Supporting information

Multi-Responsive Functionalized Mesoporous Silica Paper Based Chemosensors for Quantitative Sensing of Heavy Metals in Water

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Instruments

The surface properties including the specific surface area and the pore structure were determined by N_2 adsorption-desorption isotherms which were measured by automatic surface area and pore size analyzer (BELSORP MINI X, Microtrac MRB) was used to determine Specific surface area (S_{BET}) via adsorption-desorption of N2 gas at 77 K via applying the Barrett–Joyner–Halenda (BJH) method. The pore size distribution was determined from the adsorption isotherms by using nonlocal density functional theory. S_{BET} was calculated using multi-point adsorption data from linear segment of the N_2 adsorption isotherms using Brunauer-Emmett-Teller (BET) theory. Before the N_2 isothermal analysis, all samples were pre-treated at 80ºC for 6 h and calibrated to 10^{-3} Torr. Small- and wide-angle powder X-ray diffraction (SAXRD, and, respectively) patterns were measured by using X'Pert - PRO – TAM with monochromated CuKα (λ = 1.54060 Å) radiation with diffraction reflections recorded for 2 angles between 5◦ and 10◦ corresponding to d- and WAXRD of chemosensors scanned from 4° to 80°. Prior to analysis, the samples were outgassed at 80°C for 24 h. The Field emission scanning electron microscopy (FESEM) images were used to investigate the morphologies and obtained by Zeiss Leo Supra55 microscope. Moreover, to record the SEM micrographs, the scanning electron microscope was operated at 20 keV. The samples for FESEM observations were examined after copper coating. The scanning

electron microscope was operated at 20 keV. The absorbance spectra of the PBCs chemosensors were measured by a Shimadzu UV-2600 solid-state UV–vis spectrophotometer.

Apparatus and Software.

Scanning of the color scales was performed using the scanner of LaserJet Pro 400 in color mode RGB 24 bits with resolution 300 dpi and Digital Nikon camera (D3100). The determination of the colorimetric characteristics of the obtained images and transformation of the color coordinates were performed in the Adobe Photoshop CC 2017 (64 Bit) on a personal laptop. The crop tool called "Elliptical Marquee Tool" was used for selecting an oval region in the middle of the image of the colored sample and the ''Histogram" tool used to obtain the average color intensities values of Red, Green, and Blue (RGB) of each image. All data were transferred to Microsoft Excel 2016 (64 Bit) spreadsheet for subsequent data analysis and using Origin Pro 2016 (64 Bit) for data plotting. The color intensity can be also directly related to the absorbance concentration using the following equation:

$$A_X = -log\frac{(I_X - I_{X,b})}{(I_{X.w} - I_{X,b})} = -log\frac{(I_X)_c}{(I_{X,w})_c} = -log R_X$$

