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

Hollow Multishelled Heterostructures with Enhanced Performance for Laser Desorption/Ionization Mass Spectrometry based Metabolic Diagnosis

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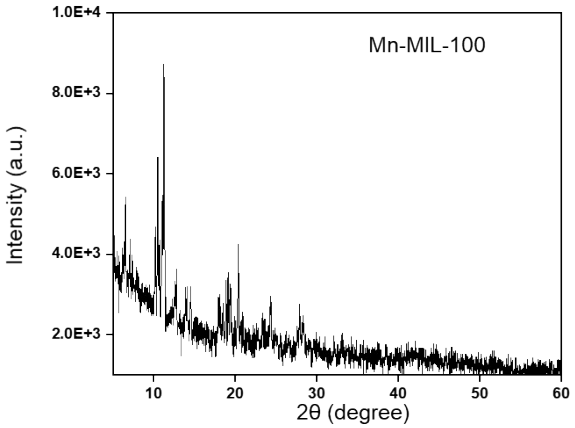

Fig. S1. XRD pattern of Mn-MIL-100.

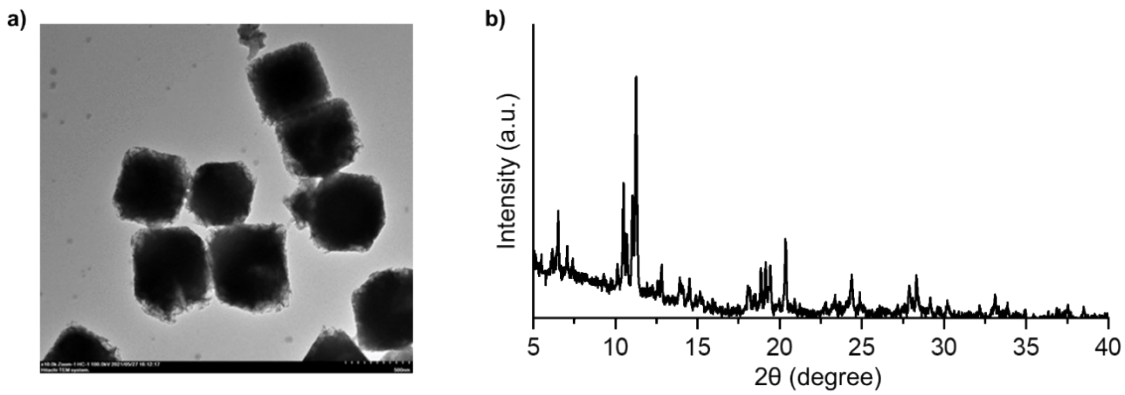

Fig. S2. a) TEM image and b) XRD pattern of slightly etched Mn-MIL-100.

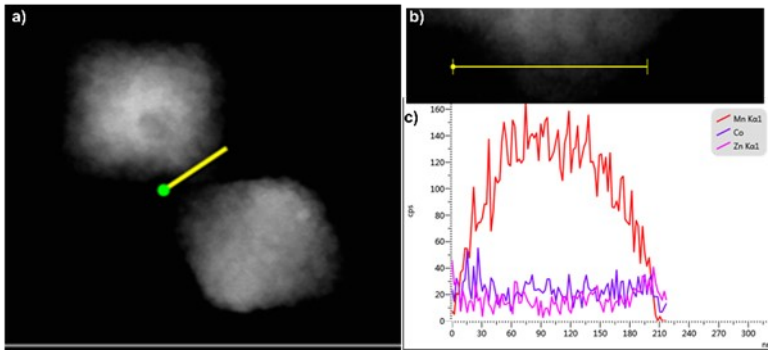

Fig. S3. STEM and line-scan (yellow line) EDX of Mn-MIL-100/ZIF.

