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Ultra-fast and probe-free cellulose biosensor for visual detection of Cu^{2+} ions in biological samples

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ABSTRACT

Novel, portable, probe-free, liquid cellulose biosensor was explored via a facile one-pot process for Cu^{2+} ions detection by naked eyes. The as-prepared biosensor displayed specific recognition towards Cu^{2+} ions in aqueous solution, even in complex urine and serum samples within 10 s, showing fast response characteristic. There is barely any interference on the Cu^{2+} ions detection by other metal ions or other complex substances in urine and serum, and the corresponding detection limit is as low as 1.185, 1.9309 and 1.9154 ppm, respectively. Moreover, the cellulose biosensor could act as an excellent candidate to sense Cu^{2+} ions in biological samples including urine and serum from SD rats with satisfying accuracies and biocompatibility. This study exploits a potential application of cellulose in biosensing and monitoring related to Cu^{2+} ions.

1. Introduction

Copper ion (Cu^{2+}) is the third abundant essential elements in human body, and participates in various physiological activities, such as redox processes, enzyme functions and signal transduction (Awual, Hasan, & Khaleque, 2016; Gurgel & Gil, 2009). The normal level of Cu^{2+} ions in blood is 100~150 μg/L (Kaler, 2011; Pall et al., 1987). Excess of Cu^{2+} ions can induce live and kidney damage, neurodegenerative diseases including Wilson's syndrome, Alzheimer's and Parkinson's diseases (Barnham, Masters, & Bush, 2004; Liu et al., 2016; Waggoner, Bartnikas, & Gitlin, 1999). Also, Cu^{2+} ions are one of the abundant contaminants of drinking water. The World Health Organization (WHO) suggested that the level of Cu^{2+} ions is 2.0 mg/L in drinking water (Zhao, Wang, Younis, Wang, & Xia, 2017). Thus, the detection of Cu^{2+} ions is imperative for the early disease diagnosis and monitoring.

To date, various analytical methods like inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption/emission spectroscopy (AAS/AES), high-performance liquid chromatography (HPLC), electrochemical method (Hu, Song, Zhao, Meng, & Wu, 2015; Yan et al., 2016), etc. have been explored for Cu^{2+} ions assay. These instrument-based methods are usually expensive, operational complexity, and need precise instruments and well-trained technicians, making them unsuitable for real time on-site detection. Recently, fluorescent sensors have been reported for the selective detection of Cu^{2+} ions owing to their simplicity, high sensitivity, continuous real-time detection and rapid response (Edwards, Prevost, French, Concha, & Condon, 2015; Liu et al., 2017; Wang & Zong, 2015). Lv et al reported a fluorescent film sensor in which a polyfluorene derivative was chemically immobilized onto a glass-plate surface for selective and sensitive detection of Cu^{2+} ions by a fluorescence quenching sensing mechanism (Lv, Feng, Tang, Liu, & Wang, 2011). Ce^{3+}/Tb^{3+}-doped SrF_2 nanocrystals were prepared as fluorescent probe to detect Cu^{2+} ions, which displayed highly selective and sensitive for Cu^{2+} detection with a sensitive detection limit of 2 nM (Sarkar, Chatti, Adusumalli, & Mahalingam, 2015). Also, a dual-colored carbon dot ratiometric fluorescent test paper was reported for the semiquantitative assay of Cu^{2+} ions with a detection limit of 8.82 nM (Ren et al., 2017). Although the use of fluorescent sensors exempts the complex sample pretreatment process, the monitoring of Cu^{2+} ions still depends on the aid of fluorescence spectrometer. Moreover, multistep and sophisticated preparation or chemical modification, water-insolubility all make them not appropriate for Cu^{2+} ions detection in biological systems. Therefore, the development of a simple, portable, probe-free, highly sensitive, cost-effective colorimetric sensor is of prime importance.

