ORIGINAL PAPER

Thiomorpholine-functionalized nanoporous mesopore as a sensing material for Cd^{2+} carbon paste electrode

Mohammad Reza Ganjali · Mehdi Asgari ·
Farnoush Faridbod · Parviz Norouzi · Alireza Badiei ·
Javad Gholami

Abstract A new thiomorpholine-functionalized nanoporous mesopore Mobil Composition of Matter No. 41 (MCM-41), abbreviated as TMMCM-41, was synthesized and applied as a sensing material in construction of a cadmium carbon paste electrode. The electrode composition of 20.1%wt TMMCM-41, 54.0% graphite powder, 25.9% paraffin oil showed the stable potential response to Cd^{2+} ions with the Nernstian slope of 28.6 mV decade^{-1} (± 1.8 mV decade^{-1}) over a wide linear concentration range of 10^{-6} to 10^{-2} mol L^{-1} with a detection limit of 6×10^{-7} mol L^{-1}. The electrode has fast response time and long-term stability (more than 4 months). The proposed electrode was used to determine the concentration of cadmium in tap water contaminated by this metal and cadmium electroplating waste water samples.

Keywords Nanoporous silica · Potentiometric sensor · Nanoporous MCM-41 · Cadmium ion · Carbon paste electrode

M. R. Ganjali (✉) · M. Asgari · F. Faridbod · P. Norouzi
Center of Excellence in Electrochemistry, Faculty of Chemistry,
University of Tehran,
Tehran, Iran
e-mail: ganjali@khayam.ut.ac.ir

M. R. Ganjali · F. Faridbod · P. Norouzi
Endocrinology and Metabolism Research Center,
University of Tehran Medical Sciences,
Tehran, Iran

A. Badiei · J. Gholami
School of Chemistry, College of Science, University of Tehran,
Tehran, Iran

Introduction

The importance of the silica-based materials is their robustness and their high specific surface area (200–1500 m^{2}g^{-1}) and a three-dimensional structure made of highly open spaces interconnected to each other. These properties cause the selection of a target analyte with a large number of accessible binding sites, which is a key factor in designing sensor devices with high sensitivity. The silica surface can be modified with a large variety of organic moieties or inorganic layers of defined reactivity. In connection to electrochemistry, these properties could be advantageously exploited in electroanalysis by inducing high selectivity at the modified electrode [1].

The family of ordered mesoporous solids was first reported in 1992 [2]. Afterward, they found wide applications in electrochemistry, catalysis, separations, adsorption, coatings, or microelectronics [3, 4]. Due to their great porosity and uniform structure, access to the organofunctional groups attached to the mesopore walls is easy [5–7] and cause fast transport of the target analyte to the binding sites [8, 9].

Two synthetic methods have been reported to get mesoporous silicas with organic surfaces: the first method is the postsynthesis grafting of organofunctional groups by silylation with the silanol moieties on the silica surface [10] and the second route is a one-step sol–gel process involving the hydrolysis and cocondensation of a mixture of tetraalkyloxy silane and organotrialkoxy silane [11, 12]. The second method offers some advantages such as an easier control of the functionalization level by adjusting the organosilane content in the starting sol [13] and a more uniform distribution of the organic groups in the mesopores, whereas the grafting process which often resulted in higher contents of these groups at the mesopore entrance [13–15].

Organic–inorganic silica-based materials have been classified into two main categories whether their organic and inorganic counterparts are linked together via either weak (class I) or strong (class II) interactions [16]. The latter is especially attractive since it provides a wide range of materials with tailor-made reactivity and long-term stability [17]. Therefore, they combine in a single material both properties of an inorganic framework (rigidity, three-dimensional structure, and mechanical stability) to the specific chemical reactivity of the organic component [10, 12, 18].

Chemical modifiers are able to preconcentrate metallic ions on the electrode surface by complexation or electrostatic attraction. This interaction lead to more sensitive electroanalytical procedures with lower detection limit values [19–21]. Dispersing materials into a conductive carbon-based composite like carbon paste is another simple way to use their properties in electrochemistry [19–21].

Various methods for the synthesis of electrochemical surface having specific charge transfer properties have been described in the literature [22, 23]. Among the techniques of incorporating electroactive species on modified substrates; in this work, thiomorpholine loading over MCM-41 mesoporous silica produces an electroactive substrate.

Carbon paste electrode (CPE) is one of the suitable conductive matrixes to set up a chemically modified electrode (CME) by simple mixing of graphite/binder paste and modifier. These kinds of electrodes are inexpensive and possess many advantages such as easy fabrication and rapid renewal [24].

