Electronic Supporting Information (ESI)

Investigation of hollow nitrogen-doped carbon spheres as non-precious $Fe-N_4$ based oxygen reduction catalyst

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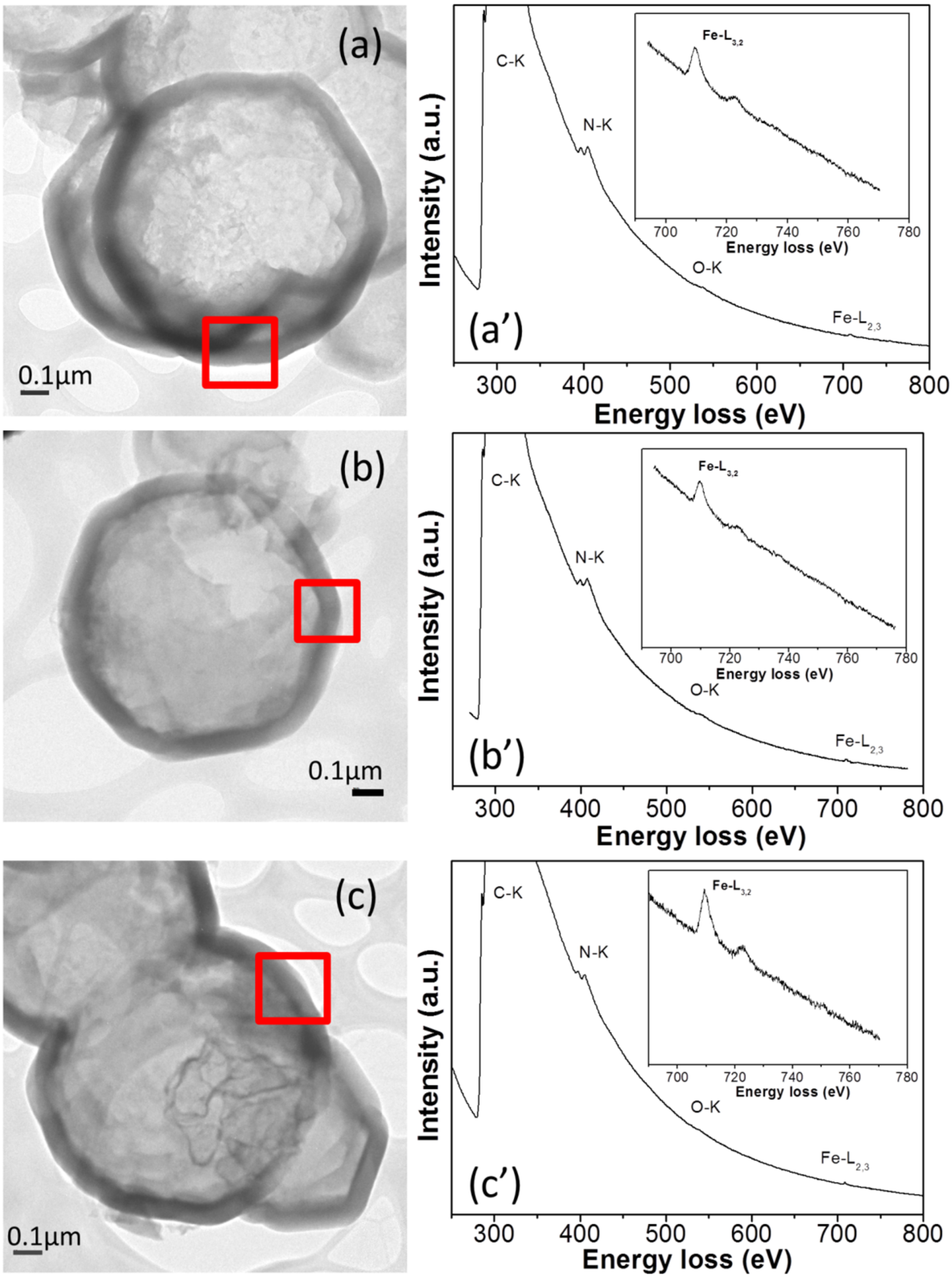

Figure S1. STEM image and EELS spectrum (red square indicated in STEM images) of (a, a') HNCS61, (b, b') HNCS81, (c, c') HNCS91, respectively.