where for each color X: (R, B, G), A_X is the absorbance of X, I_X and R_X are the intensity and the reflectance of light X, respectively, $I_{X,b} = 0$, $I_{X,W} = 256$, and C is the concentration of X.
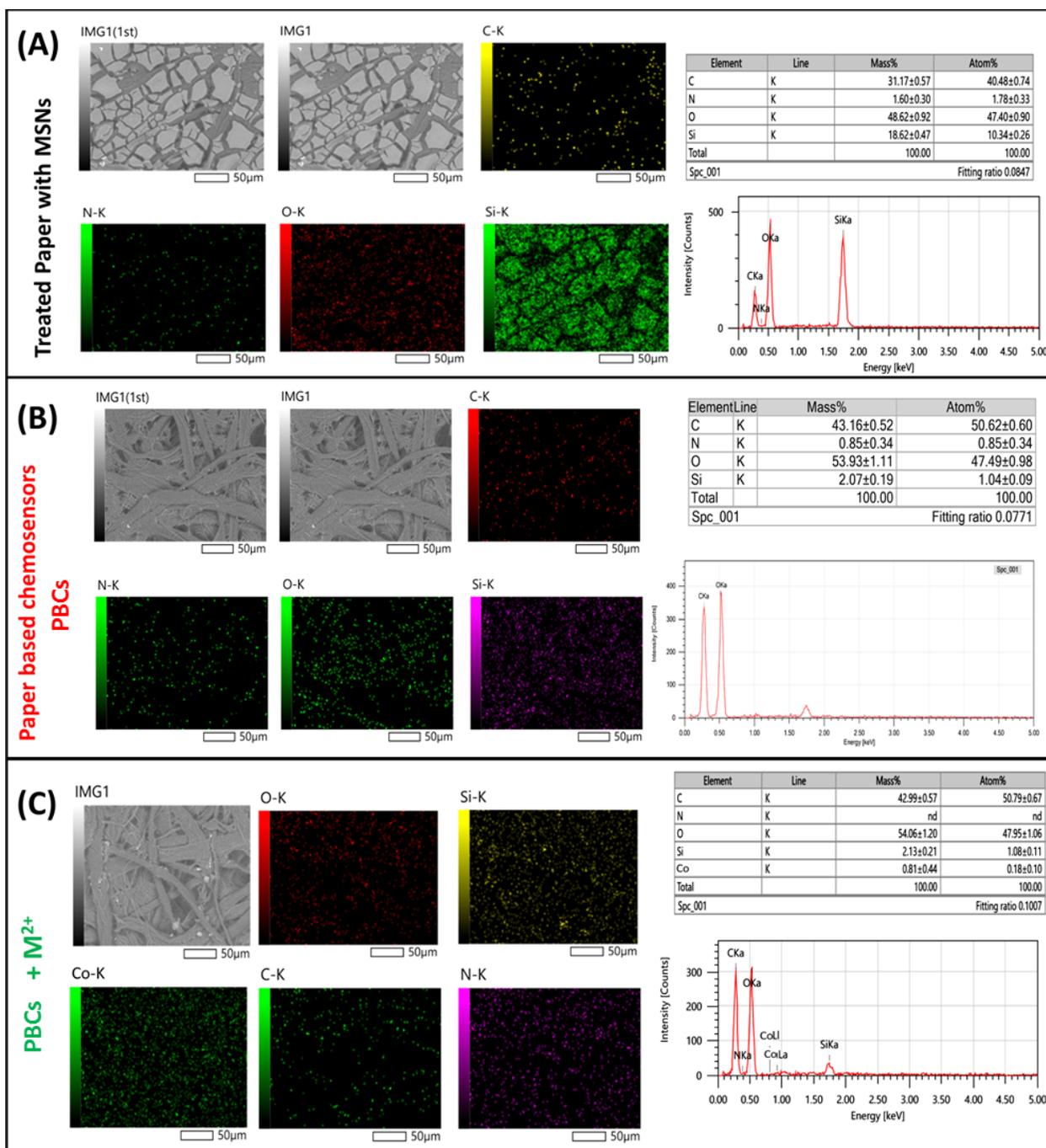
The limit of detection (LOD) was calculated using the following equation (3.3XSD of intercept/slope). The Origin lab software was used to determine the standard deviation of the intercept of the drawn calibration curve.

Table S1. Tolerance concentration for interfering matrix species during recognition of [0.5 ppm] Fe(III), Co(II), Ni(II) and Cd(II) ions by using the PBCs.

Analytes	Specific	Tolerance limits for foreign cations (ppm)									
	pH	Na(I)	Cu^{2+}	Cd^{2+}	Co^{2+}	Ni^{2+}	Pb^{2+}	Hg^{2+}	Zn^{2+}	Al^{3+}	Fe^{3+}
Co(II)	7	100	5	5	Ref	5	100	100	100	100	10
Cd(II)	10	100	5	Ref	5	5	100	100	100	100	10
Ni(II)	9	100	5	5	5	Ref	100	100	100	100	10
Fe(III)	5	100	5	5	5	5	100	100	100	100	Ref

Table S2. Determination of Co^{2+}, Cd^{2+}, Ni^{2+}, and Fe^{3+} using PBCs in water samples.

