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Communication

Superhydrophobic hierarchical porous divinylbenzene polymer for BTEX sensing and toluene/water selective detection

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ABSTRACT

This work reports a superhydrophobic divinylbenzene polymer with hierarchical porous structure as sensing material to modify the quartz crystal microbalance (QCM) to detect benzene, toluene, ethylbenzene, and xylene (BTEX) vapor. Notably, sensing results toward toluene vapor in different relative humidities indicates that this superhydrophobic polymer has favorable toluene/water selective detection performance. Besides, the limit of detection toward toluene is lower than 1 ppm.

As typical volatile organic compounds (VOCs), benzene series, especially BTEX, are easily dispersed in the air because of their extremely easy volatile nature [1]. BTEX can paralyze the central nervous system of humans, causing neurasthenia, liver disease, and even cancer [2]. Therefore, using gas sensor for real-time detection of BTEX is necessary.

Gas sensors are the most common devices used to detect harmful gases [3–6]. Compared with other sensors, QCM sensor has many advantages such as the low cost and the ability of working under room temperature [7]. By modifying sensitive materials on the surface of QCM, the target gas can be adsorbed and the surface quality of QCM changes [8]. This change can be further transformed into frequency shift by Sauerbrey equation, and then recorded by computer [9]. Based on QCM platform, some studies on benzene sensors have been reported. For example, Kumar *et al.* used tetra-*tert*-butyl copper phthalocyanine to realize the sensing of BTEX. The response to 500 ppm of toluene can reach 60 Hz [10]. But none of these reports discussed the effect of humidity on the sensor response. Our research group detected the BTEX vapor *via* using superhydrophobic polyoctadecylsiloxane (PODS) based on QCM. Besides, PODS can stably detect toluene vapor under different relative humidities. However, when the concentration of toluene is 20 ppm, the response value is only about 7 Hz. It indicated that the detection limit of PODS to toluene can not be less than 20 ppm [11].

Herein, we used one-pot process to make divinylbenzene self-polymerize into a superhydrophobic hierarchical porous polymer. The QCM sensor modified by this polymer has good sensing performance to BTEX vapors, especially toluene. The sensing limit reaches 1 ppm. The change of environmental humidity did not affect the response of the sensor to toluene vapor, as shown in Fig. 1. Besides, because the adsorption mode of polymer to toluene is weak chemical adsorption, both selectivity and reversibility are considered in the sensing process.

The synthesis process of this experiment is one-pot method. First, 0.2 g of silica nanospheres was added to 24 mL of ethyl acetate, stirred by magnetic stirrer for 30 min to obtain a uniform dispersion. Then, we added 1.8 g of divinylbenzene (DVB) and 0.07 g of azobisisobutyronitrile (AIBN) to the dispersion, stirred the mixture for 2 h. We translated the solution to a teflon reactor, and put the reactor in an oven at 383 K overnight. Then, we opened the reactor and let the liquid dry naturally at a temperature of 303 K to obtain a polymer. The surface morphology of polymer was observed by JSM 6700 F scanning electron microscopy (SEM). Transmission electron microscopy (TEM) images were recorded by JEOL JEM-20 electron microscope operated at an accelerating voltage of 120 kV. Before TEM observation, the samples were dispersed in ethanol and subjected to ultra-sonication before being

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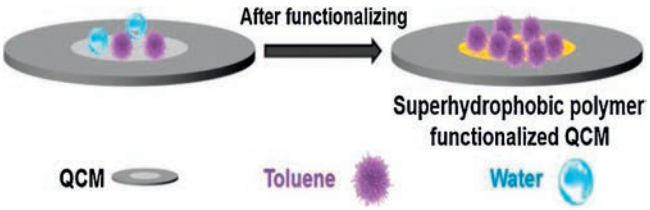

Fig. 1. Schematic of the selectively toluene/water sensing process.

drop cast onto a carbon-coated copper grid and air dried. The infrared spectrum of polymer was recorded by Nicolet iS10 FTIR system using potassium bromide as background, the scanning range was 400–4000 cm^{-1}. Nitrogen sorption isotherms were measured at 77 K using a Micromeritics ASAP 2020system with samples of ~0.1 g being degassed at 373 K for 12 h. Specific surface area and pore size were obtained using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models, respectively. Contact angle measurements of polymer modified QCMs were measured by Data physics OCA20. The static contact angles were measured in sessile drop mode. The volume of water droplet was set to 5 μL.

