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Visual and fluorescent detection of acetamiprid based on the inner filter effect of gold nanoparticles on ratiometric fluorescence quantum dots

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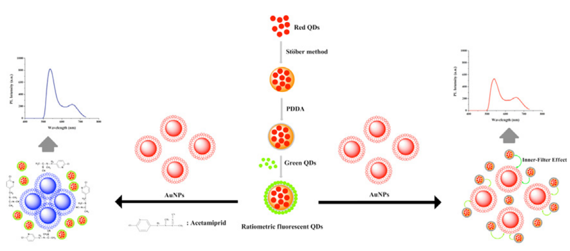
HIGHLIGHTS

- The RF-QDs were fabricated by two different QDs using layer-by-layer assembly methods.
- The PL intensity of RF-QDs could be quenched by AuNPs based on inner-filter effect.
- Acetamiprid can adsorb on AuNPs led to the PL intensity of RF-QDs recover properly.
- AuNPs serve a dual function as fluorescence quencher and colorimetric reporter in the sensor.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we develop a simple and rapid sensing method for the visual and fluorescent detection of acetamiprid (AC) based on the inner-filter effect (IFE) of gold nanoparticles (AuNPs) on ratiometric fluorescent quantum dots (RF-QDs). The RF-QDs based dual-emission nanosensor was fabricated by assembling green emissive QDs ($QDs_{539\,nm}$, λ_{em} = 539 nm) on the surface of red emissive QDs ($QDs_{661\,nm}$, λ_{em} = 661 nm)-doped silica microspheres. The photoluminescence (PL) intensity of RF-QDs could be quenched by AuNPs based on IFE. Acetamiprid can adsorb on the surface of AuNPs due to its cyano group that has good affinity with gold, which could induce the aggregation of AuNPs accompanying color change from red to blue. Thus, the IFE of AuNPs on RF-QDs was weakened and the PL intensity of RF-QDs was recovered accordingly. Under the optimized conditions, the PL intensity of the RF-QDs/AuNPs system was proportional to the concentration of AC in the range of 0.025–5.0 $\mu g\,mL^{-1}$, with a detection limit of 16.8 $\mu g\,L^{-1}$. The established method had been used for AC detection in environmental and agricultural samples with satisfactory results.

1. Introduction

Acetamiprid (AC), belongs to the new neonicotinoid class insecticides, has been widely used to control sucking-type insects [1–3]. Known as its relatively low and chronic mammalian toxicity, AC has been considered as replacement insecticide of organophosphorus and other conventional insecticides. Due to its

