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Functional Porous Cellulose Acetate / Carboxymethylcellulose Composite Microspheres for Effective Removal of Hydrogen Cyanide from Cigarette Smoke

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Background

- Hydrogen cyanide (HCN) : a smoke toxicant
  - WHO：9+9 smoke constituents
  - USA: EPA & CPSC list
  - Canada: HCI list
  - China：7 smoke constituents
- Adsorbents in the filter
  - Could reduce the harmful constituents in the cigarette smoke
  - Varies adsorbents
- Difficulty of adsorption of the harmful constituents from smoke
  - Gas-solid interface
  - high flow rate
  - Complex: a large number of chemicals (different chemical groups and functionalities)

Background

- To enhance the adsorption
  - Modifying of the micro-structure
  - Introducing chemisorption mechanism
- Cellulose based adsorbs
  - Low cost/benefit ratio
  - Safe: biocompatible and degradable

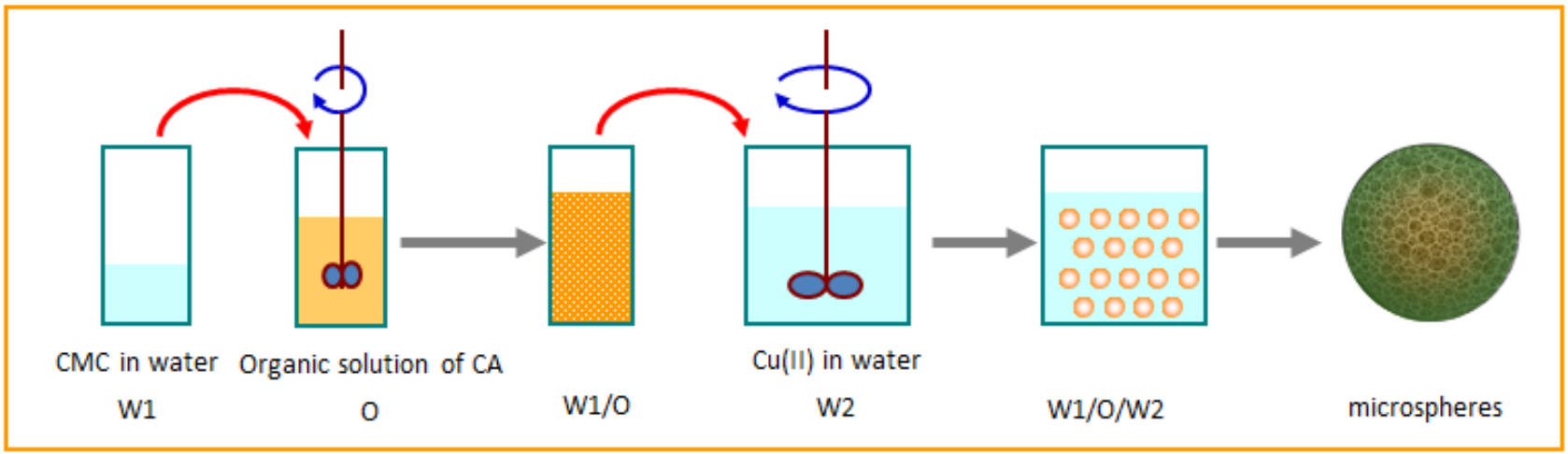
OUR STRATEGY:

Cupric loaded cellulose acetate / carboxymethylcellulose (CA/CMC) porous microspheres

