

A Hybrid-Monolayer Fluorescence Probe Towards the Detection of Ultratrace Co^{2+} Ion at Surface of SiO_2 Nanoparticles†

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This paper reports a resonance energy transfer-amplifying fluorescence quenching at the surface of silica nanoparticles for the ultrasensitive and ultratrace detection of Co^{2+} ion in solution. The nanoparticle-assembled arrays on silicon wafer can sensitively detect down to *ca.* 1 nM Co^{2+} with the use of only 10 μL of solution (*ca.* 60 pg Co^{2+}).

Key Words: Fluorescence resonance energy transfer, Silica nanoparticle, Molecular recognition, Ultratrace detection, Co^{2+} ion.

INTRODUCTION

The deleterious pollution of metal ion compounds have concurrently raised world-wide concerns of public security and environmental problem, due to their wide production and use as chemical agent in chemical engineering. The presently used detections of metal ion are usually time-consuming with the employment of cumbersome and expensive atomic absorbance, ion mobility spectrometry and neutron activation analysis¹. Therefore, the development of ultrasensitive chemosensors for the real-time detection of metal ion has attracted considerable research efforts in recent years²⁻⁵.

EXPERIMENTAL

Uniform silica nanoparticles with a size of 200 nm were synthesized by the hydrolysis of TEOS with aqueous ammonia, according to the reported Stöber method⁶. 20 μL of the stock solution was added to a spectrophotometer quartz cuvette. Subsequently, 2 mL of the known concentration of analyte was injected into the above cuvette. Fluorescence spectra were recorded immediately after fully mixing the analyte with dye-(NH_2)-silica nanoparticles in solution.

RESULTS AND DISCUSSION

FRET-based Silica nanoparticle sensors for Co^{2+} ion detection: Fig. 1 shows the schematic drawing of dye-(NH_2)-silica nanoparticle sensor for Co^{2+} detection. Co^{2+} analyte is thus attached onto the surface of silica particles in the form of Co^{2+} -amine complex. The analyte binding will lead to the

quenching of dye fluorescence through the resonance energy transfer from dye donor to Co^{2+} -amine complex. The exciting band gap of the chosen dyes is about equal to the absorption band gap of Co^{2+} -amine complex and they are of spatial proximity at the surface of nanoparticle.

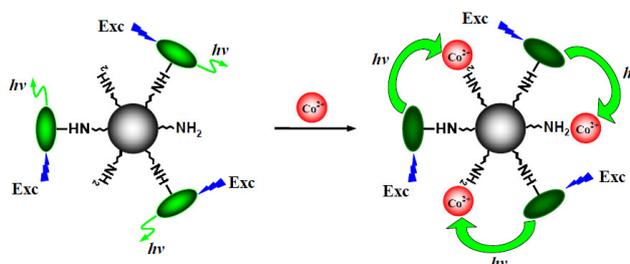


Fig. 1. (A) Schematic illustration of the FRET-based silica nanoparticle sensors for Co^{2+} detection. (B) Quenching mechanism through resonance energy transfer from FITC donor to Co^{2+} -amine complex acceptor

Confirmation of FRET quenching mechanism: Fig. 2 shows the fluorescence evolution with the increase of Co^{2+} ion concentration (A) and the Stern-Volmer plots of (B) FITC-(NH_2)-silica towards Co^{2+} , respectively. A linear Stern-Volmer relationship is observed at the Co^{2+} concentrations lower than 1×10^{-9} M for the dye systems.

Nanoparticle-assembled chips for ultrasensitive detection of Co^{2+} ion: Meanwhile, we develop the inexpensive solid-state chips for ultrasensitive detection of Co^{2+} ion by assembling the FITC-(NH_2)-silica nanoparticles into the etched microwell array of silicon wafer. Fig. 3 shows the colourful

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fluorescence images under laser excitation on a confocal microscope. The evolution of the brightness and size of fluorescent dots are clearly observed with dropping only 10 μL of Co^{2+} solution of different concentrations onto the 1 cm \times 1 cm sized chip. The brightness and size of fluorescent dots become smaller and smaller and ultimately disappear with the increase of concentration from 1×10^{-9} to 10^{-1} M. As shown in the Fig. 3, 10 μL of 1 nM Co^{2+} can result in a surprising reduction of the brightness and size of fluorescent dots under confocal microscope.

