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# The Synthesis of $Eu^{3+}$ Doped with $TiO_2$ Nano-Powder and Application as a Pesticide Sensor

**Fei Yao†, Yang Sun†, Chunlei Tan, Song Wei, Xiaojuan Zhang, Xiaoyun Hu†, and Jun Fan***
*School of chemical Engineering and Technology, Northwest University, Xi'an, Shannxi, China.*
**E-mail: fanjun@nuc.edu.cn*
*†Department of Physics, Northwest University, Xi'an, Shannxi, China*
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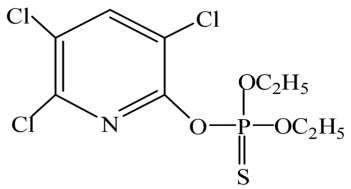
**ABSTRACT.** Using tetrabutyl titanate as precursor, $Eu^{3+}$ doped $TiO_2$ nano-powder was prepared by sol-gel method, the nature of luminescence of nano-powder was studied. The interaction of chlorpyrifos with $Eu^{3+}$ doped $TiO_2$ was studied by absorption and fluorescence spectroscopy. The results indicated the fluorescence intensity of $Eu^{3+}$ doped $TiO_2$ was quenched by chlorpyrifos and the quenching rate constant ($k_q$) was $1.24\times10^{11}$ L/mol·s according to the Stern-Volmer equation. The dynamics of photoinduced electron transfer from chlorpyrifos to conduction band of $TiO_2$ nanoparticle was observed and the mechanism of electron transfer had been confirmed by the calculation of free energy change ($\Delta G_{et}$) by applying Rehm-Weller equation as well as energy level diagram. A new rapid method for detection of chlorpyrifos was established according to the fluorescence intensity of $Eu^{3+}$ doped $TiO_2$ was proportional to chlorpyrifos concentration. The range of detection was $5.0\times10^{-10}$ - $2.5\times10^{-7}$mol/L and the detection limit ($3\sigma$) was $3.2\times10^{-11}$ mol/L.

**Key words:** $Eu^{3+}$ doped $TiO_2$, Sensor, Chlorpyrifos, Fluorescence, Analysis application

## INTRODUCTION

In recent years, there is a growing concern about harmful effects of pesticide on human health and environment. In particular, organophosphorus pesticides (OPs) are described as a group of highly toxic compounds and widely used in agriculture for protecting plants.[1]




**Chlorpyrifos**

Chlorpyrifos (CPF) is one of the most frequently used organophosphate pesticides in agriculture.[2] It is a broad-spectrum OP used to control pests in grain storage, water and a variety of leafy crop. Therefore, the detection of chlorpyrifos is significant for agriculture, environment, protection and other aspects. A wide variety of analytical methods such as gas chromatography (GC)[3] and high performance liquid chromatography (HPLC)[4] have been commonly used for an efficient determination of chlorpyrifos. However, these methods are time consuming and require labourintensive preparation of samples that involve solvent extraction and clean up of extracts.

With the rapid development of nanotechnology, there are few papers about use of nanotechnology in development of pesticide sensors. Anyway, no sensor based on the fluorescence of $Eu^{3+}$ doped $TiO_2$ was reported in the literature.

In this paper we developed a rapid and sensitive pesticide sensor. To our knowledge, this is the first report of detection of chlorpyrifos by using the fluorescence intensity of $Eu^{3+}$ doped $TiO_2$.

## EXPERIMENTAL

The $Eu^{3+}$ doped $TiO_2$ nano-powder was prepared by the Sol-gel method. Two samples were prepared, one of samples placed in vacuum drying at 50 °C for 24 h, then it was annealed at 700 °C for 2 h, to get the white powder. Another liquid sample was diluted and the ratio of distilled water to solution was 3:1. The details of the sample preparation are given in Ref.[5]

The collected nanophosphor particles were characterized by X-ray diraction (XPert-MPD System, PHILIPS) and transmission electron microscopy (TEM, JEM-2010JEOL, H-7500 HITACHI). Fluorescence spectra of liquid samples were measured by F-7000 Hitachi spectrophotometer. UV-Vis absorption spectra of samples were recorded on UV-

3600 Shimadzu spectrophotometer.

In a typical uorescence measurement, 3.0 mL liquid samples were added to a quartz cell (1.0 cm×1.0 cm). The CPF solution was then gradually titrated to the cell using a pipette. The concentrations of CPF were ranged from $2.5\times10^{10}$ to $25\times10^{10}$ mol $L^{1}$ and the volume of CPF was 20 μL every time.

