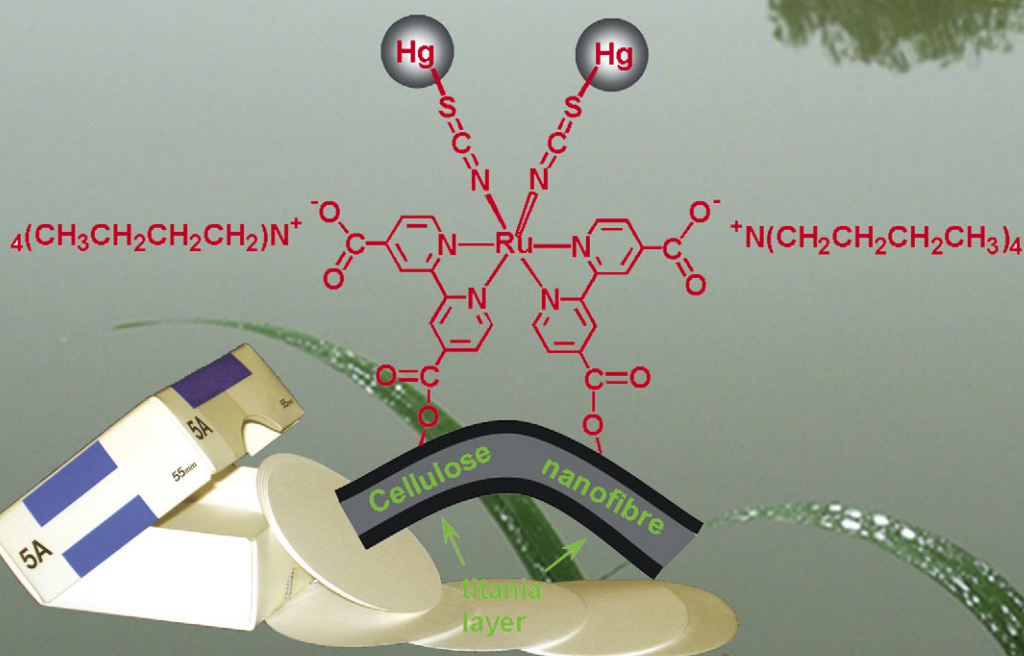
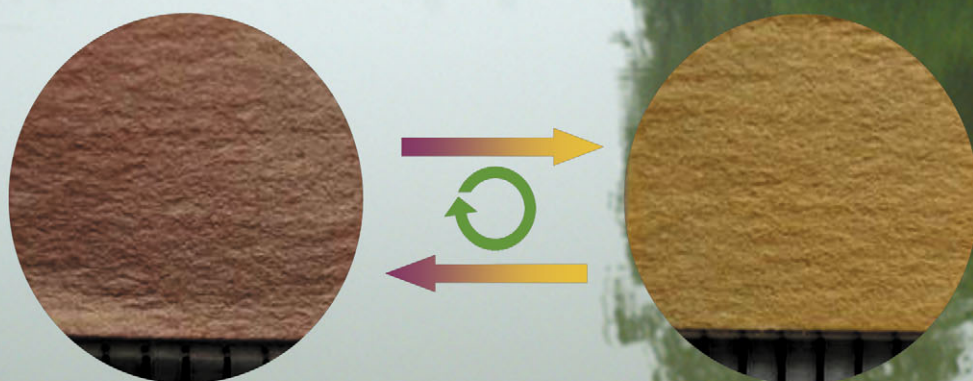


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Functional surface modification of natural cellulose substances for colorimetric detection and adsorption of Hg^{2+} in aqueous media†

