Highly active and porous single-crystal In$_2$O$_3$ nanosheet for NO$_x$ gas sensor with excellent response at room temperature†

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Porous single-crystal In$_2$O$_3$ nanosheet (ps-In$_2$O$_3$ NS) was designed and prepared through a method of calcination after liquid reflux. Compared with the other In$_2$O$_3$ with different surface morphologies, the ps-In$_2$O$_3$ NS has gas sensing properties towards NO$_x$ at room temperature. Gas sensing data strongly demonstrate that this porous single-crystal In$_2$O$_3$ nanosheet exhibits a distinguished response (89.48) and fast response time (16.6 s) to 97.0 ppm NO$_x$. Meanwhile, the ps-In$_2$O$_3$ NS sensor presents a favorable linearity and good selectivity, and the detection of NO$_x$ is down to ppb levels at room temperature. The enhancement of the sensing response is attributed to the porous, single-crystal and two-dimensional nanosheet structure of the synthesized ps-In$_2$O$_3$ NS, which has much higher BET surface area, effective gas diffusion of slit pores and thus provides more active sites for the reaction of NO$_x$ with surface-adsorbed oxygen ions. This work would be important for the low-cost and high performance of the In$_2$O$_3$ material with highly promising applications in gas sensors.

Introduction

Chemical sensing based on various nanostructures has attracted enormous attentions, as that is widely perceived as one of the most promising fields for nanotechnology to generate significant impact. Among the chemicals studied, NO and NO$_2$ are amongst the most dangerous air pollutants, which play major roles in the formation of ozone and acid rain. Continued or frequent exposure to NO$_2$ concentrations higher than the air quality standard (53 ppb) may cause increased incidence of acute respiratory illness in children. The detection and measurement of NO$_x$ gas are thus of great importance in both environmental protection and human health.

Semiconducting metal oxides, such as, In$_2$O$_3$ (ref. 14) and Fe$_3$O$_4$ (ref. 14) have been extensively studied as chemical sensing materials due to their extraordinary properties, such as good response, short response time and selectivity to the ambient conditions in addition to the simplicity in materials synthesis and sensing device fabrication. Among the semiconducting metal oxides, In$_2$O$_3$, an important functional semiconductor material with remarkable electronic properties, which has been proven to be a very good candidate with a pronounced response to detect chemicals like NO$_x$, NH$_3$, ethanol, H$_2$S, acetone, formaldehyde, Cl$_2$ (ref. 24) and so on, has attracted considerable interest for several decades. A great attention has been recently paid to the development of new material “architectures” based on In$_2$O$_3$ at the nano-scale. Since detection of a given gas involves adsorption process on the surface of the sensing material, it is expected that the higher the surface, the greater the sensor response. Thus, it is quite essential to control the size, shape, and surface characteristics of the sensing material in order to achieve reliable properties. Two-dimensional (2D) and porous oxide provide a high surface area for chemical reaction, effective diffusion of gases species into the interface/surface, and enhance gas sensing performance. Various synthetic strategies to prepare 2D and porous structures for gas sensor applications have been reported. Compared with the other methods, such as vapor phase, the hydrothermal method are proven to be environmentally benign methods, which are able to produce In$_2$O$_3$ nanostructures in mass quantities. But, 2D porous single-crystal In$_2$O$_3$ nanosheet have not yet been reported. Our research is focused on enhancing the material surface area while keeping a high crystalline degree of the nanostructured In$_2$O$_3$. 

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In this paper, we reported the synthesis of porous single-crystal In$_2$O$_3$ nanosheet by calcinations of In(OH)$_3$ for the first time. During the synthesis, urea was used as an alkaline source and ligand for assembling the porous and single crystal nanosheet. The as-obtained ps-In$_2$O$_3$ NS was applied as a high performance gas sensor to detect NO$_2$ down to 485 ppb, one order of magnitude better than the previously fabricated In$_2$O$_3$ nanosheet NO$_2$ sensors at room temperature, suggesting a great potential in sensing related application.

