Electronic Supplementary Information

Highly sensitive colourimetric anion chemosensors fabricated by functional surface modification of natural cellulose substance

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Experimental

Materials

Titanium *n*-butoxide [$Ti(O^nBu)_4$], naphthylamine, *p*-aminobenzene sulfonic acid, alizarin complexone, sodium nitrite, sodium nitrate, potassium nitrite, sodium fluoride, sodium chloride, sodium bromide, sodium acetate, tetrabutylammonium fluoride, ammonium fluoride, ammonium chloride, ammonium bromide, ammonium acetate and ammonium carbonate were purchased from Sigma-Aldrich. All the chemicals were of AR grade and were used as received. All aqueous solutions were prepared using Milli-Q water (resistivity, 18.2 MΩ cm).

Surface modification of filter paper with titania nanocoating

A piece of commercial filter paper was placed in a suction filtering unit, and was washed by suction filtration of ethanol, followed by drying with air flow. 20 mL of titanium *n*-butoxide solution (100 mM in 1:1/v:v toluene/ethanol) was then added to the filter funnel with the first 10 mL of the solution slowly suction-filtered through the filter paper, and the rest was left to stand for 3 min to ensure chemosorption of the titanium alkoxide. The remaining 10 mL of the solution was then passed through the filter paper slowly, subsequently, abundant ethanol was immediately filtered *via* suction to wash away any unreacted metal alkoxide, followed by passing through 20 mL of pure water within 3 min to promote hydrolysis of titanium alkoxide and condensation of the resultant titania gel layer. Finally, the filter paper was washed with copious ethanol and dried in flowing air, thus finishing a deposition cycle. By repeating the surface sol–gel process for ten times, each cellulose nanofibre of filter paper was coated with a uniform 5-nanometer-thick titania gel layer, resulting in cellulose/titania composite, denoted as cellulose/$(TiO_2)_{10}$.

Fabrication of the cellulose based colourimetric NO_2^- and F^- chemosensors

The resulting ultrathin titania gel film coated filter paper (the cellulose/$(TiO_2)_{10}$ paper) was immersed in 10 mM solution of naphthylamine in toluene overnight. Afterwards, it was washed with adequate ethanol, followed by drying with air flow, resulting in titania gel film and naphthylamine modified paper, denoted as cellulose/$(TiO_2)_{10}$/naphthylamine (*i.e.*, the colourimetric NO_2^- chemosensor used in this work). To fabricate colourimetric F^- chemosensor, the cellulose/$(TiO_2)_{10}$ paper was immersed in 1 mM solution of alizarin complexone (AC) in acetone at room temperature overnight. Then, it was thoroughly washed with ethanol, followed by drying with air flow, resulting in titania gel film and alizarin complexone modified paper, denoted as cellulose/$(TiO_2)_{10}$/AC (*i.e.*, the colourimetric F^- chemosensor employed in this work).

Colourimetric sensing of NO_2^- and F^-

All the aqueous analyte solutions utilized in this work were freshly prepared by dissolving a weighed amount of corresponding solid analyte in Milli-Q water and diluting the resultant aqueous solutions to the desired concentrations. The pH values of all the aqueous analyte solutions were precisely measured by pH meter and used for the colourimetric NO_2^- or F^- sensing experiments.

The NO_2^- sensing experiment with the cellulose/$(TiO_2)_{10}$/naphthylamine paper was performed by dipping it into aqueous solutions of different anions mixed with sulfonyl aniline at a molar ratio of 1:1 for 15 min. The F^- sensing experiment with the cellulose/$(TiO_2)_{10}$/AC paper was carried out by dipping it into aqueous solutions of different anions for 5 min.

Solid UV–vis absorption spectra of the related samples were measured with a Shimadzu UV-2450 spectrophotometer in the diffuse reflectance mode using an integrating sphere accessory with a piece of virgin filter paper as reference.

Sensing of NO_2^- using titania and naphthylamine modified quartz plates

Ten layers of titania film was deposited onto quartz plate by the surface sol−gel process using $Ti(O^nBu)_4$ as precursor, and a naphthylamine monolayer was successively deposited by means of the same procedure mentioned above. Due to the rather low surface area of flat substrate, the titania nanocoating and naphthylamine modified quartz plate appeared colourless, and no significant colour change and no conspicuous spectral shift were observed after exposing it to aqueous solution of $NaNO_2$ mixed with sulfonyl aniline.

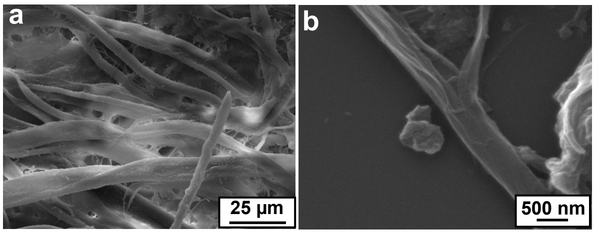

Fig. S1 FE-SEM micrographs of the bare filter paper.