The uorescence emission spectra were measured at room temperature. The width of the excitation and emission slits was set at 5.0 nm. An excitation wavelength of 450 nm was chosen and the emission wavelength was recorded from 470 nm to 700 nm.

## RESULTS AND DISCUSSION

XRD is used to investigate the phase structure of the samples. The characteristic peaks of rutile and anatase are indicated in *Fig.* 1. Which showed that $Eu^{3+}$ doped $TiO_2$ nano-powder was dominated by anatase $TiO_2$, this may be due to the low ion amount of dopants or their high dispersion in samples.

*Fig.* 2. showed TEM images of calcined samples after calcination at 700 °C. The micrographs showed the good electron diraction patterns, which indicated that the nanoparticles had crystalline nature with good crystallinity. It was found that the crystalline size of $Eu^{3+}$ doped $TiO_2$ is 25-30 nm.

The absorption spectra of CPF were recorded in the absence and in presence of $Eu^{3+}$ doped $TiO_2$ (*Fig.* 3). From *Fig.* 3. we can see in the region of 200 nm-300 nm, CPF has one characteristic absorption band with absorption maxima at 220 nm. After addition of different concentration of $Eu^{3+}$ doped $TiO_2$ to CPF solution, the shape and band maxima of absorption spectra of CPF remain unchanged, but the intensities increased greatly. The fluorescence spectra of $Eu^{3+}$ doped $TiO_2$ with varying concentrations of CPF were shown in *Fig.* 4. it is clear that the fluorescence spectra of $Eu^{3+}$ doped $TiO_2$ remain unchanged.

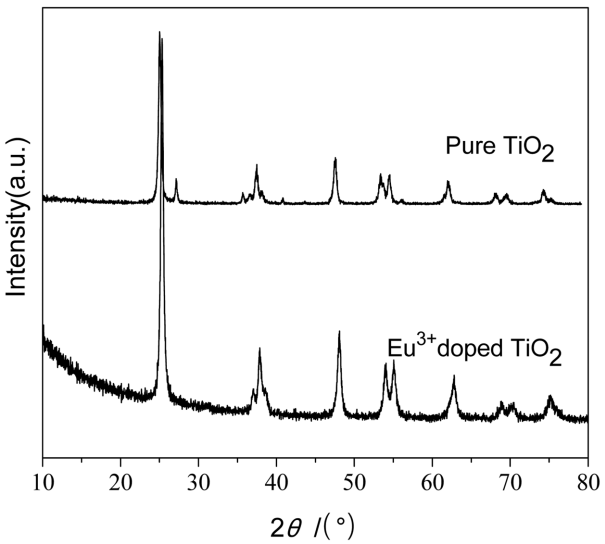



***Fig.* 1.** XRD of $Eu^{3+}$ doped $TiO_2$ and pure $TiO_2$.

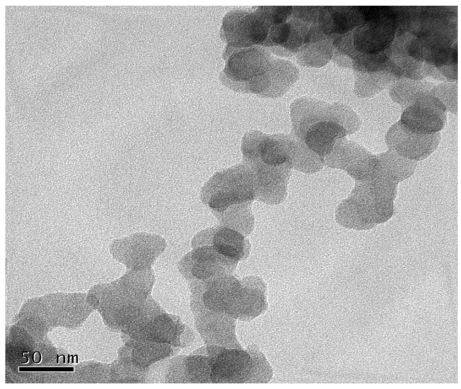



***Fig.* 2.** TEM analysis of $Eu^{3+}$ doped $TiO_2$.

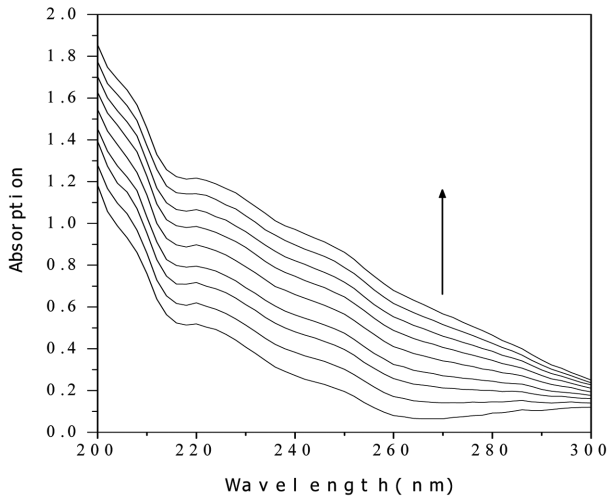



***Fig.* 3.** Absorption spectrum of CPF ($2.5\times10^{-7}$ mol/L) in the presence of $Eu^{3+}$ doped $TiO_2$ in theconcentration range of (2-16)$\times10^{-6}$ mol/L.

