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Fabrication of paper-based devices by lacquer spraying method for the determination of nickel (II) ion in waste water

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ABSTRACT

A spraying method with lacquer was developed for the fabrication of paper-based devices. A patterned iron mask was initially placed on a filter paper and held tightly attached by a magnetic plate placed on the opposite side. After that, acrylic lacquer was sprayed on the filter paper to create a hydrophobic area while the hydrophilic area was protected with the iron mask. The optimal conditions for the fabrication of this device were studied including lacquer type and particle retention efficiency of filter paper. Gloss spray lacquer and filter paper No. 4 were chosen as optimal lacquer type and particle retention efficiency of filter paper, respectively. To evaluate its efficiency, the paper-based devices were used to determine nickel using electrochemical detection. Cu-enhancer solution was employed to increase sensitivity of nickel determination with the optimal concentration of 4.5 ppm. Under the optimal conditions, linear range was observed in the range of 1–50 ppm with a coefficient of determination of 0.9971. The limit of detection (LOD) and the limit of quantitation (LOQ) were found to be 0.5 and 1.97 ppm, respectively. Moreover, these paper-based devices coupled with electrochemical detection were applied to determine nickel in waste water of a jewelry factory and compared to those obtained with inductively coupled plasma optical emission spectrometry (ICP-OES). The results indicated that there were no significant variations between this proposed method (4.15 ± 0.043 ppm) and the ICP-OES method (4.06 ± 0.013 ppm). Therefore, this spraying method was found to be an excellent alternative for the fabrication of paper-based devices due to its ease of use, affordability and simplicity.

1. Introduction

Paper-based devices have the potential to be good alternative analytical devices for healthcare related applications because they are portable, easy to use, have a low sample volume requirement and provide rapid analysis [1–3]. Paper-based device is a device made of paper in which the main component is cellulose fiber. Paper is a low-cost material that is readily available and easy to manipulate. Therefore, paper-based devices have been widely popular and have many potential benefits in fields as diverse as environmental monitoring and clinical research. Currently, paper-based devices have become an interesting technology for research units, resulting in the development of method for the fabrication of paper-based devices. A lot of methods for fabricating the pattern on paper have been proposed, including photolithography [4–11], polydimethylsiloxane (PDMS) plotting [12], inkjet printing [13], cutting [14], plasma etching [15], wax printing [16–18], wax screen-printing [19], and wax dipping [20]. Each fabrication method has its own advantages and limitations that are similar and/or different. The first reported method was based on photolithography. This method can provide a narrow barrier line between the hydrophilic and hydrophobic areas of approximately 200 μm width [6]. However, this method involves the use of organic solvents, expensive photoresists and photolithography apparatus. Moreover, the fabrication process involves many complicated processes. The PDMS plotting method also overcomes the problems of physical inflexibility of devices using photolithography [11]. This method does not use expensive photoresists, organic solvent and photolithography instrument. Unfortunately, this method needs a customized plotter [10]. The inkjet printing method involves the use of organic solvent to print onto the polymer-soaked paper by inkjet printer for creating a hydrophilic area on the paper. Plasma etching is a method to detract sizing agent [21] coating on the paper using plasma treatment. However, paper-based devices created by photolithography, inkjet printing and plasma etching methods all still require organic solvents and polymers to create hydrophilic areas. In the cutting method, a knife plotter is used to cut paper to create

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a pattern of microfluidic channels. However, this method requires the use of tape to define the paper pattern, which is difficult in implementation. The wax printing method utilizes a commercially available wax printer for the fabrication of paper-based devices. This method is easy and fast to generate a patterned paper using a wax printer. However, this method has a shallower barrier than photolithography (~850 μm of minimal barrier) because the spread of the wax is difficult to handle when wax was melted on hotplate. So, careful impregnation of wax must be regarded before creation of the pattern in this method. The wax screen-printing method is similar to the wax printing method by using a commercial wax for the fabrication of paper-based devices, but wax screen-printing does not require wax printer for fabrication. This method can create a pattern by using screen-printed block instead of the commercial printer. The advantages of the wax screen-printing method are low-cost, simple, and rapidness. Nevertheless, using wax screen-printing it is difficult to produce the exact designed pattern with high barrier due to the spread of wax. Recently, a new fabrication method for creating paper-based devices has been reported as wax dipping. Wax dipping does not demand expensive equipments and organic solvents. However, the hydrophobic areas generated by the wax printing, wax screen-printing and wax dipping methods still used the hot plate for melting wax. Moreover, limitations of these previous methods by wax are wax spreading before creating the pattern and the trained personnel for using and maintaining the instruments. To overcome these limitations, a simple, rapid and low-cost fabrication method, that also provides several advantages, needs to be developed. A spraying method with lacquer was therefore developed for the fabrication of paper-based devices.

