

# Nanoclusters prepared from a silver/gold alloy as a fluorescent probe for selective and sensitive determination of lead(II)

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**Abstract** We report on the preparation of water-soluble and fluorescent silver/gold alloy nanoclusters (Ag/Au NCs) by a galvanic replacement reaction. The alloy NCs have an average diameter of 1.5 nm and are shown to be viable fluorescent probes for the determination of lead(II) due to aggregation-induced quenching of fluorescence. The alloy NCs are characterized in terms of photoluminescence spectrum, photoluminescence excitation spectrum, transmission electron microscopy and X-ray photoelectron spectroscopy which confirm the presence of alloy NCs. Bovine serum albumin, a well known stabilizing agent, has a high-affinity site for  $\text{Pb}^{2+}$  ion, and the resulting complex acts as a quencher of fluorescence. This finding has led to a method for selective determination of  $\text{Pb}^{2+}$  with a limit of detection of about 2 nM.

**Keywords** Alloy nanoclusters · Ag/Au · Fluorescent probe · Lead(II) · Real water samples

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## Introduction

Heavy-metal ions, such as mercury(II) ( $\text{Hg}^{2+}$ ) and lead(II) ( $\text{Pb}^{2+}$ ), can result in serious and permanent damage to human organs due to their accumulative characters in the environment and biota [1, 2]. Therefore, detection of these heavy-metal ions is central to the metal monitoring of water or soil. In the past decade, some probes and/or schemes had been designed to detect heavy-metal ions selectively and sensitively due to the biotoxicity and bioaccumulative properties of heavy-metal ions which can cause damage to the kidney, liver, and nervous system and pose severe effects on human health [3–6]. Although some probes and methods (functional gold nanoparticles and quantum dots) for  $\text{Pb}^{2+}$  detection had been reported, highly sensitive and selective detection of  $\text{Pb}^{2+}$  in water is essential [7, 8]. On the other hand, DNAzyme exhibited high sensitivity for  $\text{Pb}^{2+}$  [9]. However, the expensive price made them unsuitable for many practical applications. Hence from the viewpoint of practical applications, an excellent probe should be not only highly sensitive and selective but also simple and economical in operation simultaneously.

Metal nanoclusters (NCs), an new class of fluorescent nanomaterials, was defined as isolated particles less than 2 nm in size with several to a hundred atoms [10]. Metal NCs with discrete energy levels showed molecule-like electronic transitions within the conduction band, and exhibited unique physical and chemical properties [11]. Similar to quantum dots, metal NCs exhibited size-dependent tunable fluorescence from visible to near-infrared regions with high quantum yields [12, 13]. Fluorescence NCs have been proved to be a more-powerful optical technique for the detection of low concentration analytes, owing to their handily preparation, low expense, multifunctional surface chemistry and rapid implementation [14–17]. For example, Yu groups reported luminescent Au NCs for the sensitive detection of  $\text{Cu}^{2+}$  [15]; Lin and coworkers used fluorescent Ag NCs as effective

probes for highly selective detection of  $\text{Hg}^{2+}$  at ppb levels [16]; Pradeep and co-workers prepared blue fluorescent Cu NCs which can detect highly toxic  $\text{Pb}^{2+}$  ions in water [17]. Prior to our study, these fluorescent probes were usually based on metal NCs with single component and precise number of atoms. However, there are some challenges to prepare fluorescent alloy NCs as probe for detection of heavy-metal ions.

Alloy NCs have same advantages as metal NCs: photoluminescence, facile synthesis, good biocompatibility and multifunctional surface chemistry [18]. Alloy NCs had attracted much attention due to their unique physical and chemical properties, and practical applications in various areas [19]. While there are some technical issues in preparing metal alloy NCs, such as time-consuming preparation process and low quantum yields [20, 21]. Until now, several research groups have been trying a few routes to prepare alloy NCs. Among these approaches, galvanic replacement reaction is one of particularly good methods due to the high efficiency and simplicity [22]. This method had been applied in large-scale synthesis of various shaped alloy metals nanostructures [23]. Yet, few researches about fluorescent alloy NCs appeared through this way [24].

