#### **ORIGINAL ARTICLE**



## Film sensor of a ligand-functionalized cellulose nanofiber for the selective detection of copper and cesium ions

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#### Abstract

A fluorescence sensor film for metal ion detection was prepared from a 2,2,6,6-tetramethyl-1-piperidinyloxy radicaloxidized cellulose nanofiber (TOCNF), which was chemically immobilized the metal ion selective ligand, namely, 3,5-bis (((2-hydroxynaphthalen-1-yl)methylene)amino)benzoic acid. The ligand in the TOCNF/ligand films exhibited fluorescence at a 310 nm excitation wavelength and at an ~410 nm emission wavelength. Then, the sensing efficiency and limits were evaluated from the fluorescence of the metal ion-bound ligand. The Stern–Volmer plot of the fluorescence emission intensity of the films increased with increasing of  $Cu^{2+}$  or  $Cs^+$  concentration. Accordingly, the sensing of metal ions was more effective on TOCNF with a greater amount of ligand, the sensing of  $Cu^{2+}$  was superior to that of  $Cs^+$ , and the detection range of the TOCNF/ligand film was wider for  $Cu^{2+}$  than for  $Cs^+$ . Thus, although the sensitivity of this sensor is lower than the electrochemical detection previously reported, the noticeable potential of the current sensing system is that it is a film type to be easily removable from the sensing water and there is no remaining sensing residue in the water.

#### Introduction

The steady increase in world's population and industrial activities has led to an increase in global water pollution, and this issue is a growing worldwide challenge that needs to be alleviated. One of the major causes of water pollution arises from the various types of industrial waste, especially heavy metals, and radioactive nuclide waste produced from nuclear power plants [1, 2]. The discharging of heavy metal ions into the environment is currently

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a global problem.  $Cu^{2+}$  is one of crucial environmental pollutants from industrial circles, but it is also a vital element in the human body and plays a key role in physiological processes in living organisms [3–5]. Although  $Cu^{2+}$  is a primary micronutrient for all living tissues, especially, plants and animals [6], excess  $Cu^{2+}$  has negative effects on animal and human health such as gastrointestinal, kidney, liver, and many neurological disorders [4, 5, 7].

The heavy radioactive nuclide cesium-137 ( $^{137}Cs^+$ ) was the most harmful substance emitted during the Fukushima nuclear accident due to its long half-life of 30.2 years, high water solubility, high fission yield of 6.09%, and strong  $\gamma$  radiation compared with other radioactive nuclides [8-10]. <sup>137</sup>Cs<sup>+</sup> is one of the major fission products of uranium released from a nuclear reactor [11, 12], and a total  $3.3 \times 10^{16}$  Bq of  $^{137}$ Cs<sup>+</sup> was released into terrestrial and aquatic environments [13]. Because it can also accumulate in the human body, it causes severe environmental, ecological, and human health issues, including cardiovascular disease and gastrointestinal distress [14–16]. Thus, there is a challenging task of establishing effective systems for the simple, rapid and eco-friendly detection of  ${}^{137}Cs^+$  and  $Cu^{2+}$  from widespread contamination in aquatic ecosystems.

Several analytical techniques including atomic absorption spectroscopy [17–19], ion-selective electrodes [20, 21], inductively coupled plasma-mass spectrometry [22], ion chromatography [23], fluorescence spectroscopy [6, 24, 25], and electrochemical methods [6, 26] have been previously applied for the determination of Cu and Cs ions. Although the determination limit and sensitivity of the reported methods are high, most of these methods involve complicated experimental settings and time-consuming measurements [25]. Thus, considering that the demand for sensor technology has been growing rapidly, an eco-friendly, simple, lightweight fluorescence-based sensor could be an option to detect analytes such as heavy metal ions in aqueous media.

Cellulose has been considered as a promising biomaterial due to its mechanically flexible property and environmental suitability [27-29]. However, because its structural modification is restricted owing to the limited available functional groups on cellulose [27], chemical treatment is required. Compared with many chemical treatments, 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) treatment has been shown to be effective in producing cellulose nanofibers of nanometer thickness without reducing the length [28]. TEMPO-oxidized cellulose nanofibers (TOCNFs) are uniform and ultrafine fibers that have many carboxyl groups on their chains, which are easy to chemically modify [27, 28, 30, 31]. In this respect, TOCNF has attracted particular concern due to its abundance, biodegradability, nontoxicity, and extensive use in many applications [27-32].

It has been reported that Schiff base ligands with  $\pi$  electrons in the C=N group and nitrogen of the aromatic ring can provide good chelation with metal ions to form strong metal complexes in aqueous solutions [4, 6]. This chelation could increase the intramolecular and ligand-to-metal charge transfer, and thus can be utilized for the detection of metal ions [33, 34]. In previous work, the tretradentate Schiff base ligand, 3,5-bis(((2-hydroxynaphthalen-1-yl)methylene)amino) benzoic acid (3,5-BHNMABA) was successfully synthesized to selectively detect Cu<sup>2+</sup> on indium tin oxide glass electrodes by the electrochemical methods [6].

