Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Nitrogen-Doped Hollow Carbon Hemispheres as Efficient Metal-Free Electrocatalysts for Oxygen Reduction Reaction

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Experimental Section

***Materials*:** Silver nitrate (AR, >99%), bromobutane (CP, >98%), ammonium hydroxide (NH_4OH, 25-28 wt%), ethanol (AR) were used as received from Sinopharm Chemical Reagent Co., Ltd. tetraethyl orthosilicate (TEOS, AR), $Na(CN)_2$ (>96%), 3-picoline (99%), 1-methylimidazole (99%), 4-chlorobutyronitrile (98%), NH_4HF_2 (AR, >98.5%) were used as received from Aladdin Chemistry Co., Ltd. Nafion 117 solution (5 wt%) was obtained from Aldrich Chemistry Co., Ltd. 20 wt% Pt/C was used as received from Alfa aesar Chemistry Co., Ltd. All the chemicals were used as delivered without further treatment.

Synthesis of 3-MBP-dca: 3-MBP-dca was prepared according to our previous literature.[1]

Synthesis of CMIM-Cl: 0.2 mol (16.4g) 1-methylimidazole was added into a 250 ml three-neck flask, the equal stoichiometric 4-chlorobutyronitrile (0.2 mol, 20.7 g) in a constant pressure funnel was dropped into the three-neck flask within two hours with a high speed magnetic stirring of 1000 rpm at 100 ^oC. After another 20 hours reaction, this reaction was stopped and ionic liquid CMIM-Cl was obtained.

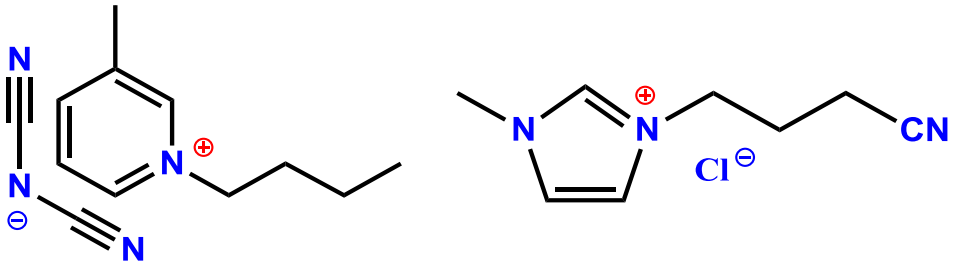
Synthesis of Silica Spheres Template: Firstly, 3.14 ml of ammonia hydroxide was added into a solution containing 74 ml of ethanol and 10 ml of deionized water, and then the mixed solution was stirred at 303 K for 0.5 h. Secondly, 6 ml of TEOS was added into the above-prepared mixture quickly under vigorous stirring and the reaction mixture was kept stirring for 1 h to yield uniform silica spheres (Stöber silica sol). Thirdly, the nanostructured silica was centrifuged, dried at 70 ^oC overnight to obtain white solid powder.

Synthesis of HCH Materials: The HCH was synthesized using ILs as the precursors and silica sphere as the hard template. Typically, taking the synthesis of HCH-dca-900 (r=1.0) as an example: Firstly, 1.0 g silica spheres was placed into a crucible, then 3.0 g deionized water and 1.0 g 3-MBP-dca were added into. They were mixed together by magnetic stirring for 24 h and then dried at 70 ^oC in an oven for another 24 h. Secondly, the mixture was calcined in a Muffle furnace at programmed temperature in N_2 flow (400 mL/min). The temperature program was shown as follow: the temperature rose from room temperature to 300 ^oC in 30 minutes, then it remained at 300 ^oC for 1 hour; After that, the temperature rose to 900 ^oC within 1 hour and remained for another 1 hour; Later, it began to cool down naturally. Thirdly, after it cooled down to room temperature, loose black solid with pore was gained. Then the black solid was ground into black powder and tranferred into a plastic bottle, 40 g NH_4HF_2 and 160 g deionized water were also added into the bottle. Furthly, the mixtures were stirred for 48 hours at room temperature. At last, filter the solution and the black solid residue was dried at 70 ^oC in an oven overnight.

Characterization: SEM images were obtained on a Zeiss Ultra 55 microscope. TEM studies were performed on a Hitachi HT-7700 microscope. The X-ray photoelectron spectra (XPS) was obtained by an ESCALAB MARK Ⅱ spherical analyzer using an aluminum-magnesium binode (Al 1486.6 eV, Mg 1253.6 eV) X-ray source. The Raman spectra was collected on a Raman spectrometer (JY, HR 800) using 514-nm

laser. The ^{1}HNMR spectrum was collected on a BRUKER Advance 2B, 400 MHz. The FT-IR spectrum was collected on a Nicolet Nexus 470. The element analysis was carried out on the Flash EA 1112, ThermoFinnigan. The BET surfaces were determined by Tristar Ⅱ3020, BET equation was used to calculate the surface areas and pore volume and samples were degassed at 150 ^{o}C for 6 h until the residual pressure was less than 10^{-4} Pa. The ICP analysis was carried out on a PerkinElmer Optima OES 8000.

Electrochemical characterization: Electrochemical measurements were performed using a computer-controlled workstation (LK2005A, China) with a typical three-electrode cell. Rotating disk electrode (RDE) was used as working electrode, a platinum sheet as counter electrode and saturated calomel electrode (SCE) as reference electrode. The activity of the HCH materials was evaluated by the CV and LSV techniques. Fabrication of the working electrode was done by pasting catalyst inks on a glassy carbon electrode (5 mm in diameter, from Pine). The carbon ink was formed by mixing 10 mg of HCH catalyst, 50 μL 5 wt% Nafion solution and 500 μL ethanol in a plastic vial under ultra-sonication for 20 min. A 5 μL aliquot of the carbon ink was dropped on the surface of the glassy carbon electrode, yielding an approximate catalyst loading of 0.09 mg. For comparison, the commercial 20 wt% Pt/C catalyst was dealt with in the same method. All the experiments were conducted at room temperature.



3-MBP-dca **CMIM-Cl**

Scheme S1. The structure of 3-MBP-dca and CMIM-Cl.

Table S1. Elemental analysis results of ionic liquid CMIM-Cl.

Entry	Catalyst	C (wt%)	N (wt%)	H (wt%)	Cl (wt%, calculated)
1	CMIM-Cl	52.0	22.3	6.5	19.2

Table S2. Elemental analysis results of HCH-dca-900 (r=0.5, 1.0 and 2.0).

Entry	Catalyst	N (wt%)	C (wt%)	H (wt%)	O (wt%, calculated)
1	HCH-dca-900 (r=0.5)	8.0	61.4	1.1	29.5
2	HCH-dca-900 (r=1.0)	10.9	76.7	1.3	11.1
3	HCH-dca-900 (r=2.0)	9.6	78.0	3.1	9.3

Table S3. The peak potential and current density of HCH.

Entry	Catalyst	Peak potential (V) [a]	Current density (mA/cm^2) [a]
1	HCH-dca-900(r=0.5)	-0.345	-3.4
2	HCH-dca-900(r=1.0)	-0.345	-4.2
3	HCH-dca-900(r=2.0)	-0.326	-2.8
4	HCH-dca-600(r=1.0)	-0.409	-2.5
5	HCH-dca-1000(r=1.0)	-0.318	-2.6
6	HCH-Cl-900(r=0.5)	-0.300	-1.4
7	HCH-Cl-900(r=1.0)	-0.309	-4.1
8	HCH-Cl-900(r=2.0)	-0.349	-4.8

[a] in O_2-saturated 0.1 M KOH at a scan rate of 50 mV s^{-1} from CVcurves.

