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ScienceDirect
Thin Solid Films 515 (2007) 3112–3119
www.elsevier.com/locate/tsf

Fluorescence behaviors of 5-dimethylamino-1-naphthalene-sulfonyl-functionalized self-assembled monolayer on glass wafer surface and its sensing properties for nitrobenzene

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Received 12 July 2005; received in revised form 27 January 2006; accepted 23 May 2006
Available online 7 July 2006

Abstract

A fluorescent film was prepared by chemically immobilizing 5-dimethylamino-1-naphthalenesulfonyl (dansyl) onto an epoxide-terminated self-assembled monolayer on glass. Steady-state fluorescence emission measurements demonstrated that the sensing molecules were homogenously and stably immobilized on the substrate surface. Fluorescence quenching results showed that the film is sensitive to the presence of nitrobenzene and has a great selectivity to it as compared with other commonly used quenchers like nitromethane, sodium nitrite, potassium iodide and acrylamide. An assumption that a less polar intermediate phase, which was composed of the long flexible spacers, the dansyl moieties and the solvent within the layer, was formed on the substrate surface was proposed to rationalize the different response of the film to those common quenchers. The explanation was supported by the results from fluorescence anisotropy studies and fluorescence quenching experiments performed in different solvents. Fluorescence lifetime studies showed that the quenching of nitrobenzene to the emission of the film is static in nature, which has been attributed to the formation of a charge transfer complex between the quencher and the fluorophore. Furthermore, the response of the film to nitrobenzene is fast and reversible, suggesting that the film might be used as a sensing film for the compound and its analogs.

Keywords: Dansyl; Fluorescence; Sensor; Nitrobenzene

1. Introduction

Surface immobilization of organic molecules on various solid supports to prepare thin films with desired properties has gained considerable research interest in the past few decades [1]. This is because, on one hand, it can offer model systems to study surface-dependent phenomena like catalysis [2], adhesion [3], wetting [4], etc., and, on the other hand, it plays a great role in the design and preparation of functionalized surface materials, of which the applications range from nonlinear optics [5] to chemical sensors [6].

For interface investigations, fluorophore has recently become more attractive to be immobilized on solid support surface due to high sensitivity of fluorescence techniques [7]. The various photophysical properties of surface-bound fluorophores like fluorescence intensity [8], emission maximum [7], anisotropy, formation of excimer or exciplex [8,9], etc. have been studied to reveal the distribution, orientation and mobility of the fluorophores on the surface [10] as well as its micro-environmental properties like polarity and density [11]. Furthermore, any variation of those photophysical properties caused by connecting or interacting with special external species could be used for sensing purposes [12].

Based upon the considerations mentioned above, different strategies for immobilizing fluorophores on solid supports have been exploited, to name a few, physical entrapment of fluorescent dyes in sol–gel thin films [13] and poly(ethylene glycol) hydrogel [14], or covalent binding on polyelectrolyte films [15] and Langmuir–Blodgett films [16]. Since some problems like poor adhesion to substrates, poor stability and polymer swelling existed in the use of these materials [5], some efforts have been focused on covalently attaching fluorophores onto solid supports based on self-assembled monolayer (SAM)

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0040-6090/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.05.035

technique [17–19]. A well-known class of solid substrates for immobilizing fluorophores is quartz and glass wafers, which are transparent and do not quench fluorescence [20]. In addition, their hydroxyl-terminated surfaces can be easily modified by the formation of SAM of silane coupling agent (SCA), which is usually bearing a functional end group responsible for the attachment and acts as spacers to link fluorophores and the solid surfaces [21].

There are only a few research groups that have made contributions in this field until now. For example, Gulino et al. reported a fluorescent thin film sensitive to NO_2 by covalent binding porphyrin molecules onto silica substrates through a SCA spacer [22]. Chrisstoffels et al. also constructed SAMs containing two chromophores (donor and acceptor) onto silica wafers [23], which may be utilized as a physical transducer for fluorescence-sensor devices. Reinhoudt et al. have chemically fabricated a series of fluorophore-functionalized SAMs on glass and oxidized silicon wafer surfaces [24–27]. They even developed a simple approach to the generation of micro-sensor arrays by sequential deposition of a fluorophore and a binding group onto SAMs [28]. However, most SCA spacers used in the works mentioned above were terminated with amino group, which limited the types of surface reaction to some extent. Other SCAs with different end groups have to be employed for fabricating fluorescent films. In the present work, 3-glycidoxypropyltrimethoxysilane (GPTS) has been adopted to make epoxide-terminated SAMs.