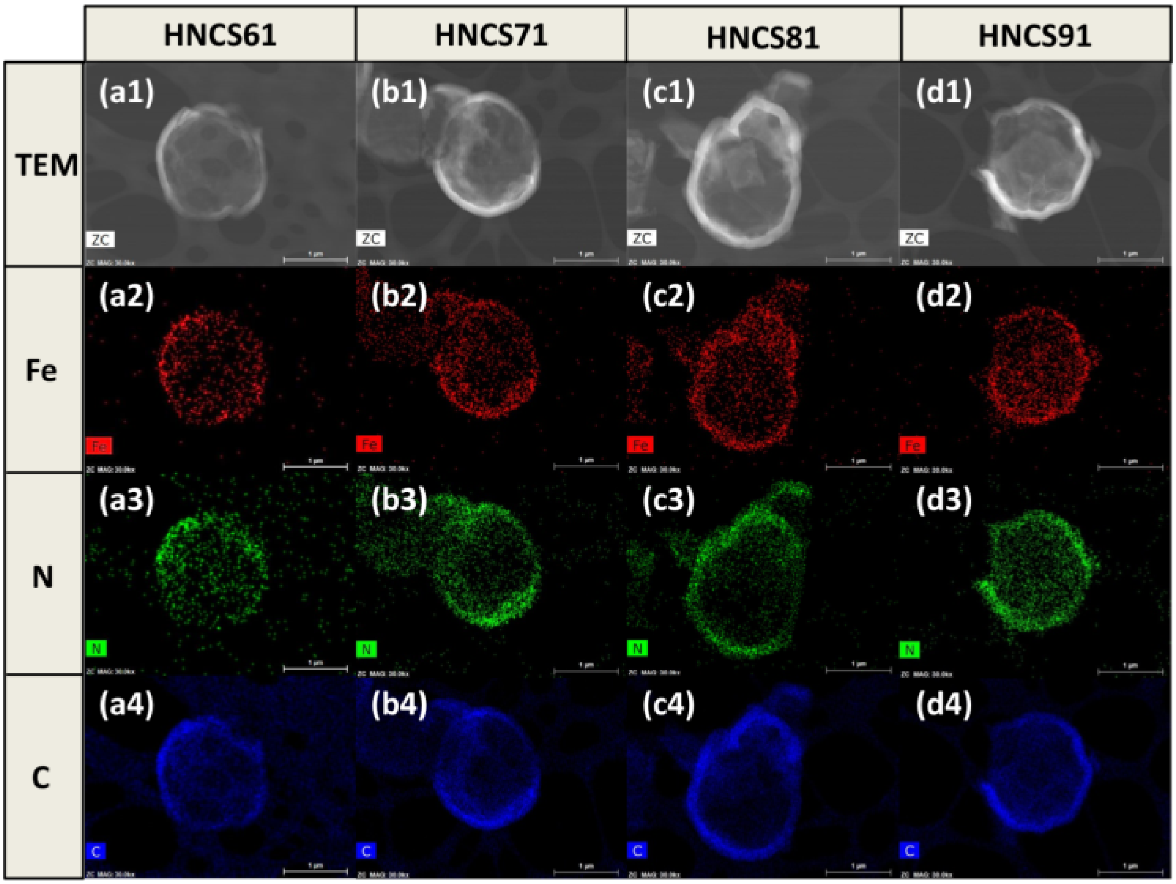

Figure S2. Arrays showing the bright field STEM image, individual of element the Fe-K edge, N-K edge and C-K edge image of catalyst Vs. HNCS61, HNCS71, HNCS81, and HNCS91.