Herein, we applied the galvanic replacement reaction to achieve Ag/Au alloy NCs with red fluorescence. As-prepared Ag/Au alloy NCs were protected by bovine serum albumin (BSA) which could work as an important scaffold to prevent NCs from growing large NPs [25]. More importantly, NCs stabilized by BSA exhibited good dispersion and high stability in aqueous solution [26, 27]. These advantages illustrated that the resultant alloy NCs were promising fluorescent probes for detection of heavy-metal ions.

## Experimental

### Materials

Reduced glutathione (GSH, molecular weight of  $307 \text{ g}\cdot\text{mol}^{-1}$ ), bovine serum albumin (BSA) were purchased from Aldrich (<http://www.sigmaaldrich.com>). Tetrachloroauric (III) acid ( $\text{HAuCl}_4$ ), silver nitrate ( $\text{AgNO}_3$ , 99 %), hydrazine hydrate ( $\text{N}_2\text{H}_4\cdot 2\text{H}_2\text{O}$ , 85 wt.%), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and isopropanol were analytical grade. All reagents were used as received without further purification. De-ionized water was used in all experiments.

The synthesis of Ag/Au alloy nanoclusters

The template of Ag nanoclusters (NCs) was prepared by chemical reducing method using  $\text{N}_2\text{H}_4\cdot 2\text{H}_2\text{O}$  as reducing agent, which was the similar as previous report [16]. The galvanic replacement reaction route was used to synthesize

Ag/Au alloy NCs, which was similar to our previously reported synthetic procedure for Ag/Au alloy NCs with a slight improvement [22]. The 100 mg BSA, 0.25 mL Ag NCs ( $10 \text{ mmol}\cdot\text{L}^{-1}$ ) and 0.25 mL  $\text{HAuCl}_4$  ( $50 \text{ mmol}\cdot\text{L}^{-1}$ ) was dissolved in 4.5 mL aqueous solution under magnetic stirring. Then, 15  $\mu\text{L}$  NaOH ( $1 \text{ mol}\cdot\text{L}^{-1}$ ) solution was introduced and the mixture was allowed to incubate at  $40^\circ\text{C}$  under vigorous magnetic stirring for 4 h. The color of the solution changed from light yellow to deep brown. The purification of resultant BSA–Ag/Au alloy NCs was centrifuging at 12,000 rpm to remove AgCl precipitate. Then the resultant BSA–Ag/Au alloy NCs were precipitated by addition of  $\text{H}_2\text{SO}_4$  ( $1 \text{ mol}\cdot\text{L}^{-1}$ ), collected through centrifugal at  $8,000 \text{ r}\cdot\text{min}^{-1}$ , and then re-dispersed in 10 mL water solution for further application.

### Application as Pb (II) probe

$\text{PbCl}_2$  was used for the study of  $\text{Pb}^{2+}$  detection. A  $2.4 \text{ mmol}\cdot\text{L}^{-1}$  stock solution of  $\text{PbCl}_2$  was prepared, from which various  $\text{Pb}^{2+}$  concentrations were prepared by serial dilution. For the quenching studies, aqueous solutions of BSA–Ag/Au alloy NCs and  $\text{Pb}^{2+}$  with different concentrations were mixed, and equilibrated for 5 min before the spectral measurements. To check the selectivity cations of this probe, we carried out other metal ions including  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . The operation was exactly similar conditions that were used for the detection of  $\text{Pb}^{2+}$ .

### Characterization methods

UV–Vis absorption spectra were obtained by using a Lambda 800 UV–Vis spectrophotometer. Photoluminescence experiments were performed with a Shimadzu RF–5,301 PC spectrofluorimeter. X–ray photoelectron spectroscopy (XPS) using Mg  $\text{K}\alpha$  excitation (1,253.6 eV) was collected in a VG ESCALAB MKII spectrometer. Binding energy calibration was based on C 1s at 284.6 eV. The Fourier transform infrared spectroscopy (FT–IR) was measured at wavenumbers ranging from  $500 \text{ cm}^{-1}$  to  $4,000 \text{ cm}^{-1}$  using a Nicolet Avatar 360 FT–IR spectrophotometer. The morphology and mean diameter of resultant Ag/Au alloy NCs were characterized by Hitachi H–800 transmission electron microscope (TEM) operating at 200 kV.