Experimental
Sample preparation

Preparation of porous single-crystal In$_2$O$_3$ nanosheet. All chemicals were purchased with analytic grade and used without further purification. In(NO$_3$)$_3$·xH$_2$O ($M_w = 300.83$) and urea (H$_2$NCONH$_2$, $M_w = 60.05$) were purchased from Aladdin Chemical Reagents Co., Ltd. sodium dodecyl benzene sulfonate (SDBS, $M_w = 348.48$) was bought from Guangfu Fine Chemical Research Institute. Deionized water was homemade.

The porous single-crystal In$_2$O$_3$ nanosheet (ps-In$_2$O$_3$ NS) were fabricated by a facile liquid reflux method with In(NO$_3$)$_3$, urea and SDBS as In source, precipitant and the structure-director, respectively. The process is schematically illustrated in Scheme 1. Typically, In(NO$_3$)$_3$ (0.90 g), urea (0.80 g), SDBS (0.17 g) and H$_2$O (50 mL) were added into a beaker reservoir and then stirred vigorously for 1 h. The homogenous mixture was refluxed at 100 °C for 3 h in a flask to obtain the precursor of ps-In$_2$O$_3$ NSs. Subsequently, the precursor was heated to 550 °C for 4 h in air with a heating rate of 2 °C min$^{-1}$. After naturally cooling to room temperature, the ps-In$_2$O$_3$ NS sample was obtained. Different dosage of In(NO$_3$)$_3$ (0.6 g, 0.7 g, 0.8 g, 0.9 g, 1.0 g and 1.2 g) was marked as In$_2$O$_3$-0.6, In$_2$O$_3$-0.7, In$_2$O$_3$-0.8, In$_2$O$_3$-0.9, In$_2$O$_3$-1.0 and In$_2$O$_3$-1.2, while other reaction conditions are the same as that described above.

Material characterizations

The X-ray diffraction (XRD) patterns were examined by using an X-ray diffractometer (XRD, Bruker NEW D8 ADVANCE, Germany) with monochromatized Cu-K$_\alpha$ radiation with an accelerating voltage of 40 kV and an applied current of 20 mA. The morphologies and structures of the ps-In$_2$O$_3$ NS were observed by scanning electron microscope (SEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL-2100). X-ray photoelectron spectra (XPS) were recorded with a AXIS ULPRA DLD (Shimadzu Corporation) system equipped to analyze the surface composition of porous single-crystal In$_2$O$_3$ nanosheet, using monochromatic Al K$_\text{z}$ radiation (1486.4 eV), and C 1s (284.6 eV) was utilized as a reference to correct the binding energy. The nitrogen adsorption/desorption isotherms were measured at 77 K using a Micromeritics Tristar II. The BET surface area was analyzed by Brunauer–Emmett–Teller (BET) theory. The pore size distribution was computed by the nonlocal density functional theory (NLDFT) method.

Fabrication and measurements of gas sensors

An interdigitated Au electrode (7 × 5 × 0.38 mm) was selected for the gas sensing detection and the electrode spacing was 20 μm. The sample materials were spin-coated onto the interdigital electrode to form a sensitive film and then dried at 70 °C for 5 h to obtain a gas sensor. The sensor was installed into a test chamber with an inlet and an outlet. The electrical resistance measurements of the sensor were carried out at room temperature and a relative humidity (RH) around 40%. The NO$_2$ gas concentration was controlled by injecting volume of the gas and the chamber was purged with air to recover the sensor resistance. The gas response can be obtained from eqn (1).

$$R = (R_N - R_0)/R_0$$

where $R_0$ and $R_N$ are the resistances measured in air and the tested gas atmosphere (NO$_2$).

The response time is defined as the time required for the variation in resistance to reach 85% of the equilibrium value after a test gas was injected. The test was conducted at room temperature (20 °C) with a relative humidity (RH) around 40%.

Results and discussion

Structure, morphology characterization of ps-In$_2$O$_3$ NS

Porous single-crystal In$_2$O$_3$ nanosheet (ps-In$_2$O$_3$ NS) were synthesized by calcinating In(OH)$_3$ precursors. The phase transformation process of the In(OH)$_3$ sample during calcinations in air was studied via TG-DSC (Fig. S1†). It is observed that the decomposition started at 200 °C in the TG curve of In(OH)$_3$. The TG-DSC curve indicates an endothermic reaction around 260 °C. The In(OH)$_3$ directly converts into cubic phase of In$_2$O$_3$ in our experiment at 290 °C. If a temperature higher than 550 °C was chosen, the nanosheets shapes were destroyed and only In$_2$O$_3$ nanoparticles were obtained. Hence, the annealing temperature is ascertained to be 550 °C in order to obtain pure In$_2$O$_3$ nanosheets.

