

Supporting Information

Olivine-type cadmium germanate: A new sensing semiconductor for the detection of formaldehyde at ppb level

Jiayu Li,^a Qihua Liang,^a Bo Zhang,^b Hui Chen,^a Xinhua Tian,^a Meihong Fan,^a Yunjia Guo,^a Ni Bai,^c Xiaoxin Zou^a and Guo-Dong Li ^{*a}

^a State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China

^b International Center of Future Science, Jilin University, Changchun13012, P. R. China

^c School of Mechanical and Metallurgical Engineering, Jiangsu University of Science and Technology, Zhangjiagang 215600, P. R. China

*Corresponding Author:

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China

E-mail address: lgd@jlu.edu.cn

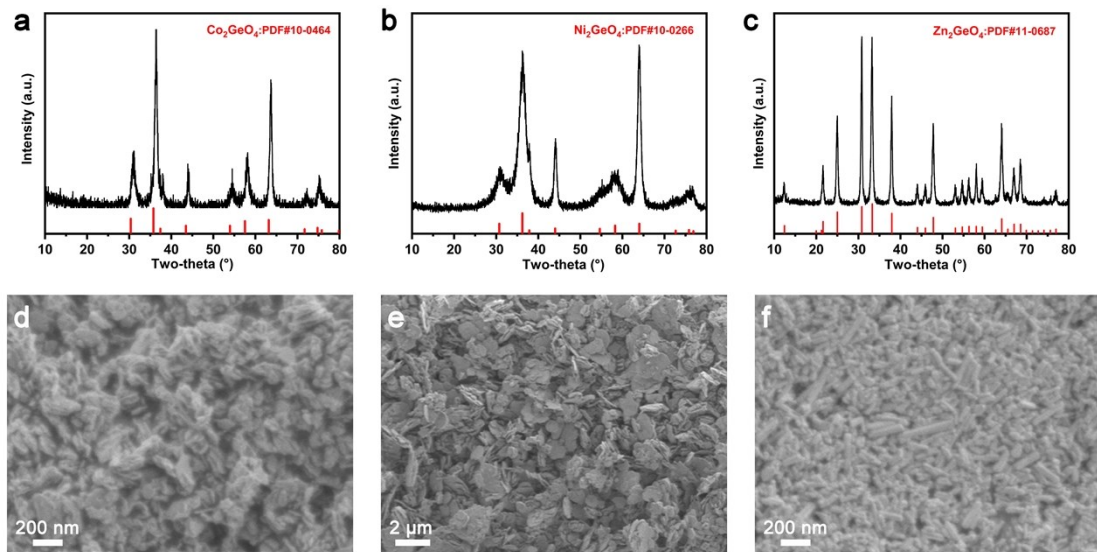


Fig. S1 (a-c) XRD patterns and (d-f) SEM images of Co_2GeO_4 , Ni_2GeO_4 and Zn_2GeO_4 , respectively.

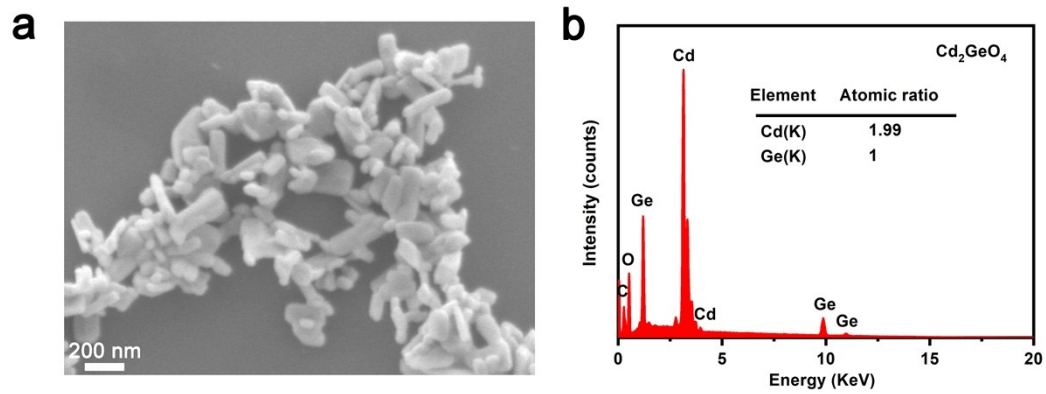


Fig. S2 (a) SEM image and (b) EDS spectrum of Cd_2GeO_4 .

