

## PAPER

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# An enhanced gas sensor based on SiO<sub>2</sub>@mesoporous MCM-41 core-shell nano-composites for SO<sub>2</sub> visual detection†

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A colorimetric sulfur dioxide (SO<sub>2</sub>) gas sensor based on a core-shell composite was developed. The composite was fabricated with a silicon dioxide core and a mesoporous MCM-41 shell (SiO<sub>2</sub>@MCM-41), and further loaded with a mixture of zinc chloride (ZnCl<sub>2</sub>), sodium nitroprusside (SNP) and hexamine as an SO<sub>2</sub> indicator. The sensing properties of SiO<sub>2</sub>@MCM-41 toward SO<sub>2</sub> were measured in solid powder, discs and a gas detection tube (GDT), respectively. Each of these sensing configurations showed a distinct color change from pale yellow to red, which indicates good potential for naked-eye detection of SO<sub>2</sub>. The limit of detection (LOD) is 2 ppm for SiO<sub>2</sub>@MCM-41 discs, which indicates high sensitivity to SO<sub>2</sub>. The performance of GDT suggested a linear relationship between the SO<sub>2</sub> concentration and the response length of the red portions in a range of 100–1000 ppm. This work shows promising potential of SiO<sub>2</sub>@MCM-41 as an easy, effective and rapid response sensing material for the *in situ* detection of SO<sub>2</sub>.

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## Introduction

SO<sub>2</sub> has drawn worldwide attention as one of the major pollutants in the atmosphere, and is mainly produced from the burning of fossil fuels. After dissolving in water vapor, SO<sub>2</sub> can interact with other particles in air and form an acid.<sup>1–4</sup> The emission of SO<sub>2</sub> has contributed to a series of problems that threaten the environment and human health, such as acid rain, eye irritation, and respiratory illnesses. The acid rain has caused great losses in forestry, agriculture, aquaculture, animal husbandry, and construction.<sup>5–7</sup> Moreover, the acid rain areas of China are the world's third largest acid rain areas next to Europe and North America, which have reached 30% of the total land area.<sup>8</sup> Without effective monitoring, air pollution and environmental acidification caused by the acid rain will increase. Therefore, it is significant to develop an SO<sub>2</sub> sensor with quick and accurate detection. Various approaches, including optics, semiconductor and electrolyte technologies, have been used to detect SO<sub>2</sub>.<sup>9–12</sup> However, the abovementioned methods for SO<sub>2</sub> detection usually suffer from the requirement of expensive instruments and complicated operation and are inconvenient for on-site monitoring.<sup>13,14</sup>

In the early 1990s, scientists in Mobil prepared M41S silicate mesoporous molecular sieves with highly uniform and ordered pore structures, which extend the pore size from micropores to mesopores.<sup>15</sup> Mesoporous materials have been vastly studied as adsorbents, sensors, catalysts, and drug carriers because of their high specific surface areas, tunable pore sizes, high mechanical strength and capability of chemical functionalization.<sup>16–20</sup> Various mesoporous materials have been reported for sensing. For example, mesoporous semiconductor metal oxides are widely used for gas sensing. Zhao *et al.* synthesised ordered mesoporous Fe doped In<sub>2</sub>O<sub>3</sub> for NO<sub>2</sub> gas sensing, and the as-prepared sensor exhibited an excellent response to NO<sub>2</sub> gas.<sup>21</sup> Izu *et al.* fabricated a V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub> resistive sensor for SO<sub>2</sub> detection, and the response range is from 20 to 5000 ppm.<sup>22</sup>

Although mesoporous materials have great potential in different areas, it is gradually becoming difficult for single-component mesoporous materials to meet the requirements of various applications. Recently, multifunctional mesoporous composites with a controlled microstructure, which can overcome the deficiencies of single-component mesoporous materials, have attracted increasing attention. Core-shell composites are nanostructures that have a core that is coated by another material, and they have been extensively explored for their unique structures and properties.<sup>23</sup> The hybrid structures of core-shell nanoparticles enhance the chemical and thermal stability. Also, the combined functionalities of cores and shells can allow them to achieve synergistic functions and have good

