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TECHNICAL PAPER

Nanofiber-based brush-distributed sensor for detecting heavy metal ions

Hsing-Cheng Chang[1] · Yu-Liang Hsu[1] · Cheng-Yan Tsai[1] · Ya-Hui Chen[1] · Shyan-Lung Lin[1]

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Abstract A brush-distributed metal oxidation sensing nanostructure is developed by growing zinc oxide (ZnO) nanorods on electrospun titanium dioxide (TiO_2) nanofibers to improve ions adsorption of lead and copper. A pair of inductive plane coils are designed to measure inductive variation induced by the adsorbed ion concentration. The brush-distributed ZnO–TiO_2 nanofibers are fabricated by using electrospinning and hydrothermal methods that are deposited on the PVDF-formed nanofiber membrane to enhance copper and lead ions adsorption efficiency. The sensitivity has been promoted based on the van der Waals force and produced hydroxyl from grown surface nanorods. The TiO_2 structure was examined by checking XRD patterns. These diffraction peaks are indexed as the (101), (004), (200), and (105) of anatase TiO_2 and are consistent with the standard data (JCPDS No. 78-2486). The circular coils are designed and simulated using the finite element method to sense metal ions by measuring concentration-dependent magnetic flux variation. The developed ZnO–TiO_2 ion sensing composites include the following advantages: simple fabrication process, low cost, high selectivity, highly effective adsorption, specific surface area and porosity, rapid response, and good repeatability and reproducibility.

✉ Hsing-Cheng Chang
hcchang@fcu.edu.tw

[1] Department of Automatic Control Engineering, Feng Chia University, Taichung 407, Taiwan, ROC

1 Introduction

Most of heavy metals are the transition metal that can induce environmental pollution due to their high residues and is difficult remove. To prevent environmental pollution from distributing heavy metals, many methods have been developed such as digestion extraction, atomic absorption spectrometry, and inductively coupled plasma mass spectrometry. There are also many methods to remove heavy metal ions such as membrane filtration, chemical precipitation, active carbon adsorption, and reverse osmosis (Karami et al. 2004; Ammann 2002; Narin et al. 2000; Fu and Wang 2011; Dabrowski et al. 2004). The nanofiber membranes with high porosity and good filtering effect by electrospinning were developed and surface modification was improved to have good adsorption efficiency (Neghlani et al. 2011). The polyamide nanofibers are fabricated by hydrothermal strategy to perform three-dimensional flower-like structures for increasing the efficiency of adsorption of chromium ions (Jia et al. 2014; Xu et al. 2012). The titanium dioxide-based nanofibers have good bonds to increase copper ions adsorption capacity (Vu et al. 2012). The chitosan nanofibers fabricated on a polyester can enhance the adsorption efficiency by a dynamic forced module (Li et al. 2016; Homaeigohar et al. 2010; Ramasundaram et al. 2013).

In this study, a non-contact sensor for detecting heavy ions of lead and copper is developed by fabricating brush-distributed ZnO–TiO_2 nanofibers doped magnetic materials. The brush-distributed nanofibers have increased specific surface about 35% to improve adsorption and sensing efficiency. Comparing traditional device developed only for executing one ion detection, the nanofiber membrane can filter and detect different heavy metal ions simultaneously. Relative to time response of other devices, the response

and recovery time of the proposed device has shown fast characteristic with reusable function. The proposed device for detecting lead and copper ions has many distinguishing characteristics of rapid detection, highly effective absorption, high selectivity, good repeatability and reproducibility, low cost, and high surface porosity.

2 Experimental details

2.1 Manufacturing process

The sensing film was fabricated by using electrospinning and hydrothermal methods. The electrospinning instrument was set up which contained a micro-infusion pump (Legato KDS 101) for controlling the solution flow rate to the spinning tip, a high-voltage generator for providing a stable electric field, and a collector plate for grounding to collect nanofibers.

The precursor tetrabutyl titanate ($Ti(OBu)_4$) solution was prepared by dissolving 1 g tetrabutyl titanate into 2 ml of glacial acetic acid and 2 ml of ethanol, then doping of 0.08 g cobalt acetate under magnetic stirring for 2 h. The polymer solution was prepared by dissolving 0.4 g polyvinylpyrrolidone to 4 ml of ethanol and 1 ml of dimethylformamide under magnetic stirring for 12 h. Finally, both solutions mixed each other for 6 h to form as-spinning solution. The TiO_2 nanofiber was fabricated by electrospinning from relative humidity of 40% RH, electric voltage of 17 kV, the spinning needle of 19 Gauge, the working distance of 13 cm (distance between the tip and the collection plate), and the constant rate of 1.0 mL/h by a syringe pump. After electrospinning, the nanofiber were dried 12 h at 90 °C and then calcinated at 420 °C in air for 3 h. Zinc oxide (ZnO) nanorods was fabricated by hydrothermal method on the nanofibers. The fabrication processes of brush-distributed nanofibers are shown as Fig. 1.

