This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
A fluorescent sensor to detect sodium dodecyl sulfate based on the glutathione-stabilized gold nanoclusters /Poly diallyldimethylammonium chloride system

Chun-Lan Zheng, Zhong-Xiang Ji, Jian Zhang and Shou-Nian Ding*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A simple method for the detection of sodium dodecyl sulfate (SDS) was developed based on glutathione-stabilized gold nanoclusters (GSH-AuNCs) and poly diallyldimethylammonium chloride (PDDA) enhanced fluorescent system. Fluorescent Au NCs were synthesized by a one-step approach employing GSH as a reducing/protection reagent. The electrostatic group repulsions between GSH-Au NCs and PDDA resulted in a strong fluorescence enhancing of the GSH-Au NCs. Moreover, the addition of SDS was able to cause a significant fluorescence recovery due to the strong affinity of PDDA and SDS. Thus the SDS can be detected. Under optimized conditions, the linear response to detect SDS ranges from 0.2 to 12 μg mL⁻¹ with a detection limit of 0.02 μg mL⁻¹.

Introduction

Sodium dodecyl sulphate (SDS), as the “industrial monosodium glutamate” has expanded from chemical industry to all areas of our daily life in the past decades. A considerable portion of these unregulated anionic surfactants pollute the aquatic ecosystems and even evoke the deterioration of drinking water quality. Various detection strategies for SDS have been developed including colorimetric, chromatographic, and biosensor analysis techniques. However, most of these techniques show some disadvantages which include expensive reagents, time-consuming and often require the use of a sophisticated instrumentation.

Poly diallyldimethylammonium chloride (PDDA), not only an electronic conducting polymer but also a strong cationic polymer, has been extensively used to combine with other materials, such as carbon nanotubes (CNTs) and metal nanoparticles to fabricate nano-composite materials with peculiar features. Moreover, PDDA as a cationic polyelectrolyte is widely used to prepare ultra-thin films by layer-by-layer method through electrostatic attraction with anionic polyelectrolyte.

There exist strong interactions between positively charged PDDA and negatively charged SDS due to the electrostatic attractions, the hydrophobic interactions from the carbon chains, or the host-guest interaction by the inclusion complexation. For example, the presence and nature of a surfactant in the CNTs/PDDA system has been found to affect their interactions. Furthermore, the formation of a surface surfactant-polyelectrolyte complex on a solid-liquid interface by sequential adsorption of SDS and then PDDA has been reported. The complex is stable in aqueous environments and does not desorb or dissociate upon rinsing with water. At the same time, PDDA contains a large number of adsorbing units and can result in the change of fluorescence signals by transferring energy. Hence, PDDA can be used as the optical platform for highly sensitive chemical and biological sensors.

Fluorescent metal nanoclusters (NCs) as a new class of metal nanostructures have attracted great attention in recent years for their unique properties and applications. Among the metal nanoclusters, Au NCs exhibit many fascinating features, including ease of synthesis, good water solubility, low toxicity, facile surface functionalities, strong fluorescence and long term stability, which makes them hold great promise in bioanalysis. Nowadays, considerable efforts have been devoted to exploration of facile one-pot synthesis strategies mostly focused on control over the size, shape, stability, functionality and solubility of Au NCs. For example, Au NCs accommodating PAMAM dendrimers have been found to emit blue light. Thiol-protected Au NCs with size less than 1.2 nm have been reported and showed favorable potential for further application. These Au NCs have been successfully used in the determination of various heavy metals such as Hg(II), Fe(III), and Pb(II) with the advantages of being simple, economical and short time analysis. Recently, a simple label-free method to monitor S²⁻ ions has been developed by using fluorescent core-shell Au@Ag NCs in our laboratory. To the best of our knowledge, there has never been a report on the application of fluorescent Au NCs for the detection of SDS till now.