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potential for applications in various research fields.<sup>24–27</sup> In particular, considering the high surface to volume ratio, core-shell mesoporous materials can enhance the gas sensing performance. Wu *et al.*<sup>28</sup> fabricated hematite hollow spheres with a mesoporous shell, and the obtained  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> exhibited high gas sensitivity toward formaldehyde and ethanol at room temperature. Li *et al.*<sup>29</sup> proposed an NH<sub>3</sub> sensor based on a Au-loaded mesoporous In<sub>2</sub>O<sub>3</sub> nanosphere@polyaniline core-shell nanohybrid, and the sensor showed excellent sensitivity, selectivity and reproducibility to NH<sub>3</sub> at room temperature.

Gas sensing involves the adsorption and desorption processes on the surfaces of materials, and core-shell mesoporous materials with high surface specific areas are favorable for gas diffusion. Herein, we report core-shell silica nanoparticles with a silica core and ordered mesoporous silica shell for SO<sub>2</sub> sensing. The SiO<sub>2</sub> core was synthesized based on the Stöber method,<sup>30</sup> and the mesoporous MCM-41 shell was obtained by using cetyltrimethyl ammonium bromide (CTAB) as a template. ZnCl<sub>2</sub>, SNP and hexamine were mixed as an SO<sub>2</sub> indicator, which was loaded on the surface of MCM-41. The sensing performance of SO<sub>2</sub> gas was measured by the as-prepared SiO<sub>2</sub>@MCM-41 in 3 different forms, and each form of SiO<sub>2</sub>@MCM-41 involved a distinct color change. Additionally, the SiO<sub>2</sub>@MCM-41 sensor exhibited remarkable repeatability, high sensitivity and perfect response concentration linearity to SO<sub>2</sub> at room temperature, which suggests its promising applications for SO<sub>2</sub> gas sensing.

## Experimental

### Chemicals & apparatus

Glycerin, SNP, ZnCl<sub>2</sub>, hydrochloric acid and hexamine were purchased from Beijing Chemical Plant. Sodium hydroxide (NaOH) and anhydrous sodium sulfate were obtained from Beijing Tongguang Fine Chemicals Co. Ltd. Tetraethyl orthosilicate (TEOS), CTAB, ethanol, isopropanol, and ammonium hydroxide (NH<sub>3</sub>·H<sub>2</sub>O) were purchased from J&K Scientific Ltd.

The heating process was carried out in a DNP-9022 electrothermal incubator (Jinghong). The calcination of SiO<sub>2</sub>@MCM-41 was carried out in a muffle furnace (Yiheng, SX2-8-10NP). The microstructure was characterized using a scanning electron microscope (SEM) (Hitachi, S-4800) and a transmission electron microscope (TEM) (JEM-2100, JEOL). The porous properties of SiO<sub>2</sub>@MCM-41 were investigated by nitrogen adsorption and desorption at 77.3 K using an ASAP 2020, Micromeritics Instrument Corp, USA. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT).

### Synthesis of SiO<sub>2</sub>@MCM-41 composites

**Preparation of SiO<sub>2</sub>@MCM-41 core-shell nanoparticles.** SiO<sub>2</sub> nanoparticles were prepared according to a previously published method.<sup>31</sup> Briefly, 2 mL TEOS was added to 2 mL NH<sub>3</sub>·H<sub>2</sub>O, 20 mL deionized H<sub>2</sub>O and 200 mL isopropanol at 35 °C under magnetic stirring. After stirring for 2 h, the resul-

tant mixture was collected by centrifugation, followed by washing with ethanol and water 3 times. The above obtained SiO<sub>2</sub> nanospheres were dispersed in the mixed solution of 100 mL ethanol and 200 mL deionized H<sub>2</sub>O. 2 mL of 1 mol L<sup>-1</sup> NaOH was added into the above solution under 500 rpm magnetic stirring for 30 min. Then, 2 g CTAB was added to the mixture. After 30-minute-stirring, 0.45 mL TEOS was added to the mixture. The product was collected by centrifugation after reaction for 8 h and then washed repeatedly with ethanol and water to remove the template CTAB. Finally, the as-prepared products were heated in a muffle furnace to 550 °C for 6 h and SiO<sub>2</sub>@MCM-41 nanoparticles were produced.