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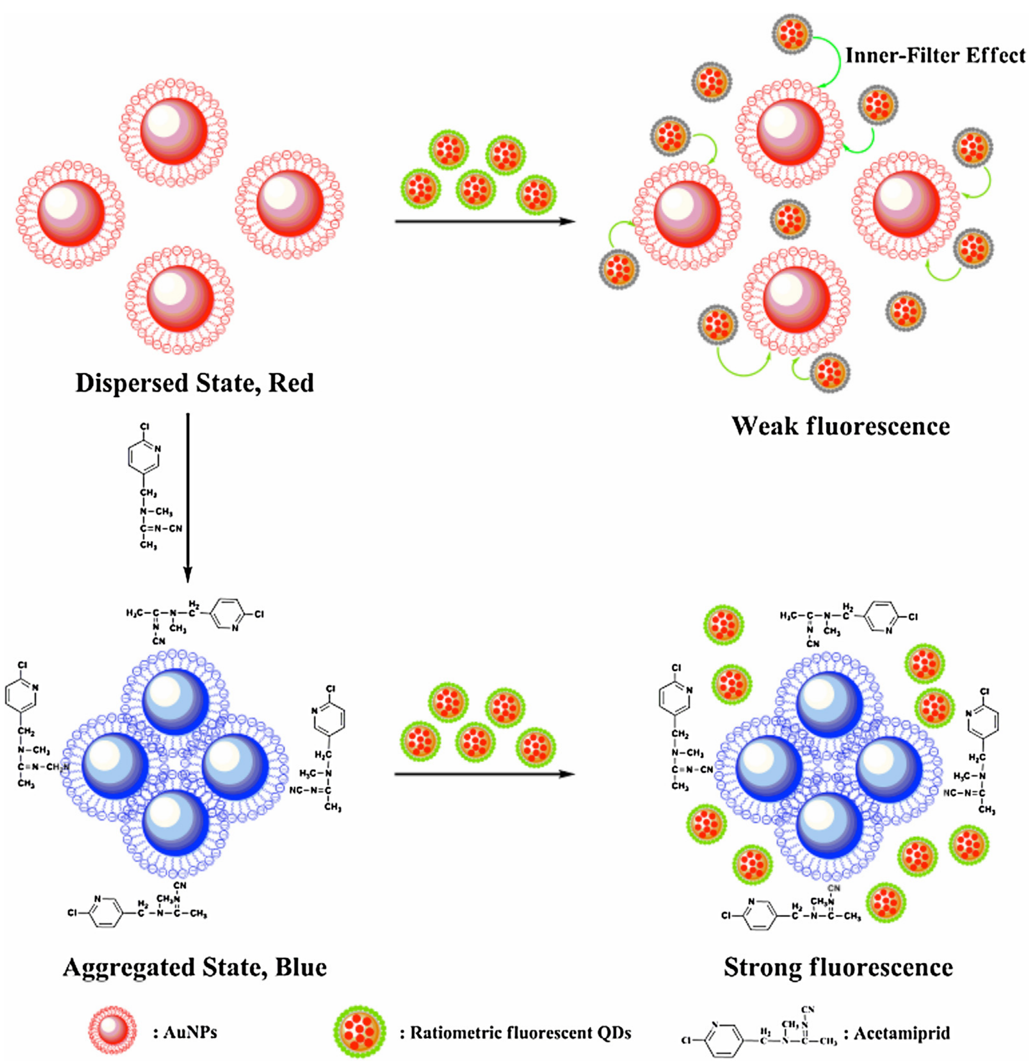
frequent and extensive usage, AC accumulated in the crops, vegetables and water will cause potential risk to human health [1,2]. Therefore, practical methods with high sensitivity and selectivity for simple and rapid detection of AC residues are crucial for human health and environment pollution monitoring. Current methods for AC detection mainly include the Association of Official Analytical Chemists methods, and enzyme-linked immunosorbent assays (ELISA) [4–6]. These methods require expensive instrumentation, complex sample preparation and purification procedures. ELISAs are susceptible to interferences from organic solvent or matrix components and also to need for costly bio-molecular reagents.

Ratiometric fluorescent (RF) methods, in which analyte concentrations are detected by measuring the ratios of photo-luminescence (PL) intensities at two wavelengths, possess a built-in correction that eliminates false signals emanating from environmental effects and therefore increases signal accuracy [7]. They are simply obtained by combining two different fluorophores in one nanoparticle, one fluorophore as reference and another as a signal report unit. RF technique has been used not only for the ratiometric fluorescent detection but also for rapid visual sensing as chemo/bio sensors [8–17]. Many ratiometric sensors employing fluorescent organic dyes are usually susceptible to photobleaching and exhibit generally broad emission bands and narrow excitation wavelength range [18–20]. Such properties of organic dyes often make it hard to construct efficient RF sensors. Compared with those ratiometric sensors employing fluorescent organic dyes, ratiometric fluorescent-quantum dots (RF-QDs) show several distinct advantages, such as better stability with respect to photobleaching, narrower spectral line-width and size-controlled luminescence properties [18,21–23]. Recently, RF-QDs sensors have been constructed for small molecule substances and pH sensors [11,12,22,23].

The combination of QDs and other functional nanoparticles (gold nanoparticles) in one micro matrix is expected to result in ideal sensors. Gold nanoparticles (AuNPs) have been successfully applied for detecting a large variety of targets owing to its unique size-dependent optical properties and the accompanying color change of solution [24–26]. It also has been used as colorimetric sensor for AC detection [2,27,28]. The inner-filter effect (IFE) of AuNPs on QDs has been considered as an efficient strategy in developing fluorescent methods. The IFE refers to the absorption of the excitation and/or emission light of fluorophores by absorbers in the detection system [29–31]. Compared to the conventional fluorescence resonance energy transfer-based fluorescent methods, IFE does not require chemical linkage between absorber and fluorophore. And it has been applied for various analytes detection [31–34].

In this study, RF-QDs are used for the construction of an effective fluorescence sensor and AuNPs are used as fluorescence



Scheme 1. Illustration of the fluorescent detection of acetamiprid through the inner-filter effect of gold nanoparticles on QDs.