

DETECTION OF UV RADIATION IN VINEYARDS BY OPTICAL ANALYSIS OF CdTe QUANTUM DOTS

¹Lenka SOCHOROVÁ, ¹Božena HOSNEDLOVÁ, ²Michaela DOČEKALOVÁ, ²Martina STAŇKOVÁ,
²Dagmar UHLÍŘOVÁ, ³Branislav RUTTKAY-NEDECKÝ, ⁴Marta KEPINSKA,
⁴Halina MILNEROWICZ, ¹Mojmír BAROŇ, ⁵Hai Xuan NGUYEN, ⁵Bach Ngoc DUONG,
⁵Hoai Viet NGUYEN, ¹Jiří SOCHOR, ²Josef RŮŽIČKA, ^{2,3,4}René KIZEK

¹ Mendel University in Brno, Faculty of Horticulture, Department of Viticulture and Enology, Lednice,
 Czech Republic, EU, sochor.jirik@seznam.cz

²Prevention Medicals, Studenka, Czech Republic, EU, docekalova@preventionmedicals.cz

³University of Veterinary and Pharmaceutical Sciences Brno, Pharmaceutical Faculty, Brno,
 Czech Republic, EU, kizek@sci.muni.cz

⁴Department of Biomedical and Environmental Analyses, Faculty of Pharmacy with Division of Laboratory
 Diagnostics, Wrocław Medical University, Wrocław, Poland, EU, zalewska.m@gmail.com

⁵Research Center for Environmental Monitoring and Modelling, VNU University of Science, Hanoi, Vietnam,
nguyenviethoai@hus.edu.vn

Abstract

The type, number, and magnitude of environmental constraints are currently undergoing changes due to shifts in climate patterns already observed for the past and predicted for the future. These changes are already affecting grape composition with observed changes in sugar and acidity concentrations. UV sensor in vineyards is therefore needed. In this work, the ability of cadmium telluride quantum dots (CdTe QDs) to respond to UV radiation was examined. Green, yellow, orange, and red CdTe QDs were freshly prepared every day and exposed to UV daily radiation for 12 hours for seven consecutive summer days. Every day, solar irradiance was measured, reaching maximal values during the day of around 200-700 W/m² with a UV index of 2-8. The highest solar and UV irradiances were on the third, fourth, sixth, and seventh days (700 W/m², UV index 8). The lowest solar and UV irradiances were on the first and fifth days (600 W/m², UV index 6). On the second day, both irradiances were average (200-500 W/m²; UV index 4-7). The physical properties of individual QDs (absorption and fluorescence maxima, electrochemical determination of cadmium concentration) were monitored. The rising dose of UV radiation led to the release of cadmium ions and the change in the size of individual QDs (a significant change of colour directed toward to the red area of the visible light spectrum). Yellow, orange, and green QDs responded most to UV radiation. This sensor will be used for detection of UV radiation in vineyards.

Keywords: UV radiation, quantum dots, electrochemical detection, fluorimetric detection, climate change

1. INTRODUCTION

The sun is a natural source of UV (ultraviolet light) radiation on Earth; however, only the UV-A and UV-B components of this radiation enter the troposphere. UV-A radiation has a wavelength range of 320-400 nm and accounts for/represents 99 % of the sun's UV rays that fall on the Earth's surface. UV-B radiation has been found to cause the release of Cd²⁺ ions from quantum dots (QDs) due to/as a result of cadmium telluride (CdTe) QDs surface oxidation [2].

Tsipotan et al. examined the effect of visible light and UV radiation on the aggregation stability of CdTe QDs [3]. In the case of ultraviolet light, photoinduced reduction of CdTe QDs size was confirmed. Typical CdTe QDs stabilised with mercaptosuccinic acid (MSA) after exposure to specific UV-B radiation at a given wavelength and energy resulted in excitation of a system capable of generating a whole group of molecularly reactive

oxidation intermediates (ROI) and reactive oxygen species (ROS) [2,4]. Due to the photodynamic effect of CdTe QDs, free cadmium ions are released.

This mechanism has been used to construct a new, very simple, and completely non-demanding qualitative UV-B radiation sensor, even in places where technical equipment is not available. Such a sensor can be used to monitor the UV-B radiation in the cultivation of vine. In this study, for the very first time, a mercaptosuccinic acid-stabilised CdTe QDs sensor for monitoring of UV-B radiation was proposed, and the possibility of it using CdTe QDs has been investigated.