The purpose of the present work is to develop a film-type sensing system for specific metal ions. The sensor film was fabricated from ligand (3,5-BHNMABA)-bound TOCNF through a chemical reaction. The nitrogen and oxygen on 3,5-BHNMABA play significant roles in the metal–ligand complex, and the complexation was detected by a fluorescence method. Finally, the detection limit of this method was assessed. The selectivity and sensitivity of Schiff base ligands toward  $Cu^{2+}$  and  $Cs^+$ , environmentally friendly sensing materials, and conventional detection techniques are merits of this study. To date, no study has been reported on the detection of a Schiff base ligand (3,5-BHNMABA)-

functionalized TOCNF sensor film. Thus, this film-type sensor should be developed.

#### **Experimental section**

#### **Materials**

The dried pulp was obtained from Canary Corporation (Taiwan). TEMPO, sodium borohydride (NaBH<sub>4</sub>), ethylenediamine (EDA), 3,5-diaminobenzoic acid (99+%), 2-hydroxynaphthalene-1-carbaldehyde (99+%), 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC), and Nhydroxysuccinimide (NHS) were purchased from ACROS Organics (USA). CsCl, Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O, and Pb (CH<sub>3</sub>COO)<sub>2</sub>·3H<sub>2</sub>O were purchased from Sigma-Aldrich (USA). Other chemicals used were of commercial analytical grade. Ultrapure water (resistivity of 18.2 M $\Omega$  cm) was obtained from a Yamato Millipore WT100 (Japan) system.

#### Instruments

Fourier-transform infrared (FTIR) absorption spectra were obtained using the KBr pellet method on an FTIR spectrophotometer (Nicolet 6700, Thermo Scientific, USA). The ultraviolet (UV)–visible absorption spectra were recorded at a scanning speed of 200 nm/min using a 2 mm quartz cell with a UV–visible spectrophotometer (V-670, Jasco, Japan). The fluorescence spectra in the solutions were measured in a 10 mm-path quartz cell, and those of the films placed on a solid holder were obtained at an incident angle of 45° at a scan speed of 2400 nm/min with a fluorescence spectrophotometer (F-7000, Hitachi, Japan). Field scanning electron microscopy (FESEM) was performed on a JEOL JSM-6500F, Japan.

### Synthesis of the TEMPO-oxidized cellulose nanofiber (TOCNF)

TOCNF was synthesized from the dried pulp as reported earlier [27–29]. Briefly, to dried pulp (1 g) dispersed in water (100 ml) containing NaBr (0.1 g/g cellulose) and TEMPO (0.016 g/g cellulose), NaOCl (5 mmol, 13 vol %) was added, and the pH was maintained at 10 for the oxidation reaction. After the oxidized pulp was filtered and washed with water, the byproduct (hydroxide group) was reduced by the addition of reducing agent (NaBH<sub>4</sub>, 1 g). The TEMPO-oxidized cellulose pulp containing sodium carboxylate groups (TOCF-COONa) was washed with water by centrifugation (6000 rpm, 5 min), dispersed in water to obtain 0.33 wt% dry weight and placed in an ultrasonicator for 40 min to produce TOCNF. Ultrasonication was carried out in an ice-cooled bath with an ultrasonic processor (Q700, Misonix, USA) equipped with a half-inch tip.

To measure the carboxylate content, a dispersion of TOCNF (160 mg) in water (50 ml) was adjusted to pH 2.5 by using aqueous 1 M HCl solution. After stirring for 10 min, the suspension was titrated using aqueous 0.1 M NaOH solution under continuous stirring. The titration was terminated at pH 12. The conductivity was monitored by using a conductivity meter throughout the titration process according to a previous study [35]. The carboxylate content in TOCNF was calculated according to the following equation [36]:

Carboxylate content(%) = 
$$\frac{V \times N \times U_W}{W} \times 100\%$$
, (1)

where N [mol/l] is the concentration of NaOH, V [l] is the volume of NaOH added at each data point during the conductivity titration, Uw [g/unit mol] is the unit weight of TOCNF, and W [g] is the dried weight of TOCNF.

# Synthesis of 3,5-bis-(((2-hydroxynaphthalen-1-yl) methylene)amino)benzoic acid (3,5-BHNMABA) and the TOCNF/3,5-BHNMABA ligand sensor film

The 3,5-BHNMABA ligand was synthesized through condensation and recrystallization reactions according to a previous report [6]. A methanol solution (20 ml) of 3,5diaminobenzoic acid (2 mmol, 0.304 g) was added dropwise to a methanol solution (20 ml) of 2-hydroxynaphthalene-1carbaldehyde (4 mmol, 0.723 g) at 40–50 °C with continuous stirring for 2 h. The mixture was left overnight at room temperature. The crude solid (brown precipitate) was collected by filtration, recrystallized from aqueous ethanol, and dried at room temperature (~25 °C).