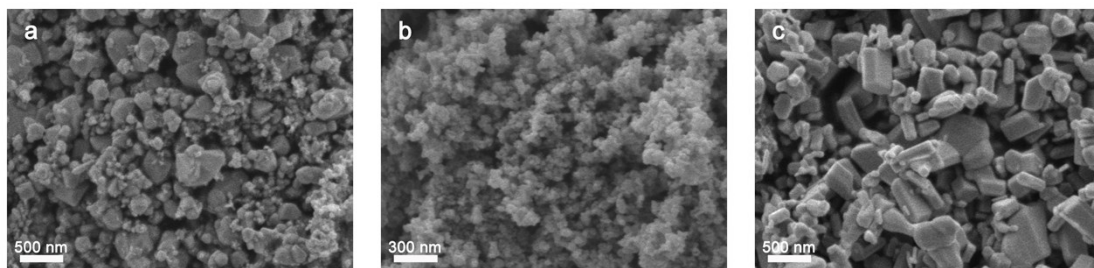


Fig. S3 SEM image of (a) SnO_2 , (b) In_2O_3 and (c) ZnO , respectively.

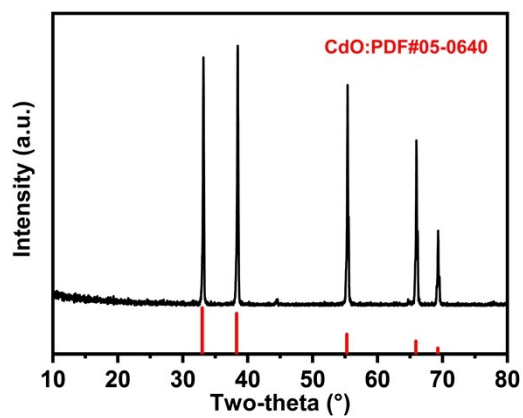


Fig. S4 XRD patterns and the standard PDF card of CdO (PDF No. 05-0640).

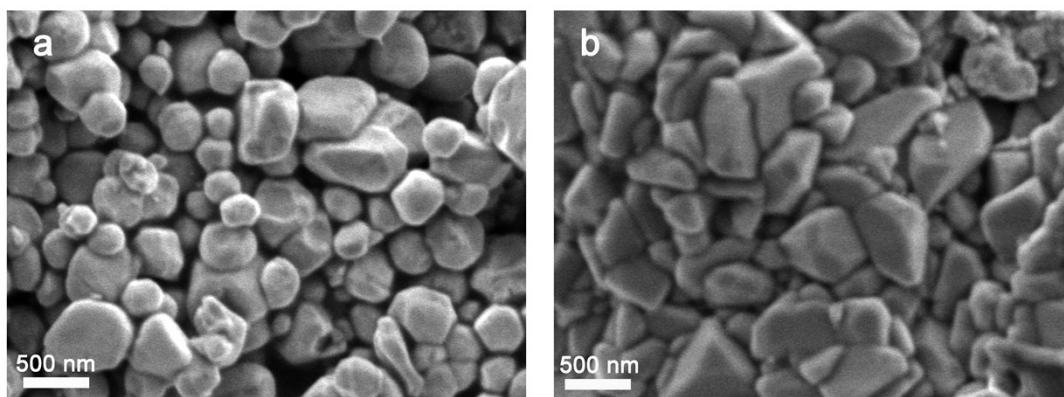


Fig. S5 SEM image of (a) CdO and (b) GeO₂.

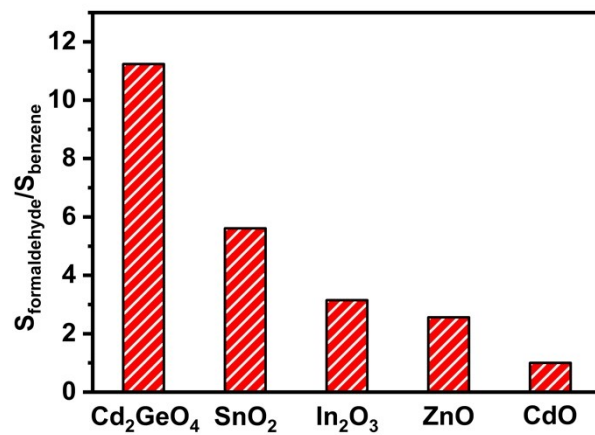


Fig. S6 The response of sensors based on Cd_2GeO_4 , SnO_2 , In_2O_3 , ZnO and CdO to 10 ppm formaldehyde vs benzene ($S_{\text{formaldehyde}}/S_{\text{benzene}}$, 140 °C).

Table S1 Gas response, operating temperature, and Response-recovery times of different nanostructured metal oxides to formaldehyde, as reported in the recent literatures 1-11 and this work.