Acrylic lacquer is made of acrylic resin. One of main characteristic features of acrylic resin is high transparency. Acrylic lacquer is a polymer (resin) generated through chemical reaction by applying polymerization. The advantages of acrylic resin are water resistance, good adhesion and fast drying [22].

The objective of this work is to present a new concept of spraying method with lacquer for the fabrication of paper-based devices. To evaluate the efficiency of this developed method, paper-based devices with electrochemical detection were used to determine nickel in waste water of a jewelry factory using the differential pulse anodic stripping voltammetry (DPASV) and copper-enhancing solution was used for increasing the sensitivity of nickel determination.

2. Materials and methods

2.1. Materials and chemicals

Whatman No. 1 (11 μm porosity) and No. 4 (20–25 μm porosity) filter papers were purchased from Cole-Parmer (Vernon Hills, IL). A patterned iron mask (1 mm thick, manufactured from steel plate) was made-to-order by a laser cutting shop in Bangkok. Magnetic plate and acrylic lacquer Leyland® manufactured by Nakoya Paint (Thailand) Co., Ltd. were purchased from a local area shop in Bangkok. Carbon ink was purchased from Gwent group (Torfaen, UK). Silver chloride ink (Electrodag 7019) was obtained from Acheson Colloids Company (Port Huron, MI). Electrochemical measurements were performed using a potentiostat (Autolab PGSTAT 30). All solutions were prepared in 18 MΩ cm^{-1} resistance deionized water (obtained from a Millipore Milli-Q purification system). A standard solution CertiPUR®, 1000 mg L^{-1} $Ni(NO_3)_2$ in HNO_3 2–3% was purchased from Merck and was used as the stock solution. Sodium chloride (NaCl) (99.5%) (Merck) and copper sulfate ($CuSO_4$) (99%) (BDH) were used as received.

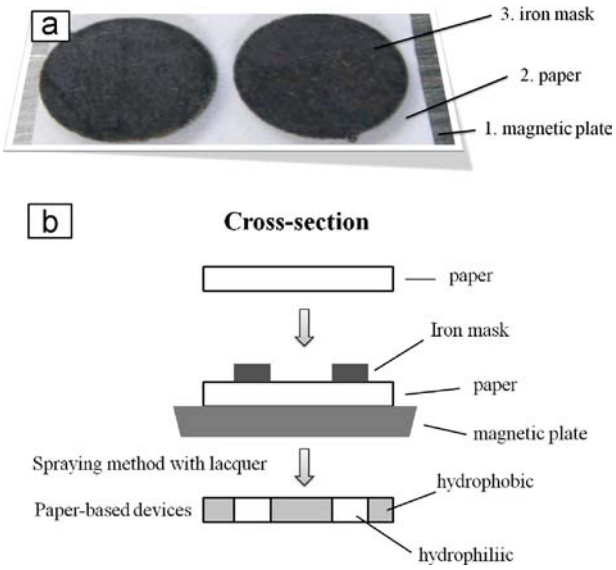

Fig. 1. Schematic representation of the procedure for the fabrication of the paper-based devices by the lacquer spraying method (a) in top view and (b) in cross-section view.

2.2. Spraying method with lacquer for fabrication of pattern on paper

The spraying method with lacquer was used to fabricate the pattern on a filter paper. The iron mask (Fig. 1a), which was designed by an Adobe Illustrator and manufactured using the laser cutting technique, was used to create cover pattern on the paper. Hydrophobic area was created by the spraying method. To fabricate paper-based devices (Fig. 1b), the paper was first put on a magnetic plate. Next, the iron mask was placed on the other side of the paper and it was temporarily attached by means of magnetic force with a magnetic plate placed on the backside of the paper. Then, the paper was sprayed with lacquer creating the hydrophobic barrier around the iron mask. After that, the paper was air-dried and the iron mask was removed from the paper. Finally, the image of hydrophobic and hydrophilic areas of the pattern on the paper were characterized using an optical microscope and scanning electron microscopy (SEM)

2.3. Preparation of electrochemical detector for paper-based devices.

The screen-printed electrodes were prepared in-house. The three electrodes were fabricated using the screen-printing method. The carbon ink was used as the working electrode (WE) and the counter electrode (CE) and the silver/silver chloride ink was used as the reference electrode (RE) and conductive pads. All electrodes were screened on the patterned paper and were cured in the oven at 65 °C for 30 min. The paper-based devices coupled with electrochemical detection are shown in Fig. 2.

