

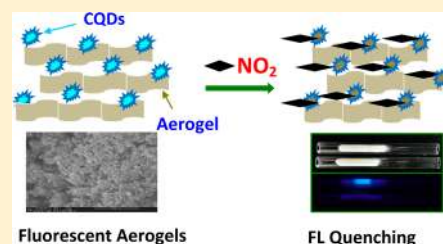
Carbon Quantum Dot-Functionalized Aerogels for NO<sub>2</sub> Gas Sensing

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## Supporting Information

**ABSTRACT:** Silica aerogels functionalized with strongly fluorescent carbon quantum dots were first prepared and used for simple, sensitive, and selective sensing of NO<sub>2</sub> gas. In the presence of ethanol, homemade silica aerogels with a large specific surface area of 801.17 m<sup>2</sup>/g were functionalized with branched polyethylenimine-capped quantum dots (BPEI-CQDs) with fluorescence quantum yield higher than 40%. The prepared porous CQD-aerogel hybrid material could maintain its excellent fluorescence (FL) activity in its solid state. The FL of CQD-aerogel hybrid material could be selectively and sensitively quenched by NO<sub>2</sub> gas, suggesting a promising application of the new FL-functionalized aerogels in gas sensing.



Aerogels are a class of porous materials, which are the world's lowest density solid,<sup>1</sup> and have been called solid smoke. Aerogels have many unique properties, such as extremely low density, high surface area, low thermal conductivity, weak dielectric permittivity, and so on. Recently, several types of aerogels, such as silicon,<sup>2,3</sup> carbon,<sup>4,5</sup> metal chalcogenides,<sup>6–8</sup> metal oxide systems,<sup>9,10</sup> metal systems,<sup>11,12</sup> and organic polymers<sup>13,14</sup> have been reported. Among the aerogels, silica aerogels are most commonly used, mainly in building insulation materials and the aerospace industry,<sup>3</sup> due to their low thermal conductivity and low density. Carbon aerogels are mainly used in electrode capacitance material,<sup>15</sup> and metal or metal compound aerogels are usually used in industrial catalysis<sup>5,9,10</sup> due to their high surface areas. Aerogels can be prepared in various ways, such as supercritical fluid drying,<sup>3,6,13</sup> chemical vapor deposition,<sup>11</sup> and solvent cross-linking.<sup>16,17</sup> However, up to now, little attention has been paid to preparation of functionalized aerogels for chemical sensing.

Carbon quantum dots (CQDs) are recently emerging zero-dimensional carbon nanomaterials with size less than 10 nm.<sup>18</sup> CQDs not only have the advantages of the traditional semiconductor quantum dots such as photoluminescence and unique optical and electrochemical properties but also have low toxicity and are environmentally friendly compared with those toxic heavy metal quantum dots.<sup>18</sup> Therefore, more and more attention has been paid to the syntheses, property studies, and applications of these emerging carbon nanomaterials.<sup>19–25</sup> Recently, we have prepared polyamine-capped carbon quantum dots by the low-temperature (<200 °C) carbonization of citric acid with branched polyethylenimine (BPEI) in one simple step.<sup>26</sup> The obtained BPEI-CQDs not only are polyamine functionalized but also exhibit high fluorescence quantum yield (FLQY >40%), thus having promising applications in chemical sensing.

It would be of considerable research interest to introduce the CQDs with high FLQY into aerogels (i.e., functionalize