To grow nanorods by hydrothermal technology, 0.05 M hexamethylene tetramine (HMT) and 0.05 g zinc acetate were stirred and mixed with TiO_2 nanofiber and then transferred into a stainless Teflon-lined autoclave. Then the autoclave was sealed and kept at 100 °C for 3 h, the reactions are shown as formulas (1)–(3). After the hydrothermal reaction, the reactant was collected and cleaned with ethanol and distilled water, and then dried at 60 °C to complete the fabrication process of ZnO–TiO_2 nanofibers.

$$(CH_2)_6N_4 + 6H_2O \xrightarrow{\Delta} 6HCHO + 4NH_3 \quad (1)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (2)$$

$$2OH^- + Zn^{2+} \rightarrow Zn(OH)_2 \rightarrow ZnO_{(s)} + H_2O \quad (3)$$

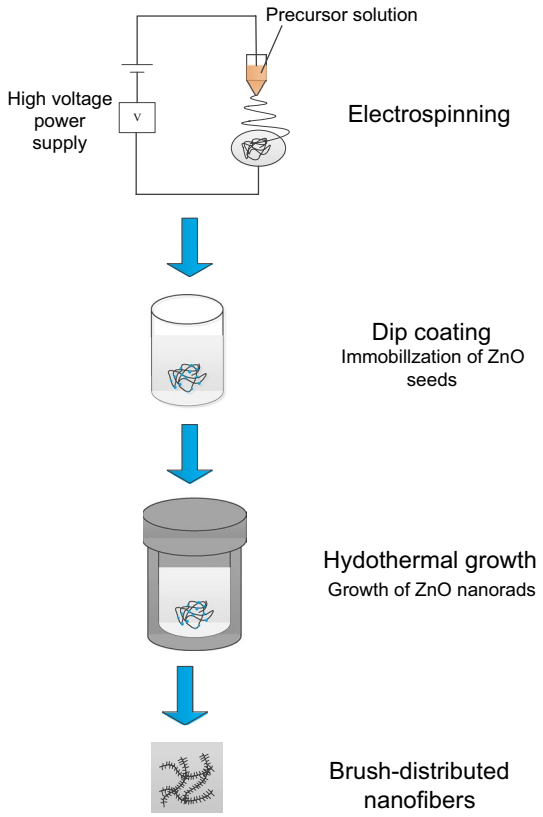

Fig. 1 Flowchart of brush-distributed nanofiber production

The microlithography and microelectroplating techniques are applied to fabricate an inductive loop-coil. First, a Ti film was deposited by evaporation as a seed layer. Second, the patterns of coils and electrodes were defined by photolithography. A Ni metal was deposited on the exposed seed layer using microelectroplating process. Finally, the photoresist was removed by acetone and the seed layers were then etched using chemical solution.

A sensing thin film on the inside of a pair of loop-type coils was arranged to sense magnetic flux changes which were simulated using finite element method (FEM) as shown in Fig. 2. A FEM meshing model for analyzing electromagnetic property has been constructed based on AC/DC model of COMSOL software as shown in Fig. 2a. One of the simulation results was shown in Fig. 2b. The magnetic flux has increased about 35.6% when the measured copper ions are caught on the nanofiber-cased film.

Anatase TiO_2 had shown good adsorption efficiency for copper ions (Vu et al. 2012). The hydroxide of the anatase TiO_2 nanofiber surface would exchange with copper ions to adsorb heavy metal ions. Their reactions should vary with different pH value as shown in formulas (4) and (5). The surface of ZnO have hydroxy groups which had good adsorption efficiency for heavy metal ions (Ma et al. 2010).

