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Electronic Supporting Information

Functional surface modification of natural cellulose substances for colorimetric detection and adsorption of Hg^{2+} in aqueous media

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Modification of filter paper with N719 monolayer. A piece of commercial filter paper was placed in a suction filtering unit, and was washed by suction filtration of methanol, followed by drying with air flow. Twenty milliliters of titania *n*-butoxide solution ($\text{Ti}(\text{O}^n\text{Bu})_4$, 100 mM in 1:1/v:v toluene/ethanol) was then added to the funnel, the first 10 mL of the solution was slowly suction-filtered through the filter paper, and the rest was left to stand for 3 min to ensure adsorption of titanium alkoxide. The remaining 10 mL of solution was then passed through the filter paper slowly, and two 20-mL portions of ethanol were immediately filtered to remove the excessively adsorbed unreacted titanium alkoxide. Twenty milliliters of water was then allowed to pass through the filter paper slowly within 2 min to promote hydrolysis and condensation. Finally, the filter paper was dried with air flow to finish the deposition cycle. Individual cellulose fibre of the filter paper was thereafter coated with 0.5-nm-thick titania gel film. The deposition cycle was repeated for a given number of times. The resultant titania ultrathin film pre-coated filter paper was immersed in 1 mM solution of N719 in 1:1 (v/v) acetonitrile and *tert*-butanol at room temperature overnight. Then it was repeatedly washed with acetonitrile and ethanol, followed by drying with air flow, resulting in $(\text{TiO}_2)_n/\text{N719}$ -modified filter paper.

Colorimetric sensing of Hg^{2+} . The sensing experiment with N719-modified filter papers was carried out by dipping it into aqueous solutions of different metal ions: $\text{Hg}(\text{NO}_3)_2$ (100 μM , 50 μM , 20 μM , 10 μM , 5 μM , 1 μM and 50 nM), $\text{Cu}(\text{NO}_3)_2$ (1

mM), $\text{Mg}(\text{NO}_3)_2$ (1 mM), $\text{Pb}(\text{NO}_3)_2$ (1 mM), $\text{Zn}(\text{NO}_3)_2$ (1 mM), and Hg^{2+} (10 μM) mixed with Cu^{2+} , Mg^{2+} , Pb^{2+} or Zn^{2+} (1 mM)) for 10 min.

Fifteen and five layer-titania film deposited filter papers modified with N719 monolayer were both subjected to the sensing of Hg^{2+} in aqueous solutions, similar sensing behaviors were observed.

Solid UV-vis adsorption spectra 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.

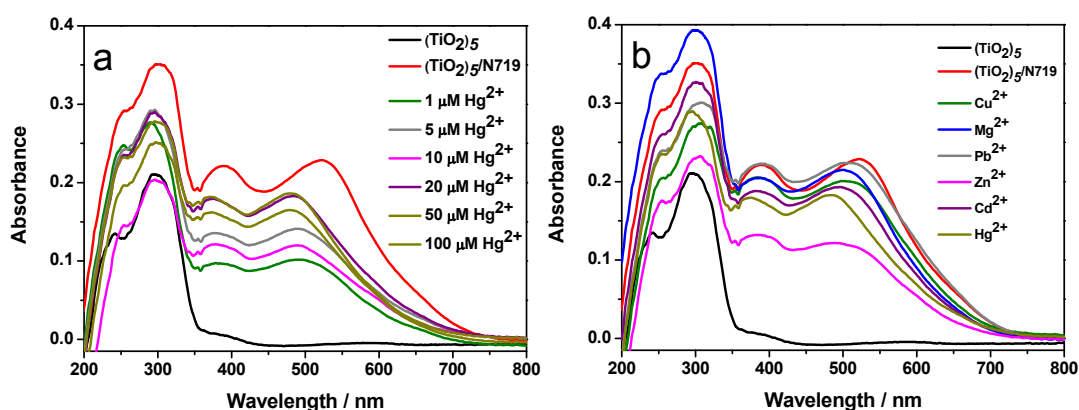


Fig. S1 (a) Solid UV-vis adsorption spectra of the $(\text{TiO}_2)_5/\text{N719}$ -modified filter paper upon exposure to aqueous solutions of different concentration of $\text{Hg}(\text{NO}_3)_2$ for 10 min. (b) Absorption spectra of the $(\text{TiO}_2)_5/\text{N719}$ -modified filter paper upon 10-min exposure to aqueous solutions of different metal ions (all as nitrates). The concentration of Hg^{2+} is 10 μM , the other metal ions are 1 mM.

