The detection of pesticides in water using ZnCdSe quantum dot films

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Abstract

This paper reports an attempt to develop a sensor system for detecting pesticides based on the effect of an analyte on the photoluminescence (PL) intensity of ZnCdSe quantum dot (QD) films. The ZnCdSe QDs were synthesized using a wet-chemical process. The sensor system comprises an excitation light source made of a laser diode, a dual arm fibre optic probe, a spectrometer and a sensor chamber. The QD films were deposited by dropping QD solution onto the probe surface and drying them at ambient temperature. The pesticides used in this study were Dipel, Siven 85% WP and Water-Dispersible Granules WG insecticides. The detection of pesticides was done by comparing the photoluminescence (PL) spectra of the films dipped in the deionized water and in pesticide solutions by varying the concentration of the pesticide solutions from 2.5 to 2500 µg l⁻¹. It was observed that the PL intensity of the films was quenched by the presence of the pesticide molecules. The quenching degree increased with the concentration of the pesticide solutions. There is a linear relationship between the pesticide solution concentrations and the QD film sensor sensitivities. The sensitivity of the sensor system depended on the type of pesticides successively from the highest to lowest sensitivity in the order Siven 85% WP, Dipel and Water-Dispersible Granules WG. The QD films could be used as fluorescence sensors to detect water that is contaminated by pesticides.

Keywords: optical sensor, pesticide sensor, photoluminescence, synthesis of quantum dots, zinc cadmium selenide

Classification numbers: 4.01, 6.08

1. Introduction

Pesticides are widely used in agriculture to improve the productivity and quality of crops. Pesticides have chemical substances that belong to different chemical groups, such as organophosphates, carbamates, organochlorine, nitro compounds, pyrethroids and amides. These chemicals are used to kill unwanted organisms so as to protect crops from damage by insects, weeds and disease. Unfortunately, pesticides act as carcinogens and can be harmful to the health of animals and humans [1]. Widely used pesticides may also cause environmental problems, such as the contamination of water, soil and vegetation [2]. Thus, it is important to detect pesticide residues in food and water. The traditionally used methods are based on chemical techniques, such as chromatography and mass spectroscopy, which require tedious sample pretreatments, highly qualified technicians and sophisticated instruments [3]. The portable method, which is faster and easier than the traditional approach, is important to detect pesticides in water. Recently, a sensor based optical sensing technique has received growing interest since current development of optical technology is able to produce low cost and portable equipment [4].

Recently, the luminescence of semiconductor quantum dots (QDs) has attracted considerable attention because of QDs’ unique optical properties that are different from their
bulk structure counterparts [5]. Some of these unique optical properties are size-tunable photoluminescence spectra [6], narrow spectral width [7], broad absorption and high quantum yield [8]. These may be changed if the QDs are placed in various media, such as gases or liquids. Hence, QDs have been utilized as sensors for medical [9], biological and environmental applications [10]. We may extend further to develop optical sensors based on luminescent QDs for the detection of pesticides.

Here, we have developed an optical sensor for the detection of pesticides in water using ZnCdSe QD films. The ZnCdSe QDs were synthesized using the wet-chemical technique and then deposited as films on the tip of a fibre optic probe. An optical system utilizing a low power laser diode and dual arm fibre optic probe was set up to study the sensing properties. The fluorescence properties of the films were studied by observing the change in PL spectra of the film dipped in water and in the solutions of three pesticides: Siven 85% WP, Dipel and Water Dispersible-Granules WG. It was observed that the pesticide molecules quenched the fluorescence spectra of the ZnCdSe QD films. The result of this study suggests that QD films can be used as sensors for the detection of pesticides.

2. Experimental

A wet-chemical technique was used to synthesize colloidal ZnCdSe QDs. The chemicals used for the synthesis were cadmium acetate hydrate, zinc acetate, octadecene, tri-n-octylphosphine (TOP), tri-n-octylphosphine oxide (TOPO), selenium powder and oleic acid. These chemicals were purchased from Sigma-Aldrich, except that oleic acid and cadmium acetate hydrate were obtained from Wako Company. The chemicals were directly used without any further purification process.

The synthesis procedure used was as reported previously [11]. In the preparation process, two precursor solutions were prepared, namely TOPSe precursor and zinc cadmium precursor. The TOPSe precursor was prepared by dissolving 16 mg of selenium powder into 3 ml of tri-n-octylphosphine (TOP). This precursor solution was heated to about 200 °C for 1 h. Subsequently, the result from whiteness TOPSe was cooled down to room temperature for the next reaction. The second precursor solution was obtained by dissolving 27 mg of cadmium acetate hydrate, 20 mg of zinc acetate and 0.8 gm of tri-n-octylphosphine oxide (TOPO) in 8.5 ml of tri-n-octylphosphine (TOP), 0.6 ml of oleic acid and 10 ml of octadecene. This solution was heated to 350 °C and it generated a colourless homogenous solution. To start nanocrystal growth, 1 ml of TOPSe solution was quickly injected into the hot solution of the zinc cadmium precursor, which was maintained at 350 °C. In this experiment, the nanocrystals of ZnCdSe were grown for 5 min. To stop the nanocrystal growth, the solution from the reaction flask was extracted and the heat was removed using an ice-cooled glass vial. The synthesized ZnCdSe was then purified by centrifugation at 4000 rpm to remove the organic by-products and residues.

The purified ZnCdSe solution was used to fabricate QD films by the drop-casting method. The films were deposited by dropping 30 μl of the solution onto the surface of the fibre optic probe and drying them at ambient temperature. The formation of the film on the probe was confirmed by observing light emission from the probe surface after exposing the probe to a UV lamp.