2.4. Applicability of paper-based devices for the determination of nickel in waste water sample of a jewelry factory

A waste water sample from a jewelry factory was obtained from the Gem and Jewelry Institute of Thailand (Public Organization). The jewelry waste sample was prepared by filtration of 20 mL of waste water with Whatman No. 1 filter paper. Then the sample was mixed with 20 mL of HNO_3 and the solution was heated at 200 °C to evaporate the solvent. After that, the sample was made up with 20 mL of Milli-Q water and was heated at 100 °C until dryness (repeated three times). Next, the sample was rinsed with

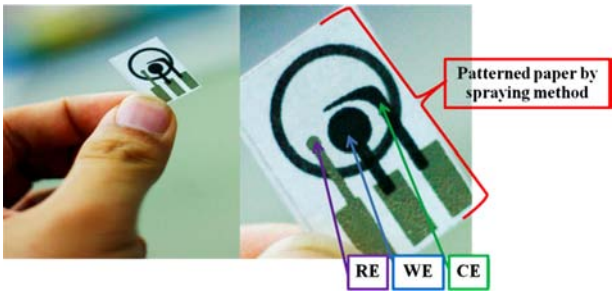

Fig. 2. Paper-based devices coupled with electrochemical detection showing the carbon ink based working (WE) and counter (CE) electrodes, plus the silver/silver chloride based reference electrode (RE).

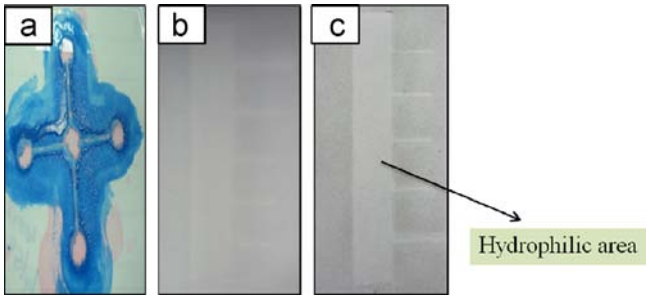

Fig. 3. The effect of the lacquer type for fabrication of the paper-based devices: (a) paint lacquer (blue color), (b) matte spray lacquer (colorless) and (c) gloss spray lacquer (colorless). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

mixed solution between 20 mL of 0.1 M NaCl and Cu solution 4.5 ppm (pH 6.7). Finally, the sample was sonicated for 30 min and clear solution was ready for analysis.

3. Results and discussions

3.1. The effect of lacquer type for the fabrication of paper-based devices

In this work, the effect of lacquer type was studied. Three types of acrylic lacquer were investigated, including paint lacquer, matte spray lacquer and gloss spray lacquer. For paint lacquer, the paper was painted with paint lacquer instead of spraying. The results indicated that it was inappropriate for fabrication of pattern on paper because the penetration of lacquer into the filter paper and the diffusion under the iron mask could not be controlled (Fig. 3a). To study the matte spray lacquer and gloss spray lacquer, the spraying method was used as the lacquer application method. With the matte spray lacquer (Fig. 3b), the hydrophobic and hydrophilic areas can be generated on the paper-based devices, however, the uniformity of pattern on paper was difficult to observe. For gloss spray lacquer, the results indicated that the hydrophobic and hydrophilic areas were clearly distinguished (Fig. 3c). Therefore, the gloss spray lacquer was chosen for fabricating the paper-based devices throughout the following work.