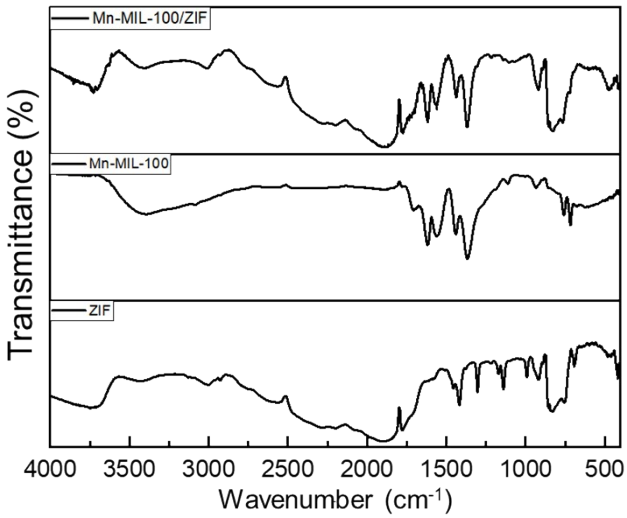

Fig. S4. FTIR spectra of ZIF, Mn-MIL-100, and Mn-MIL-100/ZIF.

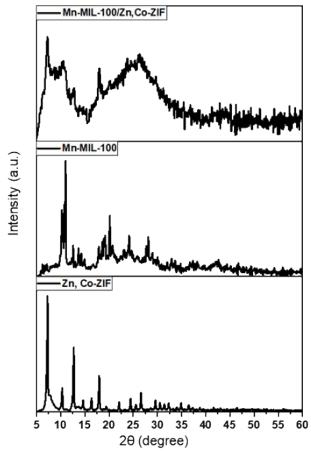

Fig. S5. XRD patterns of Zn, Co-ZIF, Mn-MIL-100, and Mn-MIL100/ZIF.

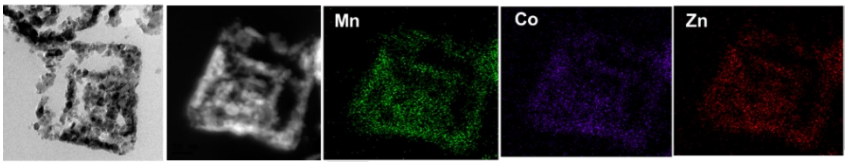

Fig. S6. TEM image, HADDF-STEM, and corresponding element mapping images of the TSH ZMO/CMO ultrathin slices.

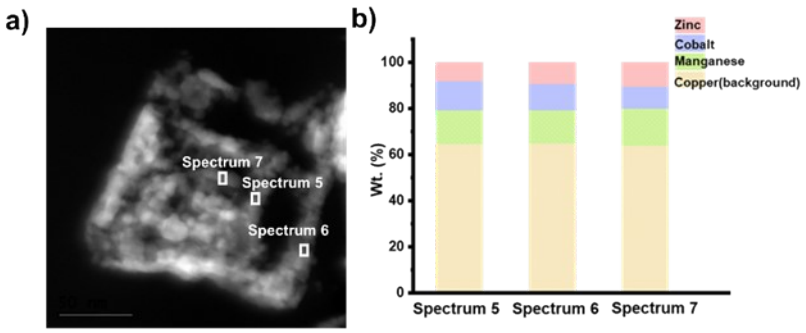

Fig. S7. a) HADDF-STEM image of ultrathin slices ZMO/CMO by ultramicrotomy; b) The wt% of elements in selected area elemental analysis of Fig. S7a.

