

Electronic Supplementary Information

**A paper-based biomimetic device for the reduction of Cu(II) to Cu(I) -
Application to the Sensing of Cu(II)**

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1. Materials

All commercial solvents and reagents were used as received without further purification from Sigma-Aldrich, Fischer Scientific Ltd, Alfa Aesar. Whatman® grade 6 filter paper (42.5 mm Ø) was used as cellulose source.

2. Analytical methods

FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer with ATR technique. Scanning Electron Microscopy (SEM) was performed on a JEOL JSH7600F (field emission gun, accelerating voltage: 5 kV, in lens detector of secondary electrons). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher Scientific K-ALPHA spectrometer for disk surface analysis with a monochromatized AlK α source ($h\nu = 1486.6$ eV) and a 200 micron spot size. A pressure of 10^{-7} Pa was maintained in the chamber during analysis. The full spectra (0–1150 eV) were obtained at a constant pass energy of 200 eV and high resolution spectra at a constant pass energy of 40 eV. Charge neutralization was required for all insulating samples. High resolution spectra were fitted and quantified using the AVANTAGE software provided by Thermo Fisher Scientific. UV-visible absorption spectra were recorded using a Varian Model Cary 5E spectrophotometer, using an integrating sphere DRA 2500. Elemental analysis were performed on a Thermo Fisher Scientific Flash 2000 CHNS organic elemental analyzer.

3. Procedure

General procedure for the pre-treatment of cellulose paper. Ten pieces of cellulose filter papers (approx. 1.50 g) were immersed in a freshly prepared aqueous solution of 10% NaOH (300 mL). This mixture was shaken overnight on an orbital agitator. The cellulose samples were washed 3 times with 50 mL of EtOH and stored in EtOH.

Procedure for the functionalization of cellulose paper with thioglycolic acid. Thioglycolic acid (257 mg, 194 μ L, 2.79 mmol) and catalytic *p*-TsOH (20 mg) were added to the pretreated filter paper (150 mg, 0.93 mmol) immersed in dry toluene (20 mL). This mixture was refluxed overnight under nitrogen. After cooling the mixture to room temperature, the cellulose paper was washed successively with MeOH, EtOH, acetone and CH₂Cl₂ under sonication bath, 5 min each, dried under vacuum and stored under nitrogen. Elemental analysis: C: 40.06%, H: 5.12%, S: 10.79%.

General procedure for the colorimetric detection of Cu(II) at different concentration.

Solutions of CuCl₂ at different concentrations were prepared in distilled water. Paper strips were immersed in the corresponding solutions for one hour, dried at 80 °C for one hour and characterized by UV-Vis.

General procedure for the colorimetric detection of cations.

Aqueous solutions of different cations as the corresponding chloride salt at 30 mM (Hg²⁺, Zn²⁺, Sn²⁺, Ni²⁺, Li¹⁺, Pb²⁺, Fe³⁺, Ag¹⁺, Cr¹⁺, Cr²⁺, Cr³⁺, Ca²⁺ and Cd²⁺) were dissolved in distilled water. Paper strips were immersed in the corresponding solutions for one hour, dried at 80 °C for one hour and characterized by UV-Vis.

General procedure for the calibration curve representing the color coordinates of the paper strips as a function of Cu(II) concentration.

The samples were placed on a white background to maintain the same environmental light and photographic conditions. Detail camera set up is shown in Table 1. Digital images were transferred to a computer without any specific software. Colors were obtained from a representative square region of approximately 900 pixels located in each sample images. The average RGB values were measured with GIMP tool color picker. The RGB data codes were converted to HSL data code by an online software (see following link <http://www.rapidtables.com/convert/color/rgb-to-hsl.htm>).

Digital camera	Canon EOS 400D DIGITAL
Camera maximum resolution	10.1 megapixels
Camera sensor	CMOS 22.2 x 14.8 mm
Exposition time	1/100 s
Focal length	34 mm
White balance	Automatic
Image format	JPEG 3888 X 2592 pixels
Color representation	sRGB (standard RGB)
RGB color measurement	Gimp

Table S1. Digital camera characteristics for Cu (II) determinations.¹

[c] / mM	Code RGB			Code HSL			2H+L	log (2H+L)	log [Cu ²⁺]
	R	G	B	H	S	L			
20	106	96.0	91.0	20.0	7.6	38.6	78.6	1.98	-1.70
10	114	102	95.0	22.0	9.1	41.0	85.0	2.01	-2.00
5	132	116	105	24.0	11.4	46.5	94.5	2.06	-2.30
1	153	137	121	30.0	13.6	57.3	117	2.14	-3
0,5	165	150	134	31.0	14.7	58.6	121	2.18	-3.30
0,3	173	158	141	32.0	16.3	61.6	126	2.20	-3.52
0,1	193	183	166	38.0	17.9	70.4	146	2.26	-4.00

Table S2. Average RGB and HSL color values for various concentrations of Cu(II).

