Novel Sol−Gel-Derived Material for Separation and Optical Sensing of Metal Ions: Propyl-ethylenediamine Triacetate Functionalized Silica

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A novel organically modified silica material has been prepared by sol−gel processing. The material incorporates an organic substituent, propyl-ethylenediamine triacetate, which is linked to the silica matrix covalently. This optically transparent material has been characterized by thermogravimetric analysis and infrared spectroscopy. Its binding capability with various metal ions has been examined. The material is porous, and almost all the covalently linked organic substituents are active in the pore space. It can be processed into monoliths or coated as thin films of widely variable shapes. The usefulness of this material as a stationary phase for chromatographic separation of metal ions has been demonstrated. The feasibility of this material as a chemical recognition phase for optical sensing of Cu^{2+} has also been illustrated. The material is highly stable and highly resistant to leaching of the organic modifier.

Introduction

The sol−gel process is very well-adapted for coating of thin films on complex shapes.[1] The porosity and pore size of these films can be controlled[2] to maximize the surface area and to ensure that diffusion rates in to and out of the film remain high. Furthermore, the sol−gel process involves low-temperature hydrolysis and condensation of appropriate monomeric precursors and is highly suitable for inclusion of organic moieties that cannot withstand high temperatures. Thus, organically modified sol−gel films have recently been of interest in various areas of analytical chemistry because of their potential uses in chemical or biochemical optical sensors,[1a,3] amperometric biosensors,[1a,4] chemically modified electrodes,[5] ion-selective electrodes or field-effect transistors,[6] capillary electrophoresis,[1c,7] liquid chromatography,[1c,8] gas chromatography,[9] and solid-phase microextraction.[10] The organic modifiers incorporated in the sol−gel processed inorganic matrixes can be doped organic or bioorganic molecules,[11] polymers or polyelectrolytes,[12] or covalently linked organic functional groups.[6b,13]

For analytical applications, the sol−gel-derived materials generally serve as host matrixes for the immobilization of organic modifiers. Methods of immobilization of organic modifiers in sol−gel-derived materials include impregnation, chemical doping, and covalent binding. In general, impregnation refers to physical or chemical sorption of organic modifiers on the preformed glass, while chemical doping refers to incorporation of organic modifiers during the formation of the sol−gel glass. Of the available immobilization techniques, co-

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valent linkage of an organic modifier to a suitable matrix appears to be the most efficient immobilization method because the resulting materials do not leach at all,[13] while doping is attractive because of its simplicity, wider generality, and effective maintenance of original reagent properties in the immobilized state.[11,14] However, no matter how attractive the simple doping process might be, it often results in leaching of organic modifiers from the doped sol−gel matrixes, especially for dopants of low molecular weight.

In this article we describe a new organically modified silica material prepared by the sol−gel process. The material, named propyl-ethylenediamine triacetate functionalized silica (PEDTAFS), incorporates an organic substituent, propyl-ethylenediamine triacetate (PEDTA), which is linked to the silica matrix covalently. Since the PEDTA moiety is similar in structure to a well-known chelating agent, ethylenediamine tetraacetate (EDTA), the material is cation-exchangeable. Also, this material retains the nanoscale porosity and optical transparency of the parent sol−gel glass and can be processed into monoliths or coated as thin films of widely variable shapes. To demonstrate the usefulness of this material as a stationary phase for chromatographic separation of metal ions, we have constructed and evaluated a prototype chromatographic column. The prototype exhibited high stability and excellent reproducibility. We have also evaluated the feasibility of using this material as a chemical recognition phase for optical sensing of Cu^{2+}. The material exhibited rapid response time and good linear dynamic range in the presence of Cu^{2+}.

Experimental Section

Materials. The following chemicals were used in the synthesis of sol−gel-derived materials: tetramethyl orthosilicate (TMOS, TCI), N−(trimethoxysilylpropyl) ethylenediamine triacetic acid, trisodium salt (TMSPEDTA, 50% w/w, Gelest), and hydrochloric acid (Merck). All reagents were used as received without further purification. Standard copper (II), cadmium (II), zinc (II), calcium (II), palladium (II), chromium (III), cobalt (II), iron (III), and nickel (II) solutions were obtained from Merck. All pH buffer solutions were prepared by the following procedure unless otherwise specified. 3.49 g sodium acetate was dissolved in 500 mL of deionized water followed by adjustment, with HNO_3 or NaOH, to the desired pH values. All aqueous solutions were prepared with deionized water.