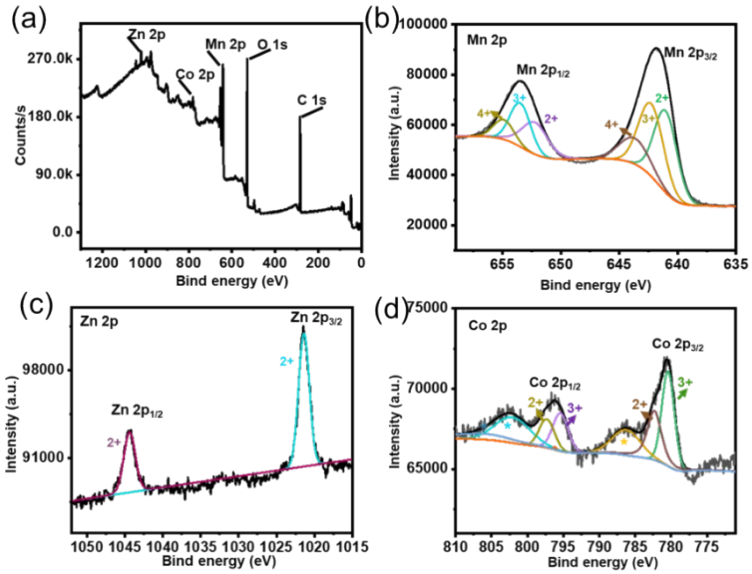

Fig. S8. XPS spectrum of TSH ZMO/CMO.

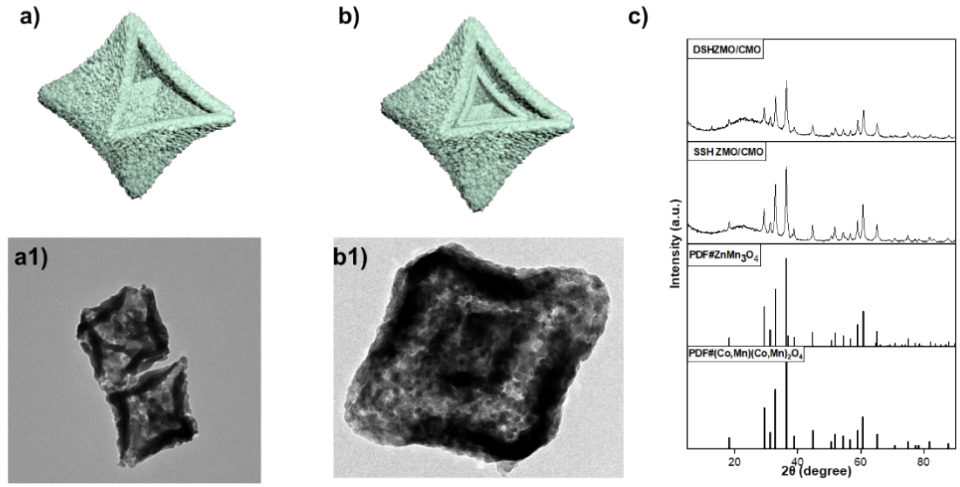

Fig. S9. TEM images of a) SSH ZMO/CMO and b) DSH ZMO/CMO; c) XRD spectrum of SSH ZMO/CMO and DSH ZMO/CMO.

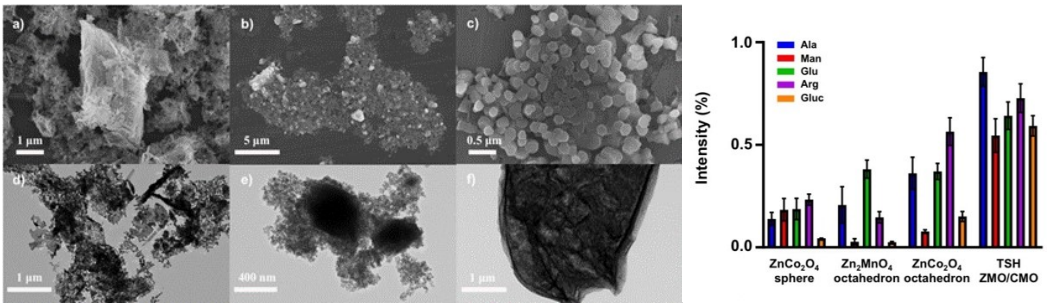

Fig. S10. (left) (a-c) SEM images of $ZnCo_2O_4$ octahedron, Zn_2MnO_4 octahedron, and $ZnCo_2O_4$ sphere; (d-f) TEM images of $ZnCo_2O_4$ octahedron, Zn_2MnO_4 octahedron, and $ZnCo_2O_4$ sphere. (right) Mean intensities of Na^+ adducted peaks for Ala, Man, Glu, Arg and Gluc using $ZnCo_2O_4$ sphere, Zn_2MnO_4 octahedron, $ZnCo_2O_4$ octahedron, and TSH ZMO/CMO as the matrices.

