Solid State Science and Technology, Vol. 19, No 1 (2011) 20-25
ISSN 0128-7389

FLUORESCENCE GAS SENSOR BASED ON CdTe QUANTUM DOTS FOR DETECTION OF VOLATILE ORGANIC COMPOUNDS GAS

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ABSTRACT

The CdTe quantum dots (QDs) synthesized using a wet chemical process was utilized an attempt to develop thin film sensor for detection of organic vapors. A sensor system was setup, comprises an excitation light source made of laser diode, a dual arm fiber optic probe, a spectrometer, a sensor chamber and a nitrogen gas for driving the vapor sample from the vapor compartment. The QDs thin film was deposited by dropping QDs solution onto the probe surface and let them dried in the ambient temperature. The detection of organic vapors was done by comparing the photoluminescence (PL) spectra the thin film exposed in the nitrogen gas and in organic vapors. The PL intensity of the CdTe thin film was quenched by the presence organic vapors with the increasing of a reaction of time until reached the saturation.

Keywords: gas sensor; quantum dots; CdTe;

INTRODUCTION

Volatile organic compounds (VOCs) formed by industrial chemical solvents, coatings and refrigerants tend to contribute to the increasing serious problem on human health and atmospheric pollution [1]. Therefore, a crucial move was drastically taken by scientists for detecting the dangerous organic vapors hidden in the whiteness of atmosphere and environment. There are a large number of techniques for measuring organic vapors but suffered from some limitation such as often costly, time-consuming and tedious sample pretreatments [2].

Recently, quantum dots (QDs) have attracted great interest due to their very appealing optical properties such as size-tunable photoluminescence (PL) spectra, narrow spectral width, tunability emission and high quantum yield [3]. Owing to their recent advance in highly luminescent semiconductor QDs, QDs (II-IV compounds) have been widely used as optical sensor for medical, biological [4] and other applications. The fluorescence intensity of QDs can be decreased by a variety of molecular interactions including excited-stated reaction, molecular rearrangement, energy transfer, forming ground state complex and fluorescence quenching [5]. In this paper, the sensing sensitivity of the presence organic vapors was detected via its quenching effect on the PL intensity of CdTe QDs thin film. The fabrication of thin film CdTe nanocrystals with size 4 nm was drop cast at ambient temperature for vapors detection by optical sensing. The optical sensing system provided a convenient, low-cost and potential application for organic vapors gas-analysis.

EXPERIMENTAL DETAILS

Quantum Dots Synthesis

The preparation process of high luminescence semiconductor nanocrystals has played a critical role in the progress of QDs applications. The colloidal CdTe QDs was prepared by mixing a two precursor solution that namely TOPTe and cadmium (Cd) precursor using wet chemical process at moderate temperature (350˚C). The TOPTe precursor was previously prepared by dissolving 26 mg of tellurium powder (Aldrich) into 3 ml of tri-n-octylphosphine (TOP) (Aldrich) at 200˚C. After that, the yellowish TOPTe was cool down at ambient temperature. In three necks round bottom flask, the cadmium precursor was obtained by dissolving 52 mg of cadmium acetate hydrate (Wako) and 34 mg of n-octadecyl phosphonic acid (ODPA) (PCL synthesis) in 0.625 ml of oleic acid (Wako) and 10 ml of octadecene (Aldrich) were then heated at 350°C. At that stage temperature, 1 ml of room temperature TOPTe solution was quickly injected into the hot solution of cadmium precursor. The reaction of QDs growth was started and the timing was begun. In this experiment, the CdTe growth at 10 second (s) was taken and ice-cooled glass vial was used to quench the nanocrystals' growth. The QDs sample was purified by centrifugation process at 5 min and 4000 rpm for further use. The PL and optical absorption properties of the CdTe QDs were collected using Perkin Elmer LS 55 Luminescence and Perkin Elmer Lamda 900 UV/VIS/NIR Spectrometer, respectively. CM12 Philips of TEM determines the size of QDs.