Xuehai Zhang and Jianguo Huang*

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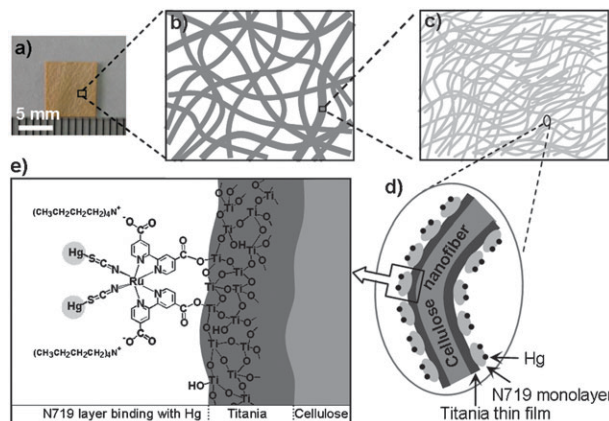
Immobilization of ruthenium dye or mercaptosilane monolayer onto metal oxide ultrathin film pre-coated cellulose nanofibres of natural cellulose substances yielded colorimetric sensing materials with high sensitivity and selectivity as well as good reversibility, and trapping materials with high efficiency for detection and adsorption of Hg^{2+} ions in aqueous media.

Mercury is well known to cause serious environmental and health problems due to its bioaccumulation through the food chain, and causes serious damage to the nervous and endocrine systems of human beings. Therefore, the development of selective and efficient methodologies for detecting and removing Hg^{2+} from aqueous media is in great demand.¹ Various methods based on the functional modification of mesoporous materials,² oligonucleotides,³ polymers,⁴ metal nanoparticles,⁵ and semiconductor quantum dots⁶ to specifically coordinate with Hg^{2+} have been reported. However, the development of facile, low-cost, highly sensitive and practical Hg^{2+} chemosensors that function in aqueous media still remains a challenge.⁷ Optical heavy metal ion sensors that allow on-site, real time detection without using any spectroscopic instruments have received a great deal of attention.⁸ In particular, colorimetric sensors are extremely attractive because of the ease of observation with the naked eye.⁹ Palomares *et al.* reported a naked-eye colorimetric sensor for Hg^{2+} using ruthenium dyes modified nanoporous TiO_2 films; color change in the presence of ppm concentrations of mercury salt was observed.^{10,11} Grätzel and co-workers fabricated a reversible optical sensor for Hg^{2+} using nanocrystalline TiO_2 films anchored with functionalized ruthenium sensitizers.¹² However, the naked-eye detection of ppb level Hg^{2+} in aqueous solution has not been achieved without the use of spectrophotometers due to the low surface area of flat TiO_2 films used for anchoring dye molecules.^{10–12}

Cellulose is the most abundant organic raw material in the world;¹³ in natural cellulosic materials such as paper, cotton and cloth, cellulose chains are organized through multiple hydrogen bonding in a well-defined cellular hierarchical structure with large surface area. Therefore, it's an ideal choice to employ natural cellulosic substances as a scaffold to fabricate chemosensors.^{14,15} We have pioneered biosensor development for the detection of protein molecules by functional surface modification of a titania thin film pre-coated natural cellulose substance, and it detected protein molecules at nanomolar

concentrations.¹⁶ Employing the surface sol–gel technique,¹⁷ ultrathin metal oxide gel film is deposited onto the individual nanofibres of the cellulose substance,¹⁸ which provides a comprehensive platform for further functional surface modification of cellulose. In the present work, a novel reversible cellulose based colorimetric Hg^{2+} sensor was fabricated by immobilization of a ruthenium dye monolayer onto titania ultrathin gel film pre-coated cellulose nanofibres of a bulk natural cellulose substance (*e.g.* common commercial filter paper, Scheme 1). The resultant sensor material exhibits extraordinary selectivity and sensitivity, gives an immediate and obvious color change from purple to orange in the presence of Hg^{2+} in aqueous solution, and the detection limit is ~ 10 ppb by the naked eye. Moreover, a cellulose substance is also an ideal matrix for the development of adsorption materials for heavy metal ions; silica ultrathin film pre-coated filter paper modified with a specific surface coating was found to efficiently adsorb Hg^{2+} or Cu^{2+} from diluted aqueous solutions.

