Fluorescence Optosensing of Triclosan by Upconversion Nanoparticles with Potassium Permanganate

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ABSTRACT: It is greatly significant to develop a simple and rapid sensing method for triclosan (TCS) because it is a widely used and a chronically toxic compound that adversely affects biological organisms and human health. This paper presents the design and development of a novel simple optosensor that uses carboxylic group-functionalized NaYF₄:Yb³⁺/Er³⁺ upconversion nanoparticles (UCNPs) coated with potassium permanganate (KMnO₄). The sensor enables the rapid, non-autofluorescence, sensitive, and selective detection of TCS based on the “turn-off” fluorescence technique through fluorescence resonance energy transfer. Under an near-infrared radiation excitation (980 nm), the “turn-off fluorescence” process involves the transfer of fluorescence resonance energy between the UCNPs and KMnO₄, whereas the “turn-on fluorescence” process occurs when KMnO₄ is reduced in the presence of TCS. TCS was detected by recovering the green emission of UCNPs. Under optimized conditions, the resulting sensor offered an excellent response to TCS with 0.2 μM of a limit of detection. The developed sensor showed higher selectivity to TCS than other phenolic compounds. Moreover, the analytical performance of the proposed probe was practically demonstrated to successfully monitor trace levels of TCS in samples of tap water and personal care products. The developed simple and sensitive method may offer a new approach for determining TCS in environmental applications.

1. INTRODUCTION

Triclosan (TCS) is widely used as an antimicrobial and preservative agent in household cleaners, toothpaste, soap, and plastics with a concentration ranging from 0.1 to 0.3% of product weight. It is found in ubiquitous environments including wastewater, drinking water, soils, and living organisms. However, once TCS has been released into the environment, it is considered as a toxic pollutant capable of disrupting endocrine compounds because its structure is similar to that of thyroid hormones. Moreover, TCS can kill normal bacteria by blocking the biosynthesis of lipids and causes mutated bacteria that become resistant to TCS and are more likely to survive and be reproduced. The growing awareness of the toxicity of TCS has led to an increasing demand for the development of highly sensitive analytical methods. In recent years, several analytical methods for the determination of TCS have been developed, among which are the methods based on chromatography, spectroscopy, immunoassay, and decomposition by an enzyme or radicals. However, these methods need expensive instrumentation and complicated procedures and require highly skilled personnel. In particular, methods that use fluorescent techniques for the determination of TCS have not yet been reported. Therefore, the development of a TCS optosensor with high sensitivity and selectivity remains a challenge that has not yet been addressed.

Potassium permanganate (Mn(VII); KMnO₄) is a strong oxidative agent that reacts with electron-rich moieties such as phenols, anilines, and olefins. Compared with other oxidants such as ozone, chlorine, and ferrate, KMnO₄ has several advantages such as its relatively low cost, ease of handling, effectiveness across a wide pH range, and comparative stability. In addition, the oxidation processes of antibiotics, phenolic endocrine disrupting chemicals, and organic pollutants have been demonstrated based on the reaction with Mn(VII) as an oxidant. The reactions of Mn(VII) with certain organic compounds commonly lead to the formation of a series of intermediates such as Mn(IV) or Mn(III) depending on the nature of the ligands. Stable Mn(III) has been found to be produced by the oxidation of organic substances in the presence of certain ligands, such as phosphate, pyrophosphate, ethylenediamine tetraacetic acid, and humic acid. In addition, Mn(IV) can be aggregated by an oxidative process to form brown colloids. This is stabilized by preventing the disproportionate oxidation of KMnO₄ and the formation of intermediates is accelerated by the oxidation of TCS by Mn(IV). Furthermore, Mn(VII) readily oxidizes TCS via several reactions including hydrogen abstraction, electron exchange, and direct oxygen transfer, thereby decreasing the adverse activity of TCS. Jiang’s group found that, during the Mn(VII)/TCS reaction, the absorption band of inherent Mn(VII) disappears from the range 490–590 nm.