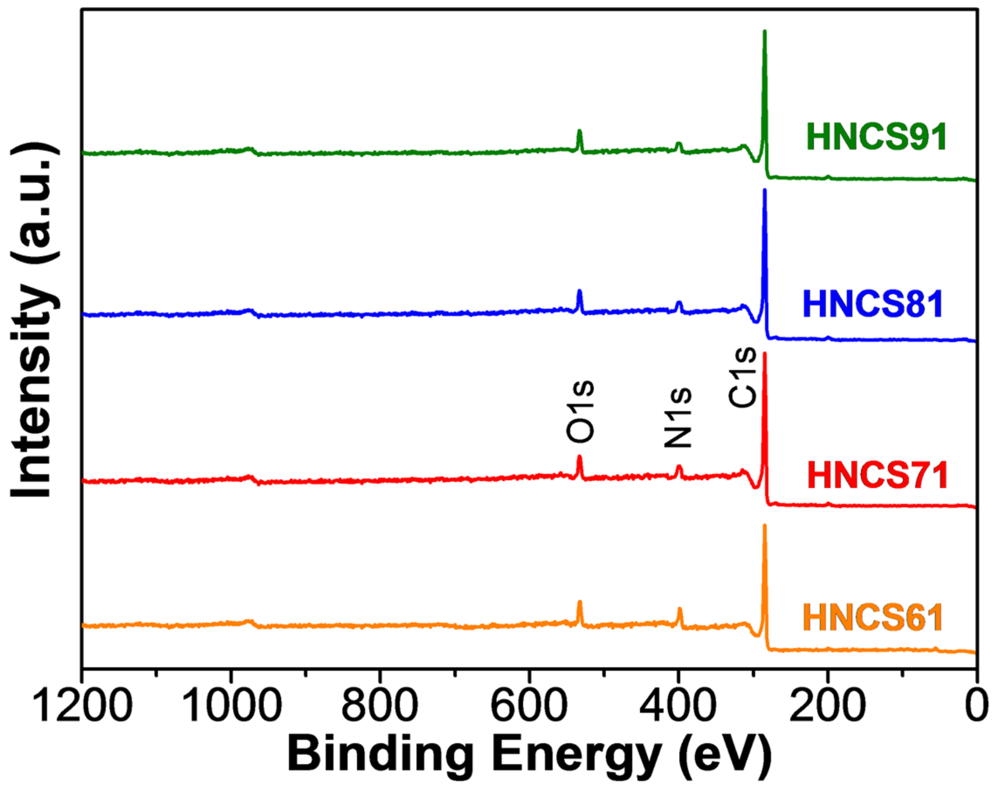

Figure S3. XPS survey spectra of HNCS catalyst.