To the 3,5-BHNMABA ligand dispersed in water, an equimolar concentration of coupling reagents, EDC and NHS, were added to activate the carboxyl functional group. After 1 h, an aqueous dispersion of the 3,5-BHNMABA ligand was adjusted to pH 10, and the bridging reagent, EDA, was added at a molar ratio of 1:1:1 (EDA:EDC: NHS). The mixture was stirred for 1 day at room temperature to complete the amidation reaction.

The nanocompound, TOCNF/3,5-BHNMABA ligand, was synthesized by a coupling reaction [28–30, 37]. Equimolar coupling reagents were added to the TOCNF dispersion (0.33 wt%) in water. The dispersion was adjusted to pH 10, mixed with the ligand solution and left for 1 day at room temperature to complete the amidation reaction. The nanocompound dispersions were dried on a Teflon plate at room temperature to mold the film. The obtained sensor films were labeled TOCNF/3,5-BHNMABA(1–3) based on the different concentrations (250, 500, and 750  $\mu$ M, respectively) of the 3,5-BHNMABA ligand, and cut into a

 $1 \times 1 \text{ cm}^2$  size for the detection of metal ions. Solutions (20 µl) of metal ions with different concentrations ranging from 5 to 600 ppm were prepared by dissolving their respective metal salts in water, dropped onto the sensor film, and dried. The binding response was monitored with a fluorescence spectrophotometer with a solid holder. In this procedure, the fluorescence is quenched by metal ions captured on the ligand in the film.

#### **Results and discussion**

### Characterization of 3,5-BHNMABA-functionalized TOCNF

In the present study, the pulp was used as a raw material, and a TEMPO-mediated oxidation reaction was performed on the pulp, since it can selectively oxidize the primary alcohol groups on the pulp fiber into carboxylate groups [29, 37, 38]. The carboxylate content of TOCNF was measured by the conductivity titration method [35] using NaOH as seen in Supporting information Fig. S1. In the titration plot, the conductivity linearly decreased in the strong acid region (pH 2-4) by the consumption of protons  $(H^+)$ , and it linearly increased at pH values >7 after the addition of NaOH due to the increase in free OH<sup>-</sup> groups in the dispersion. In the weakly acid region of pH 4-6, the conductivity remained constant because of the consumption of protons by the carboxylate groups of TOCNF. Thus, the carboxylate content in TOCNF was calculated by Eq. (1) mentioned above [36]. The carboxylate content in TOCNF reached 1.25 mmol/g, which was 22.25% of the whole cellulose unit. These values were consistent with previous reports of carboxyl content >1 mmol/g or >17.8% [38]. As seen in Fig. S2, the high transmittance (85%) in the UV-visible absorption spectrum of the aqueous TOCNF dispersion was consistent with the previous result of the cellulose nanofiber formation by the ultrasonication of TEMPO-oxidized cellulose pulp [29].

The tetradentate ligand (3,5-BHNMABA) was chemically immobilized on TOCNF by the ethylenediaminemediated amidation reaction. The products named TOCNF/ 3,5-BHNMABA(1–3), depending on the amount of ligand, were molded to form films. Figure 1 displays the photographs of the films. The TOCNF film is transparent without color, but the TOCNF/ligand films have color that becomes darker with increasing the ligand content because of the absorption band of the ligand, as described later. Figure 2 presents the FESEM images of TOCNF and the TOCNF/ 3,5-BHNMABA(1–3) films. The surface morphology of TOCNF was smooth and homogenous, and a similar smooth and homogeneous film surface was also observed for the TOCNF/3,5-BHNMABA(1–3) films, suggesting that immobilization of a small amount (~5%) of ligands did not significantly affect the film morphology.

Figure 3 shows the FTIR spectra of the TOCNF film and TOCNF/ligand films and was compared with the FTIR spectrum of the ligand. In the IR spectrum of TOCNF, characteristic bands at 3413, 2896, 1608, and 896 cm<sup>-1</sup> can be assigned to O–H, C–H, antisymmetric COO<sup>-</sup>, and

glycosidic C<sub>1</sub>–O–C<sub>4</sub> stretching vibration modes, respectively. The bands at 1420–1330 and 1200–1030 cm<sup>-1</sup> are overlapped by symmetric COO<sup>-</sup>, C–OH, pyranose C–O–C stretching vibration modes, and other modes [32, 39–41]. As seen in Fig. 3, all FTIR spectra of TOCNF/3,5-BHNMABA(1–3) films were similar to the spectra of TOCNF despite the characteristic IR bands of 3,5-BHNMABA at 3400, 2923, 1702, 1630, 1400, 1318, and



