한국환경분석학회지 제7권 (제1호) 000~000, 2004
J. of the Korea Society for Environmental Analysis

Detection of Explosives Based on Silicon Polymer

Honglae Sohn†

Department of Chemistry, Chosun University, 375 Seosuk-dong, Dong-gu, Gwangju 501-759, Korea

Polymeric silicon wires have been used to detect explosives in gas and liquid phase. Transduction mechanisms using quantum confinement derived photoluminescence have been used. Photoluminescence intensity is modulated by energy or electron transfer induced quenching. Examples of reversible sensing modes for explosives is provided.

Key words: detection, TNT, photoluminescence, polysilole

1. Introduction

Detection of TNT and DNT (a decomposition product of TNT) is desirable since there are approximately 120 million unexploded land mines worldwide.1) Very sensitive detection of TNT and its decomposition products has been achieved with thin films of silicon wires using photoluminescence quenching as a transduction mode. A complimentary method for nitroaromatics sensing has also been developed based on the photoluminescence quenching of polysilole - a polymer consisting of a catenated silicon backbone with σ-σ^* delocalization along the chain. Polytetraphenyl-1,1-silole, $(C_4Ph_4Si)_n$, which was used in this study, has a helical structure along the Si-Si backbone2) and a highly-conjugated ring system in the side chains. It also has a high luminescence quantum yield.3) Recently Yang and Swager have shown that highly π-conjugated, porous organic polymers can be used to detect vapors of electron deficient chemicals.4,5) Electron delocalization in these polymers provides a means of amplification, because interaction of an analyte molecule at any position along the polymer chain is communicated throughout the delocalized chain. A similar means of amplification is available to quantum-confined semiconductor nano-crystallites, where the electron and hole wavefunctions are delocalized throughout the nanocrystal.6) Most detection methods for explosives are only applicable to air samples due to interference problems encountered in complex aqueous media. Sensing TNT in groundwater or seawater is important for the detection of buried unexploded ordinance and for locating underwater mines.7) There are also environmental applications for characterizing soil and groundwater contaminated with toxic TNT at military bases and munitions production and distribution facilities.8) Here we report an inexpensive and highly efficient inorganic polymer sensor that can detect nitroaromatic compounds, such as nitrobenzene, 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), and and picric acid (PA) in air or seawater. The sensor employs a thin film of photoluminescent polysilole, which is stable in air, water, acids, common organic solvents, and even seawater containing bioorganisms.

2. Experimental

2.1. Polymer preparation

Polytetraphenylsilole, prepared by a previously known method,9) was coated as a thin film on substrates such as Mitex Teflon membranes (Millipore), commercial filter paper (Whatman), borosilicate glass cover slips (Fisher Scientific), porous silicon chips10) and silicon wafers. Samples were prepared by soaking the

---

† To whom correspondence should be addressed.

substrates in a toluene solution of polysilole after filtration through a 0.2 mm PTFE filter (Aldrich). Thin films of polysilole were also deposited on glass or silicon wafer substrates by spin coating. These samples were dried in vacuum before use. Samples were then placed in a quartz flow cell (1.5×1.5×2.5 cm^3) under flowing air or seawater that contained analyte for the detection experiment. The detection method involves measurement of the quenching of photoluminescence of the polysilole by the analyte (using a Perkin-Elmer LS 50B fluorescence spectrometer, 340 nm excitation wavelength). Photoluminescence quenching of polysilole in toluene solutions was observed with nitrobenzene (Aldrich, 99 % min), DNT (Aldrich, twice recrystallized from methanol), TNT (prepared from DNT[11)] and twice recrystallized from methanol) and picric acid (Aldrich 99+ %, recrystallized from ethanol).