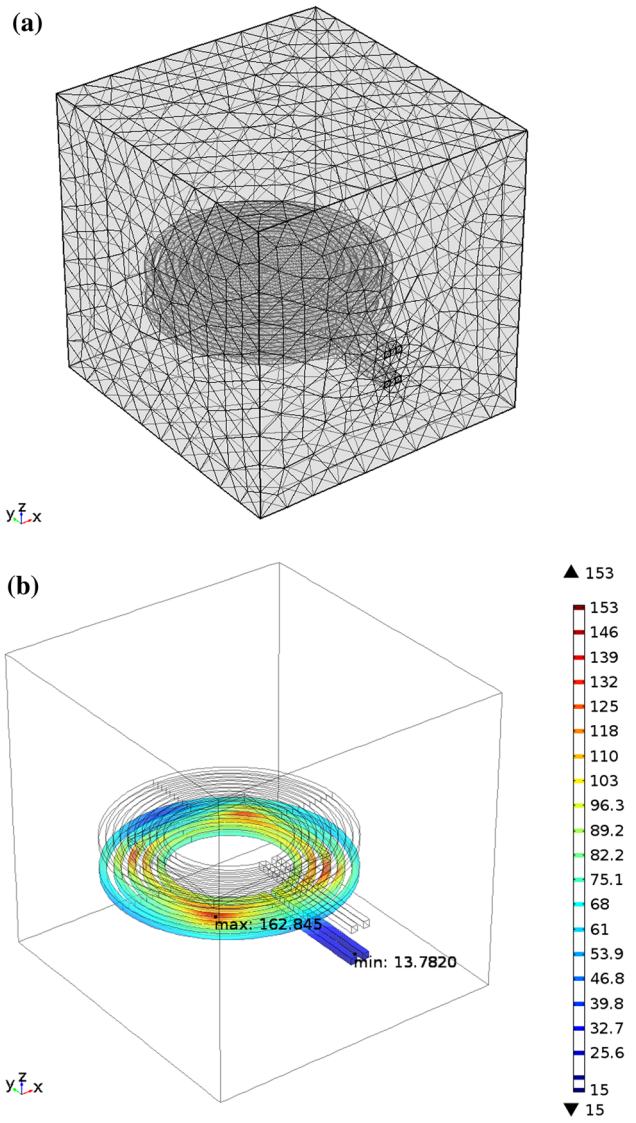

Fig. 2 **a** A FEM meshing model. **b** The magnetic flux variation of sensing coil for sensing copper ions adsorption

$$\text{Ti-OH} + \text{Cu}^{2+} \Leftrightarrow \text{TiOCu}^{+} + \text{H}^{+} \quad (4)$$

$$\text{Ti-OH(OH)}_2 + \text{Cu}^{2+} \Leftrightarrow \text{Ti-(OH)}_2\text{O-Cu}^{+} + \text{H}^{+} \quad (5)$$

Nanosized metal oxides have large surface areas to increase adsorption area and capacity. The nanofibers would generate van der Waals force and other attract force to adsorb heavy metal ions. The specific surface of ZnO–TiO_2 nanofibers are increased 35.6% than that of the TiO_2 nanofibers. The hydroxy groups of ZnO can effectively increase the adsorption efficiency and sensitivity for metal ions.

The brush-distributed nanofibers can release heavy metal ions by rinsing using 0.1 M HCl. When the acid solution reacts on the filtration membrane, the metal ions are substituted with hydrogen ions to resume the bonding ability of the nanofiber for detecting heavy metal ions. The heavy metal ions leave nanofiber surface that promises repeatable sensing and measurements.

2.2 Measurement instrumentation

A measurement system for processing proposed sensor's signal had been setup as shown in Fig. 3. A function generator was used to excite coils and an oscilloscope was used to measure sensing signal. Two set of relays and micro-pumps were selected for arranging flow rate control by a computer. The continuous dynamic sensing measurements were executed with period of 11 s. Periodic sample testing processes were executed in sequential as following: 0.1 M HCl solution washing, deionized (DI) water cleaning, pure nitrogen gas drying, and sensing device measurement, and then do same cycle again. By analyzing the results of continuous dynamic-cycle measurements, the sensor's sensitivity and repeatability can be derived. Experimental results show that the proposed sensor can be applied to measure