Fig. 1a shows a typical TEM image of the ps-In$_2$O$_3$ NS, in which the annealed In$_2$O$_3$ are porous nanosheet with a rough surface and many tiny pores with diameters of several nanometres exist along the whole area of the nanosheet. To further examine the surface morphology of the nanosheet, high-magnification TEM images were recorded, as shown in Fig. 1b and c. The selected-area electron diffraction (SAED) pattern

Scheme 1  The formation mechanism of the different porous In$_2$O$_3$.
(lower left inset of Fig. 1c) has confirmed this structure with single crystalline nature. The HR-TEM image of ps-In$_2$O$_3$ NS is displayed in Fig. 1d. The fringe spacing is about 0.29 nm, corresponding to the (222) crystal planes of the cubic In$_2$O$_3$.

Fig. 2a shows the powder X-ray diffraction (XRD) pattern of the In(OH)$_3$ precursor. All diffraction peaks are sharp and well-defined, suggesting that the sample is highly crystallized. The peaks at 2θ values of 31.8, 34.4, 36.3, 47.5, 56.6, 62.9 and 68.1° are consistent with the cubic phase In(OH)$_3$ (JCPDS no. 76-1464). The XRD pattern of the annealed ps-In$_2$O$_3$ NS is depicted in Fig. 2b. All of the detectable peaks in the pattern can be easily indexed to pure cubic In$_2$O$_3$ phase with $a = b = c = 10.140$ Å, in good agreement with the standard data (JCPDS no. 65-3170), confirming that this product is pure In$_2$O$_3$ with a cubic structure. No other diffraction peaks related to impurities are observed, indicating the formation of pure cubic In$_2$O$_3$.

In this synthesis, the indium ion concentration plays an important role in formation of different morphology In$_2$O$_3$. It can be seen that when the indium ion concentration is low (indium precursor of 0.6 g or 0.7 g seen in Fig. 3a and b and S2a and b†), In$_2$O$_3$ mainly are porous nanoparticles (NPs) with a rough surface and many tiny pores exist along the NPs. However, assembling of In$_2$O$_3$ occurred, when further increasing the indium precursor to 0.8 g seen in Fig. 3c, and S3a and b.† When indium precursor is increased to 0.9 g shown in Fig. 3d, the ps-In$_2$O$_3$ NS has been synthesized. But, when further increasing the mass of the indium precursor to 1.0 g or 1.2 g seen in Fig. 3e and f and S4a and b† the nanorods-like In$_2$O$_3$ formed with many pores on the surface. These different morphologies of In$_2$O$_3$ will affect the properties of gas sensing.

The different morphology structures of In$_2$O$_3$ prepared with different contents of In(NO$_3$)$_3$ is also studied by nitrogen adsorption–desorption measurement at 77 K. The N$_2$ adsorption desorption isotherm and pore size distribution curves of the typical synthesized In$_2$O$_3$ samples are shown in Fig. 4 and Fig. 1 (a–c) Representative TEM images of the synthesized ps-In$_2$O$_3$ NS, the inset shows the SAED pattern of the ps-In$_2$O$_3$ NS; (d) HRTEM image of ps-In$_2$O$_3$ NS, in which the (222) of cubic phase In$_2$O$_3$ can been seen.

Fig. 2 XRD patterns of (a) the In(OH)$_3$ precursors, and (b) the synthesized ps-In$_2$O$_3$ NS.

Fig. 3 Representative TEM images of the synthesized In$_2$O$_3$ with different In(NO$_3$)$_3$: (a) 0.6 g, (b) 0.7 g, (c) 0.8 g, (d) 0.9 g, (e) 1.0 g and (f) 1.2 g.
The Brunauer–Emmett–Teller (BET) surface area and total pore volume are 44.85 m² g⁻¹ and 0.28 cm³ g⁻¹, respectively. In detail, the isotherm of ps-In₂O₃ NS exhibits typical type IV curve with H₂ hysteresis loop. The pore size distribution exhibited in set of Fig. 4d also demonstrated multiple pore structure, and the average pore size about 25.51 nm. The large surface area and plentiful pores of ps-In₂O₃ NS can provide large accessible area for gas adsorption and desorption.