aerogels with the CQDs), since novel chemical sensors for gases may be developed by using the CQD-aerogel hybrid materials. To the best of our knowledge, to date, no work has been done on the preparation of CQD-aerogel hybrid materials for sensing applications; thus, the present work mainly focused on the functionalization of silica aerogels with the BPEI-CQDs and applicability of the CQD-aerogel hybrid material-based sensor for the detection of air pollutants. Nitrogen dioxide (NO<sub>2</sub>) was used as the model pollutant in the sensing, since NO<sub>2</sub> is one of the most prominent air pollutants. It has been well recognized that NO<sub>2</sub> and its derivatives are the important sources of atmospheric particulate matter (such as PM<sub>2.5</sub>), photochemical smog, and acid rain and thus are harmful to humans' respiratory systems and cause a series of diseases such as asthma,<sup>27,28</sup> chronic pharyngitis,<sup>29</sup> and pulmonary edema<sup>30</sup> and very serious damage to the ecological environment.<sup>31,32</sup> Therefore, the detection of NO<sub>2</sub> in atmosphere is very important. In this paper, we try to use the prepared novel CQD-aerogel hybrid materials to construct new gas sensors for the detection of NO<sub>2</sub>.

## EXPERIMENTAL SECTION

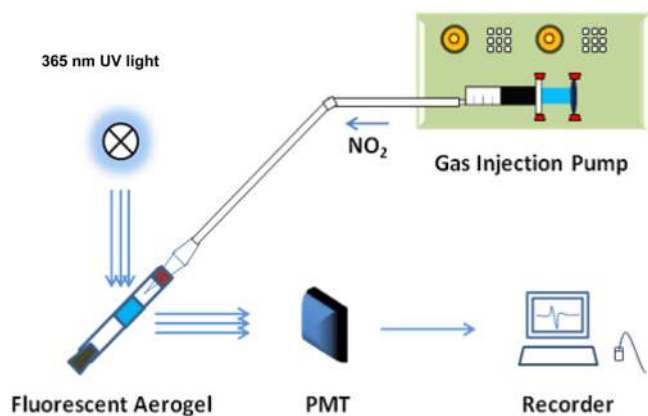
**Materials.** Tetraethylorthosilicate (TEOS), anhydrous ethanol (ETOH), hydrochloric acid (HCl), and ammonia (NH<sub>3</sub>·H<sub>2</sub>O) were of analytical grade and used as received. Citric acid and branched polyethylenimine (BPEI) used for preparing BPEI-capped carbon quantum dots (CQDs) were purchased, respectively, from Alfa Aesar and Aladdin (Shanghai, China). Doubly distilled water was used throughout the experiment.

**Instrumentation.** An autoclave (GSH, Weihai Huixin Chemical Industrial & Mechanic Co., Ltd., China) was used

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**Figure 1.** Schematic diagram of the FL aerogel-based sensor for  $\text{NO}_2$ .