**Preparation and loading of the SiO<sub>2</sub>@MCM-41 indicator.** The SiO<sub>2</sub>@MCM-41 indicator was prepared by dissolving 1 g ZnCl<sub>2</sub> in 10 mL ultrapure water with 0.5 mL hydrochloric acid, 1 g SNP in 10 mL ultrapure water with 0.5 mL glycerol, and 2 g hexamine in 10 mL ultrapure water. Afterward, we added 0.1, 0.2 and 0.1 mL as-prepared ZnCl<sub>2</sub>, SNP and hexamine solution to 30 mg SiO<sub>2</sub>@MCM-41 solid powder, respectively. After mixing the solution with SiO<sub>2</sub>@MCM-41 uniformly, the powder was dried in an oven for 30 min at 80 °C. The mechanism of ZnCl<sub>2</sub>, SNP and hexamine as an SO<sub>2</sub> indicator was referred to a previous report.<sup>32</sup> Before SiO<sub>2</sub>@MCM-41 was loaded with the SO<sub>2</sub> indicator, we weighed the SiO<sub>2</sub>@MCM-41 solid powder with an electric balance, and the weight was found to be 563 mg. Then we treated SiO<sub>2</sub>@MCM-41 with the SO<sub>2</sub> gas indicator and dried it in an oven. After the powder was completely dried, we weighed it again, and the weight was 576 mg. The weight of the SiO<sub>2</sub>@MCM-41 solid powder increased after being loaded with the SO<sub>2</sub> indicator; so we suggested that the indicator was loaded successfully.

### Gas sensing measurement

**SiO<sub>2</sub>@MCM-41 solid gas sensing test.** The gas sensing test was carried out on an as-fabricated gas sensing system, which is shown in S1.† SiO<sub>2</sub>@MCM-41 solid samples were placed inside an airbag (1L) and then different ratios of SO<sub>2</sub> and air were injected. After the balance between SO<sub>2</sub> adsorption and desorption, the color change of the SiO<sub>2</sub>@MCM-41 solid samples was recorded.

**Gas adsorption test.** The concentration of sulfate ions in solution can be obtained by ion chromatography.<sup>33</sup> 1.479 g anhydrous sodium sulfate was dissolved in ultrapure water and transferred to a 1 L volumetric flask as a sulfate ion stock liquid. We added 0.5, 1, 2.5, 5 and 7.5 mL of the sulfate ion stock liquid to 10 mL volumetric flasks, respectively. Sequentially, 50, 100, 250, 500 and 750 mg L<sup>-1</sup> sulfate ion standard solutions were obtained. Then, 30  $\mu$ L of each concentration sulfate ion standard solution was injected into the ion chromatography system, and a standard working curve was prepared based on the chromatographic peak area (S2).†

For the measurement of the gas adsorption rate of the SiO<sub>2</sub>@MCM-41 solid samples, first, 100 mL of 0.2 mol mL<sup>-1</sup> NaOH solution and hydrogen peroxide solution were mixed as the SO<sub>2</sub> adsorption solution. Afterward, we placed 30 mg of the SiO<sub>2</sub>@MCM-41 solid samples inside an airbag and injected

50 ml of  $\text{SO}_2$  at 15 °C. While waiting for the balance of gas adsorption, the remaining gas in the airbag was delivered into a sealed container with the as-prepared  $\text{SO}_2$  adsorption solution. After adsorption at 5 °C for 6 h, sulfate ions were detected by ion chromatography. Then the concentration of sulfate ions in the as-prepared  $\text{SO}_2$  adsorption solution can be obtained from the standard working curve. According to the amount of sulfate ions, the adsorption rate of  $\text{SO}_2$  was calculated.