2. MATERIAL AND METHODS

2.1. Chemicals

All chemicals used in this study ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Na_2TeO_3 , mercaptosuccinic acid, Trizma base, HCl) were purchased from Sigma-Aldrich (St. Louis, MO, USA), in ACS purity. Propanol, NaBH_4 was purchased from Merck (Darmstadt, Germany), and 25 % aqueous NH_4OH was purchased from Lach-Ner s.r.o. (Neratovice, Czech Republic). All chemicals that we used for gel electrophoresis were purchased from VWR (Germany). All plastic materials used (tubes, tips) in this study were purchased from Eppendorf (Hamburg, Germany).

2.2. CdTe quantum dots synthesis

The preparation of CdTe quantum dots (QDs) was as follows: 10 ml of solution $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.02 M), 76 ml of H_2O , 1 ml of mercaptosuccinic acid (MSA) solution (0.4 M), 5 mL of Na_2TeO_3 (0.02 M), and 40 mg of NaBH_4 was stirred with a magnetic stirrer (VMS-C4, VWR International Ltd., Darmstadt, Germany) for at least two hours until bubbling stopped. Subsequently, the volume was adjusted to 100 ml. 2 ml of the prepared solution was pipetted into the glass vials (Sigma Aldrich, St. Louis, MO, USA) with a white cap (Anton Paar, Graz, Austria) and a Teflon cap (Anton Paar, Graz, Austria). The thus prepared vial was placed in a microwave, which was set to a power of 300 W, and the heating took place for two minutes for green QDs, four minutes for yellow QDs, six minutes for orange QDs, and eight minutes for red QDs. The final concentration of QDs was 2 mM.

2.3. Spectrometry and fluorescence measurement

Absorption and fluorescence spectra were obtained with the Tecan Infinite 200 PRO Multifunctional Reader (TECAN, Switzerland). For absorption spectra, the wavelength was in the range 400-800 nm. For fluorescence spectra, there was an excitation wavelength of 250 nm and an emission wavelength in the range 350 nm to 800 nm. The optical properties of nanoparticles were studied by spectral analysis. The absorbance spectra of nanoparticles were recorded within the range of 400 to 800 nm using a UV-3100PC UV-VIS spectrophotometer (VWR, Germany).

2.4. Electrochemical determination of cadmium ions

Determination of Cd^{2+} by difference pulse voltammetry (DPV) was performed at 663 VA Stand (Metrohm, Switzerland). A standard cell with three electrodes was used, and a hanging mercury drop electrode (HMDE) with a drop area of 0.4 mm^2 was employed as the working electrode. An $\text{Ag}/\text{AgCl}/3\text{M KCl}$ electrode acted as the reference and a carbon electrode was auxiliary. For data processing, VA database software by Metrohm was employed. The analysed samples were deoxygenated prior to measurements by purging with argon (99.999 %). Acetate buffer (0.2 M sodium acetate and 0.2 M acetic acid, pH = 5) was used as a supporting electrolyte. The parameters of the measurement were as follows: initial potential -1.2 V, end potential 0 V, deoxygenating with argon 120 s, accumulation time 120 s, step potential 5 mV, modulation amplitude 25 mV, volume of injected sample: 50 μL , volume of measurement cell 10 mL. The samples, the electrolyte, and the measuring vessel were thermostated using the JULABO-200 circulation pump (Germany). The temperature was set to 20°C for all measurements.

2.5. Measurement of physical parameters

The location of the weather stations was an open non-industrial landscape in Boskovice, Czech Republic; for the monitoring, two independent measuring points with the frequency parameter of 60 s were selected. We used data from the Davis meteorological station (Hayward, USA). The station is located in Boritov, with 16° 58' 65" E longitude and 49° 43' 09" N latitude. Its altitude is 305 m a.s.l. Each weather station's temperature, humidity, and rain sensor are at 1.85 m, and solar and UV sensors are at 3.5 m. Individual parameters were collected at one-minute intervals. All data were automatically sent to the control unit and then to a computer database to store data.

