Instant Visual Detection of Trinitrotoluene Particulates on Various Surfaces by Ratiometric Fluorescence of Dual-Emission Quantum Dots Hybrid

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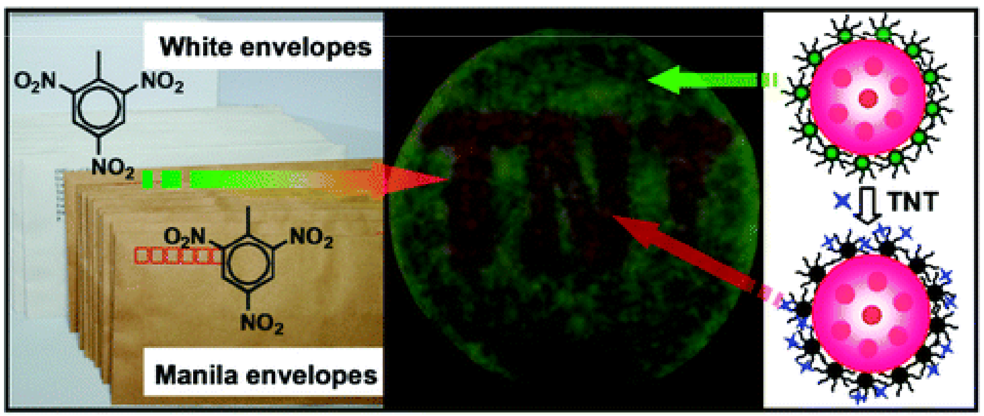

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Ammu Mathew

Introduction

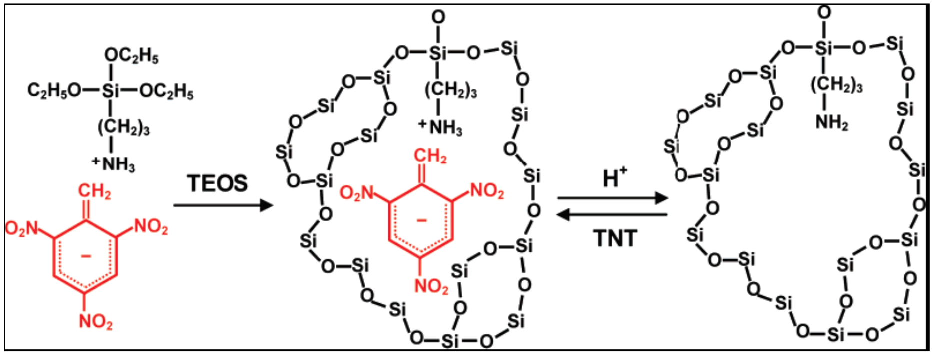
• Trace detection of TNT explosives **instantly and on-site** are in high demand for homeland security needs against terrorism (mail sorting centers, airports and luggage, transit centers, and other civilian situations).

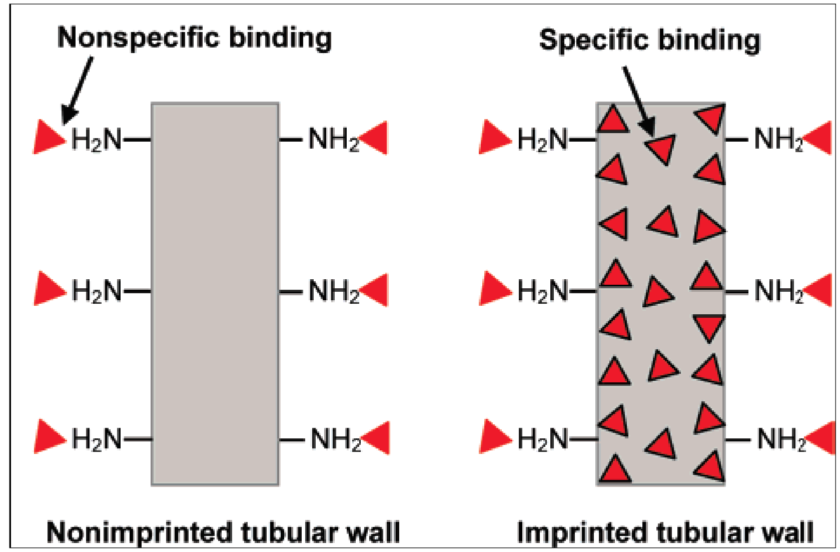
• Current methods of detection of TNT residue on solid surfaces are commonly performed **off-site** and involve **complex instrumentation** such as ion mobility spectrometry, gas/liquid chromatography, mass spectrometry, and surface acoustic wave method, which require frequent instrument calibration, sophisticated vapor sampling, and preconcentration procedures.

• Detection using chemosensors and biosensors (portable, visual, and operating ease of sensitive techniques).

• Fluorescent quantum dots - Single-excitation/multiple- emissions for signal transduction, feasibility of surface grafting for chemical recognition of TNT, which is central to ratiometric fluorescence detection.