Sensing system

Figure 1 shows the setup for the detection of organic vapors. The optical sensing system comprises an excitation light source was provided by laser diode (Arroyo Instrument) at 403.6 nm with a typical power of 40 mW, a dual arm fiber optic probe (Ocean Optics), a spectrometer HR2000 (Ocean Optics), a sensor chamber and a nitrogen gas for driving the vapor sample from the vapor compartment. The QDs thin film was deposited onto the fiber optic probe using the solvent casting technique. The sensing film on the surface of probe was prepared by dropping 50 μL of the CdTe colloid onto the probe surface and let them dried in the ambient temperature. The dual arm fiber optic is for excitation light and emission light path and at the end of probe that attached a tip structured by 45 degree slanted surface. With this geometry, the excitation light source from the excitation fiber will not enter the emission path fiber.

The formation of the QDs film on the probe tip was examined by checking the luminescence characteristic of the thin film on the probe tip through exposing them to the UV lamp irradiation. Successful film deposition was indicated by the presence of light emission from the probe surface. The detection of organic vapors was done by measuring PL spectra of the films in nitrogen gas and then in organic vapor. The organic vapors that were tested for sensing film are ethanol, 2-propanol and acetone vapor. The change in the PL spectra before and after the thin film in organic vapors was considered as the sensing sensitivity.

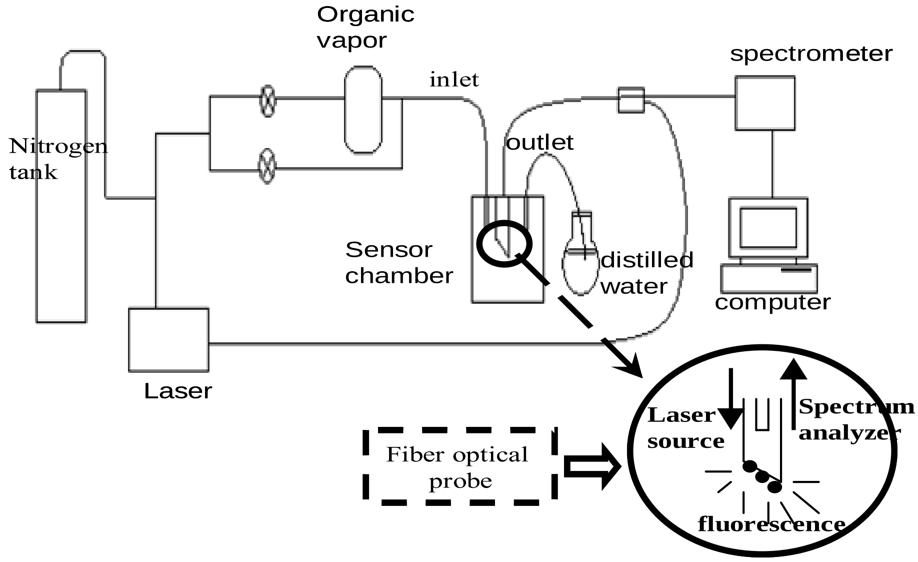
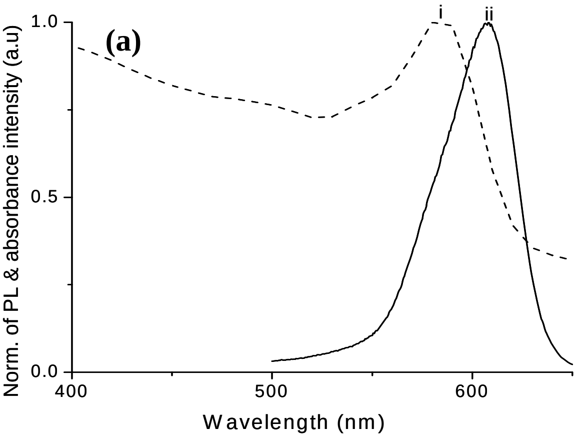


Figure 1: The optical sensing system for organic vapor detection

RESULTS AND DISCUSSION

The high luminescence CdTe synthesized has been successfully prepared using wet chemical process adopting Talapin method with several modifications [6].The colour of Cd precursor solution was quickly changed upon the injection of TOPTe from whiteness to light orange. The sample of reaction was extracted at 10 s of growth time and then dispersed into hexane solution. The CdTe QDs at 10 s was exhibited a high luminescence of orange region under UV exposure. The orange fluorescence of the PL emission from the colloidal CdTe upon exposure to the UV excitation strongly indicated the existence of QDs in the solution.