2.2. Photoluminescence Measurements

Fluorescence emission and excitation spectra were recorded on a Perkin-Elmer Luminescence Spectrometer LS 50B. The solvents were determined to be free of emitting impurities prior to use. The concentration of polysilole for the fluorescence quenching measurements was 10 mg/1 L, which is about 2.0×10^{-6} M. Fluorescence spectra were taken immediately after injection of analyte. There was no change in intensity with time. Throughout this paper, values of percent quenching are reported as $(I_0-I)/I_0$, where I_0 is the intensity of luminescence of polysilole, integrated between 350 and 650 nm, in the absence of quencher and I is the integrated intensity of luminescence of polysilole in the presence of a quencher at a given concentration.

2.3. Gas sample preparation

For the nitroaromatic, air saturated with analyte by means of a fritted glass gas bubbler was diluted with air (dry for nitroaromatics in a specially designed flow meter/mixer. The flow rates were independently adjusted to obtain the different concentrations used in the study. These chemicals were dispersed on glass beads, introduced into a glass tube and placed in one arm of the flow meter/mixer apparatus, which was then submitted to a flow of air. All the experiments were performed at atmospheric pressure, under a controlled flow of the appropriately dosed compressed air.

3. Results

3.1. Detection of TNT with nanowires of silicon

Fluorescence spectra of a toluene solution of the polysilole obtained upon successive addition of aliquots of TNT. Photoluminescence quenching of polysilole in toluene solutions with nitrobenzene (Aldrich, 99% min), DNT (Aldrich, twice recrystallized from methanol), TNT (prepared from DNT[11)] and twice recrystallized from methanol), and picric acid (Aldrich 99+ %, recrystallized from ethanol) were measured and a linear Stern-Volmer relationship was observed in the first three cases, but not for picric acid.

The mechanism of quenching is attributed to electron transfer from the conduction band of polysilole to the LUMO of the analyte. The relative efficiency of photoluminescence quenching of polysilole is 3.8 : 2.2 : 1.0 for TNT, DNT, and nitrobenzene, respectively, as indicated by the values of *K* determined from the slopes of the steady-state Stern-Volmer plots (Fig. 1). Since the reduction potential of TNT (-0.7 V vs. NHE)[12] is less negative than that of DNT (-0.9 V vs. NHE), TNT is expected to possess a larger driving force for electron transfer quenching than DNT. Nitrobenzene (-1.15 V vs. NHE), which has the most negative reduction potential among the analytes studied, exhibits the lowest

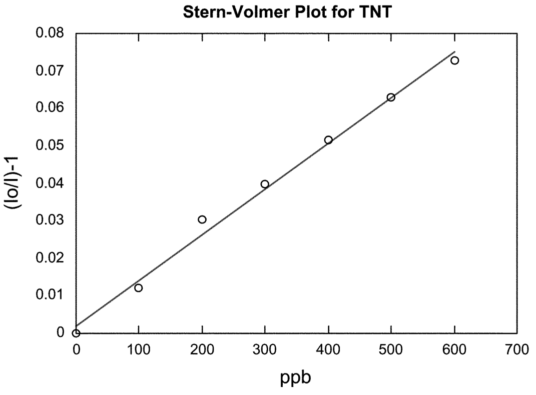

Fig. 1. Stern-Volmer plots for TNT.

quenching efficiency. Fluorescence spectra of polysilole from either toluene solution or thin polymer films displayed no shift in the maximum of the emission wavelength. This suggests that the polysilole exhibits neither π-stacking of polymer chains nor excimer formation. Photoluminescence quenching of the oligomer tersilole, $Cl(C_4Ph_4Si)_3Cl$, by TNT was also measured. The K value of (4.34 0.12)×103 M^{-1} for polysilole, which has about 15 repeat units,[9)] is 38% greater than that for the oligomer tersilole [K = (3.14 0.04)×103 M^{-1}]. This result suggests that polysilole produces an excited state that is delocalized over many repeat units. Zhou and Swager have reported that for detection of analytes by organic polymers, the sensitivity of the photoluminescence quenching technique depends on not only the polymer molecular weight but also on the diffusion length of excitation.[13]

An important aspect of the polysilole sensors is their insensitivity to common interferents. Control experiments using thin films of polysiloles (deposited on glass substrates) with oxygenated air displayed no change in the photoluminescence spectrum. Similarly, exposure to organic solvents such as toluene, THF, and methanol and the aqueous inorganic acids $H_2SO_4$and HF produced no significant decrease in photoluminescence intensity. However, 4 ppb (parts per billion) of TNT vapor in air (air stream flowing at a rate of 100 mL/min) was detected as an 8.2% decrease in photoluminescence intensity within 10 min. In toluene solution, the detection limit for TNT is about 100 ppb with quenching of 0.5% of the photoluminescence intensity observed.