## Results and discussion

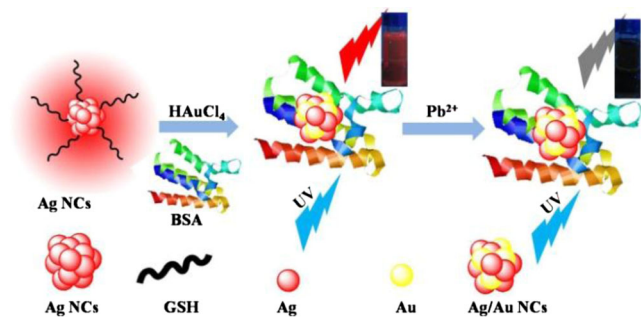
In the past few decades, lead(II) ( $\text{Pb}^{2+}$ ) levels are typically measured by using atomic absorption spectroscopy, inductively coupled plasma mass spectrometry (ICP–MS), and high performance liquid chromatography

**Table 1** The comparison of different probes for determination of  $\text{Pb}^{2+}$  (NPs=nanoparticles,  $\text{nM}=\text{nmol}\cdot\text{L}^{-1}$ )

| Methods/Materials       | Detection limit (nM) | Comments                                 | Reference |
|-------------------------|----------------------|--|-----------|
| Ag NPs                  | 13                   | Low sensitive                            | [28]      |
| EDTA-Au NPs             | 2.4                  | Low selective                            | [29]      |
| Guanine-Au NPs          | 20                   | Low sensitive and stability              | [7]       |
| Carbon electrode-Au NPs | 10                   | Complex and low selective                | [30]      |
| Quantum Dots            | 20                   | Low sensitive                            | [8]       |
| DNAzyme                 | 10                   | Expensive price                          | [9]       |
| Protein                 | 50                   | Expensive price, low sensitive           | [31]      |
| Cu nanoclusters         | 2.0                  | Blue fluorescence, difficult observation | [17]      |
| Alloy nanoclusters      | 2.0                  | Highly selective, sensitive              | This work |

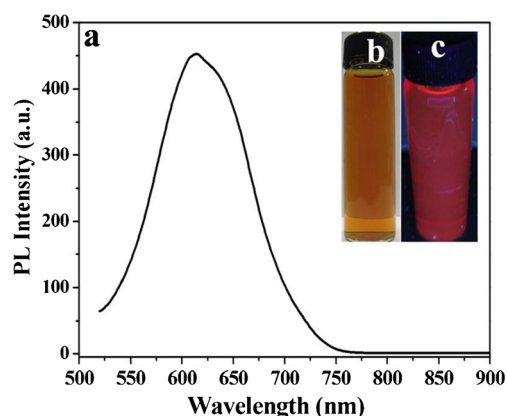
(HPLC). The drawbacks of them are time-consuming, expensive, and/or required sophisticated equipments. Compared with them, chemical probe is a sensitive, simple and fast method for quantifying  $\text{Pb}^{2+}$  and has attracted much attention [28–31]. Table 1 showed the comparison of different probes for determination of  $\text{Pb}^{2+}$ . It is apparent the Ag/Au alloy nanoclusters (NCs) could work as fluorescent probes for detection of  $\text{Pb}^{2+}$  with highly selective and sensitive.

The synthesis of Ag/Au alloy NCs through galvanic replacement reaction route is schematically illustrated in Scheme 1. In the first step, Ag NCs, as the templates, were prepared by chemical-reduced method using  $\text{N}_2\text{H}_4\cdot 2\text{H}_2\text{O}$  as reducing agent and glutathione as stabilizing agent, which was similar to previous report [16]. Then, when the  $\text{HAuCl}_4$  and BSA were added to the aqueous solution of Ag NCs, the galvanic replacement reaction occurred due to standard reduction potential of  $\text{AuCl}_4^-/\text{Au}$  pair (0.99 V vs SHE) was higher than that of  $\text{Ag}^+/\text{Ag}$  pair (0.80 V vs SHE) [32]. In this process, the Ag (0) changes to  $\text{Ag}^+$  and form the  $\text{AgCl}$  in the solution. On the other hand, the  $\text{AuCl}_4^-$  changes to Au (0). Herein the key for the formation of alloy NCs was controlled the molar ratios Ag/Au in galvanic replacement reaction. Theoretically speaking, reaction stoichiometry of Ag and  $\text{AuCl}_4^-$  is at 3:1 [33]. Hence, when molar ratios Ag/Au is higher than this