2.6. Statistic and results evaluation

Experimental work was performed in at least three independent experiments. Each sample in the experiments was analysed at least five times. The obtained data presented in this paper are average values. No experimental points were excluded from the proposed experimental study. All the obtained data are stored in the Qinslab database. If possible, data were processed and evaluated mathematically and statistically in the Qinslab database. The results were expressed as mean \pm standard deviation (S.D.). Photos were processed by the ColorTest program, which assigns intensity to the individual pixels of the studied image in a given colour area [5]. For preparing the publication, the data were processed using Microsoft software (USA).

3. RESULTS

3.1. Quantum dots as sensor for UV radiation

CdTe QDs were freshly prepared every day and exposed to UV radiation daily for 12 hours for seven consecutive summer days. After each exposure, their basic physicochemical characteristics were evaluated. The principle of our prepared sensor is shown in **Figure 1**.

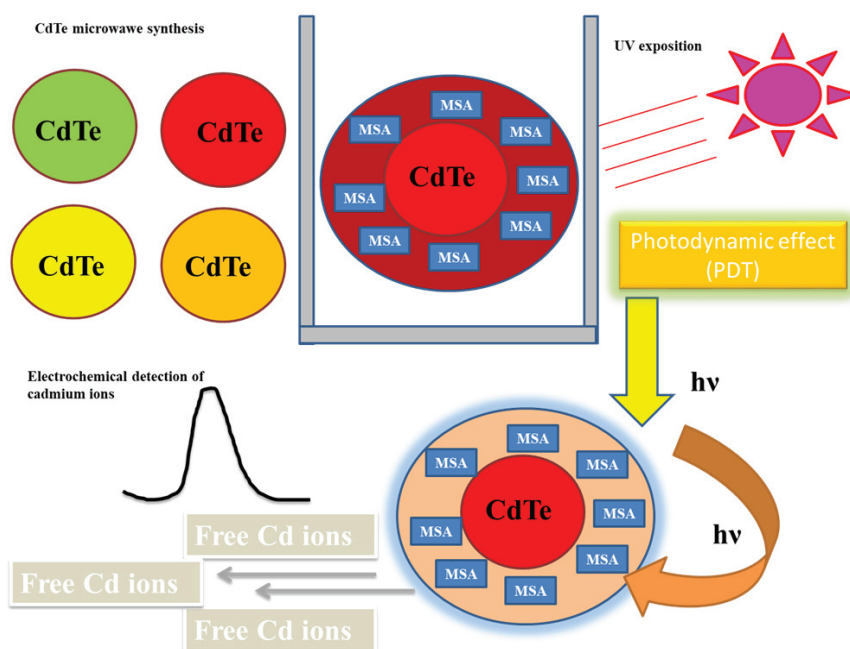


Figure 1 Schematic representation of the QDs function for sensor application. Typical CdTe QDs stabilized with mercaptosuccinic acid (MSA) after exposure to specific radiation at a given wavelength and energy leads to the excitation of a system that is capable of generating a whole group of molecular oxygen intermediates and relative oxygen species. In addition, due to the photodynamic effect of CdTe QDs, free cadmium ions are released.

3.2. Biophysical characteristics of prepared CdTe quantum dots

We decided to use CdTe QDs stabilised with mercaptosuccinic acid (MSA) in microwave synthesis. Four types of CdTe QDs: green, yellow, orange, and red (**Figure 2A**) were prepared by microwave synthesis (500 W) and under UV light (310 nm). A typical profile of the individual types of QDs on the PAGE gel after their separation is shown in (**Figure 2B**) and the intensities of the colour signals of the QDs electrophoretic bands can be seen in **Figure 2C**. Typical absorption spectra can be seen in **Figure 2D**. In the visible area of the spectrum, the absorption maxima were as follows: green QDs 519 nm, yellow QDs 544 nm, orange QDs 563 nm, and red QDs 564 nm. Typical fluorescence maxima are shown in **Figure 2E**. The fluorescence maxima were as follows: green QDs 532 nm, yellow QDs 560 nm, orange QDs 596 nm, and red QDs 654 nm. The cadmium concentration electrochemically determined was as follows: green QDs 1878 μM , yellow QDs 1739 μM , orange QDs 1636 μM , and red QDs 1181 μM (**Figure 2F,G**). The determined nanoparticle size ranged between 5 and 10 nm.