Fig. 2. Detection of TNT in seawater. Two paper tickets were coated with polysilole, then soaked for 30 s in seawater (collected off Scripps Pier, La Jolla, CA). The seawater used in the bottom ticket was spiked with purified TNT. The top ticket is the control. The image was taken under a black light.

The detection of TNT in seawater (collected off Scripps Pier, La Jolla, CA) was measured using thin films of polysilole. No quenching of photoluminescence was observed unless the seawater contained 50 ppb of TNT. Quenching was detected instantly and the amount of quenching was stable with time. Since the quenching efficiency of photoluminescence for picric acid is greater than that for TNT, we obtained a 6 ppb detection limit for picric acid using thin films in seawater (Fig. 2).

4. Conclusion

A simple and rapid method, described for detecting nitroaromatic explosives in seawater with the use of photoluminescent silicon polymers, was achieved by quenching photoluminescence via electron transfer from the conduction band of fluorescent polysiloles to electron deficient molecules such as nitrobenzene (NB), 2,4-dinitrotoluene (DNT), and 2,4,6-trinitrotoluene (TNT). The detection limit for TNT in toluene solution is 100 ppm, but it has been detected in air or seawater at concentrations as low as 4 ppb and 50 ppb, respectively. Dilute polymer solutions can also be employed as a forensic spray-on reagent to visualize TNT residues under a UV lamp.

5. References

1. A. R. Maureen,. *C&EN News* **1997**, 14-22.
2. Y. Xu, T. Fujino, H. Naito, T. Dohmaru, K. Oka, H. Sohn and R. West, *Jpn. J. Appl. Phys.* **1999**, 38, 6915-6918.
3. T. Sanji, T. Sakai, C. Kabuto and H. Sakurai, *J. Am. Chem. Soc.* **1998**, 120, 4552-4553.
4. J.-S. Yang and T. M. Swager, *J. Am. Chem. Soc.* **1998**, 120, 5321-5322.
5. S. Yamaguchi, T. Endo, M. Uchida, T. Izumizawa, K. Furukawa and K. Tamao, *Chem. Eur. J.* **2000**, 6, 1683-1692.
6. S. Content, W. C. Trogler and M. J. Sailor, *Chem. Eur. J.* **2000**, 6, 2205-2213.
7. L. C. Shriver-Lake, B. L. Donner and F. S. Ligler, *Environ. Sci. Technol.* **1997**, 31, 837-841.

8. *Approaches for the remediation of federal facility sites contaminated with explosive or radioactive wastes.* U. S. Environmental Protection Agency: Washington, D.C., **1993**.
9. H. Sohn, R. R. Huddleston, D. R. Powell and R. West, *J. Am. Chem. Soc.* **1999**, 121, 2935-2936.
10. M. J. Sailor, J. L. Heinrich and J. M. Lauerhaas, "*Luminescent porous silicon: synthesis, chemistry, and applications*", Elsevier Science B. V., Amsterdam, **1997**, Vol. 103, pp 209-235.
11. J. W. H. Dennis, D. H. Rosenblatt, W. G. Blucher and C. L. Coon, *J. Chem. Eng. Data* **1975**, 120, 202-203.
12. J.-S. Yang and T. M. Swager, *J. Am. Chem. Soc.* **1998**, 120, 11864-11873.
13. Q. Zhou and T. M. Swager, *J. Am. Chem. Soc.* **1995**, 117, 7017-7018.
14. J. C. Brosheer, F. A. Lenfesty and K. L. Elmore, *Ind. Eng. Chem.* **1947**, 39, 423-427.