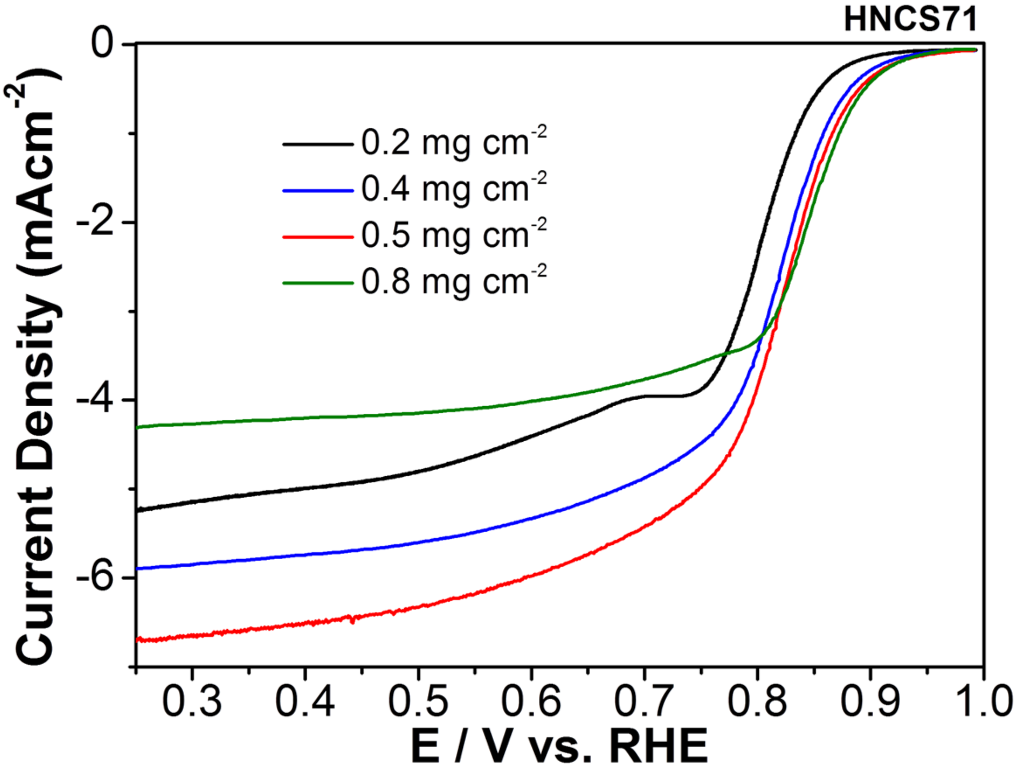

Figure S4. ORR polarization curve of HNCS71 with different loading in In O_2- saturated 0.1M KOH, 1600 rpm.

