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Cobalt-porphyrin/dansyl piperazine complex coated filter paper for “turn on” fluorescence sensing of ammonia gas†

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Filter paper has been sequentially enched with titania (TiO₂) nanoparticles and coated by a cobalt-porphyrin/dansyl piperazine complex. A series of “turn on” fluorescence sensors are demonstrated to show high sensitivity and fast response for ammonia gas.

Ammonia has been widely used in various fields such as fertilizer production, industrial refrigerant and chemical synthesis.¹ Meanwhile, gaseous ammonia is toxic to human health and corrosive to metal instruments.² Thus, several approaches have been explored to detect ammonia, such as electrochemistry,^{3,4} chromatography,^{5,6} and colorimetry.^{7,8} Among these methods, fluorescent sensors have gained increasing interest in recent years, which can be easily integrated as portable devices with high sensitivity for real-time detection.^{9,10} Mechanism with “turn on” or “turn off” mode is normally introduced into those fluorescent sensors. A series of fluorescent molecules have been synthesized for sensing applications. For example, Liu *et al.* reported a fluorogen with an aggregation-induced emission feature for CO₂ sensing.¹¹ Kim *et al.* investigated a “turn on” fluorescent sensor to detect ammonia based on a porphyrin cobalt–dansyl complex in solution.¹² This complex shows potential application in ammonia sensing although it is not suitable for detection in gas phase. Besides, we demonstrated a highly sensitive logic gates by a porphyrin derivative with protonation-induced multiple emission switches.¹³ It is found that all these sensing events were achieved in solutions, which are not convenient for gas detection.

In order to address this issue, fluorescent molecules have been anchored on solid substrates. For example, Pedrosa and co-workers prepared a transparent *meso*-tetra(4-methylpyridinium)-porphyrin/TiO₂ thin film as optochemical sensor for gaseous HCl.¹⁴ We reported a porphyrinated polyimide honeycomb film for the same purpose previously.¹⁵ However, it is still a great challenge to develop simple and convenient method by anchoring fluorescent molecules on cheap/versatile substrates and to achieve the practical detection of ammonia gas with high sensitivity and rapid response.

Filter papers (FPs) have been regarded as idea substrates to anchor fluorescent molecules for fabricating chemo-sensors.^{16–18} FPs usually combine microfibers with nano-fibers¹⁹ and this composite structure results in high surface area for fluorescent molecules functionalization as well as perforate porous morphology for gas accessibility. In this work, we present a kind of fluorescent sensors for ammonia gas by coating cobalt(II) tetraphenylporphyrin/dansyl piperazine (CoTPP/DP) complex on FPs (Whatman® filter paper No. 1, Fig. 1) pre-etched with TiO₂ nanoparticles (NPs). The TiO₂ NPs further increase the surface area of FPs and result in high sensitivity of the fluorescent sensors. Fluorescence spectra were used to monitor the “turn on” mode of the FPs-based sensors during the detection of ammonia gas.

DP was chosen as a fluorescent sensor and its quenching behaviour is used for probing molecules, such as the harmful

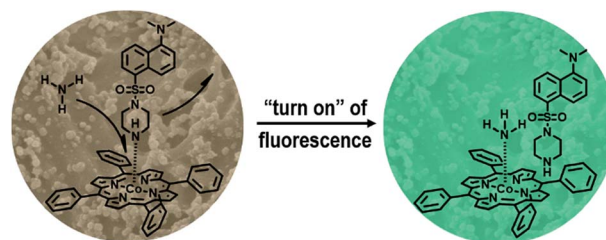


Fig. 1 Schematic illustration for mechanism of “turn on” fluorescence of the CoTPP/DP complex upon the addition of ammonia.