In our previous work, a novel cellulose-Schiff base was synthesized via polyethylenimine (PEI) modification and exhibited promising application for water treatment as well as Cu^{2+} ions detection. Although great achievements have been obtained, two-step preparation of the cellulose-Schiff base as well as its water-insolubility should be further

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overcome. Herein, we present a simple, portable, probe-free colorimetric biosensor for detection of Cu^{2+} ions using natural cellulose, whereas cellulose was oxidized and modified by PEI through a facile one-pot process. The resultant cellulose biosensor exhibited high sensitivity, selectivity, quick response, biocompatibility, and excellent practicability for Cu^{2+} ions detection in urine and blood samples, exhibiting a tremendous potential in simple, high-efficiency, non-invasive assay of Cu^{2+} ions in physiological research, disease diagnosis and monitoring.

2. Experimental section

2.1. Materials

Cellulose powder (M_w = 20,000), PEI (M_w = 600), NaOH, urea, $NaIO_4$, HCl, bovine serum, ordinary filter paper, and dialysis bag (MWCO = 8000 D) were all supplied by Shanghai Aladdin Chemical Reagent Co, Ltd. Ni^{2+}, Cd^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Ca^{2+} ions aqueous solutions were prepared from $Ni(CH_3COO)_2$, $Cd(CH_3COO)_2$, $Mg(CH_3COO)_2$, $Cu(CH_3COO)_2$, $ZnCl_2$, $Mn(CH_3COO)_2$, $Ca(CH_3COO)_2$. Deionized water was used throughout the experiments.

2.2. Synthesis of cellulose biosensor

Synthesis of biosensor from natural cellulose was preformed by a facile one-pot process. Briefly, cellulose powders and $NaIO_4$ with a mass ratio of 1:1 were dissolved in 7 wt % NaOH/12 wt % urea solution covered with a tin foil. pH value of the reaction system was adjusted to 4. At 60 °C, the reaction was carried out for 4 h with a stirring, and then adding equal PEI for 3 h reaction. Cooling down to room temperature, the products were centrifuged at 8 000 rpm for 5 min, then the obtained supernatant was dialyzed for 48 h (Huang et al., 2018; Liu et al., 2017). Finally, the liquid cellulose biosensor was harvested.

2.3. Characterization of cellulose biosensor

The chemical structure of biosensor was characterized by Fourier transform infrared spectroscopy (FTIR, Nicolet 5700, Thermo Electron Corp., USA) ranging from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}. The size of the biosensor was determined using Dynamic light scattering method (DLS, Malvern NanoSizer Nano-ZS90, UK).

2.4. Detection of Cu^{2+} ions

1 mL of cellulose biosensor was added into 20 mL metal ions solutions with a concentration of 10 ppm. The color changes of different metal ions in aqueous solution were observed by naked eye, and the resulting UV–vis spectra were recorded by a UV–vis spectrophotometer (UV, U-3900 spectrophotometer, Japan). For selectivity tests, Fe^{3+}, Ni^{2+}, Cd^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+} and Ca^{2+} ions were used, and 20 mL of mixed solution was also prepared in which the concentration of Cu^{2+} ions was 10 ppm and other metal ions was 50 ppm. For tolerance limit determination, Cu^{2+}/Fe^{3+}, Cu^{2+}/Ni^{2+}, Cu^{2+}/Cd^{2+}, Cu^{2+}/Mg^{2+}, Cu^{2+}/Zn^{2+}, Cu^{2+}/Mn^{2+}, Cu^{2+}/Ca^{2+} binary solutions were prepared with Cu^{2+} ions concentration of 10 ppm. 1 mL of liquid biosensor was added to 20 mL above solutions until no color change occurred by adjusting the concentration of other metal ions.

2.5. Real sample assay

As real samples, artificial urine and bovine serum was used to evaluate the practicability of the cellulose biosensor. 1 mL of liquid biosensor was added into 20 mL of artificial urine or bovine serum with exogenous Cu^{2+} ions (0, 2, 4, 6, 8, 10 ppm). Further, our developed test papers obtained from impregnation method (Liu et al., 2017; Zhang et al., Wang et al., 2018) were applied for the detection of Cu^{2+} ions in tap water, urine and blood from SD rats.