The fluorescence quenching behaviour is usually described by Stern-Volmer relation:[6]

$$F_0/F = 1 + K_{SV}[Q] = K_q\tau_0[Q] \quad (1)$$

where, $F_0$ and F are the fluorescence intensities in the absence and presence of quencher, respectively, $K_{SV}$ is the Stern-Volmer constant, [Q] the concentration of the quencher and $\tau_0$ is the fluorescence lifetime of $Eu^{3+}$ doped $TiO_2$. From the slope of the above plot (*Fig.* 4), the $K_{SV}$ values obtained were $4.56\times10^5$ L/mol and the fluores-

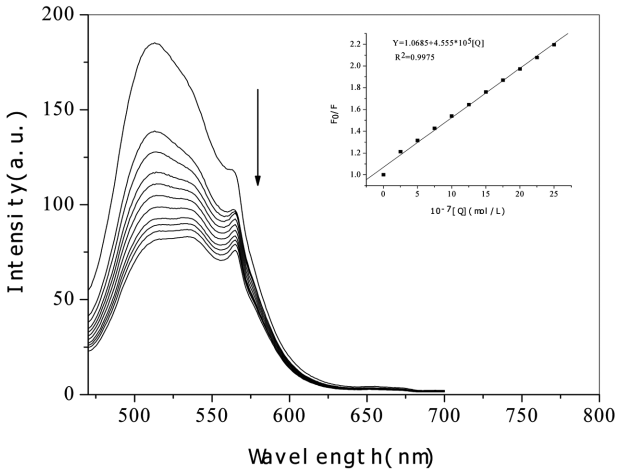



***Fig.* 4.** Fluorescence Quenching of $Eu^{3+}$ doped $TiO_2$ in the presence of various concentration of CPF(2.5-25)×$10^{-10}$ mol/L. The inset is the dependence of 1/($F_0$/F)on the reciprocal concentration of CPF.

cence lifetime of $Eu^{3+}$ doped $TiO_2$ was 3.67×$10^{-6}$ s, the $K_q$ value calculated was found to be 1.24×$10^{11}$ L/mol·s.

The decrease in fluorescence emission may be attributed to the various possibilities such as energy transfer, electron transfer or ground state complex formation between the $Eu^{3+}$ doped $TiO_2$ and CPF.

The band gap energy of $Eu^{3+}$ doped $TiO_2$ (3.0 eV) is greater than the excited state energy (2.88 eV) of CPF and there is no overlap between the fluorescence emission spectrum of $Eu^{3+}$ doped $TiO_2$ with the absorption spectrum of CPF (*Fig.* 5), so the above two inferences excluded the possibility of energy transfer from $Eu^{3+}$ doped $TiO_2$ to CPF.

The possibility of surface complex formation between $Eu^{3+}$ doped $TiO_2$ and CPF was the result out for quenching of $Eu^{3+}$ doped $TiO_2$ by CPF. Nano-$TiO_2$ had large specific surface area and strong adsorption capacity. With the

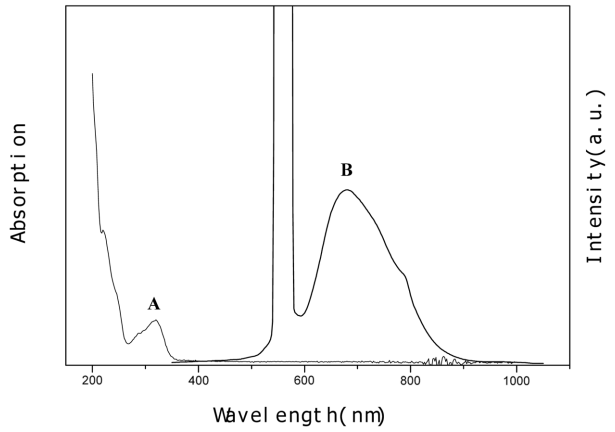



***Fig.* 5.** Absorption spectrum of CPF (A) and emission spectrum of $Eu^{3+}$ doped $TiO_2$ (B).

increasing concentration of CPF, it formed electric double layer on the surface, and impacted on the relation between surface states and of $Eu^{3+}$ doped $TiO_2$ and Fermi level,[7] it lead to carrier in the form of a non-radiative channels, thereby impacted on the luminescent of $Eu^{3+}$ doped $TiO_2$.