Cadmium, one of the 25 hazardous substances [25], is also listed by the US Environmental Protection Agency (EPA) among the 129 priority pollutants [26, 27]. Most of the cadmium in inner-city soils and waters come from landfills. Landfills contain waste lead, cadmium, and copper from industrial activities. Thus, cadmium can be absorbed by humans in small amounts from food, water, and air and causes kidney and bone-marrow diseases and emphysema [28, 29]. There is some evidence relating cadmium exposure to prostate cancer in men and animal studies [30]. An accumulation of cadmium in many tissues and a particularly long half-life, 10–30 years, has been reported for muscles, kidneys, and liver [31].

Development of selective chemical sensors has received widespread attention during the past three decades because of their possibility use in clinical and environmental monitoring as they provide a rapid, accurate, and low-cost method of analysis [32–36]. The operation mechanism of chemically modified carbon paste electrodes depends on the properties of the modifier which is used for selectivity towards the target species [37].

In this article, the construction of a selective sensor, a carbon paste electrode, modified with silica-based organic–inorganic hybrid materials containing thiol groups covalently attached to the solid framework via a propyl chain.

The proposed electrode was used to determine the concentration of cadmium in tap water contaminated by this metal and cadmium electroplating waste water samples.

Experimental part

Reagents

Toluene, 3-(triethoxysilyl)-1-iodopropane, and thiomorpholine were purchased from Merck. MCM-41 was synthesized as followed. All chemicals were used as received.

Preparation of functionalized mesoporous substrate (TM-MCM)

MCM-41 was prepared according to a synthetic procedure previously established [38, 39]. Clear gel containing fumed silica and sodium silicate is slowly added to a clear CTMAB solution with stirring at room temperature. The resulting gel is transferred into a Teflon-lined autoclave and maintained for 24 h at 130°C. The resulting powder is filtered, washed with distilled water, and dried in air. As-synthesized MCM-41 (4.0 g) was stirred in 100 mL dry toluene solution containing 13 mL 3-(triethoxysilyl)-1-iodopropane under argon atmosphere. After 24 h reflux, the solid was filtered and washed with dry toluene. The filtered sample was dried and added to 80 mL dry toluene; then, 2.8 mL thiomorpholine was added to this solution under argon atmosphere. The mixture was refluxed for 24 h. After filtering, the solid was received, and the residual reagents were removed through washing with dry toluene (Fig. 1).

Characterization

The XRD pattern shows the well-defined mesostructure of solid support with hexagonal symmetry. Nitrogen adsorption–desorption isotherm was obtained for mesoporous substrate. In summary, the BET surface area of this material is 688 $m^2 g^{-1}$, and the BJH pore diameter is 2.8 nm.

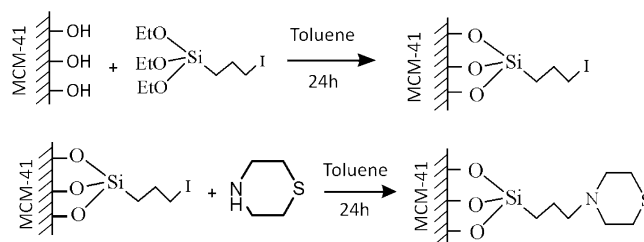From the termogeravimetric analysis of TMMCM-41 (Fig. 2), the amount of the thiomorpholine presence in the

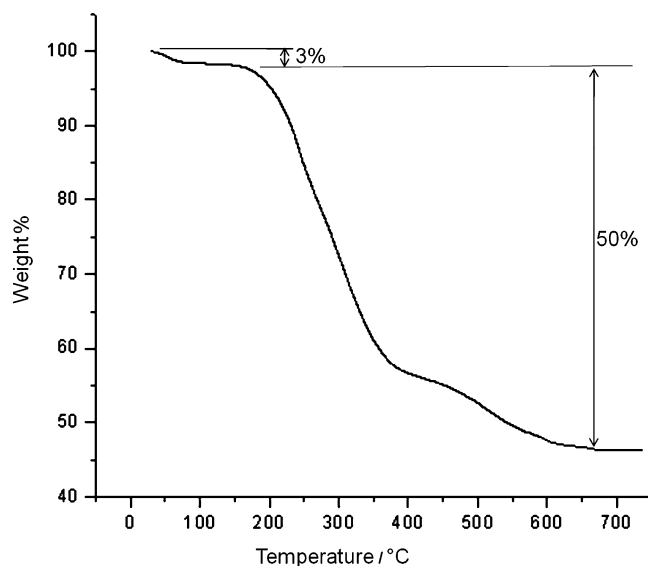Fig. 1 Schematic representation of the synthesis of TMMCM-41

Fig. 2 Thermogeravimetric analysis of TMMCM-41

material was calculated. It showed three distinct stages of decomposition. The first, between 30°C and 150°C is related to 3% adsorbed water, and the other ones, 150°C to 375°C and 375°C to 700°C are assigned to decomposition of aromatic ring, propyl group, and water from silanol group condensation. Calculation based on this analysis showed 2.3 mmol of organic matter per gram MCM. This result is adapted to elemental analysis data: C% 18.9, N% 3.5, S% 6.8.