Gas sensing performances and sensing mechanism

It is known that the response of the gas sensors is mainly related to the gas concentration. To study the gas sensor properties of the ps-In₂O₃ NS sensor, series of experiments were carried out by varying the NOₓ gas concentration from 97.0–0.485 ppm. Fig. 5a shows the representative response–recovery cyclic curves for a the synthesized ps-In₂O₃ NS sensor to 97.0–0.485 ppm NOₓ operated at room temperature. The resistance signal represents the increase from the background resistance R₀ to an equilibrium value R_N when the NOₓ gas enters the test chamber, and restores to the background value when pure air enters the chamber. Finally, the almost complete recovery of the baseline resistance values at the end of each pulse indicated a reversible interaction between the sensing element and the target analytes, a key issue in event of technological applications.

Response to NOₓ was obtained from the calculation of resistance value by using eqn (1). According experimental results, the resistance increased when NOₓ contacts the ps-In₂O₃ NS surface. The ps-In₂O₃ NS is a N-type (electron conductivity) semiconductor. Similar results were obtained by Keying Shi and co-workers using a N-type SnO₂–In₂O₃ composite sensing material. Fig. 5b shows the corresponding relationship between response and response time under different NOₓ concentrations. When the concentration of NOₓ is 97.0 ppm, the response time is only 16.6 s, while the highest response reached is 89.48. It is found that response declined gradually with the decreased concentration of NOₓ. The limitation of NOₓ detection reaches as low as 485 ppb, and the response increases with the increasing gas concentration, which means the sensor is suitable for detecting a wide concentration range of NOₓ. Compared with the gas response and response time of the In₂O₃-0.7, In₂O₃-0.8, In₂O₃-0.9, In₂O₃-1.0 and In₂O₃-1.2, In₂O₃-0.9 shows the best gas sensing performance (in Tables S2 and S3). Moreover, we list the literatures about the gas sensing device that detect NOₓ (NO or NO₂) sensing in Table S4. It is observed that the gas sensing based on ps-In₂O₃ NS shows a low working temperature (room temperature), short response time and low detection limit. The detailed data would be seen in Table S2 (In₂O₃-0.9).

Fig. 6a shows response changes as the NOₓ concentration varies from 97.0–0.485 ppm. It was revealed that the linearity of the line formed by plotting log R (response) against NOₓ was R² = 0.94379. In view of practical applications, the sensor selectivity is a key concern and, at the same time, we measured the response to some gases such as NOₓ, O₂, NH₃, H₂, C₂H₂ and CO.
at room temperature. As shown in Fig. 6b, the ps-In2O3 NS sensor exhibits an excellent selectivity for NOx, and no response to O2, NH3, H2, C2H2 and CO. The ps-In2O3 NS sensor thus is suitable for application to commercial NOx sensing systems.

When the N-type In2O3 semiconductor is used in gas sensor and exposed in air, O2 molecules will be chemisorbed and can trap the electrons of the In2O3 to be changed into O2−, O−, and O22− on the In2O3 surfaces.39–41 Such chemisorbed oxygen is suggested to act as an electron donor, which depend strongly on temperature and the nature of the material. The formation of numerous oxygen species (e.g. O2−, O−, and O22−) which are known for their good catalytic activity in gas sensors, could improve the performance of NOx sensor.42–44 After the oxidizing gas (e.g. NO2) is introduced, some oxygen species will be reduced and removed from the surfaces above a certain temperature, resulting in the variation of the resistance of In2O3. The surface area and the morphology of a sensing film can directly decide the adsorption quantity of the oxygen species and hence have important impacts on the variation of resistance and the relevant response of the sensors. The Schematic for sensing mechanism is shown in Scheme 2. When the sensor film is exposed to NOx, the NOx gas molecules could attract the electrons from which results in an increase of the In2O3 sensor, because the In2O3 sensor is a N-type semiconductor. It finally results in the rapid increase of the resistance (Scheme 2). The target gas molecules (NO2) directly adsorb onto In2O3 and react with O− the In2O3 because of the high electron affinity of the NO2 molecules, which leads to electron transfer from the In2O3 to the NO2. The adsorption of NO2 on In2O3 leads to NO−2 and the adsorption of NO on In2O3 leads to NO−3.45 The process traps electrons from the conduction band or donor level of In2O3, and generate bidentate NO3−.5,46 The target gas molecules (NO) also can adsorb onto In2O3 and react with O− and generate NO2−.6