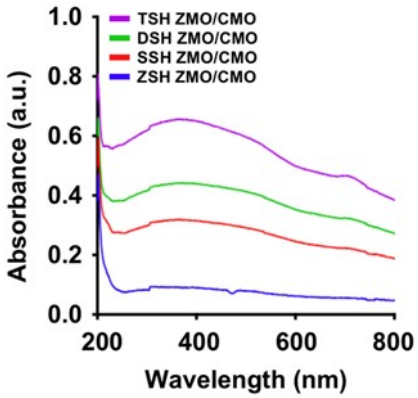

Fig. S11. The UV-vis absorption of ZSH, SSH, DSH, and TSH ZMO/CMO.

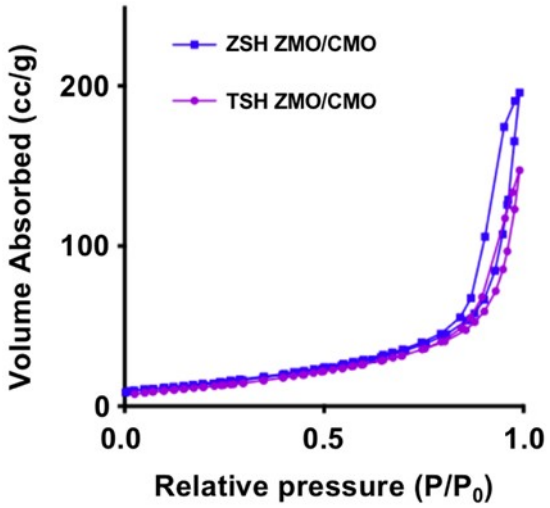

Fig. S12. Nitrogen adsorption isotherm of ZSH ZMO/CMO and TSH ZMO/CMO.

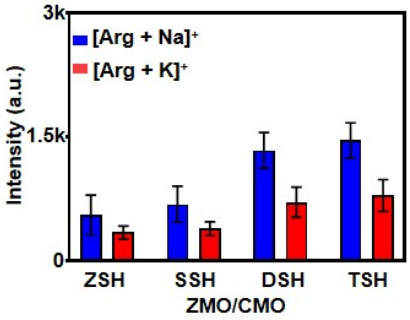

Fig. S13. Mean intensities of Na^+ and K^+ adducted peaks for 1 mg mL^{-1} Arg using ZSH ZMO/CMO, SSH ZMO/CMO, DSH ZMO/CMO, and TSH ZMO/CMO as the matrices.

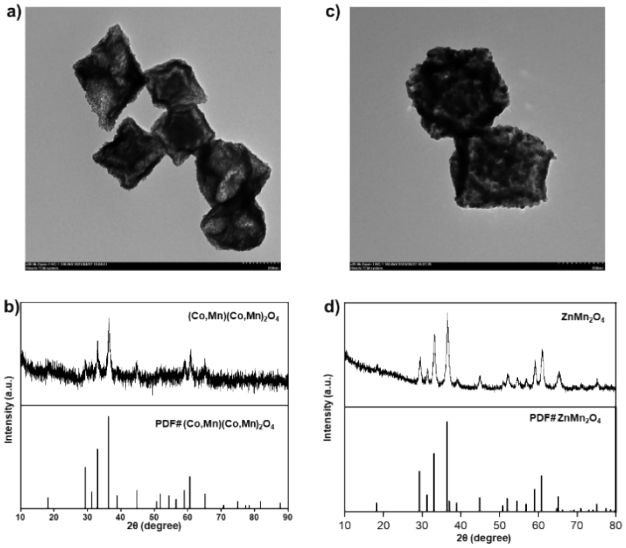

Fig. S14. a) TEM image and b) XRD pattern of $(Co,Mn)(Co,Mn)_2O_4$; c) TEM image and d) XRD pattern of $ZnMn_2O_4$.