Herein, we report a simple and rapid approach for the fluorescence detection of SDS based on the GSH-Au NCs/PDDA system, as shown in Scheme 1. Firstly, the electrostatic repulsions between GSH-Au NCs and PDDA can improve the dispersion of the Au NCs, which results in high efficiency fluorescence enhancing of GSH-Au NCs (Step 1 in Scheme 1). Secondly, due to the strong affinity between PDDA and SDS, when SDS was added to the GSH-Au NCs/PDDA system,
PDDA will preferentially adsorb the SDS (strong competitor) over GSH-Au NCs (weak competitor) to form the PDDA/SDS complex. As a result, the GSH-Au NCs gradually desorbed from the GSH-Au NCs /PDDA system, leading to the recovery of the fluorescence (Step 2 in Scheme 1), which provides a quantitative readout for the SDS. In this work, the nontoxic and biocompatible PDDA chain segments not only serve as an optical platform to enhance fluorescence but also serve as an agent to form a complex with SDS.

**Scheme 1** Schematic illustration of SDS detection based on GSH-Au NCs and PDDA system.

**Experimental**

**Apparatus**

UV-Vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer (Tokyo, Japan). The Fluorescence spectra (FL) were performed on a Fluoromax-4 fluorescence spectrofluorometer (Horiba, USA). All of the photos were taken by iPhone 4S. A vortex mixer IKA MS3 digital was used to blend the solution.

**Reagents**

Hydrogen tetrachloroaurate trihydrate (HAuCl₄-4H₂O) were of analytical grade and obtained from Shanghai Chemical Plant. Glutathione Reduced (99%) was purchased from Shanghai Sinopharm Chemical Reagent Co.Ltd. (Shanghai, China). Tris-HCl solution (pH 3.0-9.0, 0.1M) was prepared by varying the ratio of Tris(hydroxyethyl)methyl aminomethane to HCl. All chemicals and solvents were of analytical grade and were used without further purification. All aqueous solutions were prepared with doubly distilled water.

**Synthesis of GSH-Au NCs**

The glutathione-stabilized gold nanoclusters were prepared according to the literature with a slight modification. Briefly, all the glassware were thoroughly cleaned with aqua regia (HNO₃:HCl, 1:3) and rinsed extensively with doubly distilled water prior to use. The fluorescent GSH-Au NCs were synthesized by a one-step method via reduction of gold salt with glutathione as both reducing and protecting agent. Firstly, an aqueous solution of glutathione (5 mL, 15 mM) was added to an equal volume of 10 mM HAuCl₄. The mixture was vigorously stirred for 2 min. Next, an aqueous solution of NaOH (1mL, 1M) was added into the above solution. Lastly, the reaction was allowed to proceed under slow stirring at 37 °C for 24 h. Excess glutathione were thereafter removed by adding excessive methanol into the resulting aqueous solution (the ratio between water and methanol is 1:4) and then centrifuged at 15,000 rpm for 5 min. The precipitates were separated and dispersed in Tris-HCl (0.1M, pH7) solution for later use.

**Results and discussion**

**Characterization of as-prepared GSH-Au NCs**

A typical absorption spectrum of the prepared GSH-Au NCs (Curve a), GSH-Au NCs/PDDA (Curve b) and GSH-Au NCs /PDDA/SDS (Curve c) solution are shown in Fig.1(A). The UV-vis absorption spectrum of the GSH-Au NCs solution lacks the surface plasmon resonance absorption of gold nanoparticles at around 500 nm, which suggested that highly purified Au NCs have been obtained without the formation of larger Au NPs or bulk metals as by-products. Meanwhile, the absorption spectra showed that the addition of PDDA into Au NCs leads to a little increasing of absorbance due to the UV-visible absorbance properties of PDDA (Curve b), and the continuous addition of SDS does not cause the absorbance to change obviously (Curve c).

![Absorbance spectrum](image1)

**Fig. 1** (A) UV/Vis absorption spectrum of the GSH-Au NCs(a) and GSH-Au NCs /PDDA(b) GSH-Au NCs /PDDA/SDS(c). Concentrations: GSH-Au NCs (50µg mL⁻¹), PDDA (12.5µg mL⁻¹), and SDS (2µg mL⁻¹). Inset: Photographs of an aqueous solution of GSH-Au NCs in visible light (left) and UV light (right). (B) Fluorescence spectra of the GSH-Au NCs at different excitation wavelengths (a-h: 330, 340, 350, 390, 410, 420, 450, 470 nm). Concentration: GSH-Au NCs (0.2 mg mL⁻¹) (C) Typical TEM image of GSH-Au NCs.