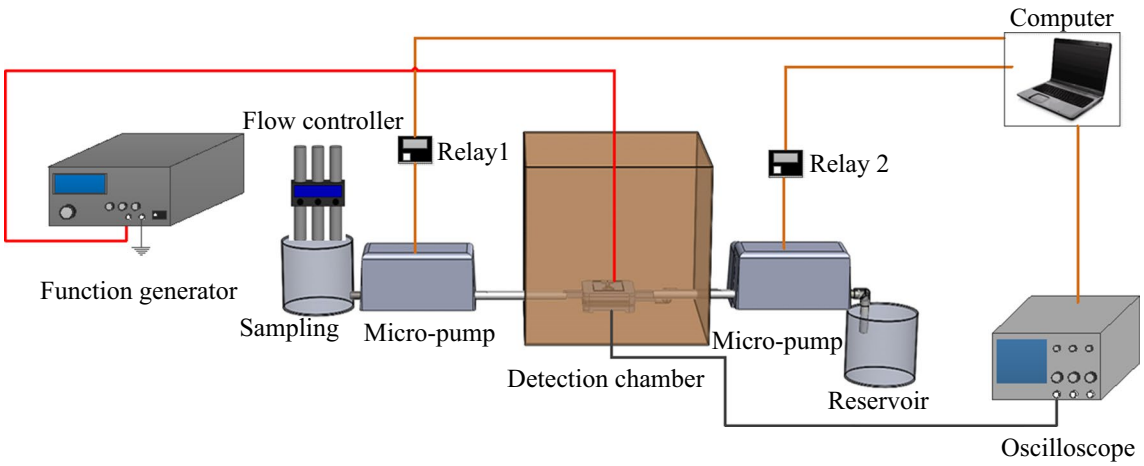

Fig. 3 A measurement system setup for sensing and measuring heavy metal ions

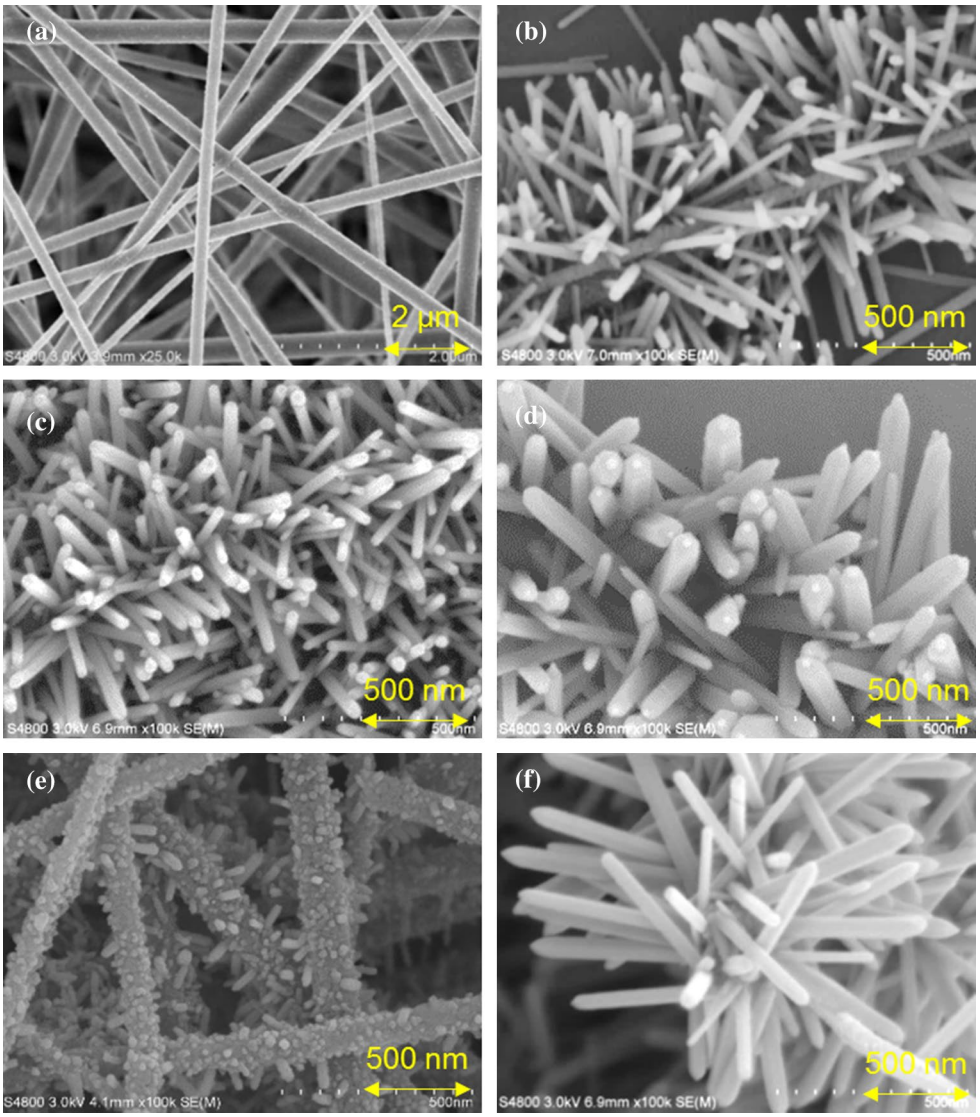

Fig. 4 The SEM images of brush-distributed ZnO–TiO_2 nanofibers. Co-TiO_2 nanofiber with different hydrathermal dip time: **a** 0 min, **b** 5 min, **c** 10 min and **d** 15 min; and with different heating time: **e** 1 h, and **f** 3 h

cooper and lead ions for 10 times with deviation below 5%. After 10 times of application, the sensor's responses decayed with a slope of 6 mV per cycle.