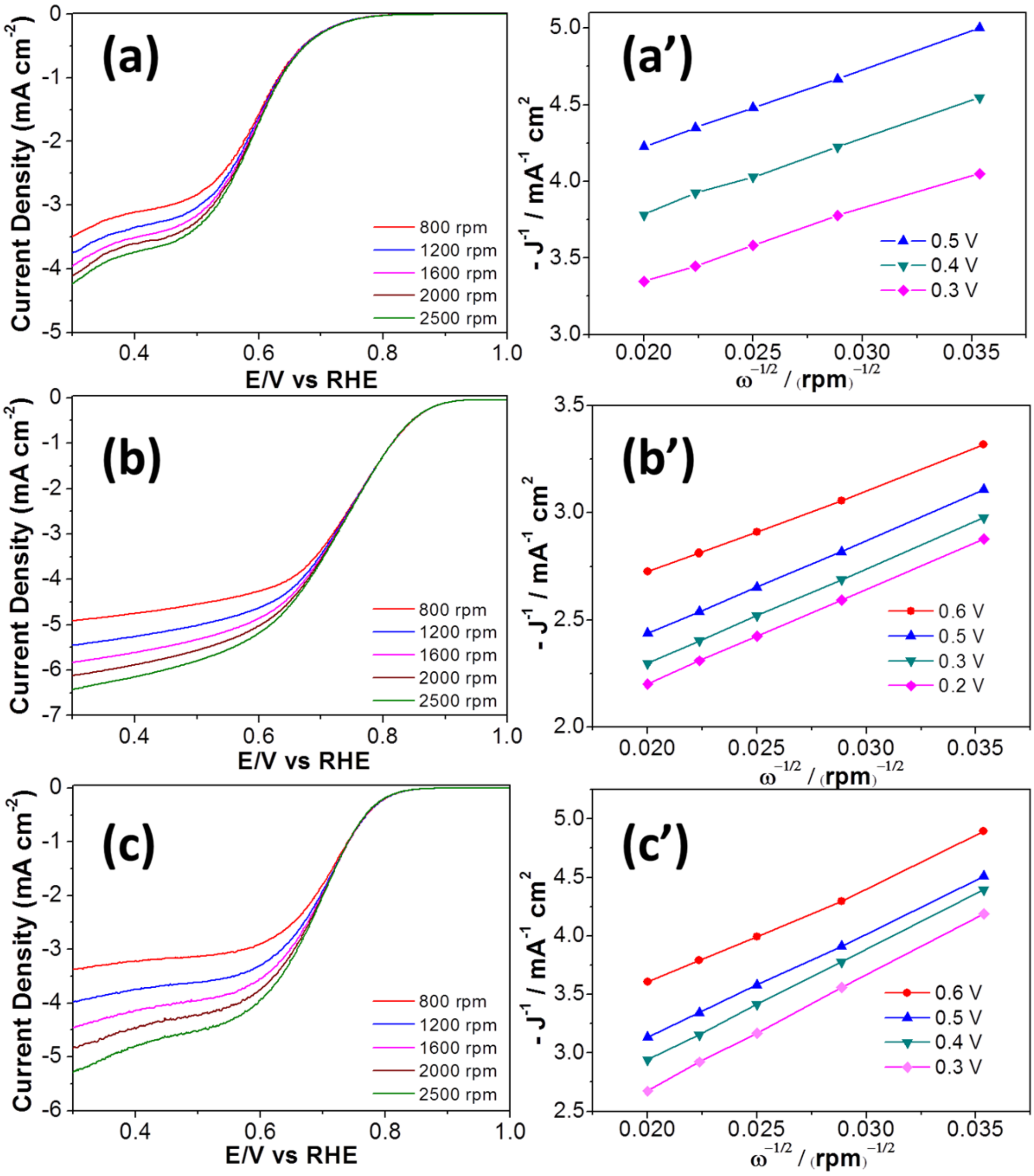

Figure S5. ORR polarization curve and K-L plot of (a, a') HNCS61, (b, b') HNCS81, (c, c') HNCS91, respectively. In O_2- saturated 0.1M KOH.

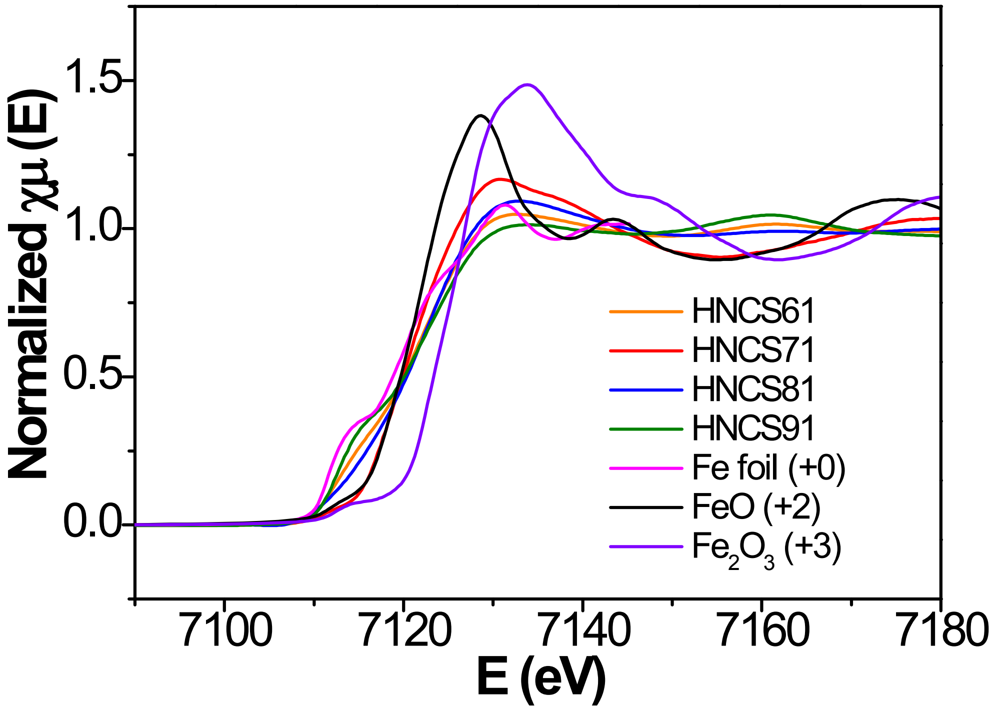

Figure S6. Fe K-edge XANES spectra of HNCS electrocatalyst with standard Fe foil, FeO and Fe_2O_3

The normalized Fe K-edge XANES spectra of HNCS61, HNCS71, HNCS81 and HNCS91 catalysts including those of the Fe foil, FeO and Fe_2O_3 standards of which oxidation state is about +0, +2 and +3, respectively. From the figure, each standard spectrum has the maximum gradient at 67112.09, 7117.04 and 7121.89 eV, respectively. In this case, the absorption Fe K-edge XANES spectra of HNCS71 samples show the maximum gradient at 7116.92 eV which is close to that of FeO and the Fe oxidation state is suggested to be +2 indicating the existence of more Fe^{+2} ion than Fe metal.