Preparation of Silica Sol−Gel Powder. Organofunctionalized silica sol−gel was prepared by adding 400 μL deionized water and 20 μL 0.1 M HCl to 160 μL TMSPEDTA. The mixture was sonicated in an ice bath for approximately 30 min and then stored in a refrigerator (at about 4 °C) for 24 h. Subsequently, 180 μL TMOS was added to the mixture. After ca. 5 min of shaking in ice water, a transparent and homogeneous sol−gel monolith resulted. The gel was aged for 24 h under ambient room conditions (temperature = 21−25 °C, relative humidity = 81−87%) and was then lyophilized into powder. Unfunctionalized silica sol−gel was prepared by adding 236 μL deionized water and 14.7 μL 0.1M HCl to 180 μL TMOS. The mixture was sonicated in ice water for approximately 30 min until a transparent and homogeneous sol−gel monolith was obtained. The gel was aged for 24 h under ambient room conditions and subsequently lyophilized to powder.

Sorption Studies of Metal Ions. Metal ion stock solutions were prepared by diluting 1000 ppm standard metal ion solutions with buffer solutions to 500 mL. Exactly 0.1 g PEDTAFS powder or TMOS-derived powder was added to 100 mL of the stock metal ion solutions. The mixtures were mechanically shaken for 72 h. Subsequently, the mixtures were filtered and the filtrates were analyzed using an atomic absorption spectrometer. The amount of Cu^{2+} sorption by PEDTAFS powder with respect to time was examined by a procedure similar to the above but with a minor change. Here a syringe with filter (cellulose acetate membrane, pore size = 0.2 mm) was used to sample the solution at appropriate times for analysis of copper content by an atomic absorption spectrometer.

Preparation of PEDTAFS-Coated Silica Gel Column. The coating solutions were prepared by adding 400 μL deionized water and 20 μL of 0.1M HCl to 160 μL TMSPEDTA. The mixture was sonicated in an ice bath for approximately 30 min and then stored in a refrigerator for 24 h. Subsequently, 0.6 g silica gel (60 mesh) was added to the mixture with sufficient stirring. Then, 180 μL TMOS was added to the mixture. After thorough stirring, the mixture was allowed to age and dry under ambient room conditions for 3 days. PEDTAFS-coated silica gel (3.5 g) was packed in a 1-cm-diameter glass column. This column was used throughout our chromatographic experiments.

Instrumentation. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50 analyzer from 25 °C to 1000 °C under nitrogen atmosphere. IR spectra were measured with a 16-PC Perkin−Elmer FTIR spectrometer by dispersing PEDTAFS powder in KBr, and pressed into a pellet form. Thermal treatment of PEDTAFS samples were performed in a Lenton LTF12/50/300 tube furnace. UV−vis spectra of the PEDTAFS powder were obtained with a Shimadzu UV-3101PC Solid State UV−vis spectrometer. The metal ion content of a solution before and after metal ion sorption by PEDTAFS or TMOS-derived silica were determined by a Perkin−Elmer 3100 atomic absorption spectrometer.

Results and Discussion

Synthesis of PEDTAFS. Several parameters were varied in an attempt to achieve a homogeneous sol−gel monolith. These parameters included the amount of catalyst, the water/silane ratio, and the prehydrolysis time of TMSPEDTA. All these factors primarily affect the rates and extents of hydrolysis of the two precursors, TMSPEDTA and TMOS, and their subsequent condensation rates. Under acidic conditions, previous work[15] suggests that the hydrolysis rate is decreased by substituents which increased steric crowding around silicon. Electron-donating substituents, which help stabilize the developing positive charges, should increase the hydrolysis rate but to a lesser extent, because the silicon acquires little charge in the transition state. Thus, difference in rates of hydrolysis between TMSPEDTA and TMOS may cause phase separation and result in an opaque gel. Our experimental results showed that either coexisting of the two sol−gel precursors, TMSPEDTA and TMOS, at the beginning of the sol−gel reaction, or prehydrolysis of TMOS prior to the addition of TMSPEDTA always yielded opaque gels, even though various compositions of TMSPEDTA, TMOS, water, and HCl were tried extensively. One likely reason is that the bulky TMSPEDTA substituent increases the steric crowding around silicon. In addition, the acetate groups in TMSPEDTA may also interact with the developing positive charge on silicon, thus making the attack of the

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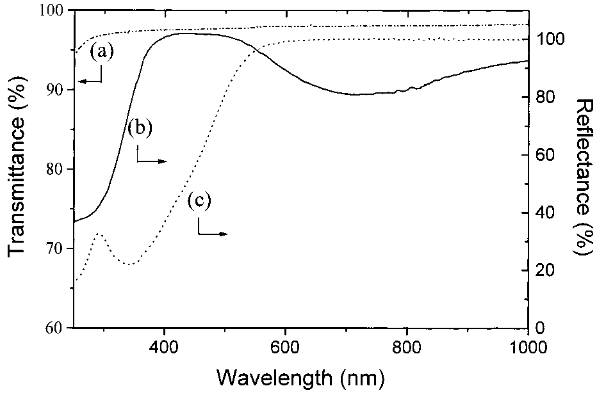

Figure 1. (a) Transmittance spectrum of a spin-coated PEDTAFS film on a glass slide. (b) Diffuse reflectance spectrum of Cu^{2+}−PEDTAFS. (c) Diffuse reflectance spectrum of Pd^{2+}−PEDTAFS.