The ability of the excited state CPF to inject its electrons into the conduction band of $Eu^{3+}$ doped $TiO_2$ is determined by energy difference between the conduction band of $Eu^{3+}$ doped $TiO_2$ and oxidation potential of excited state CPF. The oxidation potential of excited state CPF is about -1.92 V (NHE),[8] The conduction band potential of $Eu^{3+}$ doped $TiO_2$ is -0.5 V (NHE), it suggested that electron transfer from excited state CPF to the conduction band of $Eu^{3+}$ doped $TiO_2$ is energetically favorable. Therefore, we concluded that the uorescence quenching shown in *Fig.* 6 was caused by electron transfer.

The thermodynamic feasibility of the excited state electron transfer reactions was calculated by employing the well-known Rehm-Weller expression:[9]

$$\Delta G_{et} = E_{1/2}^{(OX)} - E_{1/2}^{(red)} - E_S + C \tag{2}$$

Where, $E^{(ox)}{}_{1/2}$ is the oxidation potential of CPF (0.51 V), $E^{(red)}{}_{1/2}$ is the reduction potential of $Eu^{3+}$ doped $TiO_2$, $E_S$ is the singlet state energy of CPF (2.49 eV) and C is the coulombic term. Since one of the species is neutral and the solvent used is polar in nature, the coulombic term in the above expression is neglected.[10] The Get value was calculated as -1.42 eV and this higher negative Get value indicates electron transfer process which is thermodynamically favorable.

The principle based on the fluorescence intensity of $Eu^{3+}$ doped $TiO_2$ change to detect residues of chlorpyrifos. The standard curve of the detection of chlorpyrifos using $Eu^{3+}$ doped $TiO_2$ was shown in illustration (*Fig.* 4). The

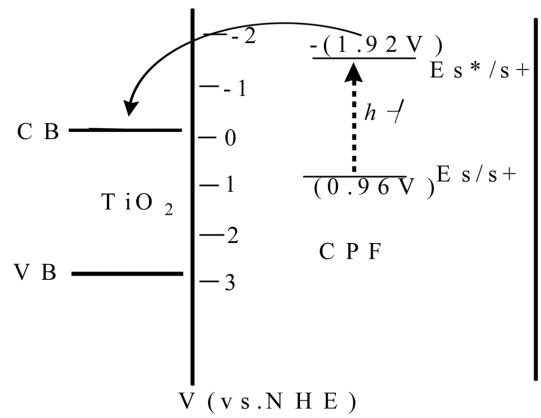



***Fig.* 6.** Schematic energy level diagram.

***Table* 1.** The detection method of chlorpyrifos

| Detection method | Range of detection (ng/mL) | Detection limit (μg/L) | Recovery (%) | References |
|---|---|---|---|---|
| Quantum dot | 15.2-205.5 | - | 90.8-108.2 | 11 |
| Immunochromatographic assay | 50-12150 | 132.91 | 102.5-107.6 | 12 |
| Electrochemical biosensor | 0.003-350 | 0.0003 | - | 13 |
| Resonance immunosensor | 45-64 | - | 80-120 | 14 |
| This methord | 0.875-87.5 | 0.0112 | 97.8-98.8 | |

***Table* 2.** Precision and recovery ($n$=5)

| Sample | Dosage×$10^{-10}$ (mol/L) | Recovery of spiked (mol/L) | Recovery (%) | RSD (%) |
|---|---|---|---|---|
| Chlorpyrifos | 2.00 | 1.975 | 98.8 | 0.43 |
| | 4.00 | 3.982 | 97.8 | 0.32 |
| | 6.00 | 5.963 | 98.7 | 0.15 |

equation is $F_0/F=1.0685+4.555\times10^5[Q]$, there is a good linear relationship between concentration of CPF ($5\times10^{-10}$ -$2.5\times10^{-7}$ mol/L) and the fluorescence intensity of $Eu^{3+}$ doped $TiO_2$, R=0.9975, the detection limit was $3.2\times10^{-11}$ mol/L and the recovery was 97.8%-98.8% (*Table* 2). This method had a wider range of pesticide concentration measurement compared with other detection methods (*Table* 1).

## CONCLUSION

Based on the above results, the electron transfer mechanism was proposed for the fluorescence quenching of $Eu^{3+}$ doped $TiO_2$ by CPF. This new rapid, simple and reproducible method should proved useful for detecting the residues of chlorpyrifos, but it can not determine the exact content of pesticide.

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