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As a result, we expect KMnO₄ to be an excellent candidate for the detection of TCS by fluorescent materials that emit light in the blue and green bands of the visible spectrum. Compared with other fluorescent materials such as organic fluorescent dyes and quantum dots, upconversion nanoparticles (UCNPs) that emit visible light following an excitation with near-infrared radiation (NIR) have been widely used in biological and chemical applications. In particular, the use of NIR irradiation has attractive properties, including sharp emission, low toxicity, non-auto-fluorescence, absence of photodamage, and deep tissue permeability. NaYF₄, which has low phonon energy, is often used as the host material of the upconversion material with doping Yb³⁺ and Er³⁺. The Yb³⁺, Er³⁺ ions are the sensitizer and the activator, respectively. Under NIR excitation (980 nm wavelength), the fluorescent upconversion process appears when there are transfers of excited energy from Yb³⁺ ions to Er³⁺ ions. The relax process of Er³⁺ ions gives radiative transitions at the green band. The observed upconversion luminescence (UCL) spectra only originate from NaYF₄:Yb,Er. Therefore, one of the advantages of the fluorescent upconversion process is non-auto-fluorescence from the matrix of the sample when the sample is excited by NIR wavelength.

However, UCNPs synthesized via general methods have low solubility and lack the functional groups required to react with analytes. Therefore, it is necessary to modify the surface of UCNPs to enable them to selectively detect the target materials. Many researchers have developed UCNPs based on the fluorescence resonance energy transfer (FRET) process for sensing specific biomolecules. For example, UCNPs coated with manganese dioxide (MnO₂) nanosheets were designed for the detection of glutathione (GSH) and glucose (Glu) by using UCNPs as the donor and MnO₂ as the acceptor, which were released from UCNPs’ surface in the presence of GSH and Glu. UCNPs coated with MnO₂ indicated that the analytes could be effectively determined by controlling the fluorescence emission band. However, in their study, they used a core–shell structure, which was synthesized in an organic solvent, and either the surface of the UCNPs had to be modified such that they became hydrophilic nanoparticles or glucose oxidase was used (for sensing Glu).

In this work, we report for the first time a simple approach for the rapid and highly selective detection of TCS by using poly(acrylic acid) (PAA)-functionalized NaYF₄:Yb³⁺/Er³⁺.
UCNs coated with KMnO₄. The method was based on the FRET process that occurs in the green emission band, which was originated from the radiative transitions of Er³⁺ ions through the energy transfer process from Yb³⁺ ions. The UCNPs were synthesized via a one-step solvothermal method at 200 °C for 12 h. The PAA-functionalized NaYF₄:Yb³⁺/Er³⁺ UCNPs are high soluble in aqueous solution and react with added KMnO₄ by electrostatic interactions. The emission of green light (500−570 nm) by NIR-excited UCNPs donor is inhibited by KMnO₄ (FRET acceptor) via the FRET process. Upon TCS addition, KMnO₄ oxidizes TCS by attacking its hydroxyl group, thereby forming MnO₂, which does not absorb 500−570 nm. Thus, FRET is disrupted, and UCNPs emit green light, as shown in Scheme 1.

2. RESULTS AND DISCUSSION

2.1. Characterization of PAA-Functionalized NaYF₄:Yb³⁺/Er³⁺ UCNPs. The obtained UCNPs were characterized with field emission scanning electron microscopy (FE-SEM), X-ray diffractometry (XRD), energy-dispersive X-ray spectroscopy (EDS), and Fourier transform infrared (FT-IR), and the results are shown in Figure 1. The FE-SEM images show that the prepared UCNPs have uniform shapes and a particle size of 100 nm (Figure 1a). The XRD pattern of the sample corresponds with the referenced peak position and intensity of hexagonal NaYF₄ (JCPDS PDF 28-1192), confirming the formation of well-crystallized UCNPs (Figure 1b). Moreover, the EDS analysis revealed the composition of NaYF₄:Yb³⁺/Er³⁺ and PAA (Figure 1c). The functional groups on the surface of the obtained UCNPs were identified by recording FT-IR spectra. As shown in Figure 1d (black line), a broad absorption band at 3400 cm⁻¹ relates with O−H stretching vibrations. The peaks at 1720 and 1392 cm⁻¹ confirm the existence of the COOH group and the carboxylate anion, respectively. Other peaks are consistent with C=C stretching at approximately 1400−1550 cm⁻¹. More information on the synthesis and characterization of UCNPs can be found in Supporting Information.

