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Cytidine-stabilized gold nanocluster as a fluorescence turn-on and turn-off probe for dual functional detection of Ag^{+} and Hg^{2+}

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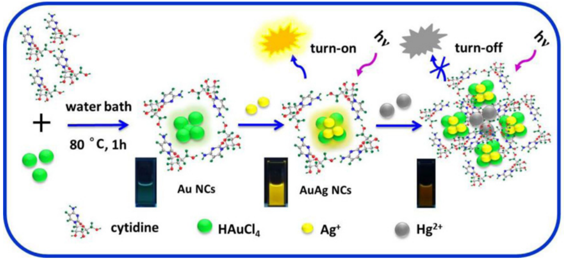
HIGHLIGHTS

- Au NCs and AuAg NCs as fluorescent turn-on and turn-off probes were synthesized.
- Au NCs recognize silver ions by fluorescence enhancement to form AuAg NCs.
- AuAg NCs can be reused to detect Hg^{2+} based on fluorescence quenching.
- The fluorescent nanoprobes are used to monitor environmental water samples.

GRAPHICAL ABSTRACT

Scheme for formation of cytidine-stabilized Au NCs and used as a fluorescent turn-on and turn-off probe for dual functional detection of Ag^{+} and Hg^{2+}.



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ABSTRACT

In this study, we have developed a label-free, dual functional detection strategy for highly selective and sensitive determination of aqueous Ag^{+} and Hg^{2+} by using cytidine stabilized Au NCs and AuAg NCs as fluorescent turn-on and turn off probes, respectively. The Au NCs and AuAg NCs showed a remarkably rapid response and high selectivity for Ag^{+} and Hg^{2+} over other metal ions, and relevant detection limit of Ag^{+} and Hg^{2+} is ca. 10 nM and 30 nM, respectively. Importantly, the fluorescence enhanced Au NCs by doping Ag^{+} can be conveniently reusable for the detection of Hg^{2+} based on the corresponding fluorescence quenching. The sensing mechanism was based on the high-affinity metallophilic Hg^{2+}–Ag^{+} interaction, which effectively quenched the fluorescence of AuAg NCs. Furthermore, these fluorescent nanoprobes could be readily applied to Ag^{+} and Hg^{2+} detection in environmental water samples, indicating their possibility to be utilized as a convenient, dual functional, rapid response, and label-free fluorescence sensor for related environmental and health monitoring.

1. Introduction

Heavy metal pollution is a global problem that has a negative impact on the environment and poses severe medical threats to human health [1–3]. Heavy metals are dangerous because they are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. It is known that mercury ion (Hg^{2+}) is a highly toxic and widely spread heavy metal pollutant that exists in water, soil, and food [4,5]. Mercury can accumulate in organisms and its damage to the brain, nervous system, endocrine system and even the kidneys is well known which constitutes a serious threat to human health and natural environment [5–8]. The silver ion (Ag^{+}) is less harmful than the mercury ion to living organisms, however, due to its wide employment in industry, such as electronics, photography, and pharmacy, a large amount of silver is being released into the environment annually from industrial wastes and emissions. Silver ions are assigned to the highest toxicity class of heavy metal

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pollutants [9,10]. Despite not being a bioaccumulative toxin, Ag^+ does inactivate sulfhydryl enzymes, bind with amine, imidazole and carboxyl groups of various metabolites, and displace essential metal ions such as Ca^{2+} and Zn^{2+} in hydroxyapatite in bone [11]. Recent studies have reported that the acknowledged antibacterial activity of Ag nanoparticles could be attributed to toxic Ag^+, which is released from the nanoparticles [12,13]. Because of the strict rules regarding human health, research into the rapid and selective detection of Ag^+ has been of intense interest [14,15]. Thus, detecting Ag^+ and Hg^{2+} is undoubtedly a significant step in environment and health monitoring.

Methods currently available for detecting heavy metal ion analysis include atomic absorption spectrometry [16], X-ray fluorescence spectrometry [17], anodic stripping voltammetry [18], microprobes [19], and inductively coupled plasma mass spectrometry [20]. These element-specific detectors are typically coupled with gas chromatography, high performance liquid chromatography, and capillary electrophoresis. However, these instrument techniques are rather complicated, costly and time-consuming for sample pretreatment procedures, as well as not being appropriate for point-of-use applications [8,21]. Therefore, developing simple methods for selective and sensitive determination of heavy metal ions is still a great challenge. To design highly selective metal ion sensors, several innovative recognizing elements based inorganic molecules [22], various polymers [23], DNAzymes [24], proteins [14], oligonucleotides [25] and nanomaterials [26,27] have been developed for determination of metal ions.

