



## Trace Detection Towards 2,4,6-Trinitro Phenol at Surface of TiO<sub>2</sub> Nanoparticles Based on Fluorescence Resonance Energy Transfer†

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This paper reports a resonance energy transfer-fluorescence quenching of 4-methyl coumarin at the surface of titanium dioxide nanoparticles for the ultrasensitive and ultratrace detection of 2,4,6-trinitro phenol in solution environments. The fluorescence resonance energy transfer-based nanoparticle sensors with high fluorescence brightness were synthesized by covalently linking a hybrid monolayer of dye and amine onto the surface of titanium dioxide nanoparticles through alkoxy silane coupling reactions. The linear range is  $1 \times 10^{-4}$ - $10^{-5}$  mol L<sup>-1</sup> with a detection limit of  $1 \times 10^{-11}$  mol L<sup>-1</sup> and the fluorescence quenching constants of 4-methyl coumarin-APTS-TiO<sub>2</sub> nanoparticles towards 2,4,6-trinitrophenol is  $2.322 \times 10^4$  mol L<sup>-1</sup> L, which is much larger than those with 2,4,6-trinitro toluene, 2,4-dinitro toluene and nitro benzene, respectively. The results show that the novel strategy is ultrasensitive for the trace detection of 2,4,6-trinitro phenol.

**Key Words:** 2,4,6-Trinitrophenol, Fluorescence quenching, 4-Methyl coumarin, TiO<sub>2</sub> nanoparticles, Fluorescence resonance energy transfer.

### INTRODUCTION

The powerful explosivity and deleterious pollution of nitroaromatic compounds have concurrently raised world-wide concerns of public security and environmental problem, due to their wide production and use as explosives in military and engineering. The presently used detections of nitroaromatics are usually time-consuming with the employment of cumbersome and expensive gas chromatography coupled to a mass spectrometer, ion mobility spectrometry and neutron activation analysis<sup>1</sup>. Therefore, the development of ultrasensitive chemosensors for the real-time detection of nitroaromatics has attracted considerable research efforts in recent years<sup>2-7</sup>. Because of overlapping between the fluorescence emission spectrum of 4-methyl coumarin (4-MU) and the ultraviolet-visible absorbance spectrum of 2,4,6-trinitro phenol (TNP), in principle, it has been demonstrated that the detection of 2,4,6-trinitro phenol based on resonance energy transfer-fluorescence quenching of 4-methyl coumarin maybe occurs at spatial-approaching between fluorophores and analytes at the surface of TiO<sub>2</sub> nanoparticles. Moreover, of various signal transducers, fluorescence quenching-based chemosensors is best suitable for the detection of aromatic nitroexplosive. Herein, the fluorescence quenching base on fluorescence

resonance energy transfer (FRET) can sensitively detect the ultratrace aromatic nitroexplosive in solution and vapour environments and selectively distinguish the different types of nitrocompounds.

### EXPERIMENTAL

**Preparation of (4-MU)-APTS-TiO<sub>2</sub> Nanoparticles:** Typically, the uniform TiO<sub>2</sub> nanoparticles with a size of 200 nm were synthesized by the hydrolysis of tetraethoxy titanium (TEOT) in aqueous ammonia solution. Then, the 4-methyl coumarin dye were prepared by the radical substitution of N-bromosuccinimide (NBS) with 7-hydroxyl-4-methylcoumarin. To prepare the TiO<sub>2</sub> nanoparticles with a hybrid monolayer of 4-MU dye and amino group, the 4-MU dye with the brooethyl group with the nucleophilic substitution reaction of 3-amino-propyl triethoxysilane (APTS) were anchored onto the surface of TiO<sub>2</sub> in absolute alcohol solution. The preparing (4-MU)-APTS-TiO<sub>2</sub> nanoparticles were carried out in dark for 24 h by slowly stirring the solution containing the 4-methyl coumarin dye with succinimide group and an excess of APTS in anhydrous ethanol by a covalence-coupling reaction of the TiO<sub>2</sub> nanoparticles. The excess of 4-methyl coumarin dye and APTS was finally removed by washing the products with ethanol.

