Supporting Information

A fish scale-like magnetic nanomaterial as a highly efficient sorbent for monitoring the changes of auxins level under cadmium stress

Qingqing Ding,[a] Hui Chen,[a] Chuanhui Huang,[a] Qiaomei Lu,[a, c] Ping Tong,[a, c] Wenmin Zhang*[b] and Lan Zhang*[a]

[a] *Ministry of Education Key Laboratory for Analytical Science of Food Safety and Biology, Fujian Provincial Key Laboratory of Analysis and Detection Technology for Food Safety, College of Chemistry, Fuzhou University, Fuzhou, Fujian, 350116, China*

[b] *College of Chemical Engineering, Fuzhou University, Fuzhou, Fujian, 350116, China*

[c] *Testing Center of Fuzhou University, Fuzhou, Fujian, 350116, China*

- ***Corresponding author:*** *Wenmin Zhang, Lan Zhang*
- ***Postal address:*** *College of Chemistry, Fuzhou University, Fuzhou, Fujian, 350116, China*
- ***Tel:*** *86-591-22866135*
- ***Fax:*** *86-591-22866135*

E-mail: *196419@fzu.edu.cn (W. Zhang); zlan@fzu.edu.cn (L. Zhang)*

Synthesis of bulk OCN

The black bulk OCN was synthesized according to the previously reported method.[1] The appropriate amount of urea and glucose solid mixture (10:1 by mass) was added into a crucible with a tightly fastened cover. The covered crucible was then heated in air with a temperature-controlled system under ambient pressure. The temperature was firstly raised to 550 °C for 1 h, then down to 200 °C for 0.5 h, and finally the temperature reached 800 °C for another 1 h. After reaction completion, the temperature naturally cooled down to room temperature. The black bulk OCN was obtained.

Synthesis of OCN nanosheets

According to the previously reported method with some modifications, the bulk OCN was synthesized into OCN nanosheets.[2] In brief, 300 mg of the obtained bulk OCN was vigorously stirred for 1 h in 50 mL of 10 M HCl at room temperature. The above mixture was centrifuged at 8000 rpm, and repeatedly washed with water until the pH reached neutral to remove residual HCl. The protonated material was then added to 100 mL of deionized water, and sonicated for 3 h to generate a stable OCN nanosheets dispersion. The concentration of the final OCN nanosheets dispersion was ~2.5 mg mL^{-1} (concentration of the OCN nanosheets dispersion was determined by measuring the mass of the OCN lyophilized from a certain volume of the dispersion).

Synthesis of granular 2D Co@Co_3O_4/OCN nanomaterials

Granular 2D nanomaterials were prepared according to the previously work with some modification. The specific steps were as follows: 1.03 mmol of $Co(Ac)_2 \cdot 4H_2O$ was added to 24.0 mL of EtOH solution, followed by addition of 2.4 mL of the obtained OCN nanosheets dispersion at RT. The reaction was kept at 80 °C with stirring for 10 h. After that, the reaction mixture was transferred to a 100 mL autoclave for hydrothermal reaction at 150 °C for 3 h. The resulted product was collected by centrifugation and washed with ethanol and water. After being dried naturally, hydrogen reduction was carried out at 300 °C for 1 h in a hydrogen atmosphere. Finally, the black magnetic powder was obtained.