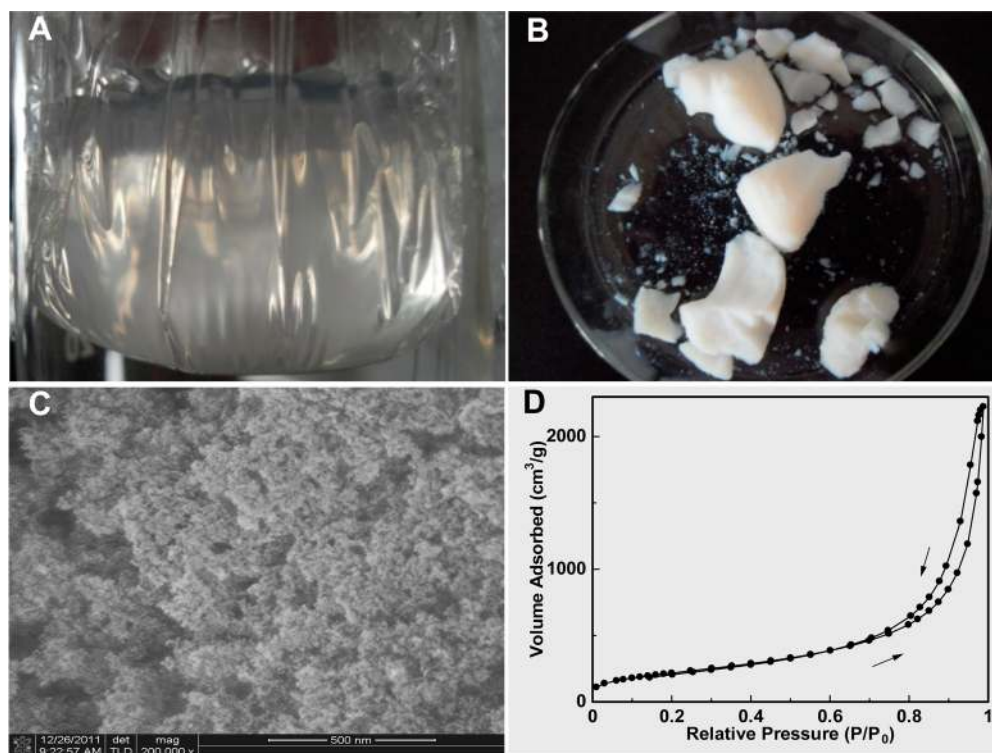
to generate ethanol supercritical fluid for drying silica wet gel. A scanning electron microscopy (SEM) image was obtained from an American FEI (Nova nano SEM-230). Surface area and porosity of the nanomaterials were measured by an ASAP 2020 accelerated surface area and porosimetry system (Micromeritics Instrument Corporation). UV–vis absorption spectra were recorded by a Lambda 750 UV/vis/NIR spectrophotometer (Perkin-Elmer). All fluorescent spectra of the prepared CQDs were obtained by a fluorescence spectrophotometer (Hitachi F-4600, Japan). A double channel microinfusion pump (WZS-50F6, Smiths Medical Instrument Co., Ltd.) was used to pump gas samples.

**Preparation of CQD-Functionalized Aerogels.** First, blank silica aerogels were prepared before functionalization with CQDs. The wet silica gel was synthesized by using tetraethylorthosilicate (TEOS) as the gel precursor and with

the method and devices described in the Supporting Information (Figure S1). The wet gel was prepared in a bag made of a piece of plastic wrap to prevent the fragile wet gel from breaking in the subsequent stripping process. The prepared wet gel was stripped carefully from the bag and then dried by ethanol supercritical fluid generated in a homemade supercritical fluid generator (Figure S2, Supporting Information) with the experimental procedures described in the Supporting Information. Finally, white and light silica aerogels were obtained after drying the wet silica gel.

The obtained blank silica aerogels were further functionalized by PEI-CQDs (Figures S3 and S4, Supporting Information) with strong FL activity (FLQY >40% at Ex 360 nm and Em 460 nm) synthesized by a previously reported method.<sup>26</sup> First, the prepared blank silica aerogels were grounded into powder; then, 1 mL of PEI-CQD solution (0.168 mg/mL) was added into a beaker containing 0.1 g of aerogel powder, followed by addition of 200  $\mu\text{L}$  of anhydrous ethanol for enhancing the interaction between CQDs and aerogels. Then, the mixture solution was stirred for 1 h to ensure the pores in the aerogels were completely filled with the CQD solution. Finally, CQD-functionalized aerogels were obtained by drying the CQD-aerogel mixture solution in an oven for 12 h at 70  $^\circ\text{C}$ . The resulting CQD-functionalized aerogels were ground once again before further sensing applications.

**Construction and Operation of FL Aerogel-Based Sensor for  $\text{NO}_2$ .** The FL aerogel-based gas sensor for  $\text{NO}_2$  was constructed as shown in Figure 1. The gas sensor consisted of a gas injection pump for injecting gas sample into the sensing unit, a UV light source to stimulate FL emission of CQD-functionalized aerogels, a FL aerogel-loading quartz tube, a PMT module for transferring light signal into electric signal, and a data processor (or a recorder). After construction, the gas