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## RESULTS AND DISCUSSION

**Ultratrace detection towards aromatics nitroexplosive 2,4,6-trinitro phenol in solution:** The SEM image of Fig. 1A shows that the (4-MU)-APTS-TiO<sub>2</sub> nanoparticles are still highly spherical and monodisperse and the surface of particles is very smooth after the chemical modification by the examination of SEM. The inset (Fig. 1B) shows the optical images of (4-MU)-APTS-TiO<sub>2</sub> nanoparticles solution under 360 nm UV lamp, respectively. The solutions of (4-MU)-APTS-TiO<sub>2</sub> nanoparticles display the fluorescence emission maximum peaks of dye fluorophores with the max at 448 nm (excited at 358.5 nm), which are identical to the emission spectra of corresponding pure dyes.

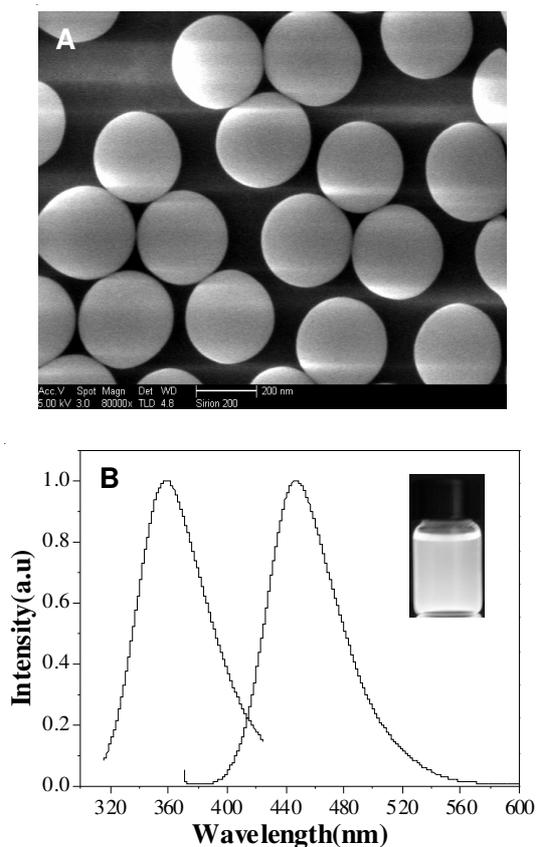


Fig. 1. (A) SEM image of (4-MU)-APTS-TiO<sub>2</sub> nanoparticles. (B) The excitation and emission spectra of (4-MU)-APTS-TiO<sub>2</sub> nanoparticles solution, the colour inset is optical image under 360 nm UV lamp

The fluorescence quenching of (4-MU)-APTS-TiO<sub>2</sub> nanoparticles sensor is applicable to detect ultratrace 2,4,6-trinitro phenol analyte. By comparison Fig. 2A with 2B, however, we can clearly find that the fluorescence intensities of the (4-MU)-APTS-TiO<sub>2</sub> nanoparticles sensor decrease with increasing successive aliquots of TNP concentrations. The liner range is  $1 \times 10^{-4}$ - $10^{-5}$  mol L<sup>-1</sup> and its detection limit is down to  $1 \times 10^{-11}$  mol L<sup>-1</sup>.

**Quenching efficiency with the different aromatic nitro-compounds:** We have further confirmed the quenching response of the (4-MU)-APTS-TiO<sub>2</sub> nanoparticles sensor to 2,4-dinitrotoluene (DNT), nitrobenzene (NB) and 2,4,6-trinitrotoluene (TNT), which are structural analogues of 2,4,6-trinitro phenol. As listed in Table-1, the quenching constants of (4-MU)-APTS-