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ammonia gas. As schematically shown in Fig. 1, DP complexes with CoTPP followed by the fluorescence quench on account of an intramolecular electron transfer. On the other hand, the central metal ion of CoTPP is served as a recognition site for NH_3 binding. This binding disrupts the CoTPP/DP complex and the fluorescence of DP is in "turn on" state.¹² The complexation of CoTPP and DP is confirmed by ^1H NMR and fluorescence analyses (Fig. S2 and S3 in ESI†). The quenched fluorescence of CoTPP/DP complex can be recovered by the addition of NH_3 in solution (Fig. S4 in ESI†). This recovery is ascribed to the stronger affinity between CoTPP and NH_3 than that between CoTPP and DP. The corresponding binding constant, K_a , is $(9.719 \pm 0.164) \times 10^4 \text{ M}^{-1}$ (Fig. S5 in ESI†) and $(2.154 \pm 0.016) \times 10^3 \text{ M}^{-1}$ (Fig. S6 in ESI†), respectively. Furthermore, CoTPP aggregates easily due to the π - π packing interaction of porphyrin molecules.²⁰ This aggregation is a disadvantage for porphyrin to be solved and coated on substrates. It can be seen that the aggregation of CoTPP is effectively suppressed by DP complexation in solution (Fig. S7 in ESI†) and on the FPs surface (Fig. S8 in ESI†).

A sequential dipping method was used to fabricate the FPs-based sensors.^{21,22} TiO_2 NPs were introduced onto FPs surface by hydrolysing process of tetrabutyl titanate to further increase the surface area.²³ These TiO_2 NPs have an average diameter of about 80 nm (Fig. 2(b) and (e)). The followed CoTPP/DP coating has no distinct changes on the surface morphology of FPs (Fig. 2(c) and (f)). It is very interesting that the surface area of FPs increases from $0.9643 \text{ m}^2 \text{ g}^{-1}$ to $6.235 \text{ m}^2 \text{ g}^{-1}$ after enshased with TiO_2 NPs (Fig. S9 in ESI†). This surface area promotion elevates the adsorption amount of CoTPP/DP, as verified by the adsorption spectra (Fig. 3). The adsorption of CoTPP/DP on the TiO_2 NPs enshased FPs is much higher than that on the FPs without TiO_2 NPs.

TiO_2 NPs not only increase the surface area of the substrates, but also improve the dispersion and coating of CoTPP/DP complex on the FPs. As illustrated in Fig. 3, the CoTPP/DP solution shows a single adsorption peak at 435 nm. The CoTPP/DP coated FPs have a hypsochromic shift peak around 410 nm that corresponds to the H-aggregation of CoTPP. This hypsochromic shift declines slightly when the complex is coated

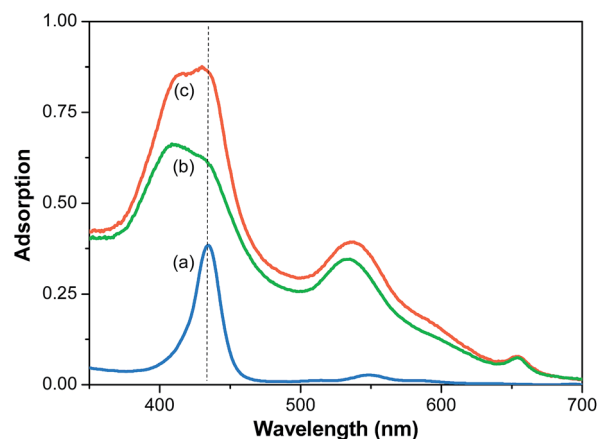


Fig. 3 Adsorption spectra of (a) 2.5 μM of CoTPP/DP in CH_2Cl_2 , (b) CoTPP/DP coated on FPs, and (c) CoTPP/DP coated on TiO_2 NPs enshased FPs, respectively.

on the TiO_2 NPs enshased FPs, indicating the suppression of CoTPP aggregation. It can be ascribed to the interaction of the unoccupied side of CoTPP with the surface of TiO_2 NPs.^{24,25}

The CoTPP/DP coated FPs were used to detect ammonia gas according to typical procedure as reported previously²⁶ (Fig. S10 in ESI†). Fig. 4(a) indicates that, upon exposing to ammonia gas, the CoTPP/DP complex coated FPs sequentially enshased with TiO_2 NPs show much more fluorescence emission intensity (2.61-folds) than the ones coated by CoTPP/DP only. The fluorescence intensity around 511 nm increases gradually with the concentration of ammonia gas increases (Fig. 4(b)). It can be mainly attributed to the dissociation of DP from the CoTPP/DP complex disrupted by ammonia and thus the fluorescence of DP recovers. The fluorescence response can be detected not only by fluorescent spectrometer or microscopy, but also by naked eye. Fluorescence images demonstrate this striking fluorescence "turn-on" effect also (Fig. 4(c)), the FPs turns bright with the increase of exposure ammonia concentration. The sensitivity of