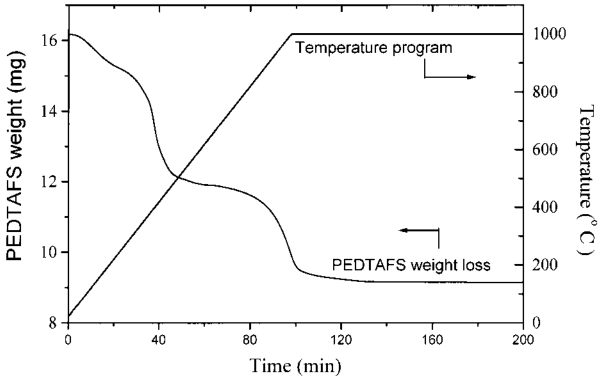

Figure 2. TGA thermogram of PEDTAFS and the corresponding temperature program used for the TGA. The heating process for the TGA run was performed at a rate of 10 °C/min.

water molecule difficult and slowing the rates of hydrolysis of the methoxyl groups. On the other hand, our experimental results showed that a long enough prehydrolysis time for TMSPEDTA would lead to clear gels. Normally, a totally transparent sol−gel monolith was formed with ca. 5 h of prehydrolysis of TMSPEDTA. Otherwise, opaque gels were obtained (for less than 5 h of prehydrolysis of TMSPEDTA). As shown in Figure 1a, a spin-coated PEDTAFS film on glass slide retains transparency even down to the mid-UV wavelength region.

The molar ratio of TMOS to TMSPEDTA also affects the condensation process. The organic moiety attached to the silicon through a Si−C bonding not only reduces the number of Si−O−Si linkages but also acts as a spacer in the inorganic network by forming an interconnected organic mesophase and, hence, a porous phase around the organic groups.[16] We found that if the molar ratio of TMOS to TMSPEDTA was less than 5.75, gelation would not occur. This is probably due to the bulky size of the PEDTA moiety. To form a three-dimensional network, at least one −O−Si−O− spacer is required between two neighboring PEDTA substituents on the inorganic network.

General Characterization of PEDTAFS. Thermogravimetric profiles for the lyophilized xerogels all contained similar features, as shown in Figure 2. The weight loss between 25 and 267 °C is possibly associated with removal of residual methanol and water trapped within the pore system or with partial dehydroxylation.[17] Above 267 °C, the hybrid glasses show two major weight losses, which are attributed to the thermal degradation of the organosilicate framework, involving Si−C, C−C, and C−N bond cleavage. Excluding the weight loss due to residual methanol and water, the total weight loss is 39.7% for the hybrid material, which is comparable to the calculated value of 40.1% organic content, assuming that all the methoxy groups are hydrolyzed and condensed and the residue consists of only SiO_2 and Na_2SiO_3. Similarly, excluding the weight loss due to residual methanol and water, the first weight loss between 267 and 667 °C is 21.5% for the hybrid material, which is comparable to a calculated value of 21.7% if this weight loss is assumed to be due to the loss of three acetate groups. In support of this assumption are the IR spectra of PEDTAFS samples heated at appropriate temperatures. As shown in Figure 3a−d, the bands at 1332 and 712 cm^{-1}, which are characteristics of the PEDTA moiety,[18] diminish in intensity at 300 °C and disappear at 500 °C, while weak bands at 2970 and 2878 cm^{-1}, which are attributed to C−H vibrations,[19] are still clearly seen at 500 °C. With the slowest possible heating rate of our instrument (10 °C/min), the weight loss did not reach steady state at 1000 °C during the scan, further heating at 1000 °C resulted in a complete weight loss. All together, this suggests that the PEDTA moiety was destroyed between 267 and 667 °C and the remaining organics were destroyed at above 667 °C.