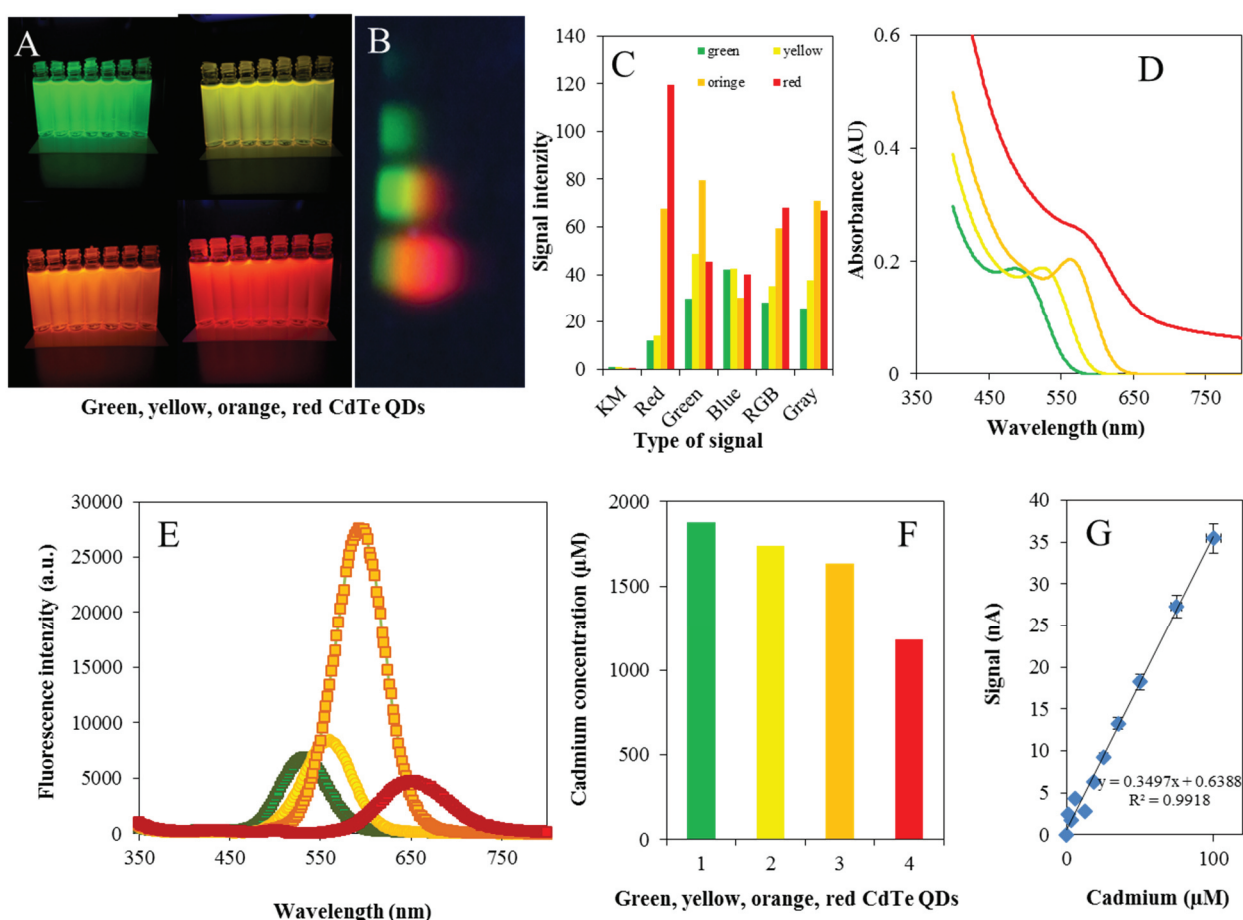


Figure 2 Biophysical characteristics of prepared CdTe quantum dots (QDs) used for environmental experiment. (A) Fluorescence of the prepared dots under UV light (310 nm) used in the experiment described above. (B) Typical profile of individual types of QDs on PAGE gel after separation (1.5h, 100V). (C) The created profile was analysed using the COLOR test program developed by us. The intensities of individual pixels are plotted in different colour profiles. (D) Spectrophotometric characterization of QDs, plastic cuvette 1 cm track, blank solution - water. (E) Fluorometric characteristics of QDs measured in a UV transparent plate at excitation of 250 nm. (F) The cadmium concentration in studied QDs. (G) Typical calibration curve for electrochemical cadmium analysis in organic form. All experiments were performed in five replicates, the displayed data being the average values. Other experimental details are described in Materials and Methods.