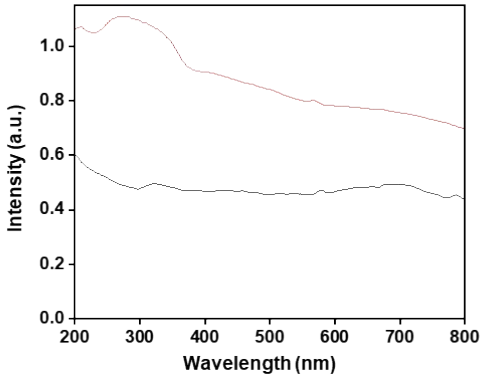

Fig. S15. The UV–vis DRS of TSH ZMO (grey line), TSH CMO (red line).

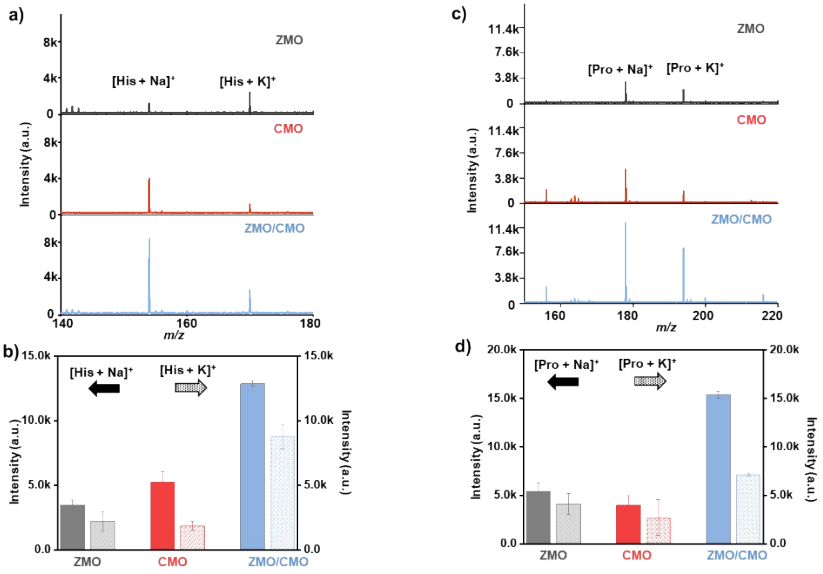

Fig. S16. Typical mass spectra of 0.1 mg mL^{-1} a) His and c) Pro using ZMO, CMO, and ZMO/CMO as the matrices; Mean intensities of Na^+ and K^+ adducted peaks for b) 0.1 mg mL^{-1} His, and d) 0.1 mg mL^{-1} Pro in 3 experiments using ZMO, CMO, and ZMO/CMO as the matrices.

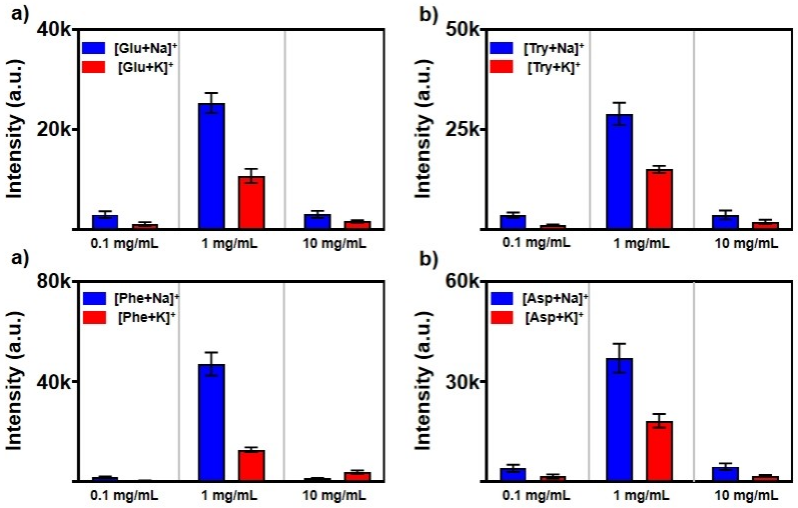

Fig. S17. Mean intensities of Na^+ and K^+ adducted peaks for Glu, Try, Phe, and Asp using 0.1 mg mL^{-1}, 1 mg mL^{-1}, 10 mg mL^{-1} TSH ZMO/CMO as the matrices.