Figure 3 shows MCM-41 alone, MCM-iodopropyl and thiomorpholine derivative FTIR spectra, up to down, respectively. The IR spectrum of MCM-41 before functionalization (upper curve, Fig. 3) clearly shows an intense band at 1,069 cm^{-1} assigned to an asymmetric stretching of siloxane groups and a broad signal (3,500–3000 cm^{-1}) resulting from hydrogen-bonded Si–OH groups. In the middle spectrum,
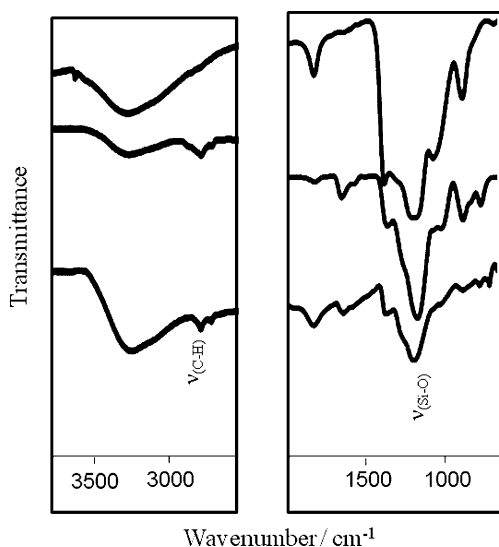
two peaks at 2,853 and 2,923 cm^{-1} are related to C–H stretching in aliphatic hydrocarbon chain that demonstrates the presence of iodopropyl groups on the surface.

## Preparation of the chemically modified carbon paste electrodes

The chemically modified carbon paste electrodes were prepared by thoroughly mixing graphite powder, 25%wt. paraffin oil and TMMCM-41 in proportions of 10.4, 14.9, 20.1, and 24.9 %wt., respectively. The electrode body was fabricated from a glass tube of i.d. 5 mm and a height of 3 cm. After the mixture homogenization, the paste was packed carefully into the tube tip to avoid possible air gaps often enhancing the electrode resistance. A copper wire was inserted into the opposite end to establish electrical contact. The external electrode surface was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the carbon paste.

Electrode conditioning

Fresh modified electrode surfaces were conditioned by exposure to 1.0×10^{-4} mol L^{-1} $Cd(NO_3)_2$. The electrodes were then rinsed with deionized water for 30 s. Figure 4 shows the interaction of the TMMCM-41 with Cd^{2+} ions. A kind of charge–dipole interaction occurs between the Cd^{2+} ions and heteroatoms (N and S) of the organic part of TMMCM-41. In general, neutral complexing agents or neutral ionophores have this type of interaction (charge–dipole).

EMF measurements

All potentials were measured on a Corning model 125 pH/mV meter versus SCE. The pH of the sample solutions was monitored simultaneously with a conventional glass pH electrode. The electrochemical cell can be represented as follows:

Ag,AgCl(s), KCl (3 mol L^{-1}) ‖ sample solution | carbon paste electrode
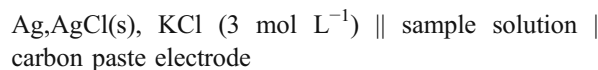
Calibration graph was drawn by plotting the potential, E, versus the logarithm of the cadmium ion concentration.

Fig. 3 Interaction of Cd^{2+} ion with TMMCM-41

Fig. 4 FTIR spectrum of MCM (*upper line*), propyl functionalized MCM (*middle line*), TMMCM (*lower line*)
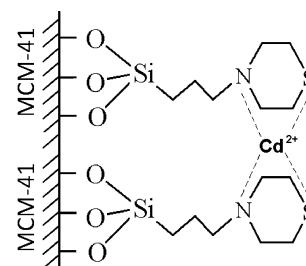
Results and discussion

General consideration

Generally, in a galvanic cell, the electromotive force (EMF) is calculated as follows [40]:

$$E_{CPE} = E_{matrix} + \Sigma E_J + \Delta E \qquad (1)$$

Where, E_{matrix} is the constant potential due to matrix resistance, ΣE_J is the summation of the liquid junction potentials, which can be kept reasonably small and constant under well-defined conditions. ΔE is the potential difference between internal and external surfaces of the conditioned electrode. In this study, ΔE of the electrode can be divided into two separate potential contributions, the phase boundary potentials at interface and the diffusion potential within the ion-selective electrode. Diffusion potential is negligible in most cases when the electrode is conditioned in the target ion solution. Therefore:

$$\Delta E = E_{Diffusion} + E_{PB} = E_{const} + E_{PB} \qquad (2)$$

E_{PB} is the phase boundary potential at the CPE sample interface which is ideally a function of the sample ion activity according to the well-known Nernst equation:

$$E_{CPE} = E'_{const} + (RT/zF)\ln a_{Cd} \qquad (3)$$

Where, z is the valency and a_{Cd} the activity of the uncomplexed Cd^{2+} ion and R, T, and F are the universal gas constant, the absolute temperature, and the Faraday constant, respectively.