Sample	ICP-MS Analysis (ppm)	Metal Ions	Amount spiked µg/L (x10^-3 ppm)	Proposed approach PBCs		
				Recovery ±RSD % µg/L (x10^-3 ppm)	E%	Error%
Sample 1	0.155 ppm Al^{3+}, 0.06 ppm Ba^{2+}, 0.0034 ppm Bi^{3+}, 524.9 ppm Ca^{2+}, 0.0007 ppm Cd^{2+}, 0.0025 ppm Co^{2+}, 0.0082 ppm Cu^{2+}, 1.73 ppm Fe^{2+}, 1.76 ppm Fe^{3+}, 0.0002 ppm Hg^{2+}, 0.14 ppm Li^+, 1066 ppm Mg^{2+}, 1.05 ppm Mn^{2+}, 0.0088 ppm Mo^{4+}, 0.0124 ppm Ni^{2+}, 0.0044 ppm Pb^{2+}, 0.95 ppm Si^{2+}, 20.3 ppm Sr^{3+}, 0.0006 ppm Tl^{4+}, 0.0005 ppm V^{5+}, 0.147 ppm Zn^{2+}	Co^{2+}	20	20.54±1.1	98.8	2.7
			50	50.13±0.48	98.3	0.26
			100	98.06±0.85	98.5	1.94
Sample 2	0.034 ppm Al^{3+}, 0.035 ppm Ba^{2+}, 616.9 ppm Ca^{2+}, 0.0005 ppm Cd^{2+}, 0.0008 ppm Co^{2+}, 0.014 ppm Cr^{6+}, 0.11 ppm Fe^{2+}, 0.08 ppm Fe^{3+}, 0.0005 ppm Hg^{2+}, 0.064 ppm Li^+, 301.3 ppm Mg^{2+}, 0.0056 ppm Mn^{2+}, 0.0076 ppm Mo^{4+}, 0.0017 ppm Ni^{2+}, 0.0072 ppm Pb^{2+}, 11.21 ppm Si^{2+}, 33.43 ppm Sr^{3+}, 0.0192 ppm Zn^{2+}	Cd^{2+}	10	9.62 ±0.52	96.2	3.8
			50	47.9 ±0.73	95.8	4.2
			100	96.7 ±1.3	96.7	3.3
Sample 3	0.0144 ppm Al^{3+}, 0.086 ppm Ba^{2+}, 77.22 ppm Ca^{2+}, 0.0008 ppm Cd^{2+}, 0.0007 ppm Co^{2+}, 0.0127 ppm Cr^{6+}, 0.0094 ppm Cu^{2+}, 0.173 ppm Fe^{2+}, 0.12 ppm Fe^{3+}, 0.0008 ppm Hg^{2+}, 0.0219 ppm Li^+, 32.04 ppm Mg^{2+}, 0.0039 ppm Mn^{2+}, 0.0068 ppm Mo^{4+}, 0.017 ppm Ni^{2+}, 44.51 ppm Si^{2+}, 4.26 ppm Sr^{3+}, 0.0019 ppm Tl^{4+}, 0.0072 ppm V^{5+}, 0.0035 ppm Zn^{2+}	Ni^{2+}	10	9.91 ±0.41	99.1	0.9
			50	49.4±0.49	98.8	1.2
			100	99.1 ±0.72	99.1	0.9
Sample 4	0.0468 ppm Al^{3+}, 0.02 ppm Ba^{2+}, 480.9 ppm Ca^{2+}, 0.0004 ppm Cd^{2+}, 0.0001 ppm Co^{2+}, 0.13 ppm Fe^{2+}, 0.14 ppm Fe^{3+}, 0.0007 ppm Hg^{2+}, 0.082 ppm Li^+, 180.1 ppm Mg^{2+}, 0.0037 ppm Mn^{2+}, 0.0092 ppm Mo^{4+}, 0.0014 ppm Ni^{2+}, 0.0124 ppm Pb^{2+}, 17.8 ppm Si^{2+}, 17.86 ppm Sr^{3+}, 0.005 ppm Zn^{2+}	Fe^{3+}	10	9.78 ±0.38	97.8	2.2
			50	49.2 ±1.05	98.4	1.6
			100	98.6 ±1.17	98.6	1.4