3.2. The effect of particle retention efficiency of filter paper for fabrication of paper-based devices

Since the distribution of the lacquer could not be controlled, the effect of particle retention efficiency of filter paper was studied. The particle retention efficiency of a depth-type filter is expressed in terms of the particle size (in μm). A retention level of 98% of the total number of particles was obtained [23]. The Whatman filter paper No. 1 and No. 4 were used to study in this work. The particle retention efficiency of Whatman filter paper No. 1 and No. 4 was 11 μm and 20–25 μm respectively. The results indicated that Whatman filter paper No. 4 gave better results than Whatman filter paper No. 1 because the former has larger porosity (Fig. 4). Therefore, the lacquer easily and rapidly penetrated into the fibers of filter paper No. 4. In this work, the Whatman filter paper No. 4 was thus chosen to fabricate paper-based devices.

3.3. The characterization of hydrophilic and hydrophobic areas on paper-based devices

The hydrophobic area was created by the sprayed lacquer on filter paper while the hydrophilic area was protected by the iron mask. The lacquer was not absorbed into the hydrophilic area. Therefore, the pattern of hydrophobic and hydrophilic areas was generated on the paper. The fabricated pattern on the paper was observed by an optical microscope (Olympus CX31), as shown in Fig. 5a and b. It was clearly seen that the surface of the paper was significantly changed as a result of lacquer coating. From Fig. 5a, the right side of the paper is the native surface, whereas the left side was coated with lacquer and completely turned into a hydrophobic area. In Fig. 5b, it was observed that a colored food dye was not able to percolate into the hydrophobic area because of lacquer coating. Fig. 5c shows the hydrophobicity of our paper-based devices following a drop of a colored food dye comparing to that of the hydrophilic zone. Then, the surface image of the pattern paper was taken by a scanning electron microscope (JSM-6400) as shown in Fig. 6a and b. Fig. 6a shows the cross-section of the surface paper uncoated with lacquer, and Fig. 6b shows the cross-section of the surface paper coated with lacquer, which clearly demonstrated the infiltration of the lacquer through the porosity of the filter paper.

3.4. The effect of Cu-enhancer solution for the determination of nickel

Based on earlier findings, copper solution is reported to enhance the sensitivity [24]. Hence in this study, we are interested in using copper to enhance the determination of nickel with the fabrication of paper-based devices. In conclusion, from the results, we found that copper can be used to enhance the sensitivity of electrochemical detection of nickel. The effect of the concentration of copper was studied in range from 0.5 to 7.5 ppm. The relationship between current and concentration of copper is shown in Fig. 7. The peak current increased until the concentration of copper was 4.5 ppm. Then peak current decreased, it could be explained that unsuitable concentration of copper may have disturbed the signal of nickel. Therefore, the optimum concentration of copper at 4.5 ppm was chosen.

3.5. Analytical performance

Under the optimum experimental conditions, the electrochemical performance of the DPASV for the determination of nickel using paper-based devices coupled with electrochemical detection on screen-printed carbon electrode was studied. A 50 μL of solution was dropped on the hydrophilic area of paper-based device. Peak potential of nickel was obtained in potential region between −0.20 and −0.10 V (versus Ag/AgCl). The obtained voltammograms provided well-defined oxidation peaks. Therefore, the developed paper-based devices are clearly an effective tool to determine nickel. The relative standard deviation (RSD) of all concentrations of nickel were within 1.25% ($n=3$), demonstrating

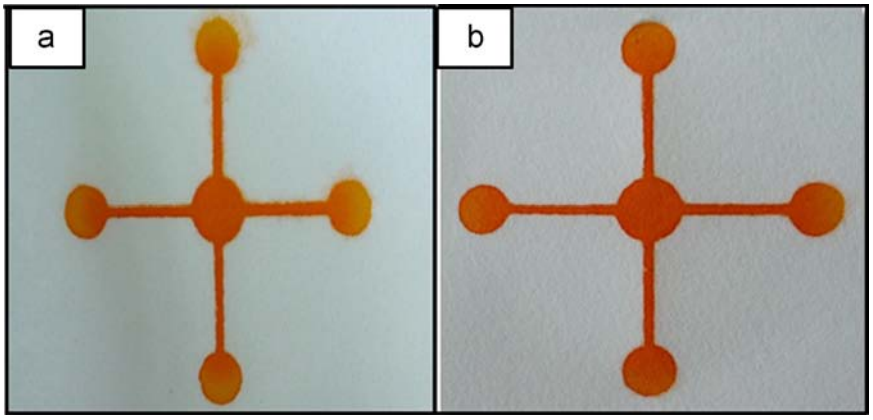

Fig. 4. The effect of the filter paper particle retention efficiency in the fabrication of a paper-based device (a) Whatman filter paper No. 1 with a porosity of 11 μm and (b) Whatman filter paper No. 4 with a porosity of 20–25 μm.