Response characteristics of the CPEs and electrode composition

The nanoporous silica used in the heavy-metal determination has been the subject of extensive research recently. This work, to the best of our knowledge, is the first attempt to apply modified TMMCM-41 for the selective cadmium ion determination in the presence of other metal ions. In preliminary experiments, we found that the carbon paste electrodes, containing TMMCM-41, generated stable potentials in the solutions with cadmium ions after conditioning in a 1.0×10^{-4} mol L^{-1} Cd(NO$_3$)$_2$ solution. The electrode revealed selectivity for Cd^{2+} in comparison with other common metal ions. This is likely due to the high selectivity of the functionalized MCM-41 toward Cd^{2+} ions with respect to the other metal ions as well as the rapid exchange kinetics of the resulting complex. The presence of both sulfur atoms, as soft coordination sites, with a more or less convenient cavity size seems to generate a great affinity between the ionophore and the Cd^{2+} ions.

The effect of the TMMCM-41 composition on the potentiometric response of the electrodes was investigated by varying the proportions of the ion carrier (TMMCM-41) and the graphite powder. Table 1 presents the compositions of several typical electrodes along with their response characteristics. Based on the IUPAC recommendations [41], the critical response characteristics of the designed electrode were assessed. Table 1 shows the slopes, linear ranges, and limit of detections (LODs) of the resulting potentiometric calibration curves for the Cd^{2+} carbon paste electrodes. Clearly, an increase at the TMMCM-41 level in the CPE caused a slope increase of the calibration curve (compare CPE2, CPE3, CPE4, and CPE5). As it can be seen from Table 1, the TMMCM-41 modified electrode with the graphite powder/paraffin oil/TMMCM-41 percentage ratio of 54.0%/25.9%/20.1% was selected as the optimal electrode ingredient composition. It exhibited a Nernstian slope of 28.6 mV decade^{-1} in a wide Cd^{2+} ion concentration range between 1.0×10^{-6} and 1.0×10^{-2} mol L^{-1}. The carbon paste electrode without modifier (CPE1) presented a nonlinear potentiometric response, and it can be seen in Table 1. From this table, it is observed that the slope was very low (~9.1 mV decade^{-1}) and the LOD for the CPE4 was equal to 6.0×10^{-7} mol L^{-1}. The LOD was calculated as the cadmium ion concentration obtained when the linear regions of the calibration graphs were extrapolated to the baseline potentials [42].

Thus, the CPE4 carbon paste composition was used for further studies. The optimum equilibration times for the electrode in the presence of 1.0×10^{-4} mol L^{-1} cadmium

Table 1 Composition of carbon paste electrodes and their potentiometric response characteristics of chemically modified electrodes

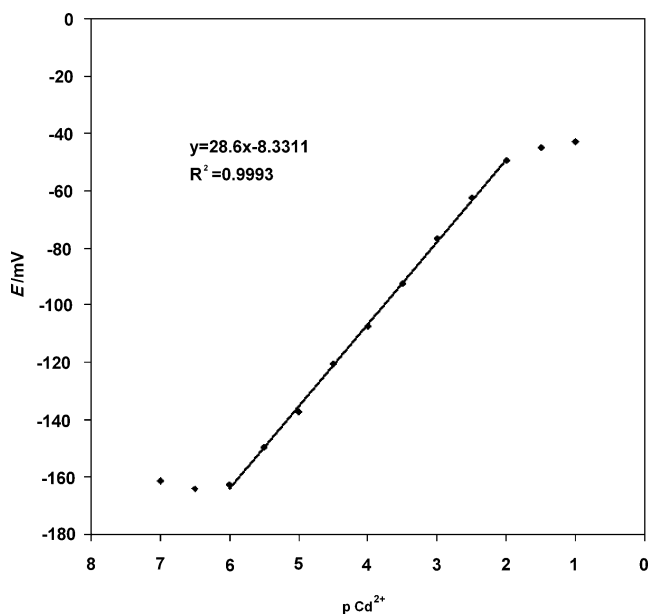| Electrode	Composition (%)			Slope (mV decade^{-1})	Linear range (molL^{-1})	LOD (molL^{-1})
	TMMCM-41	Graphite powder	Paraffin oil			
CPE1	0	75.0	25.0	9.1(±1.8)	–	–
CPE2	10.4	63.5	26.1	24.9(±1.8)	10^{-4}–10^{-2}	6.1×10^{-5}
CPE3	14.9	60.2	24.9	28.2(±1.6)	10^{-5}–10^{-2}	7.5×10^{-6}
CPE4	20.1	54.0	25.9	28.6(±1.2)	10^{-6}–10^{-2}	6.0×10^{-7}
CPE5	24.9	50.0	25.1	26.6(±1.4)	3.0×10^{-6}–10^{-2}	8.7×10^{-7}