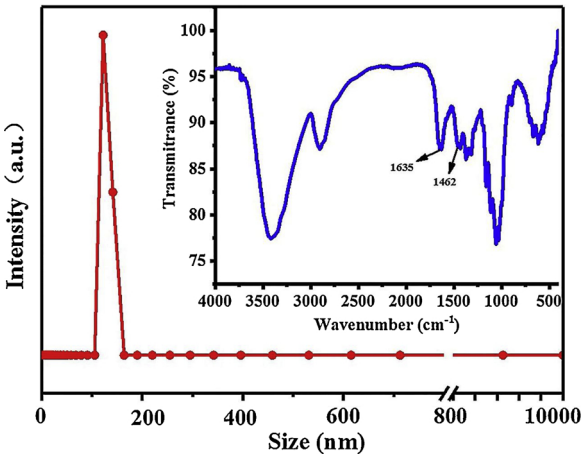

Fig. 1. FTIR spectrum and DLS analysis of cellulose biosensor.

3. Results and discussion

3.1. Synthesis and characterization

The cellulose biosensor was synthesized using natural cellulose as raw material through $NaIO_4$-mediated oxidation and subsequent graft with PEI based on Schiff base reaction (Zhang et al., Hua et al., 2018, 2018). Briefly, cellulose was oxidized at C_2−OH and C_3−OH to 2,3-dialdehyde cellulose (DAC) with $NaIO_4$, followed by grafting with PEI through forming Schiff base structure based on the aldehyde groups of DAC and amino groups of PEI. The preparation process of this biosensor was presented in Supporting Information S1. The surface functional groups were characterized by FTIR. As shown in the inset in Fig. 1, the characteristic peaks at 3490–3500 cm^{-1} were attributed to the O−H and N−H stretching vibration. The peak at 1462 $cm^{-1}$was assigned to C−N stretching vibration, and the peak at 1635 cm^{-1} corresponded to C=N stretching vibration (Hu et al., 2017; Lindh, Ruan, Stromme, & Mihranyan, 2016; Park, Choi, & Oh, 2014; Ruan, Stromme, & Lindh, 2016). All the results indicated the successful graft of PEI via Schiff base reaction, and the abundant hydrophilic groups (−OH, $-NH_2$) endowed the excellent water solubility of the cellulose biosensor. Further, the elemental analysis displayed N element contents with 9.81% in cellulose biosensor (Table S1 in Supporting Information), reconfirming the successful grafting of PEI. In addition, DLS analysis from Fig. 1 revealed that the resultant cellulose biosensor was finely-dispersed, and has homogeneous form and narrow size distribution with an average diameter of 120 nm.

3.2. Visual detection of Cu^{2+} ions in aqueous solution and biofluids

The response behaviors of the cellulose biosensor were investigated using a series of metal ions including Fe^{3+}, Ni^{2+}, Cd^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Ca^{2+}. As shown in Fig. 2a, under the same concentration with 10 ppm, the biosensor displayed specific recognition towards Cu^{2+} ions accompanied color change from colorless to blue within 10 s. Compared to other reported sensors listed in Table 1, the as-prepared liquid biosensor exhibited a fast response characteristic. In addition, the shift of absorption peak at 321 nm to 278 nm and a new absorption peak appeared at 635 nm both indicated the formation of charge transfer complexes between biosensor and Cu^{2+} ions (Fig. 2b). The color change mechanism of biosensor for Cu^{2+} ions was proposed to be such that N atoms (C=N and N−H) in the biosensor capture and concentrate Cu^{2+} ions (i.e. complexation) to form sensor-Cu^{2+} complexes,

