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Detection of Nitroaromatic Compounds with Functionalized Porous Silicon Using Quenching Photoluminescence

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Abstract

Nanocrystalline porous silicon surfaces have been used to detect nitroaromatic compounds in vapor phase. The mode of photoluminescence is emphasized as a sensing attitude or detection technique. Quenching of photoluminescence from nanocrystalline porous surfaces as a transduction mode is measured upon the exposure of nitroaromatic compounds. Reversible detection mode for nitroaromatics is, too, observed. To verify the detection afore-mentioned, photoluminescent freshly prepared porous silicons are functionalized with different groups. The mechanism of quenching of photoluminescence is attributed to the electron transfer behaviors of quantum-sized nano-crystallites in the porous silicon matrix to the analytes(nitroaromatics). An attempt has been done to prove that the surface-derivatized photoluminescent porous silicone surfaces can act as versatile substrates for sensing behaviors due to having a large surface area and highly sensitive transduction mode.

Key words : Detection, porous silicon, photoluminescence, quenching

1. Introduction

The identification and quantification of traces of nitroaromatic explosives have attracted a great attention during the last few years due to their extensive security and pollution problems for humans and ecosystems. Consequently a great number of analytical methods have been developed for monitoring these compounds, for example, mass spectrometry[1], ion mobility spectrometry[2], electrochemical methods[3], fluorescence[4], chemiluminescence[5], surface enhanced Raman spectroscopy[6], nuclear quadrupole resonance[7], energy-dispersive X-ray diffraction[8], neutron activation analysis, electron capture detection and cyclic voltammetry[9]. These techniques are highly selective , but some are expensive and others are not easily fielded in a small, low-power package. Most detection methods for explosives are only applicable to vapor sample because of interference problems encountered in aquous media. Compared to other analytical techniques, fluorescence is more attractive because of its high sensitivity, high selectivity and multiple choices in signals and parameters like emission intensity, maximum wavelength etc.

Chemical sensors for nitroaromatics[10] which offer new approaches to the rapid detection of ultra-trace analytes from explosives, have attracted attention because explosives are very important chemical species to be detected. Detection of nitroaromatics is desirable since there are millions of unexploded land mines scattered worldwide. Detection of nitroaromatics based upon adsorption into polymers has been reported. Chemoselective polymers on surface acoustic wave (SAW) device provide a detection limit of 235 ppt for dinitrotoluene (DNT)[11]. Cyclic voltammetry using gold microelectrode covered with non-volatile electrolyte shows a detection limit of 7 ppb for the trinitrotoluene (TNT)-saturated air[12]. Organic polymers have been used to detect DNT and TNT under static conditions with a detection limit of several ppb[13]. Finally silicon polymers exhibit a detection limit of 4 ppb for the TNT-saturated air[14].

2. Experimental Section

2.1. Materials and Methods

Silicon wafer (silicon sense, n-type, <100> orientation, P-doped, 1-10 ohm) were purchased from Siltron

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Inc. Aqueous HF (49%) and absolute ethanol (95%) were brought from Scientific Fisher. The alkene and alkyne i.e. 1-dodecene and phenyl acetylene were ordered from Aldrich, sparged with dry argon and used. Out of the nitroaromatics here used for sensing, DNT (97%), PA (98%), and NB (99%) are purchased from Aldrich. TNT was synthesized in the laboratory. Methylvinyl silole was synthesized in the laboratory using general procedures. The required materials lithium, diphenylacetylene, and methylvinyl silane were purchased from Aldrich. Toluene was distilled from sodium and benzophenone. Air-sensitive procedures were carried out with standard Schlenk techniques (ChemGlass dual manifold vacuum/argon lines). Thermal hydrosilylation was carried out by reflux and photochemical hydrosilylations were carried out under white bulb light and UV-light.

2.2. Etching Set-up for Porous Silicon Surface

The electrochemical etching was performed on silicon wafers to create porous surfaces which possess a network of pores to give rise to luminescence. The etching set-up was maintained in a laboratory hood where a suitable management is made for upwards flow of gas created during etching. Princeton 363 galvonostat/potentiostat was used for passage of required current density. 30 mW/cm^2 white light illumination was derived from a 300 W tungsten filament bulb. A 1.1 cm^2 exposed area of a polished crystalline n-type silicon wafer was kept for etching in a Teflon cell. Prior to this, the procedure involves the use of an aluminium foil as a cathode underneath the silicon chip. Viton O-ring seal was fixed over the chip and covered with an electrolyte/etchant in the form of a mixture of aqueous HF (49%) and absolute ethanol (95%) in required proportion (1:1) as an anode.

2.3. Availability of Nitroaromatic Compounds

Nitroaromatic (NACs) are the compounds composed of aromatic compounds with mono- or poly-nitro groups. However all the nitroaromatics (displayed in blue color) except TNT are used as received without purification.

3. Result and Discussion

3.1. Fluorescence Quenching Studies

The photoluminescent properties of nanocrystalline PSi are of interest for sensor applications. Photoluminescence from porous silicon is quenched in the presence of chemical species. We also observe that surface derivatization can be used to tune the sensor properties of porous silicon by modifying the photoluminescence quenching efficiency. The quenching mechanism is attributed to the electron transfer.

The magnitude of photoluminescence quenching can be measured by expression of photoluminescence intensity in time when various amounts of analytes were introduced into. The quenching mechanism occurs as electron transfer from porous silicon to the lowest triplet state of the molecular quenchers. We can observe a sharp decrease of photoluminescence intensity with gradual introduction of analytes and baseline stabilization after passage of a considerable amount of time.