- Porous Structures → Physisorption
- Functionality → Enhanced chemisorption

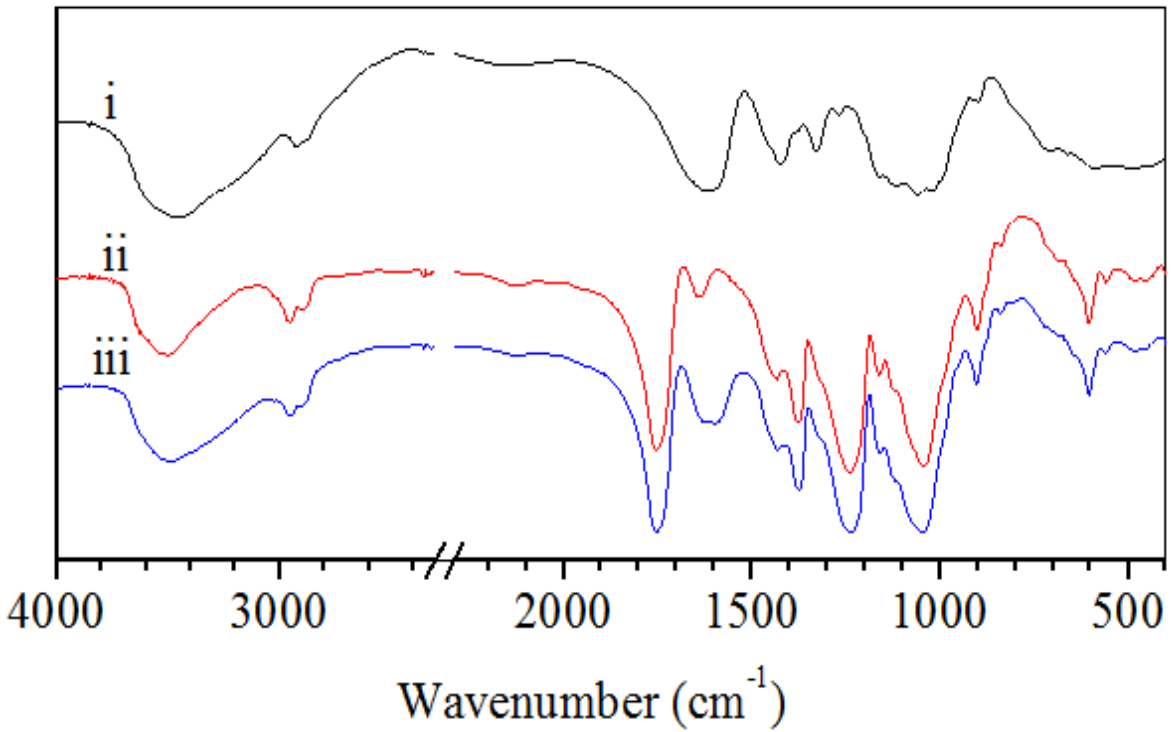
Preparation of CA/CMC microspheres

- Combination of double emulsion-solvent evaporation and in-situ cross-linking method



(1) CMC aqueous solution and CA organic solution were emulsified to form a primary emulsion;
(2) The primary emulsion was added to a aqueous solution of cupric to form a double emulsion;
(3) The evaporation of organic solvent and the crosslinking of CMC by cupric ions resulted in the solidification of the CA/CMC microspheres and the loading of cupric ions in the MS.