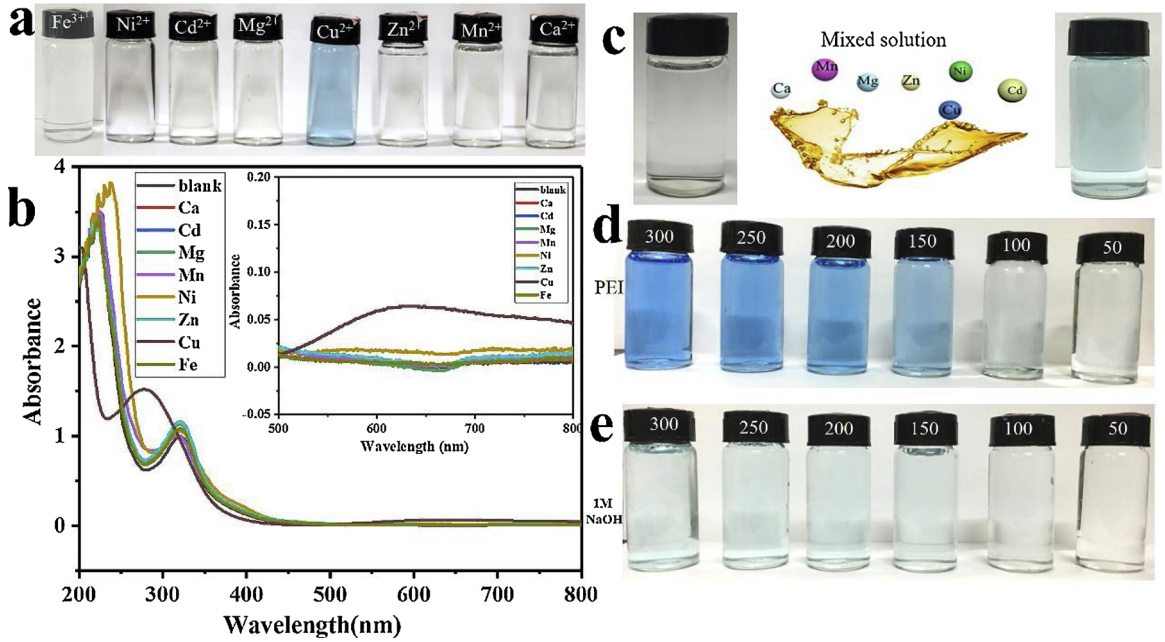

Fig. 2. Visual detection (a) and UV–vis spectra (b) of biosensor for different metal ions. Visual detection of Cu^{2+} ions with interfering metal ions (c), PEI (d), and 1 M NaOH (e).

with intramolecular charge transfer occurring as a consequence (Liu et al., 2017; Zhang et al., Wang et al., 2018). Further, the interference effect of coexisting metal ions was evaluated by monitoring the color change in the presence of excessive other interfering ions. Although the concentration of Cu^{2+} ions (10 ppm) in the mixture was much lower than that of other interfering ions (50 ppm), the solution color could still turn blue within 10 s (Fig. 2c). Considering the effect of PEI and NaOH, the recognition of PEI and NaOH was explored for sensing Cu^{2+} ions, in which the concentration of Cu^{2+} ions was in the range of 50–300 ppm. As shown in Fig. 2d and Fig. 2e, PEI and NaOH (1 M) can sense Cu^{2+} ion when its consentration was more than 100 ppm. Further, tolerance limit of the interfering metal ions was determined. As shown in Table 2, keeping the concentration of Cu^{2+} ions with 10 ppm, the tolerance limit of Fe^{3+}, Ni^{2+}, Cd^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Ca^{2+} ions were 252 ppm, 510 ppm, 227 ppm, 558 ppm, 500 ppm, 451 ppm and 730 ppm, respectively. These results

confirmed the excellent selectivity and anti-interference ability of the cellulose biosensor for Cu^{2+} ions detection.

To investigate the stability of cellulose biosensor for Cu^{2+} ions detection, absorption intensity was recorded under various pH conditions, and shown in Fig. 3. The absorption intensity was stable with pH range from 5 to 7. The −OH and $-NH_2$ on the surface of biosensor was protonated in the strong acid condition, reducing the complex reaction

Table 2
Tolerance limite of cellulose sensor to different metal ions in the detection of Cu^{2+} ions.

Metal ions	Fe^{3+}	Ni^{+}	Cd^{2+}	Mg^{2+}	Zn^{2+}	Mn^{2+}	Ca^{2+}
Tolerance limit (ppm)	252	510	227	558	500	451	730

between biosensor and Cu^{2+} ions. As well known, the pH of biological samples is nearly neutral, thus this cellulose biosensor has a good stability, benefiting the practical application. Moreover, the storage stability of the cellulose biosensor was also investigated, in which the biosensor has been stored for 3 months. As shown in Fig. S2, it is clear that the cellulose biosensor still holds specific recognition towards Cu^{2+} ions in aqueous solution, indicating the excellent storage stability of the cellulose biosensor.