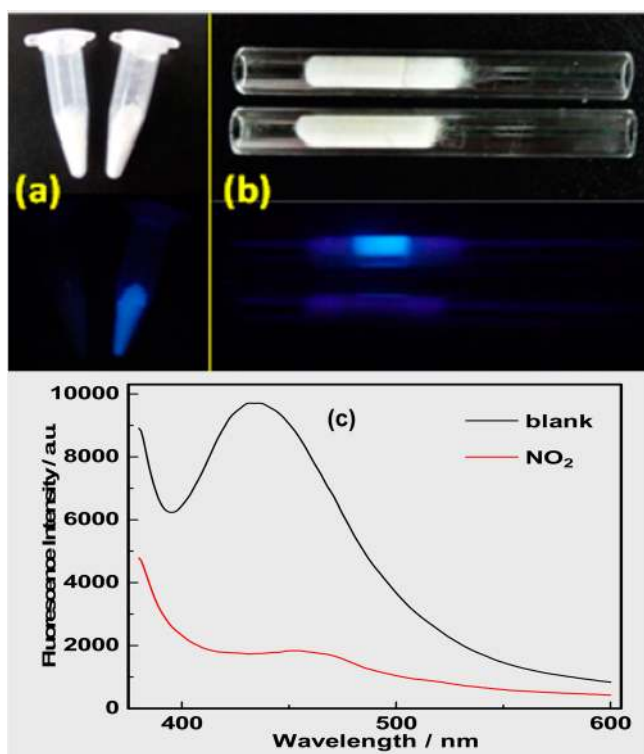


**Figure 2.** The preparation of silica aerogels. (A) The wet silica gel contained in a bag made of a piece of plastic wrap; (B) the as-prepared silica aerogels; (C) SEM image obtained for the silica aerogels; (D)  $\text{N}_2$  adsorption–desorption isotherms measured for the silica aerogels.

sensor was performed as follows: First,  $N_2$  used as the carrier gas was pumped into the sensing tube for 10 min to remove air in the sensor. Then, the excitation and emission wavelengths were set at 360 and 430 nm, respectively. 50 mL gas samples with various  $NO_2$  concentrations (prepared by the dilution of concentrated  $NO_2$  with  $N_2$ ) were passed into the sensor with the flow rate of 10 mL/min (i.e., the injection of  $NO_2$  gas sample was finished within 5 min). Finally, the FL spectra (from 380 to 600 nm) were recorded at 5 min intervals until the total measurement time reached 60 min.

