

Supporting Information

A Carboxylated Cellulose Aerogel for Rapid Detection of Aniline Vapor

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1. Synthesis of carboxylated cellulose aerogel

3.5 g of sodium hydroxide and 6.0 g of urea were successively added to 40 mL of deionized water, and stirred to obtain a sodium hydroxide/urea aqueous solution. The mixed aqueous solution was frozen in a low-temperature refrigerator, and taken out to thaw after 12 h. Subsequently, microcrystalline cellulose with a mass fraction of 2% was weighed, slowly poured into the sodium hydroxide/urea aqueous solution and stirred for 6 h to obtain a clear aqueous cellulose solution. Then, the above solution was put into the refrigerator for freezing, and taken out to thaw after 12 hours. The cellulose aqueous solution was poured into ethanol to solidify for a period of time until the cellulose hydrogel was completely floated in the ethanol. Then, the cellulose hydrogel was washed with 0.1 mol/L hydrochloric acid aqueous solution and deionized water until neutral, and finally placed in a refrigerator for use. The obtained cellulose aerogel was named CA.

The carboxylation process of cellulose aerogel is shown in Figure 2. A certain amount of cellulose aerogel was weighed and placed in 5 mL of deionized water to obtain a suspension. Then, a certain amount of sodium bromide (0.10 mmol/g cellulose aerogel) and 2,2,6,6-tetramethylpiperidine-1-oxyl (0.01 mmol/g cellulose aerogel) were weighed as catalysts for the carboxylation reaction. The oxidation reaction was started by adding certain amounts of NaClO aqueous solution (1, 3, 5, 7 mmol/g cellulose aerogel). The pH value was maintained between 10.0 and 10.5. The reaction continued for 6 h under stirring condition and then was terminated by adding ethanol. Aqueous hydrochloric acid and deionized water are added to keep the

product chemically neutral, and then the carboxylated cellulose hydrogel is freeze-dried to obtain the carboxylated cellulose aerogel. The carboxylated cellulose aerogels with different sodium hypochlorite addition (1, 3, 5, 7 mmol/g cellulose aerogel) were named CA-C-1, CA-C-3, CA-C-5, and CA-C-7, respectively.

2. Characterization

2.1. Morphology and structure characterization

The surface morphologies of the materials were observed by Zeiss Sigma300 field emission scanning electron microscope (FESEM). For the characterization of the functional groups, we employed Fourier-transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet iS20, Thermo Fisher Scientific).

2.2. Carboxyl content characterization

The content of carboxyl group was characterized by conductometric titration. First, 0.1 g carboxylated cellulose aerogel was suspended in 100 mL deionized water, then 0.01 mol of sodium chloride was added, and then 0.1 mol/L of aqueous hydrochloric acid was added for stirring to fully acidify the carboxylated cellulose aerogel to ensure that the sodium carboxylate (-COONa) is completely converted into carboxyl groups (-COOH), and the pH is maintained at 2.5-3.0. The 0.025 mol/L sodium hydroxide aqueous solution was added dropwise to the suspension until the pH reached 11.0. The change in the conductivity of the suspension and the dropwise amount of the aqueous sodium hydroxide solution were recorded. The formula for calculating the carboxyl content (n_{COOH} , mmol/g) is equation (1):

$$n_{COOH} = c \times (V_2 - V_1)/m \quad (1)$$

Where c (mol/L) is the concentration of standard sodium hydroxide aqueous solution. V_1 (mL) is the minimum value of standard sodium hydroxide consumption when the conductivity is the lowest. V_2 (mL) is the maximum value of the standard sodium hydroxide consumption when the conductivity is the lowest. m (g) is the absolute weight of the sample mass.

2.3. Porosity characterization

By using absolute ethanol as the medium, the pycnometer method was used to characterize the porosity of carboxylated cellulose aerogels with different addition amounts of sodium hypochlorite. The calculation formula of porosity is equation (2):

$$P = \frac{m_2 - m_3 - m_s}{m_1 - m_3} \times 100\% \quad (2)$$

Where P (%) represents the porosity. m_1 (g) represents the total mass of the pycnometer and ethanol. m_2 (g) represents the total mass of the pycnometer and ethanol after repeated vacuuming after adding the sample. m_3 (g) represents the total mass of the pycnometer and the remaining ethanol after the sample is taken out after repeated vacuuming. m_s (g) represents the dry weight of the aerogel.