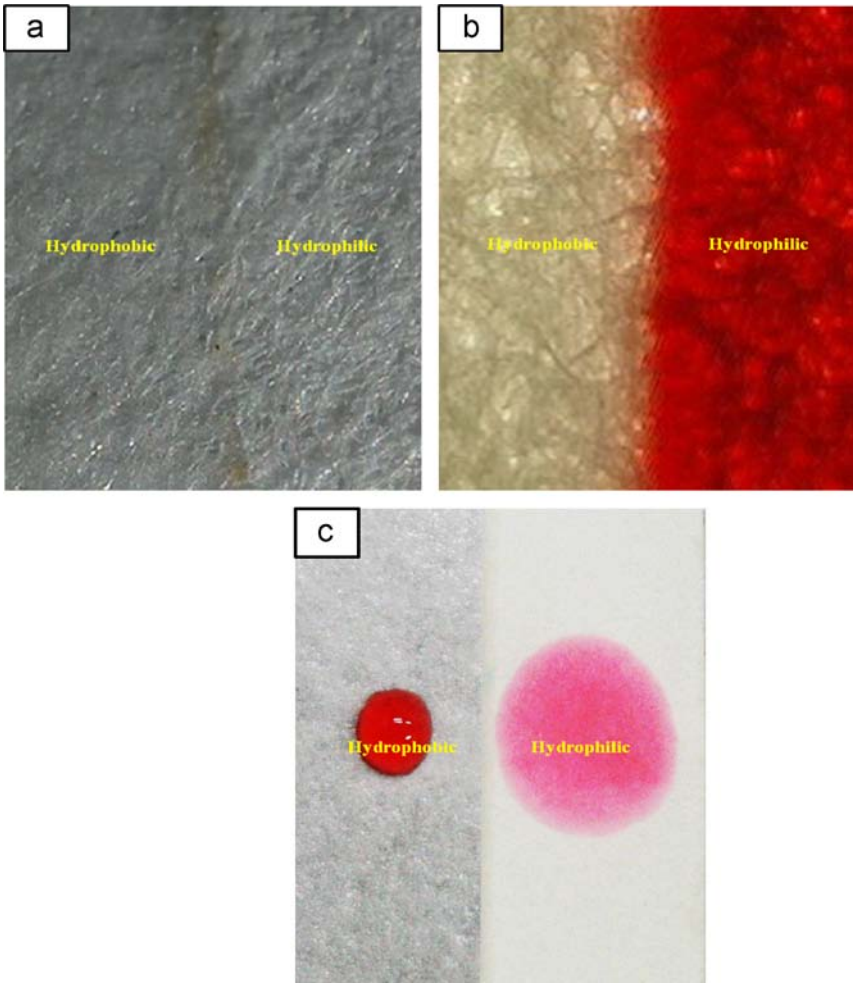

Fig. 5. The paper-based device fabricated by the gloss lacquer spraying method, showing: (a) the hydrophobic (left side) and hydrophilic (right side) areas captured under an optical microscope at 4× magnification, (b) the hydrophilic zone soaked with food dye color and (c) a comparison of the hydrophilic and hydrophobic areas of the paper after applying a drop of colored food dye.

acceptable reproducibility for this device. Calibration curve of the anodic current against concentrations generated linear range between 1 and 50 ppm with a high coefficient of 0.9971 (Fig. 8). The limit of detection (LOD) and the limit of quantitation (LOQ) were found to be 0.5 and 1.97 ppm, respectively.

3.6. Analytical application

To evaluate the efficiency of this developed method, the paper-based devices with electrochemical detection were used to detect nickel in waste water of a jewelry factory. The determination of

nickel in real sample was carried out using the optimal conditions. In addition, this proposed method was compared with the ICP-OES method. The results indicated that the concentration of nickel in waste water were found to be 4.15 ± 0.043 ppm for electrochemical detection and 4.06 ± 0.013 ppm for the ICP-OES method ($n=3$). For the reproducibility study, RSD values ($n=9$) for determination of nickel using our proposed paper-based devices and ICP-OES system were found to be 1.32% and 1.25%, respectively. The paired *t*-test was used to validate our method versus the ICP-OES method. No significant difference of the analyzed values of nickel in the jewelry waste water was found at the 95% confidence level.