**Fig. 1** Photographs of the **a** TOCNF, **b** TOCNF/3,5-BHNMABA(1), **c** TOCNF/3,5-BHNMABA(2), and **d** TOCNF/3,5-BHNMABA (3) films



Fig. 3 FTIR spectra of TOCNF, the TOCNF/3,5-BHNMABA ligand 1–3 films, and 3,5-BHNMABA powder



Fig. 2 FESEM images of the a TOCNF, b TOCNF/3,5-BHNMABA(1), c TOCNF/3,5-BHNMABA(2), and d TOCNF/ 3,5-BHNMABA(3) films



Fig. 4 UV-visible absorption spectra of a TOCNF, b TOCNF/3,5-BHNMABA(1), c TOCNF/3,5-BHNMABA(2), and d TOCNF/3,5-BHNMABA(3) (A) in solution and (B) on films

1317 cm<sup>-1</sup> assigned to O–H, C–H, C=O, C=N, aromatic ring, C–N, and C–C/C–O stretching vibration modes, respectively [6]. The reason for this result is the lower contribution of ligand in the FTIR spectra since the ligand exists in only a small portion (~5%) of the nanocompound films.

#### Optical properties of TOCNF/3,5-BHNMABA(1-3)

The optical properties were examined for of TOCNF and TOCNF/3,5-BHNMABA(1–3) both in solutions and on films. Figure 4 shows the UV–visible absorption spectra of the solutions and the films of TOCNF and TOCNF/3,5-BHNMABA(1–3). Five absorption bands appeared at 220, 250, 310, 417, and 442 nm in the TOCNF/3,5-BHNMABA (1–3) solutions, and they intensified with increasing ligand content, although pristine TOCNF did not exhibit any UV–visible absorption bands (Fig. 4A). These results are



Fig. 5 a UV–vis absorption, b fluorescence excitation, and c fluorescence emission spectra of TOCNF/3,5-BHNMABA(2) (A) in solution and (B) on films

attributed to the aromatic  $\pi$ - $\pi$ \* transition, C=N bond  $\pi$ - $\pi$ \* transition, and n- $\pi$ \* transitions of 3,5-BHNMABA [42]. The same five UV-visible absorption bands of 3,5-BHNMABA were detected even in the TOCNF/3,5-BHNMABA(1–3) films and their absorbances increased with increasing ligand content as well (Fig. 4B).

The fluorescence emission bands of TOCNF/3,5-BHNMABA(1) and TOCNF/3,5-BHNMABA(2) solutions were at 407 nm, while that of the TOCNF/3,5-BHNMABA (3) solution was at 402 nm, when the solutions were excited at 310 nm (Figs. 5A and S3A). The TOCNF/3,5-BHNMABA films excited at 310 nm also displayed fluorescence emission bands, but these emission bands were at 400 nm for the TOCNF/3,5-BHNMABA(1 and 2) films and at 396 nm for the TOCNF/3,5-BHNMABA(3) film (Figs. 5B and S3B).

## Sensing of $Cu^{2+}$ and $Cs^+$ on the TOCNF/3,5-BHNMABA(1-3) film sensors

In this study, different concentrations of  $Cu^{2+}$  and  $Cs^{+}$  ranging from 5 to 600 ppm were monitored by fluorescence



Fig. 6 Fluorescence emission spectra of the TOCNF/3,5-BHNMABA(2) film upon addition of different concentrations of a  $Cu^{2+}$  and b  $Cs^+$ 

intensity on the TOCNF/3,5-BHNMABA(1–3) film sensors. Figures 6a and S4A show the fluorescence spectra of TOCNF/ligand films with the addition of  $Cu^{2+}$  at different concentrations. The emission intensity of the TOCNF/3,5-BHNMABA(1–3) films decreased as the  $Cu^{2+}$  concentrations increased from 5 to 600 ppm. A similar trend was observed for the emission spectra of Cs<sup>+</sup> on the TOCNF/ 3,5-BHNMABA(1–3) films, as seen in Figs. 6b and S4B. The addition of 5–600 ppm Cs<sup>+</sup> on the TOCNF/ligand films led to a decrease in the emission intensity.

