

Electronic Supplementary Information (ESI†)

Modified mesoporous silica optical nanosensor for selective monitoring of multiple analytes in water

Madhappan Santha Moorthy, Hun-Jeong Cho, Eun-Jeong Yu, Young-Sik Jung and Chang-Sik Ha*

*Department of Polymer Science and Engineering, Pusan National University,
Busan-609-735, Korea.*

Experimental

4-aminomethylpyridine, salicylaldehyde, cetyltrimethylammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), 3-(Triethoxysilyl)propylisocyanate (ICPTES) and ethylenediaminetetraacetic acid (EDTA) were analytical grade. All chemicals and reagents were obtained from Sigma-Aldrich, USA, and used as-received.

Synthesis of sensor probe 1

1.77 g (0.016 mmol) of 4-aminomethylpyridine in 10 mL of methanol was slowly added into a reaction flask containing 2.0 g (0.016 mmol) salicylaldehyde in 40 mL of methanol, and the reaction mixture was stirred at room temperature for 3 h. Upon reaction completion, the solvent was removed under reduced pressure and the obtained product was then purified using silica gel by eluting with 3:7 ethyl acetate/hexane mixture. The yield of sensor probe **1** was 86 %. ¹H NMR (400 MHz, MeOH-d₄): δ_H 1.89 (t, 4H, CH₂), δ_H 4.1 (t, 4H, CH=N), δ_H 6.6–7.3 (m, 18H, aromatic). ¹³C NMR (400 MHz, MeOH-d₄): δ_C 27.8 (CH₂), δ_C 46.3 (CH=N), δ_C 135–142 (aromatic). FTIR (KBr): 2848, 2916 cm⁻¹ (ν_{C-H}), 1617 cm⁻¹ (ν_{C=N}), 1454 cm⁻¹ (ν_{C=C}), 1264 cm⁻¹ (ν_{C-O-H}).

Synthesis of silylated SAPy precursor

1.0 g (0.04 mmol) of sensor probe **1** was dissolved in 10 mL of dry tetrahydrofuran (THF). To this, 1.16 g (0.047 mmol) of ICPTES was added with vigorous stirring under nitrogen

atmosphere in the presence of a catalytic amount of triethylamine base. Then, the mixture was refluxed at 70 °C for 24 h under nitrogen atmosphere. After cooling, the solvent was removed by rotor vacuum and the obtained viscous product was dispersed in diethyl ether and stirred for 1 h. The obtained greenish yellow viscous liquid mass was dried under a vacuum condition overnight with a N₂ purge. ¹H NMR (400 MHz, MeOH-d₄): δ 0.49 (t, 4H, SiCH₂), δ 1.09 (t, 18H, CH₂CH₂O), δ 1.7 (t, 4H, SiCH₂CH₂), δ 3.6 (t, 4H, CH=N), δ 6.8–7.3 (m, 18H, aromatic). ¹³C NMR (400 MHz, MeOH-d₄): δ 1.8 (CH₂Si), δ 10.9 (CH₃), δ 16.5 (CH₂), δ 32.3 (CH=N), δ 52.5 (aromatic), δ 128.4 (C=O). FTIR (KBr): 2886, 2965 cm⁻¹ (ν_{C-H}), 1623 cm⁻¹ (ν_{C=N}), 1454 cm⁻¹ (ν_{C=C}), 1536 cm⁻¹ (ν_{C-N}), 1727 cm⁻¹ (ν_{C=O}).

Preparation of modified mesoporous silica nanosensor (SAPy-MMS)

In a typical synthesis of SAPy-MMS nanosensor, 1.0 g (2.7 mmol) of CTAB was dissolved in 47 mL water, and then 13.5 mL of aqueous ammonia (25 %) was added to the above solution. The resultant mixture was stirred at 35 °C for 30 min. To this, a premixed solution of silylated SAPy-precursor and TEOS in ethanol (5 mL) was added drop-wise to the mixture solution under vigorous stirring. The resultant suspension was further stirred at 35 °C for 24 h and then aged at 90 °C for another 24 h under static conditions. The molar ratio of TEOS/SAPy/CTAB/NH₃/H₂O was (1-x):x:0.08:5.3:76, where x = 0.25. The obtained solid was washed with copious amounts of water and dried in air at 60 °C. The surfactant was finally extracted by solvent extraction method using acidified ethanol (150 mL of 0.5 M ethanolic HCl for per gram of the SAPy-MMS at 60 °C for 12 h. The extracted material was filtered and dried under vacuum. All the synthesis procedures described above are illustrated in the Scheme 1.