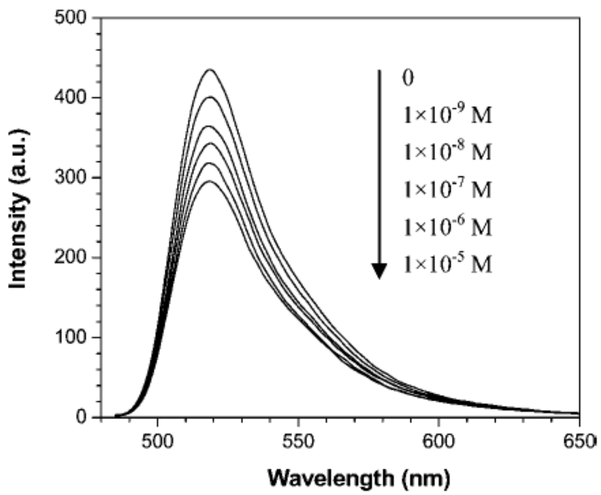
Molecular Imprinting at Walls of Silica Nanotubes for TNT Recognition

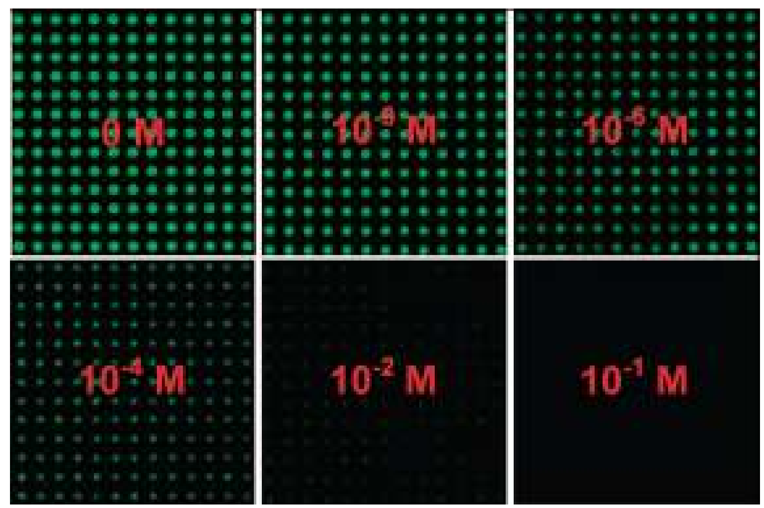




Anal. Chem. 2008, 80, 437-443

Fluorescence Quenching at Surface of Silica Nanoparticles -Ultrasensitive Detection of TNT