The composition of the hybrid material treated at a few selected temperatures was further characterized by IR absorption spectroscopy. Here each PEDTAFS sample was heated at the specified temperature for ca. 60 min. Figure 3 shows the IR transmission spectra of the PEDTAFS samples after treatments at different temperatures. Between room temperature and 100 °C, the band at ca. 1636 cm^{-1}, which is attributed to molecular water that is weakly physisorbed on the surface,[17,20] decreases in intensity, and there is a decrease in relative intensity at ca. 3452 cm^{-1}, which is attributed to stretching modes of hydrogen-bonded Si−OH and trapped molecular water.[17,20] Furthermore, Figure 3a−b show that band at 962 cm^{-1}, which is identified as stretching of terminal Si−OH on the silica surface,[17b,20,21] decreased in intensity when PEDTAFS was heated from room temperature to 100 °C. All of the above results suggest that when PEDTAFS was heated from room temperature to 100 °C, most of the weakly adsorbed or trapped molecular water would be removed and there would also be a partial dehydration of the surface

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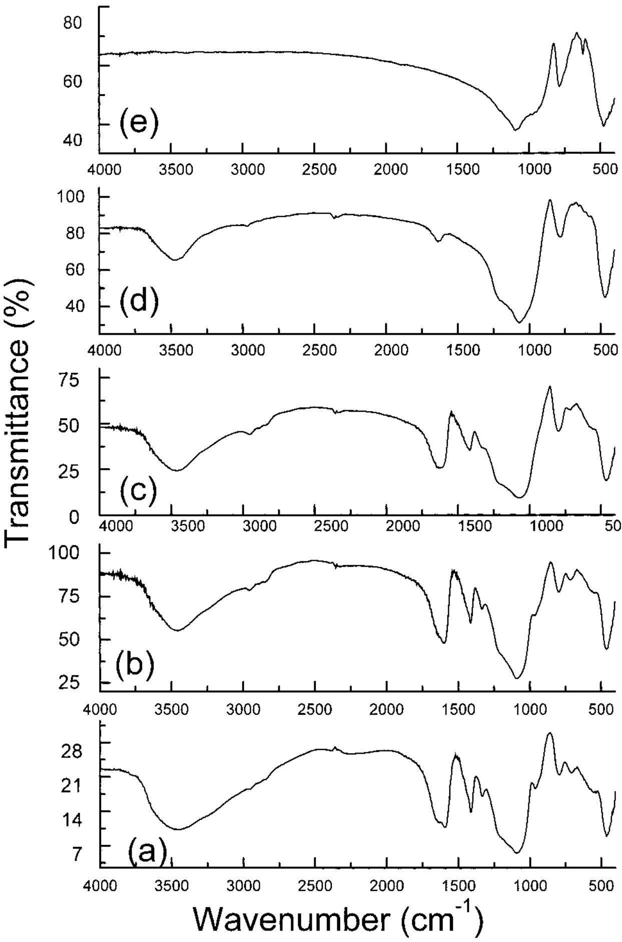

Figure 3. IR transmission spectra of PEDTAFS samples (a) at room temperature; and after thermal treatment at (b) 100 °C, (c) 300 °C, (d) 500°, and (e) 1000 °C.

hydroxyls. Previous studies[17a] suggest that the dehydration process at below 450 °C is completely reversible.

When PEDTAFS was heated from 300 °C to 500 °C, as shown in Figure 3c–d, there was a further decrease in relative intensity at ca. 3452 cm^{-1}, indicating that some strongly bound molecular water may be removed. In addition, the disappearance of the band at 962 cm^{-1} probably indicates that further condensation occurs among silica nanoparticles. One other noticeable feature is that, up to 100 °C, the organic functional groups are still stable, as indicated by the presence of $-CO_2$-stretching at 1592 and 1412 cm^{-1},[19] the bands at 1332 and 712 cm^{-1} due to the PEDTA moiety,[18] and the presence of $-CH_3$ stretching at ca. 2956 and 2842 cm^{-1}.[22] The band at 2880 cm^{-1} is probably an overlapping band of the $-CH_2$- stretching modes. The intensity of these bands mostly disappeared after thermal treatment of PEDTAFS at 500 °C, indicating the PEDTA moiety was decomposed. This is consistent with the TGA results. Nevertheless, the bands at ca. 3452 and 1636 cm^{-1} still existed. This can be attributed to the rehydration of the silica surface where the dehydration of the surface hydroxyls becomes progressively more irreversible from 450 °C to 800 °C.[17a] Above 800 °C, the dehydration is "irreversible", as illustrated in Figure 3e, where the bands at ca. 3452 and 1636 cm^{-1} disappeared when the temperature reached 1000 °C, leaving just the silica network with Si–O–Si vibrating modes at 1096, 788, and 476 cm^{-1}.[17b,20]

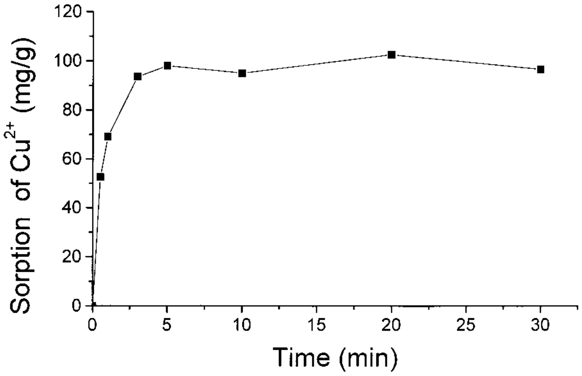

Figure 4. Amount of Cu^{2+} sorption in mg by 1 g of PEDTAFS powder with respect to time. Ammonia/ammonium nitrate buffer, pH = 8.3.