As shown in the inset of Fig. 1(A), the color of the as-prepared GSH-Au NCs solution was pale yellow under visible light and orange-red under UV light of 365 nm wavelength indicating that highly luminescent species were formed. The maximum of the fluorescence intensity of the GSH-Au NCs was obtained at 410 nm excitation wavelength, which was consistent with the UV-vis absorption spectrum. As demonstrated in Fig.1(B), when the excitation wavelength changes from 330 to 470 nm, the emission spectra always centered at 660 nm with a Stokes shift of 250 nm. Meanwhile, the increase or decrease in the excitation wavelength around 410 nm causes a gradual decrease fluorescence intensity.
Thus, the as-prepared GSH-Au NCs should be a single component owing to the same emission peak wavelength in the fluorescence spectra for the excitation. To further confirm the formation of GSH-Au NCs, transmission electron microscopy (TEM) image was performed. As shown in Fig.1C, the gold clusters are spherical in shape and well dispersed (average radius: 1.2 ± 0.3 nm).

Fig. 2 shows the fluorescence emission spectra of GSH-Au NCs (curves a) GSH-Au NCs/PDDA (curves b), and GSH Au NCs/PDDA/SDS (curves c) at the excitation wavelength of 410 nm. As demonstrated in Fig.2, the GSH-Au NCs showed weak fluorescence emission in the absence of PDDA at 660 nm in pH 5.0 Tris-HCl buffer solution (curve a in Fig. 2). When the PDDA was introduced to the GSH-Au NCs solution, the fluorescence emission intensity was greatly enhanced (curves b in Fig. 2) due to the electrostatic group repulsions. Subsequently, with the addition of SDS to the GSH-Au NCs/PDDA system, the significant fluorescence recovery (curve c in Fig. 2) was observed due to the competitive reaction of SDS and PDDA. Other cationic water-soluble polymer, such as poly(allylamine hydrochloride) has the similar enhancing fluorescence effect on GSH-Au NCs as PDDA. However, SDS addition could not make its fluorescence recovery very well.

![Fluorescence emission spectra](image)

**Fig. 2** Fluorescence emission spectra of GSH-Au NCs (a), GSH-Au NCs/PDDA (b), and GSH-Au NCs/PDDA/SDS (c) in the wavelength range of 550–780 nm upon excitation at 410 nm. Inset: the corresponding fluorescence photographs (from left to right represent a, b and c) under UV light (365 nm). Concentrations: GSH-Au NCs (0.2 mg mL⁻¹), PDDA (0.05 mg mL⁻¹), and SDS (8 μg mL⁻¹).

**Influence of PDDA Concentration on Efficiency of Fluorescence Recovery**

As shown in Fig. 3, when the GSH-Au NCs concentration was fixed at 0.2 mg mL⁻¹, the fluorescence signal of GSH-Au NCs was gradually enhanced with the increasing concentrations of PDDA from 20 to 65 μg mL⁻¹. However, a higher concentration of PDDA (70 μg mL⁻¹) can cause the aggregation of GSH-Au NCs, leading to the quenching of the fluorescence signal. In order to obtain the optimal experimental condition to detect SDS, the fluorescence intensities of GSH-Au NCs/PDDA system with various PDDA concentrations were measured before and after incubation with 8 μg mL⁻¹ SDS. The inset of Fig.3 is the plot of relative fluorescence intensity ((F₀-F)/F₀) vs. the concentration of PDDA, where F₀ and F denote the fluorescence intensity of GSH-Au NCs/PDDA complex in the absence and presence of SDS at the emission wavelength of 660 nm, respectively. After incubation with SDS, the efficiency of fluorescence recovery increased at first and then decreased with the further increasing PDDA concentration. The reason may be that excess PDDA would cause difficult release of GSH-Au NCs from PDDA to affect the efficiency of fluorescence recovery. Thus, the optimum concentration of PDDA was 50 μg mL⁻¹ chosen for the following experiments.

![Influence of PDDA concentration](image)

**Fig. 3** Effects of the concentrations of PDDA on the fluorescence intensities of GSH-Au NCs/PDDA (a), GSH-Au NCs/PDDA/SDS (b). Inset: the plot of relative fluorescence intensity ((F₀-F)/F₀) vs. the concentration of PDDA, where F₀ and F denote the fluorescence intensity of GSH-Au NCs/PDDA complex in the absence and presence of SDS at the emission wavelength of 660 nm, respectively. Concentrations: GSH-Au NCs (0.2 mg mL⁻¹), PDDA (20-70 μg mL⁻¹), and SDS (8 μg mL⁻¹). Tris-HCl buffer solution, pH 5.0.