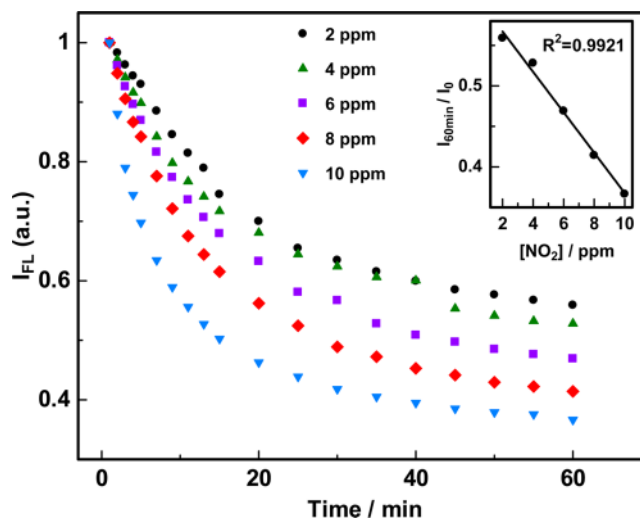
## RESULTS AND DISCUSSION

**Characterization of Silica Aerogels and CQD-Functionalized Aerogels.** The wet silica gels (Figure 2A) were

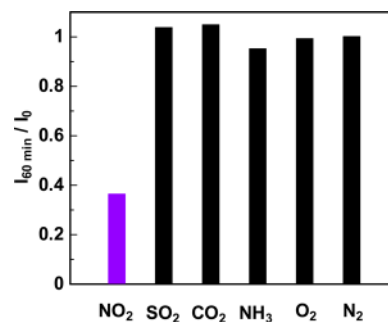


**Figure 3.** (a) The photos of CQD-functionalized aerogels (right) and blank aerogels (left) under a visible light (upper section) and illuminated by a UV beam of 365 nm (lower section). (b) The photos of CQD-functionalized aerogels in quartz tubes without (top) and with (bottom) passing 1000 ppm  $NO_2$  under a visible light (upper section) and illuminated by a UV beam of 365 nm (lower section). (c) The fluorescence spectra of the CQD-functionalized aerogels exposed to  $N_2$  (black curve) and 1000 ppm  $NO_2$  (red curve).

changed to white and light silica aerogels (Figure 2B) after being dried in the ethanol supercritical fluid. SEM shows that the obtained silica aerogels are sponge-like and have abundant nanopores (Figure 1C). The test of Brunauer–Emmet–Teller (BET) demonstrates that the blank silica aerogels have a large specific surface area (801.17  $m^2/g$ ), suggesting that these silica aerogels are very suitable to be used as gas adsorption material. The nitrogen adsorption–desorption isotherms show that the adsorption and desorption of  $N_2$  by the silica aerogels are completely reversible (Figure 1D), implying that the silica aerogels may be used as a reversible absorbent in the detection of the pollutant gases such as  $NO_2$ .



**Figure 4.** Fluorescent responses of CQD-functionalized aerogels to various concentrations of  $NO_2$  gas samples (from top: 2, 4, 6, 8, and 10 ppm). Inset: Linear calibration plots of FL quenching ratio ( $I_{60 \text{ min}} / I_0$ ) versus the concentration of  $NO_2$ .  $I_{60 \text{ min}}$  was the FL intensity obtained after reacting CQD-functionalized aerogels with  $NO_2$  for 60 min.



**Figure 5.** Selectivity of CQD-functionalized aerogel sensor for  $NO_2$  over other gases ( $SO_2$ ,  $CO_2$ ,  $NH_3$ ,  $O_2$ , and  $N_2$ ); the concentrations of gases were all 10 ppm, respectively.

Under the white light, both the CQD-functionalized aerogels and blank aerogels are white powders (see the upper section in Figure 3a); however, under the excitation of 365 nm UV light, they exhibit very different FL activities. CQD-functionalized aerogels give strong blue emission whereas the blank aerogels have no any FL emission (see the lower section in Figure 3a), suggesting that CQDs have been successfully loaded on the silica aerogels and CQDs can keep their excellent FL activity in solid state. Therefore, it is envisioned that the well FL functionalization of aerogels may enable their application in gas sensing. It should be noted here that the maximum emission wavelength of the CQD-aerogel hybrid materials is 430 nm (see the black curve in Figure c), which is 30 nm blue-shifted from that of CQDs in aqueous solution (Figure S4, Supporting Information). The blue shift in emission wavelength might be attributed to the well-known strong electrostatic interaction between the positively charged PEI polyelectrolytes (from the surfaces of the CQDs) and the negatively charged silica surfaces (from the silica aerogels).<sup>33</sup> Obviously, the strong electrostatic interaction facilitates the immobilization and stability of CQDs on silica aerogels.

