Supporting information

Mesoporous Nanosensors for Sensitive Monitoring and Removal of Copper Ions In Wastewater Samples

Islam.M. El-Sewify [a,*] , Mostafa M.H. Khalil[a]
[a]Department of Chemistry, Faculty of Science, Ain Shams University, 11566, Abbassia, Cairo, Egypt.
*Corresponding author: islamelsewify@gmail.com & eslamelsewify@sci.asu.edu.eg
Islam.M. ElSewify [a,*] , Mostafa M.H. Khalil[a]

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Instruments

Small angle X-ray diffraction (SAXRD) patterns were obtained by using XPERT – Analytical with monochromatic CuKα (λ = 1.54060 Å), wide angle X-ray diffraction (WAXRD) patterns were measured by using Bruker D8 Discover diffractometer with monochromated CuKα (λ = 1.54178 Å) at 40 kV, and 45 mA. The adsorption/desorption isotherms were collected using Quantachrom Autosorb system at 77 K. Prior to analysis, the samples were outgassed at 80 °C for 24 h. The BET surface areas pore volume and pore size distribution were calculated from N2 adsorption data. The pore size distributions were obtained using the adsorption branch of the nitrogen isotherms by applying the Barrett–Joyner–Halenda (BJH) method. Field emission scanning electron microscopy (FESEM) images were obtained with a Zeiss Leo Supra55 microscope. The samples for FESEM observations were observed without any metal coating. High resolution transmission electron microscope (HR-TEM, Tecnai G20, FEI, and Netherland) was used for the purpose of imaging and elemental analysis. The concentrations of Cu^{+} ions were analyzed by using a Seiko SPS-1500 inductively coupled plasma atomic emission spectrometer (ICP-AES) before and after detection. The absorbance spectrum of the FHNS chemosensors were measured by a Shimadzu UV-2600 solid-state UV–vis spectrophotometer.

Calculation of adsorption capacity

The adsorption capacity (Q, mmol g^{1}) of the FHNS sensor at saturation was deduced by the following equation;

$$Q_t = \frac{(C_o - C_t)\,V}{m} \qquad (1)$$

Where Q_t is the adsorbed amount at saturation time t, V is the solution volume (L), m is the mass of silica nanosphere carriers (g), C_o and C_t are the initial concentration and the concentration at saturation time, respectively.

adsorption capacity was calculated form the equation (2),

$$C_e/q_e = C_e/q_m + 1/K_L q_m \qquad (2)$$

where C_e is the concentration of Cu^{2+} ions in solution at equilibrium (ppm), q_e is the amount of copper ion adsorbed on the FHNS sensor at equilibrium (mg/g), q_m is the amount of mecury ion adsorbed to form a monolayer coverage (mg/g), and K_L is the Langmuir adsorption equilibrium constant. The adsorption capacity (Q, mmol g^{-1}) of the organic probe in the FHNS chemosensors at saturation was determined by the following equation: $Q_t = (C_o\text{-}C)\ V/m$, where Q_t is the adsorbed amount at saturation time t, V is the solution volume (L), m is the mass of the carriers (g), and C_o and C are the initial and saturation concentrations at time t, respectively.

