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Carbon Quantum Dot-Functionalized Aerogels for NO_2 Gas Sensing

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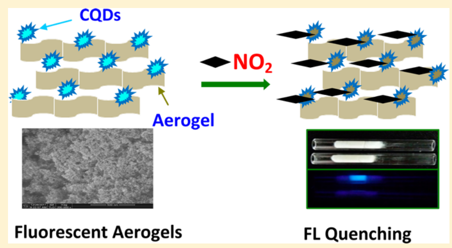
Supporting Information

ABSTRACT: Silica aerogels functionalized with strongly fluorescent carbon quantum dots were first prepared and used for simple, sensitive, and selective sensing of NO_2 gas. In the presence of ethanol, homemade silica aerogels with a large specific surface area of 801.17 m^2/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_2 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,[1] 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,[2,3] carbon,[4,5] metal chalcogenides,[6−8] metal oxide systems,[9,10] metal systems,[11,12] and organic polymers[13,14] have been reported. Among the aerogels, silica aerogels are most commonly used, mainly in building insulation materials and the aerospace industry,[3] due to their low thermal conductivity and low density. Carbon aerogels are mainly used in electrode capacitance material,[15] and metal or metal compound aerogels are usually used in industrial catalysis[5,9,10] due to their high surface areas. Aerogels can be prepared in various ways, such as supercritical fluid drying,[3,6,13] chemical vapor deposition,[11] and solvent cross-linking.[16,17] 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.[18] 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.[18] Therefore, more and more attention has been paid to the syntheses, property studies, and applications of these emerging carbon nanomaterials.[19−25] 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.[26] 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_2) was used as the model pollutant in the sensing, since NO_2 is one of the most prominent air pollutants. It has been well recognized that NO_2 and its derivatives are the important sources of atmospheric particulate matter (such as PM2.5), photochemical smog, and acid rain and thus are harmful to humans' respiratory systems and cause a series of diseases such as asthma,[27,28] chronic pharyngitis,[29] and pulmonary edema[30] and very serious damage to the ecological environment.[31,32] Therefore, the detection of NO_2 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_2.

■ EXPERIMENTAL SECTION

Materials. Tetraethylorthosilicate (TEOS), anhydrous ethanol (ETOH), hydrochoric acid (HCl), and ammonia ($NH_3{\cdot}H_2O$) 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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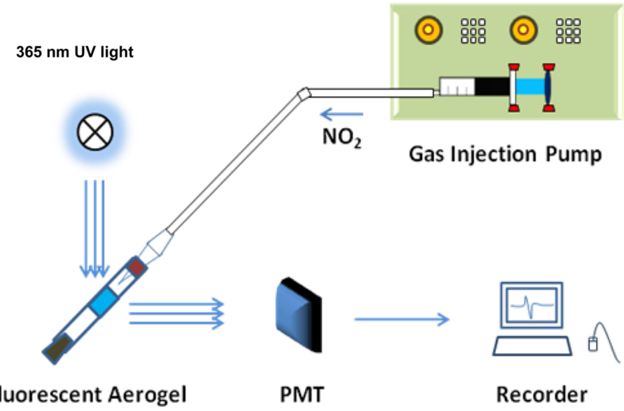

Figure 1. Schematic diagram of the FL aerogel-based sensor for NO_2.

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.[26] 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 μL 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. Finaly, CQD-functionalized aerogels were obtained by drying the CQD-aerogel mixture solution in an oven for 12 h at 70 °C. The resulting CQD-functionalized aerogels were ground once again before further sensing applications.

Construction and Operation of FL Aerogel-Based Sensor for NO_2. The FL aerogel-based gas sensor for 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