Further, artificial urine and bovine serum by adding exogenous copper ions (2–10 ppm) were employed to evaluate the validity of the cellulose biosensor for the visual detection of Cu^{2+} ions. As shown in Fig. 4, adding the biosensor into urinary copper and blood copper solutions, color change quickly occurred within 10 s. Compared with our previous work (Zhang et al., Wang et al., 2018), this liquid biosensor

Table 1
Comparison of response time of cellulose biosensor with other sensors for Cu^{2+} ions detection.

Sensors	Detection method	Response times	Ref.
Pyoverdine biosensor	Fluorescence	30 min	Yin et al. (2016)
Ag NPs based SPR sensor	Colorimetric	2 min	Peng, Liu, Yuan, Feng, and Zhou, (2017))
Benzothiazolenhydrazone moiety sensor	Fluorescence	30 min	Wang et al. (2013)
Quinoline with 2-picolinic sensor	Fluorescence	5 min	Wang and Zong (2015)
L-cysteine sensor	Colorimertric	50 min	Yin, Li, Wang, Zhang, and Chen, (2015))
Bovine serum albumin sensor	Fluorescence	10 min	Liu et al. (2012)
SrF_2 Nanocrystals sensor	Fluorescence	1 min	Sarkar et al. (2015)
Polypyrrole-modified electrodes	Potential and voltammetry	2 h	Zanganeh et al. (2008)
Cellulose-Schiff base	Colorimetric	30 s	Zhang et al. (2018)
Cellulose biosensor	Colorimetric	10 s	This study

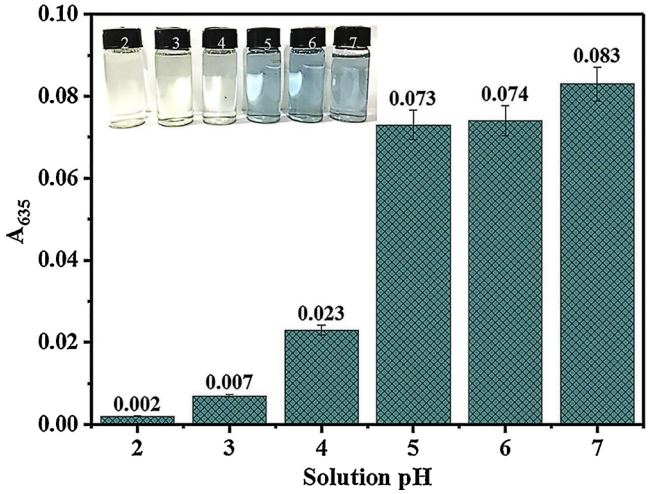

Fig. 3. Absorption intensity of biosensor-Cu^{2+} at various pH.

exhibited more fast response and anti-interference ability. The light green biosensor-Cu^{2+} complex in bovine serum derived from the combination between the serum with inherent pale yellow and blue of biosensor-Cu^{2+} complex. Moreover, the absorption intensity increased gradually with the increases of exogenous Cu^{2+} concentrations, consistenting with the deepening color. The results confirmed that the liquid cellulose biosensor has a strong recognition ability in complex biological samples, providing a promising prospect for early disease diagnosis.

3.3. Sensitivity

The sensitivity of the biosensor for sensing Cu^{2+} ions in water, urine and serum was investigated using UV–vis titration, by which the working curve, and limit of detection (LOD) were obtained. As shown in Fig. 5a, c and e, the absorption peak at 330 nm was gradually shifted to 275 nm, and a new absorption peak at 635 nm appeared. All the absorption intensities increased progressively with the increases of Cu^{2+} concentrations, indicating more complex formation. According to the calculation formula LOD=3∅/k (where ∅ is the standard deviation of blank measurement, k is the slope between the absorption intensity versus Cu^{2+} ions concentration) (Awual et al., 2013; El-Safty, Prabhakaran, Ismail, Matsunaga, & Mizukami, 2008), the LOD was calculated to be 1.185, 1.9309, and 1.9154 ppm for Cu^{2+} ions in water, urine, and serum, respectively (Fig. 5 b, d and f). The low limit detection indicated that the resultant cellulose biosensor could be considered as an excellent colorimetric sensor for sensing Cu^{2+} ions in water and biological sample sensitively.