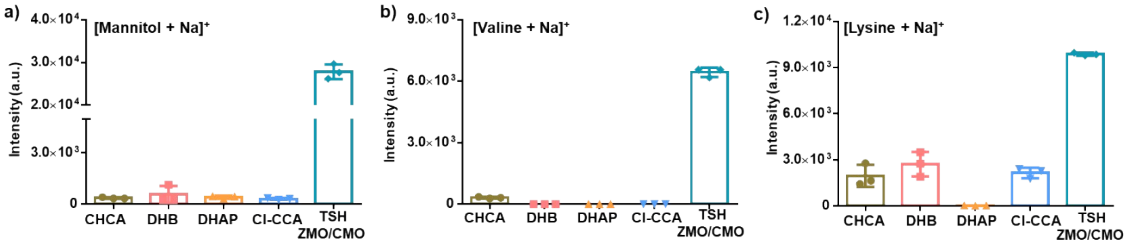

Fig. S18. The reproducibility of Na^+ adducted peaks for a) 0.1 mg mL^{-1} Man, b) 0.1 mg mL^{-1} Val, and c) 0. 1 mg mL^{-1} Lys in 3 experiments using CHCA, DHB, DHAP, Cl-CCA, and TSH MO/CMO as the matrices.

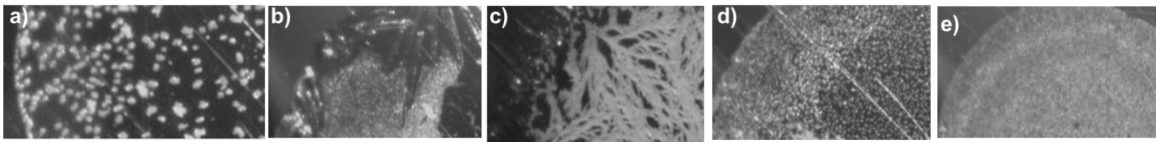

Fig. S19. The micrograph images of sample distribution with a) CHCA, b) DHB, c) DHAP, d) Cl-CCA, and e) TSH ZMO/CMO matrices.

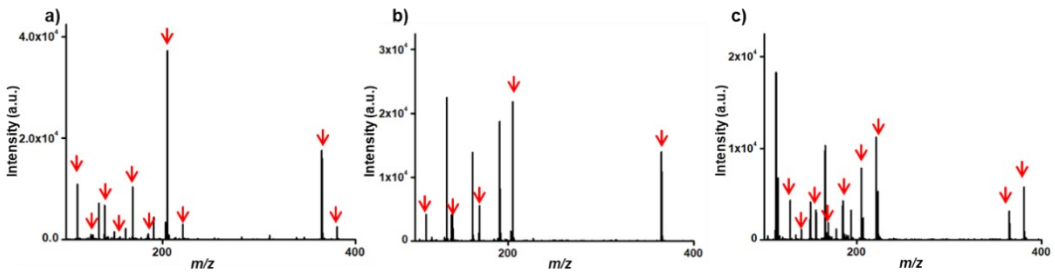

Fig. S20. Mass spectra of Ala, Lys, Val, Man, and Suc in a) 5.00 mg mL^{-1} BSA and b) 0.50 M NaCl; c) 0.50 M KCl solutions using TSH ZMO/CMO as the matrix.

