GOLD NANOPARTICLE-BASED FLUORESCENT SENSOR FOR THE ANALYSIS OF DITHIOCARBAMATE PESTICIDES IN WATER

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ABSTRACT

Pesticides play a key role in the high yields achieved in modern agricultural food production. Besides their positive effect on increasing productivity they are intentionally toxic, often towards non-target organisms and contaminated food products can have a serious impact on human and environmental health. This paper demonstrates the potential of a gold nanoparticle-based microfluidic sensor for in field detection of dithiocarbamate pesticides at remote locations. Combining the attractive optical properties of gold nanoparticles with on chip mixing and detection, using a simple digital camera, a detection limit of 16 µg L^{-1} for Ziram, a dithiocarbamate pesticide, was obtained.

KEYWORDS

Dithiocarbamate Detection, Gold Nanoparticle, Fluorescence, Environmental Monitoring.

INTRODUCTION

Dithiocarbamates (DTC) are a group of organo sulfur compounds, widely used in agriculture and some of the most frequently detected pesticides residues in plant products in the European Union and environmental contaminates near agricultural fields [1, 2]. They are suspected developmental neurotoxicins and have been associated to Parkinson's disease developed by agricultural workers [3, 4]. Generally, DTCs are determined by acidic hydrolysis which involves the generation of gaseous carbon disulfide and the subsequent analysis with traditional chromatographic and UV or mass spectrometric detection methods, with limits of detection (LOD) ranging from low µg L^{-1} to mg L^{-1} levels [5]. Here, microfluidic sensors would offer a highly advantageous alternative with fast and low cost pesticide analysis options and the possibility to monitor food product quality and environmental contaminations at any step in the production chain.

Gold Nanoparticles (AuNPs) are, due to their physico-chemical properties, an excellent mediator for new sensing applications. DTCs, as sulfur containing compounds, have a high affinity for gold. This property in combination with AuNP-based detection schemes and a microfluidic device would form a portable platform, ideal for pesticide screening at remote locations. In this report we demonstrate the detection of the DTC pesticide ziram using our recently reported AuNP-based method [6].

EXPERIMENT

AuNPs were prepared by the Frens-Turkevitch method as described by Grabar *et al.* [7]. Briefly, in a round bottom flask equipped with a condenser, sodium citrate (38 mM, 1.5 mL) was added to a boiling solution of chlorauric acid (0.25 mM, 100 mL) under vigorous stirring. The addition of sodium citrate to the vortex of the solution causes a colour change from pale yellow to burgundy. The solution was heated under reflux for 10 min and stirred for an additional 15 min. The resulting AuNP solution was characterized by UV-Vis spectra with extinction coefficients provided by Haiss *et al.* [8]. AuNP probes were diluted with 5mM sodium tetraborate (2.5 mL AuNP solution to 2.5 mL sodium tetraborate) and further functionalized by adding 5 µL of 0.2 mM Rhodamine 6G (R6G) to the diluted AuNP probe and left to equilibrate for 2h. All chemicals were of analytical grade and were obtained from Sigma Aldrich (Saint Louis, MO, USA). The AuNP mediated ziram detection scheme is illustrated in Figure 1 and based on the rapid "turn-on" fluorescence sensing [9].

In their unbound state, R6G molecules are highly fluorescent but when adsorbed onto the surface of AuNPs their fluorescence is quenched. Here, we take advantage of the high affinity of the sulfur containing DTC pesticides (Figure 1 (a)) to gold. Upon ziram addition to the R6G-AuNP probe, R6G molecules are released from the AuNP surface and their native fluorescence is restored providing a measure for the ziram concentration (Figure 1(b)).

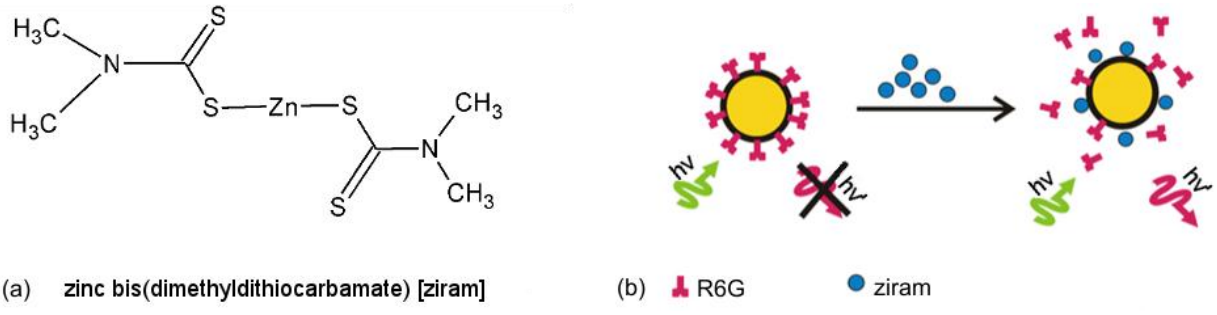

Figure 1. (a) Chemical structure of ziram (b) Gold nanoparticle detection scheme for ziram. Fluorescence of surface adsorbed R6G molecules is quenched but is recovered once they are displaced by ziram molecules.