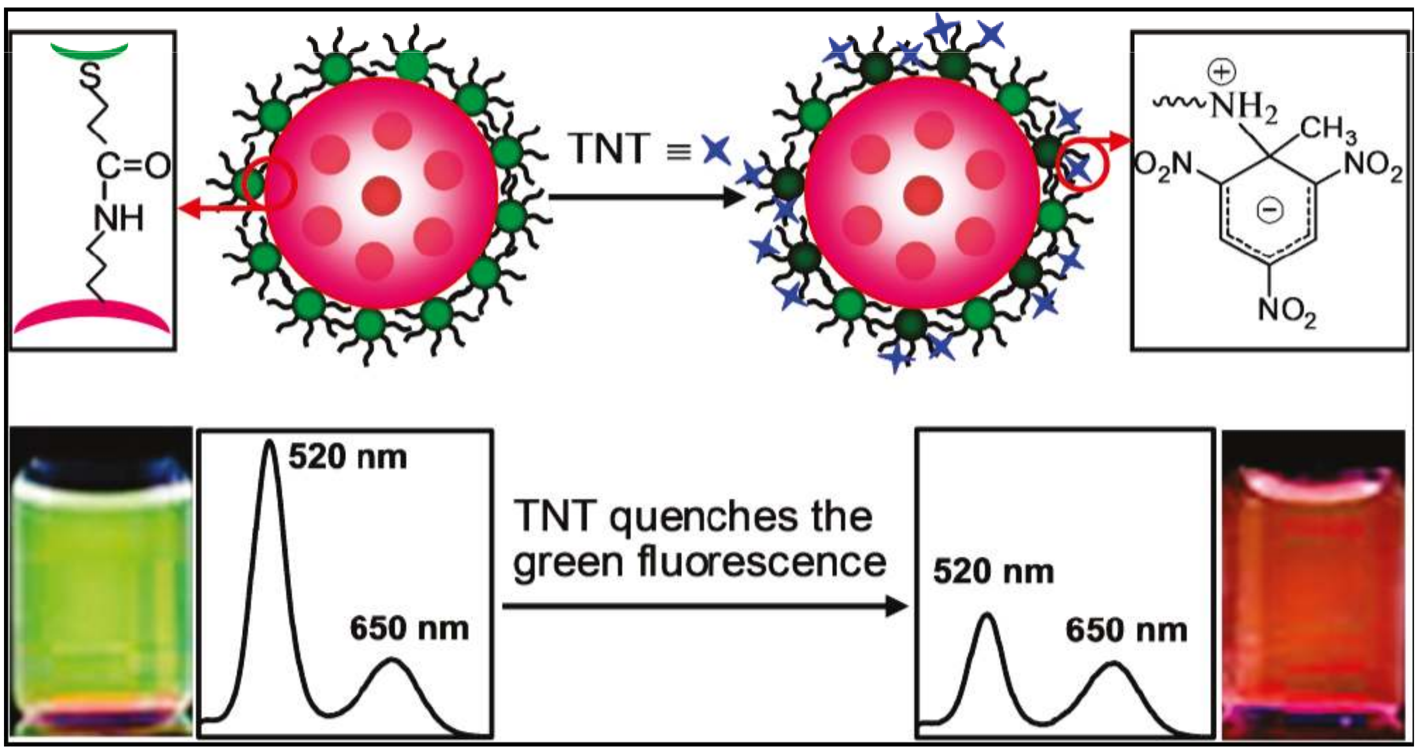


Anal. Chem. 2008, 80, 8545–8553

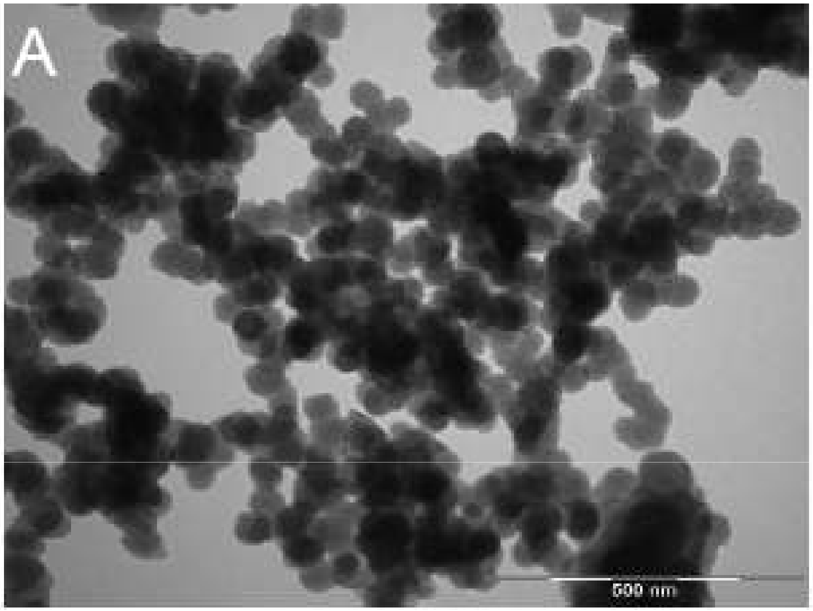
In this paper:

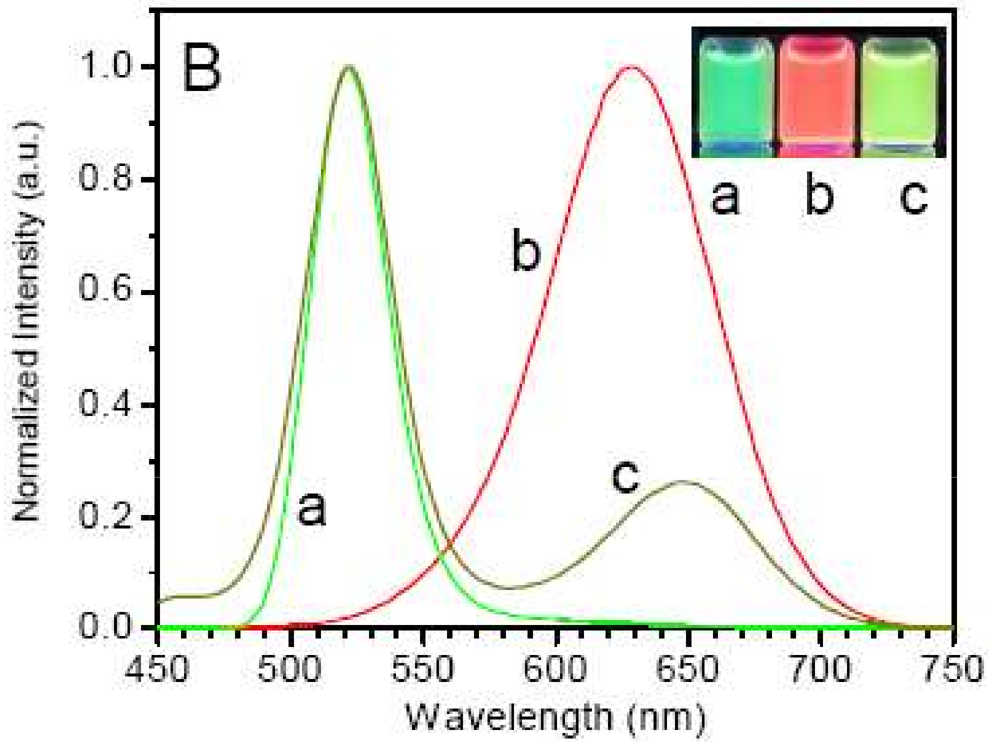
- Two differently sized CdTe QDs (emitting red and green fluorescences) have been hybridized by embedding the red-emitting one in silica nanoparticles and covalently linking the green-emitting one to the silica surface, respectively, to form a dual-emissive fluorescent hybrid nanoparticle.
- The fluorescence of red QDs in the silica nanoparticles stays constant, whereas the green QDs