Figure S1. SEM-EDS analysis and mapping of (A) treated filter paper with mesoporous silica nanospheres, (B) paper based chemosensors (PBCs), and (C) PBCs with Co^{2+}.
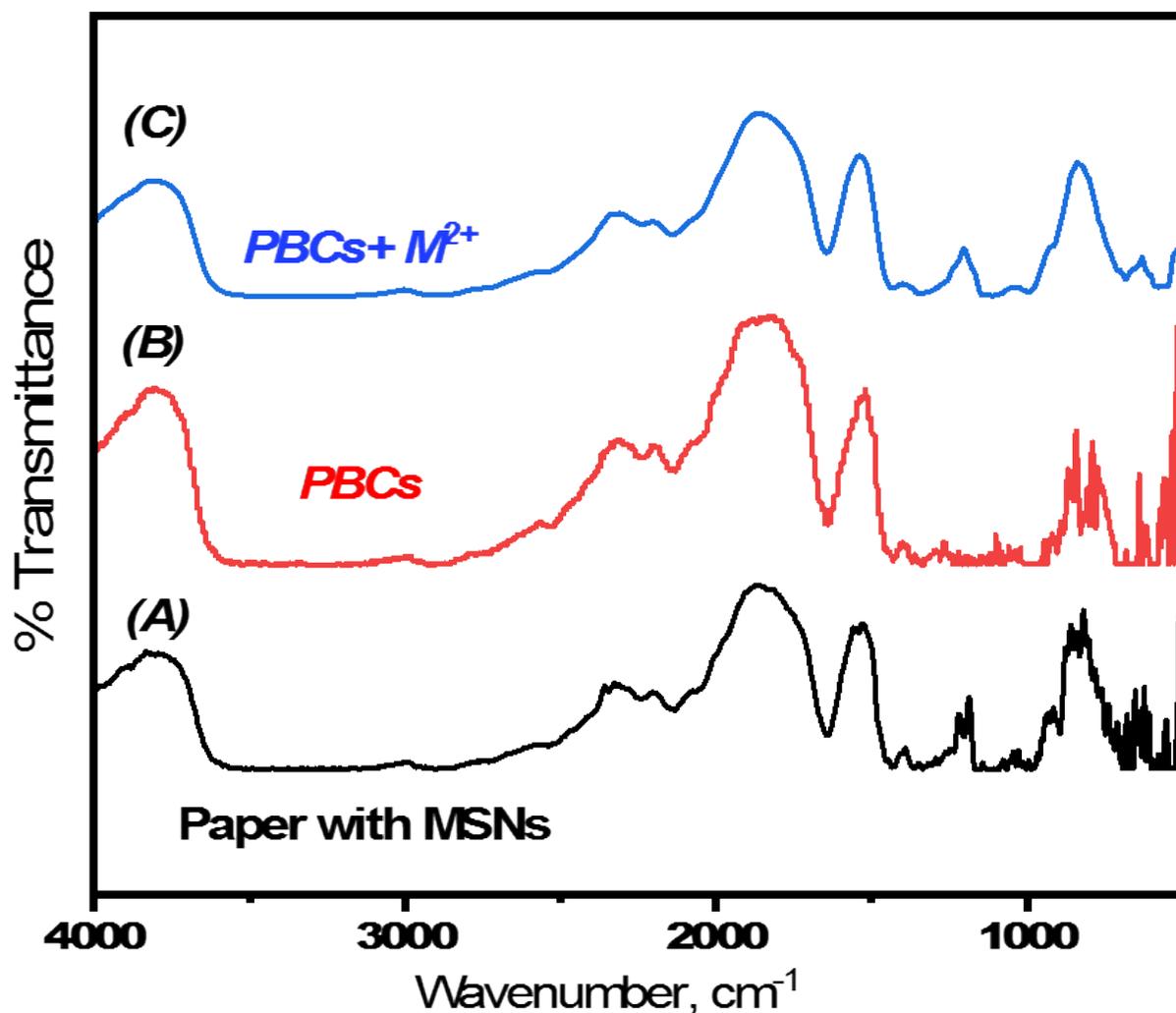
Figure S2. FTIR spectra of (A) filter paper treated with mesoporous silica nanospheres (MSNs), (B) paper based chemosensors (PBCs), and (C) PBCs with M^{2+}.

