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SPR Enhanced molecular imprinted sol–gel film: A promising tool for gas-phase TNT detection

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An innovative surface plasmon resonance (SPR) approach for the detection of 2,4,6-trinitrotoluene (TNT) gas traces, obtained using an engineered molecular imprinted sol–gel film as recognition layer onto a plasmonic gold grating, is here proposed. The SPR substrate combined with the sol–gel matrix is able to trap gas phase TNT molecules from a TNT-saturated environment (4.9 ppb). Taking advantage of the azimuthally-controlled grating-coupled SPR, this sensing platform demonstrates the potentiality to detect TNT traces <1 ppb with a sensitivity of 0.47°/ppb.

1. Introduction

In recent years, improvements of explosive trace detection systems in terms of sensitivity, costs and handiness became of growing interest for increasing applications to terrorism prevention, trace monitoring from unexploded land mines, industrial leakage from manufacturing facilities and other fields [1–3].

A particularly relevant goal is trinitrotoluene (TNT) detection with stable, portable and simple sensing systems, e.g. for safety of airports and air travel [4].

In this context, a large variety of TNT nanosensors has been explored in the last decades, including colorimetric [1], laser photoacoustic spectroscopy- [5] and cantilever- [6,7] based devices. Among the various approaches, surface plasmon resonance (SPR) sensors emerge as promising tools in terms of miniaturization, scalability and sensitivity [8]. SPR nanosensors require a recognition layer, usually represented by a chemical receptor able to capture the analyte, and they can be divided into two categories: prism-coupled (PC-) and grating-coupled (GC-) SPR sensors. Standard GC- and PC-SPR methods typically have refractive index sensitivities of 50–150°/RIU, but exploiting an azimuthal control of the grating SPR substrate the sensitivity could be increased of up to one order of magnitude [9–11].

Recently Bao et al. [12] introduced an innovative approach in the TNT sensing field by combining a molecular imprinted polymer (MIP) with PC-SPR and demonstrating TNT detection from a liquid sample. MIPs are generally synthesized via the interaction of functional monomers, bearing suitable pendant groups, with explosive template molecules and a cross-linking agent. Templates are then removed, leaving cavities that can only be occupied by molecules matching the template shape and properties, providing high shape-selective binding sites [13,14]. Once TNT molecules match the template cavities, a change in the MIP refractive index occurs, leading to a change in the plasmonic response of sensing platform. MIPs integrated with Surface Enhanced Raman Scattering (SERS) substrates [15] and optical fibers or waveguides [8,16] were also reported as sensing strategies towards different explosives. However, the exposure of the sensor to explosive analytes is generally performed by immersion of the sensitive substrate in a liquid.

Molecular imprinting approach is also increasingly used in combination with sol–gel materials for several applications [16–17]. The low temperature processing conditions and versatility of the sol–gel synthesis make these materials very suitable matrices for the molecular imprinting technique.

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Starting from these fundamentals, we here present a molecular-imprinted sol–gel/azimuthally-controlled GC-SPR sensing platform for TNT gas trace detection, i.e. a device in which a sol–gel porous matrix was deposited onto a gold sinusoidal grating monitored under azimuthal control. This approach takes advantages of both the high selectivity of the molecular imprinted sol–gel matrix and the high sensitivity of azimuthally-controlled GC-SPR, combined into a cheap and miniaturized sensing device, capable of gas-phase detection.

2. Materials and methods

2.1. Chemicals and solutions

The sensing platforms were fabricated by combining laser interference lithography (LIL) and soft lithography techniques. S1805 photoresist was purchased from Microposit (Shipley European Limited, UK), while MF319 Developer and PGMEA (propylene glycol monomethyl ether acetate) were purchased from MicroChem Corp (Newton, MA, USA). PDMS (polydimethylsiloxane; Sylgard 184) was purchased from Dow-Corning Corp. (Midland, MI, USA), and thiolene resin NOA 74 (Norland Optical Adhesive) was purchased from Norland Products Inc. (Las Vegas, NV, USA).

For the sol–gel synthesis, tetramethoxysilane 98% (TMOS), aminopropyltriethoxysilane 98% (APTES) and mercaptopropyltrimethoxysilane 95% (MPTMS) were all purchased from Sigma-Aldrich and used without further purification. Sodium Hydroxide 1 N and Ethanol 99.8% (EtOH) were used as catalyst and solvent, respectively.