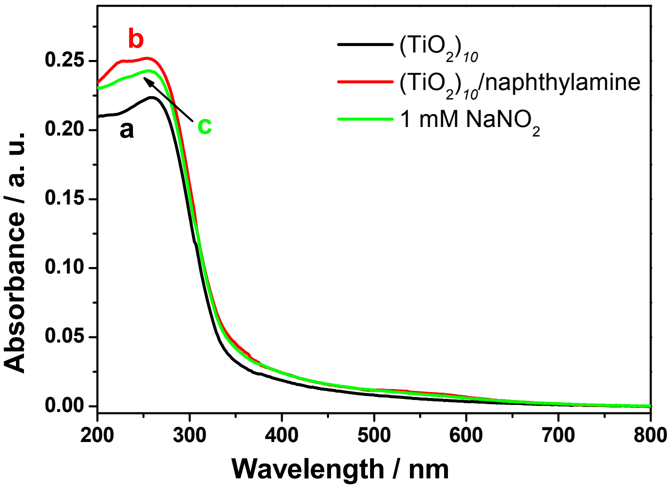

Fig. S2 UV–vis spectra of titania gel film coated quartz plate (a), titania nanocoating and naphthylamine modified quartz plate before (b) and after (c) exposure to aqueous solution of $NaNO_2$ (1 mM) mixed with sulfonyl aniline (1 mM). The pH value of the aqueous analyte solution is 3.80.

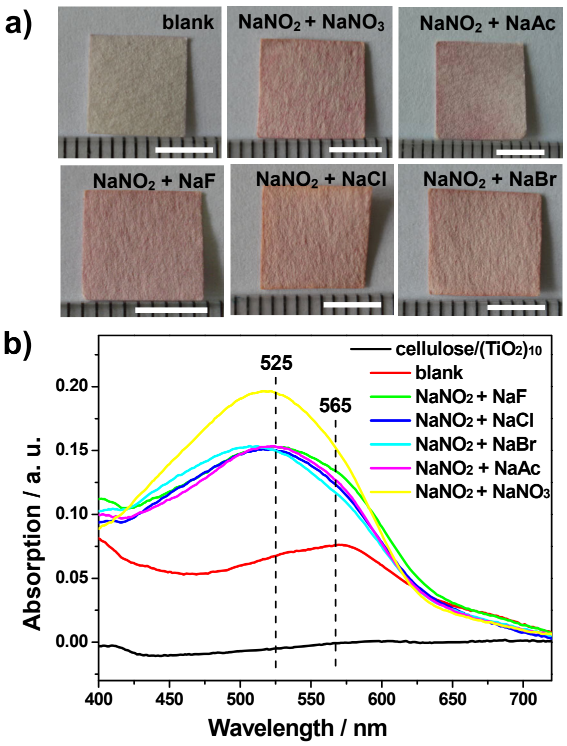

Fig. S3 (a) Colour change of the cellulose/$(TiO_2)_{10}$/naphthylamine papers upon exposure to aqueous solutions of NO_2^- (1 mM) mixed with sulfonyl aniline (1 mM) and different anions (F^-, Cl^-, Br^-, Ac^- or NO_3^-, 1 mM). The pH values of the aqueous analyte solutions are 3.76, 3.83, 3.85, 4.24 and 3.81 respectively. Scale bars: 5 mm. The sample denoted as "blank" is the initial cellulose/$(TiO_2)_{10}$/naphthylamine paper. (b) Solid UV–vis spectra of the cellulose/$(TiO_2)_{10}$ paper, the initial cellulose/$(TiO_2)_{10}$/naphthylamine paper and the cellulose/$(TiO_2)_{10}$/naphthylamine papers after exposure to aqueous solutions of NO_2^- (1 mM) mixed with sulfonyl aniline (1 mM) and different anions (F^-, Cl^-, Br^-, Ac^-or NO_3^-, 1 mM).

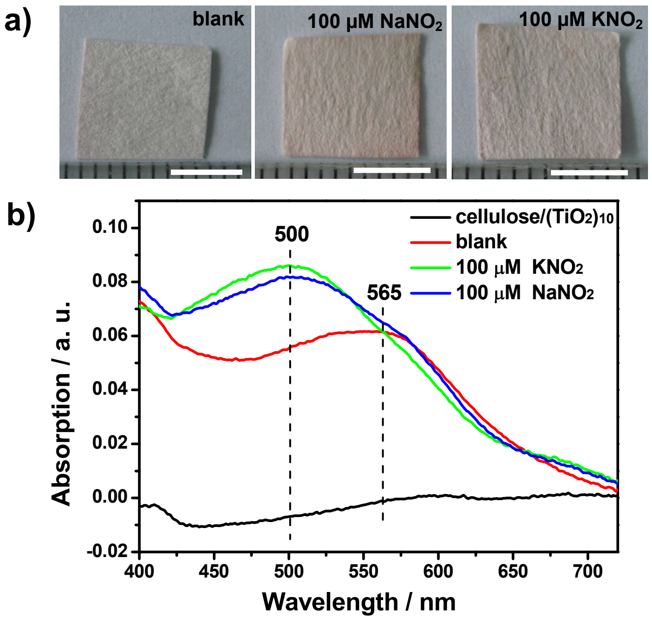

Fig. S4 (a) Colour change of the cellulose/(TiO_2)$_{10}$/naphthylamine papers upon exposure to aqueous solutions of $NaNO_2$ (100 μM) mixed with sulfonyl aniline (100 μM), and KNO_2 (100 μM) mixed with sulfonyl aniline (100 μM), the corresponding pH values of the analyte solutions are 4.52 and 4.58. Scale bars: 5 mm. The sample denoted as "blank" is the initial cellulose/(TiO_2)$_{10}$/naphthylamine paper. (b) Solid UV–vis spectra of the cellulose/(TiO_2)$_{10}$ paper, the initial cellulose/(TiO_2)$_{10}$/ naphthylamine paper and the cellulose/(TiO_2)$_{10}$/naphthylamine papers after exposure to aqueous solution of $NaNO_2$ (100 μM) mixed with sulfonyl aniline (100 μM), and KNO_2 (100 μM) mixed with sulfonyl aniline (100 μM).