**FL Interaction between CQD-Functionalized Aerogels and  $NO_2$ .** In order to investigate the interaction of the FL



CQD-functionalized aerogels with NO<sub>2</sub> gas, equal amounts (i.e., 0.01 g) of CQD-functionalized aerogels were loaded, respectively, in the middle of two quartz tubes (with 4 mm in inner diameter) and fixed with a small amount of cotton at both ends (see the upper section in Figure 3b). 1000 ppm NO<sub>2</sub> was passed through one of above fixed tubes whereas pure N<sub>2</sub> was passed through the other as the control experiment. From the comparison, it is evident that the FL intensity of the CQD-functionalized aerogels can be quenched obviously by NO<sub>2</sub> gas whereas no FL change can be investigated upon exposure of CQD-functionalized aerogels to N<sub>2</sub> (see the lower section in Figure 3b). FL spectra (see Figure 3d) clearly show that the characteristic FL emission peak at 430 nm not only decreases significantly but also shifts to longer wavelength (460 nm). The strong quenching of FL by NO<sub>2</sub> might result from the interaction of electron-donating PEI (from the surfaces of CQDs) and electron-withdrawing NO<sub>2</sub>,<sup>34</sup> thus preventing the radiative recombination of electrons and holes trapped on the CQD surfaces.<sup>35</sup>

**Evaluation of FL Aerogel-Based Gas Sensor for NO<sub>2</sub>.** Apparently, on the basis of the strong FL interaction between CQD-functionalized aerogels and NO<sub>2</sub>, a new aerogel-based FL sensor can be developed for the detection of NO<sub>2</sub>. After the construction of the gas sensor as shown in Figure 1, several major performances of the sensor, including signal response time, concentration dependence of FL, and detection selectivity were evaluated for future applications under the optimum FL conditions (i.e., 360 and 430 nm as the maximum excitation and emission wavelengths of PEI-CQDs, respectively).<sup>26</sup> First, the FL responses of the CQD-functionalized aerogels to various concentrations of NO<sub>2</sub> were investigated and shown in Figure 4. It was found that, under the exposure of the FL-functionalized aerogels, the FL intensities all decreased with time and reached relatively constant values (around 95%) in 60 min. The time dependence of FL response might be attributed to the aerogels having abundant nanosized pores and large inner surface areas and thus slowing down the exchange of sample gas and the air in the functionalized aerogels. Consequently, the FL signals sampled after passing the NO<sub>2</sub> gas for 60 min were used for further quantitative analysis. From the inset of Figure 4, it can be shown that there is a good linear relationship ( $R^2 = 0.9921$ ) between the quenching ratio ( $I_{60 \text{ min}}/I_0$ ) and the concentration of NO<sub>2</sub> in the observed ppm levels (2–10 ppm). The limit of detection (LOD) was 250 ppb at signal-to-noise ratio of 3. This shows that the presently developed sensor has practical utility in measurement of NO<sub>2</sub> gas.

High selectivity is very important for the development of a good sensor; thus, five other gases including N<sub>2</sub>, O<sub>2</sub>, SO<sub>2</sub>, CO<sub>2</sub>, and NH<sub>3</sub> that are common gases or usually exist in the atmosphere were chosen to evaluate whether the presently developed gas sensor is specific for the detection of NO<sub>2</sub> (Figure 5). The concentrations of O<sub>2</sub>, SO<sub>2</sub>, CO<sub>2</sub>, and NH<sub>3</sub> were all 10 ppm, and N<sub>2</sub> was used as the carrier. Under the same experimental conditions, all of the potential interfering gases show virtually no FL quenching activities since the quenching ratios ( $I_{60 \text{ min}}/I_0$ ) are similar with that of N<sub>2</sub>. In contrast, NO<sub>2</sub> exhibits much larger FL quenching activity, indicating that the functionalized aerogel sensor has good selectivity in sensing NO<sub>2</sub> gas.

## CONCLUSION

A new CQD-aerogel hybrid material has been prepared and used for sensing for the first time. The PEI-capped CQD-functionalized aerogels have abundant pores and exhibit strong FL activities. The strong FL of the CQD-functionalized aerogels can be sensitively and selectively quenched by NO<sub>2</sub> gas, and there is good linear response between FL quenching ratio and the concentration of NO<sub>2</sub>. It is envisioned that a novel and promising aerogel-based gas sensor can be developed and applied for the detection of NO<sub>2</sub> gas.

## ASSOCIATED CONTENT

### Supporting Information

Materials, instruments, the preparation of silica wet gel, silica aerogels, and BPEI-CQDs, Figures S1–S4, and Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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