ChemComm

RSC Publishing

COMMUNICATION

View Article Online
View Journal

Cite this: DOI: 10.1039/c3cc42513d

Received 7th April 2013,
Accepted 28th May 2013

DOI: 10.1039/c3cc42513d

www.rsc.org/chemcomm

A 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*

A new modified mesoporous silica nanosensor was synthesized by the co-condensation method. Under basic conditions, the obtained mesoporous silica nanosensor responds selectively to Fe^{2+} (pH = 8) and Cu^{2+} (pH = 12) with a distinguishable colour change perceivable by the naked eye and a detection limit of approximately 50 ppb.

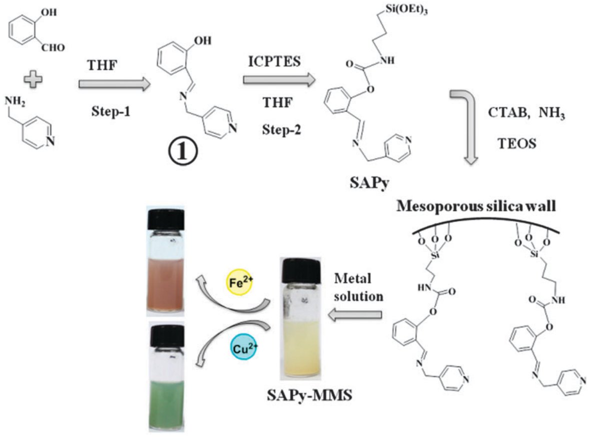
Heavy metal (transition metal) ions generally play crucial roles in both biological systems and the evolving field of bionanotechnology.[1] Recent research efforts tend to focus on the potential impact of transition metal ions and their toxicity on human health and the environment.[2] Among the first row transition metal ions, Cu^{2+} and Fe^{2+} play important roles in extra- and intracellular functions of metabolic processes.[3] On the other hand, the excess quantities of these metal ions can cause serious neurodegenerative conditions, like Wilson's disease,[4] Alzheimer's disease,[5] and prion diseases.[6] The development of materials for the detection of significant metal cations is a synergistic advancement while considering both the environmental and biological importance.[7] Recently, the development of metal-sensitive chromogenic probes has been receiving increased attention because of their various potential applications, and it is crucial to pursue more simplistic nanosensor designs to very selectively detect important physiological and environmental metal cations. So far, a variety of homogeneous chemosensors have been reported,[8] and they can be utilized for the immediate optical detection of various metal cations by an instant colour change that can be perceived by the naked eye. However, these homogeneous sensors have some drawbacks that critically affect their recovery/reuse. Alternatively, recently developed heterogeneous solid-state chemosensors, such as silica nanoparticles,[9] magnetic silica,[10] and silica nanowires,[11] are highly applicable due to their rapid detection and recyclability in practical applications. Currently, very few solid-based chemosensor materials have been reported for the simultaneous colorimetric detection of two metal cations.[12] The development of mesoporous nanoparticles MCM-41 and SBA-15 for solid-type nanosensors is key to designing highly sensitive and selective heterogeneous optical sensors, which have several advantages over the homogeneous probes; *e.g.* large surface area, pore volume, hydrophilicity, thermal and mechanical stability, and easy recyclability.[13] In this study, we prepared a modified mesoporous silica nanosensor (SAPy-MMS) that allows for the selective detection of two analytes with distinct spectral responses (absorption shifted) and colour changes; specifically, the colorimetric response only occurs with the addition of Fe^{2+} (dark brown, λ_{max} 325 nm) and Cu^{2+} (green, λ_{max} 365 nm), whereas other metal ions do not interfere with the absorption spectra of SAPy-MMS or its ability to detect Fe^{2+} and Cu^{2+}.

In Fig. S1 (ESI†), the FTIR spectrum of SAPy-MMS shows typical bands at 2869 and 2941 cm^{-1} attributed to C–H stretching vibrations of silylated SAPy segments. The peak appearing at 1492 cm^{-1} indicates the presence of the N–H bands of SAPy groups. The vibration bands at 1638 and 1718 cm^{-1} are characteristic of C=N and C=O groups, confirming that the covalently bonded SAPy functional organosilane moieties are integrated into the mesoporous silica network. The bands at 1075 cm^{-1} and 963 cm^{-1} indicate the presence of Si–O–Si bonds and Si–OH bonds, respectively. A broad band appearing in the range 3200–3500 cm^{-1} suggests the presence of silanol groups in the silica nanosensor.[14] The FTIR result confirms the successful incorporation of SAPy groups in the silica network (Scheme 1).