Table S4. ICP analysis of silicon content.

Entry	Catalyst	Si / %
1	HCH-dca-900 (r=0.5)	0.05
2	HCH-dca-900 (r=1.0)	0.09
3	HCH-dca-900 (r=2.0)	0.08

Table S5. compare HCH with the other N-doped carbons for ORR

Entry	Catalyst	ORR activity vs. Pt/C	Fuel tolerance	$4e^-$ Reduction	Refs.
1	HCH	Comparable	CH_3OH	√	This paper
2	N-CNT	Comparable	CH_3OH	×	[2]
3	N-CNT fibre	Better		√	[3]
4	N-CNC	Better	CH_3OH	√	[4]
5	N-mesoporous carbon	Comparable	CH_3OH	√	[5]
6	N-graphitic array	Better	CH_3OH	√	[6]

Table S6. The FWHM of N1s XPS peaks.

FWHM	401.4 eV	400.2 eV	398.6 eV
	Graphitic N	Pyrrolic N	Pyridinic N
HCH-dca-900 (r=0.5)	1.80	1.87	1.29
HCH-dca-900 (r=1.0)	1.73	1.70	1.36
HCH-dca-900 (r=2.0)	1.79	1.66	1.29
HCH-dca-600 (r=1.0)	1.28	2.02	1.20
HCH-dca-1000 (r=1.0)	2.19	2.01	1.25

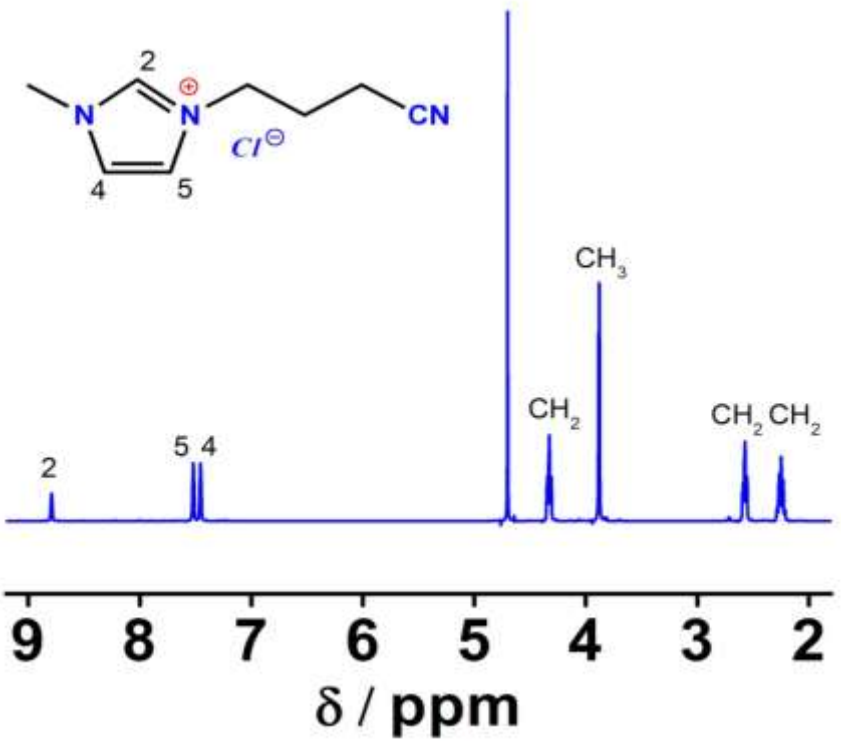


Figure S1. ^{1}HNMR of ionic liquid CMIM-Cl.

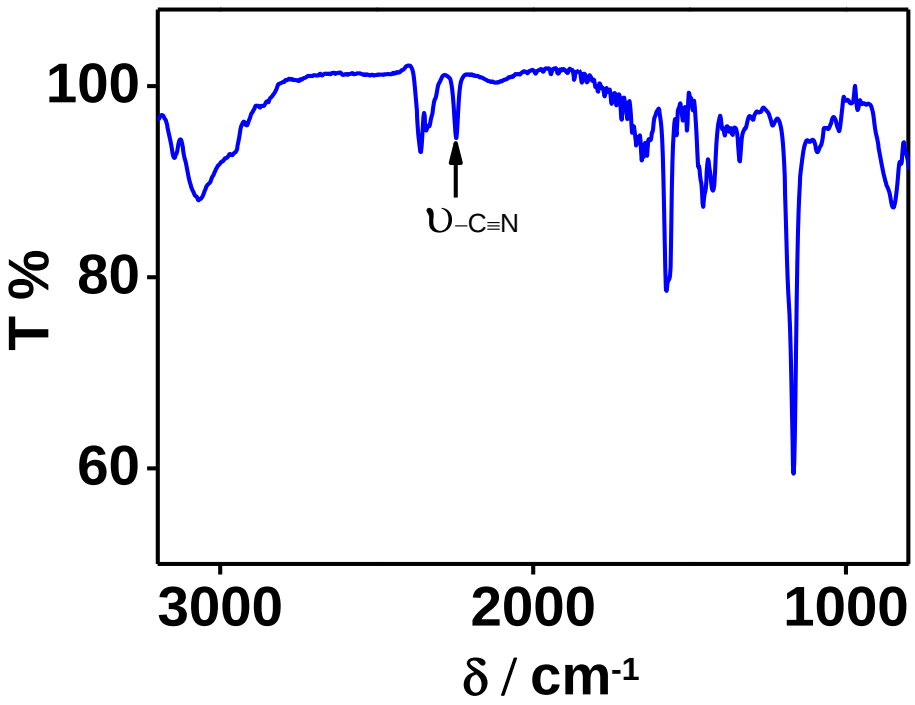


Figure S2. FT-IR spectrum of ionic liquid CMIM-Cl.