Figure 2. (a) Absorption spectrum of KMnO₄ (blue line) and emission of the prepared UCNPs (black line), (b) absorption spectra at various concentrations of KMnO₄, and (c) effect of KMnO₄ concentration on UCL spectra after a reaction time of 2 h.

Figure 3. (a) Effect of reaction time on absorption spectra of UCNPs@KMnO₄ in the presence of TCS. (b) UCL spectra of UCNPs@KMnO₄ before (black line) and after addition of TCS (red line).
The COOH group on the surface of the UCNPs ensures good solubility and reacts with KMnO4. The peak at 528 cm$^{-1}$, which is the Mn=O stretching vibration, confirms the existence of this bond on the UCNPs.

2.2. Fluorescent Property of UCNPs@KMnO4. The UV−vis and UCL spectra of UCNPs@KMnO4 show that the absorption band of KMnO4 and the emission of UCNPs overlap in the region of 500−550 nm (Figure 2a). This overlap can lead to FRET from the UCNPs (as donor) to the KMnO4 (as acceptor) in the green emission band to decrease the UCL intensity of the UCNPs. The effect of the KMnO4 concentration on the absorbance and UCL intensity of UCNPs was assessed. We found that the absorption band appeared in the range of 400−450 nm when the concentration of KMnO4 exceeded 0.825 mM (Figure 2b). This band can be related to MnO2 because KMnO4 exists as MnO2 under neutral or slightly alkaline conditions.23 As shown in Figure 2c, the green emission of UCNPs decreased with increasing KMnO4 concentration and was completely quenched when the concentration of KMnO4 reached 1.65 mM. On the basis of this result, the value of 1.65 mM KMnO4 was selected for subsequent experiments.

The time dependence of the reaction between UCNP@KMnO4 and TCS was studied. Figure 3a shows the absorption spectra of a mixture of UCNP@KMnO4 and TCS after different reaction times. We found that the change of absorbance in the range of 500−550 nm was negligible with increasing the reaction time, whereas the nonspecific absorbance at a short range <500 nm corresponding to colloidal manganese oxides Mn(IV) gradually increased with increasing reaction time. The brown colloid Mn(IV), which was formed as the intermediate when Mn(VII) oxidizes TCS, can be observed by the naked eye. Although Mn(VII) is generally converted to the Mn(III) state when TCS is oxidized in the presence of a ligand, in the case of PBS, Mn(IV) rather than Mn(III) is formed.20−22 Therefore, a certain amount of MnO2 was formed and increased in the presence of TCS in the UCNPs@KMnO4 solution. The UCL intensity of UCNPs was quenched by coating KMnO4 because of the overlap between the absorption spectrum of KMnO4 and emission spectrum of UCNPs. By adding TCS, the UCL intensity was recovered. The UCL spectra of UCNPs@KMnO4 before and after adding TCS are shown in Figure 3b.