**$3\text{SO}_2$  gas detection tube (GDT) test.** A homemade sensing system of  $\text{SO}_2$  GDT is presented in S3.† We injected different concentrations of  $\text{SO}_2$  gas prepared in airbags through a tube using a 100 mL syringe. After the gas passed through the  $\text{SO}_2$

GDT, it was collected by another 100 mL syringe, which was connected to the end of the tube. For each concentration, the experiment was repeated 10 times, and the color change and response length of the  $\text{SO}_2$  GDT were recorded. Scheme 1 shows a schematic illustration of the fabrication and sensing processes of  $\text{SiO}_2@\text{MCM}-41$ .

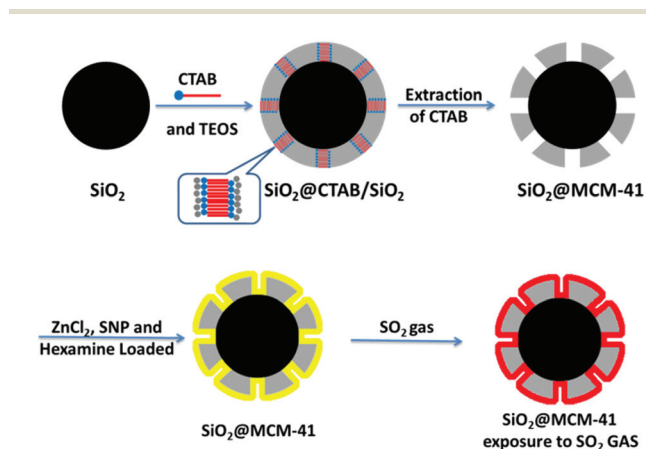
## Results and discussion

### Characterization of $\text{SiO}_2@\text{MCM}-41$

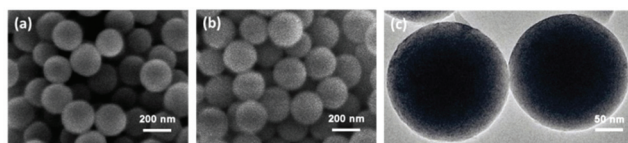
From the SEM image (Fig. 1a), the mean diameter of  $\text{SiO}_2$  particles is found to be  $206 \pm 5$  nm, and the sizes of these particles are uniform.  $\text{SiO}_2$  nanoparticles showed good monodispersity and sphericity. After the combination of  $\text{SiO}_2$  with MCM-41, the SEM image showed that the mean diameter of  $\text{SiO}_2@\text{MCM}-41$  increased to  $235 \pm 5$  nm, and the TEM image revealed a distinct core-shell structure of  $\text{SiO}_2@\text{MCM}-41$  composite nanoparticles, and both implied that the MCM-41 shell integrated with the  $\text{SiO}_2$  core successfully (Fig. 1b and c). The adsorption curves of  $\text{SiO}_2@\text{MCM}-41$  exhibited the type-IV isotherm (Fig. S4†), which is characteristic of mesoporous materials. A Brunauer–Emmett–Teller (BET) surface area of  $656 \text{ m}^2 \text{ g}^{-1}$  was estimated for  $\text{SiO}_2@\text{MCM}-41$ . The NLDFT gave rise to a narrow pore size distribution with an average pore width of 10.6 nm (Fig. S4†).