Figure 2a shows the optical properties of the CdTe QDs using PL and absorption spectroscopy. The center of wavelength emission of CdTe was appeared at 590 nm. The spectrum show relatively high intensity and narrow width. Based on the spectrum, it was found that the quantum yield as high as 85% and full width at half maximum (FHWM) as narrow as 38 nm. From this result, it can be concluded that the QDs was exhibited high quantum efficiency and pure colour emission. It was also exhibited that the center peak of corresponding absorbance is at 580 nm.



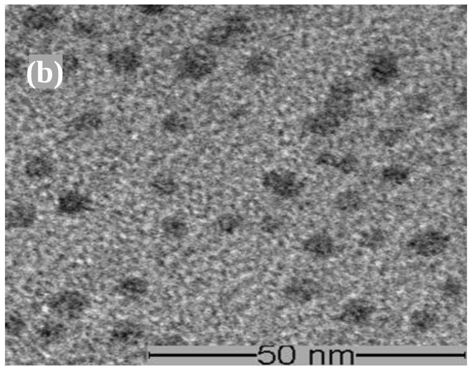


Figure 2: (a) The resulting optical properties of CdTe-prepared (i) absorbance spectrum and (ii) PL spectrum, (b) TEM image of CdTe synthesized for 10 s of growth time

By taking small drop of the sample after centrifugation and dropped on the transmission electron microscopy grid, we performed the electron microscopic investigation on the QDs. Figure 1B shows TEM image of the QDs that was taken from the sample grown for 10 s. It can be vividly seen that the presence of black dot in the images, represented the CdTe QDs. The low magnificent TEM shows the homogenous spherical QDs with size as small as 4 nm. From the lower magnification, it can also be concluded that the QDs size distributed is relatively very narrow and single shape.

The sensing properties of thin film were firstly studied by observing the change of PL intensity when nitrogen (N_2) and ethanol vapor react on the surface of CdTe thin film. Figure 3 shows the PL spectra of the thin film in nitrogen and ethanol towards time. The PL peak of CdTe thin film is observed at 595 nm, and its PL intensity progressively decreases along with the increasing of time but the shifted and shape of spectra was not significantly changed. It can be seen that the PL peak in N_2 is ca. 50.0 but dramatically decreases from ca. 44.0, 40.0, 36.6, 28.9 and 20.0 in the first 30 mins. The quenching effect of ethanol vapor on the PL intensity of CdTe thin film achieved saturation more than one hour. The insertion curve shows the quenching of PL peaks with time up to 120 minutes. The PL quenching can result from energy transfer between donor/acceptor systems (7), which is there possibility of electrons transfer occurred when the ethanol vapor in contact with the QDs surface. The QDs is may be considered as electron donor and the ethanol molecules as acceptor. Qiang et. al has been reported that the electron acceptor adsorbed on the surface of thin film can quench the PL intensity of QDs by fast electron transfer and increase the fluorescence decay rate. The lost of excited electrons from QD will reduced the intensity of emission light.