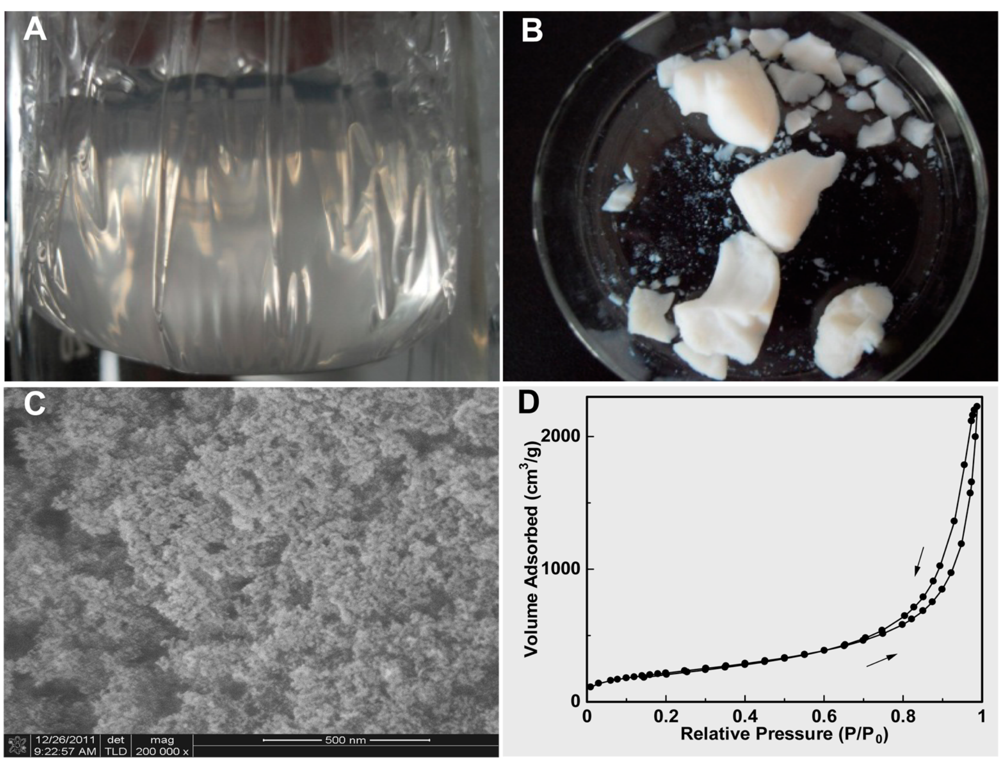

Figure 2. The preparation of silica aerogels. (A) The wet silica gel contained in a bag made of a piece of plastic wrap; (B) the as-prepared silica aerogels; (C) SEM image obtained for the silica aerogels; (D) N_2 adsorption−desorption isotherms measured for the silica aerogels.

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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

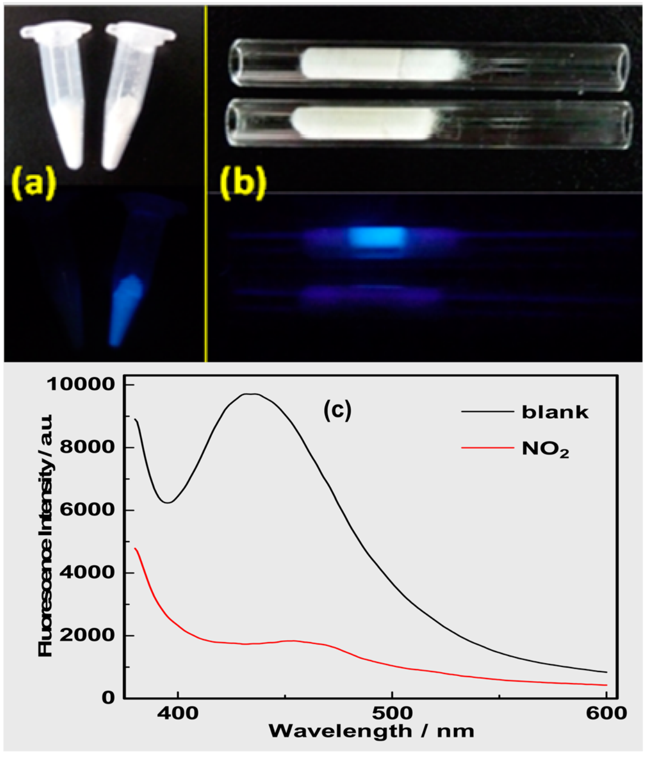

Figure 3. (a) The photos of CQD-functionalized aerogels (right) and blank aerogels (left) under a visible light (upper section) and illuminated by a UV beam of 365 nm (lower section). (b) The photos of CQD-functionalized aerogels in quartz tubes without (top) and with (bottom) passing 1000 ppm NO_2 under 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 slica aerogels may be used as a reversible absorbent in the detection of the pollutant gases such as NO_2.