Binding of Metal Ions. As expected, the new material was able to bind various metal ions. Presumably, the metal ion-binding capability is due to the presence of the PEDTA substituent, which remains active in PEDTAFS. This has direct significance for applications in chemical sensing and chemical separation. When PEDTAFS powder was added to standard metal ion solutions (pH = 0), e.g., Cu^{2+}, Pd^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, and Cr^{3+}, which were blue, yellow, colorless, light blue, red, and navy blue, respectively,[23] the colors of PEDTAFS powder became sky blue for Cu^{2+}–PEDTAFS, yellow for Pd^{2+}–PEDTAFS, pale yellow for Fe^{3+}–PEDTAFS, light blue for Ni^{2+}–PEDTAFS, violet for Co^{2+}–PEDTAFS, and violet for Cr^{3+}–PEDTAFS. The diffuse reflectance spectra recorded for M^{n+}–PEDTAFS powder had a spectral maximum at 730, 590, 338, and 266 nm for $M^{n+} = Cu^{2+}$, Ni^{2+}, Pd^{2+}, and Fe^{3+}, respectively, while the transmittance spectra of M^{n+}–TMSPEDTA complexes in aqueous solution had a spectral maximum at 697, 600, 306, and 290 nm for $M^{n+} = Cu^{2+}$, Ni^{2+}, Pd^{2+}, and Fe^{3+}, respectively. Figures 1b and 1c display the representative diffuse reflectance spectra of Cu^{2+}–PEDTAFS and Pd^{2+}–PEDTAFS. Analogous to the case of sol–gel encapsulated EDTA,[23] the spectral shifts observed for spectra of M^{n+}–PEDTAFS as compared to those of M^{n+}–TMSPEDTA in solution are due to the change in the chelating strength of the M^{n+}–PEDTA in the gel compared to that in solution. This change in the chelating strength also indicates that the orientation of the PEDTA substituent is restricted in the pores of the silica matrix.

As shown in Figure 4, the response time for the formation of Cu^{2+}–PEDTAFS, which was presented as the amount of Cu^{2+} sorption by PEDTAFS powder with respect to time, was less than 5 min. This suggests that the PEDTAFS powder is porous enough that reagents can diffuse in to and out of the powder freely. The response time for the formation of M^{n+}–PEDTAFS was also less than 5 min for Pd^{2+}, Fe^{3+}, or Ni^{2+}, while the response time for Co^{2+} or Cr^{3+} was ca. 20 h in the

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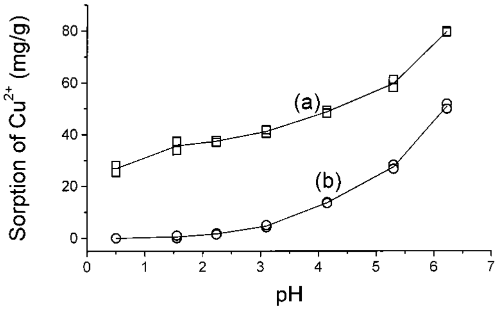

Figure 5. The amount of Cu^{2+} sorption in mg by 1 g of (a) PEDTAFS powder or (b) TMOS-derived powder with respect to pH.

absence of heating. Nevertheless, formation of colored M^{n+}−TMSPEDTA complexes for all the above M^{n+} in solution were observed instantaneously. Furthermore, when the Co^{2+} or Cr^{3+} solution was heated to boiling, only a few minutes was needed to develop the color of Co^{2+}−PEDTAFS or Cr^{3+}−PEDTAFS. The formation of colored Co^{2+}−EDTA or Cr^{3+}−EDTA complexes for Co^{2+} or Cr^{3+} has been suggested to be a thermal-activated process that requires boiling the solution for a few minutes.[23] This excludes the use of PEDTAFS for optical sensing of Co^{2+} and Cr^{3+}. In addition, we have found that the colored Co^{2+}−PEDTA or Cr^{3+}−PEDTA complexes could form without pretrapping of Co^{2+} or Cr^{3+} during the sol−gel process.[23] This suggests that the PEDTA substituent remains active, but its motion is restricted in the rigid sol−gel-derived cage.