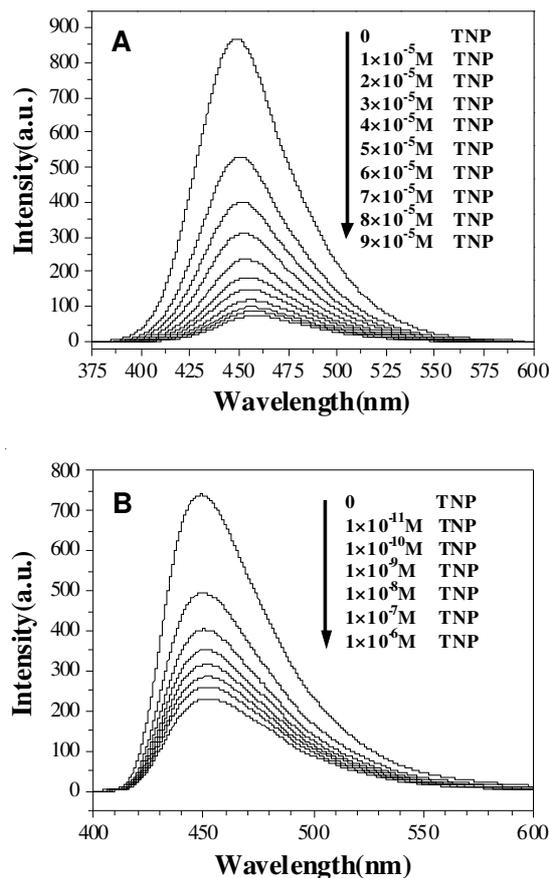


Fig. 2. Evolution of fluorescence spectra of (4-MU)-APTS-TiO<sub>2</sub> with increasing TNP concentration (A) and the detection limit to TNP (B)

TABLE-1  
SUMMARY OF QUENCHING CONSTANTS  $K_{sv}$  WITH NITROCOMPOUNDS ANALYTES IN SOLUTION

|                              | $\lambda_{exc}$<br>(nm) | $K_{sv}$<br>(TNP)   | $K_{sv}$<br>(TNT)   | $K_{sv}$<br>(DNT)   | $K_{sv}$<br>(NB)    |
|------------------------------|-------------------------|---------------------|---------------------|---------------------|---------------------|
| (4-MU)-APTS-TiO <sub>2</sub> | 448                     | $2.322 \times 10^4$ | $4.628 \times 10^3$ | $4.724 \times 10^3$ | $3.009 \times 10^3$ |

TiO<sub>2</sub> nanoparticles with TNP is  $2.322 \times 10^4$  and it is much larger than those with 2,4-dinitrotoluene, nitrobenzene and 2,4,6-trinitrotoluene, respectively. The larger quenching constants for the (4-AU)-APTS-TiO<sub>2</sub> nanoparticles towards TNP mainly is the partially overlapping between the emission spectrum of (4-AU)-APTS-TiO<sub>2</sub> nanoparticles and the UV-visible absorbance spectrum of TNP, resulting to FRET occurring at spatial approach. However, the other aromatic nitrocompounds, such as nitrobenzene, 2,4-dinitrotoluene and 2,4,6-trinitrotoluene do not overlap the spectra between them, therefore, their quenching constants are much smaller, as shown in Fig. 3.

### Conclusion

We have demonstrated the fluorescence quenching toward the ultrasensitive detection of 2,4,6-trinitro phenol by the use of dye fluorophores at the surface of TiO<sub>2</sub> nanoparticles. Mean while, the non-emissive fluorescence resonance energy transfer between the dye-APTS-TiO<sub>2</sub> nanoparticles and the 2,4,6-trinitro phenol in the spatial proximity leads to a quenching response. The processes have achieved the ultrasensitive

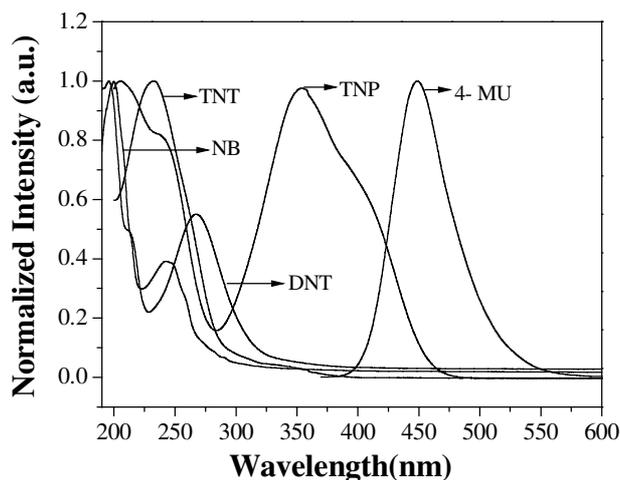


Fig. 3. Normalized intensity absorbance spectra of DNT, NB, TNT and TNP and emission spectrum of (4-MU)-APTS-TiO<sub>2</sub>, respectively

detection of 2,4,6-trinitro phenol in solution and selectively distinguished 2,4,6-trinitro phenol from other types of aromatic nitrocompounds.

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