From all the above, the good gas sensing for NOx of the In2O3 sensor can be ascribed to the following two factors. First, effective gas diffusion and contact from pores of the In2O3 may also contribute to the good gas sensing. The porous structure can act as channels for gas diffusion, and thus provide more active sites for the reaction of NOx with surface-adsorbed oxygen ions. Second, the good gas sensing for NOx of the In2O3 sensor can be ascribed to the single crystal In2O3 and its own nanosheet structure which have a beneficial effect on the performance of the In2O3 sensor.47–48 The ideal structure is considered to be single crystal, because such gas sensing materials can exhibit high electron conductivities, and have abundant interfacial active sites and excellent stability.49,50 When the porous coupled with single crystallinity provides for the ease of gas diffusion and more active sites for the formation of reactive oxygen species.51 Then the oxygen species are benefit to the gas sensing performance. So the single crystal structure will lead to good gas sensing performance. These factors improve the performance of the ps-In2O3 NS sensor together.

Conclusions

In summary, we have demonstrated that the porous single-crystal In2O3 nanosheet via a liquid reflux method. The ps-In2O3 NS have gas sensing properties towards NOx and gas sensing data shows this porous single-crystal In2O3 nanosheet exhibit an excellent response (89.48), fast response time (16.6 s) and low testing limit to the NOx at room temperature,
respectively. The good gas sensing is attributed to the effective gas diffusion and contact by the pore canals on the surface of the In$_2$O$_3$ nanosheet.