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The microfluidic network for the on-chip mixing and detection of ziram was made by laser ablation of polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning, Midland, MI, USA) slabs. As shown in Figure 2, the flower shaped meandering channel allows mixing of three different solutions by diffusion. R6G fluorescence is detected at the end of the mixing channel in a 1.5 mm deep and 100 µm wide through hole that continues into the waste channel. The structured PDMS slab is laminated between two PDMS slabs containing inlet and outlet holes (Oxygen plasma bonding, 50 W, 13.56 MHz, 90 s).

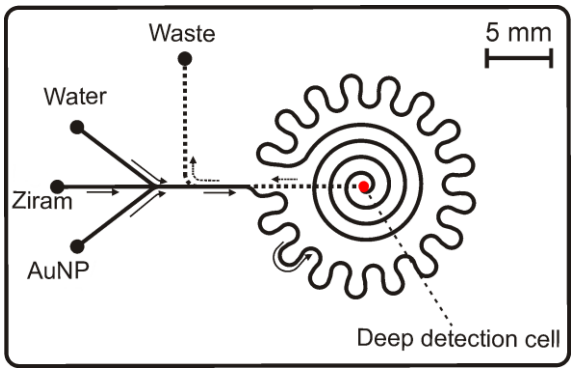

Figure 2. Illustration of the microfluidic chip. The 1.5 mm deep detection cell is located at the center of the flower shaped meandering channel (red dot) and the waste channel (dotted line) is located on the back side of the chip. The mixing channel has a Gaussian shape profile, width= 300 µm, depth= 100 µm.

High precision syringe pumps (neMESYS, Cetoni GmbH, Korbussen, Germany) are used to establish a fluid flow with a total flow rate of 10 µL min^{-1}. To allow on chip mixing of different pesticide concentrations, the flow rate for the AuNP probe was kept constant at 6 µL min^{-1} while the flow rates of water and ziram varied between 0 and 4 µL min^{-1}. Fluorescence was measured on an Olympus IX71 (Olympus Corporation, Tokyo, Japan) inverted microscope equipped with a Canon 550 D digital camera (Tokyo, Japan). Images were acquired with 3 s integration time and further analyzed with Matlab (MathWorks, Natick, MA, USA).

RESULTS AND DISCUSSION

The fluorescent "turn-on" approach of the described method is demonstrated in Figure 3, showing microfluidic cells filled with AuNP probe (23 nm at 0.03 nM). The AuNP adsorbed R6G molecules exhibit very weak fluorescence as shown in Figure 3(a) whereas the content of the cell in Figure 3(b) shows bright red fluorescence due to the addition of ziram to the AuNP probe and consequent release of R6G into solution.

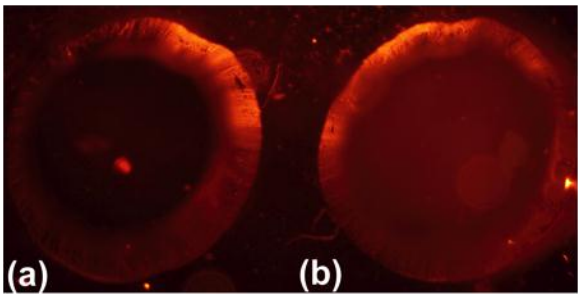

Figure 3. Microfluidic cells filled with (a) 23 nm R6G-AuNP probe, and (b) the R6G-AuNP with 100 µg L^{-1}ziram.

As shown in *Figure 4* the fluorescence enhancement was proportional to the ziram concentration from 16 µg L^{-1} to 150 µg L^{-1} with a LOD of 16 µg L^{-1} (calculated as 3 σ_{blank}). Maximum residue levels (MRL) established by the European Commission for ziram range from 0.1 to 5 mg Kg^{-1} [10].

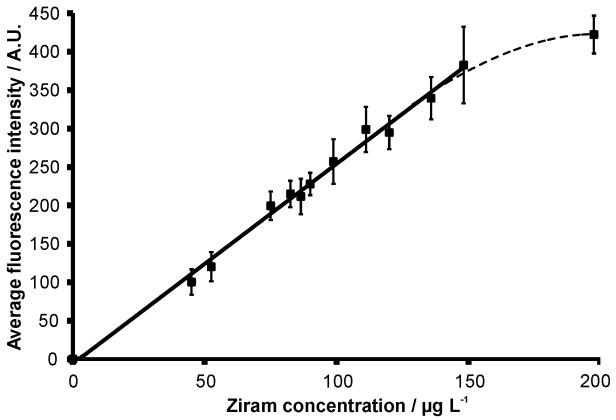

Figure 4. On-chip detection of ziram using R6G-AuNP probes. R^2=0.99(3) LOD=16µg L^{-1}.Error bars shown for 95% confidence level (<2% error)

CONCLUSION

These results demonstrate the great potential of AuNP based microfluidic sensors for rapid monitoring of DTC pesticides. The low LOD and wide detection range as well as the possibility to use small and low cost readout electronics such as a smartphone camera make this microfluidic device suitable for on field monitoring of pesticides. Coupled with an on-chip separation, several DTC pesticides could be detected.

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