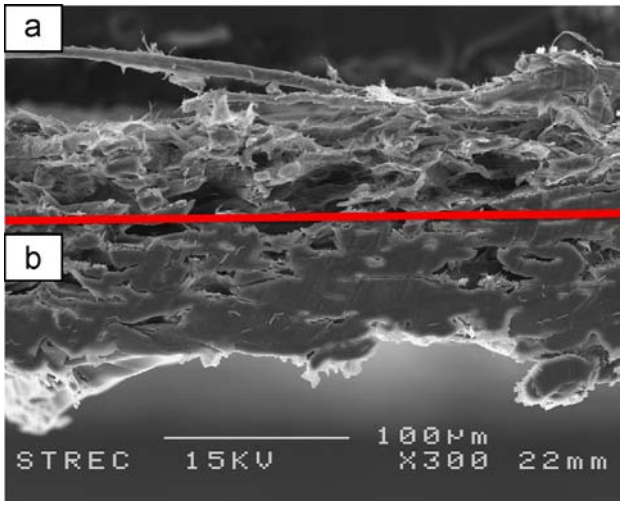

Fig. 6. SEM image (300× magnification) of the cross-section surface of the Whatman filter paper No. 4, either (a) uncoated or (b) coated with gloss spray lacquer.

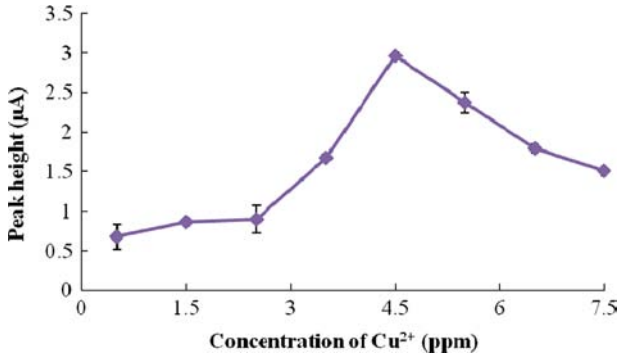

Fig. 7. The effect of the Cu^{2+} concentration on enhancing the 0.5 ppm Ni^{2+} signal in 0.1 M NaCl.

4. Conclusions

The lacquer spraying method was successfully employed for the fabricating paper-based devices. This spraying method is an alternative method due to its ease of use, affordability and simplicity. In addition, there is no requirement for complicated and expensive instruments or organic solvents. The iron mask was used to create the pattern of hydrophilic area and hydrophobic area was obtained by spraying with lacquer. The spraying method does not suffer from problems of interference from residues remaining in the hydrophilic area after fabrication. Moreover, the paper-based devices were shown to be useful for electrochemical detection methods, and were applied for the determination of nickel in real samples. Therefore, to fabricate paper-based devices, the spraying method with lacquer is one of the effective promising method.

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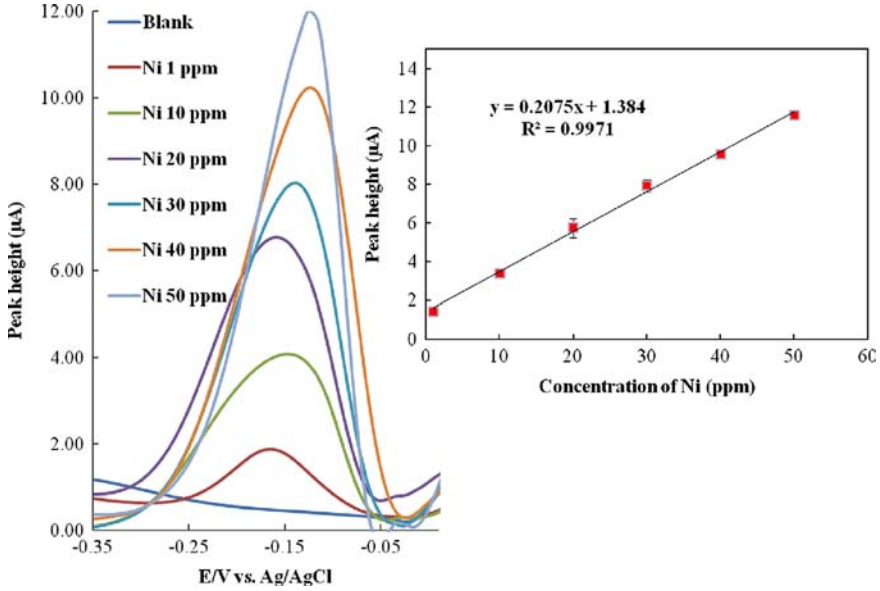