3 Results and discussion

The brush-distributed ZnO–TiO_2 nanofibers are fabricated using electrospinning and hydrothermal technologies. The SEM images of TiO_2 nanofibers and nanorods distribution are observed to analyze nanostructure variation with different dip time and hydrothermal time, shown as Fig. 4. The pure TiO_2 nanofibers had smooth surface with an average diameter of 300 ± 20 nm (Fig. 4a). The average diameters of the TiO_2 nanofibers hydrothermally dipped 5 and 10 min were 50 ± 2 and 50 ± 5 nm, respectively. After hydrothermally dipped 10 min, the nanorods were distributed grown

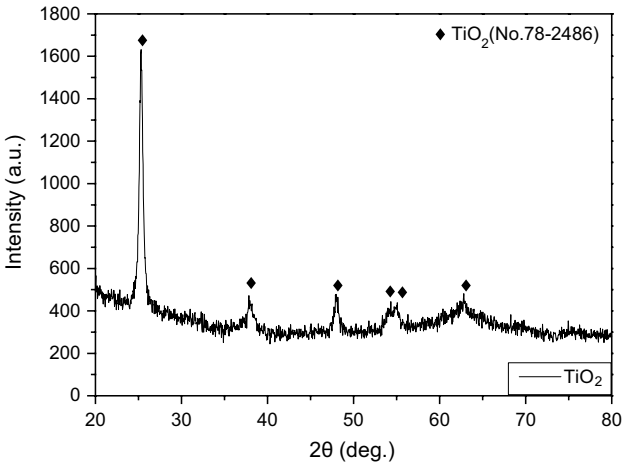

Fig. 5 The XRD patterns of TiO_2 nanofibers

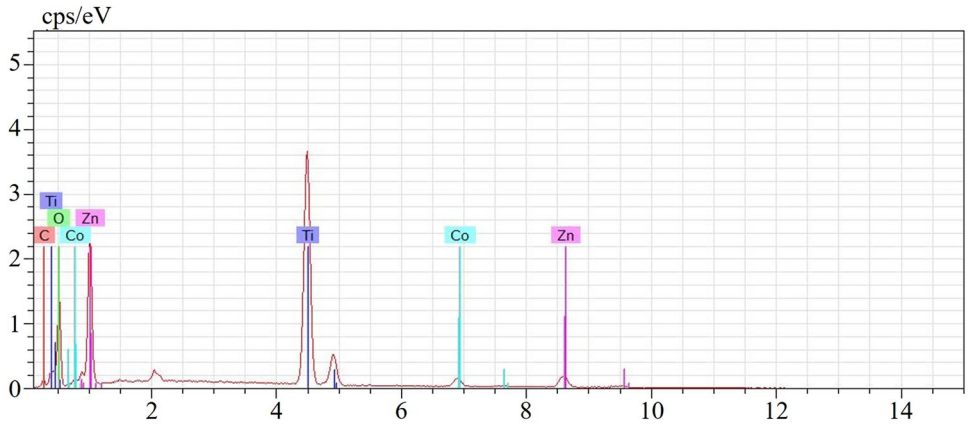

Fig. 6 The EDS patterns of brush-distributed ZnO–TiO_2 nanofibers

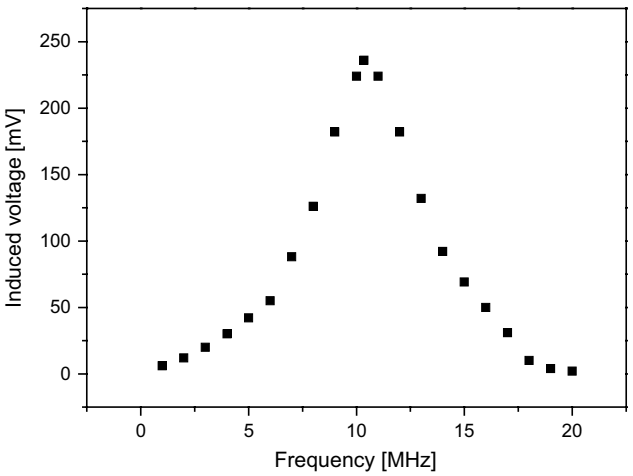

Fig. 7 The response voltage of sensing coils induced from different frequencies

uniformly on the nanofiber surfaces (Fig. 4b, c). When the dip-coated time was over 15 min, the ZnO nanorods had an average diameter of 50 ± 30 nm (Fig. 4d). The nanorods can not grow when the hydrothermal heating time is less than 1 h (Fig. 4e). After three hours heating, the nanorods had an average length of 250 ± 30 nm (Fig. 4f). By dipping 5 min and heating 3 h, the optimal brush-distributed nanofibers were grown. There are 35% increase in specific surface to improve adsorption reaction effectively.

The lattice structure of TiO_2 was examined by checking XRD patterns, shown as Fig. 5. The TiO_2 peaks are ranged from 20° to 80°, and the typical diffraction peaks of anatase TiO_2 are indexed as the (101), (004), (200) and (105). These peaks match well with those of the standard data (JCPDS No. 78-2486). Figure 5 shows that the incorporation of Co^{2+} ions do not change the structure of TiO_2 nanofibers since no diffraction peak related to Co^{2+} ions.

The elements of brush-distributed ZnO–TiO_2 nanofibers were analyzed by energy spectroscopy to determine elements proportion as shown in Fig. 6. The analytic main composition are Ti, Zn, Co, and O, whose occupation are 46.59 wt% Ti, 5.87 wt% Co, 19.21 wt% Zn, and 27 wt% O.