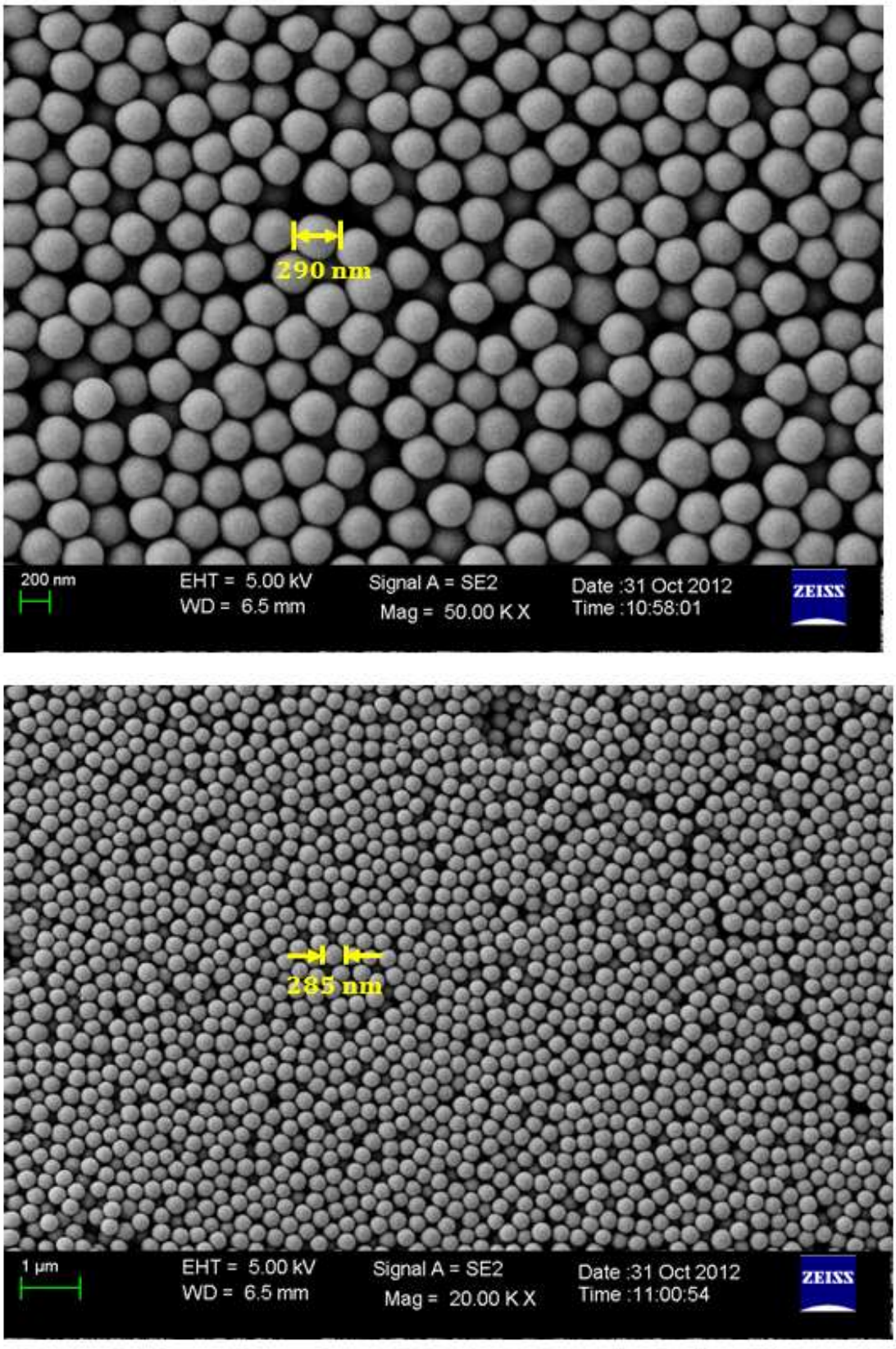


Figure S3. SEM images of spherical silica template .

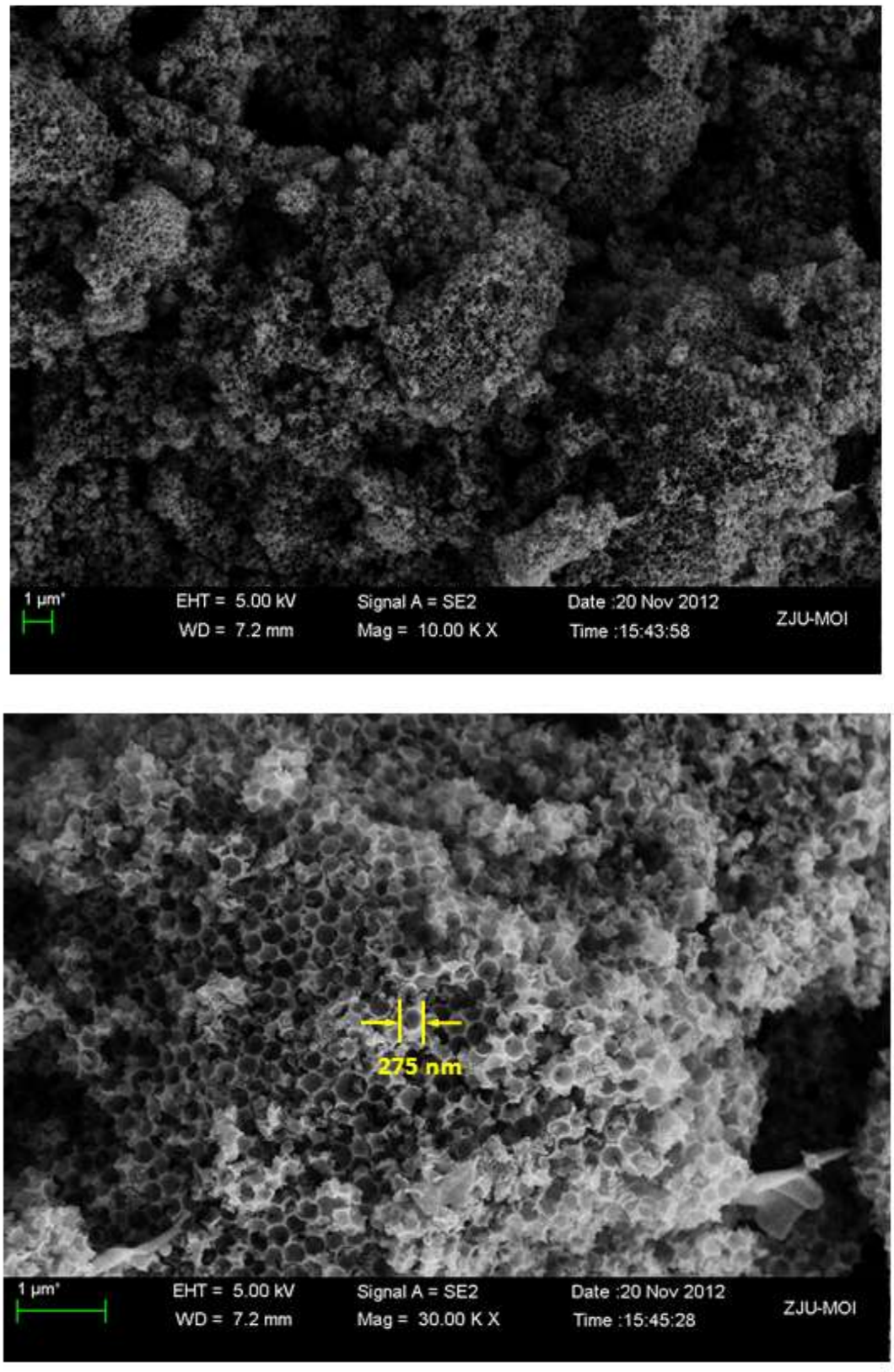


Figure S4. SEM images of HCH-dca-900 (r=1.0).