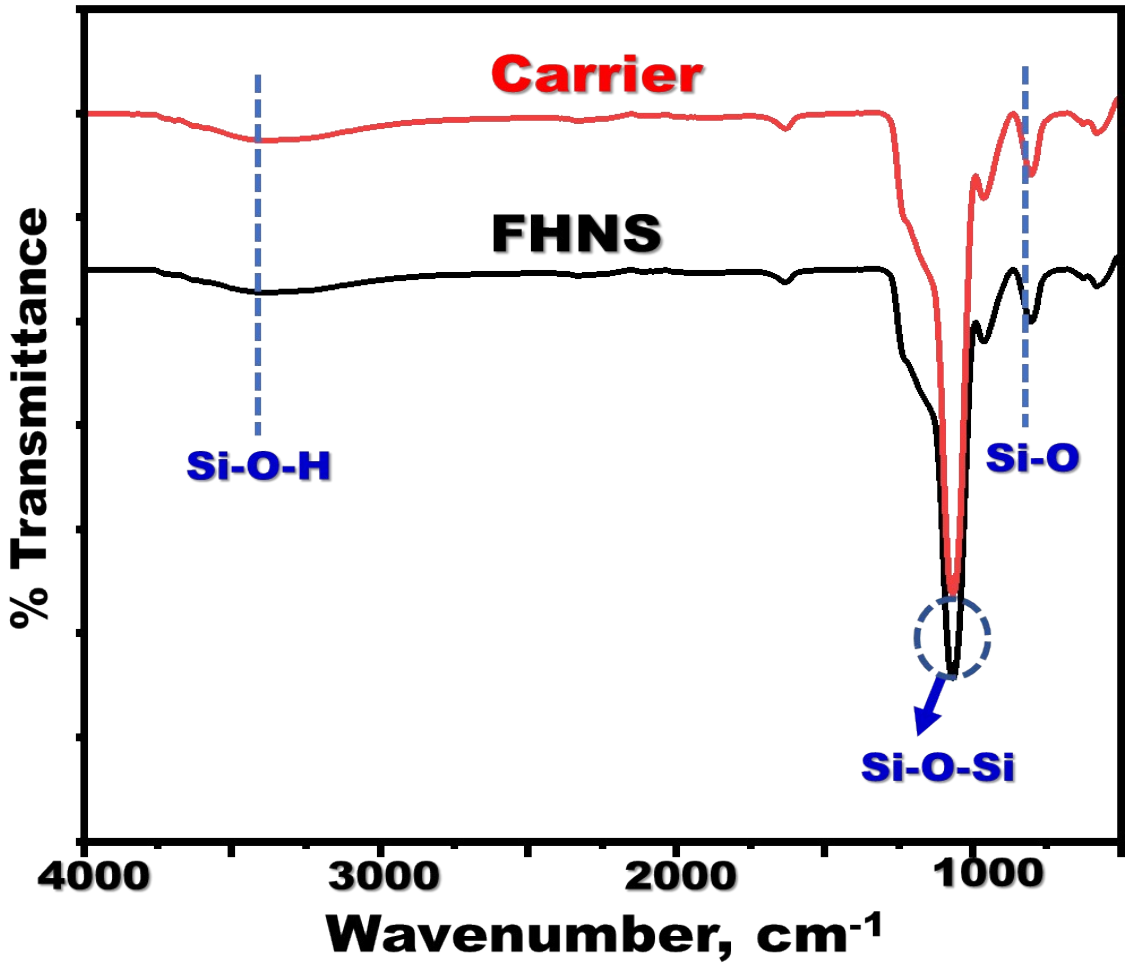

Figure S1. FTIR spectra of the mesoporous carrier nanosphere and the fabricated optical chemosensors FHNS nanomonitors.