Fig. 1A shows the nitrogen adsorption–desorption isotherm of SAPy-MMS and the corresponding pore size distributions. The sample displays a type IV isotherm with a H1 type hysteresis loop,[15] characteristic of mesoporous materials with uniform pore size distributions. The specific surface area (S_{BET}), pore volume, and pore diameter values are listed in Table S1 (ESI†), and they indicate ordered mesoporosity with uniform mesopore size distribution.[16] Fig. S2 (ESI†) shows the XRD patterns of the as-synthesized and surfactant extracted SAPy-MMS. Both as-synthesized and surfactant extracted SAPy-MMS show a sharp (100) XRD reflection peak around $2\theta = 2.38^\circ$ with a *d*-spacing value of 3.8 nm, while the peak intensity of (100) reflection becomes sharper and the additional (110), (200)

Department of Polymer Science and Engineering, Pusan National University, Geumjeong-gu, Busan, 609-735, Korea. E-mail: csha@pnu.edu; Fax: +82-51-514-4331; Tel: +82-51-510-2407

† Electronic supplementary information (ESI) available: Experimental details and supporting figures. See DOI: 10.1039/c3cc42513d



Scheme 1 Synthesis and preparation of the SAPy functionalized mesoporous silica nanosensor.

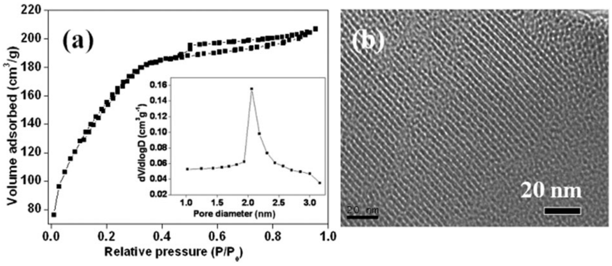


Fig. 1 (A) Nitrogen adsorption–desorption isotherm and pore size distribution (inset) and (B) transmission electron microscopic image of the SAPy-MMS nanosensor.

and (210) peak intensities become increased after the surfactant extraction process, as expected. The reflection peaks of SAPy-MMS after solvent extraction suggest the formation of an ordered mesoporous silica network. The TEM image of SAPy-MMS shows also well-ordered, hexagonally arranged mesochannels, as seen in Fig. 1(b), corroborating that the prepared sample possesses an ordered mesostructure. Fig. S3(a) (ESI†) shows the SEM image of SAPy-MMS. The SEM image reveals that some of the particles have been aggregated or grown together. This most likely happened during the drying step. As shown in Fig. S3(b) (ESI†) the particle size was in the range of approximately 400 nm–1.1 μm.

The formation of a covalent bond between the silylated SAPy precursor and tetraethyl orthosilicate (TEOS) was confirmed by the solid state ^{29}Si MAS NMR spectroscopy (Fig. S4A, ESI†). The Q signals appeared at −109.1, −100.4, and −90.8 ppm for Q^4 [$(SiO)_4Si$], Q^3 [$(SiO)_3Si(OH)$], and Q^2 [$(SiO)_2Si(OH)_2$] structures, respectively; the peaks at −64.0 ppm and −56.3 ppm were assigned to T^3 [$RSi(OSi)_3$] and T^2 [$RSi(OSi)_2(OH)$] sites, respectively,[17] indicating the high degree of condensation of organosilane functional groups in the silica pore walls. In the ^{13}C CP MAS NMR spectrum (Fig. S4B, ESI†), the alkyl carbon resonance signals appeared at 12.4 ppm, 22.6 ppm, and 36.2 ppm for the respective Si–CH$_2$, CH$_2$–CH$_2$–CH$_2$, and CH$_2$–O groups, indicating the presence of silylated functional moieties. An intense resonance signal appeared at 177.5 ppm for the aromatic carbon atoms of benzene and pyridine. Furthermore, the resonance peaks at 60.4 ppm, 117.8 ppm and 237.0 ppm can also be observed (albeit with weak intensities), which can be attributed to CH$_2$, C═N, and C═O, respectively.[18] From the elemental analysis of carbon and nitrogen content, the amount of loaded SAPy functionalities in SAPy-MMS was determined to be 10.9 mol% (Table S1, ESI†).