3.4. Assay of Cu^{2+} ions in tap water and SD rats

To further assess the applicability and validity of the cellulose biosensor, test strip was developed by impregnating test paper into liquid biosensor (Liu et al., 2017; Zhang et al., Wang et al., 2018). Three types of samples, tap water, urine and blood from SD rats were collected for determine Cu^{2+} ions. As shown in Supporting Information S3, test strips exhibited a series of color changes as increasing the concentration of Cu^{2+} ions from 2 to 10 ppm, revealing a semi-quantitative detection ability. Further, it can be found from Table S2 that the measured values using test strip basically consisted with atomic absorption spectroscopy (AAS). The accuracy of cellulose biosensor for Cu^{2+} ions in tap water, urine and blood from SD rats was 84.03%, 80.24% and 76.05%, respectively, which indicated that complex other substances in tap water, urine and blood could not interfere with the assay of Cu^{2+} ions.

3.5. Biocompatibility of cellulose biosensor

Biocompatibility of cellulose biosensor toward Raw 264.7 cells was carried out using Methylthiazolyldiphenyl-tetrazolium bromide (MTT) assay. As shown in Supporting Information S4, when the concentration of cellulose biosensor was 50 μg/mL, the cell viability was still over 97% after 48 h. Additionally, cell viability was still maintained over 88% at a high concentration of cellulose biosensor up to 400 μg/mL. The results indicated that this visual biosensor could be used in intracellular assay for Cu^{2+} ions.

4. Conclusions

We developed a facile and green one-pot process to synthesis a liquid biosensor from natural cellulose. The as-prepared cellulose biosensor displayed specific recognition towards Cu^{2+} ions in aqueous solution, even in complex urine and serum samples within 10 s, showing fast response characteristic. There is barely any interference on the Cu^{2+} ions detection by other metal ions or other complex substances in urine and serum, and the corresponding detection limit is as low as 1.185, 1.9309 and 1.9154 ppm, respectively. Moreover, the cellulose biosensor was proved to be an effective candidate to sense Cu^{2+} ions with excellent sensitivity, selectivity, fast response, and biocompatibility in tap water, urine and serum from SD rats. This study exploits a potential application of cellulose in biosensing and monitoring related to Cu^{2+} ions.

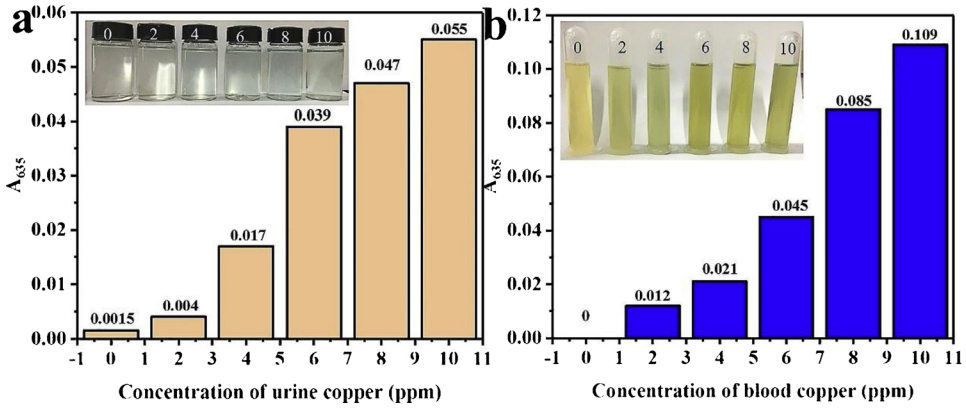

Fig. 4. Absorption intensity of biosensor-Cu^{2+} in urine (a) and serum (b).