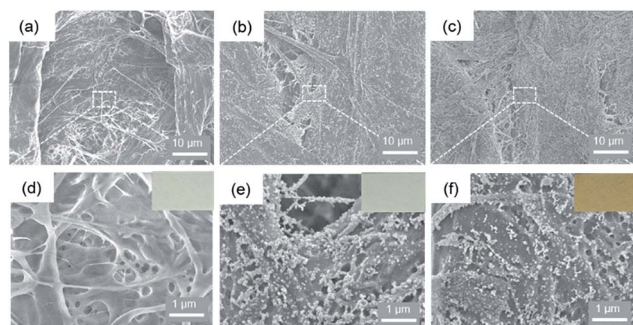


Fig. 2 SEM images of (a) nascent FPs, (b) FPs enshased with TiO_2 NPs, (c) FPs sequentially enshased with TiO_2 NPs and coated with CoTPP/DP complex. (d), (e), (f) are the partial enlargement of (a), (b), (c), respectively.

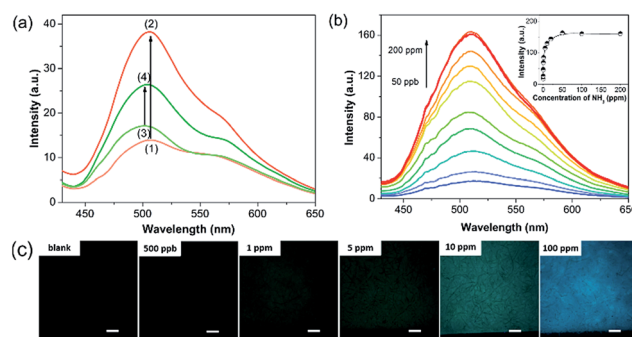


Fig. 4 (a) Fluorescent response of FPs-based sensors to ammonia gas: (1) to (2), the CoTPP/DP coated on the TiO_2 enshased FPs; (3) to (4), the CoTPP/DP coated on the nascent FPs. (b) Fluorescence spectra of the CoTPP/DP coated on the TiO_2 enshased FPs after exposed to ammonia gas in nitrogen atmosphere with different concentrations. (c) Fluorescence images of the CoTPP/DP coated on the TiO_2 enshased FPs for the detection of gaseous ammonia. Scale bar is 200 μm .

FPs, defined as the slope of the fluorescence/concentration curve, was calculated by calibration curve of fluorescence/concentration relation (Fig. S11 in ESI†), with a sensitivity linearly related to concentration in the range between 0 and 10 ppm. It shows the sensitivity of the FPs sensor is 8.385 ppm^{-1} . After fluorescent enhancement was achieved upon exposing to ammonia gas, the FPs sensor can not be regenerated due to the high affinity between CoTPP and NH_3 , showing lack of the reversibility. The selectivity of the FPs sensors was also explored (Fig. S12 in ESI†). After exposing to organic amine vapors with nitrogen donor moieties (ammonia, diethylamine and triethylamine), the FPs sensors exhibit similar fluorescence enhancement, but with little response to toluene vapour in the same conditions. This selectivity property ensures the FPs sensors being suited for the ammonia sensing application with the absence of nitrogen donor moieties. Response time of the sequential coated FPs to ammonia gas (100 ppm) was further measured by time-course fluorescent spectra (Fig. S13 in ESI†). It is defined as the time required for the fluorescent sensor to reach 90% of the final equilibrium values after exposing to the ammonia gas. Results show that the fluorescence increases quickly in 5 s and reaches equilibrium in next 15 s. This quick response time is associated with the high surface area of the TiO_2 NPs enched FPs.

Conclusions

In conclusion, we present a kind of FPs-based sensors for ammonia gas on the basis of “turn on” fluorescent emission. These sensors are facilely fabricated by sequential coating TiO_2 NPs and cobaltporphyrin/dansyl piperazine complex on FPs. SEM images show that there are abundant of NPs enched on the FPs surface. The surface area is increased for more than 6 times by the enched TiO_2 NPs and thus the coating of cobaltporphyrin/dansyl piperazine complex is obviously improved with declined aggregation. The sensors show high sensitivity and fast response to ammonia gas. This work provides a simple, efficient, and convenient method to fabricate substrate-based chemosensors.

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