Magnetic relaxation switching assay based on three-dimensional assembly of Fe₃O₄@ZIF-8 for detection of cadmium ion

Zhou Xu^a, ShiQin Dai^a, YiXuan Wang^a, YanQiu Chen^a, Yun-Hui Cheng^{a, c}, and Shuang Peng*^{a, b}

^a Hunan Provincial Key Laboratory of Cytochemistry, School of Food Science and Bioengineering, Changsha University of Science & Technology, Changsha, 410114, Hunan, China

^b College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, Hunan, China ^c School of Food Science and Engineering, Qilu University of Technology, Jinan, Shandong, 250353, China

Reagents and apparatus

Reagents

Zn (NO₃)₂·6H₂O, oleic acid (90%), Fe(acac)₃, 2-methylimidazole, phenyl ether (99%), 1,2hexadecanediol (97%), n-hexane, N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC), and N-hydroxysulfosuccinimide (sulfo-NHS) were purchased from J&K Scientific Ltd. (Beijing, China). The antigens and monoclonal mouse anti-Cd²⁺ were acquired from Lvkang (Wuxi, China). Meso-2,3-DMSA and oleylamine (>70%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Milli-Q ultrapure (18.2 MQ) water (Millipore, Billerica, MA, USA) was used throughout the study. Other solvents were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All the reagents and solvents were used directly without further purification.

Apparatus

 T_2 was determined with a 0.5 T NMI 20-CA magnetic resonance imaging instrument (Shanghai Niumag Corporation Limited, Shanghai, China). The size and zeta-potentials of the formed nanomaterials were measured with a dynamic laser light scattering instrument using a Zetasizer nano ZS (Malvern Instruments, Malvern, UK). FTIR spectroscopy was employed to analyze the molecular structures of the samples. The N₂ adsorption-desorption isotherms were recorded using a Quadrasorb-SI instrument at 77 K. The weighed samples were degassed at 150°C for 2 h before being measured. Crystal phases were investigated using a BRUKER AXS D8-Advance X-ray diffraction (XRD) system. X-ray photoelectron Spectroscopy (XPS) analyses were performed using an Escalab 250Xi. The concentration of Fe was determined by inductively coupling plasma spectrometry (Agilent 720ES). The specific surface areas and pore-size distributions were calculated using the Brunauer-Emmett-Teller (BET) model and the Barrett-Joyner-Halenda (BJH) method, respectively. The magnetic properties of the NPs were determined with a TM-VSM2014-MHR vibration sample magnetometer (Tamakawa, Sendai, Japan)



Figure S1. TEM image of ZIF-8.



Figure S2. The Size distribution of ZIF-8.



Figure S3. The XPS spectrum of Fe₃O₄@ZIF-8 (A); deconvoluted high-resolution Zn 2p (B), C 1s (C), and O 2p (D).

•

Determination method	Materials	Linear range (ng mL ⁻¹)	LOD (ng mL ⁻¹)	Refs.
Electrochemical	graphene oxide-bismuth nanoparticles	20.00-400.00	2.80	1
Surface plasmon resonance	competitive immunoassay combined SPR	3.57-758.37	1.25	2
Fluorescence Sensing	benzothiazole-based fluorescent probe	0-11241.10	130.39	3
Electrochemical	(AuNPs-GN-Cys) composites	0.50-40.00	0.10	4
colorimetry	MSA-AuNPs	7868.77- 22482.20	7868.77	5
whole-cell bioassay	Cell biosensor	10.00-200.00	5.00	6
Magnetic relaxation switch sensor	Au-Fe ₃ O ₄	0-11241.10	296.76	7
Magnetic resonance sensing	Fe ₃ O ₄ @ZIF-8	2.00-200.00	0.65	This work

 Table S1 Comparison for Cd²⁺ detection between this work and other methods.

References

- P. K. Sahoo, B. Panigrahy, S. Sahoo, A. K. Satpati, D. Li and D. Bahadur, *Biosens. Bioelectron.*, 2013, 43, 293-296.
- 2. G.-F. Kang, Y. Z. Wang, Y. F. Bai, Z.-Z. Chen and F. Feng, RSC Adv., 2017, 7, 44054-44058.
- J. Li, Y. Chen, T. Chen, J. Qiang, Z. Zhang, T. Wei, W. Zhang, F. Wang and X. Chen, Sens. Actuators B. Chem., 2018, 268, 446-455.
- 4. L. Zhu, L. Xu, B. Huang, N. Jia, L. Tan and S. Yao, *Electrochim. Acta.*, 2014, 115, 471-477.
- N. Chen, J. Chen, J. H. Yang, L. Y. Bai and Y. P. Zhang, J. Nanosci. Nanotechnol., 2016, 16, 840-843.
- 6. S. Kumar, N. Verma and A. K. Singh, Sens. Actuators B. Chem., 2017, 240, 248-254.
- 7. Y. Zhang, Y. Zhao, Y. Yang, J. Shen, H. Yang, Z. Zhou and S. Yang, *Sens. Actuators B. Chem.*, 2015, **220**, 622-626.