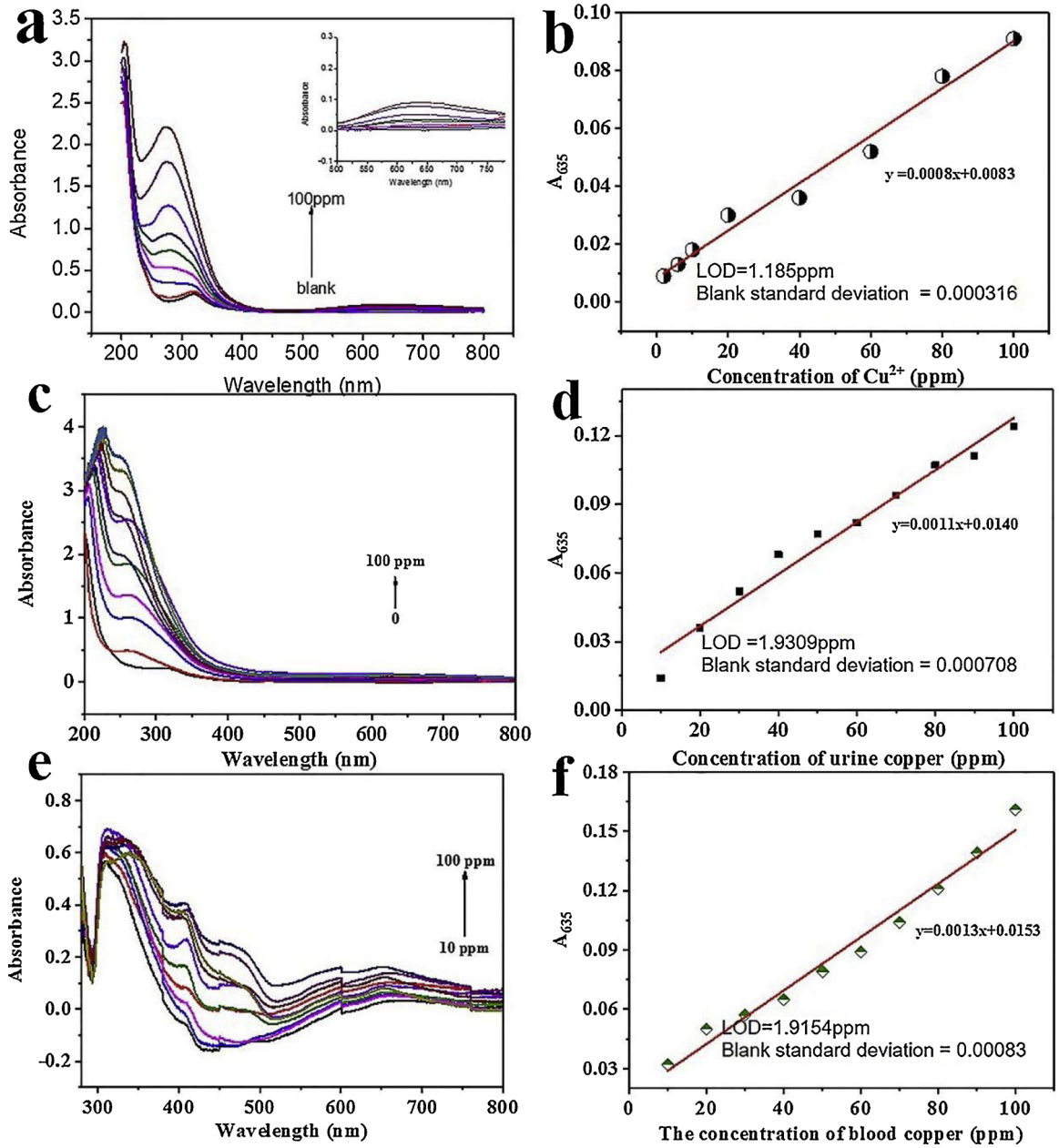

Fig. 5. UV–Vis spectral changes of cellulose biosensor with different concentrations of Cu^{2+} ions in aqueous solution (Inset: Magnification curves at 635 nm) (a), urine (c) and serum (e). The linear correlation between absorption intensity and Cu^{2+} ions concentration in aqueous solution (b), urine (d) and serum (f) at 635 nm.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.carbpol.2019.115117.

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