The coating of ruthenium dye N719 (di-tetrabutylammonium *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II), see Scheme 1) molecules was applied onto titania film pre-coated cellulose nanofibres of a bulk natural cellulose substance (filter paper) for the detection of Hg^{2+} in aqueous solutions. Thin titania gel film (thickness ~ 7.5 nm) was firstly deposited onto the cellulose nanofibre surfaces of commercial filter paper by 15 cycles of the surface sol–gel process using $\text{Ti}(\text{O}^n\text{Bu})_4$ as precursor.^{18a} Subsequently, N719 molecules were adsorbed onto the titania film surface forming a monolayer by soaking in 1 mM solution of the dye in a 1 : 1 (v/v) mixture of acetonitrile/*tert*-butanol at room temperature overnight (ESI†). The sensing tests were carried out by exposing the 15-layer titania film and N719 monolayer



Scheme 1 Schematic representation of Hg^{2+} sensing using titania/N719 multilayer modified natural cellulose substance (common commercial filter paper).

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† Electronic supplementary information (ESI) available: Experimental details, Hg^{2+} sensing using titania/N719 film modified quartz plates, and study of heavy metal ion adsorption using specifically surface modified filter paper. See DOI: 10.1039/c0cc01072c

(denoted as $(\text{TiO}_2)_{15}/\text{N719}$) modified filter paper to aqueous solutions of Hg^{2+} . The color change of the sensor material is due to the selective coordination of mercury ions with the thiocyanate groups of N719 dye.^{10,11} Depending on the concentrations of the Hg^{2+} solutions, the sensor material showed an obvious color change within 1–10 min.

As displayed in Fig. 1a, the $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter paper underwent an obvious color change from purple to orange after being dipped into $\text{Hg}(\text{NO}_3)_2$ aqueous solutions. Because of the high surface areas of filter paper, as expected, the color change could be clearly seen by naked eye inspection even down to 50 nM (10 ppb) Hg^{2+} solution, which was much more sensitive than the reported N719 film deposited on a flat surface (detection limit was only 20 μM by the naked eye).¹⁰ UV-vis absorption spectra of the $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter paper before and after sensing of Hg^{2+} are shown in Fig. 1b. The former sample shows an adsorption band at 520 nm, while it shifted to 480 nm for the latter samples. The 40 nm hypsochromic shift indicates that mercury ions coordinate to the NCS groups of N719.¹² However, for $(\text{TiO}_2)_{15}/\text{N719}$ hybrid film modified quartz plates, no conspicuous color change was observed by exposing them to Hg^{2+} aqueous solutions due to their much lower surface area compared with a cellulose substance (ESI†).

Except for Hg^{2+} , no color change was observed for the $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter paper upon exposing it to aqueous solutions of other metal ions such as Cu^{2+} , Mg^{2+} , Pb^{2+} and Zn^{2+} (all as nitrates, 1 mM), as shown in Fig. 2a. These metal ions did not cause any hypsochromic shift of the initial 520 nm adsorption band of the $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter paper (Fig. 2b). Furthermore, the coloration response in the presence of Hg^{2+} is not influenced by addition of other metal ions. Upon exposing the $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter paper to aqueous solutions of Hg^{2+} (10 μM) mixed with Cu^{2+} , Mg^{2+} , Pb^{2+} or Zn^{2+} (1 mM), it showed the same purple to orange