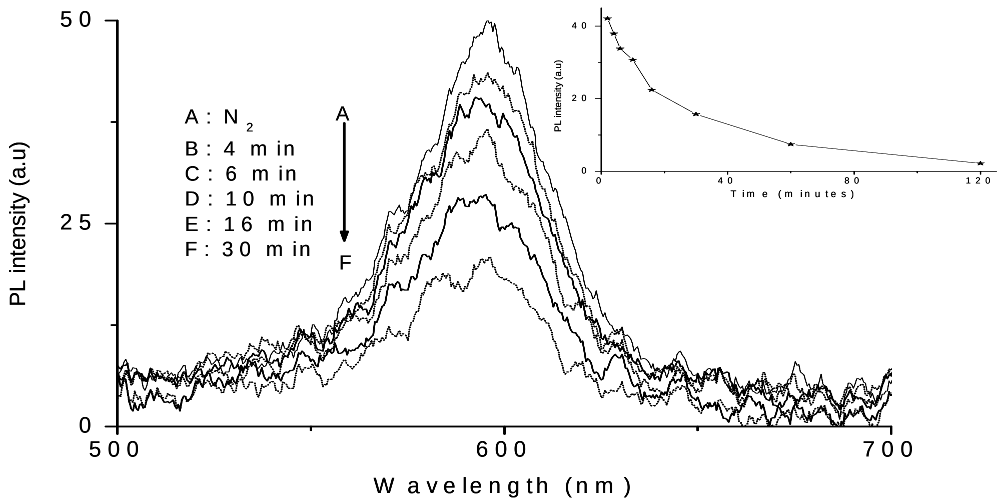


Figure 3: PL spectra of CdTe thin film in N_2 and ethanol vapor. The inset curve shows the relation between PL intensity and the reaction time

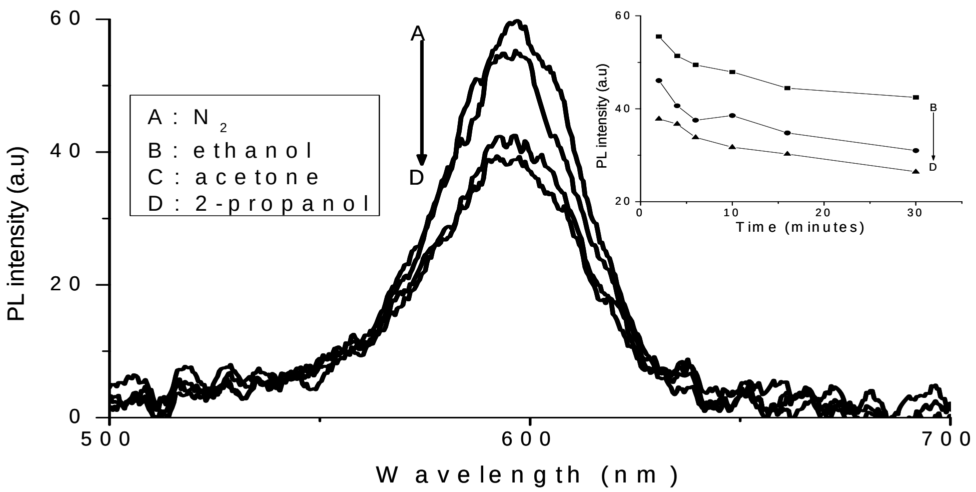


Figure 4: PL intensity of thin film in nitrogen and in ethanol, acetone and 2-propanol vapor after exposing within four minutes. The inset curves show the PL intensity with the increasing of reaction time

We further study the sensing sensitivity of CdTe thin film when the three different organic vapors react on the surface of the fluorescent thin film. As the result, the PL intensity is ca 60.0 in N_2 but when the three different vapors in contact on the surface thin film within four minutes, the PL intensity drastically decreases to be ca. 55.4, 42.6 and 38.7 for ethanol, acetone and 2-propanol vapor respectively (Figure 4). The inset of Figure 4 shows the PL intensity of three different vapors quenched towards time. It can be vividly seen that the PL intensity's 2-propanol vapor shows the highest of the drop PL intensity than ethanol and acetone. There possibility that the 2-propanol molecules absorbed the electron of CdTe thin film is more easily and difficult to escape from the arrangement of nanocrystals' thin film causing the longer of quenching PL intensity. As the result, the 2-propanol vapor was exhibited more sensitivity than ethanol and acetone that was only by-passed on the surface of thin film.

CONCLUSION

The high luminescence of CdTe has been successful prepared using the wet-chemical process and the organic vapors gas-analysis was developed. The sensing thin film was showed the good sensitivity by quenching effect of PL intensity when organic vapors' molecules free transfer and deposit on the surface of CdTe thin film. The PL intensity of CdTe was quenched with the increasing of time and reached the saturation exceed than 1 hour. The 2-propanol vapor was exhibited more sensitivity than ethanol and acetone according the highest of the drop of PL intensity. The quenching of PL intensity by organic vapors makes it possible to develop a competent detection method for organic vapors.

ACKNOWLEDGEMENT

The authors acknowledge the support from the Malaysian Ministry of Higher Education Universiti Kebangsaan Malaysia under Research University Grant.

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