Analogous to EDTA, which behaves like an amino acid with a double-zwitterionic structure when dissolved in water,[23] TMSPEDTA in water also showed a spectral band at 2138 cm^{-1}. This band is associated with the $=$NH^{+} stretching vibration of the amino acid zwitterions $=$NH^{+}−CH$_2$COO^{-}. In the sol−gel matrix, as shown in Figure 3, PEDTAFS showed no vibrational band at around 2100 cm^{-1}, suggesting that the PEDTA moiety in a silica gel matrix does not form a double betaine structure.

Silica is well-known to have an isoelectric point at about pH 2;[24] that is, its surface will become negatively charged upon immersion in solutions with pH > 2. As a result, silica is a weak cation exchanger in solutions with pH > 2. To evaluate how well the PEDTA substituent in PEDTAFS behaves, we need to examine its metal ion binding capability at a solution pH where the silanol group on the silica surface does not bind metal ions. Thus, the relation between the binding capability the of metal ion and the solution pH for both PEDTAFS and TMOS-derived silica was studied. Figure 5 showed that the Cu^{2+} binding capability of both PEDTAFS and TMOS-derived silica increased when the solution pH increased. The increase of Cu^{2+} binding capability by the TMOS-derived silica with an increase in solution pH likely is due to the increase of surface negative charge when the solution pH increases.

At a solution pH below 2, where a surface silanol does not bind metal ions, the increase of Cu^{2+} binding capability by PEDTAFS with an increase in solution pH is probably due to the increase in the α_3 value[25] of the PEDTA substituent at increasing solution pH. For example, the α_4 value for EDTA changes from 3.7×10^{-14} at pH 2 to 2.2×10^{-5} at pH 6.[25] In this study, we limited our solutions to the acidic pH range because depolymerization of the silica network is more likely to take place at solution pH values greater than 8.5.[26]

Table 1. Sorption of Metal Ions by PEDTAFS Powder

metal ion	pH	molar ratio of metal ion sorption to PEDTA substituent in PEDTAFS
Cu^{2+}	0.5	0.868 ± 0.021
	1.6	1.02 ± 0.02
	2.2	1.15 ± 0.01
Cd^{2+}	0.5	0.477 ± 0.017
	2.2	0.815 ± 0.047
Zn^{2+}	0.5	0.292 ± 0.005
	2.2	0.781 ± 0.027
Ca^{2+}	0.5	0.108 ± 0.002
	2.2	0.165 ± 0.003

The binding capabilities for Cd^{2+}, Zn^{2+}, and Ca^{2+} by PEDTAFS were also studied. These metal ions were colorless and their M^{n+}−PEDTAFS powders were white. As shown in Table 1, the binding capability for the metal ions by PEDTAFS decreases in the order Cu^{2+} > Cd^{2+} > Zn^{2+} > Ca^{2+}. Except for Cd^{2+} and Zn^{2+} (which showed similar binding capability with PEDTAFS), the trend of metal ion binding capability by PEDTAFS is similar to the trend of formation constants for EDTA with the above metal ions.[27] The deviation from the latter trend is probably due to the different geometric requirements for metal ion binding between the PEDTA substituent and EDTA. It is also important to note that, as shown in Table 1, the molar ratio of Cu^{2+} sorption to PEDTA substituent in PEDTAFS at a solution pH of 1.6 (where a surface silanol does not bind Cu^{2+}) is very close to 1, indicating that almost all the PEDTA substituents in PEDTAFS are active and are exposed on the surfaces of the sol−gel-derived pores.

Optical Monitoring of Metal Ion. To test the suitability of PEDTAFS as an optical sensing material, preliminary analytical tests were performed with PEDTAFS powder. The aim of the experiment was to find out if the binding of PEDTAFS with a metal ion would lead to a quantitative relationship between the optical signal and the concentration of the metal ion. It should be noted that PEDTAFS is versatile in various forms of sensing platforms, for example, as a coating on a glass slide or optical fiber.

In this experiment, 0.1 g of PEDTAFS was added to 100 mL of standard Cu^{2+} solution (pH $=$ 2). The mixture was mechanically shaken for 5 min. Subsequently, the mixture was filtered and the optical spectra of the powder residue was measured by diffuse reflectance spectroscopy. Figure 6 showed that the absorbance, which is given by the Kubelka−Munk function,[28] increases linearly with the increase of Cu^{2+} concentration. As shown in the previous section, the response time of PEDTAFS powder is reasonably good; hence, application

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(27) The formation constants of M^{n+}-EDTAs for Cu^{2+}, Cd^{2+}, Zn^{2+}, and Ca^{2+} are 6.3×10^{18}, 2.9×10^{16}, 3.2×10^{16}, and 5.0×10^{10}, respectively.[25]

(28) Wendlandt, W. W. *Reflectance Spectroscopy*; Wiley: New York, 1966; Chapter III.