The sensing test methods of the polymer are all in the supporting information. Fig. S2 (Supporting information) is the infrared spectrum of the polymer we synthesized. The peaks at 2932 cm^{-1} and 1109 cm^{-1} are stretching vibrations derived from $-CH_2-$ and Si—O—Si, and the stretching vibration peaks of the C=C functional group and C—H in divinylbenzene were located at 3083 cm^{-1} and 1632 cm^{-1}. This result is consistent to the infrared spectrum of the divinylbenzene polymer in the literature, indicating the successful synthesis of the polymer with divinylbenzene as the monomer [12]. Fig. S3a (Supporting information) is the XPS spectrum of the surface of the polymer, and Fig. S3b (Supporting information) is the XPS spectrum of the interior of the polymer. It is obvious that the polymer contains oxygen (O), carbon (C) and silicon (Si) elements. The elemental composition of the internal part and of the surface part are generally uniform. Fig. 2a shows the results of nitrogen physical adsorption-desorption test of the polymer. The specific surface area of the polymer is 818.94 cm^2/g. Besides, the porous polymer has a typical type IV adsorption-desorption curve and a H4 type hysteresis loop. In the relative pressure range from 0.4 to 0.8, the adsorption amount has an upward trend, indicating that this porous polymer possesses mesopores. With the relative pressure larger than 0.8, the nitrogen adsorption capacity still rises significantly, indicating that there are macropores in the porous polymer. The pore size distribution of the multistage pore polymer is shown in the inset of Fig. 2a. It is obviously that the pore size of the polymer is distributed in the range from 10 nm to 100 nm, indicating its hierarchical porous structure.

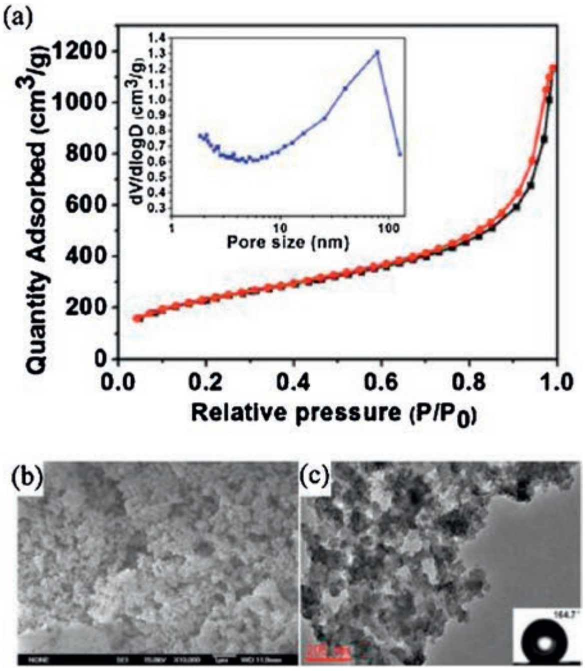

Fig. 2. (a) N_2 adsorption-desorption isotherms of the polymer. (b) The SEM image of the porous polymer. (c) The TEM image of the porous polymer. The inset is the contact angle test of QCM modified by the porous polymer.