functionalized with polyamine can selectively bind TNT by the formation of Meisenheimer complex, leading to the green fluorescence quenching due to resonance energy transfer.
- The variations of the two fluorescence intensity ratios display continuous color changes from yellow-green to red upon exposure to different amounts of TNT.

Schematic illustration of the structure of the ratiometric fluorescent probe and the working principle for the visual detection of TNT.



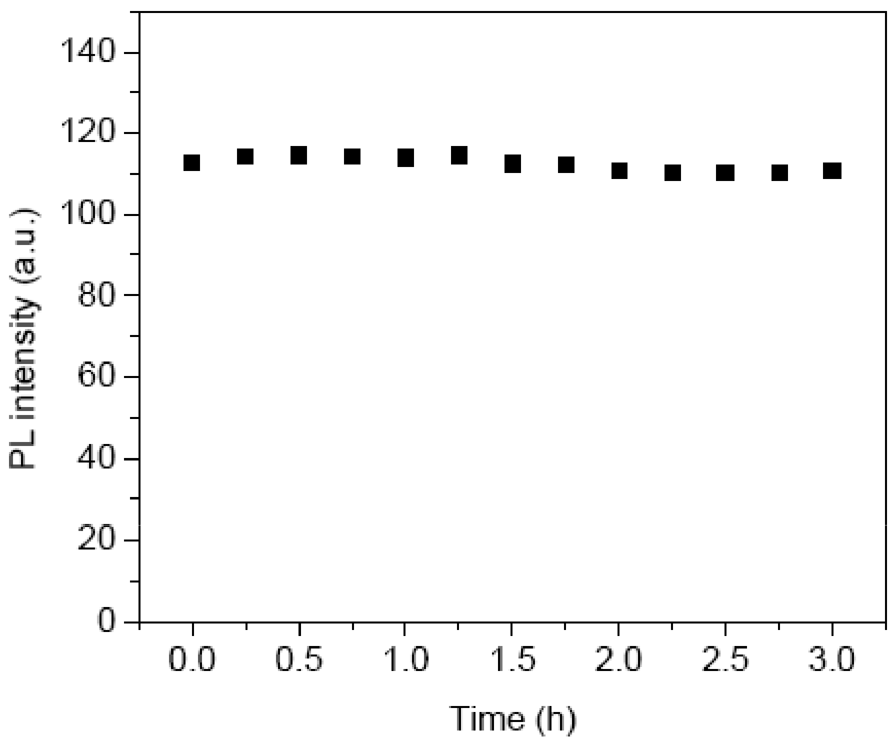
Dual-emission quantum dots hybrid silica nanoparticles