The quenching of emission intensity was plotted as a function of  $Cu^{2+}$  or  $Cs^+$  concentration based on the Stern–Volmer equation as follows:

$$Fo/F = K_{\rm sv}[M^{\rm x+}] + 1,$$
 (2)

where Fo and F are the emission intensities at metal ion concentrations of 0 and  $[M^{x+}]$ , respectively, and  $K_{sv}$  is a



**Fig. 7** Stern–Volmer plots of **A** Cu<sup>2+</sup> and **B** Cs<sup>+</sup> on the TOCNF/ligand sensor films: **a** 3,5-BHNMABA(1), **b** 3,5-BHNMABA(2), and **c** 3,5-BHNMABA(3)

Stern–Volmer constant. As presented in Fig. 7, the quenching efficiency mostly increased with increasing the concentration of ions for all TOCNF/ligand films. Then the Stern-Volmer constant in ppm<sup>-1</sup> was 0.0052 ( $R^2 = 0.996$ ), 0.0060 ( $R^2 =$ 0.993), and 0.0022 ( $R^2 = 0.999$ ) for the addition of Cu<sup>2+</sup> and 0.0017 ( $R^2 = 0.997$ ), 0.0027 ( $R^2 = 0.998$ ), and 0.0037 ( $R^2 =$ 0.995) for the addition of Cs<sup>+</sup> onto the TOCNF/3,5-BHNMABA(1-3) films, respectively. When the fluorescence was quenched, the Stern-Volmer constant increased. Thus, the Stern-Volmer constant is the barometer for sensing metal ions. The sensing of metal ions is more effective on TOCNF with a larger amount of ligand, and the sensing of  $Cu^{2+}$  was superior to that of Cs<sup>+</sup>. By way of exception, the sensing of the TOCNF/3,5-BHNMABA(3) film for  $Cu^{2+}$  was lower than that of the TOCNF/3.5-BHNMABA(1 and 2) films. A possible reason for this result is that Cu<sup>2+</sup> could easily bind to two ligands at the same time on films with a larger amount of ligands, because divalent ions have this ability. Separately,



Fig. 8 Fluorescence emission of the TOCNF/3,5-BHNMABA(2) sensor film upon the addition of a Cu<sup>2+</sup>, b Cs<sup>+</sup>, c Pb<sup>2+</sup> at 500 ppm, and d no metal ion.  $\lambda_{\text{excitation}} = 310 \text{ nm}$ 

the highest limit of detection can be evaluated as the concentration deviating from linearity on the Stern–Volmer equation, and the lowest detection limit is the lowest concentration that shows the significant fluorescence quenching. Thus, the detection range was 5–600 ppm for the sensing of  $Cu^{2+}$  on the TOCNF/3,5-BHNMABA(1 and 2) films, 5–400 ppm for the sensing of  $Cu^{2+}$  on the TOCNF/3,5-BHNMABA(3) film, and 5–500 ppm for the sensing of  $Cs^+$  on the TOCNF/3,5-BHNMABA(1–3) films. Thus, the detection range of the TOCNF/ligand film was superior for  $Cu^{2+}$  compared with  $Cs^+$ .

A previous report [6] confirmed the selective detection of  $Cu^{2+}$  by a free tetradentate (3,5-BHNMABA) ligand in acetone/water, where other divalent ions (Ni<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, Co<sup>2+</sup>, Pb<sup>2+</sup>, and Cd<sup>2+</sup>) were not selected. Figure 8 indicates that the addition of 500 ppm Pb<sup>2+</sup> is inappreciable on the present film-type sensor. Thus, the TOCNF/ligand sensor is selective for Cu<sup>2+</sup> even its film state and useful for Cs<sup>+</sup> sensing.

Scheme 1 illustrates the coordination complex of metal ions ( $Cu^{2+}$  or  $Cs^+$ ) with the tetradentate ligand (3,5-BHNMABA) on the TOCNF chain in the film state. The nonbonding lone pair electrons exist in the center of the tetradentate ligand to capture the metal ions, which raises the quenching effect of the ligand in the fluorescence spectra. Namely, the Schiff base ligand (3,5-BHNMABA) forms a complex with metal ions and thus the intramolecular charge transfer increases [6, 33, 34]. This indicates a strong coordination complex between the tetradentate ligand (3,5-BHNMABA) and Cs<sup>+</sup> or Cu<sup>2+</sup>. More detailed insight into the selectivity or complexation of Cu<sup>2+</sup> and Cs<sup>+</sup> on ligand sensors is an issue to be addressed in the near future.

In addition, the current TOCNF/ligand sensor for the  $Cu^{2+}$ and  $Cs^+$  detection was compared with previously reported



Scheme 1 Schematic illustration of the TOCNF/3,5-BHNMABA ligand sensor with  $\mbox{Cu}^{2+}$  or  $\mbox{Cs}^+$ 

sensors with different detection techniques and sensing materials, as presented in Table 1. Compared with previous studies, the current sensor showed some great potential, including simple preparation, inexpensive and eco-friendly materials and techniques, good selectivity for Cu<sup>2+</sup> and Cs<sup>+</sup>, broad linear range of detection (10-600 ppm), on-site detection, and short detection time. The inadequacy is that the sensitivity of the fluorescence film sensor in the current study is lower than those previously reported using the same ligand or other ligands and electrochemical detection, calorimetric, or fluorescent methods [6, 8, 25, 43-48]. However, electrochemical detection methods require the effort to prepare the electrode sensors and spectroscopic detection methods must undergo a removal process of sensor ligand after binding of the metal ions. By contrast, as the most noticeable potential, the current ligand film sensor is a sheet-like figure and is usable by cutting into an adequate size, and after the detection process, it can just be removed from the wastewater.