Two major parameters, the coil's resonance frequency and the detection chamber's pH condition, were concerned with sensitivity. The temperature-dependence output responses had shown that the output response decreased with increasing temperature, hence sensor operation at room temperature (25 °C) was set. To obtain optimal sensitivity for sensing ion concentrations of lead and copper, the maximum adsorption reaction condition and the maximum output frequency must be assured. By analyzing output frequency responses, the operation at 10 MHz had the maximum output voltage response as shown in Fig. 7. Experiments of metal ion measurements at 25 °C and 10 MHz with different pH-value conditions were executed and statistically analyzed to find an optimal pH parameter. Figure 8 shows that the highest output voltage response had been discovered at pH-6 condition. Therefore, the output responses with different ions concentrations had shown that the optimal sensitivity was happened at coil's frequency of 10 MHz and at chamber condition of pH-6.

To grow highly sensitive nanostructures of ZnO–TiO_2, different hydrothermal heating tests were executed by measuring the cycle of varied concentrations (0–10–0 ppm) of lead ions. The dynamic behavior is shown in Fig. 9 which shows the best heating time of 3 h.

The results of concentration measurements are shown in Fig. 10 where the measured samples were pump-pushed to the developed nanostructures with flow rate of 1.0 ml/min. The piecewise linear approach is applied to analyze the sensing behavior. The sensitivities of lead and copper ions are 8.3 and 0.59 mV/ppm for the concentration above 5 ppm, respectively. And they are 3.6 and 2.8 mV/ppm for the concentration below 5 ppm, respectively. As the results, the sensing film had better sensitivity for measuring lead ions.