Sensing reversibility. The purple colored $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter paper was firstly exposed to a 50 μM aqueous solution of $\text{Hg}(\text{NO}_3)_2$, upon which it turned orange; after washing with water and drying, it was soaked in 10 mM KI aqueous solution, by which it returned to the original purple color immediately. This procedure was repeated up to six cycles.

Sensing of Hg^{2+} using $(\text{TiO}_2)_{15}/\text{N719}$ -modified quartz plates. Fifteen layers of titania film was deposited onto quartz plate by the surface sol-gel process using $\text{Ti}(\text{O}^n\text{Bu})_4$ as precursor (J. Huang, I. Ichinose, T. Kunitake and A. Nakao, *Langmuir*, 2002, **18**, 9048; *Nano Lett.* 2002, **2**, 669.), and a N719 monolayer was successively deposited by means of the same procedure mentioned above. The $(\text{TiO}_2)_{15}/\text{N719}$ -modified quartz

plate appeared colorless, and no color change was observed by naked eyes by exposing it to Hg^{2+} solutions.

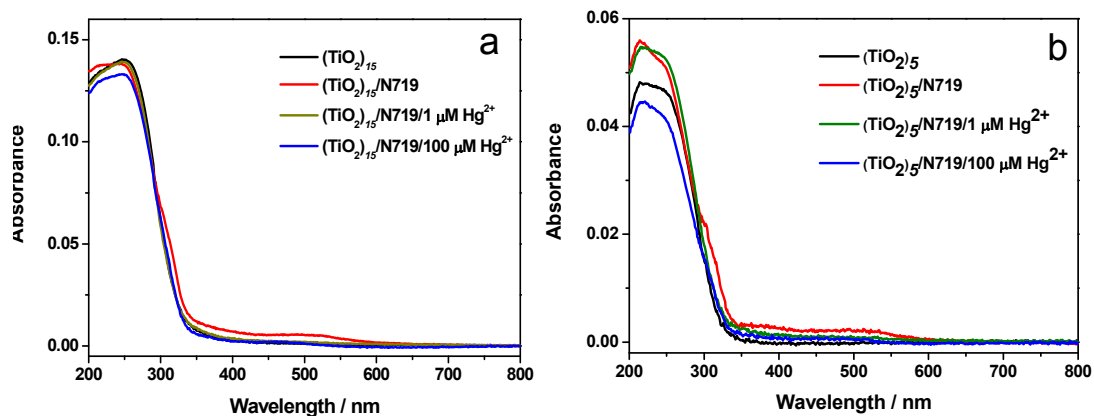


Fig. S2 UV-vis absorption spectra of $(\text{TiO}_2)_{15}/\text{N719}$ (a) and $(\text{TiO}_2)_5/\text{N719}$ -modified quartz plate (b) before and after exposing to aqueous solutions of different concentration of $\text{Hg}(\text{NO}_3)_2$ (1 μM and 100 μM).

Calcination treatment. Calcination of the Hg^{2+} adsorbed $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter paper was carried out at 450 °C in air to remove the organic components, resulting in nanotubular TiO_2/HgO composite sheet, as shown below.

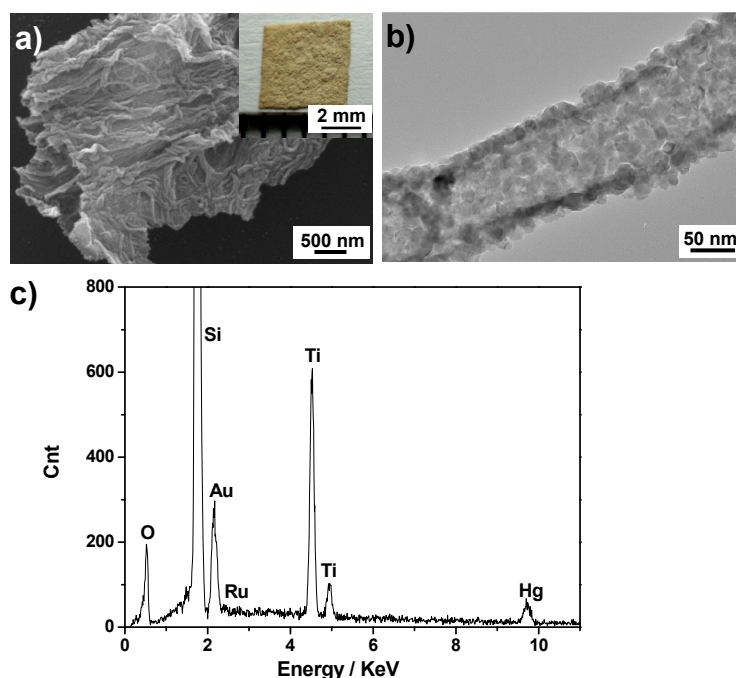
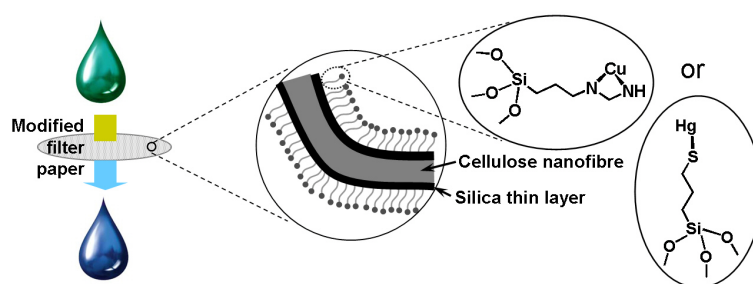