Regeneration and Reuse of PBCs

Metal ion recovery via elution/desorption is an essential metric to consider when evaluating materials with regard to cost-effectiveness. Elution studies were carried out using various concentrations of EDTA to determine the best eluent for adsorbent renewal and reusability. A simple treatment with 0.1 M EDTA was shown to efficiently remove Fe(III), Co(II), Ni(II), and Cd(II) ions (i.e. decomplexation) while preserving the adsorbent's residual functionality for reuse in several cycles. To liberate the metal ions and get a "metal–free" sensor surface, these procedures were repeated numerous times using a liquid-exchange method. After being regenerated and cleaned with water, the optical chemosensors were vacuum dried before being reused. PBCs were regenerated/reused for five cycles. Figure S3 shows that increasing the recovery cycles had a minor effect on the sensitivity of the produced optical

chemosensors. Accordingly, the constructed optical chemosensors for sensing Fe(III), Co(II), Ni(II), and Cd(II) ions can be used multiple times.
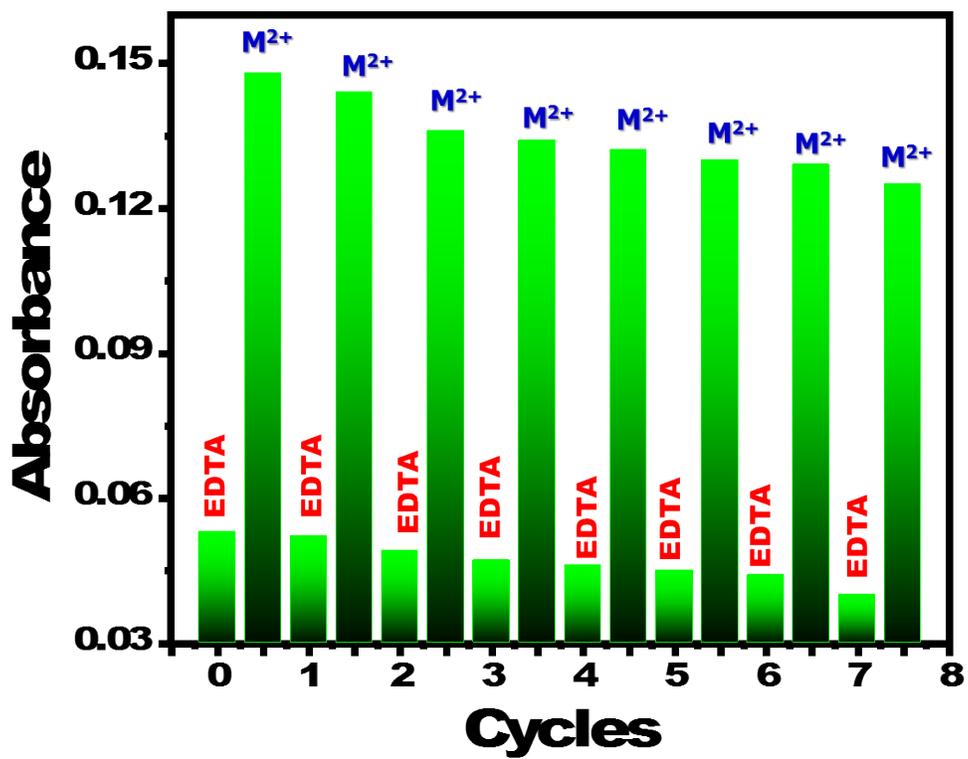

Figure S3. Elution and regeneration of PBCs for multiple cycles using 0.1 M EDTA as the stripping agent.