Fig. 8. (a) Anodic stripping voltammogram of Ni^{2+} (1–50 ppm) determination with the screen-printed carbon electrode on a Whatman No. 4 paper-based device at a deposition potential of −0.9 V versus Ag/AgCl. (b) The calibration plot of anodic currents at 180 s of deposition time for determination of the Ni^{2+} level. Data are (a) representative of, or (b) derived from, three independent repeats.

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References

[1] F.S.R.R. Teles, L.A.P.D.T. Tavira, L.J.P. Fonseca, Crit. Rev. Clin. Lab. Sci. 3 (2010) 139–169.
[2] S. Haeberle, R. Zengerle, Lab Chip 7 (2007) 1094–1110.
[3] S. Sun, M.H. Yang, Y. Kostov, A. Rasooly, Nature 442 (2006) 412–418.
[4] A.W. Martinez, S.T. Phillips, G.M. Whitesides, E. Carrilho, Anal. Chem. 82 (2009) 3–10.
[5] A.W. Martinez, S.T. Phillips, M.J. Butte, G.M. Whitesides, Angew. Chem. Int. Ed. 46 (2007) 1318–1320.
[6] A.W. Martinez, S.T. Phillips, E. Carrilho, S.W. Thomas, H. Sindi, G.M. Whitesides, Anal. Chem. 80 (2008) 3699–3707.
[7] A.W. Martinez, S.T. Phillips, B.J. Wiley, M. Gupta, M. Whitesides, Lab Chip 8 (2008) 2146–2150.
[8] W. Dungchai, O. Chailapakul, C.S. Henry, Anal. Chem. 81 (2009) 5821–5826.
[9] Z. Nie, C.A. Nijhuis, J. Gong, X. Chen, A. Kumachev, A.W. Martinez, M. Narovlyansky, G.M. Whitesides, Lab Chip 10 (2010) 477–483.
[10] R.F. Carvalhal, M. Sima~o Kfouri, M.H. de Oliveira Piazetta, A.L. Gobbi, L. T. Kubota, Anal. Chem. 82 (2010) 1162–1165.
[11] A. Apilux, W. Dungchai, W. Siangproh, N. Praphairaksit, C.S. Henry, O. Chailapakul, Anal. Chem. 82 (2010) 1727–1732.
[12] D.A. Bruzewicz, M. Reches, G.M. Whitesides, Anal. Chem. 80 (2008) 3387–3392.
[13] K. Abe, K. Suzuki, D. Citterio, Anal. Chem. 80 (2008) 6928–6934.
[14] E.M. Fenton, M.R. Mascarenas, G.P. L_opez, S.S. Sibbett, ACS Appl. Mater. Interfaces 1 (2008) 124–129.
[15] X. Li, J. Tian, T. Nguyen, W. Shen, Anal. Chem. 80 (2008) 9131–9134.
[16] E. Carrilho, A.W. Martinez, G.M. Whitesides, Anal. Chem. 81 (2009) 7091–7095.
[17] L.Y. Shiroma, M. Santhiago, A.L. Gobbi, L.T. Kubota, Anal. Chim. Acta 725 (2012) 44–50.
[18] M. Santhiago, L.T. Kubota, Sens. Act. B. 177 (2013) 224–230.
[19] W. Dungchai, O. Chailapakul, C.S. Henry, Analyst 136 (2011) 77–82.
[20] T. Songjaroen, W. Dungchai, W. Chailapakul, W. Latwattanapaisal, Talanta 85 (2011) 2587–2593.
[21] X. Li, J. Tian, G. Garnier, W. Shen, Colloids Surf. B: Biointerf. 76 (2010) 564–570.
[22] R. Lu, T. Honda, T. Ishimura, T. Miyakoshi, Polym. J. 37 (2005) 309–315.
[23] ⟨http://www.Whatman.com/References/FiltrationSimplified.pdf⟩.
[24] A. Apilux, W. Siangproh, N. Praphairaksit, C.S. Henry, O. Chailapakul, Talanta 97 (2012) 288–394.