#### Conclusions

A simple and robust film-based sensor was successfully developed from Schiff base ligand (3,5-BHNMABA)functionalized TOCNF for the selective and specific  $Cu^{2+}$ and  $Cs^+$  detection. The TOCNF-based film sensor exhibits outstanding mechanical properties, flexibility, high transmittance, and easy functionalization. Although the detection of heavy metal ions by the TOCNF/3,5-BHNMABA film sensor is less sensitive compared with other methods, the current sensor provides some benefits, such as the film type, and can be recovered and reused. Moreover, the current fluorescence sensor possesses great potential for portable and convenient on-site detection of heavy metal ions. In

#### Table 1 Previous studies of $Cu^{2+}$ and $Cs^+$ detection by different methods

Detection method	Sensing material	Detection limit (ppm)	Detection range (ppm)	Ref.
Colorimetric	EBMS-based mesoporous silica	$[Cu^{2+}] = 9.7 \times 10^{-2}$	$[Cu^{2+}] = 0.5-60.0$	[43]
Colorimetric	DHDM-mesoporous inorganic silica	$[Cu^{2+}] = 1 \times 10^{-4}$	$[Cu^{2+}] = 0-2.0$	[7]
Colorimetric	Probe Cy-NB	$[Cu^{2+}] = 5.46 \times 10^{-8}$	$[Cu^{2+}] = 6.35 \times 10^{-4} - 1.73 \times 10^{-3}$	[44]
Colorimetric	MQNL/MeCM composite material	$[Cu^{2+}] = 3.3 \times 10^{-4}$	$[Cu^{2+}] = 0-2.0$	[45]
Electrochemical	ITO/APTES/3,5-BHNMABA (electrode)	$[Cu^{2+}] = 1.27$	$[Cu^{2+}] = 1.27 \times 10^{-2} - 1.65$	[6]
Electrochemical	Pi-A/RGO/GCE nanocomposite (electrode)	$[Cu^{2+}] = 6.7 \times 10^{-4}$	$[\mathrm{Cu}^{2+}] = 5 \times 10^{-3} - 3 \times 10^{-1}$	[46]
Fluorescence	N-acylhydrazone acridone derivative	$[Cu^{2+}] = 5.08 \times 10^{-2}$	$[Cu^{2+}] = 0 - 1.91$	[47]
Fluorescence	TBTA/SA/DNA probe	$[Cu^{2+}] = 2.28 \times 10^{-8}$	$[Cu^{2+}] = 3.17 \times 10^{-7} - 1.90$	[48]
Fluorescence	2,4-bis[4-(N,N-dihydroxyethylamino) phenyl]squaraine	$[Cs^+] = 6.1 \times 10^{-3}$	$[Cs^+] = 63.55 \times 10^{-2} - 63.55$	[25]
Fluorescence	TOCNF/Schiff base ligand 3,5-BHNMABA nanocomposite (film)	$[Cu^{2+}] = 5$ $[Cs^{+}] = 5$	$[Cu^{2+}] = 5-600$ $[Cs^+] = 5-500$	This work

\*EBMS: 3-(((5-ethoxybenzenethiol)imino)methyl)-salicylic acid

\*DHDM: N,N(octane-1,8-diylidene)di(2-hydroxy-3,5-dimethylaniline)

\*Cy-NB: L-cysteine - p-nitrobenzoyl

\*MQNL/MeCM: 2-methyl-8-quinolinol immobilized onto the mesoporous silica solution

- \*APTES: 3-(aminopropyl)triethoxysilane
- \* Pi-A/RGO: N-(2-(1-(p-tolyl)-1Hphenanthro[9,10-d]imidazol-2 yl)phenyl)picolinamide decorated reduced graphene oxide

\*TBTA/SA: Tris-(benzyltriazolylmethyl)amine/sodium ascorbate

particular, the present procedure can contribute to the treatment of radioactive waste.

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#### **Compliance with ethical standards**

**Conflict of interest** The authors declare that they have no conflict of interest.

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#### References

- Mon M, Bruno R, Ferrando-Soria J, Armentano D, Pardo E. Metalorganic framework technologies for water remediation: towards a sustainable ecosystem. J Mater Chem A. 2018;6:4912–47.
- Howarth AJ, Liu Y, Hupp JT, Farha OK. Metal-organic frameworks for applications in remediation of oxyanion/cation-contaminated water. CrystEngComm. 2015;17:7245–53.
- Awual MR, Ismael M, Khaleque MA, Yaita T. Ultra-trace copper (II) detection and removal from wastewater using novel mesoadsorbent. J Ind Eng Chem. 2014;20:2332–40.
- 4. Kim MS, Lee SY, Jung JM, Kim C. A new Schiff-base chemosensor for selective detection of Cu<sup>2+</sup> and Co<sup>2+</sup> and its copper complex for colorimetric sensing of S<sup>2-</sup> in aqueous solution. Photochem Photobio Sci. 2017;16:1677–89.
- Awual MR. New type mesoporous conjugate material for selective optical copper (II) ions monitoring & removal from polluted waters. Chem Eng J. 2017;307:85–94.
- ReddyPrasad P, Imae T. Selective detection of copper ion in water by tetradentate ligand sensor. J Taiwan Inst Chem E. 2017; 72:194–9.