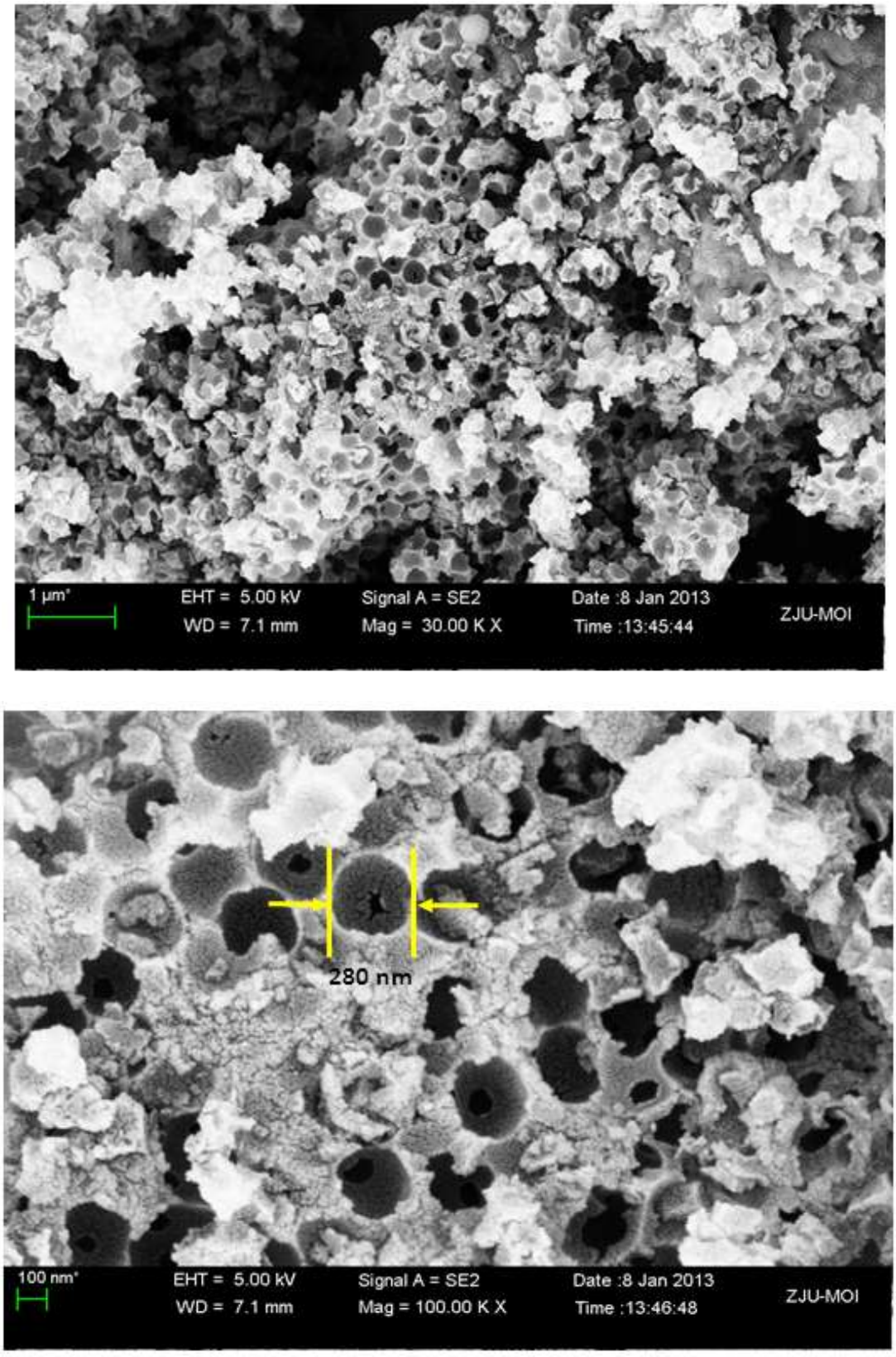


Figure S5. SEM images of HCH-dca-900 (r=2.0).

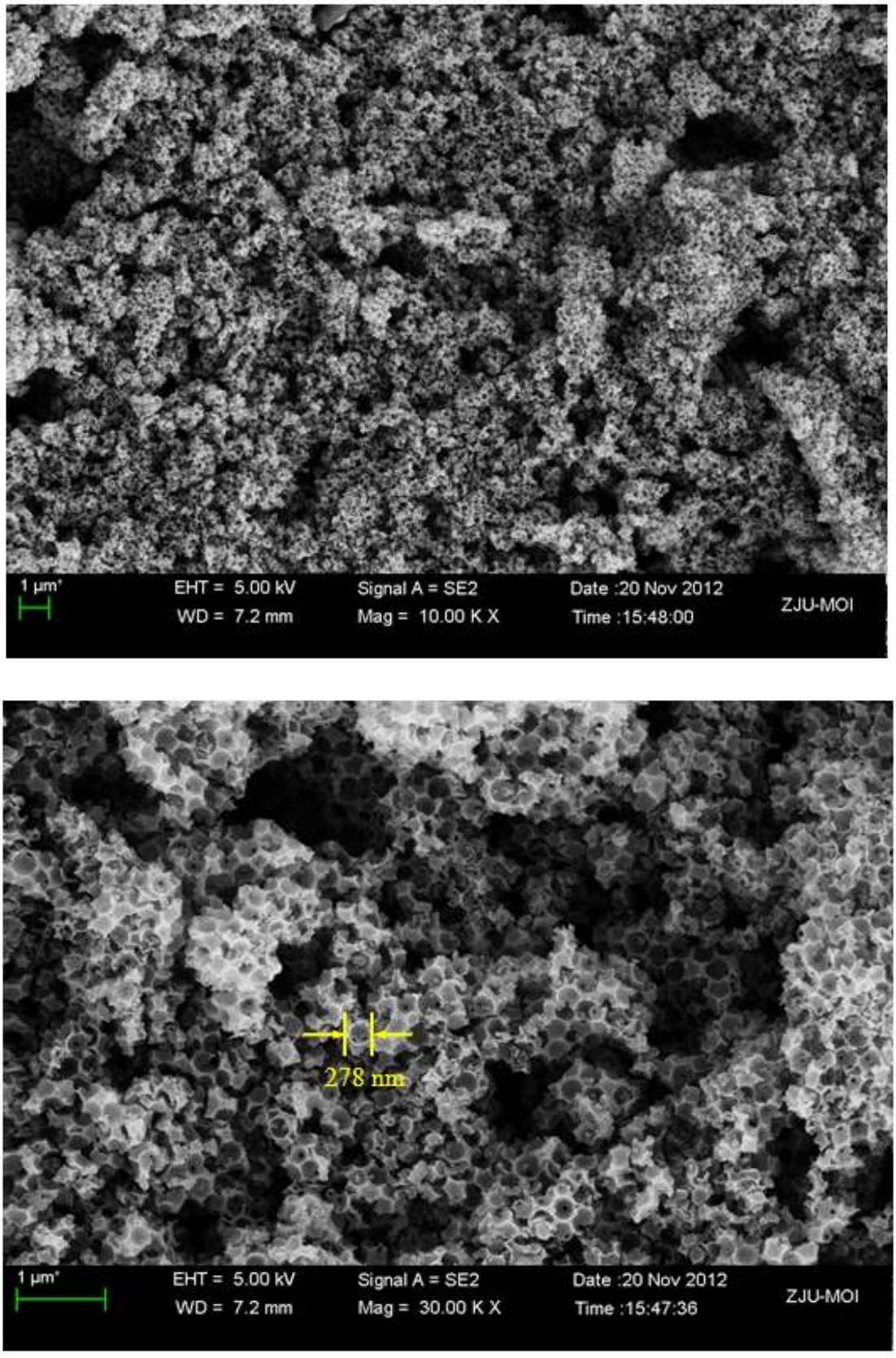


Figure S6. SEM images of HCH-dca-600 (r=1.0).