$y=28.6x-8.3311$
$R^2=0.9993$

Fig. 5 Calibration curve of the Cd^{2+} CPE based on TMMCM-41 (CPE 4)

nitrate was 24 h; after this time period, the electrode generated stable potentials in contact with the cadmium solution. In the case of all the TMMCM-41-modified electrodes, the standard deviations of ten replicate potential measurements were ±1.2 (for CPE4). For the study of the regeneration step effect on the reproducibility of the electrode response, the electrode surface was scrubbed and used under the same conditions.

Cleaning solution

By washing the electrode only with distilled water, more than ten successive potentiometric measurements were performed from 1.0×10^{-5} to 1.0×10^{-3} mol L^{-1} cadmium solution and vice versa without any deterioration of the potential signal (Fig. 5). The washing step, required for the electrode to return to the starting potential after performing calibration, was ~5 min with a standard deviation in the potential of ±1.4 mV.

Response time

The response time of an ion-selective electrode is also an important factor for any analytical application. In the case of all electrodes, the average response time was defined as the required time for the electrodes to reach a cell potential of 90% of the final equilibrium values after successive immersions in a series of solutions each having a ten-fold concentration difference [43–47]. Figure 6a shows the static response time of the sensor for 1.0×10^{-3} mol L^{-1} of Cd^{2+} ions. Results of the dynamic potential–time responses for

the mentioned electrode were obtained upon changing the Cd^{2+} concentration from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} (by fast injection of microliter-amounts of a concentrated solution). The results shown in Fig. 6b clearly indicate that the potentiometric response time of the electrode was 20 s.

To evaluate the reversibility of the electrode, the practical potential response of the modified electrode was
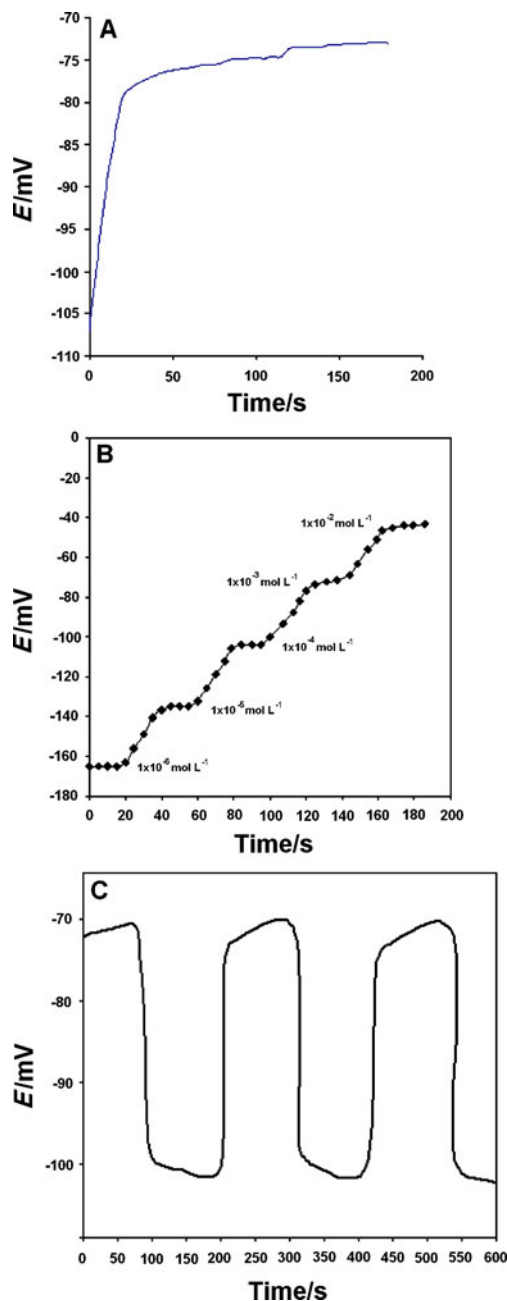