### The visual detection of $\text{SO}_2$

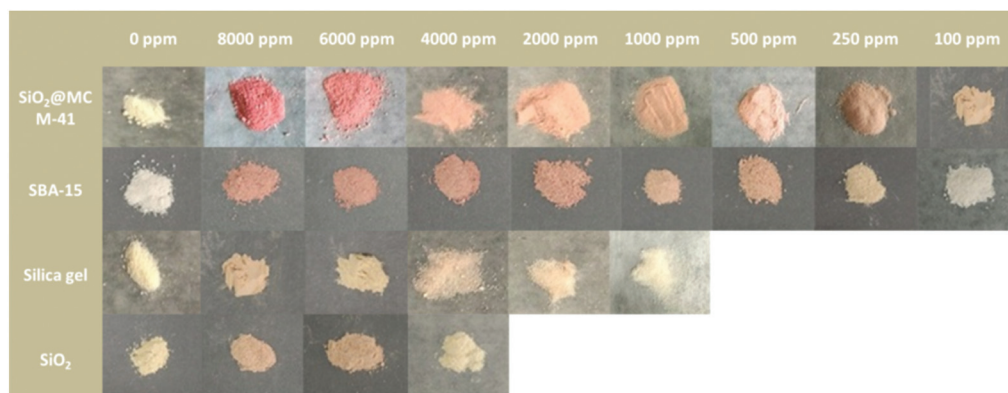
The response of the  $\text{SiO}_2@\text{MCM}-41$  nanocomposite toward  $\text{SO}_2$  was investigated over a range of 100–8000 ppm, and the results are presented in Fig. 2. After exposure to  $\text{SO}_2$ , the color of the  $\text{SiO}_2@\text{MCM}-41$  nanocomposite changed from pale yellow to red visually. In the presence of  $\text{SO}_2$  with different concentrations, the powder showed a different color. In this enclosed environment of  $\text{SO}_2$ , the observed response time is typically around 20 s. Based on the above experiment studies and literature findings, we proposed a mechanism for the sensing of  $\text{SiO}_2@\text{MCM}-41$ . After the gas adsorption,  $\text{SO}_3^{2-}$  is generated. When SNP and  $\text{SO}_3^{2-}$  are mixed, a deep red coloration develops. The coloration results from what is commonly



**Scheme 1** Schematic illustration of the fabrication and detection processes of  $\text{SiO}_2@\text{MCM}-41$ .

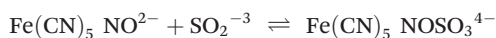


**Fig. 1** SEM images of (a)  $\text{SiO}_2$  nanoparticles and (b)  $\text{SiO}_2@\text{MCM}-41$  composite nanoparticles. (c) TEM image of  $\text{SiO}_2@\text{MCM}-41$  composite nanoparticles.



**Fig. 2** The visual color changes of  $\text{SiO}_2@\text{MCM}-41$ , SBA-15, silica gel and  $\text{SiO}_2$  in response to different concentrations of  $\text{SO}_2$  gas.

called the Boedeker reaction.<sup>34</sup> SNP and sulfite interact to give the red, highly dissociated sulphonitroprusside ions as follows:



According to the previous research,<sup>35</sup> the addition of zinc ions results in the formation of sparingly soluble zinc sulphonitroprusside and markedly increases the sensitivity of the Boedeker reaction. The alkaline medium can form ion-pairs of the type  $\text{Fe}(\text{CN})_5 \text{NOSO}_3 \text{M}^{3-}$ , where M is an alkaline medium. So we added  $\text{ZnCl}_2$  and hexamine to help increase the sensitivity of the Boedeker reaction. Also, the larger the volume of  $\text{SO}_2$  that  $\text{SiO}_2@\text{MCM-41}$  adsorbed, the larger the volume of sulphonitroprusside ions it reacted with, so that the color change of the response becomes more significant.