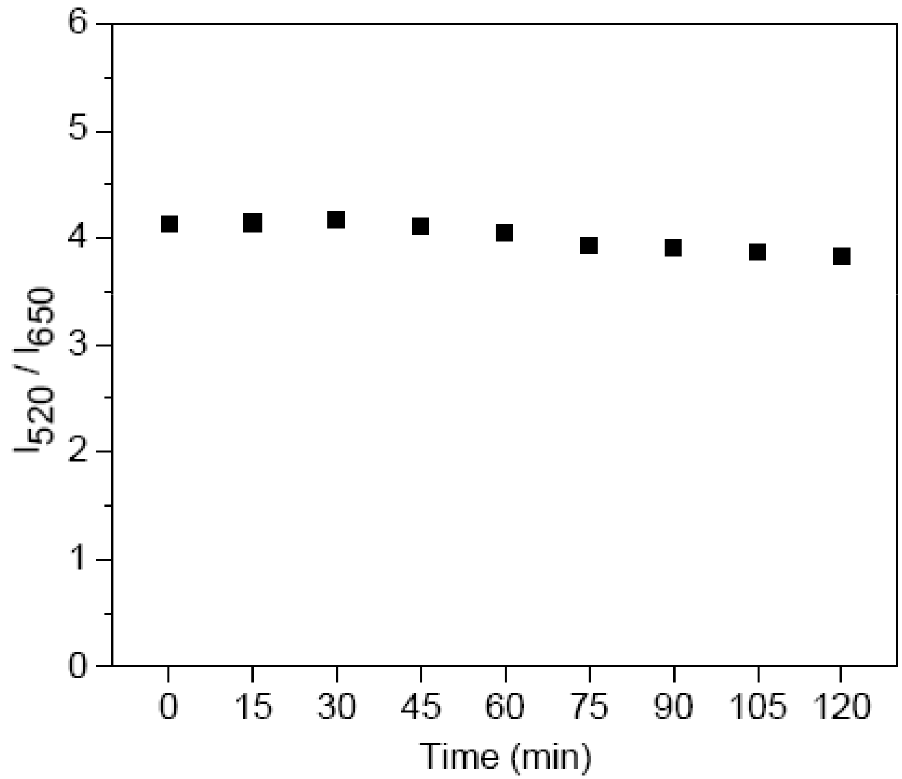




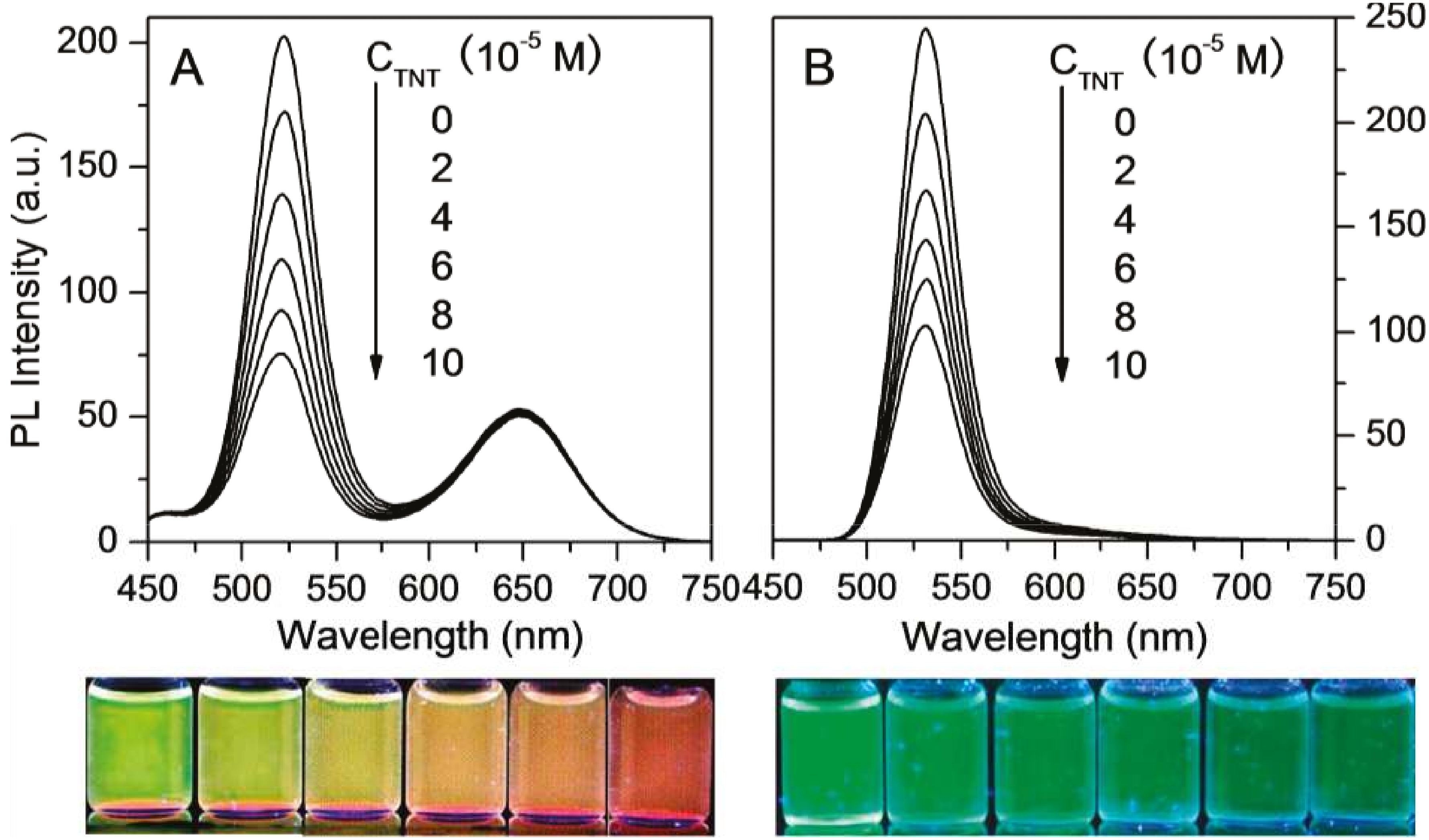
(A) TEM image of dual-emission quantum dots hybrid silica nanoparticles.
(B) Normalized fluorescence emission spectra of (a) green QDs (b) red QDs and (c) the ratiometric probe solution. The inset shows the optical photos of green QDs, red QDs and the ratiometric probe solution under a 365 nm UV lamp, respectively.