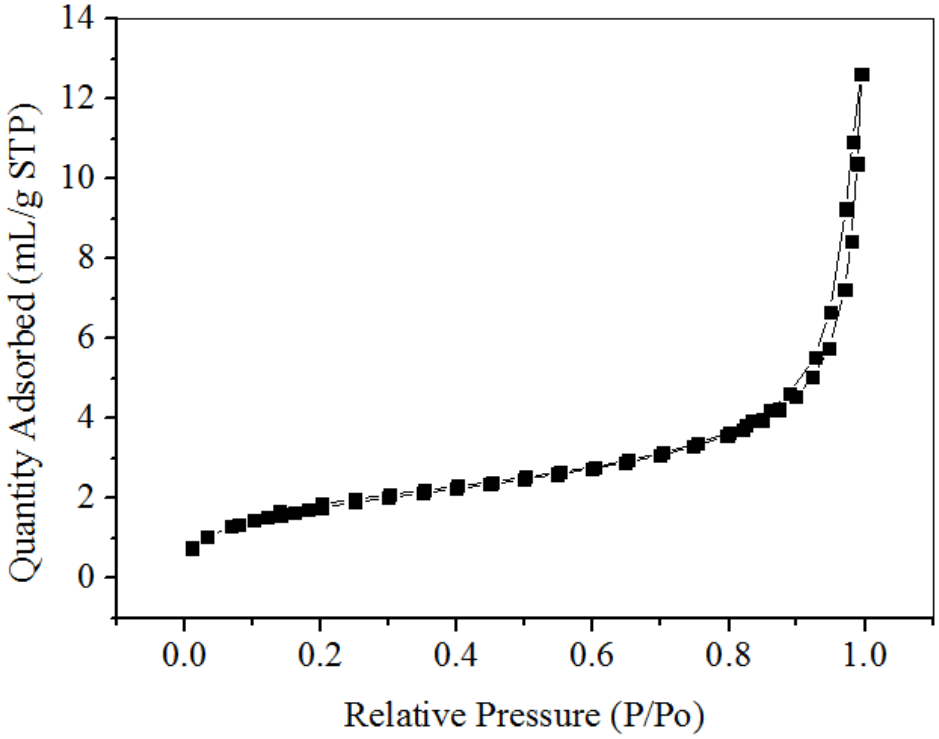
FTIR spectrum of CA/CMC microspheres

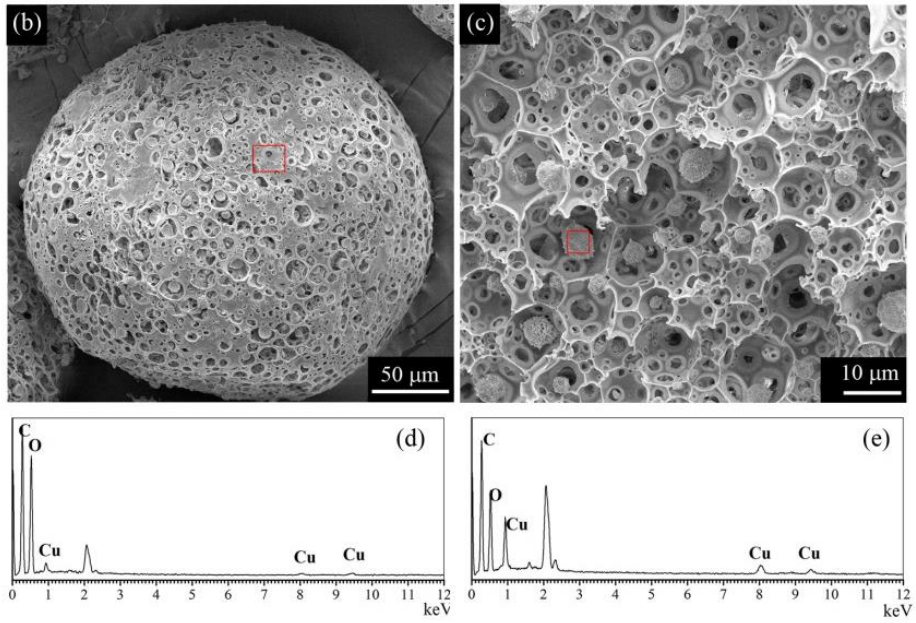


(i) CA
(ii) CMC
(iii) CA/CMC MS

- acetyl group vibrations in CA at 1753 cm^{-1} ; CMC: 1597cm^{-1} ←1640cm^{-1}
- The redshift indicated the complexion of CMC and the cupric ions

N_2 adsorption and SEM/EDS





- Type IV isotherm and SEM images showed the microsphere are porous, with a predominantly macroporous structure.
- Smaller micro-partial were observed in the cave of the composite microsphere
- Cupric content of the inner micro-partial: ca. 10.5%; surface cupric content 3.1%.