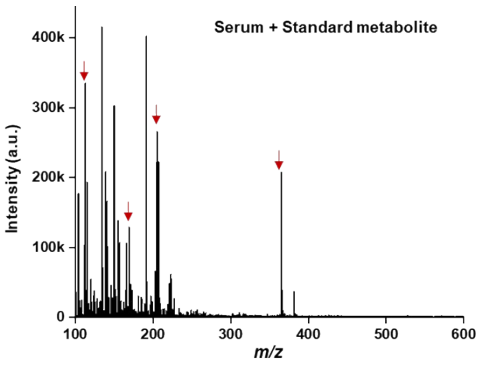

Fig. S21. The serum metabolic fingerprints of typical HCC serum and standard metabolites using TSH ZMO/CMO as the matrix.

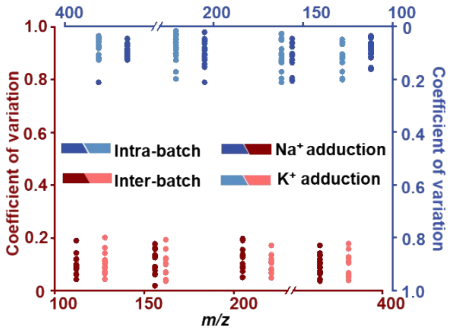

Fig. S22. CV distribution of intensities for the mixture of 4 analytes was loaded in serum.

Table. S1. Comparison of methods for multishelled materials.

Number	Cost (RMB)	Hazarous raw materials	Time	Morphology	Size	Component	Reference
1	0.79	/	24 h	triple-shelled octahedron	250 nm	$ZnMn_2O_4$/(Co, Mn) $(Co, Mn)_2O_4$	Our work
2	1.08	/	37 h	Single-shelled octahedron	6 μm	$ZnCo_2O_4$	[1]
3	1.11	Nitric acid	24 h	Single-shelled octahedron	1.5 μm	Zn_2SnO_4	[2]
4	10.48	/	32 h	triple-shelled sphere	1μm	$ZnCo_2O_4$	[3]
5	2.53	/	28.5 h	triple-shelled sphere	1μm	$CuNiFe_2O_4$	[4]
6	24.76	/	60.5 h	triple-shelled sphere	500 nm	Ni-Co-O	[5]
7	87.27	Sodium hydroxide	40.3 h	triple-shelled sphere	2 μm	$NiCo_2O_4$	[6]
8	0.98	/	90 h	triple-shelled sphere	800 nm	Co_2MnO_4	[7]
9	67.60	/	51 h	triple-shelled sphere	1 μm	TiO_2/Fe_2TiO_5	[8]
10	0.37	/	29 h	triple-shelled sphere	700 nm	$ZnMn_2O_4$	[9]
11	673.85	Sodium hydroxide	21 h	double-shelled cube	1μm	Zn_2SnO_4-SnO_2	[10]

Table. S2. The LOD and S/N ratio of the creatinine, Asp, and Glu.

	ZMO	CMO	SSH ZMO/CMO	DSH ZMO/CMO	TSH ZMO/CMO
Creatinine	0.005 mg/mL S/N=18.7	0.005mg/mL S/N=20.4	0.00005 mg/mL S/N=9.3	0.00001 mg/mL S/N=6.2	0.00001 mg/mL S/N=7.2
Aspartic acid	0.0005 mg/mL S/N=8.3	0.00001 mg/mL S/N=12	0.0001 mg/mL S/N=9.4	0.00001 mg/mL S/N=4.1	0.00001 mg/mL S/N=6.2
Glucose	0.01 mg/mL S/N=16.4	0.005 mg/mL S/N=10.8	0.0005 mg/mL S/N=8.1	0.00005 mg/mL S/N=8.7	0.00005 mg/mL S/N=16.4

Table. S3. Clinical characteristics of HCC patients and controls for training and test.

Characteristic	Training cohort		P value	Test cohort	
	HCC patient	control		HCC patient	control
Sex			0.911[a]	/	/
Male	42	35	/	10	7
Female	30	26	/	6	2
Age (Median(ange))	61(41-81)	57(40-78)	0.414[b]	/	/

[a]) P value was calculated by Chi-Square test; [b]) P value was calculated by t-test.

Notes and references

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