Recently, gold nanoparticles (Au NPs)-based assays have attracted much attention due to their unique electronic, photonic, optoelectronic, and catalytic properties [28,29]. It is reported that functional Au NPs can be used as a colorimetric sensor for metal ions [30] because of their extremely high extinction coefficients and strongly distance-dependent surface plasmon resonance (SPR) absorption [31,32]. Meanwhile, a photoluminescence (PL) quenching assay for the detection of Hg^{2+} has also been developed based on excellent PL properties of Au NPs [30,33]. Compared with PL Au NPs, gold nanoclusters (Au NCs) have smaller particle size and higher PL quantum yield [8,34–36]. Thus, Au NCs have attracted an increasing interest due to their simplicity and low detection limit in both fundamental research and research toward practical applications [37–41]. Advances in synthesis and application of Au NCs as fluorescence probes have drawn wide attention due to their ultra-small size, large Stokes shift, low toxicity, strong fluorescence, and long term stability. A number of methods have been reported to synthesize Au NCs by using specific capping agents such as thiol ligands [42], or using templates such as DNA [7,43] and polymers [44]. These Au NCs have been used in the determination of various heavy metals such as Hg^{2+} [8,34,35,45,46], Ag^+ [14,15,38], Cu^{2+} [30], Fe^{3+} [47], As^{3+} [48], and Pb^{2+} [49] with advances of being simple, rapid, and economical. Thus it is possible to utilize Au NCs as a fluorescent probe for selective determination of Ag^+ and Hg^{2+}, which is valuable for monitoring the relevant environment and human health [10,50].

Herein, in this contribution, we report a dual functional, rapid, ultrasensitive and label-free fluorescent sensor for the detection of ionic silver and mercury based on cytidine-stabilized gold nanoclusters (Au NCs) (Fig. 1). This new fluorescent sensor can be employed for the sensitive and selective detection of Ag^+ by fluorescence turn-on. Meanwhile, the Au NCs by doping Ag^+ could produce fluorescence enhanced gold and silver nanoclusters (AuAg NCs) that can be reusable for the detection of Hg^{2+} based on the fluorescence turn-off.

2. Experimental

2.1. Materials and instruments

Cytidine was purchased from Sigma–Aldrich and was used as received. Auric chloride acid ($HAuCl_4 \cdot 6H_2O$) and silver nitrate ($AgNO_3$), trisodium citrate, citrate, ethylenediaminetetraacetic acid (EDTA) and other reagents were of analytical grade from Sinoreagent, China. All the solutions were prepared by doubly distilled water.

Fluorescence measurements were carried out using SHIMADZU RF-5301 PC instrument. The slit wavelength for excitation and emission was set as 3 nm. Thermo Scientific, BioMate 3S UV–vis spectrophotometer was used for the UV/vis adsorption measurements. Spectra were typically measured in the range of 200–600 nm. Transmission electron microscopy (TEM) images were collected using a JEM-2100 microscope to characterize the size and size distribution. A diluted solution was spotted on carbon coated copper grid (300 meshes) and was dried in laboratory ambiance.

2.2. Synthesis and separation of cytidine stabilized Au NCs and AuAg NCs

The synthesis of Au NCs is as follows: 40 μL of 50 mM cytidine was added in 1.82 mL water (final concentration: 1 mM), to this

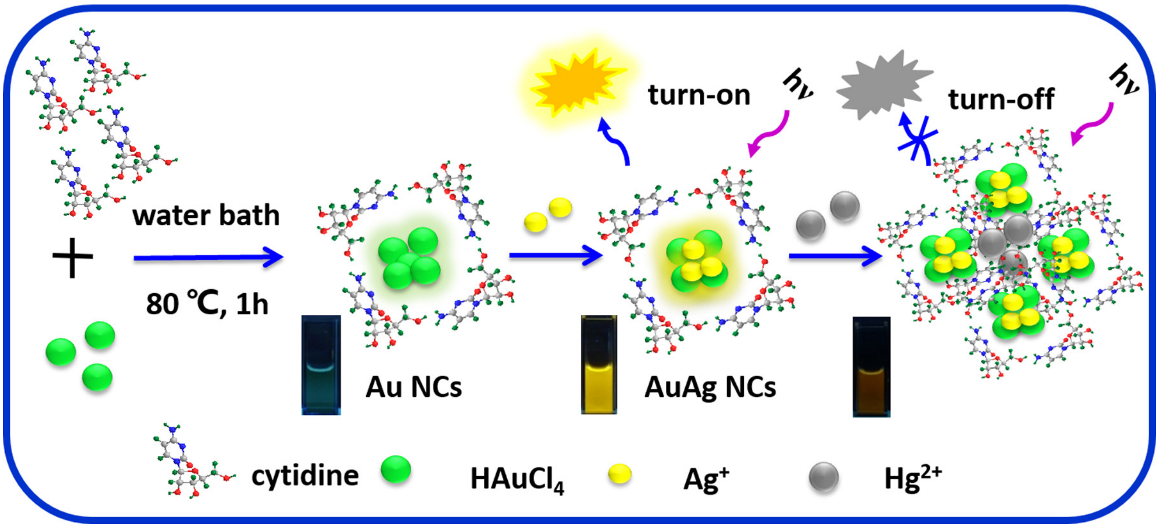

Fig. 1. Schematic of the formation of cytidine-stabilized Au NCs and used as a fluorescent turn-on and turn-off probe for dual functional detection of Ag^+ and Hg^{2+}.