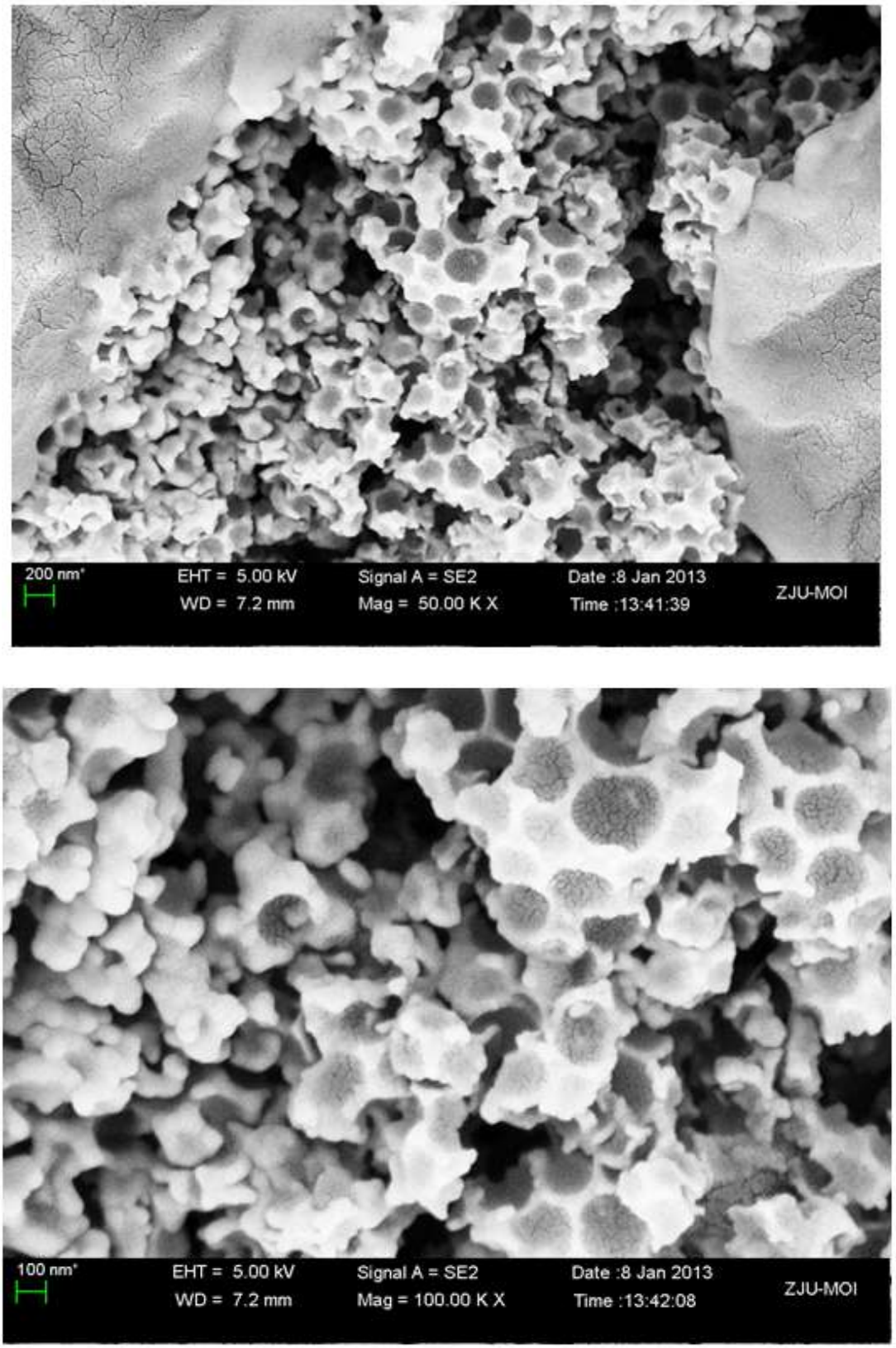
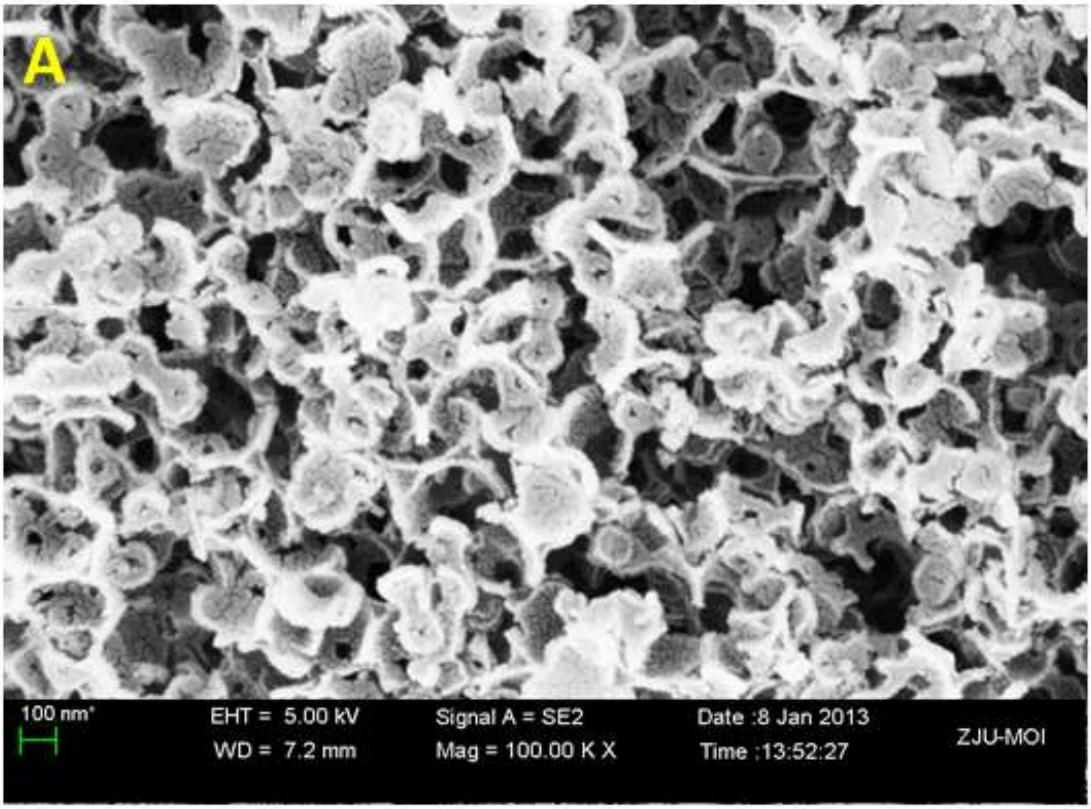
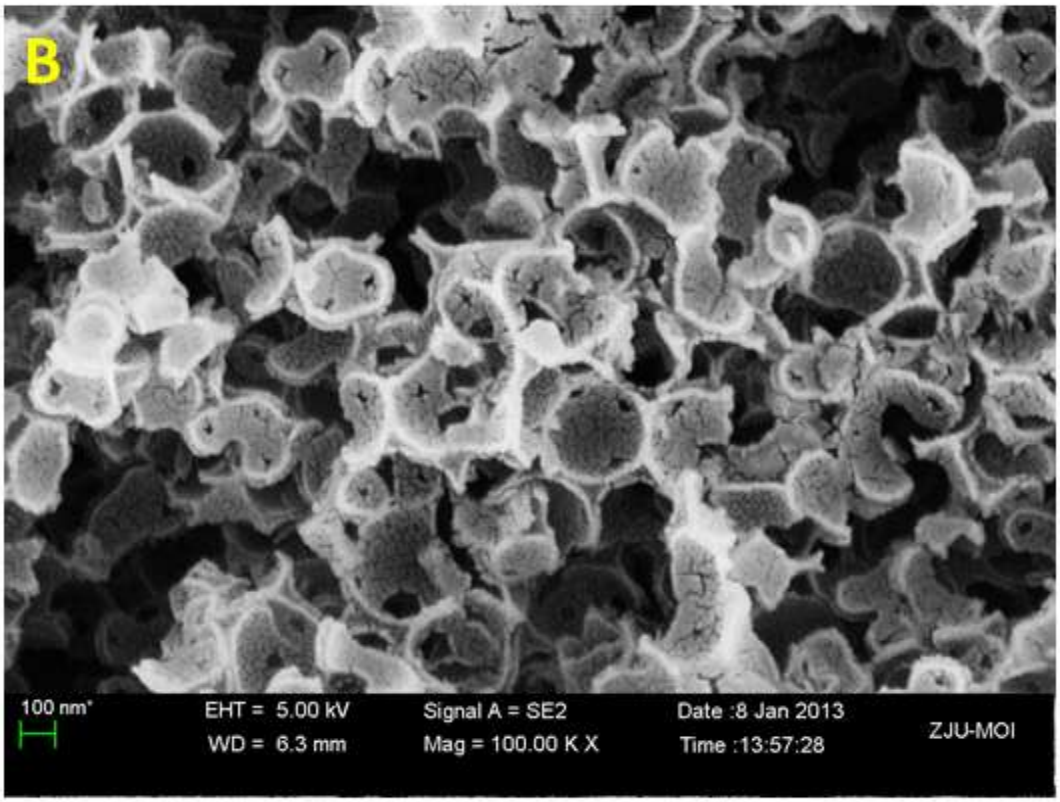
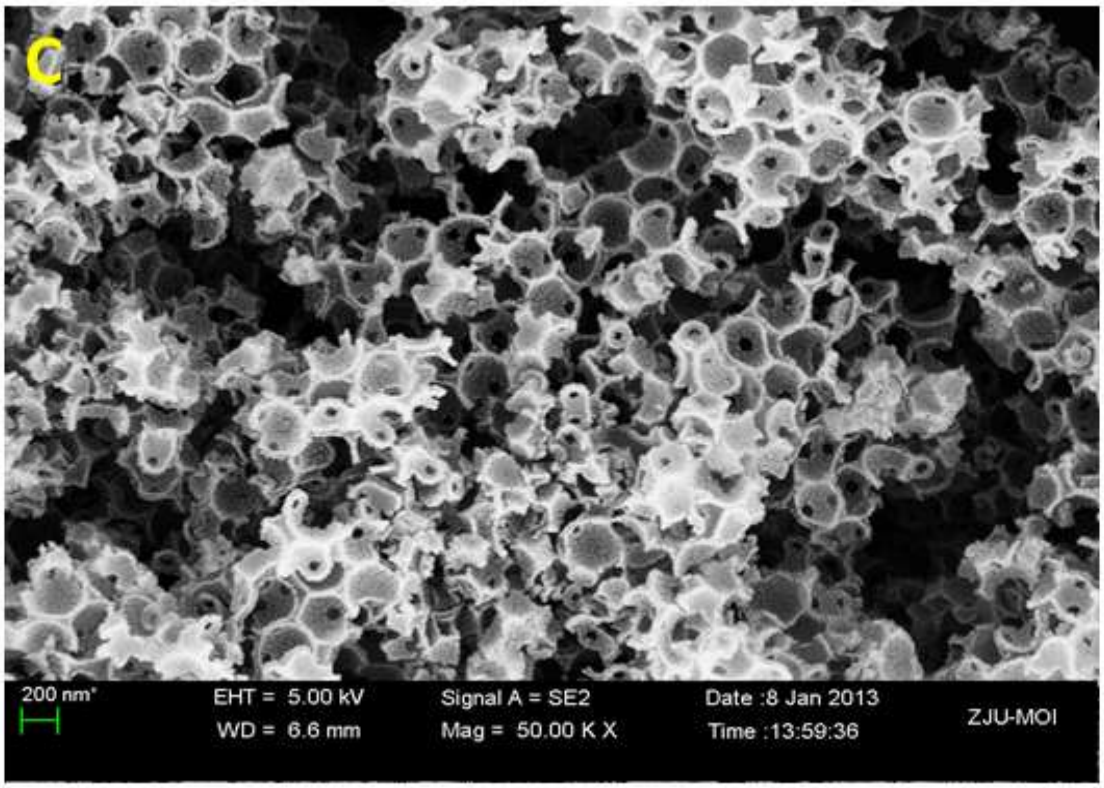