Adsorption of HCN using MS as filter additive

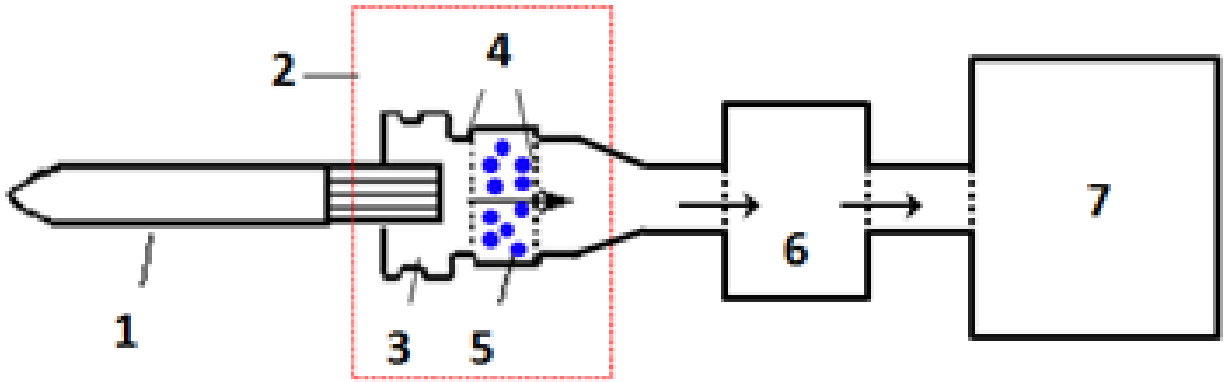


Figure 1. Device for evaluation the adsorption of HCN from cigarette smoke.

1. Cigarette; 2. Homemade device; 3. Cigarette holder; 4. Sieve (120 mesh);

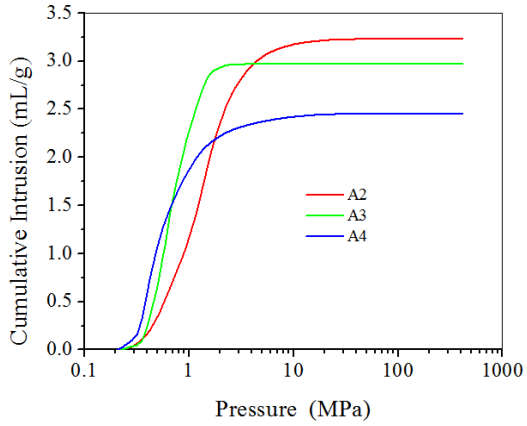
5. Sample; 6. Cambridge filter pad; 7. Smoking machine

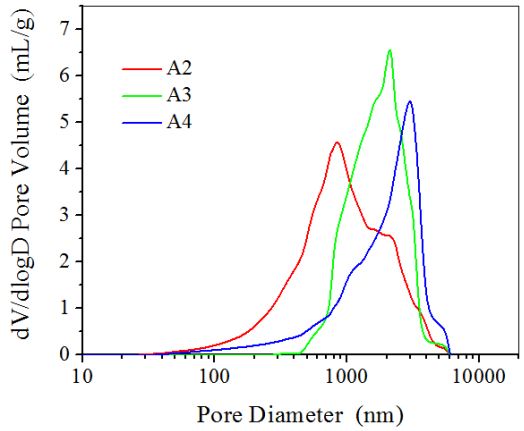
Influence of preparation parameters on the MS properties

Sample Group	Sample	CMC/wt%	W1/O	$[Cu^{2+}]$/mM	T/°C
A	A2	2	50:100	50	40
	A3[a]	3			
	A4	4			
B	B1	3	10:100	50	40
	B2		30:100		
	B3[a]		50:100		
	B4		70:100		
	B5		90:100		
C	C1	3	50:100	25	40
	C2[a]			50	
	C3			100	
	C4			200	
D	D1	3	50:100	50	20
	D2				30
	D3[a]				40
	D4				50