The photoluminescence and optical absorption properties of the ZnCdSe QDs were measured using a Perkin-Elmer LS 55 luminescence and Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer, respectively. A low-resolution TEM image was recorded by a CM12 Philips to determine the size of the QDs. The PL properties of the ZnCdSe films were studied by dipping the films in water.

The pesticides with trade names Dipel, Siven 85% WP and Water-Dispersible Granules WG insecticides were used in this study. The active ingredient for Dipel is Bacillus thuringiensis, Siven 85% WP is carbaryl and Water-Dispersible Granules WG is Acibenzolar. These pesticides were directly used as purchased without any further purification process. The pesticide solutions in deionized water were prepared with nine concentrations of 2.5, 10, 20, 25, 50, 150, 250, 1250 and 2500 μg l⁻¹. The solutions were then shaken for several seconds to form homogenous solutions.

The optical sensing system comprises an excitation light source that was provided by laser diode (Arroyo Instrument) at 403.6 nm with a typical power of 40 mW, a dual arm fibre optic probe (Ocean Optics), a spectrometer HR2000 (Ocean Optics) and a sensor chamber that contains the pesticide solution sample. Figure 1 shows the setup for the detection of pesticides. The dual arm fibre optic is used as the excitation and emission light path where at the end of probe a tip with a 45° slanted surface is attached. With this geometry, the excitation light source from the excitation fibre will not enter the emission path fibre. The pesticides were detected by comparison of the PL spectra of the sensing films that were first dipped in water and then in the pesticide solutions. The change in the PL spectra before and after the films were dipped in the pesticide solutions were considered as the sensing sensitivity.
3. Results and discussion

Ternary ZnCdSe QDs were synthesized by a wet chemical technique and the nanocrystals were grown for 5 min. Figure 2 shows a TEM image of the colloidal nanocrystals of the ZnCdSe QDs. The QDs appear as spherical black dots with a narrow size distribution. The average size examined by TEM was 5 nm.

The optical properties of the QDs in solution were studied. Figure 3 shows the photoluminescence (PL) and absorption spectra of the colloidal QDs. The PL spectrum is narrow with the emission centre at 590 nm, compatible with a narrow distribution of nanocrystals. The estimated full width at half maximum (FWHM) is 38 nm. The synthesized QDs have the orange PL emission spectrum. Meanwhile, the QDs have a broad optical absorption where the peak is at 574 nm, i.e. at the left side of the PL peak.

The ZnCdSe QDs films were deposited by drop-casting the colloidal solution onto the glass probe surface. Using our optical system setup, we measured the PL spectrum of the films dipped in water. The result is shown in figure 3(c). The PL spectrum curve of the films in water is broader and the centre of the emission wavelength is shifted to the right from the original peak of the material in the solution, i.e. at 593 nm.

These may be due to various factors, such as the change in the shape or size of the QDs or the effect of the fibre optic.

The sensing sensitivity of the QD films was studied by comparing the PL spectra of the films dipped first in deionized water and then in the pesticide solutions: Sevin 85% WP, Dipel and Water-Dispersible Granules WG. Figure 4 shows the PL spectra of the films in deionized water and in 20 µg l⁻¹ of Sevin 85% WP solution. It is clear that the PL curve of the films was quenched by the presence of the pesticide in the solution. Similar results were obtained for the solutions of other pesticides. It was observed that the shape and position of the peaks of the PL curves were not significantly changed with the presence of the pesticide molecules. Since the wavelength emission depends on the QD size and shape, this means that the physical properties of the QDs are stable in the pesticides solutions. We found that the PL curves of the films in water and in the pesticides solutions were stable within 30 min of the experiment. For a particular of the QD film, similar results are repeated for at least seven cycles of the sensing experiments.

There are several possible mechanisms that can be proposed to explain how the pesticide molecules quench the fluorescence of the QDs films. They include Förster (fluorescence) resonance energy transfer, inner filter effects, electron transfer processes and ion-binding interactions [12]. The electron transfer might occur when the pesticide molecules are in contact with the QD surface [13]. The QDs may be considered as electron donors and the pesticide molecules as acceptors. Hence the pesticide molecules acquire some excited electrons from the QD surface. The lost excited electrons from the QDs will reduce the intensity of the emitted light.

The sensing sensitivity of the QD films with varying pesticide solutions concentration, from 2.5 to 2500 µg l⁻¹, was studied. Figure 5 shows the results for Sevin 85% WP pesticide. The percentage of the PL peak dropped increases with pesticide solution concentration. There is a linear relationship between the pesticide solution concentration and the QD film sensor sensitivity. Figure 6 displays the calibration curves of the QD film sensor towards three
pesticides solutions, i.e. Sevin 85% WP, Dipel and Water-Dispersible Granules WG, based on 12 repeating experiments. The calibration curves showed good linear correlation coefficients ($r$) of $0.90$. This result may be used to estimate the amount of pesticide residue in water. The sensitivity of the QD films depended on the type of pesticide successively from the highest to lowest sensitivity in the order Sevin 85% WP, Dipel and Water-Dispersible Granules WG.

4. Conclusion

The high luminescence of ZnCdSe QDs was successfully synthesized using the wet-chemical technique. The drop-casting QD films were used to study pesticide detection in water. The presence of pesticide was detected from the drop of the peak of the PL spectrum of the films. The percentage of the PL peak dropped increases with the concentration of the pesticide solutions. There is a linear relationship between the pesticide solution concentrations from 2.5 to 2500 $\mu$g l$^{-1}$ and the QD films sensor sensitivities. Hence, the QD films could be used as fluorescence sensors to detect water that is contaminated by pesticides.

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