- Awual MR, Hasan MM. Colorimetric detection and removal of copper (II) ions from wastewater samples using tailor-made composite adsorbent. Sens Actuators B Chem. 2015; 206:692–700.
- Yang H, Luo M, Luo L, Wang H, Hu D, Lin J, et al. Highly selective and rapid uptake of radionuclide cesium based on robust zeolitic chalcogenide via stepwise ion-exchange strategy. Chem Mater. 2016;28:8774–80.
- Wang J, Zhuang S. Removal of cesium ions from aqueous solutions using various separation technologies. Rev Environ Sci Biotechnol. 2019;18:231–69.
- 10. Ma F, Li Z, Zhao H, Geng Y, Zhou W, Li Q, et al. Potential application of graphene oxide membranes for removal of Cs(I) and Sr(II) from high level-liquid waste. Sep Purif Technol. 2017;188:523–9.
- 11. Yoon JY, Zhang H, Kim YK, Harbottle D, Lee JW. A highstrength polyvinyl alcohol hydrogel membrane crosslinked by sulfosuccinic acid for strontium removal via filtration. J Environ Chem Eng. 2019;7:102824.
- Kim Y, Eom HH, Kim YK, Harbottle D, Lee JW. Effective removal of cesium from wastewater via adsorptive filtration with potassium copper hexacyanoferrate-immobilized and polyethyleneimine-grafted graphene oxide. Chemosphere. 2020;250:126262.
- Liu X, Chen GR, Lee DJ, Kawamoto T, Tanaka H, Chen ML, et al. Adsorption removal of cesium from drinking waters: a mini review on use of biosorbents and other adsorbents. Bioresour Technol. 2014;160:142–9.
- Jia F, Wang J. Separation of cesium ions from aqueous solution by vacuum membrane distillation process. Prog Nucl Energ. 2017;98:293–300.
- 15. Qian J, Han X, Yang S, Kuang L, Hua D. A strategy for effective cesium adsorption from aqueous solution by polypentacyanoferrate-grafted polypropylene fabric under γ-ray irradiation. J Taiwan Inst Chem Eng. 2018;89:162–8.
- Guria UN, Mahapatra AK, Ghosh AK, Bindal RC. Fluorescent chemosensor for lethal cesium detection using thin film membrane. Sep Sci Technol. 2019;54:1687–96.

- Arida HAM, Aglan RF, El-Reefy SA. A new cesium ion selective graphite rod electrode based on Cs-Molybdophosphate. Anal Lett. 2004;37:21–33.
- Greda K, Jamroz P, Pohl P. The improvement of the analytical performance of direct current atmospheric pressure glow discharge generated in contact with the small-sized liquid cathode after the addition of non-ionic surfactants to electrolyte solutions. Talanta. 2013;108:74–82.
- Karadas C, Turhan O, Kara D. Synthesis and application of a new functionalized resin for use in an on-line, solid phase extraction system for the determination of trace elements in waters and reference cereal materials by flame atomic absorption spectrometry. Food Chem. 2013;141:655–61.
- Radu A, Peper S, Gonczy C, Runde W, Diamond D. Trace-level determination of Cs<sup>+</sup> using membrane-based ion-selective electrodes. Electroanal. 2006;18:1379–88.
- Cho ES, Kim J, Tejerina B, Hermans TM, Jiang H, Nakanishi H, et al. Ultrasensitive detection of toxic cations through changes in the tunnelling current across films of striped nanoparticles. Nat Mater. 2012;11:975–85.
- 22. Chrastny V, Komarek M. Copper determination using ICP-MS with hexapole collision cell. Chem Pap. 2009;63:512–9.
- Tofalvi R, Horvath K, Hajos P. High performance ion chromatography of transition metal chelate complexes and aminopolycarboxylate ligands. J Chromatogr A. 2013;1272:26–32.
- 24. Jung JY, Kang M, Chun J, Lee J, Kim J, Kim J, et al. A thiazolothiazole based Cu<sup>2+</sup> selective colorimetric and fluorescent sensor via unique radical formation. Chem Commun. 2013;49:176–8.
- Radaram B, Mako T, Levine M. Sensitive and selective detection of cesium via fluorescence quenching. Dalton Trans. 2013;42:16276–8.
- Zuang J, Zhang L, Lu W, Shen D, Zhu R, Pan D. Determination of trace copper in water samples by anodic stripping voltammetry at gold microelectrode. Int J Electrochem Sci. 2011;6:4690–9.
- Shah KJ, Imae T. Selective gas capture ability of gas-adsorbentincorporated cellulose nanofiber films. Biomacromolecules. 2016;17:1653–61.
- Shah KJ, Imae T. Photoinduced enzymatic conversion of CO<sub>2</sub> gas to solar fuel on functional cellulose nanofiber films. J Mater Chem A. 2017;5:9691–701.
- Ujihara M, Hsu MH, Liou JY, Imae T. Hybridization of cellulose nanofiber with amine-polymers and its ability on sick house syndrome gas decomposition. J Taiwan Inst Chem Eng. 2018;92:106–11.
- Ramaraju B, Imae T. Renewable catalyst with Cu nanoparticles embedded into cellulose nano-fiber film. RSC Adv. 2013;3:16279–82.
- Ramaraju B, Imae T, Destaye AG. Ag nanoparticle-immobilized cellulose nanofibril films for environmental conservation. Appl Catal A-Gen. 2015;492:184–9.
- Prasannan A, Imae T. One-pot synthesis of fluorescent carbon dots from orange waste peels. Ind Eng Chem Res. 2013;52:15673–8.