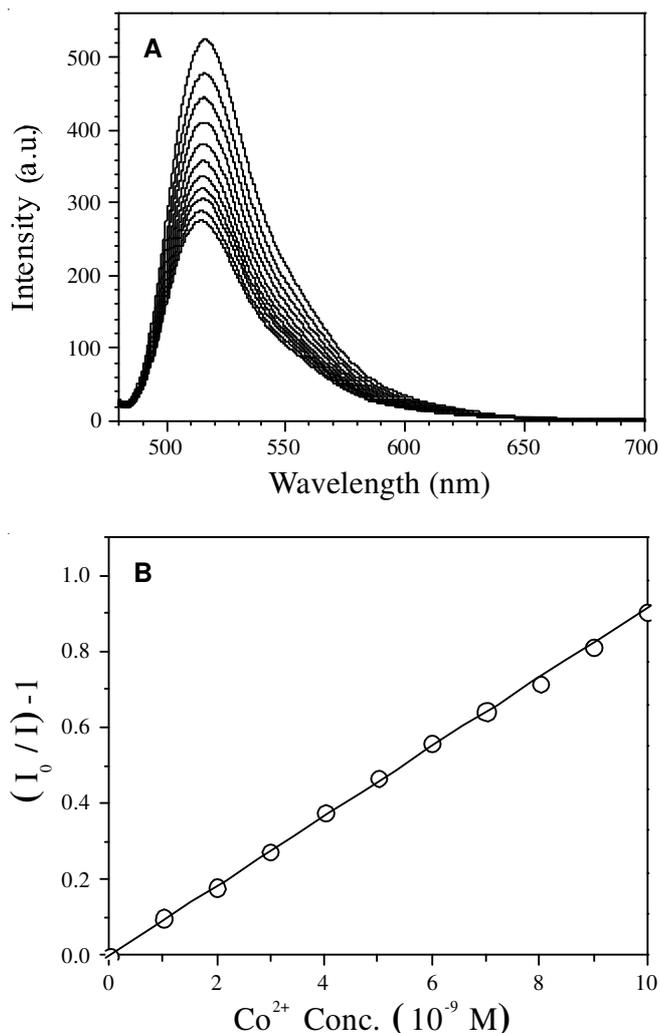


Fig. 2. (A) the evolution of fluorescence intensity with the increase of Co^{2+} ion concentration. (B) The Stern-Volmer plots of FITC-(NH_2)-silica towards Co^{2+} , respectively

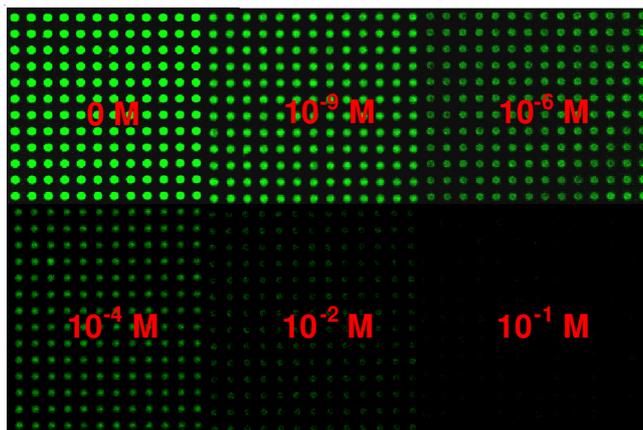


Fig. 3. Regular array assembly of FITC-(NH_2)-silica nanoparticles on the silicon wafer with etched microwells. Confocal fluorescence images show the evolution of the brightness and size of fluorescent dots with dropping 10 μL of Co^{2+} solution of different concentrations

Conclusion

We have demonstrated the resonance energy transfer-amplifying fluorescence quenching toward the ultrasensitive detection of Co^{2+} ion by the use of a hybrid monolayer of dye fluorophores and amine ligands at the surface of silica nanoparticles. The primary amine ligands at the surface of silica particles can specifically bind Co^{2+} species from environment by the formation of Co^{2+} -amine complex. Meanwhile, the non-emissive FRET between the dye and the resultant Co^{2+} -amine complex in the spatial proximity leads to an enhanced quenching response.

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