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Notes and references

1 (a) Y. H. Hang and H. E. Katz, J. Mater. Chem. C, 2017, 5, 2160–2166; (b) Y. L. Guo, T. Wang, F. H. Chen, X. M. Sun, X. F. Li, Z. Z. Yu, P. B. Wan and X. D. Chen, Nanoscale, 2016, 8, 12073–12080.
2 J. Zhang, Z. Y. Qin, D. W. Zeng and C. S. Xie, Phys. Chem. Chem. Phys., 2017, 19, 6313–6329.
3 Z. M. Liu, H. Y. Liu, H. Zeng and Q. Xu, Catal. Sci. Technol., 2016, 6, 8063–8071.
4 Z. J. Feng, J. Q. Wang, X. Liu, Y. W. Wen, R. Chen, H. F. Yin, M. Q. Shen and B. Shan, Catal. Sci. Technol., 2016, 6, 5580–5589.
5 J. Gao, H. Y. Wu, J. Zhou, L. Y. Yao, G. Zhang, S. Xu, Y. Xie, L. Li and S. Y. Shi, New J. Chem., 2016, 40, 1306–1311.
6 L. Y. Yao, K. Kan, Y. F. Lin, J. B. Song, J. C. Wang, J. Gao, P. K. Shen, L. Li and K. Y. Shi, RSC Adv., 2015, 5, 15515–15523.
7 X. M. Xu, H. J. Zhang, C. Z. He, C. Y. Pu, Y. M. Leng, G. Q. Li, S. J. Hou, Y. S. Zhu, L. Fu and G. Y. Lu, RSC Adv., 2016, 6, 47083–47088.
8 J. B. Sun, P. Sun, D. L. Zhang, J. Xu, X. S. Liang, F. M. Liu and G. Y. Lu, RSC Adv., 2014, 4, 43429–43435.
9 P. Sun, X. Zhou, C. Wang, K. Shimanoe, G. Y. Lu and N. Yamazoe, J. Mater. Chem. A, 2014, 2, 1302–1308.
10 N. B. Tanvir, O. Yurchenko, C. Wilbertz and G. Urban, J. Mater. Chem. A, 2016, 4, 5294–5302.
11 Z. Li, C. K. Dong, J. Yang, S. Z. Qiao and X. W. Du, J. Mater. Chem. A, 2016, 4, 2699–2704.
12 J. C. Liao, Z. C. Li, G. J. Wang, C. H. Chen, S. S. Lv and M. Y. Li, Phys. Chem. Chem. Phys., 2016, 18, 4835–4841.
13 N. Qin, Q. Xiang, H. B. Zhao, J. C. Zhang and J. Q. Xu, CrystEngComm, 2014, 16, 7062–7073.
14 T. Y. Yang, L. Y. Du, C. B. Zhai, Z. F. Li, Q. Zhao, Y. Luo, D. J. Xing and M. Z. Zhang, J. Alloys Compd., 2017, 718, 396–404.
15 Y. Yang, C. G. Tian, J. C. Wang, L. Sun, K. Y. Shi, W. Zhou and H. G. Fu, Nanoscale, 2014, 6, 7369–7378.
16 H. Y. Wu, L. L. Wang, J. Zhou, J. Gao, G. Zhang, S. Xu, Y. Xie, L. Li and K. Y. Shi, J. Colloid Interface Sci., 2016, 466, 72–79.
17 X. M. Xu, X. Li, H. J. Zhang, C. H. Feng, C. Wang, F. M. Liu, Y. F. Sun, P. Sun and G. Y. Lu, RSC Adv., 2015, 5, 30297–30302.
18 H. F. Yang, X. Zhang, J. F. Li, W. T. Li, G. C. Xi, Y. Yan and H. Bai, Microporous Mesoporous Mater., 2014, 200, 140–144.
19 W. H. Zhang, W. C. Zhang, B. Chen, R. Shao, R. F. Guan, W. D. Zhang, Q. F. Zhang, G. H. Hou and L. Yue, Sens. Actuators, B, 2017, 239, 270–278.
20 Y. Y. Wang, G. T. Duan, Y. D. Zhu, H. W. Zhang, Z. K. Xu, Z. F. Dai and W. P. Cai, Sens. Actuators, B, 2016, 228, 74–84.
21 X. S. Liang, G. X. Jin, F. M. Liu, X. S. Zhang, S. S. An, J. Ma and G. Y. Lu, Ceram. Int., 2015, 41, 13780–13787.
22 J. Wang, X. P. Gan, Z. Y. Li and K. C. Zhou, Powder Technol., 2016, 303, 138–146.
23 L. T. Ma, H. Q. Fan, H. L. Tian, J. W. Fang and X. Z. Qian, Sens. Actuators, B, 2016, 222, 508–516.
24 P. Li and H. Q. Fan, Mater. Sci. Semicon. Process., 2015, 29, 83–89.
25 X. Y. Bai, W. J. Ji, S. N. Li, Y. C. Jiang, M. C. Hu and Q. G. Zhai, Cryst. Growth Des., 2017, 17, 423–427.
26 Y. Ren, X. R. Zhou, W. Luo, P. C. Yu, Y. H. Zhu, X. X. Li, X. W. Chang, Y. H. Deng and D. Y. Zhao, Chem. Mater., 2016, 28, 7997–8005.