- 33. Kim KB, Kim H, Song EJ, Kim S, Noh I, Kim C. A cap-type Schiff base acting as a fluorescence sensor for zinc (II) and a colorimetric sensor for iron(II), copper(II), and zinc(II) in aqueous media. Dalton Trans. 2013;42:16569–77.
- 34. Lee JJ, Choi YW, You GR, Lee SY, Kim C. A phthalazine-based two-in-one chromogenic receptor for detecting Co<sup>2+</sup> and Cu<sup>2+</sup> in an aqueous environment. Dalton Trans. 2015;44:13305–14.
- Isogai A, Saito T, Fukuzumi H. TEMPO-oxidized cellulose nanofibers. Nanoscale. 2011;3:71–85.
- Kumar V, Yang T. Analysis of carboxyl content in oxidized celluloses by solid-state <sup>13</sup>C CP/MAS NMR spectroscopy. Int J Pharm. 1999;184:219–26.
- 37. Kebede MA, Asiku KS, Imae T, Kawakami M, Furukawa H, Wu CM. Stereolithographic and molding fabrications of hydroxyapatite-polymer gels applicable to bone regeneration materials. J Taiwan Inst Chem Eng. 2018;92:91–6.
- Isogai A. Development of completely dispersed cellulose nanofibers. Proc Jpn Acad Ser B. 2018;94:161–79.
- Kebede MA, Imae T, Sabrina, Wu CM, Cheng KB. Cellulose fibers functionalized by metal nanoparticles stabilized in dendrimer for formaldehyde decomposition and antimicrobial activity. Chem Eng J. 2017;311:340–7.
- Kondo T. The assignment of IR absorption bands due to free hydroxyl groups in cellulose. Cellulose. 1997;4:281–92.
- Liu CF, Ren JL, Xu F, Liu JJ, Sun JX, Sun RC. Isolation and characterization of cellulose obtained from ultrasonic irradiated sugarcane bagasse. J Agric Food Chem. 2006;54:5742–8.
- 42. Zare AJ, Ataeinia P. Synthesis and study of complexes of tetradentate Schiff base and bridging ligand of thiocyanate with transition metals of Fe, Cr and Co. Life Sci J. 2012;9:2396–405.
- Awual MR, Ismael M, Yaita T, El-Safty SA, Shiwaku H, Okamoto Y, et al. Trace copper(II) ions detection and removal from water using novel ligand modified composite adsorbent. Chem Eng J. 2013;222:67–76.
- Gao Q, Ji L, Wang Q, Yin K, Li J, Chen L. Colorimetric sensor for highly sensitive and selective detection of copper ion. Anal Methods. 2017;9:5094–100.
- Awual MR, Hasan MM, Rahman MM, Asiri AM. Novel composite material for selective copper(II) detection and removal from aqueous media. J Mol Liq. 2019;283:772–80.
- 46. Yang L, Huang N, Huang L, Liu M, Li H, Zhang Y, et al. An electrochemical sensor for highly sensitive detection of copper ions based on a new molecular probe Pi-A decorated on graphene. Anal Methods. 2017;9:618–24.
- Aarjane M, Slassi S, Amine A. Novel highly selective and sensitive fluorescent sensor for copper detection based on Nacylhydrazone acridone derivative. J Mol Struct. 2020;1199:126990.
- Qiu S, Wei Y, Tu T, Xiang J, Zhang D, Chen Q, et al. Triazolestabilized fluorescence sensor for highly selective detection of copper in tea and animal feed. Food Chem. 2020;317:126434.