CMC concentration in W1 ~ MS structure

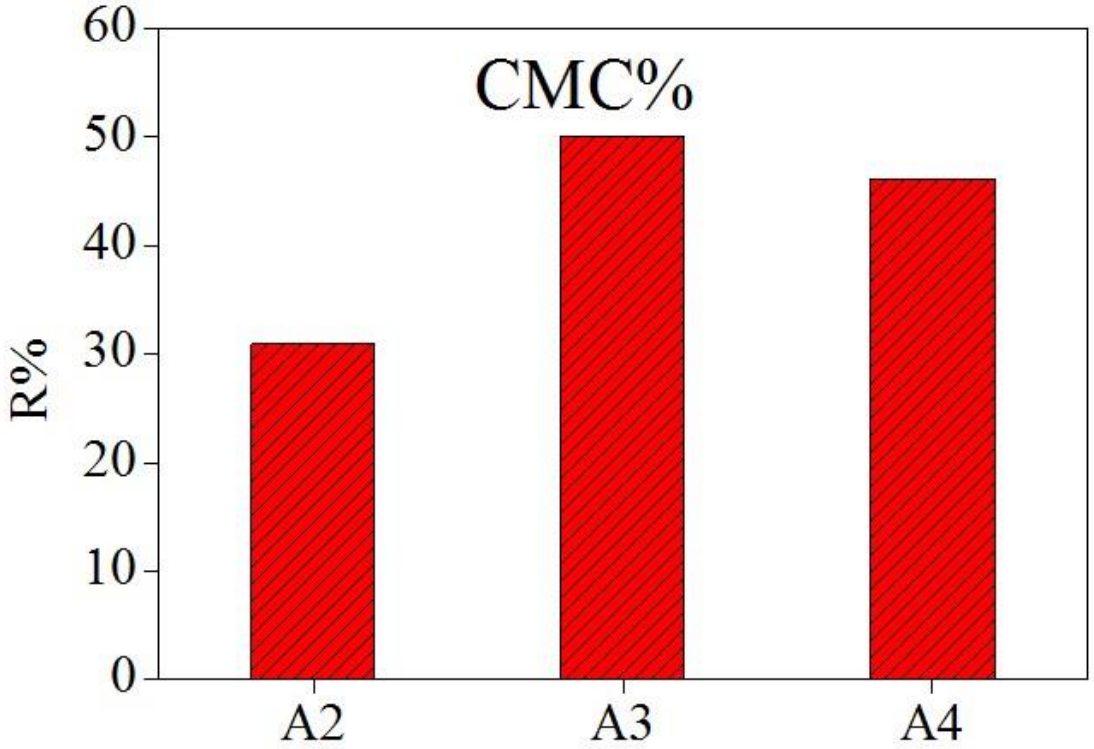
Sample (c_{CMC})	BET surface areas (m^2/g)	Cu% (wt%)	Mean diameter (nm)	Pore volume (mL/g)
A2(2%)	5.06	1.8	952	3.23
A3(3%)	6.46	2.6	1780	2.97
A4(4%)	5.75	3.3	2264	2.45





With CMC concentration in W1 increased from 2% to 4%
1. Pore size increased while the pore volume decreased;
2. More Cu(II) could be complexed to the CA/CMC microspheres.

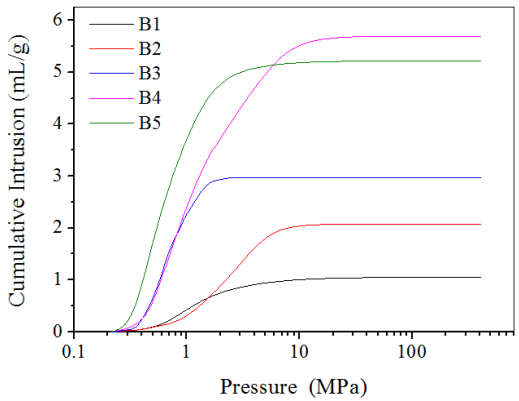
CMC concentration in W1 ~ HCN reduction

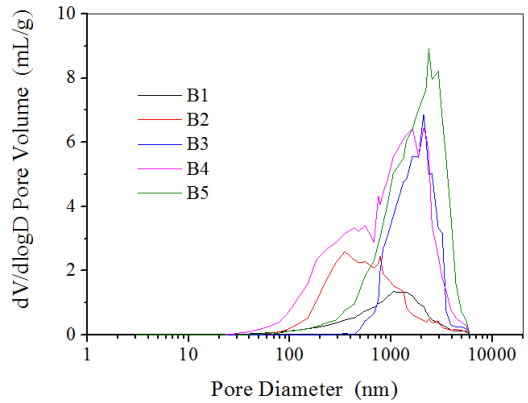


sample	blank	A2 (2%)	A3 (3%)	A4 (4%)
HCN (μg/cig)	129.5	89.6	64.6	69.8
The decrease of HCN(%)	/	30.9	50.1	46.1
TPM (mg/cig)	12.3	11.6	11.6	12.3