27 X. H. Sun, H. R. Hao, H. M. Ji, S. Cai and C. M. Zheng, ACS Appl. Mater. Interfaces, 2014, 6, 401–409.
28 A. Shanmugasundaram, P. Basak, S. V. Manorama, B. Krishna and S. Sanyadanam, ACS Appl. Mater. Interfaces, 2015, 7, 7679–7689.
29 S. Y. Choi, Y. H. Kim, H. S. Chung, A. R. Kim, J. D. Kwon, J. Park, Y. L. Kim, S. H. Kwon, M. G. Hahm and B. Cho, ACS Appl. Mater. Interfaces, 2017, 9, 3817–3823.
30 M. Zhang, G. X. Feng, Z. G. Song, Y. P. Zhou, H. Y. Chao, D. Q. Yuan, T. T. Y. Tan, Z. G. Guo, Z. G. Hu, B. Z. Tang, B. Liu and D. Zhao, J. Am. Chem. Soc., 2014, 136, 7241–7244.
31 B. A. Prakasam, M. Lahtinen, A. Peuronen, M. Muruganandham and M. Sillanpää, Mater. Chem. Phys., 2016, 184, 183–188.
32 A. Qurashi, J. A. Rather, T. Yamazaki, M. Sohail, K. D. Wael, B. Merzougui and A. S. Hakeem, Sens. Actuators, B, 2015, 221, 167–171.
33 B. F. Wu, L. L. Wang, H. Y. Wu, K. Kan, G. Zhang, Y. Xie, Y. Tian, L. Li and K. Y. Shi, Microporous Mesoporous Mater., 2016, 225, 154–163.
34 H. X. Sun, Z. Y. Chu, D. H. Hong, G. Zhang, Y. Xie, L. Li and K. Y. Shi, J. Alloys Compd., 2016, 658, 561–568.
35 J. J. Liu, G. Chen, Y. G. Yu, Y. L. Wu, M. J. Zhou, H. Q. Zhang, C. D. Lv, H. Qin and X. Qi, RSC Adv., 2016, 6, 14615–14619.
36 S. Li, Z. F. Shi, Z. J. Tang and X. J. Li, J. Alloys Compd., 2017, 705, 198–204.
37 W. Yang, P. Wan, X. D. Zhou, J. M. Hu, Y. F. Guan and L. Feng, ACS Appl. Mater. Interfaces, 2014, 6, 21093–21100.
38 S. Xu, J. Gao, L. L. Wang, K. Kan, Y. Xie, P. K. Shen, L. Li and K. Y. Shi, Nanoscale, 2015, 7, 14643–14651.
39 H. Y. Wu, K. Kan, L. L. Wang, G. Zhang, Y. Yang, H. Li, L. Q. Jing, P. K. Shen, L. Li and K. Y. Shi, CrystEngComm, 2014, 16, 9116–9124.
40 P. Li, H. Q. Fan, Y. Cai, M. M. Xu, C. B. Long, M. M. Li, S. H. Lei and X. W. Zou, RSC Adv., 2014, 4, 15161–15170.
41 R. Q. Xing, Q. L. Li, L. Xia, J. Song, L. Xu, J. H. Zhang, Y. Xie and H. W. Song, Nanoscale, 2015, 7, 13051–13060.
42 S. Park, S. Kim, G. J. Sun and C. Lee, ACS Appl. Mater. Interfaces, 2015, 7, 8138–8146.
43 L. L. Wang, J. Gao, B. F. Wu, K. Kan, S. Xu, Y. Xie, L. Li and K. Y. Shi, ACS Appl. Mater. Interfaces, 2015, 7, 27152–27159.
44 M. Q. Huang, Z. D. Cui, X. J. Yang, S. L. Zhu, Z. Y. Li and Y. Q. Liang, RSC Adv., 2015, 5, 30038–30045.
45 Q. Y. Yang, X. B. Cui, J. Y. Liu, J. Zhao, Y. L. Wang, Y. Gao, P. Sun, J. Ma and G. Y. Lu, New J. Chem., 2016, 40, 2376–2382.
46 J. Gao, L. L. Wang, K. Kan, S. Xu, L. Q. Jing, S. Q. Liu, P. K. Shen, L. Li and K. Y. Shi, J. Mater. Chem. A, 2014, 2, 949–956.
47 Z. P. Li, H. Yan, S. L. Yuan, Y. J. Fan and J. H. Zhan, J. Colloid Interface Sci., 2011, 354, 89–93.
48 J. Rombach, A. Papadogianni, M. Mischo, V. Cimalla, L. Kirste, O. Ambacher, T. Berthold, S. Krischok, M. Himmerlich, S. Selve and O. Bierwagen, Sens. Actuators, B, 2016, 236, 909–916.
49 L. J. Guo, X. P. Shen, G. X. Zhu and K. M. Chen, Sens. Actuators, B, 2011, 155, 752–758.
50 S. Elouali, L. G. Bloor, R. Binions, I. P. Parkin, C. J. Carmalt and J. A. Darr, Langmuir, 2012, 28, 1879–1885.
51 J. J. Liu, G. Chen, Y. G. Yu, Y. L. Wu, M. J. Zhou, H. Q. Zhang, C. D. Lv, H. Qin and X. Qi, RSC Adv., 2016, 6, 14615–14619.