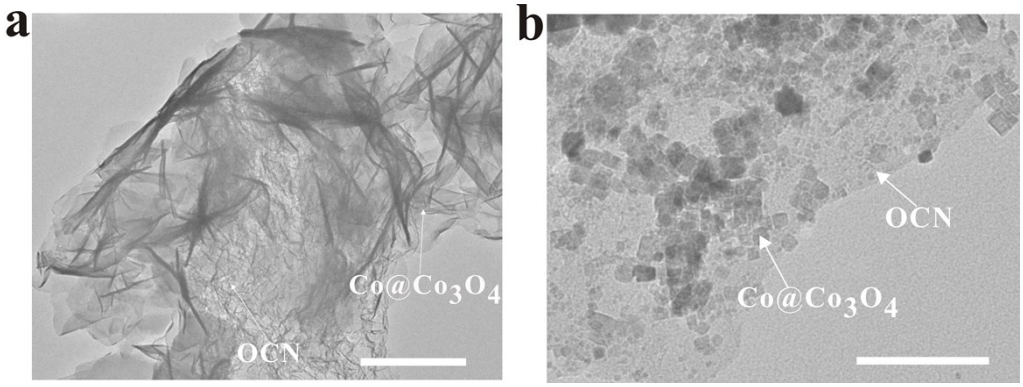

Fig. S1 TEM images of (a) fish scale-like and (b) granular Co@Co_3O_4/OCN nanomaterials. Scale bar, 500 nm for (a) and 200 nm for (b).

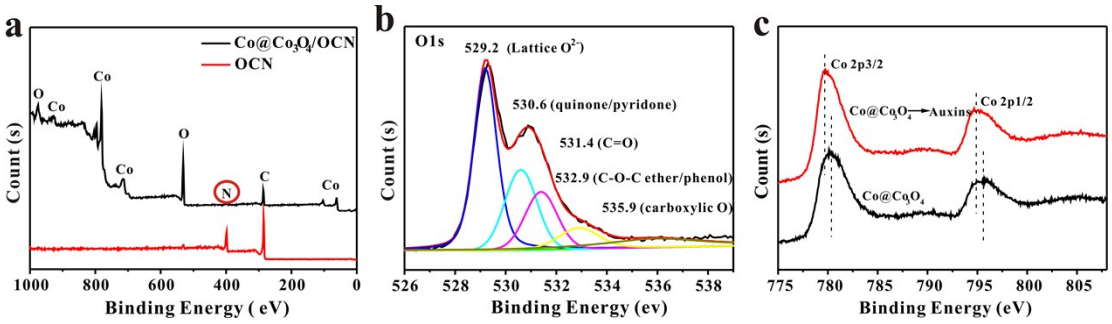

Fig. S2 The XPS spectra of (a) OCN nanosheets and Co@Co_3O_4/OCN nanomaterials; (b) O 1s XPS spectrum and (c) Co 2p XPS spectra before and after adsorption of auxins by Co@Co_3O_4. The O 1s XPS spectrum of Co@Co_3O_4/OCN was shown in Fig. S2b, the main peak of 529.2 eV was identified as O^{2-} in Co@Co_3O_4, and the other three peaks were considered to be highly conjugated forms of quinone or pyridone O at 530.6 eV, carbonyl O (C=O) at 531.4 eV and ether or phenol O (C-O-C or C-OH) at 532.9 eV, respectively. The appeared peak at 535.9 eV was identified as carboxylic O (C(O)OH). Thus, the doped of O can enhance the interaction between the material and auxins by introducing carboxyl and hydroxyl groups into the material.

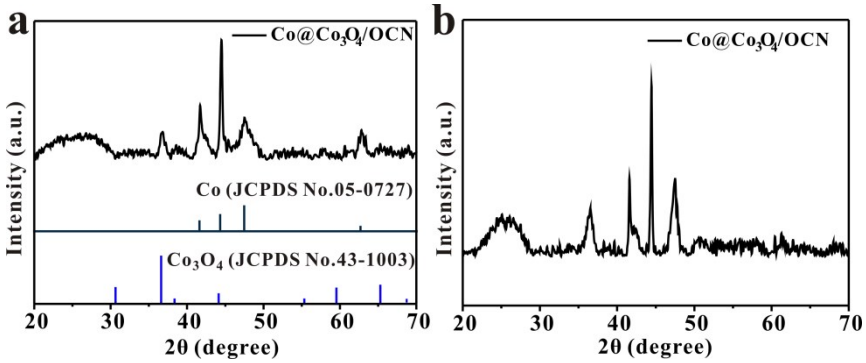

Fig. S3 Typical XRD patterns of (a) fish scale-like Co@Co_3O_4/OCN nanomaterials, and (b) granular Co@Co_3O_4/OCN nanomaterials.