The W1/O ratio ~ MS structure

sample	BET surface areas (m^2/g)	Cu% (wt%)	Mean diameter (nm)	Pore volume (mL/g)
B1(10/100)	2.24	0.8	1058	1.04
B2(30/100)	3.87	1.8	540	2.07
B3(50/100)	6.46	2.6	1780	2.97
B4(70/100)	13.50	3.4	1037	5.69
B5(90/100)	7.42	4.1	1905	5.20



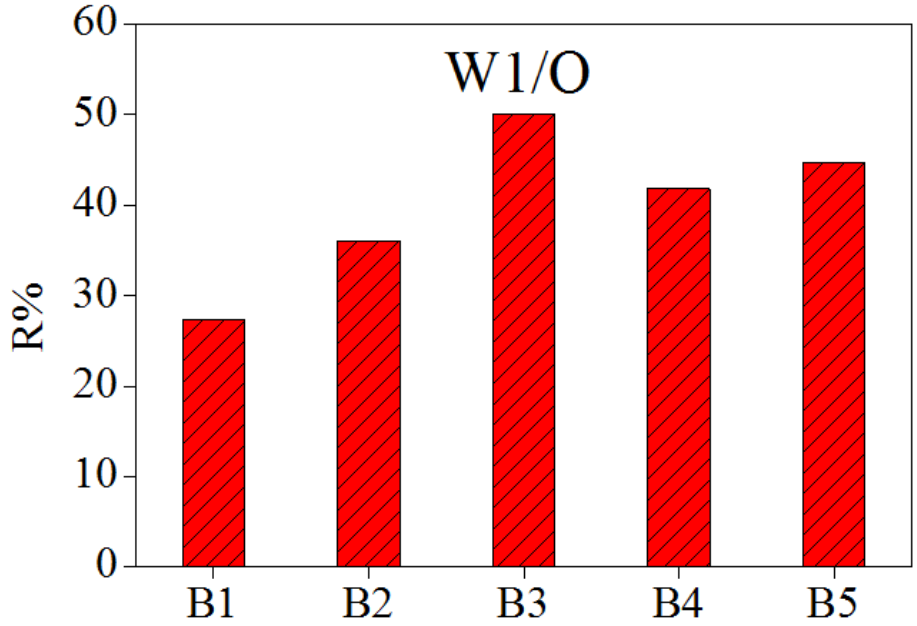


With W1/O ratio increased from 10/100 to 70/100

- BET surface areas increased
- Pore volume increased
- Cu content increased

A higher W1/O ratio 90/100 Deformation of the W1/O emulsion resulted in the decrease of BET and pore volume

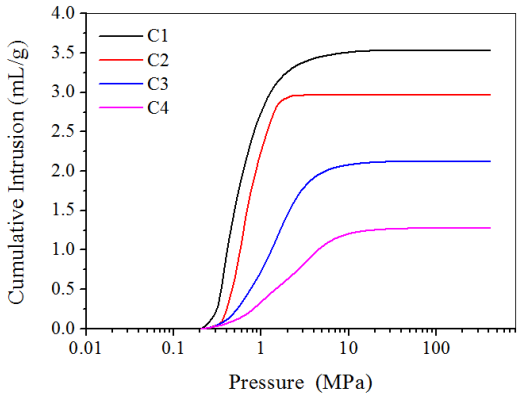
The W1/O ratio ~ HCN reduction

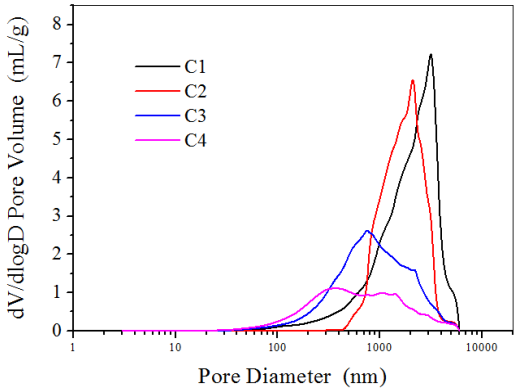


sample	blank	B1 (10/100)	B2 (30/100)	B3 (50/100)	B4 (70/100)	B5 (90/100)
HCN (μg/cig)	129.5	94.1	82.7	64.6	75.4	71.5
The decrease of HCN(%)	/	27.3	36.1	50.1	41.8	44.8
TPM (mg/cig)	12.3	12.9	11.3	11.6	12.5	11.8