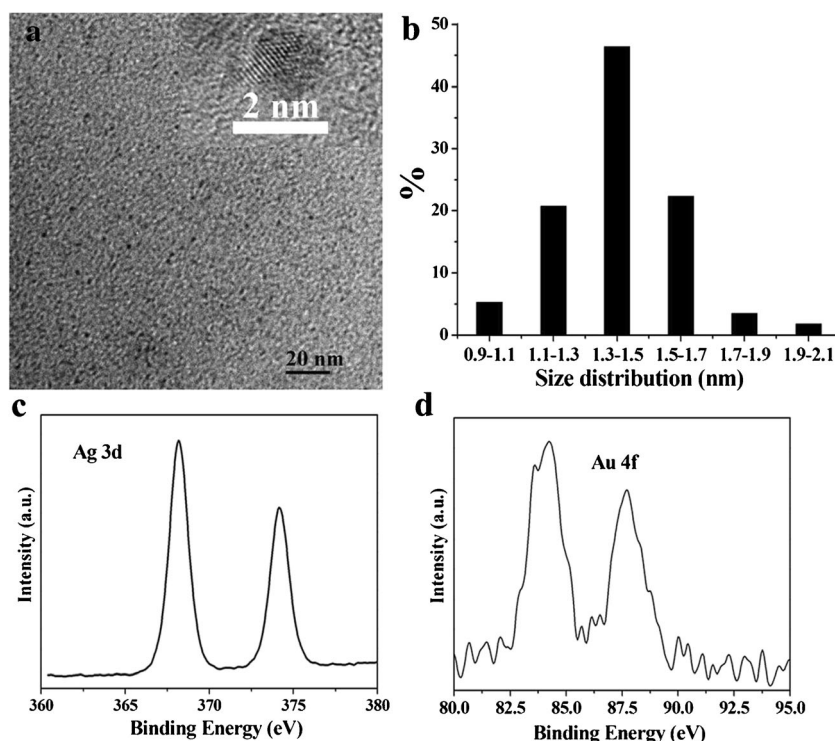
**Scheme 1** Schematic illustration of the formation and the  $\text{Pb}^{2+}$  induced quenching of Ag/Au alloy nanoclusters

value, the product would be alloy NCs [22]. Besides, BSA play an important role in the stability of alloy NCs. BSA worked as the model protein to stabilize the clusters and provide steric protection due to the 17 disulfide bonds and 1 free cysteine, which had been widely used in the synthesis of fluorescent Ag and Au NCs [34, 35].

By adjusting molar ratios of Ag/Au at 5:1, Ag/Au alloy NCs would be formed. Resultant alloy NCs exhibited intense red fluorescence with peak maximum at 620 nm under a wavelength of excitation of 500 nm (Fig. 1a). Both the solution and the freeze-dried forms of clusters showed strong red emission under UV light (365 nm) (Fig. 1c and Fig. S1, Electronic Supplementary Material, ESM). The fluorescence quantum yields of resultant alloy NCs reached up to 2.4 % using Rodamine 6G (quantum yields, 0.95 in ethanol) as the standard, which was suitable for preparing fluorescent probes for detecting heavy-metal ions. Moreover, resultant alloy NCs had good dispersion in aqueous solution and there was no noticeable precipitation, which was attributed to capping layer of BSA to prevent NCs from agglomeration (Fig. 1b). Different from reported NCs, this newly developed Ag/Au

**Fig. 1** a, the photoluminescence spectrum of Ag/Au alloy NCs in aqueous solution. The inset images show the photographs of Ag/Au alloy NCs: b, in room light and c, under a UV light source emitting 365 nm light