2.3. Detection on TCS-Possible Mechanisms. In this study, UCNPs@KMnO4 nanoparticles were used to detect TCS based on the “turn off−on fluorescence intensity” process. TCS oxidation by KMnO4 mainly involves two pathways, which are cleavage of the ether bond of TCS by free chlorine ferrate, O3, MnO2, and a benzene ring-opening reaction.23 On the basis of this information, we predicted cleavage of the ether bond because of the formation of MnO2 during the reaction of UCNPs@KMnO4, but the −OH stretching band on the FT-IR spectra (Figure 1d, red line) largely disappears after TCS is added. More significantly, the Mn−O stretching vibration at 528 cm$^{-1}$ increased compared to UCNPs@KMnO4. These results indicate that the hydroxyl group of TCS is attacked by KMnO4, after which the benzene ring-opening reaction occurs. After the addition of TCS, KMnO4 separated from the surface of the UCNPs. This is a result of the oxidation of TCS by KMnO4. As a result, the UCNPs' surface was exposed and released emission in the green band, as shown in Figure 3b. The addition of TCS to the UCNPs@KMnO4 solution strongly enhanced the green emission band of UCNPs@KMnO4 approximately 36 times upon exposure to 980 nm excitation.

On the basis of the abovementioned mechanisms, the TCS analytical performance of the proposed optosensor was investigated by measuring the recovery of the UCL intensity.
When TCS was directly added to UCNPs that have not been coated with KMnO₄, the UCL intensity remains unchanged, as shown in Figure 4a. However, the UCL intensity of UCNPs@KMnO₄ gradually increased with the addition of different TCS concentrations. The dependence of the UCL intensity of UCNPs@KMnO₄ on the TCS concentration is presented in Figure 4b.

The relationship between the UCL intensity and TCS concentration was estimated, as shown in Figure 4c. A calibration curve was established based on the relationship between the TCS concentration and UCL intensity $F_0/F$ ratios ($F_0$ and $F$ are the UCL intensities at 542 nm in the absence and presence of TCS, respectively), as displayed in Figure 4c. The results show that there are two linear ranges: the first one is in the range of 2–10 μM and the second one is in the range of 10–200 μM. The regression equation in the range of 2–10 μM is $F_0/F = -0.03364[TCS] + 0.43441$, where [TCS] is the concentration of TCS (μM) and the correlation coefficient is 0.9807. The detection limit (LOD) of the proposed sensor for TCS was calculated to be 0.2 μM according to the $3.3 \times SD/S$ equation (SD is standard deviation of the signal and $S$ is the slope of the calibration curve). The performance of the proposed method was additionally examined by comparing the results with those obtained by other methods, as shown in Table 1. Although the LOD value of the proposed method is comparable to those of electrochemical methods, the proposed optical method does not require sophisticated equipment and highly skilled personnel. Moreover, by using diluted acetone for dissolving TCS, the proposed method can be used to detect a high TCS concentration (to 200 μM).

The selectivity of the UCNPs@KMnO₄ optosensor was evaluated. The UCL response of UCNPs@KMnO₄ was assessed with compounds related to TCS, including bisphenol A (BPA), 4-chlorophenol (CP), 2,4-dichlorophenol (DCP), and pentachlorophenol (PCP) after reacting for 1 h at a concentration of 10 μM (Figure 4d). Compared to the other species, the UCL intensity was strongly recovered in the presence of TCS, showing the loss of the hydroxyl group as a consequence of the oxidation of TCS. However, all the other compounds except for PCP also have a hydroxyl group. Considering the second-order rate constants of the reaction of each of these compounds with KMnO₄ under neutral conditions, it is clear that the reaction of KMnO₄ with TCS is much faster than with the other compounds. Moreover, among the substituted phenols, the oxidative reactivity of TCS with manganese oxide (Mn(IV)) is comparable or higher. These results show the high sensitivity and selectivity toward TCS based on the UCNPs@KMnO₄ fluorescence properties.

### 2.4. Determination of TCS in Real Samples
To evaluate the applicability of the fluorescence sensing system, UCNPs@KMnO₄ was employed for the determination of TCS by analyzing tap water samples and commercially available personal care products. The tap water hand-wash samples were spiked with different amounts of TCS and the samples were analyzed to determine the TCS concentration. The results are summarized in Table 2. The recovery of TCS in tap water is 92 and 106.7, and 97 and 98% for hand-wash products with RSD < 4%, respectively. These values indicate that the proposed optosensor is satisfactory and suitable for the detection of TCS in practical applications.