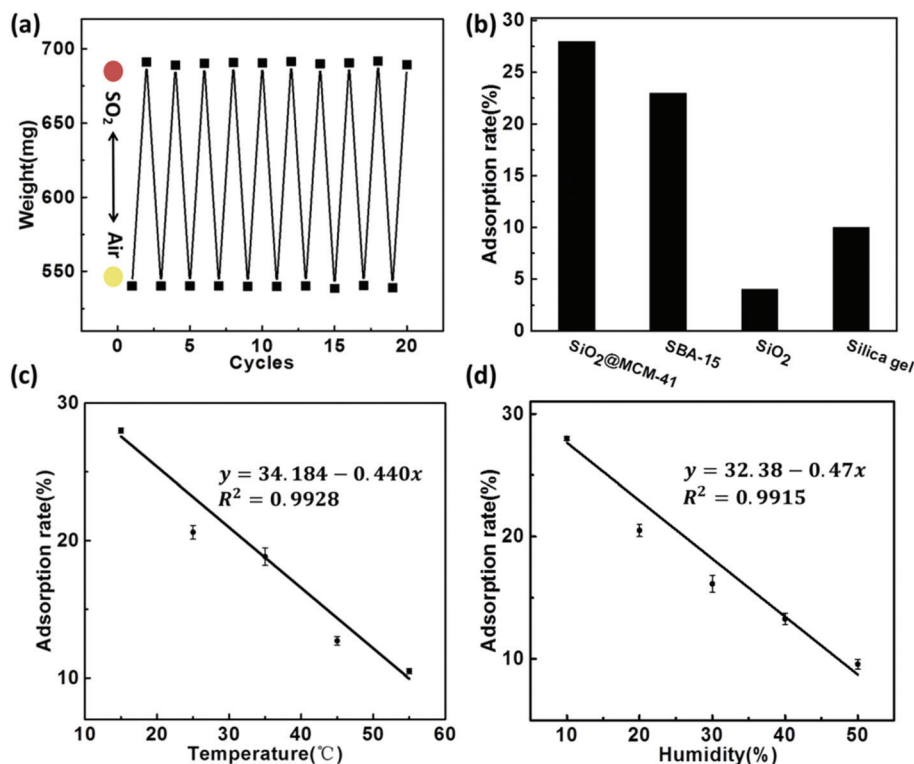
The  $\text{SO}_2$  sensing properties for other porous solids were also measured (Fig. 2). The  $\text{SiO}_2@\text{MCM-41}$  nanocomposite exhibits a higher response than SBA-15, silica gel and  $\text{SiO}_2$ , which is in agreement with their adsorption properties. Compared to  $\text{SiO}_2@\text{MCM-41}$ , the color changes of these materials are less obvious. The LOD value of  $\text{SiO}_2@\text{MCM-41}$  is lower than 100 ppm while the LOD values of SBA-15, silica gel and  $\text{SiO}_2$  are 250 ppm, 2000 ppm and 6000 ppm, respectively. These results are due to the difference in the specific surface areas of these solids.  $\text{SiO}_2@\text{MCM-41}$  has a higher specific

surface area than others, which can provide more binding sites and lead to more rapid adsorption of  $\text{SO}_2$  on the surface.

### The adsorption properties of the $\text{SiO}_2@\text{MCM-41}$ solid

The reproducibility of the  $\text{SiO}_2@\text{MCM-41}$  sensing system was evaluated as the weight changes of  $\text{SiO}_2@\text{MCM-41}$  for 10 cycles (Fig. 3a). The  $\text{SiO}_2@\text{MCM-41}$  nanoparticles were alternately placed under air and  $\text{SO}_2$  atmosphere at 15 °C. The initial weight of the solids was 540 mg in air, and changed to ~691 mg after exposure to  $\text{SO}_2$  gas. With the adsorption and desorption of  $\text{SO}_2$  from the pore structure of  $\text{SiO}_2@\text{MCM-41}$ , the weight changed and the adsorption rate was maintained after 10 cycles. Moreover, after  $\text{SO}_2$  gas bound with the indicator that loaded on  $\text{SiO}_2@\text{MCM-41}$ , the nanoparticles changed from white to red accordingly. The color change of  $\text{SiO}_2@\text{MCM-41}$  upon exposure to  $\text{SO}_2$  and air is reversible, which implies the remarkable stability and repeatability of this sensor.

Fig. 3b illustrates the adsorption capacity of a series of nanoparticles including  $\text{SiO}_2@\text{MCM-41}$ , SBA-15, silica gel and  $\text{SiO}_2$ . Owing to the porous structure and high specific surface area of  $\text{SiO}_2@\text{MCM-41}$ , which allow them to adsorb more gas, the adsorption capacity of  $\text{SiO}_2@\text{MCM-41}$  is higher than that of other porous materials. The adsorption rate for  $\text{SO}_2$  is 28% for  $\text{SiO}_2@\text{MCM-41}$  while the rates are 23%, 10% and 4% for



**Fig. 3** (a) Reversible changes of the weight of  $\text{SiO}_2@\text{MCM-41}$  when alternately exposed to air and  $\text{SO}_2$  gas, and the corresponding color changes. (b) The adsorption rates of  $\text{SiO}_2@\text{MCM-41}$ , SBA-15, silica gel and  $\text{SiO}_2$  toward  $\text{SO}_2$  gas. (c) The relationship between the adsorption rate and the temperature of  $\text{SO}_2$  gas. (d) The relationship between the adsorption rate and the humidity of  $\text{SO}_2$  gas.