**Fig. 2** **a**, Typical TEM image of as-prepared Ag/Au alloy NCs (inset, high-resolution TEM image); **b**, size distribution: the average size was  $1.5 \pm 0.2$  nm; XPS spectra of resultant Ag/Au alloy NCs: **c**, Ag 3d and **d**, Au 4f

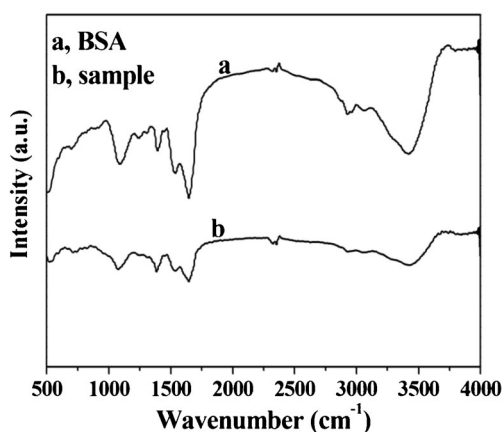


alloy NCs can not give a well-defined excitation band (Fig. S2, ESM) [16].

The transmission electron microscope (TEM) image of the Ag/Au alloy NCs was shown in Fig. 2a. As indicated, this galvanic replacement method gave the average size of resulting alloy NCs was  $1.5 \pm 0.2$  nm (Fig. 2b). Moreover, there was no formation of larger size nanoparticles or aggregation, which highlighted the unique template effect by BSA for the preparation of small-size alloy NCs. Moreover, the template of Ag NCs was too small to produce hollow or core-shell nanostructures, which was confirmed by high-resolution

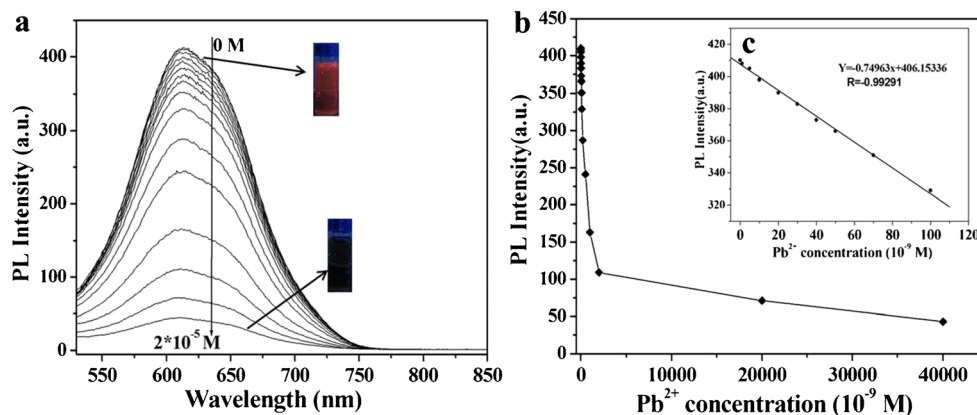
TEM image (inset of Fig. 2b). On the other hand, X-ray photoelectron spectroscopy (XPS) analysis is carried out to determine the oxidation state and elemental composition of as-prepared alloy NCs. In the present study, the binding energy of Ag  $3d_{5/2}$  and Ag  $3d_{3/2}$  appeared at 368.2 eV and 374.1 eV, which indicated the presence of  $\text{Ag}^0$  (Fig. 2c) [36]. The binding energy of Au 4f located at 88.1 eV and 84.3 eV respectively, could explicitly demonstrate that the electronic structure of Au in the alloy NCs was the coexistence of Au (0) and Au (I) (Fig. 2d) [37]. The results of photoluminescence, photoluminescence excitation, transmission electron microscopy and X-ray photoelectron spectroscopy confirmed one fact the Ag/Au alloy NCs were synthesized.