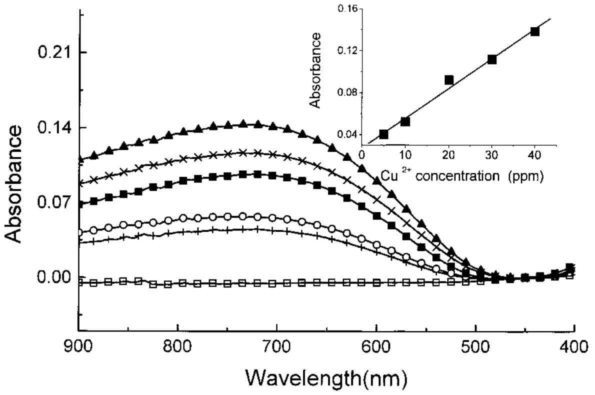


Figure 6. Diffuse reflectance spectra of PEDTAFS powder after standing in a Cu^{2+} solution with a concentration of (a) 0 ppm (□), (b) 5 ppm (+), (c) 10 ppm (○), (d) 20 ppm (■), (e) 30 ppm (×), and (f) 40 ppm (▲). The inset in the figure is a plot of the absorbance at 742 nm versus Cu^{2+} concentration. The correlation coefficient of the plot is 0.9935.

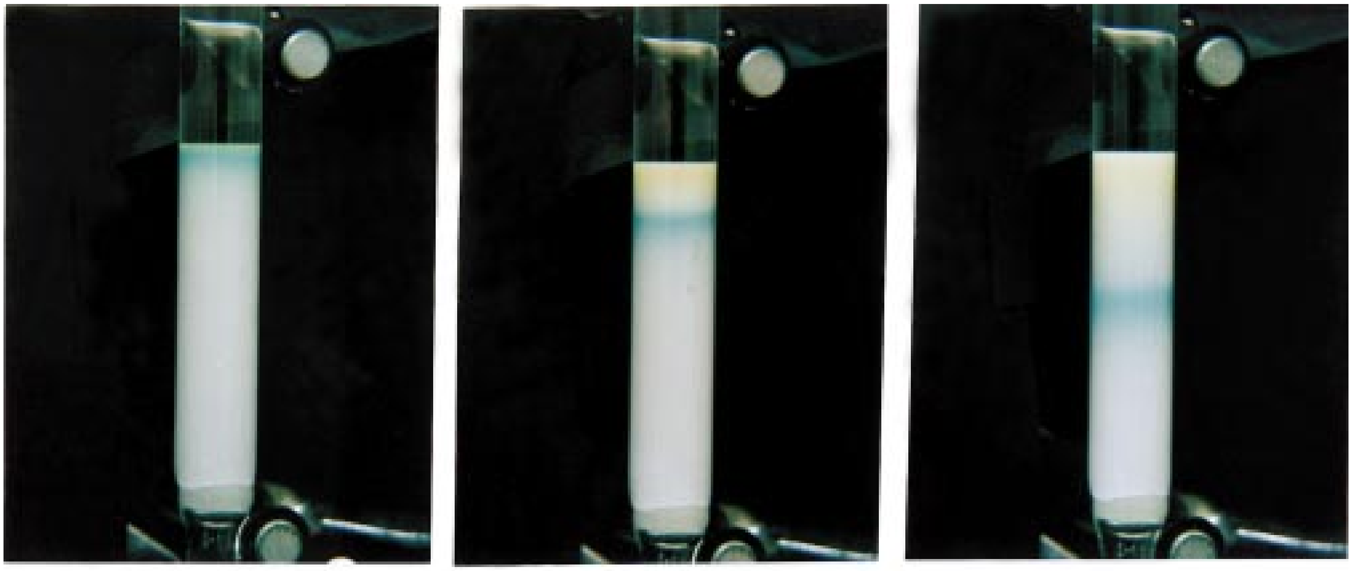
of PEDTAFS as a thin coating certainly will shorten the response time. Experiments are under way to examine the response time and the sensing capability of PEDTAFS in the form of thin films. Nevertheless, the above experiment shows that PEDTAFS can be used to monitor metal ions quantitatively.

Chromatographic Applications. Two basic types of packings have been used in liquid chromatography: pellicular and porous particle. In principle, because of its porous nature, our PEDTAFS material could be used for both types of packings. However, in this study, PEDTAFS was used only as a porous layer around the silica core just to demonstrate its feasibility as a chromatographic packing material.