Colourimetric detection of metal ions

1.25 × 10⁻³ M of stock metal cationic solutions were prepared from the nitrate salts of (Zn²⁺, Pb²⁺, Cr²⁺, Cd²⁺, Cu²⁺, Ni²⁺, Co²⁺, Hg²⁺, In²⁺ and Fe²⁺). The suspensions of SAPy-MMS (0.1 g·L⁻¹) were prepared in aqueous solution at various pH conditions, which were adjusted with 0.2 M NaOH or HCl. Each time, 2 mL portion of suspension was filled in a 1 cm quartz cell and then different stock solutions of cations were gradually added into the quartz cell. The colour change of the suspension of metal cations was monitored by bare sight, while the amount of Fe²⁺ and Cu²⁺ was determined quantitatively using UV-visible

spectrometry at 325 nm for Fe²⁺ and 365 nm for Cu²⁺.

Characterization

Powder XRD patterns were recorded with a MiniFlex instrument using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 40 mA in the 2θ range of 1.2° – 10° . Nitrogen adsorption-desorption data were measured using a Nova 4000e surface area and pore size analyzer. The Brunauer-Emmet-Teller (BET) method was used to calculate the specific surface area. The pore size distribution curve was obtained from the analysis of the adsorption branch using the Barrett-Joyner-Halenda (BJH) method. FTIR spectroscopy was performed using a JASCO FTIR 4100 analyzer for samples in KBr pellets. UV-visible spectra were recorded using an OPTIZEN 3220 UV spectrometer. All ²⁹Si and ¹³C cross polarization magic angle spinning (CP MAS) NMR (Bruker DSX 400) spectra were obtained with a 4-mm zirconia rotor spinning at 6 kHz (resonance frequencies of 79.5 and 100.6 MHz for ²⁹Si and ¹³C CP MAS NMR, respectively; 90° pulse width of 5 μ s, contact time of 2 ms, and recycle delay of 3 s for both ²⁹Si MAS and ¹³C CP MAS NMR). Scanning Electron Microscopy (SEM) characterisation was performed using a JEOL 6400 microscope operated at 20 kV. Particle size distributions in suspension were measured by using dynamic light scattering on a Malvern Zetasizer Nano-ZS (Malvern Instruments).

Supporting Figures

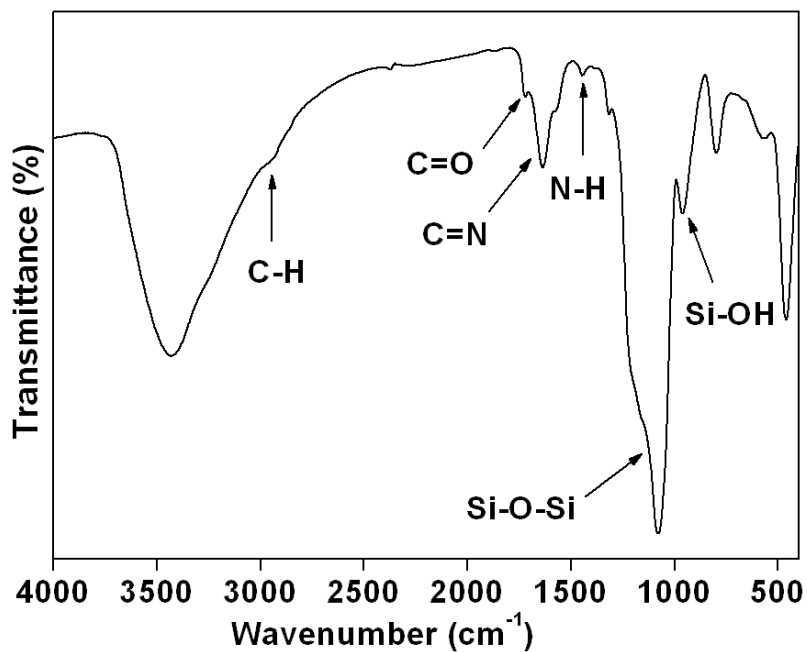


Fig. S1 FTIR spectrum of the SAPy-MMS.