The SEM image of the hierarchical porous polymer is shown in Fig. 2b. The SEM image shows that the hierarchical porous polymer is constructed of many stacked small particles. In orderto see the pore structure of these small particles, we used high- resolution TEM for further characterization, as shown in Fig. 2c. We found that the polymer contains many pores with different sizes. It should be attributed to the volstilization of ethyl acetate. Ethyl acetate is used as the solvent, which does not participate in the polymerization reaction. It stays in the interior of the polymer during the self-polymerization of divinylbenzene. During the drying process, ethyl acetate turned into gas, vaporizes away from the polymer, and leaving a large number of pores with different sizes [13]. The inset of Fig. 2c is the result of the water droplet contact angle test. The tested surface is the QCM surface modified by the hierarchical porous polymer. The contact angle is 164.7°. It is indicating that the hierarchical porous polymer is superhydrophobic.

In the testing environment with 65% relative humidity, we tested the sensing performance of the superhydrophobic hierarchical porous polymer to four BTEX vapors (benzene, toluene, ethylbenzene and xylene). The concentrations of BTEX were kept at 20 ppm. The corresponding response data is shown in Fig. 3a. The superhydrophobic hierarchical porous polymer has good response to all four BTEX vapors with the concentration of 20 ppm. The response rank is toluene > xylene > ethylbenzene > benzene. The response of the toluene is greater than 160 Hz, which is larger than that of PODS we designed to 20 ppm toluene vapor (7 Hz). This significant improvement in response may attribute to the large number of benzene ring structures and large specific surface areas in the superhydrophobic hierarchical porous polymer. The π-π interaction was formed between these benzene ring structures and toluene, enhancing the ability of adsorption. In addition, the polymer possesses rich pore structure. The porous structure can offer more adsorption sites for toluene molecules. Fig. 3b shows the responses to 5 ppm toluene under different relative humidity environments. The change of the relative humidity has very little effect on the response. Besides, the response of the sensor to several groups of high humidity (75% RH, 85% RH and 97% RH) is not obvious, and the maximum response is only 12 Hz (Fig. S7 in Supporting information). The hierarchical porous polymer is superhydrophobic, so no water molecules can adhere to its surface regardless of the increase or decrease of the ambient humidity. This result demonstrates that the superhydrophobic hierarchical porous polymer has the ability to detect toluene vapor stably in different relative humidity environments. Fig. 3c is the real-time response-recovery curve of the polymer to different concentrations of toluene vapor. With the toluene concentration is increasing from 5 ppm to 200 ppm, the response increases too, indicating that the polymer has excellent capability of detecting different concentrations of toluene vapor continuously. The inset in Fig. 3c is the real-time response- recovery curve of the polymer to 1 ppm toluene vapor. The response is about 8 Hz and the response time is about 50 s, the recovery time is about 20 s.