2.2. Sol–gel-based SPR sensing platform fabrication

The whole fabrication procedure could be divided into three steps, summarized in Fig. 1: (a) plasmonic substrate fabrication; (b) sol–gel synthesis and (c) sol-gel-SPR substrate combination.

2.2.1. Plasmonic substrate fabrication

A sinusoidal grating (period of 500 nm; peak-to-valley amplitude of 40 nm) was fabricated by means of laser interference lithography (LIL). The pattern was transferred to a polydimethylsiloxane (PDMS) mold and replicated onto a thiolene

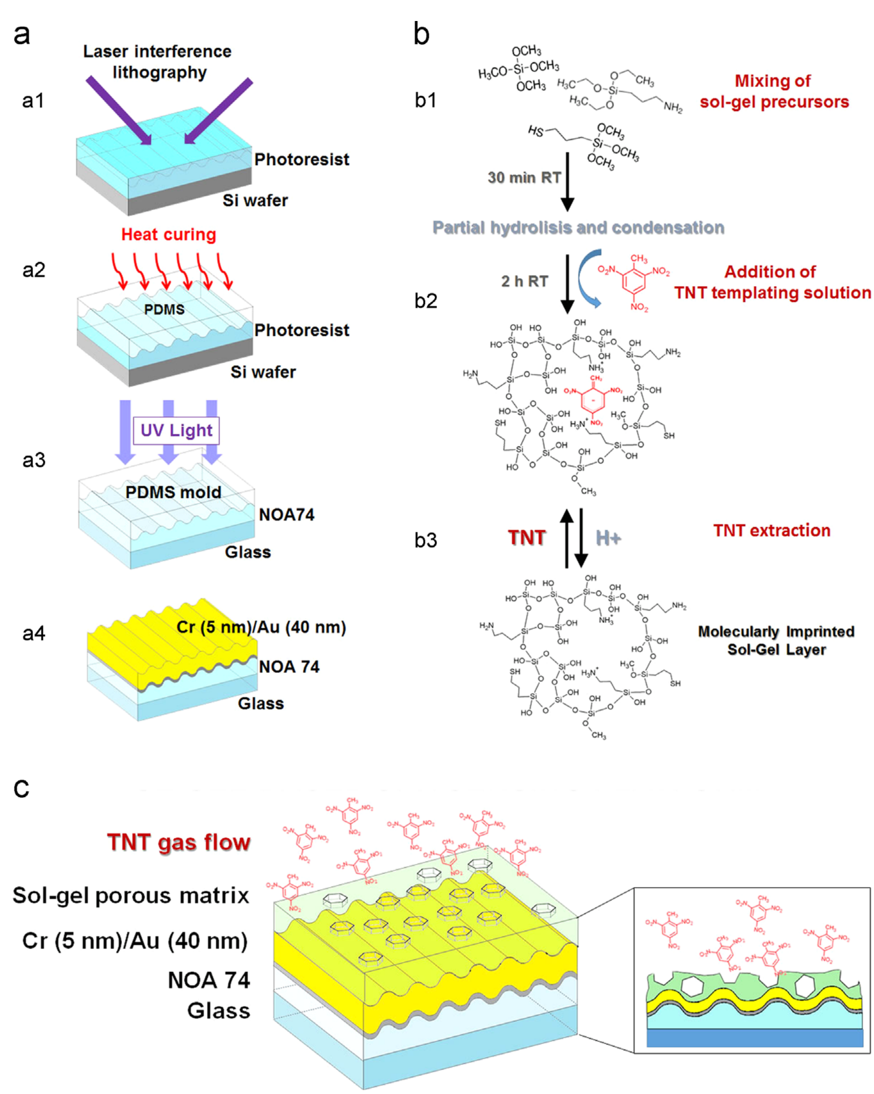

Fig. 1. Sol-gel-based SPR sensing platform fabrication. (a) SPR substrate fabrication: a photoresist sinusoidal grating realized by means of laser interference lithography (a.1) was replicated onto a thiolene resin film through replica-molding techniques (a.2–3) and covered by a Cr(5 nm)/Au(40 nm) layer. (b) Molecularly imprinted layer was synthesized by sol–gel method through hydrolysis and condensation reactions of silicon alkoxides (b.1) TNT was added as templating molecules to the sol–gel (b.2) and then removed using an acidic alcoholic solution (b.3). (c) Sol-gel-based SPR sensing platform after the deposition of the molecularly-imprinted sol–gel onto the SPR substrate (in the inset the side view of the sol-gel-based SPR sensing platform working principle is shown).