To test its separation capability as a chromatographic packing material, we applied a solution mixture of Cu^{2+} (1 mL, 1000 ppm) and Pd^{2+} (1 mL, 1000 ppm) to the top of the PEDTAFS-coated silica gel column. Two color bands, blue and yellow, on the top of the column were observed immediately after the addition of the sample. As shown in Figure 7a, the yellow band was above the blue band and was narrower than the blue band. During this separation, 0.05 M EDTA (sodium salt) was used as an eluent (pH 4.5), and the flow rate was adjusted to be ca. 0.06 mL/min. Figure 7b showed that, after 50 min, the blue band moved forward while the yellow band broadened but barely moved. After 145 min, as shown in Figure 7c, the blue band broadened and moved to the middle of the column, while the yellow band almost remained on the top of the column and became broader. After 4 h of elution, the blue band was eluted from the column completely, but the yellow band still remained on the top part of the column. However, if 0.25 M EDTA (sodium salt) was used as an eluent, the yellow band was eluted from the column completely. The longer elution time of the yellow band when compared to that of the blue band indicates that the PEDTA substituent chelates Pd^{2+} better than Cu^{2+}.

In this study, the chromatographic conditions, such as column diameter, particle size, flow rate, type and concentration of eluent, and pH, were not optimized. The Cu^{2+}/Pd^{2+} mixture was chosen as an example merely because the color bands of Cu^{2+} and Pd^{2+} could be easily visualized. However, many other metal ions, such as Cd^{2+}, Zn^{2+}, Ca^{2+}, Ni^{2+}, and Fe^{3+}, should also be able to be separated by using PEDTAFS as the chromatographic packing material.

The use of PEDTAFS as a packing material for preconcentration columns was also evaluated. When a standard solution of Cu^{2+} (100 mL, 5 ppm) was injected onto the top of the column (same column as above) with a flow rate of 0.17 mL/min, a blue band gradually formed and remained on the top of the column. The concentrations of the standard Cu^{2+} solution before and



(a) right after addition of sample (b) 50 minutes (c) 145 minutes

Figure 7. Photographs of the chromatographic bands of a solution mixture of Cu^{2+} and Pd^{2+} through the PEDTAFS-coated silica gel column (a) right after addition of sample, (b) at 50 min, and (c) at 145 min. Eluent: 0.5 M EDTA (sodium salt).

after sorption by the preconcentration column were examined by atomic absorption spectroscopy. The percent sorption by the column was calculated by eq 1.

$$\text{Sorption (\%)} = [(C_i - C_f)/C\text{i}] \times 100\% \qquad (1)$$

where C_i is the initial concentration of Cu^{2+} before sorption and C_f is the final concentration of Cu^{2+} after sorption. Results of three runs give a percent sorption of 98.4 ± 1.1%.

To evaluate the preconcentration capability, 10 mL of 0.25 M EDTA (sodium salt) solution was used to elute the Cu^{2+} remaining on the column; i.e., a preconcentration factor of 10 was tried in this experiment. The concentration of eluted Cu^{2+} was again examined by atomic absorption spectroscopy. The percent recovery was calculated by eq 2.

$$\text{Recovery (\%)} = [C_e/(C_i - C_f)] \times 100\% \qquad (2)$$

where C_e is the concentration of eluted Cu^{2+}. Results of three runs give a percent recovery of 96.1 ± 4.4%. All together, the above results show that PEDTAFS is a suitable material for preconcentration of metal ions.

When evaluating the suitability of a chromatographic or sensing material, stability is one of the major concerns. Previous studies[23] showed that EDTA, upon encapsulation in sol−gel-derived silica matrixes, will rapidly leach out of the matrixes when soaked or flooded with water. Hence, it is important to check whether the PEDTA moiety remains active after extended use. Here, we evaluated the percent sorption and the percent recovery (without preconcentration) with respect to the number of reuses as indicators of the stability of the PEDTAFS material. For up to 25 reuses, the percent sorption is 96.1 ± 2.6% and the percent recovery is 98.1 ± 2.8%. Both trends, the percent sorption and the percent recovery versus the number of reuses, did not show a decrease but merely fluctuated randomly. This suggests that, due to the covalent nature of the PEDTA substituent, it is stable and will not leach out of PEDTAFS under normal chromatographic and sensing environments.

Conclusions

We have prepared a new organically modified silica material via the sol−gel process. The synthesis of this organic/inorganic hybrid material involved the use of a hybrid precursor and an SiO_2 precursor, which offered the advantage of independent control of reaction kinetics of the organic and inorganic components without the problem of phase separation. The advantages of such an approach to incorporate organic modifiers in a silica matrix include (1) high stability and no leaching, (2) simple fabrication and excellent reproducibility, (3) widely variable forms of coating available, and (4) rapid response. The incorporation of organic functional groups through covalent bonding is highly specific and provides leak-free, bulk-modified coatings, which is an indisputable must for analytical separation and in vivo medical applications and a prerequisite for most on-line sensors.

In summary, the microscale homogenity, nanoscale pososity, and optical transparency of this material, together with the chemical functionality of its PEDTA substituent, suggests that it is a suitable material for separation and optical sensing of metal ions. Further research is under way to develop this material for practical applications.

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