SAPy-MMS shows remarkable chromogenic selectivity for Fe^{2+} and Cu^{2+} ions when tested against various physiologically important and environmentally toxic metal ions in water (Fig. S5, ESI†). It is interesting to observe that the metal cations Fe^{2+} and Cu^{2+} caused a remarkable colour change of SAPy-MMS from pale yellow to dark brown and green, respectively. On the other hand, the other tested metal ions caused no noticeable colour change, validating that the prepared SAPy-MMS can be used to quantitatively and selectively detect Fe^{2+} and Cu^{2+} at lower concentrations under basic conditions. For spectrometric detection, metal free SAPy-MMS in aqueous suspension (0.5 g L^{-1}) shows an absorbance maximum at 410 nm. When the analytes were introduced, the absorption band of SAPy-MMS shows a noticeable blue shift from 410 nm to 325 nm (85 nm) for Fe^{2+} and a blue shift from 410 nm to 365 nm (45 nm) for Cu^{2+} ions (Fig. 2). The absorption shifts were caused by the formation of SAPy-MMS–Fe^{2+} and SAPy-MMS–Cu^{2+} complexes. In addition, the SAPy-MMS–Fe^{2+} and SAPy-MMS–Cu^{2+} complex formation caused an internal charge transfer (ICT), which can be observed as a wavelength shift or colour change.[19] Addition of Fe^{2+} and Cu^{2+} produced prominent absorbance enhancements at A_{325} nm/A_{410} nm and A_{365} nm/A_{410} nm, respectively.

The effect of pH on SAPy-MMS was determined to investigate the viable operating range. Fig. 3A(a, b) and B(a, b) show the absorbance of free SAPy-MMS and SAPy-MMS with the addition of Fe^{2+} and Cu^{2+}, respectively, at various pH values. There was no deviation in the absorption characteristics of free SAPy-MMS within the pH range of 1 to 14. When Fe^{2+} or Cu^{2+} was added, the absorbance intensity is enhanced throughout the entire pH range,

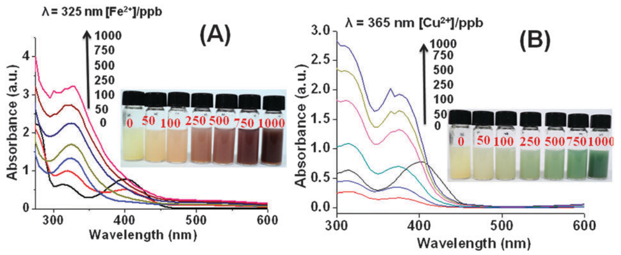


Fig. 2 UV-vis absorption spectra of SAPy-MMS with different concentrations of (A) Fe^{2+} ions at pH 8 and (B) Cu^{2+} ions at pH 12.

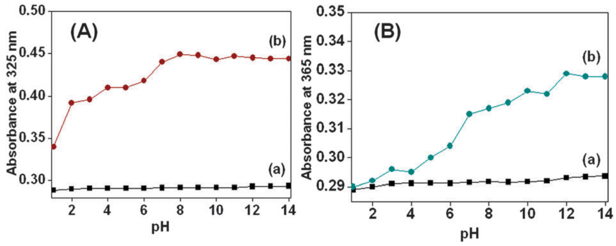


Fig. 3 Effect of pH on absorbance at 325 nm for (A) Fe^{2+} and 365 nm for (B) Cu^{2+}, respectively, in UV-vis spectra of (a) free SAPy-MMS and (b) SAPy-MMS–Fe^{2+} and SAPy-MMS–Cu^{2+}, respectively (6.25×10^{-6} M).

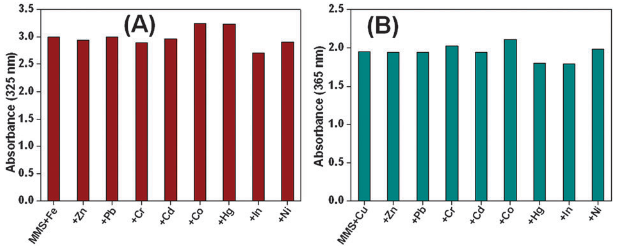


Fig. 4 Absorption of (a) Fe^{2+} at 325 nm and (b) Cu^{2+} at 365 nm upon the addition of SAPy-MMS to Fe^{2+} and Cu^{2+} over the selected competitive metal ions.