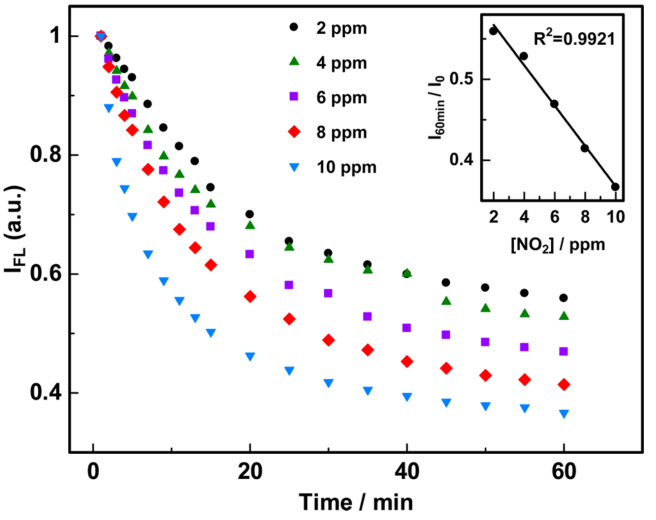

Figure 4. Fluorensent responses of CQD-functionalized aerogels to various concentrations of NO_2 gas samples (from top: 2, 4, 6, 8, and 10 ppm). Inset: Linear calibration plots of FL quenching ratio ($I_{60\ min}/I_0$) versus the concentration of NO_2. $I_{60\ min}$ was the FL intensity obatined after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

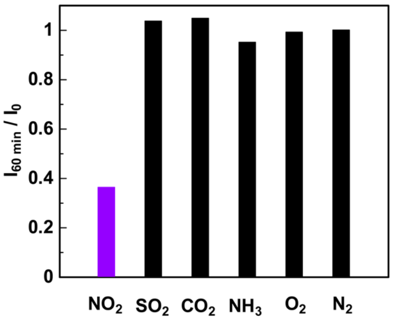

Figure 5. Selectivity of CQD-functionalized aerogel sensor for NO_2 over other gases (SO_2, CO_2, NH_3, O_2, and N_2); the concentrations of gases were all 10 ppm, respectively.

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 emssion 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 postively charged PEI polyelectrolytes (from the surfaces of the CQDs) and the negatively charged silica surfaces (from the silica aerogels).[33] Obviously, the strong electrostatic interaction facilitates the immobiliziation 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_2 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_2 was passed through one of above fixed tubes whereas pure N_2 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_2 gas whereas no FL change can be investigated upon exposure of CQD-functionalized aerogels to N_2 (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_2 might result from the interaction of electron-donating PEI (from the surfaces of CQDs) and electron-withdrawing NO_2,[34] thus preventing the radiative recombination of electrons and holes trapped on the CQD surfaces.[35]

Evaluation of FL Aerogel-Based Gas Sensor for NO_2. Apparently, on the basis of the strong FL interaction between CQD-functionalized aerogels and NO_2, a new aerogel-based FL sensor can be developed for the detection of NO_2. 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).[26] First, the FL responses of the CQD-functionalized aerogels to various concentrations of NO_2 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_2 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 ($I_{60\ min}/I_0$) and the concentration of NO_2 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_2 gas.

High selectivity is very important for the development of a good sensor; thus, five other gases including N_2, O_2, SO_2, CO_2, and NH_3 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_2 (Figure 5). The concentrations of O_2, SO_2, CO_2, and NH_3 were all 10 ppm, and N_2 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 ($I_{60\ min}/I_0$) are similar with that of N_2. In contrast, NO_2 exhibits much larger FL quenching activity, indicating that the functionalized aerogel sensor has good selectivity in sensing NO_2 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_2 gas, and there is good linear response between FL quenching ratio and the concentration of NO_2. It is envisioned that a novel and promising aerogel-based gas sensor can be developed and applied for the detection of NO_2 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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