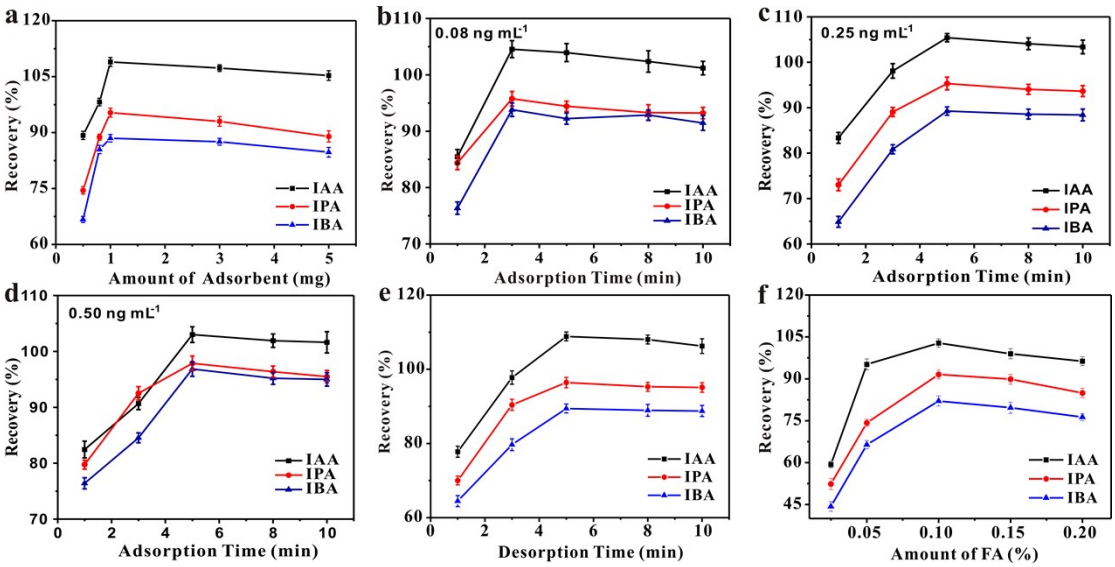

Fig. S4 Factors affecting the extraction efficiency for 0.25 ng mL^{-1} auxins. (a) Effect of the amounts of Co@Co_3O_4/OCN nanomaterials; (b) Effect of extraction time (0.08 ng mL^{-1}); (c) Effect of extraction time (0.25 ng mL^{-1}); (d) Effect of extraction time (0.50 ng mL^{-1}); (e) Effect of desorption time; (f) Effect of FA concentration. Error bars showed the standard deviations for three replicate extractions.

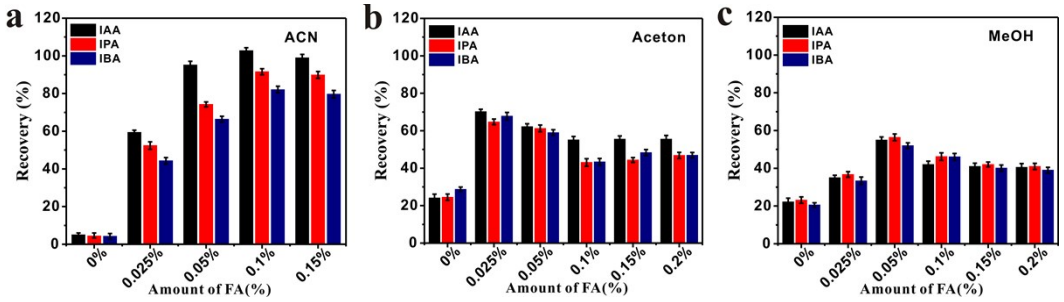

Fig. S5 Effect of FA in different solvents. (a) ACN (b) Aceton (c) MeOH. Error bars showed the standard deviations for three replicate extractions.