Fluorescence quenching has proved an effective approach in chemical sensing and surface studies[15]. In the present work, fluorescence quenching was expected to occur due to possible electron transfer from surface-derivatized porous silicon to nitroaromatics. In order to examine the role of electron transfer in the quenching process of nitroaromatics to the fluorescence surface, the response of the porous surfaces to a series of nitroaromatics such as DNT, TNT, NB, and PA were investi-

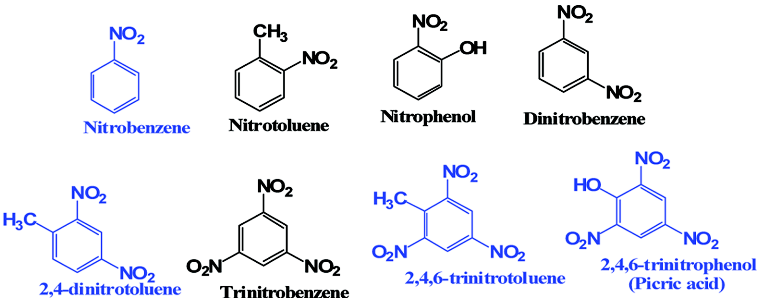

Fig. 1. Chemical structures of some nitroaromatics.

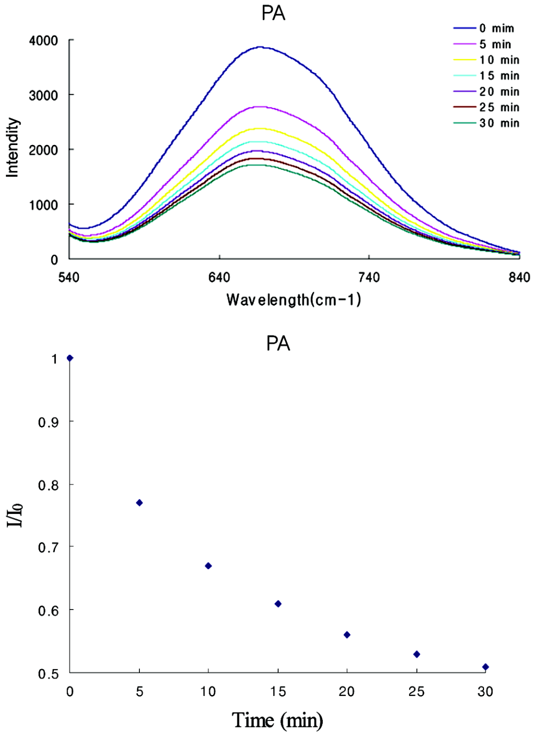

Fig. 2. PL quenching sprectrum and Stern-Volmer plot based on freshly etched PSi sample for the detection of picric acid.

gated. The fluorescence response of the porous films to the vapors of various analytes was ascertained by adjusting the porous films at room temperature upon which a flow of analytes is carried out. Glass wool is placed adjoining the analyte in order to prevent direct contact between analyte and porous film and helps to maintain a constant vapor pressure. Figure 2 shows that PL quenching sprectrum and Stern-Volmer plot based on freshly etched PSi sample for the detection of picric acid.

The fluorescence spectra were recorded immediately after exposing the porous films to analytes for a specific time. The quenching studies on porous films were performed with excitation wavelengths of 460 and 380 nm and the analyte's equilibrium vapor pressures are assumed to be similar as noted from certain documents[16].

Figure 3 shows that comparison of Stern-Volmer plots based on freshly etched PSi sample for the detection of nitoaromatic compounds (TNT, DNT, and picric acid).

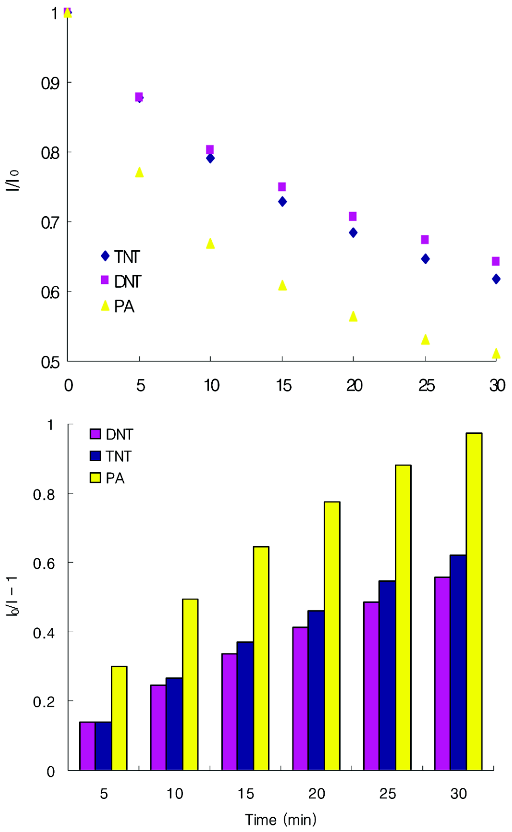

Fig. 3. Comparison of Stern-Volmer plots of freshly etched PSi sample for the detection of nitoaromatic compounds (TNT, DNT, and picric acid).

4. Conclusion

A new chemosensors for the detection of nitroaromatic compounds based on porous silicon have been developed. Interferometric porous silicon sensor using various etching parameters was obtained The PL quenching spectra of porous silicon are measured against the detection of nitroaromatics as analytes.

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