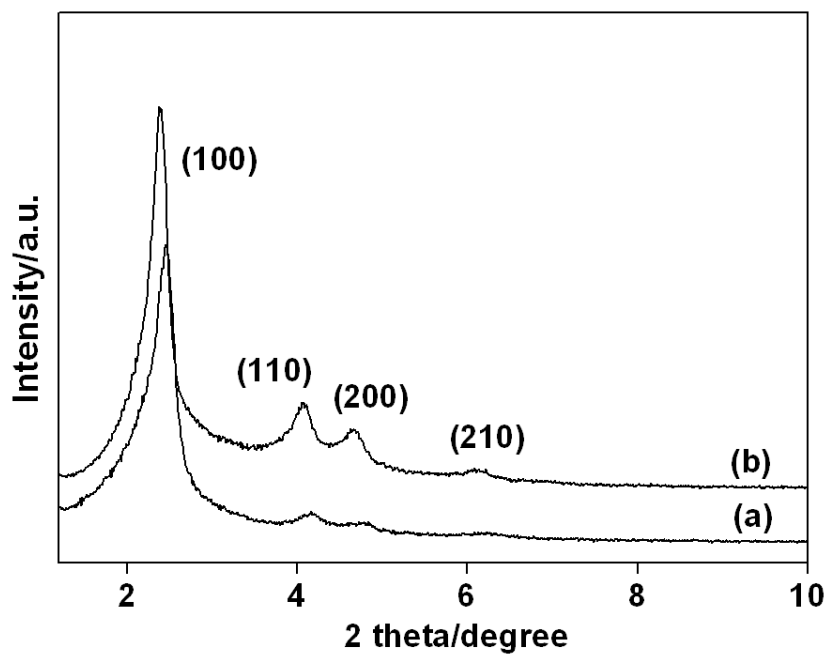


Fig. S2 XRD patterns of the (a) as-synthesized and (b) surfactant extracted SAPy-MMS.

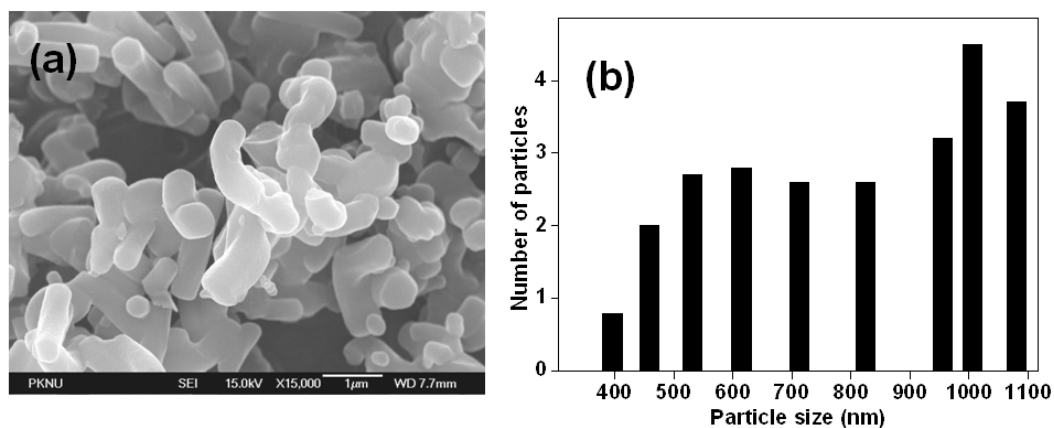


Fig. S3 (a) SEM image and (b) particle size distribution (PSD) of the SAPy-MMS.

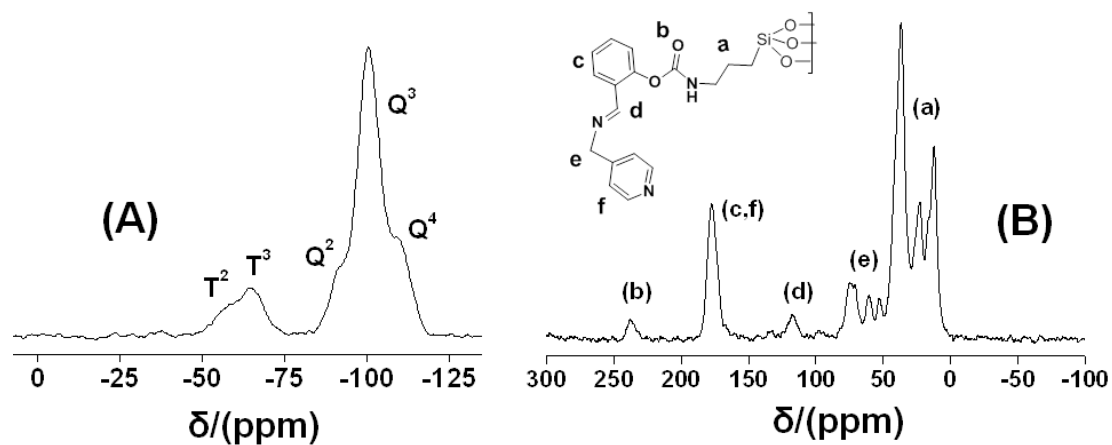


Fig. S4 (A) ^{29}Si MAS and (B) ^{13}C CP MAS NMR spectra of the SAPy-MMS.