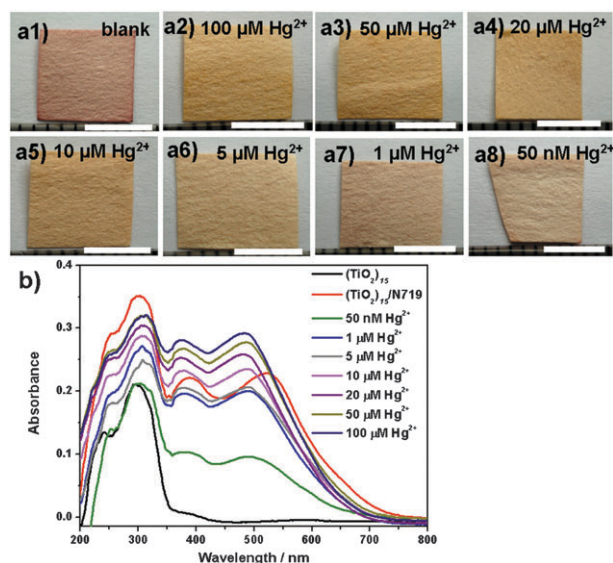


Fig. 1 (a1–a8) Color change of the $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter papers upon exposure to $\text{Hg}(\text{NO}_3)_2$ aqueous solutions of different concentrations, scale bars: 5 mm. (b) Solid UV-vis spectra of the $(\text{TiO}_2)_{15}$ thin film and $(\text{TiO}_2)_{15}/\text{N719}$ multilayer modified filter papers, and spectra of the latter material upon sensing of Hg^{2+} with varied concentrations.

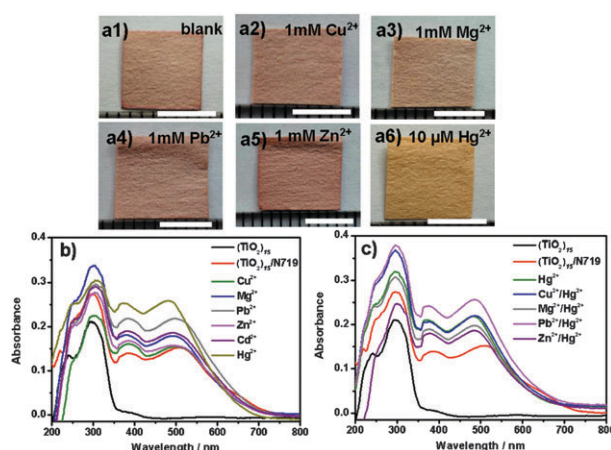


Fig. 2 (a1–a6) Color change of the $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter papers upon exposure to aqueous solutions of different metal ions (1 mM), scale bars: 5 mm. (b) Solid UV-vis spectra of the $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter papers after dipping in aqueous solutions of different metal ions. (c) Absorption spectra of the $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter papers upon contact with aqueous solution of Hg^{2+} (10 μM) mixed with Cu^{2+} , Mg^{2+} , Pb^{2+} or Zn^{2+} (1 mM).

color change as well as the 520 nm to 480 nm band shift in the absorption spectra. These results indicate the high selectivity of the $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter paper for the detection of Hg^{2+} from mixed aqueous solutions of various metal ions.

It was reported that sensors fabricated using ruthenium complexes anchored onto mesoporous oxide films were applied for the detection of mercury ions in acetonitrile,¹² inferred from which the current titania/N719-modified filter paper could be used for the detection in non-aqueous solutions.

The $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter paper possesses preferable detection reversibility of Hg^{2+} (Fig. 3a). By treatment with KI aqueous solution (10 mM), the bound mercury ions can be dissociated from the N719 molecules. As shown by the adsorption spectra, the 480 nm adsorption band shifted back to 520 nm after the KI solution treatment (Fig. 3b). The orange color of the $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter paper in the presence of mercury ion returned to the initial purple color immediately upon immersing in KI solution, and again turned orange by once more exposing to Hg^{2+} solution. This repetition procedure was repeated up to six cycles, which commendably demonstrated the reversibility of the $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter paper for Hg^{2+} detection.

During the detection process of Hg^{2+} with $(\text{TiO}_2)_{15}/\text{N719}$ -modified filter paper, mercury was adsorbed into the cellulose matrix at the same time. Calcination of the mercury-loaded filter paper to remove the organic components resulted in TiO_2/HgO composite sheet (Fig. S3, ESI†). The hierarchical morphologies and structures of the initial filter paper were faithfully replicated in the calcined sample. Cellulose nanofibres were precisely copied as composite metal oxide nanotubes with *ca.* 10 nm wall thickness. EDX analysis demonstrated that the content of Ru and Hg in the resultant calcined sample is 0.18% and 0.33% (at%), respectively. It reveals a *ca.* 1:2 molar ratio of ruthenium and mercury elements, indicating that each NCS group of N719 coordinates to one Hg^{2+} ion, which is in agreement with the reported result.¹²