Fig. 6 Response time of the CPE based on TMMCM-41, on changing Cd^{2+} concentration **a** static response time for 1.0×10^{-3} mol L^{-1} of Cd^{2+} ion; **b** dynamic response time from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}; **c** response time of the proposed sensor for several high-to-low sample cycles
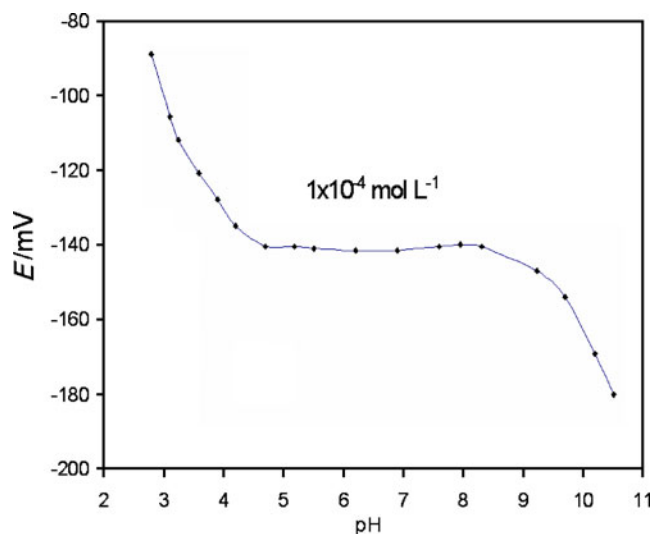
Fig. 7 pH effect on the potential responses of the Cd^{2+} CPE (CPE 4) based on TMMCM-41 on test solution of the Cd^{2+} ion (1.0×10^{-2} mol L^{-1})

recorded by changing solutions with different Er(III) concentrations from 1.0×10^{-3} to 1.0×10^{-4} mol L^{-1}. The measurements were performed from the highest concentration to the lowest, and the results are shown in Fig. 6c. The potentiometric response of the sensor was reversible and had no memory effect, although the time needed to reach equilibrium was longer than that when the solution sequence was reversed.

pH effect of the test solution

The potentiometric response of the membrane electrodes, based on the TMMCM-41, was found to be sensitive to the pH changes. Figure 7 shows a typical pH response curve for the freshly prepared CPE4, over a pH range of 3.0–10.5, where the pH was adjusted with dilute nitric acid and

Table 2 Potentiometric selectivity coefficient, $K_{Cd,X}^{MPM}$, for Cd^{2+} CPE (electrode CPE4) obtained by using the matched potential method (concentration of the reference solution of Cd^{2+} ion was 1.0×10^{-6} mol L^{-1} and the concentration of interfering ions was between 1×10^{-4} to 1.0 mol L^{-1}; the pH of the all solutions adjusted to 4.6 with acetate buffer)

Interfering ion, X	$\log K_{Cd,X}^{MPM}$	Interfering ion, X	$\log K_{Cd,X}^{MPM}$
Cr^{3+}	−3.0	Fe^{3+}	−5.7
Mg^{2+}	−2.8	Zn^{2+}	−2.3
Ni^{+}	−3.9	K^{+}	−4.6
Co^{2+}	−3.2	Ca^{2+}	−5.3
Pb^{2+}	−2.9	Ba^{2+}	−3.2
Mn^{2+}	−3.2	Sr^{2+}	−2.9
Na^{+}	−3.5	Cu^{2+}	−5.0
Ag^{+}	−2.9	Hg^{2+}	−3.8

Table 3 Results of the cadmium recovery experiment in tap water by proposed electrode (CPE 4)

Sample	Added cadmium ($\mu g m L^{-1}$)	Found cadmium ($\mu g m L^{-1}$)	%Recovery=found/added×100
Tap water	1.124	1.056 (±1.8)	94.0
	5.62	5.35 (±1.1)	95.2
	13.50	13.07 (±1.0)	96.8
	22.48	22.09 (±2.2)	98.3

sodium hydroxide solutions. When the same membrane electrode was conditioned in 1.0×10^{-4} mol L^{-1} $Cd(NO_3)_2$ (for~12 h), the electrode response was hardly affected by the pH change from 4.0 up to 8.0, implying that this electrode could be used to measure many environmental and industrial water samples without pH adjustment. However, outside this range, the electrode responses changed significantly. The decreased response at pH<4 seemed ascribable to the competitive binding of protons (or hydrated protons) to the ligands on the electrode surface. The diminished potential at pH>8.0 was due to some cadmium hydroxide formation in the sample solutions. In this pH range, neither the precipitation of the metal hydroxide nor the protonation of the thiol group was expected [48, 49].

