Tetrahedron Letters 57 (2016) 2468–2473

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Pamam built-on-silicon wafer thin-layer extraction devices for selective metal contamination detection

Oscar Valdés [a], Claudia Vergara [b], Fabiane M. Nachtigall [a,b], Zoraya Lopez-Cabaña [b], Jaime Tapia [c], Leonardo S. Santos [a,b,*]

[a] Nanobiotechnology Division at University of Talca, Fraunhofer Chile Research Foundation—Center for System Biotechnology, FCR-CSB, PO Box 747, Talca, Chile
[b] Laboratory of Asymmetric Synthesis, Chemistry Institute of Natural Resources, University of Talca, PO Box 747, Talca, Chile
[c] Chemistry Institute of Natural Resources, University of Talca, PO Box 747, Talca, Chile

ARTICLE INFO

Article history:
Received 1 March 2016
Revised 11 April 2016
Accepted 17 April 2016
Available online 22 April 2016

Keywords:
Silicon wafer
Polyamidoamine
MALDI-TOF

ABSTRACT

Silicon wafer surface was modified with polyamidoamine (PAMAM G0) dendrimer and further characterized by AFM, MALDI-MS, SEM, and EDX to provide a new sensor for metallic ions. The characterization showed the effective immobilization of dendrimer on the surface, and the analysis performed by MALDI-MS also showed a characteristic signal for each dendrimer–metal complex, which confirms the presence of the metal in solutions. The proof-of-concept of this device was tested as sensor for metal ions such as Cu(II) and U(VI) and using calibration curves the amount of metallic ions dissolved in solution can be easily assessed. The PAMAM G0 supported in silicon wafer can also be envisaged as possible built-on-silicon thin-layer chromatography (TLC) extraction device for metal determination with 'on-spot' MALDI-TOF-MS detection.

© 2016 Elsevier Ltd. All rights reserved.

Introduction

Chemical detection using sensors has been the focus of interest and study of various research groups.[1] These sensors are preferably used for qualitative detection or quantitative determination of the concentration of a substance using a specific chemical reaction.[2,3] In this context, one of the major environmental problems is the pollution by toxic metals.[4] Soluble and mobile toxic metals are not biodegradable, therefore they accumulate in organisms causing various disorders and health damages such as renal disturbances,[5,6] decreased lung capacity,[7,8] bone lesions,[9] and cancer.[10]

The detection and quantification for metal intoxication is limited, and atomic absorption spectroscopy (AAS) is one of the most used techniques. However, AAS can be expensive, complex and in some cases inefficient and time consuming, which challenges analytical chemists to explore alternative techniques in the last years.

Recent advances in nanotechnology focused on the development of dendrimers have provided several opportunities to improve efficiency and decrease cost of different processes, as metal detection.[11] Moreover, the physical and chemical properties of dendrimers can be controlled by modification of the structure and the terminal functional groups. Dendrimers are highly branched polymers with controlled composition and architecture consisting of three structural components: a core, interior branch cells and terminal branch cells. As a result of their unique behavior, structure and properties, dendrimers are suitable for a wide range of applications such as environmental remediation,[12] nanoparticle synthesis,[13] and nanomedicine.[14]

PAMAM dendrimers, first synthetized by Tomalia and coworkers, possess functional nitrogen and amide groups arranged in regular patterns that increase progressively with the number of generations.[15,16] PAMAM dendrimers appear as an attractive high capacity chelating agent for metal ions, mainly due to the high density of nitrogen groups and the possibility to modify their surface with various functional groups, which enhances its capabilities. Functional group modifications can improve the ability to chelate a variety of metals such as Cu(II), Ag(I), Cr(VI), Fe(III), among others.[17,18] Due to the possibility of modifying their surface and according to a wide range of applications, we figured out to employ PAMAM dendrimers of low generation (G0) to detect and quantify Cu(II) and U(VI) metal ions as a proof-of-principle. In this study, the use of a silicon wafer, as a solid support for the PAMAM dendrimers, in order to achieve a novel functional material for sensor applications in detecting metals in aqueous solutions is described.

---

* Corresponding author. Tel.: +56 71 2201575; fax: +56 71 2200448.
E-mail address: lssantos@utalca.cl (L.S. Santos).

http://dx.doi.org/10.1016/j.tetlet.2016.04.063
0040-4039/© 2016 Elsevier Ltd. All rights reserved.