The applicability of the proposed method was further assessed by determining the TCS in commercial toothpaste samples by the standard addition method. The results indicated that TCS levels of four different brands of toothpaste [2 g of toothpaste diluted into 1 L of distilled water (DW)] are 3.44, 9.32, 9.99, and 7.52 μM, which are comparable or similar to TCS levels compared with those with other methods. These results confirmed that this probe demonstrates good sensitivity and accuracy to monitor TCS in real samples.

### 3. CONCLUSIONS
In summary, this paper presents the first demonstration that TCS can be detected based on the "turn off→on" fluorescence of UCNPs@KMnO₄. A possible mechanism for the determination of TCS is that the UCL intensity of UCNPs@KMnO₄ is quenched in the green band by an energy transfer process between UCNPs and KMnO₄ and then recovered again in the presence of TCS. The novel TCS sensor possesses high sensitivity and selectivity. This study confirmed that UCNPs@KMnO₄ is a useful probe for determining TCS and that the method is broadly applicable to the environmental field.

### 4. MATERIALS AND METHODS

#### 4.1. Reagent and Materials
Ammonium fluoride (NH₄F), yttrium oxide (Y₂O₃, 99.99%), erbium oxide (Er₂O₃, 99.99%), ytterbium oxide (Yb₂O₃, 99.99%), TCS, cerificated reference material (CRM), BPA, DCP, PCP, potassium permanganate (KMnO₄), and phosphate buffer saline (PBS, pH = 7.4) were purchased from Sigma-Aldrich. PAA (M₆, = 2000) was obtained from Acros Organics. Concentrated hydrochloric acid (HCl) and ethylene glycol (EG) were obtained from Alfa Aesar. Sodium chloride (NaCl) and CP were purchased from Oriental Chemical Industries and Junsei Chemical Company, respectively. A stock solution of TCS (0.345 mM) was prepared in 5 mL of acetone solution (acetone/water = 5:95, v/v). All other reagents were of analytical grade and used as received without any further purification.

#### 4.2. Preparation of Hydrophilic NaYF₄:Yb³⁺/Er³⁺ UCNPs and Coated by KMnO₄
PAA-capped NaYF₄:Yb³⁺/Er³⁺ UCNPs were synthesized by a hydrothermal method and coated with KMnO₄. The details of the synthesis and modification process are described in our previous work. The fluorescence properties of the resulting UCNPs@KMnO₄ were measured using a fluorescence spectrophotometer (Hitachi F-7000, Japan) and the optical properties of the synthesized UCNPs were characterized by TEM (Hitachi H-7650, Japan) and X-ray diffraction (XRD) (Bruker D8 Advance, Germany). The sensitivity of the UCNPs@KMnO₄ optosensor was evaluated under different TCS concentrations, and the results showed that the UCL intensity of UCNPs@KMnO₄ is quenched in the green band by an energy transfer process between UCNPs and KMnO₄ and then recovered again in the presence of TCS. The novel TCS sensor possesses high sensitivity and selectivity. This study confirmed that UCNPs@KMnO₄ is a useful probe for determining TCS and that the method is broadly applicable to the environmental field.

### Table 1. Comparison with Other Methods

| method | LOD (μmol/L) | detection range (μmol/L) |
|--------|--------------|--------------------------|
| HPLC-sorptive extraction | 0.002 | 0.001–0.4 |
| electrochemical-polymer | 0.250 | 1–100 |
| capillary electrophoresis-UV | 0.015 | 0.07–7 |
| electrochemical-graphe | 0.6 | 0.6–30 |
| electrochemical-carbon nanotube | 0.005 | 0.003–7 |
| electrochemical-carbon NP | 10 | 1–120 |
| electrochemical-Au/graphene | 0.04 | 0.2–14 |
| electrochemical-multivalled carbon nanotube | 0.06 | 0.2–6 |
| FRET upconversion NP | 0.2 | 2–10 |