Interference studies

The potentiometric selectivity coefficients, describing the preference of the suggested electrode for an interfering ion, X, with reference to the cadmium ion, Cd^{2+}, were determined by the matched potential method (MPM). The MPM is recommended by IUPAC [39, 49] to overcome the difficulties associated with the methods based on the Nicolsky–Eisenman equation [50].
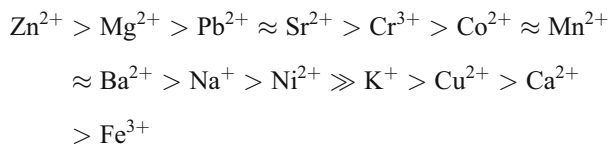
According to this method, the specified activity (concentration) of the primary ion is added to a reference solution (1.0×10^{-5} mol L^{-1} cadmium nitrate, in this case) and the potential is measured. In a separation experiment, interfering ions (X) are successively added to an identical

Table 4 Cadmium electroplating waste water sample analysis by using proposed cadmium sensor (CPE 4) and ICP-AES

Samples	The proposed sensor[a] ($\mu g m L^{-1}$)	ICP-AES[a] ($\mu g m L^{-1}$)	Relative error (%)
Sample 1	4.73±0.34	4.56±0.23	3.72
Sample 2	5.10±0.42	4.90±0.33	4.08
Sample 3	4.0±0.27	3.87±0.30	3.35

[a] The results are based on triplicate measurements

reference solution until the measured potential matched that obtained before the addition of the primary ions. The matched potential method selectivity coefficient, $K_{Cd,X}^{MPM}$ is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K_{Cd,X}^{MPM} = \Delta a_{Cd}/a_X$ [51–56]. The resulting values for the cadmium ion-selective electrode are listed in Table 2. The selectivity sequence of the employed thiomorpholine-functionalized MCM-41 for different inorganic cations more or less obeys the order:

$$Zn^{2+} > Mg^{2+} > Pb^{2+} \approx Sr^{2+} > Cr^{3+} > Co^{2+} \approx Mn^{2+}$$
$$\approx Ba^{2+} > Na^+ > Ni^{2+} \gg K^+ > Cu^{2+} > Ca^{2+}$$
$$> Fe^{3+}$$

Lifetime

The lifetime of the TMMCM-41-modified electrode was studied by periodically recalibrating the potentiometric response to Cd^{2+} ion in standard cadmium nitrate solutions. After the conditioning step, the electrode repeatedly calibrated three times during a period of one month; no significant change in the performance of the electrode was observed. This shows that the lifetime of the proposed electrode was about 4 months.

Analytical application

To assess the applicability of proposed electrode in real samples, an attempt was made to determine cadmium in tap water. The analysis was performed by using the standard addition technique. The results are given in Table 3. Good recoveries were obtained in all samples.

The proposed sensor was also applied to determination of the cadmium content of industrial cadmium electroplating wastewater samples. The obtained results are shown in Table 4. As it can be seen from Table 4, there is a satisfactory agreement between the results of this sensor and those with inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. Thus, the recommended sensor could be successfully used in the environmental monitoring of cadmium ions.

Conclusion

The results of this study show that the potentiometric method using TMMCM-41 doped in carbon paste electrode provides an attractive alternative for the determination of Cd^{2+} ion. The electrode exhibited linear response over a wide concentration range with a Nernstian slope, fast response time, selective to cadmium, and is easy to prepare.

Another unique feature of the present sensor for cadmium is its good long-term stability (more than 4 months).