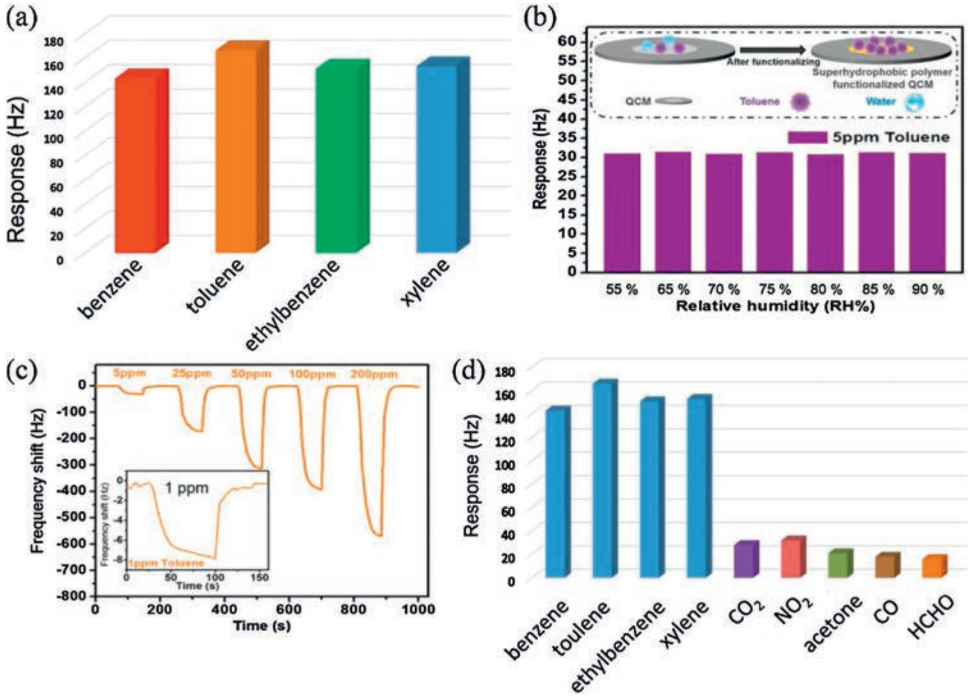

Fig. 3. (a) Response of the polymer to BTEX vapor (20 ppm). (b) Response of the polymer to toluene under different relative humidity environments. (c) Response curves of the polymer to toluene with different concentrations. The inset shows the response c urve of the polymer to 1 ppm toluene. (d) Responses of the polymer-based sensor to various kinds of interfering gases compared to BTEX. The concentration of all gases is 20 ppm.

As shown in Fig. S4 (Supporting information), we performed a two-week toluene vapor (20 ppm) sensing test. Before each test, we dropped the polymer modified QCM sensor into the water and then lifted it out. The sensing test was performed after the sensor was completely dried.

The maximum response of the superhydrophobic hierarchical porous polymer to 20 ppm toluene vapor is 173 Hz, and the minimum response was 162 Hz. Therefore, the response of the superhydrophobic hierarchical porous polymer based sensor to 20 ppm toluene vapor is stable. This stability is attributed to the stability of the benzene ring skeleton in the polymer. Besides, the self-cleaning ability of the superhydrophobic material also plays a role [14]. The superhydrophobic hierarchical porous polymer is able to maintain their properties better and ensure the stability of sensing application. In order to provide more evidence for the stability of the polymer, we characterized the TEM image and SEM image of the polymer after the sensing test, as shown in Figs. S5 and S6 (Supporting information). Comparing with the original TEM image (Fig. 2c), the pore structure of the polymer is well maintained, which verified the structure of the polymer is stable. Therefore, this superhydrophobic hierarchical porous polymer has the potential to stably detect toluene vapor over a long period of time.

In order to evaluate the selectivity of the sensor, we selected five common gases with a concentration of 20 ppm, including carbon dioxide, nitrogen dioxide, acetone, carbon-monoxide and formaldehyde (Fig. 3d). The responses of the superhydrophobic hierarchical porous polymer to 20 ppm BTEX are much larger than those of the other gases. It is indicating that this polymer is selective for the detection of BTEX vapors.

The excellent reversible sensing performance of this superhydrophobic hierarchical porous polymer is owed to the adsorption of toluene. The adsorption enthalpy (ΔH) between the polymer and toluene molecule can reflect the adsorption mode [15]. When the adsorption enthalpy is less than −40 kJ/mol, the adsorption mode is reversible physical adsorption. When the adsorption enthalpy is greater than −80 kJ/mol, the adsorption mode is a selective chemical reaction. When the adsorption enthalpy is between −40 kJ/mol and −80 kJ/mol, the adsorption mode is weak chemical adsorption, and it is selective and reversible. Therefore, we use the enthalpy extraction experiment, combined with the Clausius-Clapeyron equation to calculate the ΔH between the toluene and the polymer. Then, the adsorption mode can be extracted [16]. The results are shown in Fig. 4. The ΔH of the polymer to toluene is −50.29 kJ/mol, which is between −80 kJ/mol and −40 kJ/mol. The ΔH value indicates that the adsorption is selective and reversible, which is in accordance with the sensor test results [17]. The adsorption mode between toluene and the polymer is in the weak chemical adsorption. The mechanism of this adsorption should be the π-π adsorption between the toluene and the benzene ring structure in the polymer.