3. Fabrication and test method of QCM sensor

The carboxylated cellulose aerogels were cut into a cylinder with a diameter of 5 mm and a height of 1 mm by using the cutting equipment. Then, the cut aerogels were glued to QCM by the aid of araldite. According to Sauerbrey equation ($\Delta F = -2.2 \times 10^{-6} f^2 \Delta m / A$), the frequency shift of QCM resonator (ΔF) is proportionate with the

increased mass on silver electrode (Δm)¹. As shown in Figure 3, QCM chip was vertically suspended inside a sealed chamber with gas inlet/outlet. This sealed chamber integrates the functions of temperature and humidity control. The air (15 sccm) generated by an air generator was used as the carrier gas. Because the evaporation point of aniline is relatively high, a heater is indispensable. All tests were conducted at ambient temperature and relative humidity (RH) of 50%. Two running fans can accelerate the dispersion of gaseous aniline homogeneously. As a typical process, QCM sensor was flushed with air until a steady fundamental frequency was obtained. Then, the liquid aniline analyte with calculated volume was introduced to the chamber by a microliter syringe. The exact volume of the injected aniline analyte liquid was concretely calculated in μl based on the following equation: $V_l = \frac{cVM}{10^6/22.4dp}$, where V_l represents the volume of liquid in μl , c is the liquid concentration in ppm, M represents the molecular weight, d is the liquid density, and p represents the degree of purity. Then, following the sensing test, a frequency shift to analyte would be obtained after a period of time. The frequency shift was living measured by a digital controller and recorded by a desk top computer. At the end of each testing cycle, continuous air would wash away the analyte to re-establish the fundamental frequency. Moreover, the sealed chamber can be operated with humidity control to test the response changes in different relative humidity environments.

4. Gaussian calculations

Based on the previous literature, we explored the sensing mechanism by means of simulation calculation². We utilized Gaussian 09 software with a DFT method and

the hybrid B3LYP functional and 6-311++G(d,p) basis set to optimize the geometries of the molecules and frequency. The optimized structures were confirmed to be minima on the potential energy surface via vibration frequency analysis. To verify which group plays a key role in aniline detection, the interaction energies between aniline molecule and the multiple functional groups of carboxylated cellulose aerogel were calculated according to the following equation (3). The sensing material will be named C:

$$\Delta H_{aniline - C} \left(\frac{kJ}{mol} \right) = H_{aniline - C} \left(\frac{kJ}{mol} \right) - H_{aniline} \left(\frac{kJ}{mol} \right) - H_C \left(\frac{kJ}{mol} \right) \quad (3)$$

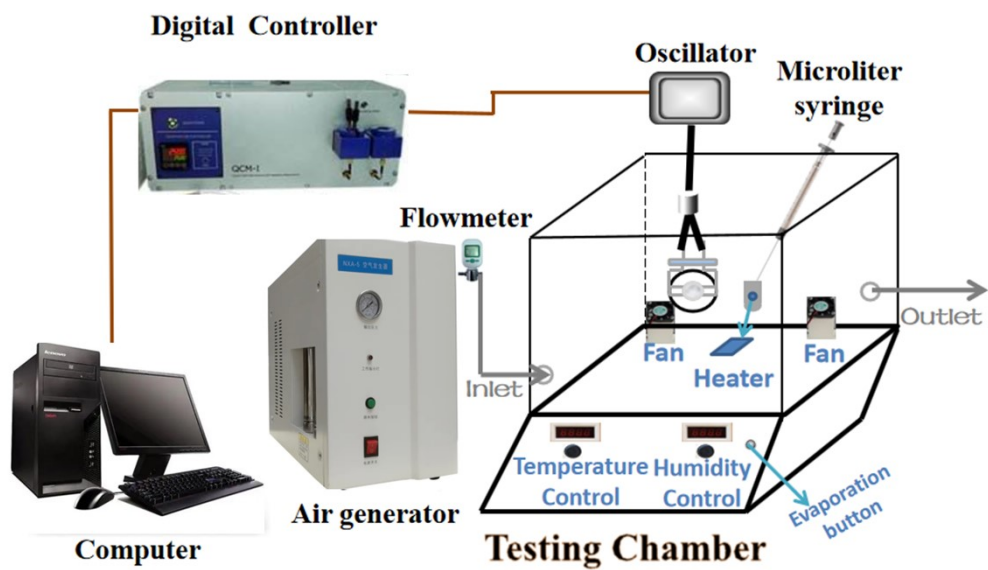


Figure S1. Schematic of the sensing testing system.

References

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