attributed to the deprotonation of amide NH groups and pyridine. In the UV-vis absorption spectra, the relative absorbance maxima were observed at pH 7–8 for Fe^{2+} and pH 12 for Cu^{2+} ions, indicating the formation of the respective SAPy-MMS–Fe^{2+} and SAPy-MMS–Cu^{2+} complexes.[20]

The absorbances plateau at pH values above 8 for Fe^{2+} and above 12 for Cu^{2+}. The results indicate that there is a minimum alkalinity to drive the complete complexation between Fe^{2+} or Cu^{2+} and the SAPy functional ligand on the surface of SAPy-MMS, and that pH 8 and pH 12 are the respectively suitable conditions for the sensitive and selective detection of these cations at low concentrations. Furthermore, the competitive effects of various metal ions were investigated in the presence of Fe^{2+} or Cu^{2+}, respectively (Fig. 4). The absorption shifts for Fe^{2+} and Cu^{2+} complexing with SAPy-MMS were unchanged in the presence of the other metal ions. These results indicate that other metal ions neither interfere nor compete with iron and copper at the surface of SAPy-MMS.[21] Fig. S6 (ESI†) shows the addition of Fe^{2+} and Cu^{2+} at a concentration of 6.25×10^{-6} M, where the absorbance increases rapidly within 1 minute and then remains constant over time due to the fact that the complexation reaction has reached equilibrium. The quickly established equilibrium further demonstrates just how efficient colorimetric detection is with SAPy-MMS. To expand on that, regeneration is quite important for the practical application of solid-state chemosensors. Fig. S7 (ESI†) shows the initial pale-yellow colour of free SAPy-MMS and the dark brown/green colours with the addition of Fe^{2+}/Cu^{2+} (6.25×10^{-6} M). By adding 7.5×10^{-6} M ethylenediaminetetraacetic acid (EDTA) solution to SAPy-MMS–Fe^{2+} or SAPy-MMS–Cu^{2+}, the suspension returns to the original pale-yellow colour (Fig. S7, ESI†), indicating that EDTA forms more stable complexes with the cations.[22] Subsequently, the addition of excess Fe^{2+} or Cu^{2+} instigated the expected colour changes, and this cycle can be repeated at least 5 times with consistent results. Therefore, employing EDTA allows SAPy-MMS to be used repeatedly to monitor Fe^{2+} or Cu^{2+} in aqueous solution with the naked eye at a detection limit of 50 ppb, as determined from Fig. S8 (ESI†).

In conclusion, a novel modified SAPy-MMS was developed for the selective detection of both Fe^{2+} and Cu^{2+} ions simultaneously by an obvious colour change under basic conditions that could be perceived without relying on spectroscopic instrumentation. SAPy-MMS is sensitive enough to allow the detection of Fe^{2+} and Cu^{2+} cations at concentrations as low as 50 ppb. Thus, SAPy-MMS shows very favourable properties for its use as an optical solid sensor with the advantages of simple fabrication, high selectivity, short response time, regeneration, easy handling, low detection limit, and low production and operation costs. This method offers the ability to screen for Fe^{2+} and Cu^{2+} in competitive media by UV-visible spectroscopy or bare human sight. This approach may aid in the design and development of a new generation of solid-based optical sensors.

We thank the National Research Foundation of Korea (NRF) Grant funded by the Ministry of Science, ICT & Future Planning, Korea (Acceleration Research Program (No. 2013003956), Pioneer Research Center Program (No. 2013008174/2013008201)).