3.3. Summary of biophysical characteristics of QDs after their exposure to UV radiation

Four types of CdTe QDs (green, yellow, orange, and red) were exposed to UV radiation daily for 12 hours (QDs were freshly prepared each day) and the measurements were repeated for seven consecutive days in the summer. The course of the whole experiment, expressed in terms of average differential changes, is shown in **Figure 3**. The integral sum of the areas of the measured solar irradiance (W/m^2) and the UV index is shown in **Figure 3A** and **Figure 3B**. The highest solar and UV radiations were on the third, fourth, sixth, and seventh days, whereas the lowest solar and UV radiations were on the first and fifth days. On the second day, they were average. The cadmium concentration reached the highest values for non-irradiated (freshly prepared) QDs (day 0). The lowest Cd values were then reached on the sixth and seventh day (**Figure 3C**).

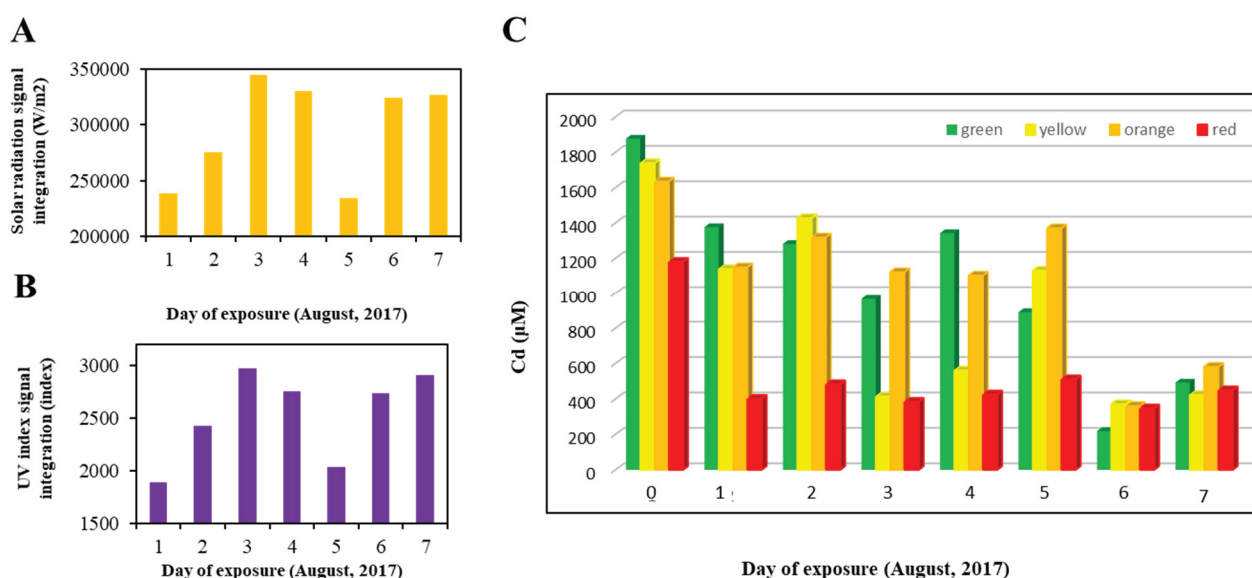


Figure 3 Changes in the observed biophysical parameters of CdTe QDs after exposure to the environment. The above figure shows the integral sum of the areas measured by solar irradiance (W/m^2) (A) and the UV index values (B) on the observed days in the experimental locality. On individual days, fluctuations in the integral radiation values are well traceable. The cadmium concentration (μM) of CdTe QDs on the observed days where in day 0 the initial cadmium concentration in CdTe QDs is given (C). The individual tested colour QDs are marked in the graphs with the appropriate colours. The results were evaluated as averages of five replicates. Other experimental details are described in Materials and Methods

4. CONCLUSION

This study provides an important basis for further understanding the relationship between the behaviour of CdTe QDs and UV radiation, and offers valuable information for their potential practical use as a sensor in the near future. The findings show that MSA-stabilised CdTe QDs are a suitable platform for the measurement of UV irradiance. This unique feature of the designed sensor seems to be a promising prospect for its versatile use in a variety of industrial and environmental applications, particularly in vineyards.

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