Results and discussion

The use of silanes as coupling agents to immobilize biomolecules by surface activation was to introduce new reactive sites to the SiO_2/Si/GPTMS, which allowed the binding of PAMAM dendrimer on the surface of silicon wafer. The silane agent was chosen due to the homogeneity and surface morphology of silane films that is important for controlling the structural order of final immobilized PAMAM. The chosen coupling agent was 3-glycidoxypropyltrimethoxy silane (GPTMS).[19,20] The epoxide ring of 3-glycidoxypropyltrimethoxy is reactive toward nucleophiles such as amines, thiols, alcohols, and acids, and the functionalization of the SiO_2 surface involves condensation of the methoxy groups in the GPTMS with silanol groups from the surface using toluene as solvent.

The pre-cut silicon pieces (approx. 1.0 cm^2) were cleaned with a 7:3 (v/v) mixture of concentrated sulfuric acid and 30% hydrogen peroxide for 30 min at room temperature, rinsed successively with deionized (DI) water and ethanol, blown dry with nitrogen. Then, it was immersed in 1.0 mM toluene solution of (3-Glycidyloxypropyl)trimethoxysilane at room temperature for 30 min to form a monolayer on silicon wafer of epoxy functional (SiO_2/Si/GPTMS) groups toward the outside (step 1, Fig. 1). Subsequently, the substrates were sonicated in toluene for 10 min, rinsed with toluene and ethanol 5 times, and blown dry with nitrogen. The silicon wafers functionalized were then incubated overnight in solutions containing PAMAM G0 synthesized previously (1%, w/v) in DMSO at 60 °C under gentle shaking (step 2, Fig. 1). Finally, the substrates (SiO_2/Si/GPTMS/PAMAM G0) were rinsed thoroughly with DMSO twice in an ultrasonic bath (5 min $\times 2$), followed by ethanol rinse and drying in a gentle stream of nitrogen (Fig. 1).

The surface morphology of silicon wafer modified with PAMAM and further treatments with Cu(II) and U(VI) solutions were observed using AFM. All images were collected in air using the semicontact mode in a microcopy NTegra Prima. The drive frequency was 300 ± 50 kHz, and the voltage was between 3.0 and 4.0 V. In all the measurements described, Olympus rectangular Silicon Nitride cantilevers with a pyramid-like tip shape and spring constant of 0.06 Nm^{-1} were used. AFM data on the PAMAM G0, PAMAM G0 with Cu(II) and U(VI) supported on silicon wafer are depicted in Fig. 2a–c. It was observed in the topography area that the surface was characterized by regular small grains distributed on the surface. The micro-roughness of root-mean-square of PAMAM G0, PAMAM G0 with Cu(II), and PAMAM G0 with U(VI) supported on silicon wafer were about 2.23, 3.12 and 8.3 nm, respectively. Those analyses indicated that the surfaces were rather smooth. Finally, the surface profile along the line indicated variations of $\approx$2.5, 9.0 and 20 nm in surface height of SiO_2/Si/GPTMS/PAMAM G0, SiO_2/Si/GPTMS/PAMAM G0 + Cu(II) and SiO_2/Si/GPTMS/PAMAM G0 + U(IV), respectively. Furthermore, some accumulations on the surface for the three modified silicon wafers were observed. The accumulations can be controlled by time/concentrations of PAMAM solutions in the surface modification processes.