The surface chemistry of alloy NCs was confirmed by FT-IR spectroscopy. Comparing with the FT-IR spectra of alloy NCs and pure BSA, there were no differences in their spectra, inferring that the alloy NCs embedded in BSA would not affect the surface-structure of BSA (Fig. 3). BSA-capping fluorescent metal NCs displayed good dispersion and high stability in aqueous phase [26, 27]. Especially, BSA has a much-stronger affinity toward metal ions, including  $\text{Pb}^{2+}$ , which is important for practical applications in ion detection. So with this fluorescence active, water soluble alloy NCs in hands, we then investigated their ability as probe in selective metal  $\text{Pb}^{2+}$  detection. It was found that the luminescence of alloy NCs was quenched in the presence of  $\text{Pb}^{2+}$  ion (Fig. 4a). The emission spectra displayed a gradual decrease in emission intensity with the increase in the solution  $\text{Pb}^{2+}$  concentration (Fig. 4). Moreover, as shown in Fig. 4c, a linear relationship



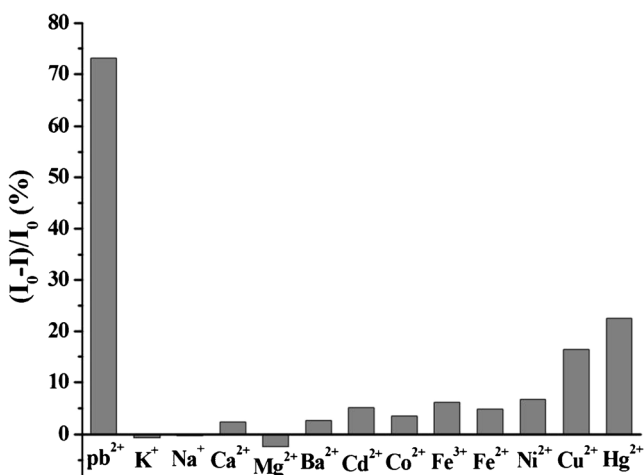
**Fig. 3** The FT-IR spectra of **a** pure BSA and **b** as-prepared Ag/Au alloy NCs, which confirmed the surface of resultant sample was protected by BSA

**Fig. 4** **a**, Changes in emission spectra ( $\lambda_{\text{ex}}=500$  nm) of as-prepared Ag/Au alloy NCs upon the addition of  $\text{Pb}^{2+}$  ions in different concentrations. **b** Maximum emission intensity changes of **a** as a function of the solution  $\text{Pb}^{2+}$  concentration. **c** Expanded linear region of the calibration curve ( $0.5\text{--}100$  nmol·L $^{-1}$  of  $\text{Pb}^{2+}$ )



was observed between the intensity of the fluorescence of resultant alloy NCs and the concentration of  $\text{Pb}^{2+}$  ions over the range from  $0.5$  nmol·L $^{-1}$  to  $100$  nmol L $^{-1}$ , which based on the result of fluorescence spectra of Fig. 4a. The limit of detection (LOD) was estimated to be  $2$  nmol·L $^{-1}$ , which was much lower than the maximum safety level of  $\text{Pb}^{2+}$  ( $75$  nmol L $^{-1}$ ) in drinking water defined by the U.S. Environmental Protection Agency (EPA).

To test the selectivity of this quenching behavior by  $\text{Pb}^{2+}$ , other metal ions were used for the probe study, such as  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . These ions were carried out as same as  $\text{Pb}^{2+}$  concentration ( $10^{-6}$  mol·L $^{-1}$ ) and exactly similar study conditions. The PL intensity variation of alloy NCs toward a variety of metal ions was presented in Fig. 5 (Based on the fluorescence spectra of Fig. S3 and S4, ESM). The results clearly showed that little emission intensity changes were observed in the presence of these interference metal ions, which



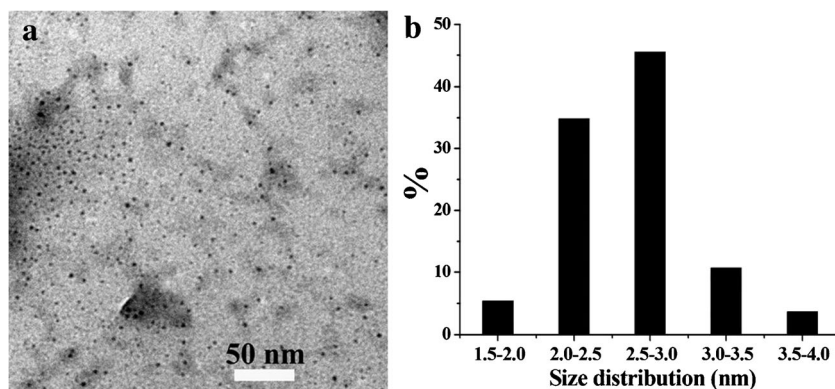
**Fig. 5** Relative emission intensity  $[(I_0-I)/I_0]$  of as-prepared Ag/Au alloy NCs after the addition of  $10^{-6}$  mol L $^{-1}$  of different metal ions.  $I_0$  and  $I$  were the maximum emission intensity of the Ag/Au alloy NCs before and after the addition of the metal ions