Sensing materials	Synthetic method	BET surface area (m²/g)	Conc. (ppm)	S_{formaldehyde}	T_{sens} (°C)	t_{res}/t_{rec} (s)	Ref.
ZnO	Hydrothermal	-	100	9.6	275	16/28	1
In ₂ O ₃	Hydrothermal	129.81	20	≈5	130	-	2
SnO ₂	Hydrothermal	38.31	100	10.6	200	53/99	3
WO ₃	Hydrothermal	-	100	6.5	350	9/6	4
NiO	Hydrothermal	109	100	≈12	300	-	5
CuO	Hydrothermal	6.91	0.8	≈1.2	300	45/106	6
ZnSnO ₃	Precipitation	37	100	10.7	220	6/80	7
LaFeO ₃	Sol-gel	-	50	14.2	100	33/27	8
ZnCo ₂ O ₄	Hydrothermal	121	100	7.4	180	9/12	9
CdGa ₂ O ₄	Electrospinning	27	10	18.4	100	7/130	10
Zn ₂ SnO ₄	Hydrothermal	-	10	10.1	160	-	11
Cd ₂ GeO ₄	Hydrothermal	≈10	10	14.1	140	5/99	This work

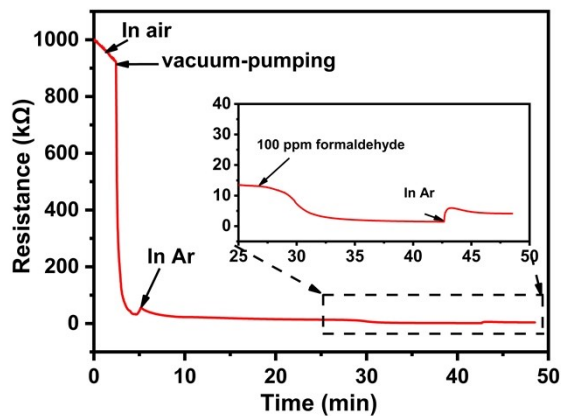


Fig. S7 The change in resistance of sensor based on Cd₂GeO₄ during vacuum extraction and gas-sensing properties of sensor based on Cd₂GeO₄ was measured in the absence of background oxygen using a homemade device.

References for SI

- 1 X. San, M. Li, D. Liu, G. Wang, Y. Shen, D. Meng and F. Meng, A facile one-step hydrothermal synthesis of NiO/ZnO heterojunction microflowers for the enhanced formaldehyde sensing properties, *Journal of Alloys and Compounds*, 2018, **739**, 260-269.
- 2 Z. Wang, C. Hou, Q. De, F. Gu and D. Han, One-Step Synthesis of Co-Doped In₂O₃ Nanorods for High Response of Formaldehyde Sensor at Low Temperature, *ACS Sens*, 2018, **3**, 468-475.
- 3 D. Meng, D. Liu, G. Wang, Y. Shen, X. San, M. Li and F. Meng, Low-temperature formaldehyde gas sensors based on NiO-SnO₂ heterojunction microflowers assembled by thin porous nanosheets, *Sensors and Actuators B: Chemical*, 2018, **273**, 418-428.
- 4 H. Yu, J. Li, Y. Tian, and Z. Li, Gas Sensing and Electrochemical Behaviors of Ag-doped 3D Spherical WO₃ Assembled by Nanostrips to Formaldehyde, *International Journal of Electrochemical Science*, 2018, **13**, 9281-9291.
- 5 X. Lai, G. Shen, P. Xue, B. Yan, H. Wang, P. Li, W. Xia and J. Fang, Ordered mesoporous NiO with thin pore walls and its enhanced sensing performance for formaldehyde, *Nanoscale*, 2015, **7**, 4005-4012.
- 6 H. J. Park, N. J. Choi, H. Kang, M. Y. Jung, J. W. Park, K. H. Park and D. S. Lee, A ppb-level formaldehyde gas sensor based on CuO nanocubes prepared using a polyol process, *Sensors and Actuators B: Chemical*, 2014, **203**, 282-288.
- 7 T. Zhou, T. Zhang, R. Zhang, Z. Lou, J. Deng and L. Wang, Hollow ZnSnO₃ cubes with controllable shells enabling highly efficient chemical sensing detection of formaldehyde vapors, *ACS Appl Mater Interfaces*, 2017, **9**, 14525-14533.
- 8 Y. Zhang, B. Jiang, M. Yuan, P. Li, W. Li and X. Zheng, Formaldehyde-sensing properties of LaFeO₃ particles synthesized by citrate sol-gel method, *Journal of Sol-Gel Science and Technology*, 2016, **79**, 167-175.
- 9 T. Zhou, N. Sui, R. Zhang and T. Zhang, Cabbage-shaped zinc-cobalt oxide (ZnCo₂O₄) sensing materials: Effects of zinc ion substitution and enhanced formaldehyde sensing properties, *J Colloid Interface Sci*, 2019, **537**, 520-527.
- 10 H. Chen, L. Sun, G. D. Li and X. Zou, Well-tuned surface oxygen chemistry of cation off-stoichiometric spinel oxides for highly selective and sensitive formaldehyde detection, *Chemistry of Materials*, 2018, **30**, 2018-2027.
- 11 X. Li, N. Zhang, C. Liu, S. Adimi, J. Zhou, D. Liu and S. Ruan, Enhanced gas sensing properties for formaldehyde based on ZnO/Zn₂SnO₄ composites from one-step hydrothermal synthesis, *Journal of Alloys and Compounds*, 2021, **850**.