SEM images of SiO_2/Si/GPTMS/PAMAM G0 + Cu(II) and SiO_2/Si/GPTMS/PAMAM G0 + U(VI) silicon wafer are given in Figures 3 and 4, respectively. SEM images of the silicon wafer were obtained with a FEI scanning electron microscope, Inspect F50 model, coupled with EDS detector, operating at accelerating voltage of 10 kV. The images show that the topographic morphology of silicon wafer is composed of agglomerated PAMAM molecules. The EDX spectrum derived from the silicon wafers after deposition of Cu(II) or U(VI) ions indicated the presence of copper (Cu), uranium (U) and oxygen (O) in different percentages. Qualitative analysis by EDX is based on empirical standards, and the energies of the commonly used core shell transitions of elements have been tabulated for all the natural elements. EDX spectrum of U(VI) is illustrative and shows five characteristic peaks that can be used to determine the composition of uranium samples. Thus, Figure 4b shows the most intense peak U Mα resulting from ionization of uranium M shell (around 3.7 keV). Furthermore, other peaks as U L1 (around 11.9 keV), U Lα (around 13.0 keV), U Lβ3 and U Lβ6 (around 16.5 and 17.5 keV, respectively) are also observed and assure the presence of uranium capture by the PAMAM modified silicon wafer. Similar EDX behavior results were observed by Elzbieta et al. and Sakthi et al. for the characterization of U(VI) and Cu(II), respectively.[21,22] Moreover, according to EDX spectra, the presence of Si from the silicon wafer used to support the PAMAM is also observed in Figures 3b and 4b as well as other minor impurities from the work medium (glass materials and reagents). Other morphologies observed in SEM images also show the presence of some minor impurities. Finally, Tables 1 and 2 summarize EDX surface results of SiO_2/Si/GPTMS/PAMAM G0 in the presence of Cu(II) and U(VI), respectively.

Finally, Figure 5 shows the MALDI mass spectra of SiO_2/Si/GPTMS/PAMAM G0, SiO_2/Si/GPTMS/PAMAM G0 + Cu^{2+} and SiO_2/Si/GPTMS/PAMAM G0 + UO_2^{2+} supported on silicon wafer. In MALDI, neutral molecules are transferred from the solid–solid solution of the plate to the gas phase, where these molecules are ionized via either electron abstraction, protonation, or deprotonation promoted by a series of ion/molecule reactions with the matrix.[23] Therefore, the mass spectrometric detection is expected to closely reflect the composition of the surface after cleavage of the PAMAM-supported molecules. Moreover, for metal identification, the metal coordination spheres are also expected to be fully preserved. Reagents, intermediates, and products present in SiO_2/Si should therefore all be transferred directly to the gas phase and then ionized and mass analyzed. To structure characterize the SiO_2/Si/GPTMS/PAMAM G0 by MALDI, a previously technique developed by us was employed. [24]

Silicon wafer samples with net SiO_2/Si/GPTMS/PAMAM G0 and SiO_2/Si/GPTMS/PAMAM G0/metal (Cu^{2+} or UO_2^{2+}) added to their surfaces were analyzed by MALDI-MS in the positive ion-mode. The solid support was coupled to the MALDI Imaging plate, then matrix was homogeneously sprayed over the solid surface and let to dry. α-Cyano-4-hydroxycinnamic acid (CHCA) was used as matrix and prepared as follows: 10 mg of CHCA in total of 1 mL solution containing 0.5 mL of 0.1% TFA and 0.5 mL of 100% ACN.

Thus, MALDI analyses of the SiO_2/Si/GPTMS/PAMAM G0 shows the ion of m/z 517 (Fig. 5a) in the spectra, which was identified and characterized as the protonated PAMAM G0 molecule of the ideal (defect-free) structure. Additionally, signals at higher m/z values are also observed, which correspond to sodium ($[M+Na]^+$, m/z 539) and potassium ($[M+K]^+$, m/z 555) adducts of PAMAM. Then, the SiO_2/Si/GPTMS/PAMAM G0 after exposure to metal solutions was analyzed. It was observed in the MALDI spectra a signal at m/z 579, which was identified and characterized as the addition of one copper ion to the PAMAM structure (Fig. 5b). The same behavior was observed when uranyl ions were analyzed, which afforded an expected ion at m/z 802 ($[M+UO_3]^+$, Fig. 5c). Moreover, MALDI-MS technique is a useful tool for identifying metals present in solutions, because it has the ability to discriminate isotopic

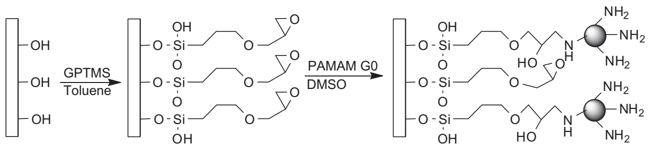

Figure 1. Steps for surface functionalization of silicon substrates with GPTMS followed by PAMAM dendrimer.

Download English Version:

https://daneshyari.com/en/article/5258886

Download Persian Version:

https://daneshyari.com/article/5258886

Daneshyari.com