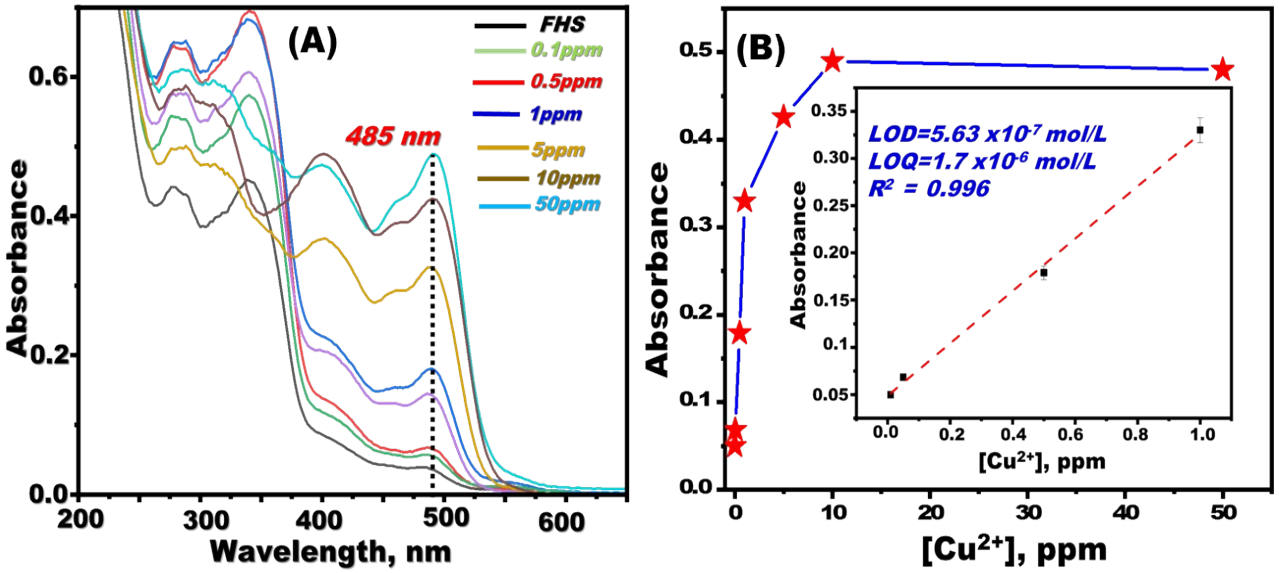

Figure S2. (A) Changes in the UV-vis absorption spectra of FHS probe with different standardized Cu^{2+} ions concentrations at pH 8. Calibration plots for FHNS optical chemosensors with absorbance spectra measured for the Cu^{2+} ions at λ_{485}, linear-fit line is inserted in the linear concentration range before the saturation of the calibration plots for the colorimetric spectra of FHS probe with different [Cu^{2+}] concentrations.

Table S1: Sensing of Cu^{2+} ions parameters for FHS probe in solution and FHNS in solid

Parameter	FHS	FHNS
Solvent	Methanol	Milli-Q water
Excitation wavelength	490 nm	495 nm
LOD	5.63 $x10^{-7}$ mol/L	2.4$x10^{-10}$ mol/L
LOQ	1.7 $x10^{-6}$ mol/L	7.3 $x10^{-10}$ mol/L
Linear rang	3.14 $x10^{-10}$ – 7.87 $x10^{-10}$ mol/L	3.14 $x10^{-10}$ – 7.87 $x10^{-10}$ mol/L
Residual square	0.996	0.979
Specific pH	8	8

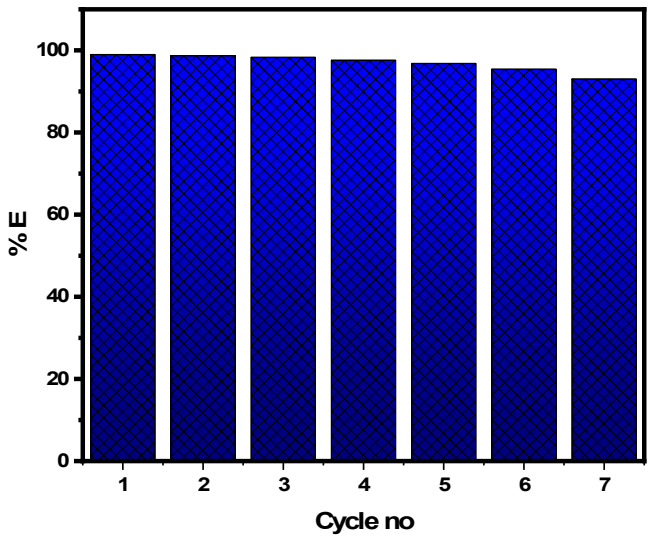

Fig. S3. The adsorption, elution and regeneration of FHNS nanomonitors for multiple cycles where the decomplexing agent was 0.1 M EDTA. The efficiency (%E) of the FHNS nanomonitors was calculated for each cycled.

Table S2: Determination of Cu^{2+} in different wastewater samples.

Wastewater	ICP-MS Analysis (ppm)	Amount spiked of Cu(II) µg/L (ppb)	Proposed method FHNS Chemosensors		
			Recovery ± * RSD % µg/L (ppb)	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+}	5	4.8 ±0.46	98.8	2.2
		10	9.6±0.62	98.3	1.7
		50	50.2±1.24	98.5	1.5
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+}	5	5.2 ±0.52	98.2	1.8
		10	10.1 ±0.73	97.6	2.4
		50	50.1 ±1.37	97.9	2.1
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+}	5	4.9 ±0.41	99.1	0.9
		10	10.3±0.49	98.8	1.2
		50	99.1 ±0.72	99.1	0.9

* Relative Standard deviation percentage

Table S3: Evaluation of intra-day and inter-day accuracy and precision

Wastewater	Amount spiked of Cu(II) µg/L (ppb)	Intra-day accuracy and precision (n=3)			Inter-day accuracy and precision		
		Measured ± * CL % µg/L (ppb)	%RSD	%RE	Measured± CL % µg/L (ppb)	%RSD	%RE
Sample 1	50	50.17 ±0.028	0.25	1.7	50.05±0.047	0.45	0.5
Sample 2	50	50.24 ± 0.022	0.2	2.4	49.96±0.017	0.2	0.4
Sample 3	50	50.14± 0.11	0.098	1.4	49.98± 0.018	0.2	0.2

%RE. Percent relative error,%RSD. relative standard deviation and CL. Confidence limits were calculated from: CL = ± tS/√n. (The tabulated value of t is 4.303, at the 95 % confidence level; S standard deviation and n number of measurements)