SBA-15, silica gel and  $\text{SiO}_2$ . Hence, we believe that  $\text{SiO}_2@\text{MCM-41}$  is an ideal material for  $\text{SO}_2$  gas sensing.

For practical applications, temperature and humidity are critical influencing factors for gas sensors. Fig. 3c and d show how the adsorption rate toward  $\text{SO}_2$  varies with its temperature and humidity, respectively. With the increasing temperature, the absorption capacity decreased, suggesting an exothermic process (Fig. 3c). This indicated that low temperature is in favor of  $\text{SO}_2$  absorption. In a high-moisture environment, water vapor can block the adsorption sites on the surface of  $\text{SiO}_2@\text{MCM-41}$  and compete with  $\text{SO}_2$  gas for these sites. As a result, the adsorption rate for  $\text{SO}_2$  decreased (Fig. 3d). These adsorption behaviours under different temperatures and humidity are consistent with the references.<sup>36–38</sup>

### $\text{SO}_2$ sensing properties

The  $\text{SiO}_2@\text{MCM-41}$  solid was pressed into discs with a manual hydraulic press at 20 MPa to detect the gases of low-concentration  $\text{SO}_2$  (Fig. 4). When the  $\text{SO}_2$  gases with different concentrations were injected into the airbag, these discs exhibited different color changes in 10 s. With the increase of the  $\text{SO}_2$

concentration, more red reaction products were obtained and the color change became more obvious. Moreover, the LOD of  $\text{SiO}_2@\text{MCM-41}$  was also investigated. When the concentration of  $\text{SO}_2$  is lower than 2 ppm, the amount of gas  $\text{SiO}_2@\text{MCM-41}$  absorbed is too small to obtain sufficient red reaction products that the human eyes can observe. Thus, we suggest that the LOD of  $\text{SiO}_2@\text{MCM-41}$  is 2 ppm, which exhibits high sensitivity for  $\text{SO}_2$  naked-eye detection.

By observing the color change of the  $\text{SiO}_2@\text{MCM-41}$  solid, we can estimate the approximate concentration of  $\text{SO}_2$  gas. However, for a practical, visual and rapid  $\text{SO}_2$  gas sensor, it should be able to detect  $\text{SO}_2$  quantitatively. Therefore, we proposed an  $\text{SO}_2$  GDT. The apparatus consists of a transparent glass tube with iron meshes at both ends, and the  $\text{SiO}_2@\text{MCM-41}$  solid samples were fixed between the iron meshes. After the injection of different concentrations of  $\text{SO}_2$  gases through a 100 mL syringe, the color of the  $\text{SO}_2$  GDT turned to red at different lengths (Fig. 5a). The response lengths of the red portions toward 100, 200, 400, 800 and 1000 ppm are about 1.6, 3.2, 6.5, 12.5 and 17.4 mm, respectively. By measuring the length of the product, we can infer the concentration of  $\text{SO}_2$  gas quantitatively. Fig. 5b shows the relationship between the  $\text{SO}_2$  concentration and the color change length of the  $\text{SO}_2$  GDT. According to the calibration curve, a very good linear correlation with  $R^2 = 0.9971$  is achieved, which reveals a good potential application for *in situ*  $\text{SO}_2$  gas monitoring. Besides, the red reaction product of the GDT cannot remain stable in air for a long time. So after exposure to air for 2 days, the red reaction product vanished, and the  $\text{SO}_2$  GDT could be reused again.