References

1 (*a*) E. Katz and I. Willner, *Angew. Chem., Int. Ed.*, 2004, **43**, 6042; (*b*) H. N. Kim, M. H. Lee, H. J. Kim, J. S. Kim and J. Yoon, *Chem. Soc. Rev.*, 2008, **37**, 1465.
2 (*a*) A. Ajayaghose, P. Carol and S. Sreejith, *J. Am. Chem. Soc.*, 2005, **127**, 14962; (*b*) M. K. Amini, B. Khezri and A. R. Firooz, *Sens. Actuators, B*, 2008, **131**, 470.
3 B. L. Valle and K. H. Falchuk, *Physiol. Rev.*, 1993, **73**, 79.
4 D. J. Waggoner, T. B. Bartnikas and J. D. Gitlin, *Neurobiol. Dis.*, 1999, **6**, 221.
5 B. Bruijin, T. M. Miller and D. W. Cleveland, *Annu. Rev. Neurosci.*, 2004, **27**, 723.
6 D. R. Brown and H. Kozlowski, *Dalton Trans.*, 2004, **13**, 1907.
7 (*a*) W. Denk, J. H. Strickler and W. W. Webb, *Science*, 1990, **248**, 73; (*b*) I. W. Lichtman and J. A. Conchello, *Nat. Methods*, 2005, **2**, 910.
8 (*a*) J. Du, J. Fan, X. Peng, P. Sun, J. Wang, H. Li and S. Sun, *Org. Lett.*, 2010, **12**, 476; (*b*) T. Gunnlaugsson, J. P. Leonard and N. S. Murrag, *Org. Lett.*, 2004, **6**, 1557; (*c*) J. Wang, X. H. Qian and J. Cui, *J. Org. Chem.*, 2006, **71**, 4308.
9 P. Teolato, E. Rampazzo, M. Arduini, F. Mancin, P. Tecilla and U. Tonellato, *Chem.–Eur. J.*, 2007, **13**, 2238.
10 H. Y. Lee, D. R. Bae, J. C. Park, H. Song, W. S. Han and J. H. Jung, *Angew. Chem., Int. Ed.*, 2009, **48**, 1239.
11 L. Mu, W. Shi, J. C. Chang and S. T. Lee, *Nano Lett.*, 2008, **8**, 104.
12 (*a*) N. Kaur and S. Kumar, *Tetrahedron Lett.*, 2008, **49**, 5067; (*b*) H. Komatsu, T. Miki, D. Citterio, T. Kubota, Y. Shindo, K. Yoshiichiro, K. Oka and K. Suzuki, *J. Am. Chem. Soc.*, 2005, **127**, 10798.
13 (*a*) S. A. El-Safty, A. A. Ismail, H. Matsunaga and F. Mizukami, *Chem.–Eur. J.*, 2007, **13**, 9245; (*b*) R. Metivier, I. Leray, B. Lebeue and B. Valeur, *J. Mater. Chem.*, 2005, **15**, 2965; (*c*) E. Kim, H. E. Kim, S. J. Lee, S. S. Lee and M. L. Seo, *Chem. Commun.*, 2008, 3921.
14 M. Kruk, T. Asefa, M. Jaroniec and G. A. Ozin, *J. Am. Chem. Soc.*, 2002, **124**, 638.
15 (*a*) M. Kruk and M. Jaroniec, *Chem. Mater.*, 2001, **13**, 3169; (*b*) W. H. Zhang, X. B. Lu, J. H. Xiu, Z. L. Hua, L. X. Zhang, M. Robertson, J. L. Shi, D. S. Yan and J. D. Holmes, *Adv. Funct. Mater.*, 2004, **14**, 544.
16 R. Richer and L. Mercier, *Chem. Mater.*, 2001, **13**, 2999.
17 (*a*) O. Dag, C. Y. Ishii, T. Asefa, M. MacLachlan, H. Grondey, N. Coombs and G. A. Ozin, *Adv. Funct. Mater.*, 2001, **11**, 213; (*b*) H. Zhu, D. J. Jones, J. Zajac, R. Dutarture, M. Rhomari and J. Roziere, *Chem. Mater.*, 2002, **14**, 4886.
18 (*a*) O. Olkhovyk, S. Pikus and M. Jaroniec, *J. Mater. Chem.*, 2005, **15**, 1517; (*b*) G. Arrachart, C. Carcel, P. Trens, J. J. E. Moreau and M. W. ChiMan, *Chem.–Eur. J.*, 2009, **15**, 6279.
19 (*a*) C. Bhaumik, S. Das, D. Maity and S. Baitalik, *Dalton Trans.*, 2011, **40**, 11795; (*b*) N. Kaur and S. Kumar, *Dalton Trans.*, 2006, 3766; (*c*) N. Kaur and S. Kumar, *Chem. Commun.*, 2007, 3069.
20 Z. Q. Liang, C. X. Wang, J. X. Yang, H. W. Gao, Y. P. Tian, X. T. Tao and M. H. Jiang, *New J. Chem.*, 2007, **31**, 906.
21 S. A. El-Safty, A. A. Ismail, H. Matsunaga, H. Nanjo and F. Mizukami, *J. Phys. Chem. C*, 2008, **112**, 4825.
22 M. Zenki, Y. Iwadou and T. Yokoyoma, *Anal. Sci.*, 2002, **18**, 1077.