demonstrated that the assay method was highly selective for  $\text{Pb}^{2+}$  detection.

The reason for highly sensitive and selective fluorescence probe for  $\text{Pb}^{2+}$  is the aggregation-induced fluorescence quenching of Ag/Au alloy NCs. According to above discussion, the surface of alloy NCs was protected by BSA which was confirmed by FT-IR. This was important for highly selective and sensitive for  $\text{Pb}^{2+}$  detection, due to the alloy NCs aggregation induced by the complexation between BSA and the  $\text{Pb}^{2+}$  ion. BSA contains a high-affinity site for  $\text{Pb}^{2+}$  ion; the binding involves carboxylate groups [17]. The aggregation of alloy NCs induced by  $\text{Pb}^{2+}$  was confirmed by TEM image as shown in Fig. 6. We found that the  $\text{Pb}^{2+}$ -induced aggregation of the as-prepared fluorescent alloy NCs completed and left only larger aggregation (Fig. 6a) with the size about  $2.5\pm 0.5$  nm (Fig. 6b), which caused the luminescence quenching of alloy NCs. This sensing mechanism based on aggregation-induced fluorescence quenching had been widely adopted for NCs as probe to determine metal ions [17, 38, 39].

It is well known that highly sensitive and selective detection of  $\text{Pb}^{2+}$  in water is crucial in environmental and biological fields. Herein, to evaluate whether the alloy NCs-based fluorescent probe is applicable to natural systems, drinking water solution and lake water collected from Taihu Lake at Wuxi City were investigated. The experimental results showed that although the fluorescence was affected in the real water samples due to the complex environment including the various cations and pH value, the fluorescence of as-prepared alloy NCs was quenched with increasing the  $\text{Pb}^{2+}$  concentration and the detection for  $\text{Pb}^{2+}$  was also highly sensitive (Fig. S5a and S5b, ESM) and a linear relationship was observed between the intensity of the fluorescence of resultant alloy NCs and the concentration of  $\text{Pb}^{2+}$  ions over the range from  $5$  to  $20$  nmol·L $^{-1}$  (Fig. S5, ESM). These results further reveals that such a sensing system is highly selective toward  $\text{Pb}^{2+}$  over other compositions in real water samples.

**Fig. 6** **a**, TEM image of the aggregated Ag/Au alloy NCs in the presence of  $Pb^{2+}$  ions; **b**, size distribution: the average size was  $2.5 \pm 0.5$  nm



## Conclusions

A practical and robust synthesis of water-soluble and fluorescence active, small-size Ag/Au alloy nanoclusters (NCs) was successfully developed through galvanic replacement reaction. As-prepared alloy NCs exhibited red fluorescence with peak maximum at 620 nm and quantum yields up to 2.4 %. More importantly, the surface of as-prepared Ag/Au alloy NCs were protected by bovine serum albumin (BSA), which made them have good dispersion in aqueous solution and high stability. Besides, BSA have a much-stronger affinity toward metal ions, which suggested the resultant alloy NCs were promising fluorescent probes for detection of heavy-metal ions based on aggregation-induced fluorescence quenching mechanism. The results confirmed this newly developed alloy NCs indicated excellent selectivity and sensitivity for  $Pb^{2+}$  detection in water. Furthermore, the alloy NCs probe could detect  $Pb^{2+}$  ion in drinking water and lake water, which indicated that this novel sensing system has great potential for detection of  $Pb^{2+}$  in environmental samples.

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