Stability of the fluorescence intensity of the red fluorescent QDs doped silica nanoparticles.



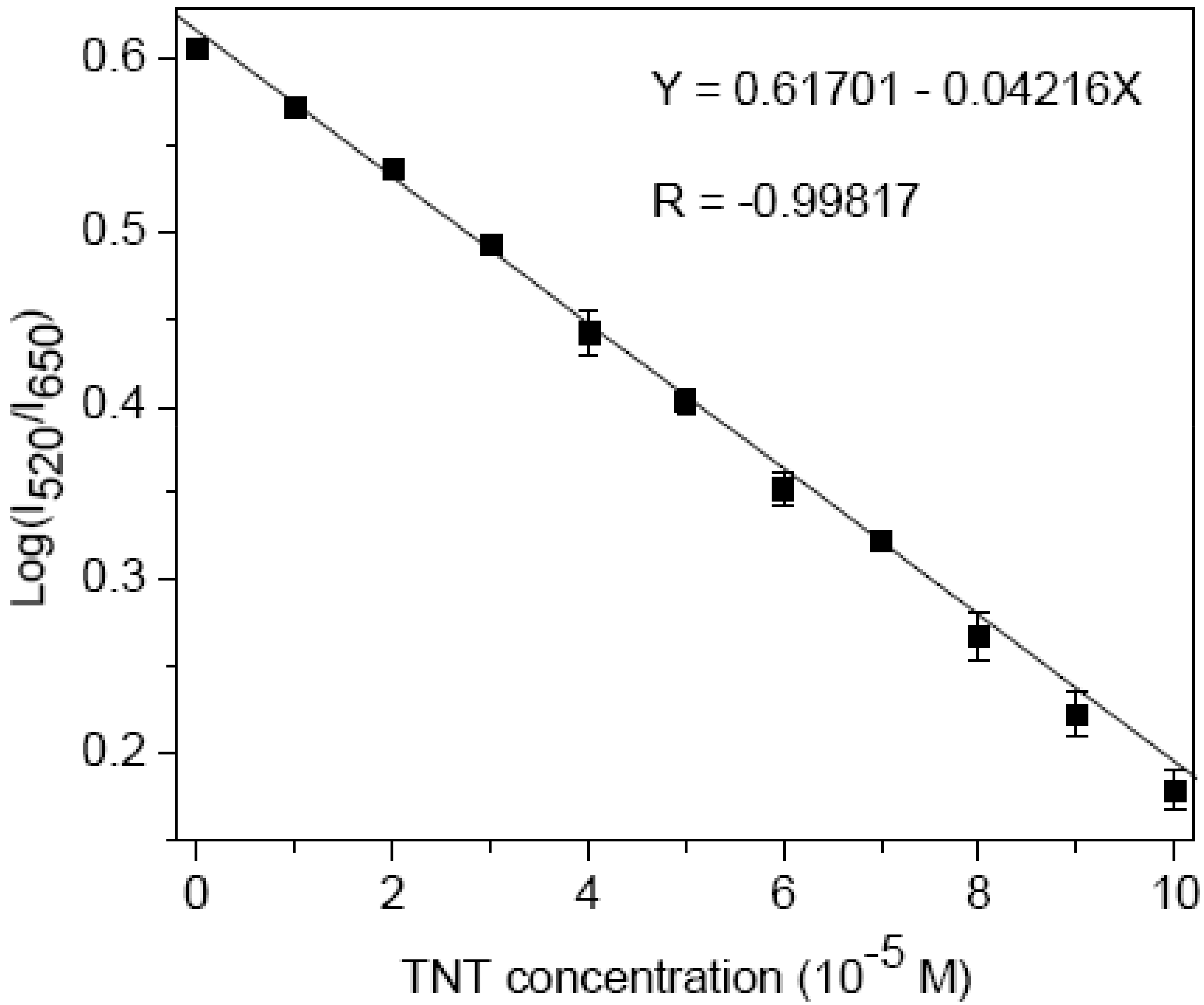


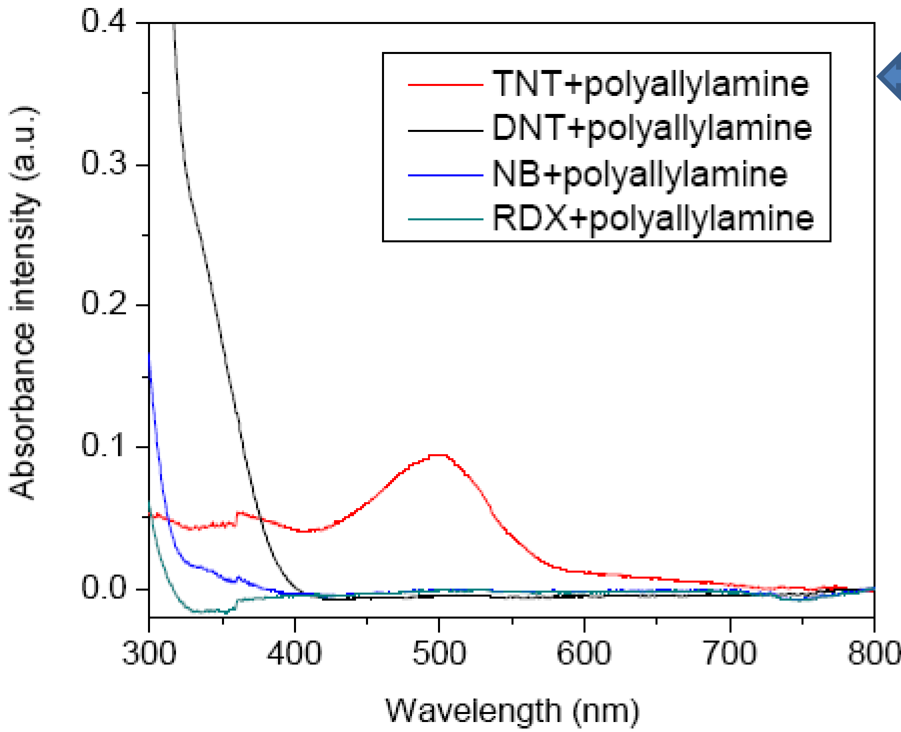
Stability of the fluorescence intensity of the ratiometric probe at 520 nm versus that at 650 nm. The change of the relative intensity (I_{520}/I_{650}) is not significant (<5 %) in 2 hours.



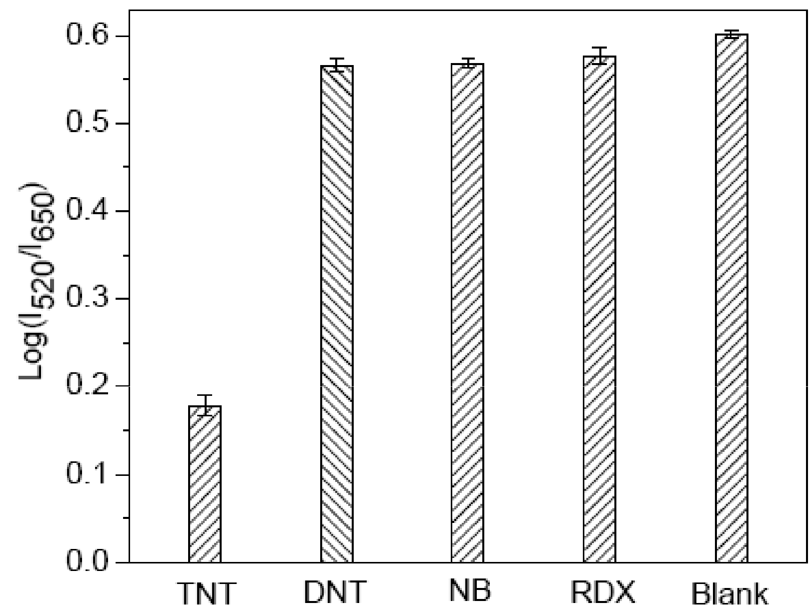
Dependence of the fluorescence spectra (λex = 365 nm) of (A) the ratiometric probe and (B) the pure green QDs modified with polyallylamine upon exposure to different amount of TNT. (Bottom panel) Comparison between the fluorescence colors of the ratiometric probe solutions (left) and the pure green QDs solutions (right) after exposure to TNT. The concentrations of TNT from left to right are 0, 2×10^{-5}, 4×10^{-5}, 6×10^{-5}, 8×10^{-5}, and 10×10^{-5} mol/L, respectively. Photos were taken under a 365 nm UV lamp.

Changes in the fluorescence intensity of the ratiometric probe solution at 520 nm versus that at 650 nm upon the addition of TNT.

