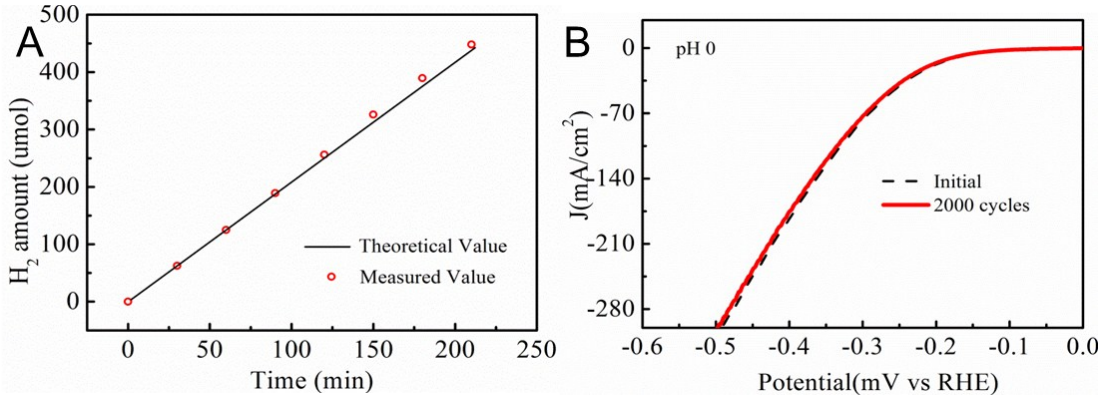

Fig. S9. (A) Hydrogen production efficiency for HER under potentiostatic electrolysis with VC@NCNT at the overpotential η=310 mV at pH 0; (B) LSV curves obtained with VC@NCNT.

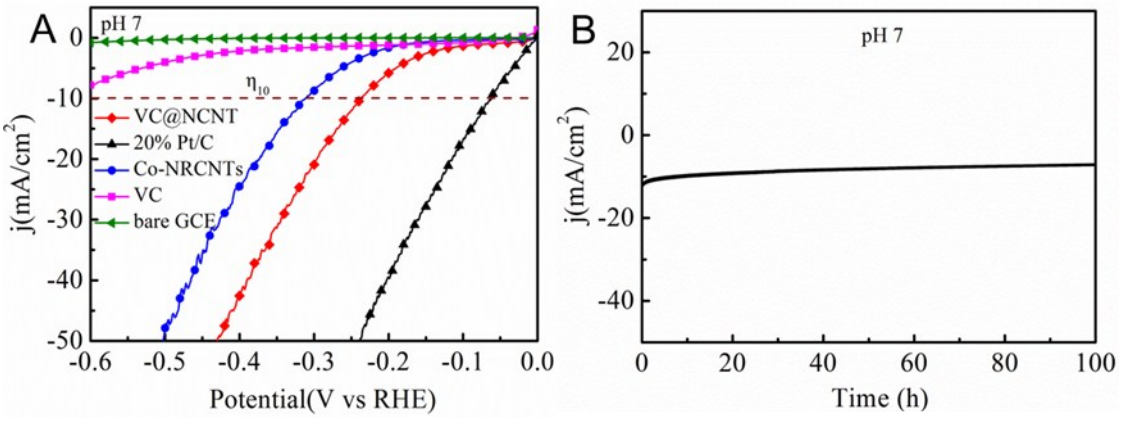

Fig. S10. (A) Polarization curves of bare GCE, VC, Co-NRCNTs, 20% Pt/C, VC@NCNT in phosphate buffer solution; (B) I-t curve obtained for HER with VC@NCNT at the overpotential η = 266 mV at pH 7.

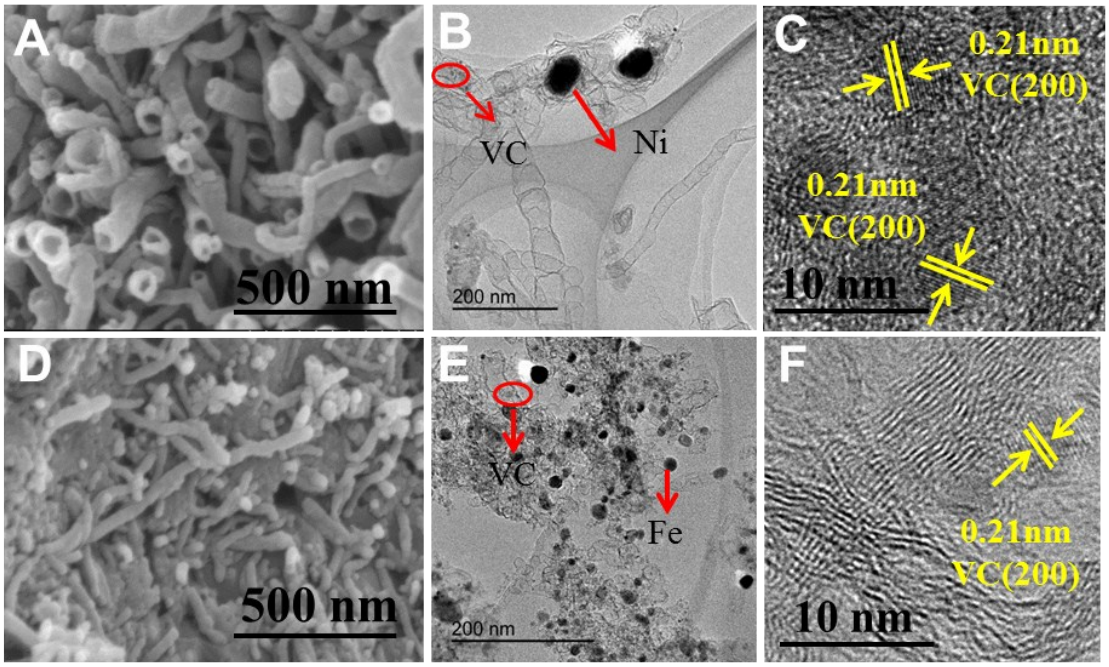

Fig. S11. SEM, TEM, HRTEM images of samples: (A-C): VC@NCNT (Ni); (D-F):VC@NCNT (Fe).

Table S3 Comparison of representative precious-metal-free HER electrocatalysts.

Catalyst	Electrolyte	Current density (j)	Overpotential at the corresponding j (mV)	Stability test	Reference
VC@NCNT	**1 M KOH**	**10 mA/cm^2**	**159**	**100 h**	**This work**
	0.5 M H_2SO_4	**10 mA/cm^2**	**161**	**100 h**	
	1 M phosphate buffer solution	**10 mA/cm^2**	**266**	**100 h**	
WC-CNTs	1 M KOH	10 mA/cm^2	235	1000 cycles	*ACS Nano* **2015,** *9*, 5125.
	0.5 M H_2SO_4	10 mA/cm^2	189	1000 cycles	
Mo_2C-CNT	0.5 M H_2SO_4	10 mA/cm^2	179	2000 cycles	*J. Mater. Chem. A* **2015,** 3, 5783.
	1 M KOH	10 mA/cm^2	257		
WC@NPC	0.5 M H_2SO_4	10 mA/cm^2	51	15 h	*J. Am. Chem. Soc.* **2017,** *139*, 5285.
MoC@NC nanoribbon	0.5M H_2SO_4	10 mA/cm^2	~ 170	70 h	*ACS Appl. Mater. Interfaces* **2018.**
Mo_2C QDs/NGCLs	0.5M H_2SO_4	10 mA/cm^2	136	20 h	*Chem. Commun.**2016,** 52, 12753*
	1 M KOH	10 mA/cm^2	111		