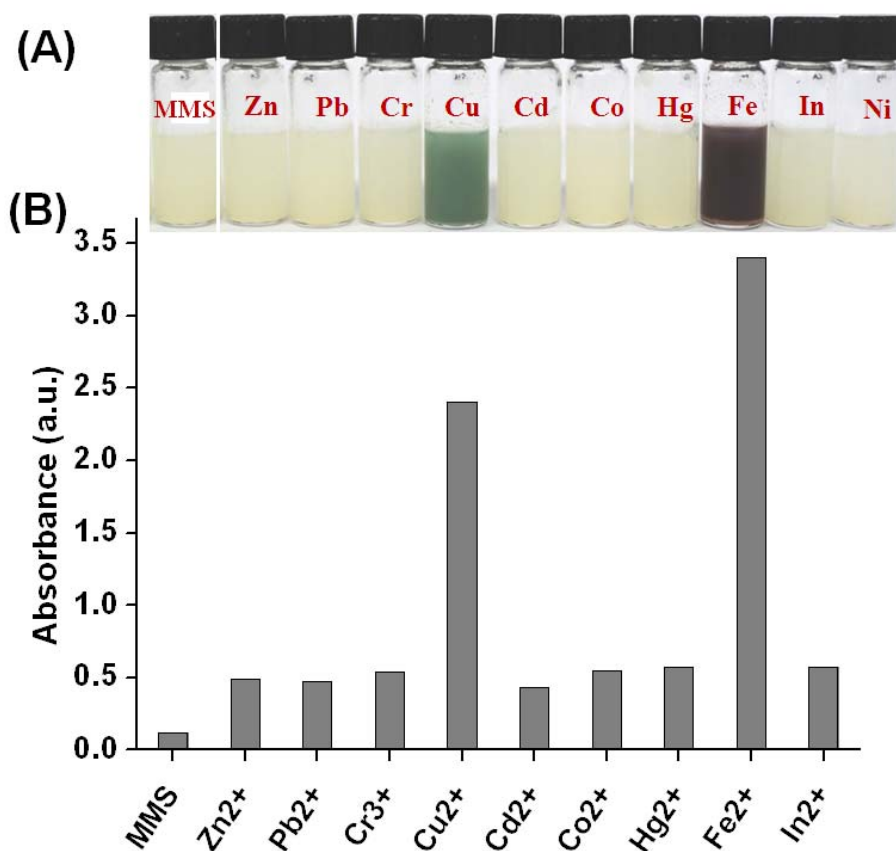


Fig. S5 Colour changes of Fe²⁺ and Cu²⁺; the absorption responses of (a) A₃₂₅/A₄₁₀ for Fe²⁺ and A₃₆₅/A₄₁₀ for Cu²⁺ and (b) of the SAPy-MMS with different heavy metal ions (6.25 × 10⁻⁶ M).

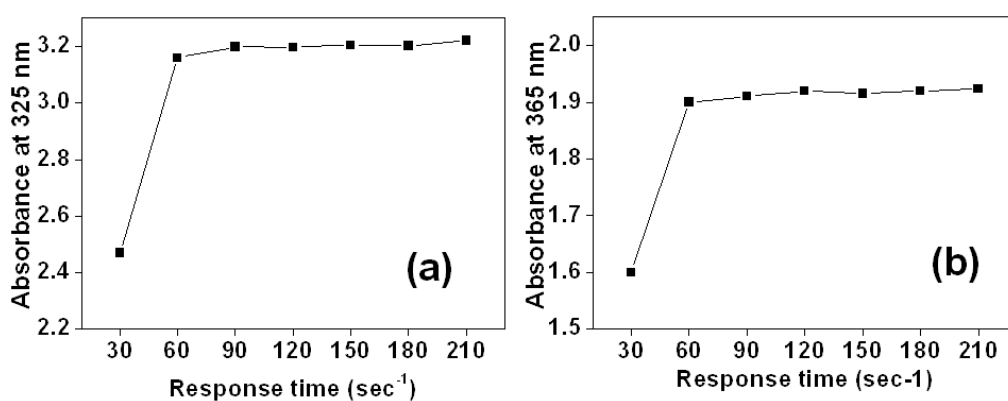


Fig. S6 Response time of the SAPy-MMS (0.5 g L⁻¹) with Cu²⁺ and Fe²⁺, both at the concentration of (6.25 × 10⁻⁶ M).