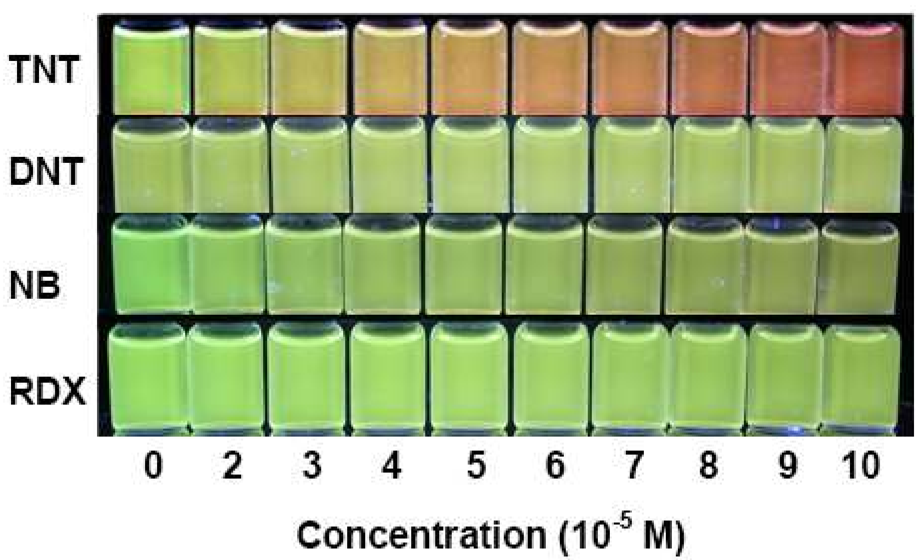




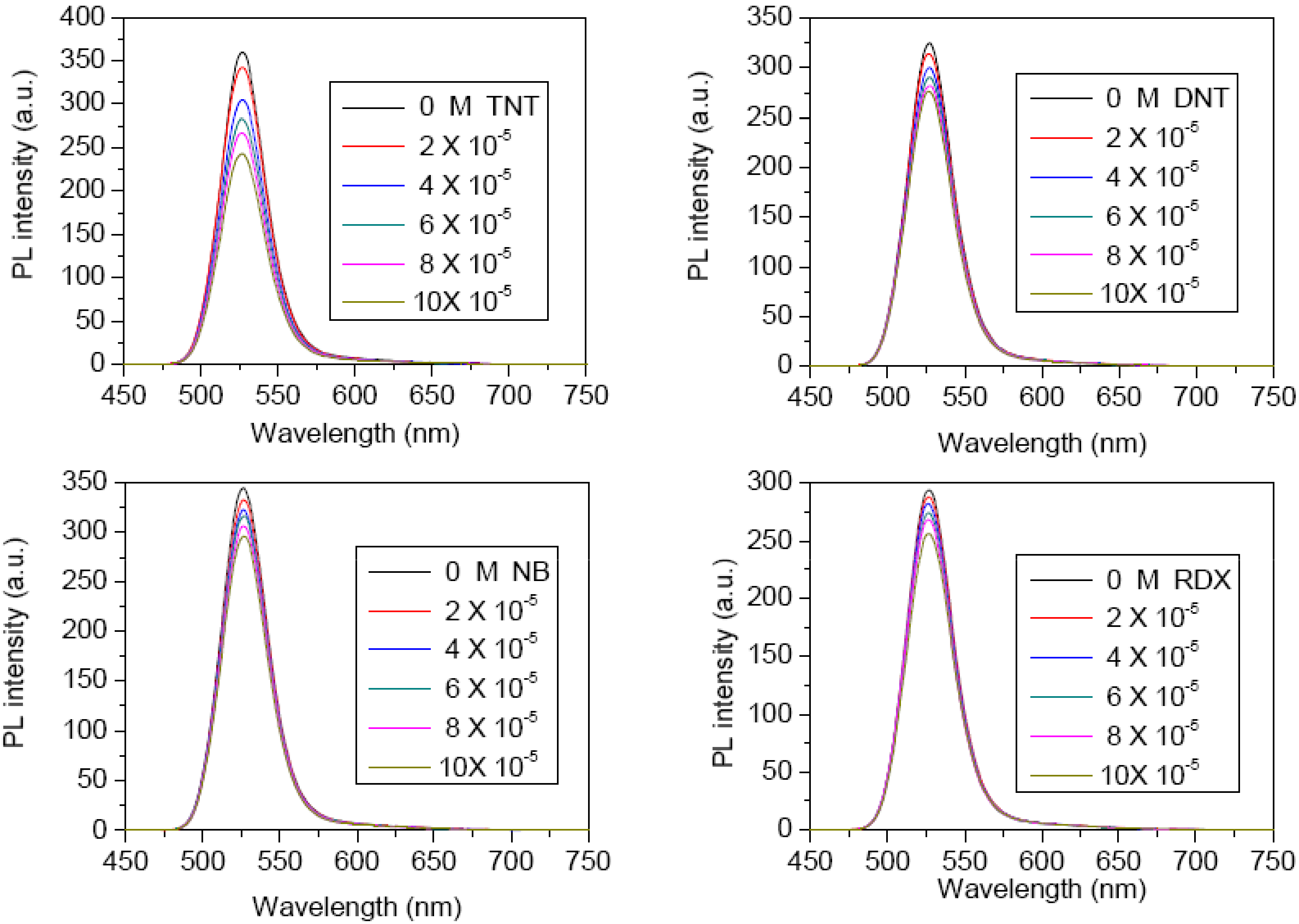
The evolution of UV-visible spectra with adding 20 mg of polyallylamine into 20 mL of 1 mM TNT, DNT, NB, and RDX, respectively.



Changes in the fluorescence intensity of the probe solution at 520 nm versus that at 650 nm upon the addition of 1×10^{-4} M of nitro analytes, respectively.