Our group has specially focused on designing, fabricating pyrene-functionalized thin films based on SAM technique and the detailed fluorescence studies of the surface-bound fluorophores [29,30]. Among these studies, the effect of the length and chemical nature of the spacers adopted on the photophysical properties and sensing performances of the final fluorescent films were studied systematically during the last few years [30–33]. As expected, the flexibility, the length and the functionality of the spacers, the nature of the substrates and, of course, the identity of the fluorophore have a great effect upon the fluorescence behaviors and sensing properties of the films. There is no doubt that these kinds of studies are of significance and will definitely help to design and prepare more practical fluorescent sensing films and to know better of the photophysical behaviors of fluorophores in immobilized states.

For surface immobilization, 5-dimethylamino-1-naphthalenesulfonyl (dansyl) is another attractive choice in terms of high quantum yield, large Stokes shift and ease to be immobilized [16,24,34]. In the current study, dansyl was employed as sensing element and chemically immobilized on glass wafer surface via a relatively long flexible spacer based on surface reaction between its ethylenediamine derivatives and epoxide-terminated SAM. Our initial results from fluorescence quenching studies and other fluorescence-based experiments showed that the introduction of the long spacer may induce conformational changes which affect the accessibility of surface-bound fluorophores to different common quenchers, which endows the film with great selectivity to nitrobenzene.

2. Experimental details

2.1. Materials

Glass wafers used in the experiment were microscope slides (25.4 mm × 76.2 mm, 1–1.2 mm thick) by cutting them into ~0.9 cm × 2.5 cm pieces. Dansyl chloride (99%) and the silane coupling agent, GPTS (97%), were both purchased from Acros and used directly without further purification. Ethylenediamine was washed with KOH solution and then distilled before use. All other reagents were of at least analytical grade. Water used throughout was deionized and then double distilled.

2.2. Preparation of dansyl derivative

The amino derivative of dansyl, *N*-(2-aminoethyl)-5-(dimethylamino)-naphthalene sulfonamide (DANSA), was obtained by reacting ethylenediamine with dansyl chloride according to a method previously reported by others [35]. Thus, dansyl fluorophore can be easily attached to the SAM films formed by GPTS on glass through surface reaction with epoxide. The product, DANSA, a kind of light-green needles, was characterized, and the results are listed below: m.p. 149–151 °C. IR (KBr): 3349 cm^{-1}, 2945 cm^{-1}, 2841 cm^{-1}, 2796 cm^{-1}, 1571 cm^{-1}, 1455 cm^{-1}, 1403 cm^{-1}, 1318 cm^{-1}, 1146 cm^{-1}, 1102 cm^{-1}, 943 cm^{-1}, 902 cm^{-1}, 799 cm^{-1}, 620 cm^{-1}, 570 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.53 (d, 1H, ArH), δ 8.31 (d, 1H, ArH), δ 8.24 (d, 1H, ArH), δ 7.53 (m, 2H, ArH), δ 7.20 (d, 1H, ArH), δ 2.83 (m, 9H, $N(CH_3)_2$ and SO_2NHCH_2), δ 2.72 (m, 2H, CH_2NH_2).

2.3. Fabrication of dansyl-functionalized film

The film was prepared in three steps. (i) Clean glass wafers (~0.9 cm × 2.5 cm) were first activated with "piranha solution" [20] (98% H_2SO_4/30% H_2O_2 70:30 v/v) at 98 °C for 1 h, then rinsed thoroughly with double-distilled water when cooled to room temperature, and finally dried at 100 °C in a dust-free oven for 1 h. (*Caution*: piranha solution is a very strong oxidant and reacts violently with many organic materials, and so must be handled with extreme care.) (ii) The freshly activated glass wafers were immersed at 50 °C in a toluene solution of GPTS (0.6%, v/v), containing a trace amount of water, for at least 12 h. After that, the GPTS-modified wafers were washed successively with fresh toluene and dichloromethane (CH_2Cl_2) for several times to remove any physically adsorbed GPTS. (iii) After the treatment, these wafers were further put into a solution of DANSA in CH_2Cl_2 at room temperature for 48 h. Finally, the dansyl-functionalized wafers were washed with plenty of CH_2Cl_2 and then rinsed with acetone and water successively. The whole coupling process is schematically shown in Fig. 1.

2.4. Characterization techniques

Infrared (IR) spectra were measured on the samples of DANSA in KBr pellets by using a Bruker Equinox 55 Fourier Transfer Infrared Spectrometer with a resolution of 1 cm^{-1}, and