Fig. S3 (a) FE-SEM of the titania/mercuryoxide composite nanotubular material yielded by calcination of Hg^{2+} adsorbed $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter paper. The inset is photograph of the material. (b) TEM image of one individual titania/mercuryoxide composite nanotube. (c) EDX spectra of the composite material. Si peaks come from silicon wafer substrate to support the specimen, and Au peaks come from gold coating used to increase conductivity to make SEM observation.

Cellulose substance based heavy metal ion trapping materials. The surface sol–gel deposition of silica gel layers onto the nanofibres of filter paper was carried out at 50 °C using $\text{Si}(\text{OMe})_4$ as precursor (500 mM in methanol). The film deposition cycle was repeated ten times, and the thickness of the resulted silica film was *ca.* 7.5 nm. The silica film pre-coated filter paper was immersed in toluene solution of (3-mercaptopropyl)trimethoxysilane or N-[3-(trimethoxysilyl)propyl] ethylenediamine (both 10 mM) overnight to deposit the corresponding monolayer, followed by washing with toluene, chloroform and ethanol, and finally dried with air flow.



Scheme S1 Schematic illustration of the adsorption of Cu^{2+} or Hg^{2+} ions from aqueous solutions using the specifically surface modified filter paper.

To absorb Hg^{2+} or Cu^{2+} ions from aqueous solutions, a piece of the modified filter paper (diameter 3 cm) was placed in a suction filter funnel, and 50 mL of aqueous solution of Hg^{2+} (30 ppm, nitrate) or Cu^{2+} (10 ppm, nitrate) was passed through the filter paper slowly for ten times. ICP-MS was employed to determine the concentration of Cu^{2+} or Hg^{2+} in the solutions before and after the adsorption.

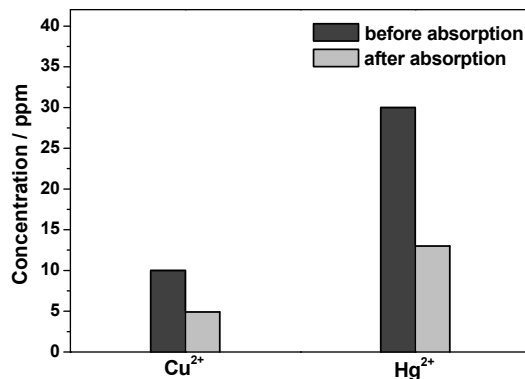


Fig. S4 The concentration of Cu^{2+} and Hg^{2+} in aqueous solutions before and after adsorption by the specifically surface modified filter paper.

The mercury or copper ion adsorbed filter paper was calcined in air at 450 °C, yielding bulk SiO₂/HgO or SiO₂/CuO nanotubular hybrid sheet.