The Cu^{2+} content in W2 ~ MS structure

sample	BET surface areas (m^2/g)	Cu% (wt%)	Mean diameter (nm)	Pore volume (mL/g)
C1(25mM)	5.86	2.7	2252	3.54
C2(50mM)	6.46	2.6	1780	2.97
C3(100mM)	3.86	2.6	898	2.12
C4(200mM)	2.80	2.6	610	1.28

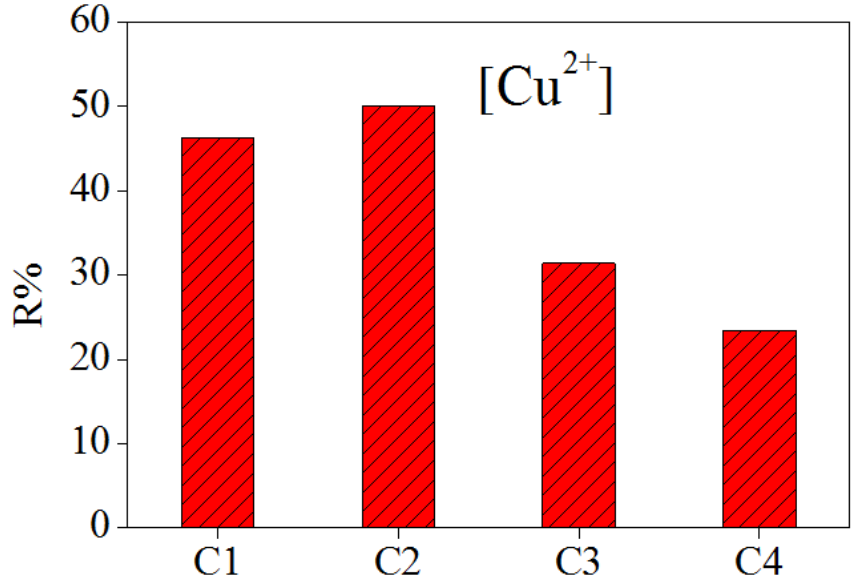




With Cu2+ content in W2 increased from 25mM to 200mM

- BET surface areas decreased
- Pore size and pore volume decreased

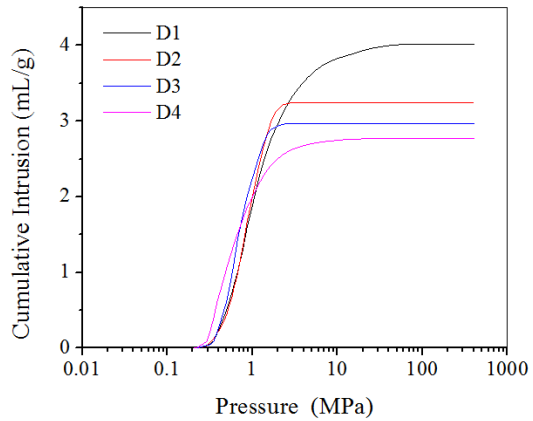
The Cu^{2+} content in W2 ~ HCN reduction

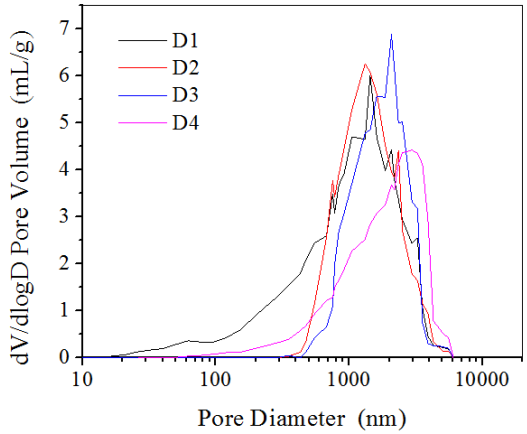


sample	blank	C1 (25mM)	C2 (50mM)	C3 (100mM)	C4 (200mM)
HCN (μg/cig)	129.5	69.6	64.6	88.8	99.2
The decrease of HCN(%)	/	46.3	50.1	31.4	23.4
TPM (mg/cig)	12.3	10.9	11.6	12.8	11.9