References

1. Walcarius A (2001) Electroanalysis 13:701–718
2. Kresge CT, Leonowicz ME, Roth WJ, Vartuli JC, Beck JS (1992) Nature 359:710–712
3. Beck JA, Vartuli JC (1996) Curr Opin Solid State Mater Sci 1:76–87
4. Feng X, Fryxell GE, Wang LQ, Kim AY, Liu J, Kemner KM (1997) Science 27:923–926
5. Mercier L, Pinnavaia TJ (1997) Adv Mater 9:500–503
6. Brown J, Richer R, Mercier L (2000) Micropor Mesopor Mater 37:41–48
7. Yantasee W, Lin Y, Fryxell GE, Busche BJ, Birnbaum JC (2003) Separ Sci Technol 38:3809–3825
8. Bibby A, Mercier L (2002) Chem Mater 14:1591–1597
9. Walcarius A, Etienne M, Bessiere J (2002) Chem Mater 14:2757–2766
10. Moller K, Bein T (1998) Chem Mater 10:2950–2963
11. Sayari A, Hamoudi S (2001) Chem Mater 13:3151–3168
12. Stein A, Melde BJ, Schroden RC (2000) Adv Mater 12:1403–1419
13. Mercier L, Pinnavaia TJ (2000) Chem Mater 12:188–196
14. Corriu RJP, Lancelle-Beltran E, Mehdi A, Reye C, Brandes S, Guilard R (2002) J Mater Chem 12:1355–1362
15. Lim MH, Stein A (1999) Chem Mater 11:3285–3295
16. Sanchez C, Ribot F (1994) New J Chem 18:1007–1047
17. Walcarius A (2004) Electrochim Acta 49:3775–3783
18. Corriu RJP, Leclercq D (1996) Angew Chem Int Ed Engl 35:1420–1436
19. Javanbakht M, Badiei A, Ganjali MR, Norouzi P, Hasheminasab A, Abdouss M (2007) Anal Chim Acta 601:172–182
20. Javanbakht M, Fard SE, Abdouss M, Mohammadi A, Ganjali MR, Norouzi P, Safaraliee L (2008) Electroanalysis 20:2023–2030
21. Javanbakht M, Ganjali MR, Norouzi P, Badiei A, Hasheminasab A, Abdouss M (2007) Electroanalysis 19:1307–1314
22. Badiei A, Norouzi P, Tousi F (2005) Europ J Sci Res 12:39–45
23. Badiei A, Bonneviot L, Crowther N, Mohammadi Ziarani G (2006) J Organomet Chem 691:5923–5931
24. Lawrence NS, Deo RP, Wang J (2004) Anal Chem 76:3735–3739
25. Department of Health and Human Services and US Environmental Protection Agency (1987) Federal Register 52:12866
26. Keith LH, Telliard WA (1979) Environ Sci Toxicol 13:416–423
27. US Environmental Protection Agency (1991) Water quality criteria summary list. USEPA, Washington, DC
28. US Environmental Protection Agency (1996) EPA integrated risk information system (IRIS). USEPA, Washington, DC
29. Green M. Chapter on Pollutants, Chemical. Grolier Electronic Publishing Ink, (1988) Danbury, CT
30. National Library of Medicine (1996) Hazardous substances data bank (HSDB)
31. Friberg L, Nordberg GF, Kessler E, Vouk VB (1986) Handbook of toxicology of metals, 2nd Edn. 1:11
32. Faridbod F, Ganjali MR, Dinarvand R, Norouzi P, Riahi S (2008) Sensors 8:1645–1703
33. Bakker E, Buhlmann P, Pretsch E (1997) Chem Rev 97:3083–3132
34. Faridbod F, Ganjali MR, Dinarvand R, Norouzi P (2007) African J Biotechnol 6:2960–2987
35. Granzhan AV, Charykov AK (1993) Pharm Chem J 27:517–523

36. Faridbod F, Ganjali MR, Dinarvand R, Norouzi P (2008) Sensors 8:2331–2412
37. Mashhadizadeh MH, Mostafavi A, Allah-Abedi H, Sheikhshoai I (2006) Sens Actuators B 113:930–936
38. Reddy KM, Song C (1996) Catal Lett 36:103–109
39. Badiei A, Bonneviot L (1998) Inorg Chem 37:4142–4145
40. Lorencetti LL, Gushikem Y, Kubota LT, Oliveria Neto G, Fernandes JR (1995) Microchim Acta 117:239–244
41. IUPAC Analytical Chemistry Division, Commission on Analytical Nomenclature. Recommendations for nomenclature of ion-selective electrodes (1976) Pure Appl Chem 48:127
42. Ganjali MR, Memari Z, Faridbod F, Dinarvand R, Norouzi P (2008) Electroanalysis 20:2663–2670
43. Gupta VK, Al Hayat M, Singh AK, Pal MK (2009) Anal Chim Acta 634:36–43
44. Ganjali MR, Norouzi P, Faridbod F, Yousefi M, Naji L, Salavati-Niasari M (2007) Sens Actuators B 120:494–499
45. Ganjali MR, Norouzi P, Faridbod F, Riahi S, Ravanshad J, Tashkhourian J, Salavati-Niasari M, Javaheri M (2007) IEEE Sensor J 7:544–550
46. Gupta VK, Jain S, Chandra S (2003) Anal Chim Acta 486:199–207
47. Gupta VK, Singh AK, Gupta B (2006) Anal Chim Acta 575:198–204
48. Ganjali MR, Norouzi P, Mirnaghi FS, Riahi S, Faridbod F (2007) IEEE Sens J 7:544–550
49. Faridbod F, Ganjali MR, Larijani B, Norouzi P, Riahi S, Mirnaghi FS (2007) Sensors 7:3119–3135
50. Buck PR, Lindner E (1994) Pure Appl Chem 66:2527–2532
51. Umezawa Y, Umezawa K, Sato H (1995) Pure Appl Chem 67:507–518
52. Riahi S, Faridbod F, Ganjali MR (2009) Sensor Lett 7:42–49
53. Ganjali MR, Norouzi P, Faridbod F, Sepehrifard A, Ghandi M, Moghimi A (2007) Can J Anal Sci Spec 52:46–56
54. Ganjali MR, Norouzi P, Dinarvand R, Faridbod F, Moghlimi M (2008) J Anal Chem 63:684–689
55. Gupta VK, Goyal RN, Sharma RA (2009) Int J Electrochem Sci 4:156–172
56. Gupta VK, Chandra S, Agarwal S, Lang H (2005) Sens Actuators B 107:762–767