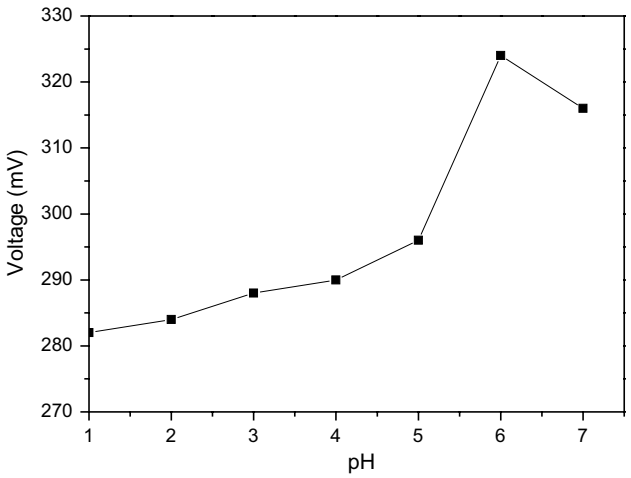

Fig. 8 The variation of sensing voltage for different pH values

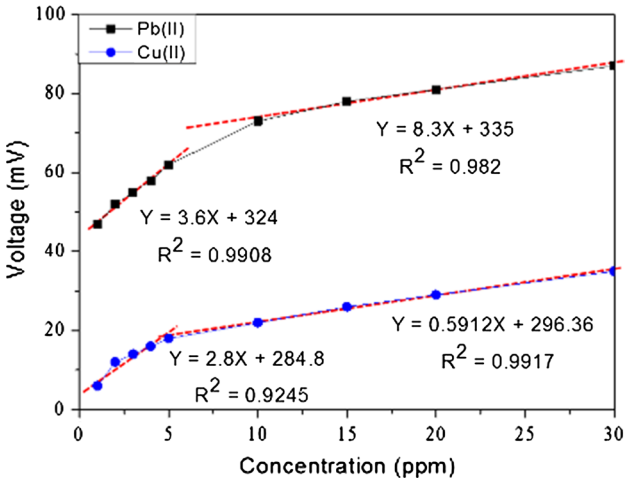

Fig. 10 The analysis of response voltage for lead and copper ions concentration

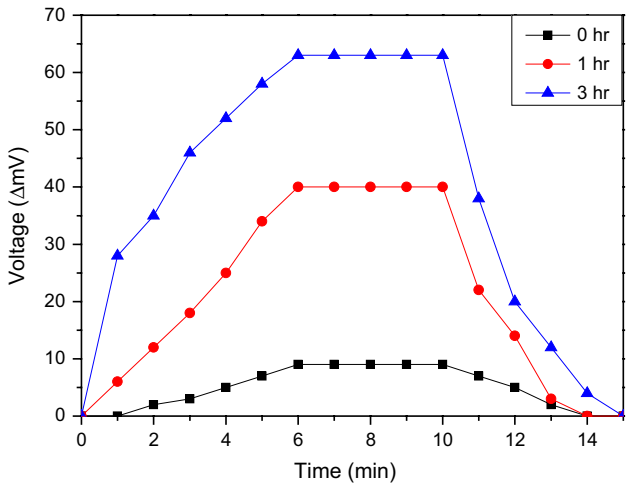

Fig. 9 The time response of output voltage with different hydrothermal time

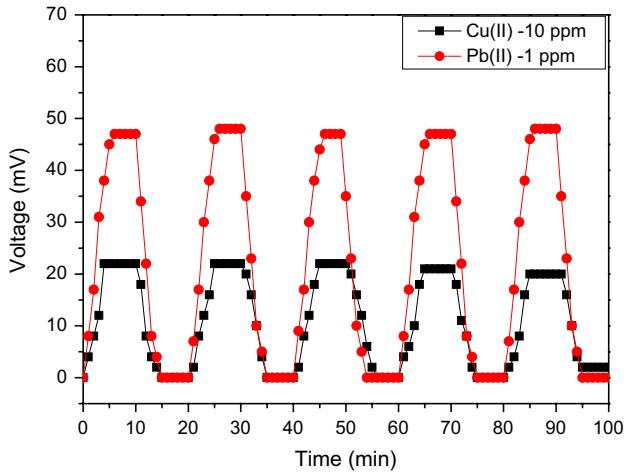

Fig. 11 Dynamic sensing measurements for testing dynamic repeatability

The zinc oxide nanorods grown on a titanium dioxide surface can enhance sensing selectivity. The TiO_2 nanofibers have good adsorption to both copper and lead, and the hydroxy groups of ZnO have better adsorption to lead. Experimental result shows that the ZnO–TiO_2 nanofibers have better sensing ability to lead ions.

To check the device's characteristic of repeatability and recoverability, dynamic sensing measurements are executed by measuring time-dependence ion concentration variation. The periodic responses of different copper ions concentrations by adjusting concentration from 0 to 10 ppm and then back to 0 ppm were executed to observe output time responses. And the same processes were arranged for lead ions measurements by adjusting concentration from 0 to 1 ppm and then back to 0 ppm. After each testing cycle, 0.1 M HCl solution and DI water were used to clean the device for 5 min to recover initial sensing condition. The curves of output time responses were shown in Fig. 11. The response time is defined by analyzing the rising response curve from 10 to 90% in the range of initial to saturation. And the recovery time is defined by analyzing the falling response curve from 90 to 10% in the range of saturation to initial. After continuously periodic sensing cycles, the adsorption rate of devices had kept over 95% for ten times test cycle. Figure 11 shows that the response time and the recovery time are 6 and 5 min, respectively.

The ZnO–TiO_2 adsorption and filtration efficiency were tested by using a peristaltic pump. Electromagnetic measurements show that the heavy metal ion concentration always reaches the highest stable level within 15 min. Table 1 compared nanoscale-based relevant ion sensing

Table 1 The comparison of ion sensing and adsorption properties

Morphology	Material	Heavy metal ion	Adsorption time (min)	References
Particles	MBC + $CoFe_2O_4$	Pb^{2+}	60	Reddy and Lee (2014)
Nanofiber	APAN	Cu^{2+}	20	Neghlani et al. (2011)
Nanofiber	P123-TiO_2	Cu^{2+}	300	Vu et al. (2012)
Nanofiber	PA6@$Mg(OH)_2$	Cr^{3+}	–	Jia et al. (2014)
Nanofiber	TPEE	Cr^{3+}	30	Luo et al. (2015)
Brush-distributed nanofiber	ZnO–TiO_2	Pb^{2+}	15	This work

Table 2 The characteristics comparison of heavy metal ions sensing

Sensing form	Heavy metal ion	Sensitivity	Response time (min)	Recovery time (min)	References
Capacitance	Pb^2	–	15	–	Tsekenis et al. (2015)
Florescence	Cd^{2+}	3.65 (a.u./ppm)	60	–	Zhang et al. (2011)
Florescence	Cr^{3+}	8.58 (a.u./μM)	15	–	Wu et al. (2015)
Electro-chemistry	$Pb^{2+}Cd^{2+}$	3.0 (MΩ/μM)	7	7	Avuthu et al. (2014)
Inductance	Pb^{2+}	8.3 (mV/ppm)	6	5	This work

literatures, and the results show that our ZnO–TiO_2 film outperforms other nanofibers in adsorption time. The characteristics comparison of our ZnO–TiO_2 film and other devices are summarized in Table 2. The first three columns of recovery time in Table 2 were empty because those devices were developed in the stage only for disposable application that the recovery time was not concerned. By comparing the APAN electrospining film developed for adsorbing copper ions by Neghlani et al. (2011), the P123 polymer doped TiO_2 film developed for adsorbing copper ions by Vu et al. (2012), and the electrospining fluorescence film developed for detecting cadmium ions by Zhang et al. (2011), the electospining and hydrothermal grown ZnO–TiO_2 films were developed with increasing sensing surface and multifunctional application for measuring cooper and lead ions efficiently by improving adsorption, filtration and detection efficiency. The results show our ZnO-TiO_2 film with good sensitivity, fast response time, and good repeatability.