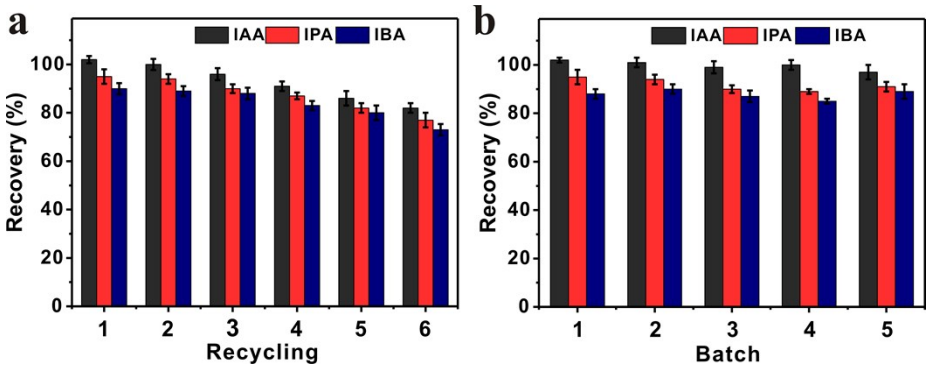

Fig. S6 The relative recovery of three auxins from different reuse time (a), and different batches (b) of Co@Co_3O_4/OCN. Error bars show the standard deviations for three replicate extractions.

Table S1. The gradient elution conditions for HPLC-MS/MS

Time (min)	mobile phases A (%)
0	50
5	50
6	45
9	50
10	45
10.1	95
10.2	50
12	50

Table S2. MS parameters by auto tuning for IAA, IPA, IBA

Compounds	Assignment	Parent (Q1, m/z)	Product (Q3, m/z)	SRM Collision Energy (eV)	Tube Lens Voltage (V)
IAA	$[M+H]^+$	176.044	130.118[a], 103.212[b]	17/30	69
IPA	$[M+H]^+$	190.045	130.121[a], 77.317[b]	12/42	63
IBA	$[M+H]^+$	204.071	186.140[a], 130.230[b]	13/31	69

[a] Quantification ion.

[b] Qualitative ion.

Table S3. Relative recoveries for phytohormones determination in leaves of *Perilla frutescens* by $Co@Co_3O_4$/OCN-based MSPE-HPLC-MS/MS method (mean ± SD[a], n = 3)