The temperature of W2 ~ MS structure

sample	BET surface areas (m^2/g)	Cu% (wt%)	Mean diameter (nm)	Pore volume (mL/g)
D1 (20°C)	13.01	2.5	1172	4.02
D2 (30°C)	7.44	2.7	1457	3.24
D3 (40°C)	6.46	2.6	1780	2.97
D4 (50°C)	4.72	2.5	2055	2.77

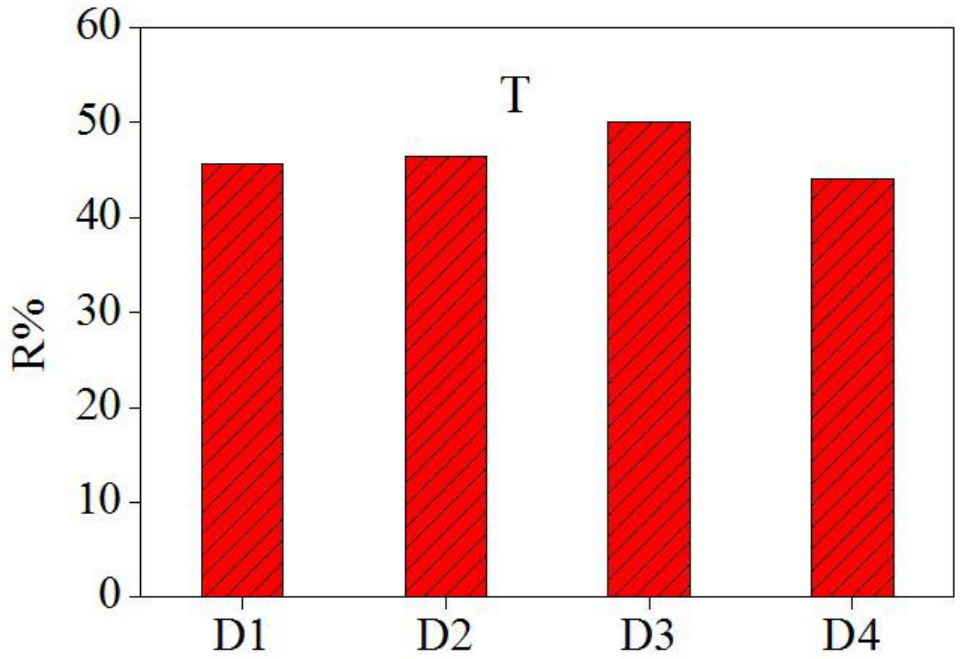




With the temperature increased from 20 to 50°C

- BET surface areas decreased
- pore size increased
- pore volume decrease

The temperature of W2 ~ HCN reduction



sample	blank	D1 (20°C)	D2 (30°C)	D3 (40°C)	D4 (50°C)
HCN (μg/cig)	129.5	72.4	69.4	64.6	70.3
The decrease of HCN(%)	/	45.7	46.4	50.1	44.1
TPM (mg/cig)	12.3	11.2	11.0	11.6	11.7

Summary

- Porous CA/CMC MS were prepared via the combination of emulsion-solvent evaporation and in-situ ion cross-linking method.
  Cupric (II) ions, which have high complexing ability to HCN, were introduced to the CA/CMC microspheres during the in-situ cross-linking process.
  The microspheres have connect macroporous structure and a high cupric(II) ions loading amount of 0.8~4.1wt%.

- A conspicuous reduce of HCN yield of cigarette smoke could be achieved using these microspheres as filter additive.

- HCN reduction efficiency was dependent on both the Cu content and the microstructure of the MS.

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Thank you !