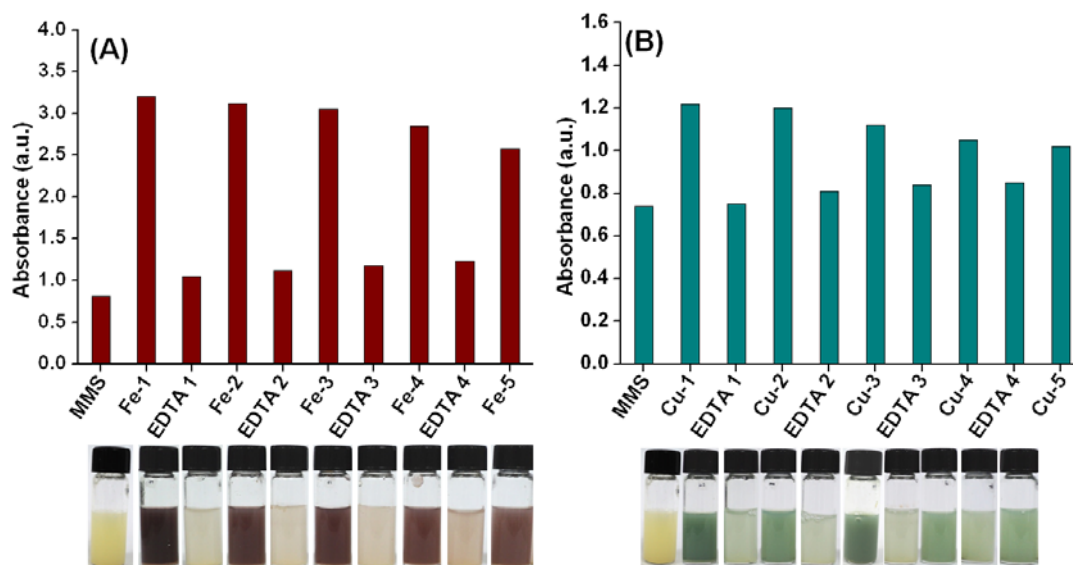


Fig. S7 UV-vis absorption spectra and colour change of the SAPy-MMS with (A) Fe²⁺ and EDTA and (B) Cu²⁺ and EDTA.

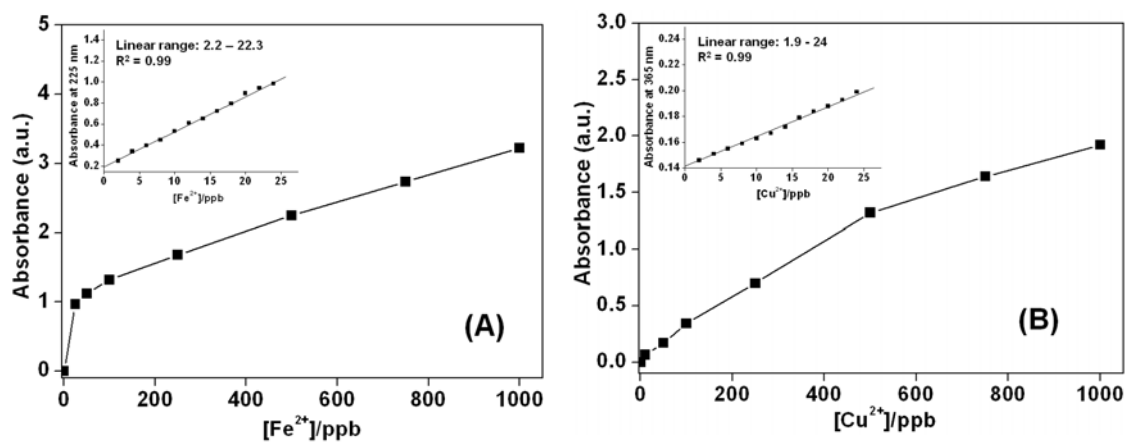


Fig. S8 Calibration curves of the absorbance of the SAPy-MMS with varied concentrations of (A) Fe²⁺ at 325 nm at pH 8 and (B) Cu²⁺ at 365 nm at pH 12.

Table S1 Textural properties of the SAPy-MMS.

Material	d_{100}/nm^a	a_0/nm^b	Pore diameter/ nm	Wall thickness/ nm^d	BET surface area/ m^2/g	Pore volume/ cm^3/g^e	C/N (mol%) ^f
SAPy-MMS	3.8	4.4	2.4	2.0	624	0.32	10.9

^a Calculated from XRD analysis.

^b $a_0 = 2d_{100}/3^{1/2}$

^c Calculated from adsorption branch of nitrogen isotherm using BJH model.

^d Wall thickness = a_0 – pore diameter.

^e Calculated from volume adsorbed of P/P_0 at 0.95.

^f Elemental analysis.