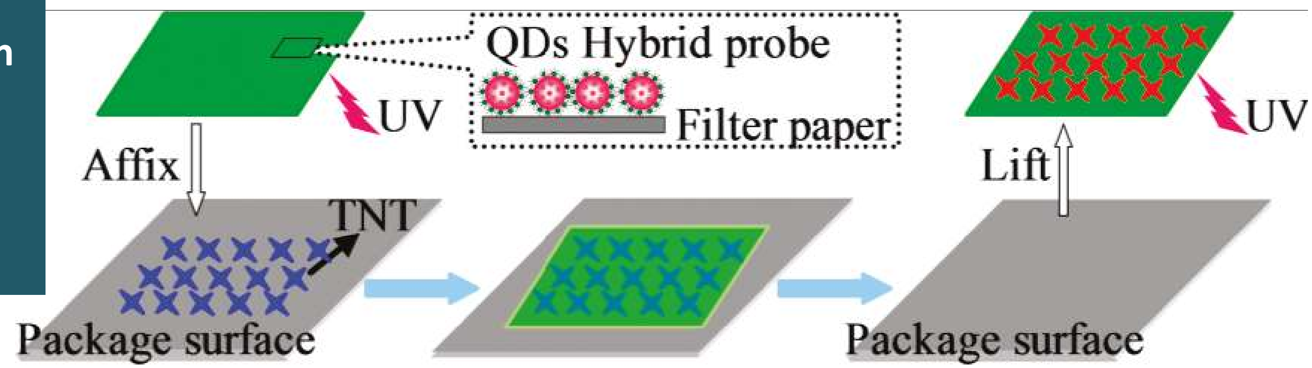


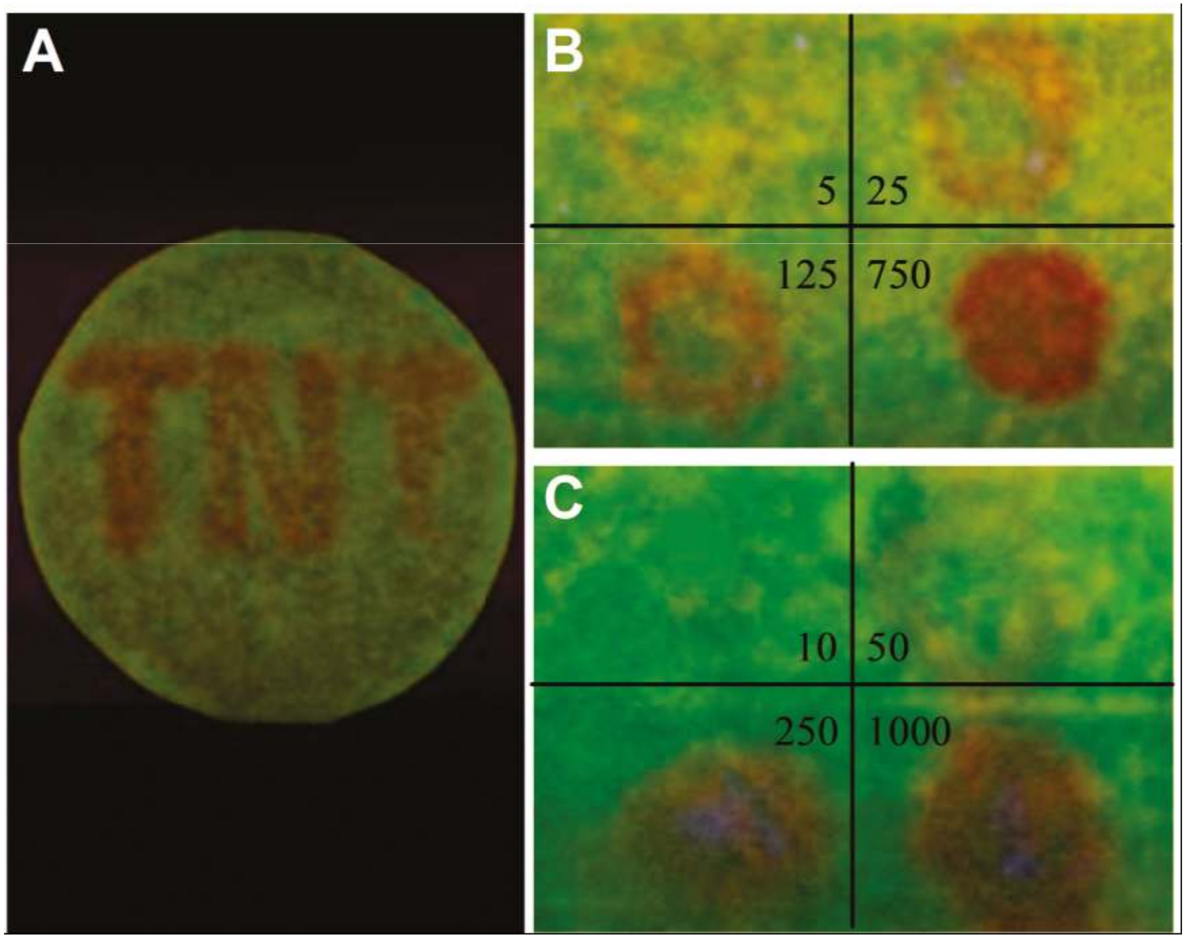
Fluorescence colorimetric visualization for specific identification of TNT from other similar nitroarmoatics.



The evolutions of fluorescence spectra of the as-prepared green QDs (without polyallylamine coating) with increasing TNT, DNT, NB, and RDX concentrations. The analyte concentrations from top to bottom are 0, 2×10^{-5}, 4×10^{-5}, 6×10^{-5}, 8×10^{-5}, and 1×10^{-4} mol/L, respectively.

Fingerprint lifting technique for visual detection of TNT on the surfaces using the ratiometric hybrid probe immobilized on a piece of filter paper.





The TNT particulates are first captured by the primary amino groups on the probe and then lifted from the surfaces. The lifted TNT particulates are visualized as differently colored spots in the yellowgreen background under UV illumination.

(A) a rubber surface (B) a manila envelope with amounts of 5 ng, 25 ng, 125 ng, and 750 ng (C) a synthetic fabric bag with amounts of 10 ng, 50 ng, 250 ng, and 1000 ng, respectively.

Conclusion

• A dual-emission quantum dots probe has been constructed by hybridization of two differently sized quantum dots, and its utility has been established for visual detection of TNT particulates on various surfaces using an approach resembling the fingerprint lifting technique.

• The presence of TNT particulates on the surfaces can be revealed by the fluorescence color change of the probe. The probe can also be used to quantitate TNT in solutions on the basis of the measurement of ratiometric fluorescence.

• The method shows high selectivity and sensitivity for TNT particulates on an envelope with the naked eye.

• The sensitivity could be further improved by judiciously selecting an initial fluorescence color more sensitive to the naked eye, which can be optimized by tuning the ratios of the differently sized quantum dots.

• This concept reported herein could be significant and could be extended to the visual detection of a wide range of organic and biological molecules through properly functionalizing the green quantum dots on the silica surfaces.

Thank you