



Enhancing Sensitivity of Novel Hg²⁺ Fluorescent Sensor via Plasmonic Enhancement of Silver Nanoparticles



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ABSTRACT

Contamination of Hg²⁺ in an aqueous environment is dangerous for all living species including human. In this work, a new rhodamine B derivative fluorescent sensor (sensor **RBS**) for Hg²⁺ detection was successfully synthesized. In addition, the synthesized yellow silver nanoparticles (**Y-AgNPs**) were incorporated into sensor **RBS** to obtain sensor **RBS + Y-AgNPs**. The sensitivity studies for Hg²⁺ detection of the sensors showed that the Hg²⁺ detection limit of sensor **RBS** and sensor **RBS + Y-AgNPs** were 12.9 ppb and 0.7 ppb, respectively. The result indicated that incorporation of **Y-AgNPs** into sensor **RBS** led to significantly lower Hg²⁺ detection limit of sensor **RBS + Y-AgNPs**, which could be attributed to plasmonic enhancement of **Y-AgNPs**. Furthermore, the selectivity studies of the sensors showed that sensor **RBS** and sensor **RBS + Y-AgNPs** were highly selective toward Hg²⁺ against interference ions. We also showed that sensor **RBS + Y-AgNPs** could be used to detect Hg²⁺ in real samples. Importantly, we have demonstrated that utilization of plasmonic enhancement could improve the sensitivity of the Hg²⁺ fluorescent sensor, which could pave the way for development of portable fluorescent sensor for the on-site Hg²⁺ detection.

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1. Introduction

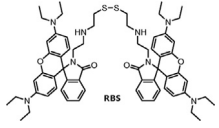
Contamination of hazardous substances such as heavy metals and chemicals in an aqueous environment can lead to serious human health and environmental problems. Heavy metal ions such as Fe²⁺, Mn²⁺ and Hg²⁺ can form a complex with the bioorganic molecule which contains oxygen, nitrogen or sulfur atom. This process can interrupt and cause the abnormalities in biological system such as change of protein structure, enzyme structure and can even lead to death [1]. The Hg²⁺ contamination was mainly caused by Hg²⁺ emission from several sources such as coal power plant, petroleum production, and waste incineration. In human, Hg²⁺ can damage neurologic, gastrointestinal, and renal organ systems. The well-known example toxicity of mercury is the Minamata disease. Exposure to Hg²⁺ is often occurred by consumption of water or contact to an aqueous solution in an environment. Conventionally, methods for Hg²⁺ detection in an aqueous sample require expensive and complicated instruments. In addition, these methods are often time consuming. The examples of these methods are induc-

tively coupled plasma atomic emission spectroscopy (ICP-AES) and Flame Atomic Absorption Spectrometry (AAS). Recently, detection of Hg²⁺ by fluorescence spectroscopy has received a lot of interests due to its high selectivity, its usability, and its low interferential signal. Besides that, the fluorescence sensor can be designed to operate through “Off-On” or “On-Off” fluorescence switching which allows rapid and clear detection in the presence of the Hg²⁺ [2–6]. However, most of the fluorescent sensors exhibit poor quantum yields which lead to moderated sensitivities of the sensors. Therefore, these sensors are still not practical for the on-site uses. One possible way to improve the quantum yield of the fluorescent sensors is utilizing plasmonic enhancement of metal nanoparticles (MNPs). Many MNPs exhibit optical phenomenon called “Surface Plasmon Resonance, (SPR)”, this phenomenon is originated from the coherent oscillations of the surface-bound electrons, which are induced by excitation of electromagnetic wave. After excitation of electromagnetic wave, SPR of metal nanoparticle (MNP) undergoes dampening and can dissipate energy via a radiative pathway as a scattering or via a non-radiative pathway as a heat or hot electrons [7]. For a MNP with a size in the range of tens of nanometers, most of the energy is dissipated to the surrounding via non-radiative pathway, which can enhance the electromagnetic field of the surrounding in the vicinity of the MNP [7–9]. The electromagnetic field

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Table 1
Analytical parameters of sensor **RBS** and sensor **RBS + Y-AgNPs**.

| Sensor | Working system | $\lambda_{ex}/\lambda_{em}$ (nm) | Detection limit | K_{assoc} (M^{-1}) | ϕ_f |
|---|---------------------------------|----------------------------------|------------------------------------|--------------------------|----------|
|  | water/acetonitrile (8:2 v/v) | 555/594 | 6.4×10^{-8} M or 12.9 ppb | 1.58×10^8 | 0.15 |
| Y-AgNPs (1.33 nM) | water/acetonitrile (8:2 v/v) | | 3.8×10^{-9} M or 0.7 ppb | 5.70×10^9 | 0.47 |