4 Conclusions

The heavy metal ions sensor is developed based on the brush-distributed nano-sensing structure of ZnO–TiO_2 nanofibers and nanorods. The copper and lead metal ion sensing capability is enhanced by van der Waals force and hydroxyl adsorption to perform good adsorption and detection capabilities. The adsorption efficiency has above 95% with good repeatability and sensing efficiency. As the results, the sensor measurement had better sensitivity for lead ions than for copper ions. The lead ions sensitivity of 3.6 mV/ppm for concentration below 5 ppm is achieved, and the sensitivity of 8.3 mV/ppm for concentration above 5 ppm is also achieved with good selectivity. After cyclic tests, the response and recovery times are 6 and 5 min, respectively.

References

Ammann AA (2002) Speciation of heavy metals in environmental water by ion chromatography coupled to ICP-MS. Anal Bioanal Chem 372:448–452

Avuthu SGR, Narakathu BB, Eshkeiti A, Emamian S, Bazuin BJ, Joyce M, Atashbar MZ (2014) Detection of heavy metals using fully printed three electrode electrochemical sensor. 13th IEEE Sens Conf. doi:10.1109/ICSENS.2014.6985087

Dabrowski A, Hubicki Z, Podkoscielny P, Robens E (2004) Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. Chemosphere 56:91–106

Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: A review. J Environ Manag 92:407–418

Homaeigohar SS, Buhr K, Ebert K (2010) Polyethersulfone electrospun nanofibrous composite membrane for liquid filtration. J Membr Sci 365:68–77

Jia BB, Wang JN, Wu J, Li CJ (2014) "Flower-Like" PA6@ $Mg(OH)_2$ electrospun nanofibers with Cr(VI)-removal capacity. Chem Eng J 254:98–105

Karami H, Mousavi MF, Yamini Y, Shamsipur M (2004) On-line preconcentration and simultaneous determination of heavy metal ions by inductively coupled plasma-atomic emission spectrometry. Anal Chim Acta 509:89–94

Li L, Li Y, Yang C (2016) Chemical filtration of Cr(VI) with electrospun chitosan nanofiber membranes. Carbohydr Polym 140:299–307

Luo C, Wang J, Jia P, Liu Y, An J, Cao B, Pan K (2015) Hierarchically structured polyacrylonitrile nanofiber mat as highly efficient lead adsorbent for water treatment. Chem Eng J 262:775–784

Ma X, Wang Y, Gao M, Xu H, Li G (2010) A novel strategy to prepare ZnO/PbS heterostructured functional nanocomposite utilizing the surface adsorption property of ZnO nanosheets. Catal Today 158:459–463

Narin I, Soylak M, Elçi L, Doğan M (2000) Determination of trace metal ions by AAS in Natural water samples after preconcentration of pyrocatechol violet complexes on an activated carbon column. Talanta 52:1041–1046

Neghlani PK, Rafizadeh M, Taromi FA (2011) Preparation of aminated-polyacrylonitrile nanofiber membranes for the adsorption of metal ions: comparison with microfibers. J Hazard Mater 186:182–189

Reddy DHK, Lee SM (2014) Magnetic biochar composite: facile synthesis, characterization, and application for heavy metal removal. Colloids Surf A 454:96–103

Ramasundaram S, Yoo HN, Song KG, Lee J, Choi KJ, Hong SW (2013) Titanium dioxide nanofibers integrated stainless steel filter for photocatalytic degradation of pharmaceutical compounds. J Hazard Mater 258:124–132

Tsekenis G, Filippidou MK, Chatzipetrou M, Tsouti V, Zergioti I, Chatzandroulis S (2015) Heavy metal ion detection using a capacitive micromechanical biosensor array for environmental monitoring. Sens Actuators B Chem 208:628–635

Vu D, Li Z, Zhang H, Wang W, Wang Z, Xu X, Dong B, Wang C (2012) Adsorption of Cu(II) from aqueous solution by anatase mesoporous TiO_2 nanofibers prepared via electrospinning. J Colloid Interface Sci 367:429–435

Wu J, Jiang W, Xu S, Wang Y, Tian R (2015) Synthesis of highly selective and sensitive magnetic targeted nanoprobe for Cr^{3+} detection in aqueous solution and its application in living cell imaging. Sens Actuators B Chem 211:33–41

Xu GR, Wang JN, Li CJ (2012) Preparation of hierarchically nanofibrous membrane and its high adaptability in hexavalent chromium removal from water. Chem Eng J 198:310–317

Zhang L, Zhao YH, Bai R (2011) Development of a multifunctional membrane for chromatic warning and enhanced adsorptive removal of heavy metal ions: application to cadmium. J Membr Sci 379:69–79