### Conclusions

This paper reports a core-shell  $\text{SiO}_2@\text{MCM-41}$  sensor synthesized by an easily operated method and loaded with  $\text{ZnCl}_2$ , SNP and hexamine as indicators. The  $\text{SiO}_2@\text{MCM-41}$  sensor was made into solid powder, discs and a GDT. The as-prepared three  $\text{SiO}_2@\text{MCM-41}$  sensors were measured by exposure to different concentrations of  $\text{SO}_2$  gas, and the sensing properties

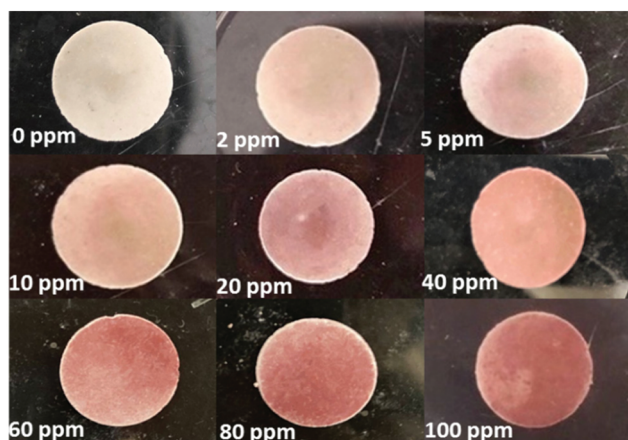


Fig. 4 The visual color changes of  $\text{SiO}_2@\text{MCM-41}$  discs in response to low concentrations of  $\text{SO}_2$  gases.

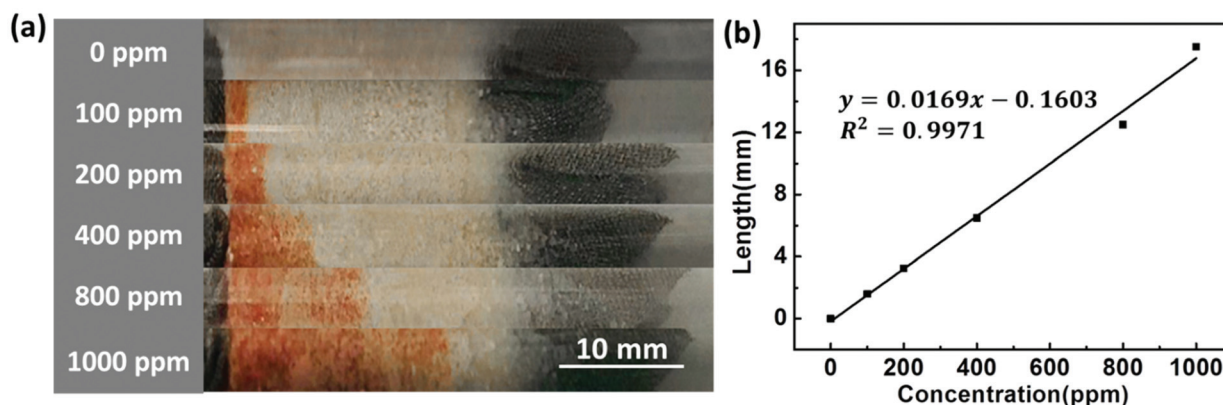


Fig. 5 (a) The visual color change length and (b) corresponding fitting curve of the  $\text{SO}_2$  GDT in response to various concentrations of  $\text{SO}_2$  gases.

were systematically investigated. As a result, the SiO<sub>2</sub>@MCM-41 sensor displayed different color changes with various concentrations and a quick response. The LOD of SiO<sub>2</sub>@MCM-41 is 2 ppm, which indicated that the sensor is highly sensitive. Moreover, the SO<sub>2</sub> GDT performed colorimetric quantitative detection, and hence we suggest the potential application of practical SO<sub>2</sub> sensing. In summary, this SiO<sub>2</sub>@MCM-41 sensor is easy to fabricate and operate. The research results in this paper show high sensitivity, outstanding stability and perfect response concentration linearity to SO<sub>2</sub>. Besides, the distinct color change of SiO<sub>2</sub>@MCM-41 after exposure to SO<sub>2</sub> makes naked-eye detection possible. Thus, we believe it is a qualified candidate for SO<sub>2</sub> *in situ* monitoring.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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