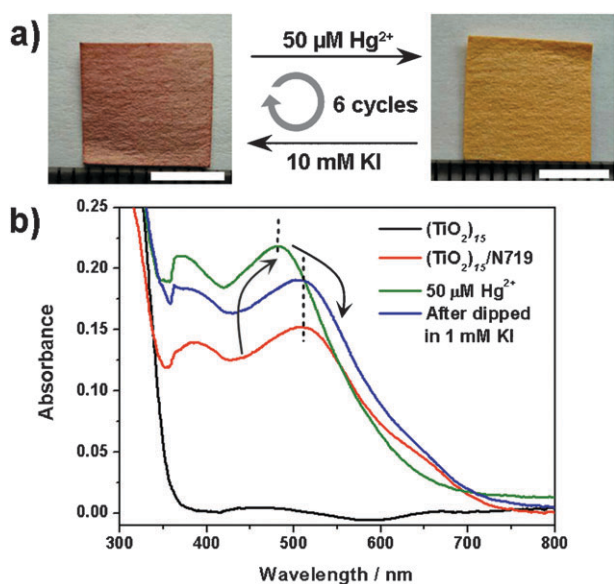


Fig. 3 (a) The reversible colorimetric detection of Hg^{2+} using the $(\text{TiO}_2)_{15}$ /N719-modified filter paper, scale bars: 5 mm. (b) Solid UV-vis spectra of the $(\text{TiO}_2)_{15}$ /N719-modified filter paper in the absence and presence of Hg^{2+} and after being dipped in KI solution.

The ultrathin titania coating of cellulose nanofibres provides the essential platform for N719 molecules to be deposited, without which the detection of Hg^{2+} would be impossible. Compared with the $(\text{TiO}_2)_{15}$ /N719-modified filter paper (thickness of the titania film is *ca.* 7.5 nm) mentioned above, filter paper modified with 5-layer titania gel film (thickness *ca.* 2.5 nm) and N719 monolayer showed similar selectivity and sensitivity for the detection of Hg^{2+} in aqueous solutions (ESI†).

Apart from being employed as a scaffold for the fabrication of a chemosensor for Hg^{2+} as discussed above, a natural cellulosic substance is also an ideal matrix for developing heavy metal ion-trapping materials due to its high surface area. By deposition of (3-mercaptopropyl)trimethoxysilane monolayer onto silica thin film (thickness *ca.* 7.5 nm) pre-coated filter paper, a new Hg^{2+} adsorbent was obtained which showed excellent absorption ability for Hg^{2+} from diluted aqueous solution (ESI†). A piece of as-such modified filter paper with 3-cm diameter was found to absorb half of the mercury ions from 50 mL solution of 30 ppm Hg^{2+} by facile filtration of the solution through the modified filter paper for ten cycles. Moreover, silica thin film and *N*-[3-(trimethoxysilyl)propyl]ethylenediamine monolayer modified filter paper could remove half of the copper ions from 50 mL of 10 ppm Cu^{2+} solution by a similar process. Calcination of the mercury or copper ion adsorbed filter paper resulted in bulk SiO_2/HgO or SiO_2/CuO hybrid sheet composed of nanotubes with the corresponding components, which was confirmed by FT-IR and EDX analysis (ESI†). The specific surface modification of a natural cellulose substance not only provides a facile pathway for the development of heavy metal ion trapping materials, but also a shortcut for the preparation of composite metal oxide nanotubes.

In summary, a highly selective, sensitive, and reversible chemosensor based on an N719 modified cellulose substance for the colorimetric detection of Hg^{2+} was developed. The

detection limit was ~ 10 ppb by the naked eye. The selectivity for Hg^{2+} over other metal ions (100 times the concentration of Hg^{2+}) is remarkably high. Specific surface modification of a cellulose substance to adsorb heavy metal ions from aqueous solutions was also achieved. The currently developed methodology sheds new light on the detection and adsorption of heavy metal ions from aqueous media for practical applications.

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