Figure S7. SEM images of HCH-dca-1000 (r=1.0).







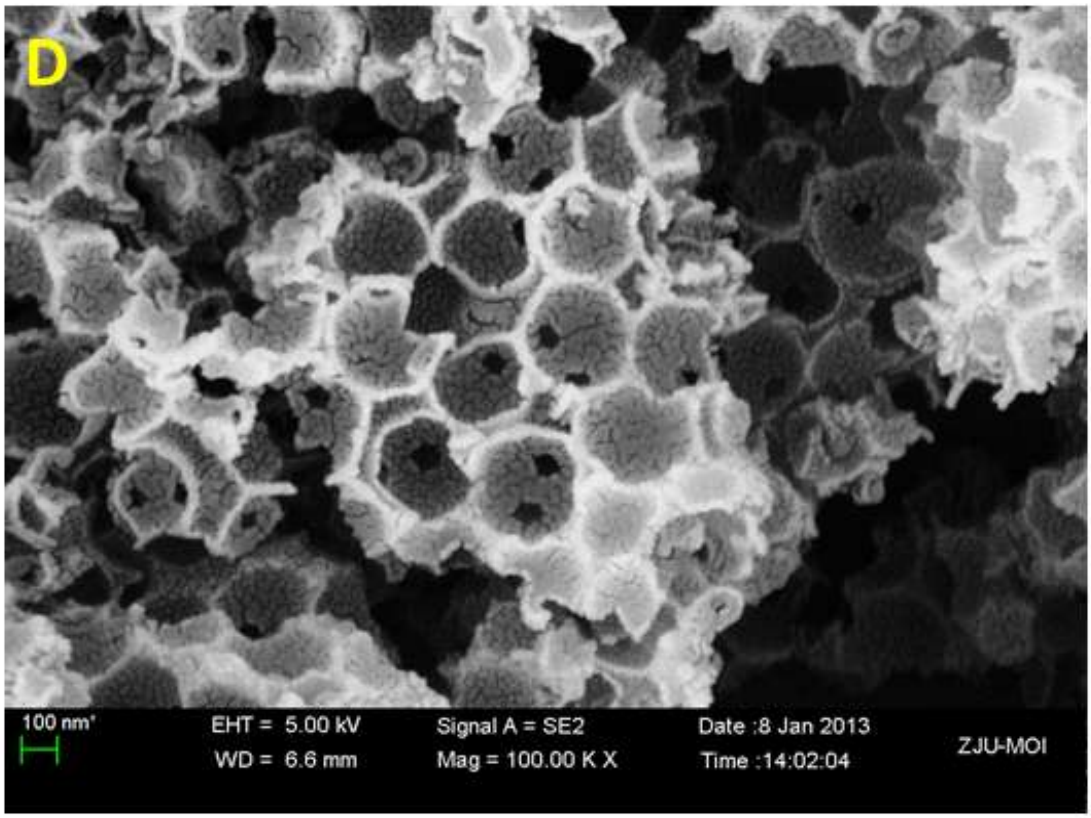


Figure S8. SEM images of HCH-Cl-900 (A) r=0.5 (B) r=1.0 (C) and (D) r=2.0.