enhancement from SPR of MNPs could be utilized to enhance signal strengths or sensitivities in many spectroscopy applications such as fluorescence spectroscopy [8,9], and surface-enhanced Raman spectroscopy (SERS) [10–12]. For example, several studies have reported that the Raman signal of Raman-active molecules could be improved up to 6 order of magnitudes (10^6 times) when MNPs were used as a substrate for the detection [10–13]. Furthermore, fluorescence enhancement up to 3 order of magnitudes has been achieved by incorporation of MNPs with the fluorescence molecules [8,9]. These enhancements of the spectroscopic signals were caused by the strong electromagnetic field enhancement of the area in close proximity to surface of the MNPs, which led to larger transition of electrons to the higher (excited or vibrational) energy states. Consequently, the stronger spectroscopic signals were observed [8–13]. Therefore, utilization of the electromagnetic field enhancement of the MNPs for fluorescence sensing requires employing the MNPs to the close proximity of a fluorescent sensor. In addition, it has been confirmed that the sharp edge or asymmetric MNPs could give stronger electromagnetic field enhancement. These MNPs included star-shaped MNPs [10,11,14,15], triangular-shaped MNPs [16], rod-shaped MNPs [17], and cube-shaped MNPs [18]. Incorporation of MNPs into a fluorescence sensor could be achieved by self-assembly [19], chemical bonding or electrostatic interaction [20]. For example, gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs) can be chemically attached to a fluorescent sensor through proper chemical functional groups, which include alkyl [21], carboxylate [22], thiols [23] and amine [24]. Moreover, SPR of MNPs can be tuned by varying types of metal, sizes and shapes of the synthesized MNPs [25]. And the energy of SPR of MNPs in the ranges of ultraviolet, visible and infrared frequencies can be achieved [25]. Matching SPR of MNPs to the absorption of the fluorescent molecule could enhance the absorption of the molecule and led to stronger fluorescence emission [8,9]. Therefore, incorporation of the MNPs with suitable SPR into the fluorescent sensor could improve detection sensitivity of the sensor.

Here in, the new rhodamine B derivative fluorescent sensor (sensor **RBS**) for Hg^{2+} detection was successfully synthesized. In order to enhance the sensitivity of sensor **RBS**, the synthesized yellow silver nanoparticles (**Y-AgNPs**) were incorporated into sensor **RBS** to create sensor **RBS + Y-AgNPs**. We found that the Hg^{2+} detection limit of sensor **RBS + Y-AgNPs** was drastically improved compared to the Hg^{2+} detection limit of sensor **RBS**. The calculated Hg^{2+} detection limit of sensor **RBS** and sensor **RBS + Y-AgNPs** were 12.9 ppb and 0.7 ppb, respectively. The improved Hg^{2+} detection limit of sensor **RBS + Y-AgNPs** could be attributed to plasmonic enhancement of **Y-AgNPs** that occurred through non-radiative energy transfer from SPR of **Y-AgNPs** to sensor **RBS**, which led to stronger fluorescence emission, and consequently led to lower Hg^{2+} detection limit. Furthermore, our developed method that utilized the plasmonic enhancement from SPR of MNPs to improve the sensitivity of the fluorescent sensor could be applicable to the other fluorescent sensors. Therefore, the developed method could promote the application of a fluorescent sensor for an on-site detection.

2. Experimental

2.1. Materials

Reagents and solvents were purchased from Sigma–Aldrich and Fluka Chemical, and they were used as received. All perchlorate metal salts were purchased from Sigma–Aldrich and Strem Chemicals, Inc.

2.2. Methods

NMR spectra were measured by a Bruker Avance 300 spectrometer operating at 300 MHz for 1H and 75 MHz for ^{13}C . All NMR spectra were carried out in $CDCl_3$ solutions with TMS as the internal standard. Melting points were determined by Stuart Scientific melting point apparatus SMP2. Mass spectra were obtained by a ThermoElectron LCQDECA-XP, electrospray ionization ion trap mass spectrometer. Absorption spectra were recorded by a single beam Hewlett Packard 8453 spectrophotometer. Fluorescence spectra were measured by a Perkin Elmer Luminescence spectrometer LS 55. The excitation and emission slit widths were both 5.0 nm. Optimizations of **RBS** and **RBS-Hg²⁺** complex were obtained by density functional theory (DFT) calculations using a Gaussian 09 program [26]. Both of all geometry optimization were performed in 80% v/v water/acetonitrile by B3LYP level using 6-311G** for main group element and LanL2DZ [26,27]. HOMOs, LUMOs, and molecular figures were achieved by VMD program [28].

2.3. Synthesis: Sensor **RBS**

The synthesis procedure of **RBOH** was modified from the previous synthesis procedure [29]. In 25 mL round bottom flask, rhodamine B (1.00 g, 2.0 mmol) was dissolved in dry EtOH (10 mL) and the solution was stirred under argon atmosphere. Then 2-aminoethanol (1.00 mL, 16.5 mmol) was added into the solution and the reaction was refluxed for 24 h under argon atmosphere. After that, the reaction was cooled to room temperature and the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 (30 mL) and then was washed by water (3×30 mL). The organic phase was dried over anhydrous Na_2SO_4 , and the solvent was removed under vacuum. Then the crude product was purified by column chromatography using 10% v/v MeOH/ CH_2Cl_2 ($R_f = 0.85$) as eluent to obtain the white solid (0.88 g, 90% yield, mp 216–217 °C); 1H NMR ($CDCl_3$, 300 MHz): δ 1.64 (t, 12H, $J = 6.9$ Hz), 3.27–3.37 (m, 10H), 3.46 (d, 2H, $J = 3.9$ Hz), 6.29 (dd, 2H, $J = 2.7, 6.3$ Hz), 6.38 (d, 2H, $J = 2.4$ Hz), 6.49 (d, 2H, $J = 8.7$ Hz), 7.05–7.08 (m, 1H), 7.42–7.46 (m, 2H), 7.89–7.91 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.6 (4 CH_3), 44.4 (4 CH_2), 44.6 (2 CH_2), 62.6 (2 CH_2), 65.9 (C), 97.9 (2CH), 104.9 (2C), 108.3 (2CH), 122.9 (CH), 123.8 (CH), 128.1 (CH), 128.5 (2CH), 130.5 (2C), 132.7 (CH), 149.0 (2C), 153.3 (C), 154.0 (C), 170.0 (C) ppm; HR-ESI MS calcd for $C_{30}H_{36}N_3O_3^+$ ($M + H$)⁺ 486.2751 m/z, found 486.2760 m/z.

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