4. Characterization

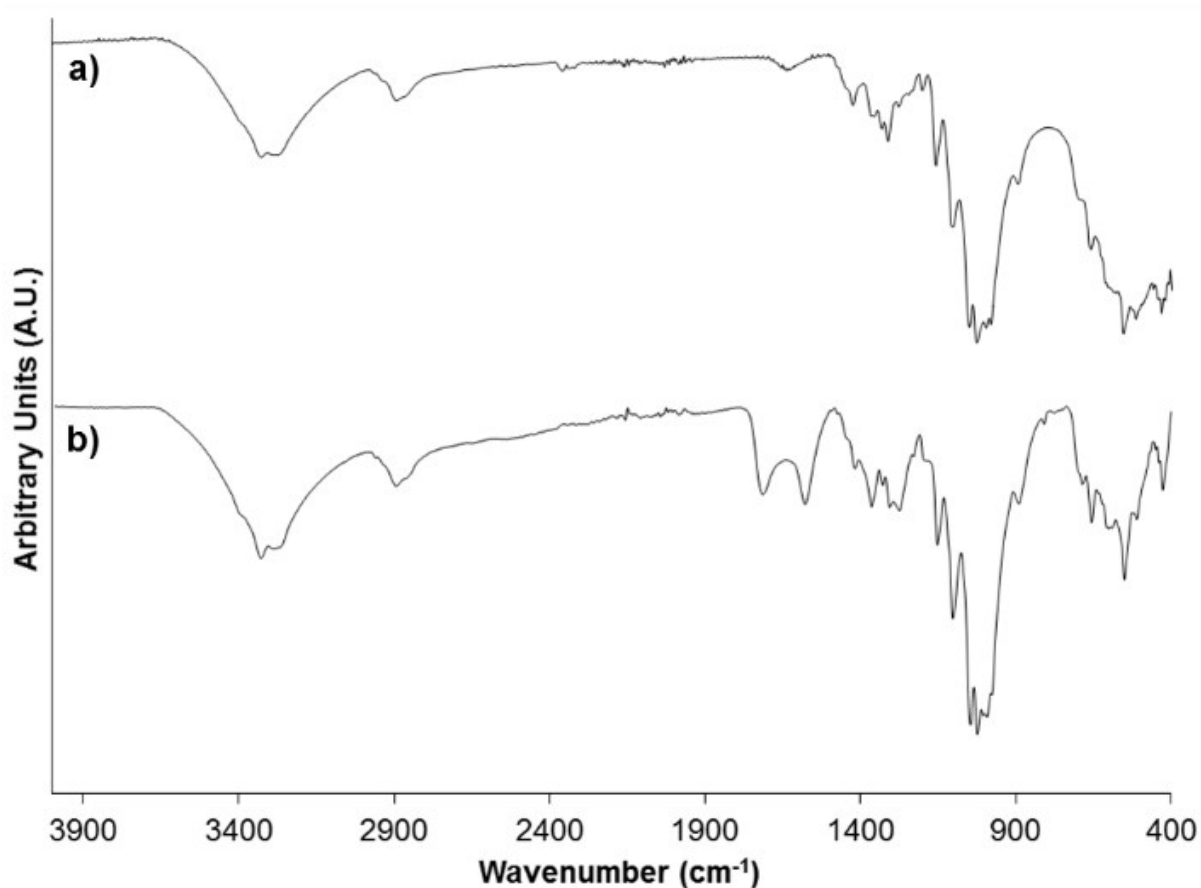


Fig. S1. FT-IR spectra of (a) pristine cellulose paper, (b) paper-grafted thioglycolic acid.

- 1 M. L. Firdaus, W. Alwi, F. Trinoveldi, I. Rahayu, L. Rahmidar and K. Warsito, *Procedia Environ. Sci.*, 2014, **20**, 298-304.