**Effect of pH**

In order to achieve the highly sensitive detection of SDS by using GSH-Au NCs/PDDA, the pH value of solution from 3 to 9 was studied and optimized. The fluorescence of the system was tested at different pH values (Fig.4).

![Effect of pH](image)

**Fig. 4** (A) Effect of the pH on the fluorescence intensity of GSH-Au NCs (a), GSH-Au NCs/PDDA (b), and GSH-Au NCs/PDDA/SDS (c). (B) The plot of relative fluorescence intensity ((F₀-F)/F₀) vs. the pH value. Concentrations: GSH-Au NCs (0.2 mg mL⁻¹), PDDA (50 μg mL⁻¹), and SDS (8 μg mL⁻¹). Tris-HCl buffer solution (0.1M, pH 3.0 - 9.0).

As shown in Fig.4 (A), the fluorescence signal of GSH-Au NCs was greatly quenched at pH 3 due to the aggregation of the GSH-Au NCs, and reached the maximum value at pH 4, then gradually decreased (Curve a). The fluorescence signal of GSH-Au NCs was greatly enhanced by PDDA in the range of pH 4 to pH 9...
The addition of SDS leads to the recovery of fluorescence over the wide pH range from 3 to 9 (Curve c). However, the efficiencies of fluorescence recovery at these pH values are quite different. The addition of SDS can cause greater fluorescence recovery in acidic media than in alkaline solutions. As shown in Fig. 4 (B), the efficiency of fluorescence recovery has the highest value at pH 5.0, suggesting that 5.0 can be chosen as the optimum pH value in the following experiments.

Sensitivity

The fluorescence at 660 nm of the GSH-Au NCs/PDDA decreased upon increasing the concentration of SDS from 0 to 20 μg mL⁻¹. As indicated in Fig. 5, the sensitivity and linearity of the GSH-Au NCs/PDDA/SDS system was evaluated by varying the SDS concentrations in Tris–HCl buffer solution (0.1M, pH 5.0). With the increase of the concentrations of SDS, the fluorescence emission intensity of the GSH-Au NCs/PDDA decreased gradually. From the inset of Fig. 5, it can be seen that the efficiency of fluorescence recovery is sensitive to the concentration of SDS. A linear equation \( (F_0 - F) / F_0 = 0.02699c + 0.05373 \) can be obtained in the SDS concentration range from 0.2 to 12 μg mL⁻¹, where \( F_0 \) and \( F \) denote the meanings mentioned above, and \( c \) (μg mL⁻¹) is the concentration of SDS. A good linear correlation (\( R^2 = 0.998 \)) was obtained. In this work, the detection limit for SDS was approximately 0.02 μg mL⁻¹. The fluorescence sensing system shows a wide linear range and a very low detection limit.

Conclusions

In summary, the fluorescent GSH-Au NCs were synthesized via a facile one-step method. The introduction of PDDA into the obtained Au NCs can enhance the fluorescence of the as-prepared Au NCs through the electrostatic group repulsions between GSH-Au NCs and PDDA. SDS can react with PDDA to form a complex and result in the sensitive fluorescence recovery of GSH-Au NCs via competing reaction. A sensitive fluorescence sensing platform to detect SDS was fabricated based on the above mechanism. Under optimal conditions, this method displayed a low detection limit and good selectivity over other substances. The above results revealed that the proposed fluorescence sensor is promising for the selective determination of SDS in environmental water samples using luminescent Au NCs.

Acknowledgements

This work was supported by the Natural Science Foundation of China (No. 21345008), the Fundamental Research Funds for the Central Universities, the Open Research Fund of State Key Laboratory of Bioelectronics, Southeast University, and the Open Research Fund of State Key Laboratory of Analytical Chemistry for Life Science (SKLACLS1211).
**Notes and references**

School of Chemistry & Chemical Engineering, Southeast University, 211189 Nanjing, China  
E-mail: nding@seu.edu.cn; Tel/Fax: +86-25-52090621;

Glutathione-stabilized gold nanoclusters and poly diallyldimethylammonium chloride enhanced fluorescent system was used to detect sodium dodecyl sulfate.