*This work.*

### Table 2. Recovery Study in Real Samples

| samples | spike (μM) | found (μM) | recovery (%) | RSD (n = 3, %) |
|---------|------------|------------|--------------|----------------|
| tap water | 3 | 3.2 | 106.7 | 3.68 |
| 5 | 4.6 | 92 | 3.96 |
| hand wash | 3 | 2.9 | 97 | 3.97 |
| 5 | 4.9 | 98 | 1.79 |

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Er\textsuperscript{3+} nanoparticles were synthesized using the following method\textsuperscript{44}. Typically, NaCl (2.4 mmol), RECl\textsubscript{3} (Y:Er:Yb = 80:2:18, 0.1 mmol), PAA 0.3 g were dissolved in 15 mL of EG and then NH\textsubscript{4}F (5 mmol) in 5 mL of EG was added while stirring. The resulting mixture was stirred at room temperature for 30 min and then transferred to a 30 mL Teflon-lined autoclave. The autoclave was heated at 200 °C for 12 h. After cooling to room temperature, the precipitates were separated from the mixture by centrifugation and washed with DW and ethanol several times, and dried in a vacuum oven at 50 °C overnight. The obtained UCNPs were dispersed in PBS buffer at a concentration of 0.2 mg/mL. To use the UCNPs for the detection of TCS, 1.65 mmol of K\textsubscript{3}MnO\textsubscript{4} was dissolved in PBS buffer and was added to the solution of UCNPs with stirring at room temperature for 2 h. The obtained UCNPs@K\textsubscript{3}MnO\textsubscript{4} samples were washed with DW for removing excess potassium, free manganese ions, and then re-dispersed in PBS buffer.

4.3. Detection of TCS. To a solution of 1.625 mL of the UCNPs coated with K\textsubscript{3}MnO\textsubscript{4} (UCNPs@K\textsubscript{3}MnO\textsubscript{4}) were added various amounts of TCS and then filled up to 3 mL by PBS buffer (pH 7.4). The TCS concentration in this experiment was in the range of 2–200 μM. The mixture was stirred at room temperature for 1 h. After the reaction, the fluorescence intensity was recorded under an excitation wavelength of 980 nm.

4.4. Sample Preparation. The availability of the proposed sensor was assessed by studying samples of tap water, handwash product, and four tubes of toothpastes. The tap water samples were collected from our laboratory at Changwon National University. Before use, the water samples were filtrated by using a 0.22 μm syringe filter and maintained at 4 °C in the dark.\textsuperscript{35} The commercial hand-wash product (0.5 g) was dissolved in 25 mL methanol with sonication for 30 min. After filtration, the solution was diluted 25-fold with DW. A stock solution of TCS (0.345 mM) was prepared by dissolving 99.89 mg of TCS in 5 mL of acetone and diluted with deionized water. Spiked samples were obtained by adding TCS solutions with different concentrations. The toothpaste samples that were analyzed to determine their TCS content were acquired at local markets. These samples were prepared by dispersing 1.25 g of toothpaste in 25 mL of DW under sonication for 15 min. The resulting suspension was diluted 25-fold with DW, and filtered by using a 0.45 μm syringe filters.\textsuperscript{46}

4.5. Characterizations. The crystal structure was determined using XRD (X’Pert PW3040/00, PANalytical; Almelo, The Netherlands) using Cu Kα (ratio Kα/2/β1 = 0.5) radiation with step mode (step size 0.02). The morphology of the samples was determined by FE-SEM (CZ/MIRA II LMH, Tescan, Czech). EDS emission spectra were measured using an EDAX X-ray detector incorporated with the FE-SEM. The electron beam was accelerated at 20 kV. FT-IR spectra were obtained using a Nicolet iS10 FT-IR spectrometer (Thermo Fisher Scientific, Madison, USA). The UCL emission spectra were recorded with a fluorescence spectrophotometer (Acton SpectraPro 750-triplet grating monochromator) containing a charge coupled device detector (Princeton EEV 1024 × 1024 and PI-Max 133 controller). A 980 nm laser diode was used as an excitation source, and was placed at an angle of 45° in front of the sample holder.

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