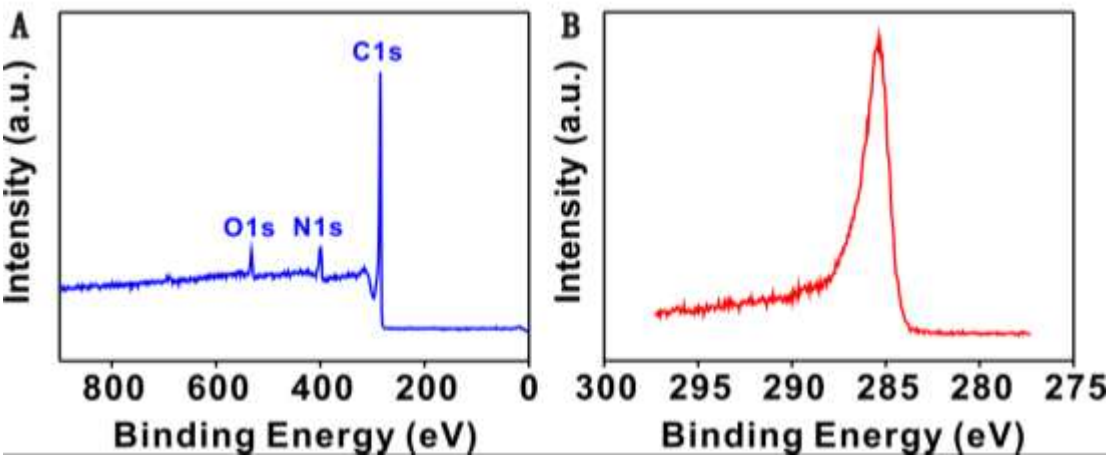


Figure S9. XPS spectra of HCH-dca-900 (r=1.0): (A) the wide spectra.

(B) the typical C1s spectra.

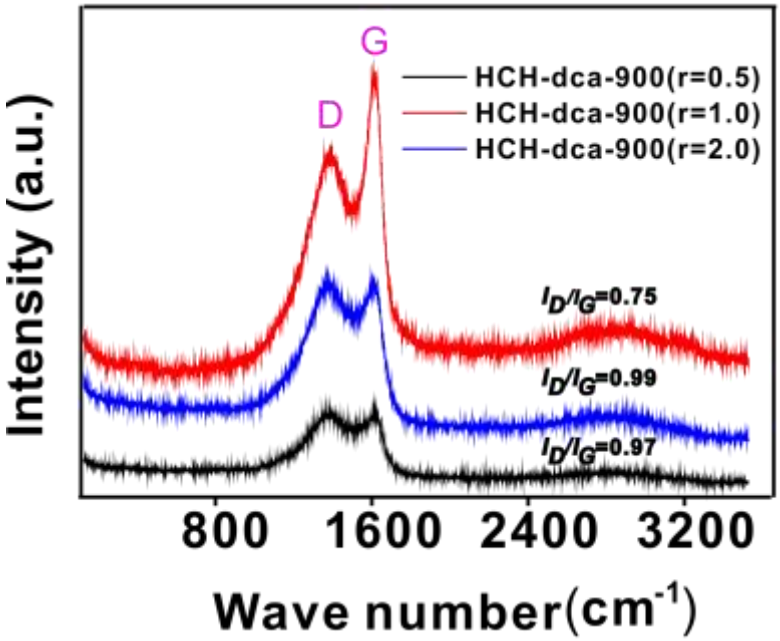


Figure S10. Raman spectra of HCH-dca-900 with different r.

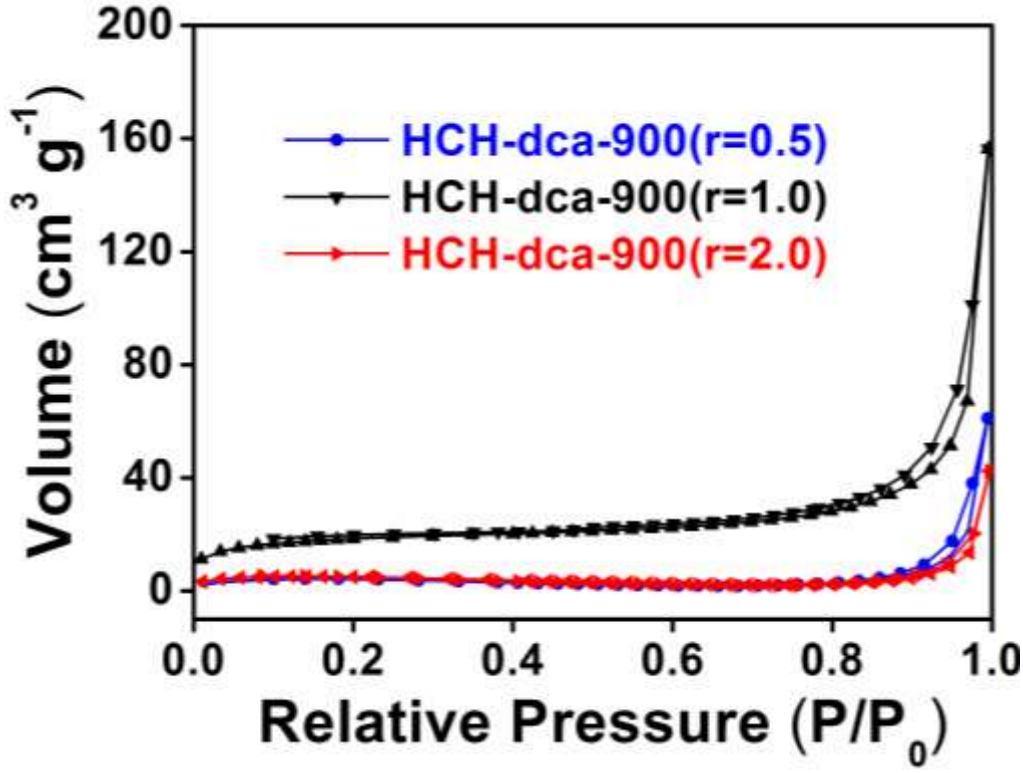


Figure S11. Nitrogen adsorption / desorption isotherms of HCH-dca-900.