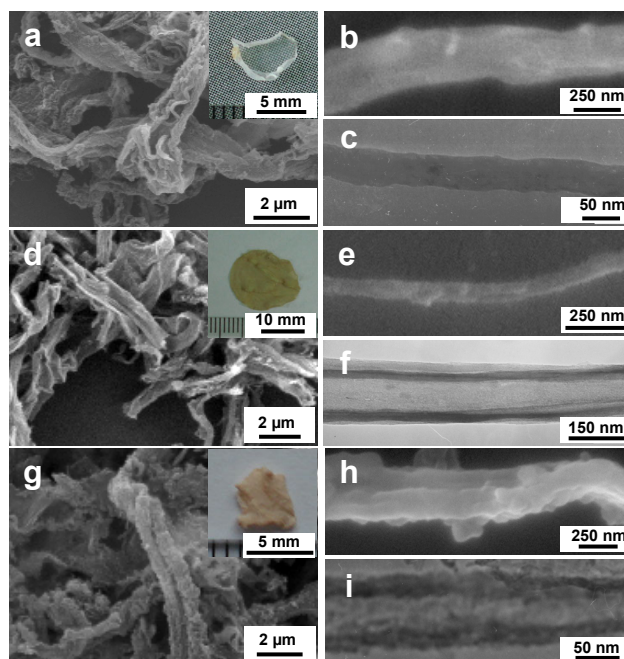


Fig. S5 Electron micrographs of metal oxide nanotubular materials yielded by calcination of mercury or copper ion adsorbed filter paper. (a) and (b), Field emission scanning electron micrographs (FE-SEM) of the silica sheet; (d) and (e), FE-SEM images of the silica/copperoxide hybrid sheet; (g) and (h), FE-SEM images of the silica/mercuryoxide hybrid sheet. (c), (f) and (i), Transmission electron micrographs (TEM) of corresponding individual nanotubes. The insets of (a), (d) and (g) are photographs of the corresponding calcined sheets.

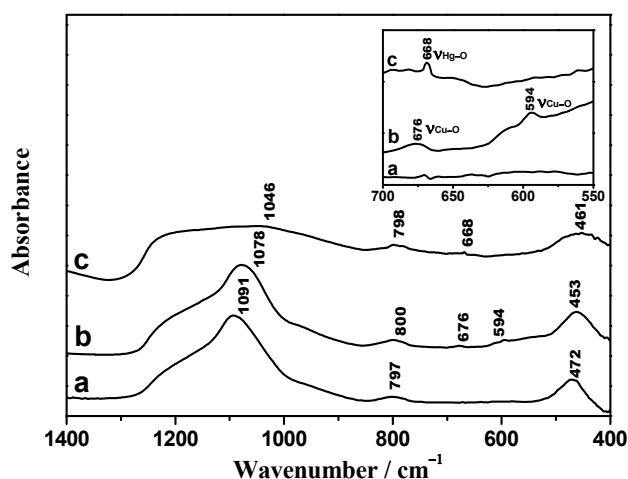


Fig. S6 FT-IR spectra of silica nanotube (a), silica/copperoxide hybrid nanotube (b) and silica/mercuryoxide hybrid nanotube (c) obtained from calcination of mercury or copper ion adsorbed filter paper.

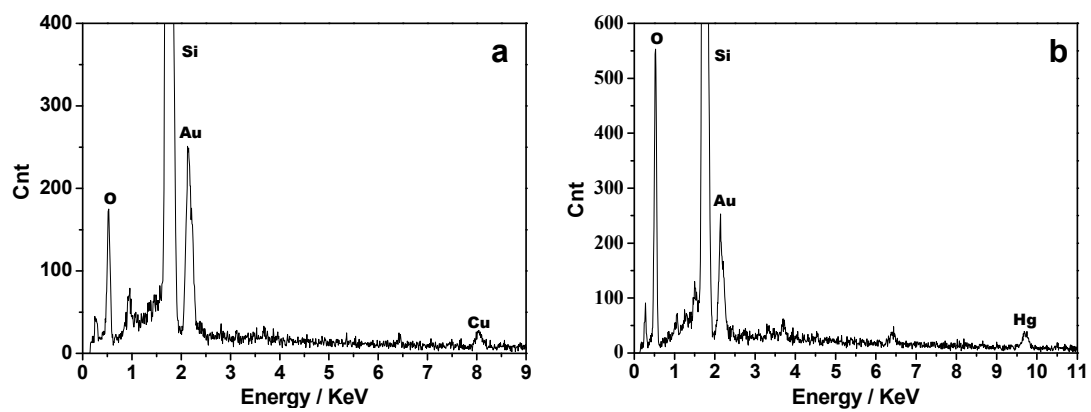


Fig. S7 Energy dispersive X-ray (EDX) spectra of silica/copperoxide hybrid (a), and silica/mercuryoxide hybrid (b) yielded by calcination of mercury or copper ion adsorbed filter paper.