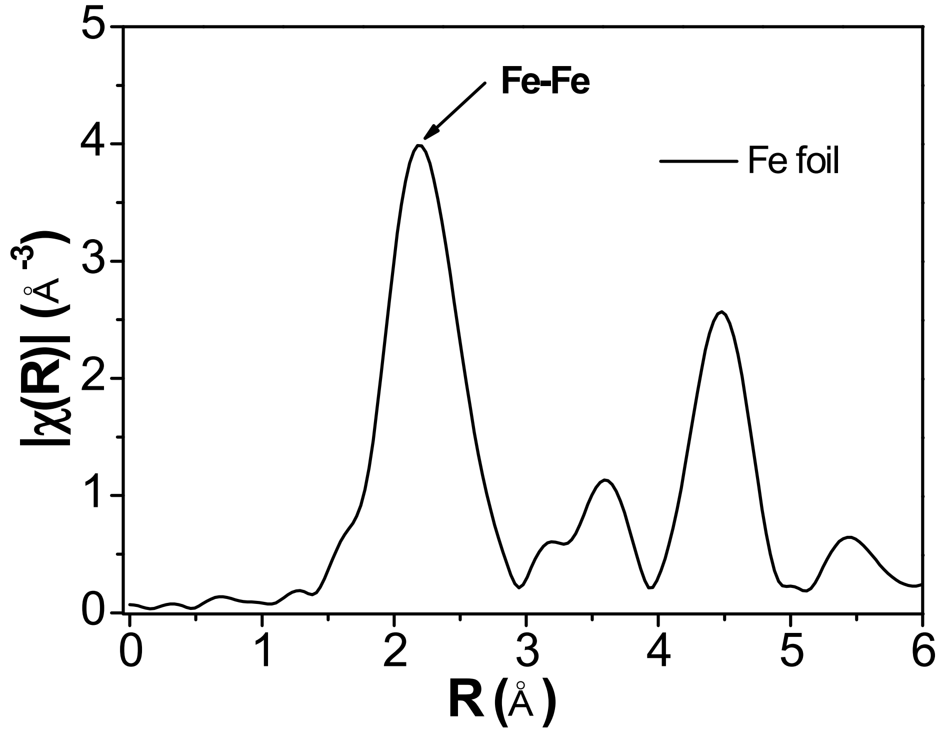

Figure S7. Fe K-edge of k^2-weighted Fourier transforms EXAFS spectra of standard Fe foil.

Table S1. The physical and electrochemical properties of HNCSs

Catalyst	no of electron transfer	Nitrogen distribution (%)				Total N content (%)[a]	N/C ratio
		N1	N2	N3	N4		
HNCS61	2.41	4.85	2.02	5.66		12.55	0.16
HNCS71	3.90	4.15	1.41	4.93	0.31	10.81	0.13
HNCS81	3.59	2.39	0.85	3.41	0.26	6.91	0.08
HNCS91	2.96	1.09	0.42	2.31	0.21	4.04	0.04
Pt/C	3.95	-	-	-	-	-	-

(a) Measured by X-ray photoelectron spectroscopy (XPS)

Table S2. The CHN elemental analysis of HNCSs

Catalyst	C	H	N	N/C ratio
HNCS 61	78.9	2.1	13.19	0.167
HNCS 71	83.38	0.7	11.4	0.136
HNCS 81	88.2	0.7	6.79	0.076
HNCS 91	91.47	0.2	3.89	0.042

Table S3. The alkaline membrane fuel cells performance data electrocatalyst with commercial membrane in H_2-O_2 system, no added back pressurization, reported in the literature

Cathode material	Operating Temperature (˚C)	Maximum power density (mW cm^{-2})	Reference
HNCS71	60	68	*
NpGr-72	50	27	1
N-CNT	50	37.3	2
MnO_x-GC	70	98	3
Ag/C	RT	10	4
Ag/C	60	48	5
Au/C	60	21	
CoPc/MWCNT	50	120	6
FePc/MWCNT	50	60	

* This study

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