C_{Cd}^{2+} (mg L^{-1})	Compounds	7 Days			10 Days			17 Days		
		Recoveries (%)			Recoveries (%)			Recoveries (%)		
		Low	Medium	High	Low	Medium	High	Low	Medium	High
0 mg L^{-1}	IAA	93.2 ± 2.0	90.5 ± 2.1	95.1 ± 3.2	96.5 ± 1.6	104.7 ± 2.2	95.2 ± 2.3	101.3 ± 1.3	100.4±2.8	99.7±2.6
	IPA	91.6 ± 2.3	94.6 ± 1.9	93.4 ± 3.9	87.9 ± 3.2	85.4 ± 2.1	90.2 ± 3.6	87.6 ± 3.1	88.2±2.9	86.4±1.4
	IBA	101.2 ± 3.1	103.7 ± 2.0	97.4 ± 4.2	102.5 ± 2.3	98.1 ± 2.3	95.3 ± 4.1	97.5 ± 2.6	96.5±2.1	98.7±3.9
2 mg L^{-1}	IAA	89.3 ± 2.8	90.1 ± 3.3	94.5 ± 2.1	97.6 ± 2.8	98.3 ± 1.5	89.9 ± 2.7	107.9 ± 3.8	110.2±1.6	103.2±4.0
	IPA	104.3 ± 4.2	101.6 ± 1.7	98.2 ± 1.5	90.2 ± 1.7	91.8 ± 4.4	92.6 ± 1.5	94.4 ± 1.7	89.9±3.3	90.0±2.5
	IBA	88.9 ± 1.3	90.8 ± 2.7	86.3 ± 1.9	104.9 ± 1.5	93.7 ± 3.6	87.1 ± 2.1	95.7 ± 2.0	93.2±1.4	96.8±3.6
4 mg L^{-1}	IAA	92.0 ± 1.9	97.6 ± 4.6	95.2 ± 3.6	96.4 ± 2.5	102.7 ± 2.8	100.2 ± 1.3	101.1 ± 1.9	100.9±2.2	102.2±1.7
	IPA	85.1 ± 2.6	88.1 ± 3.2	89.4 ± 2.8	86.3 ± 3.1	87.9 ± 3.9	90.1 ± 3.7	85.4 ± 4.6	86.1 ± 3.6	88.4 ± 3.9
	IBA	98.7 ± 2.6	95.1 ± 2.3	99.3 ± 1.7	112.3 ± 5.2	104.5 ± 2.1	97.4 ± 1.5	100.5 ± 1.5	98.3 ± 1.2	97.5 ± 2.1
6 mg L^{-1}	IAA	101.4 ± 2.2	100.6 ± 1.4	103.8 ± 4.3	103.7 ± 4.4	96.2 ± 1.7	97.5 ± 3.3	103.4 ± 3.7	101.8 ± 3.7	100.5 ± 2.1
	IPA	90.7 ± 2.0	98.2 ± 5.1	96.7 ± 3.5	92.6 ± 3.6	88.8 ± 4.1	96.3 ± 4.5	92.9 ± 2.3	97.1 ± 4.2	98.2 ± 3.5
	IBA	95.1 ± 1.8	96.6 ± 3.1	100.9 ± 2.9	91.9 ± 1.7	92.4 ± 3.0	100.7 ± 5.4	96.4 ± 2.8	98.1 ± 2.0	99.1 ± 1.2
8 mg L^{-1}	IAA	106.2 ± 2.1	103.2 ± 1.3	99.6 ± 1.8	111.4 ± 2.9	95.9 ± 2.5	87.3 ± 1.8	99.2 ± 3.8	100.1 ± 1.7	98.5 ± 2.7
	IPA	91.7 ± 1.8	93.6 ± 3.7	92.4 ± 2.8	91.5 ± 1.8	86.7 ± 3.3	88.0 ± 6.1	88.8 ± 1.6	89.2 ± 4.5	86.7 ± 3.1
	IBA	97.3 ± 1.9	95.9 ± 2.2	93.2 ± 4.1	94.8 ± 2.1	95.2 ± 3.2	87.9 ± 4.7	103.2 ± 3.4	100.6 ± 1.5	101.7 ± 2.3
10 mg L^{-1}	IAA	108.1 ± 2.0	103.4 ± 4.7	102.3 ± 2.4	110.1 ± 3.0	97.3 ± 2.8	89.2 ± 3.2	100.5 ± 3.3	99.3 ± 2.6	98.1 ± 4.3
	IPA	96.2 ± 3.9	97.8 ± 1.6	94.6 ± 3.5	89.9 ± 4.2	91.8 ± 1.2	91.4 ± 2.8	97.2 ± 1.4	93.7 ± 4.0	89.9 ± 2.7
	IBA	95.5 ± 2.7	94.2 ± 3.0	97.7 ± 1.5	90.5 ± 2.7	102.4 ± 5.6	89.0 ± 4.1	98.2 ± 3.5	96.8 ± 2.8	97.1 ± 4.4

Auxins standards were spiked in sample at three different concentrations (0.01, 0.05 and 0.25 ng mL^{-1}).

[a] Standard deviation.

References

1 J.H. Liu, W.F. Li, L.M. Duan, X. Li, L. Ji, Z.B. Geng, K.K. Huang, L.H. Lu, L.S. Zhou, Z.R. Liu, W. Chen, L.W. Liu, S.H. Feng, Y.G. Zhang, *Nano Lett.,* 2015, **15**, 5137-5142.

2 T.Y. Ma, S. Dai, M. Jaroniec, S.Z. Qiao, *Angew. Chem.*, 2014, **126**, 7409-7413.