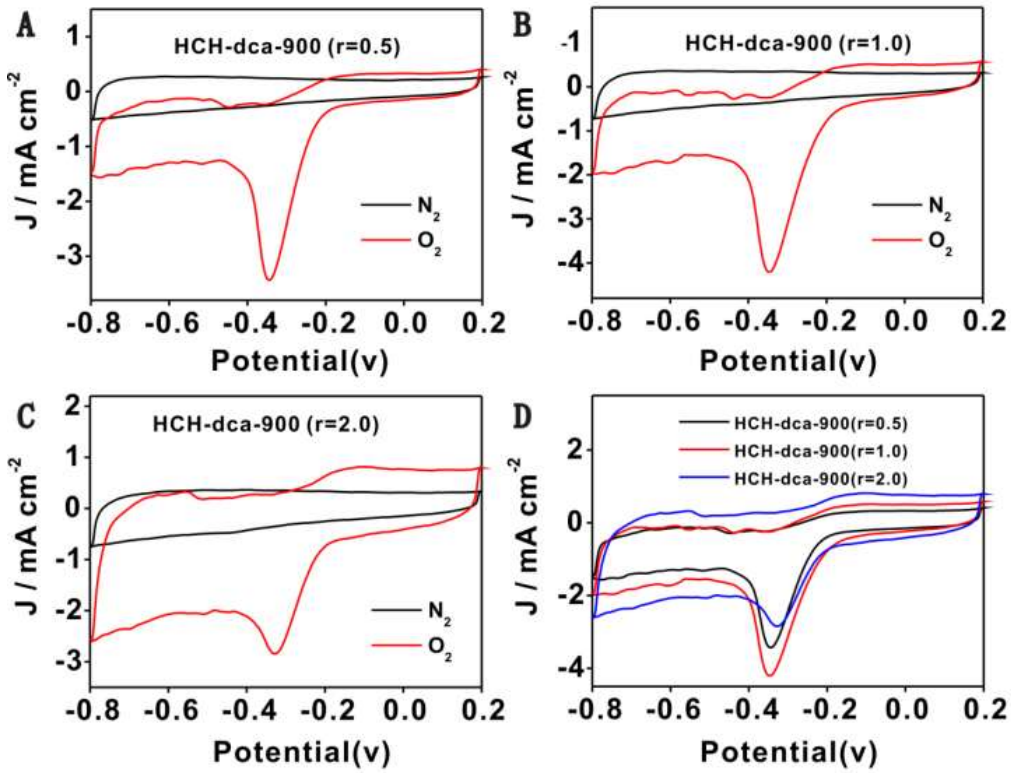


Figure S12. The cyclic voltammograms of HCH-dca-900 (A) r=0.5 (B) r=1.0 (C) r=2.0 and (D) compare of HCH-dca-900

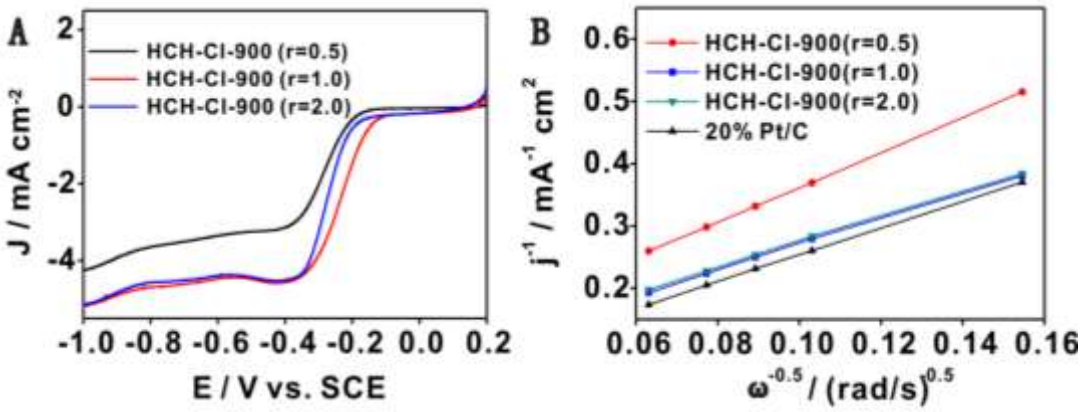


Figure S13. (A) Polarization curves on a glassy carbon rotating disk electrode for HCH-Cl-900 in O_2-saturated 0.1 M KOH at a scan rate of 10 mV s^{-1}.(B) Koutecky-Levich plots of HCH-Cl-900 (r=0.5, 1.0 and 2.0) and 20 wt% Pt/C at -0.60V.

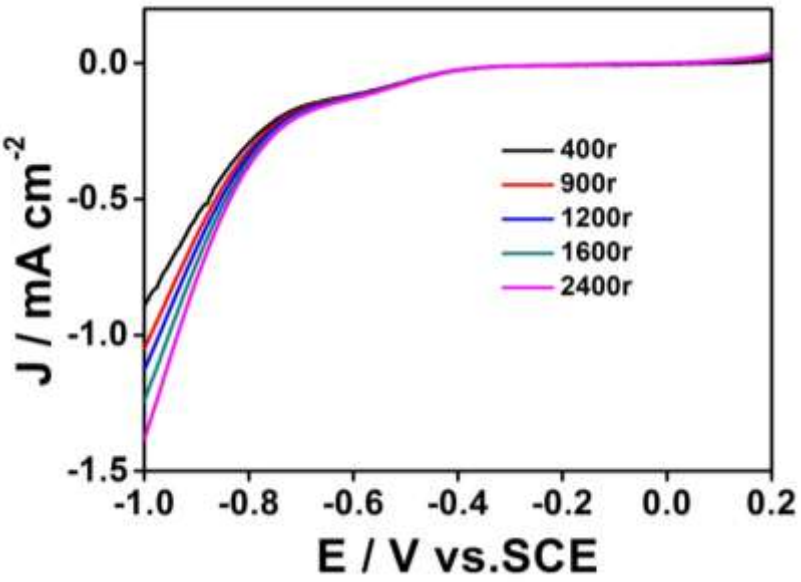


Figure S14. LSV curves of ORR of blank experiment on the GC electrode

Equation S1. The equation of the shifted electrons n of ORR in alkaline electrolyte.

$$4e^-:\ O_2 + 4e^- + 2H_2O \longrightarrow 4OH^-$$

$$2e^-:\begin{cases} O_2 + 2e^- + H_2O \longrightarrow HO_2^- + OH^- \\ HO_2^- + 2e^- + H_2O \longrightarrow 3OH^- \end{cases}$$

Equation S2. The Koutecky-Levich equations.

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{0.5}}$$

where j_k is the kinetic current and B is Levich slope which is given by:

$B = 0.62\ n\ F\ (D_{O2})^{2/3}\ \nu^{(-1/6)}\ C_{O2}$

Here n is the number of electrons transferred in the reduction of one O_2 molecule, F is the Faraday constant (F = 96485 C/mol), Do_2 is the diffusion coefficient of O_2 (Do_2 = 1.9×10^{-5} $cm^2\ s^{-1}$), ν is the kinematics viscosity for KOH (ν= 0.01 $cm^2\ s^{-1}$) and Co_2 is concentration of O_2 in the solution (Co_2 = 1.2×10^{-6} mol cm^{-3}). The constant 0.62 is adopted when the rotation speed is expressed in rps.

References

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