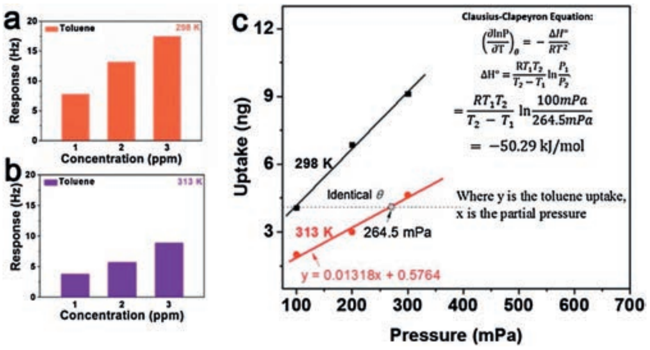

Fig. 4. Sensing curves of the polymer at (a) 298 K and (b) 313 K to toluene with different concentrations (1, 2 and 3 ppm). On the basis of the temperature-varied microgravimetric curves, plotted isotherms are used to extract the value of ΔH. (c) On the basis of the experimental results of the polymer in (a) and (b), two isotherms are plotted to calculate the value of ΔH.

In summary, useing divinylbenzene as the monomer and ethyl acetate as the solvent, a superhydrophobic hierarchical porous polymer was synthesized quickly. As sensing material for QCM, the sensing result shows that the sensor can detected BTEX, and stably detect toluene vapor under various relative humidity conditions. In addition, the sensor is capable of detecting toluene with the concentration of 1 ppm. The selectivity and long-term stability of the sensor are satisfactory. By using variable temperature experiment and Clausius-Clapeyron equation, we demonstrated the weak chemical adsorption between superhydrophobic hierarchical porous polymer and toluene molecule.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2020.02.051.

References

[1] L. Miller, X. Xu, A. Grgicak-Mannion, J. Brook, A. Wheeler, Atmos. Environ. 61 (2012) 305–315.
[2] F. Zhang, X. Wang, J. Dong, N. Qin, J. Xu, Sens. Actuator. B –Chem. 186 (2013) 126–131.
[3] X. Chu, J. Wang, L. Bai, et al., Sens. Actuator. B –Chem. 255 (2018) 2058–2065.
[4] H. Liu, Y. Zhang, Y. Dong, X. Chu, Talanta 199 (2019) 507–512.
[5] B. Wang, Y. Wang, Y. Lei, et al., J. Mater. Chem. C 4 (2016) 295–304.
[6] C. Qin, B. Wang, N. Wu, et al., Appl. Surf. Sci. 506 (2020) 144900.
[7] L. Wang, J. Gao, J. Xu, Sens. Actuator. B –Chem. 293 (2019) 71–82.
[8] D.Z. Shen, T.T. Cai, X.L. Zhu, et al., Chin. Chem. Lett. 26 (2015) 1022–1025.
[9] Y. Lu, S. Song, C. Hou, et al., Chin. Chem. Lett. 29 (2018) 65–68.
[10] A. Kumar, J. Brunet, C. Varenne, et al., Sens. Actuator. B -Chem. 210 (2015) 398–407.
[11] L. Wang, X. Cha, Y. Wu, et al., ACS Omega 3 (2018) 2437–2443.
[12] Y. Li, Z. Zhang, B. Ge, X. Men, Q. Xue, Green Chem. 18 (2016) 5266–5272.
[13] F. Svec, J.M. Frechet, Chem. Mater. 7 (1995) 707–715.
[14] F. Wang, T. Shen, C. Li, W. Li, G. Yan, Appl. Surf. Sci. 317 (2014) 1107–1112.
[15] D. Yan, P. Xu, Q. Xiang, et al., J. Mater. Chem. A 4 (2016) 3487–3493.
[16] P. Xu, H. Yu, X. Li, Anal. Chem. 88 (2016) 4903–4908.
[17] P. Xu, H. Yu, S. Guo, X. Li, Anal. Chem. 86 (2014) 4178–4418.