Sensors and Actuators B 253 (2017) 283–291

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

A dual-functional spectroscopic probe for simultaneous monitoring Cu^{2+} and Hg^{2+} ions by two different sensing nature based on novel fluorescent gold nanoclusters

Shu Chen[a,b,*], Yangfang Kuang[a], Pingping Zhang[a], Yuanzhi Huang[a], Aoli Wen[a], Xuyao Zeng[c], Ruihong Feng[a], Huidong Nie[a], Xiaochun Jiang[b], Yunfei Long[a,**]

[a] Key Laboratory of Theoretical Organic Chemistry and Function Molecule of Ministry of Education, Hunan Provincial Key Laboratory of Controllable Preparation and Functional Application of Fine Polymers, Hunan Province College Key Laboratory of QSAR/QSPR, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, 411201, PR China
[b] Hubei Key Laboratory for Processing and Application of Catalytic Materials, Huanggang Normal University, Huanggang, 438000, PR China
[c] College of Chemistry, Nankai University, Tianjin, 300071, PR China

ARTICLE INFO

Article history:
Received 28 December 2016
Received in revised form 17 June 2017
Accepted 19 June 2017
Available online 21 June 2017

Keywords:
Gold nanoclusters
Dual-functional probe
Fluorescence quenching
Resonance light scattering (RLS)
Copper ions (Cu^{2+})
Mercury ions (Hg^{2+})

ABSTRACT

Here a dual-functional spectroscopic probe was developed based on novel gold nanoclusters (Au NCs) for highly selective and sensitive detection of heavy metal ions targeting copper ions (Cu^{2+}) and mercury ions (Hg^{2+}). Small sized Au NCs (3.9 nm) with highly orange emitting fluorescent were synthesized via an one-pot reaction by using citrate-stabilized stannous ions (Sn(II)-citrate) as reducing and capping agent. The dual spectroscopic probe was conceived in such a way to utilize both the fluorescence (FL) quenched by Cu^{2+} and resonance light scattering (RLS) enhanced by Hg^{2+}. Two different ions in the corresponding discrete spectral response appeared completely independent of each other by different mechanism. The intensity of fluorescence decreasing at 575 nm in FL spectra and the scattering increasing at 520 nm in RLS spectra, show linear relationships with Cu^{2+} and Hg^{2+} ion concentrations in the ranges of 0.5–70 and 0.25–10 $\mu mol\,L^{-1}$, respectively. The detection limits are as low as 0.38 $\mu mol\,L^{-1}$ and 0.05 $\mu mol\,L^{-1}$ for Cu^{2+} and Hg^{2+} ions, respectively. Furthermore, these Au NCs could be readily applied to Cu^{2+} and Hg^{2+} detection in environmental water samples, indicating it is promising to serve as a convenient, dual-functional, and label-free probe for related ions monitoring.

1. Introduction

The detection of various metal ions with selective and sensitive probes are of considerable interest due to their vital role in the human body even in trace amounts [1]. Among these, copper is the third most abundant essential trace element. The alternations of copper ions (Cu^{2+}) in cellular homeostasis are connected to serious neurodegenerative diseases, including Alzheimer's disease, amyotrophic lateral sclerosis (ALS), Menkes and Wilson's diseases and prion diseases [2–4]. On other hand, mercury is one of the most ubiquitous non-biodegradable toxic element that easily contaminates foods and natural environments. Mercury ions (Hg^{2+}) can be transformed into the human body through food chain due to their water solubility, and its excessive accumulation can cause Minamata disease, cognitive disorder and kidney damage [5–7]. Accordingly, many traditional techniques are readily available to quantify these two ions (Cu^{2+} and Hg^{2+}) independently by sophisticated analytical equipment [8–10]. The fluorescent, scattering and colorimetric spectrum for the monitoring have been rapidly developed in recent years, due to their simplicity in approach, fast response time and cost effectiveness [11–15]. However, challenges still exist in using single probes for simultaneous detection of Cu^{2+} and Hg^{2+} in multi-ion systems [16–21].

Recently, various spectroscopic probes including small organic molecules [22], polymer particles [23], quantum dots [24] and fluorescent metal nanoclusters (FM NCs) [25] have been developed and attracted tremendous attention for sensing metal ions. FM NCs

* Corresponding author.
** Corresponding author at: Key Laboratory of Theoretical Organic Chemistry and Function Molecule of Ministry of Education, Hunan Provincial Key Laboratory of Controllable Preparation and Functional Application of Fine Polymers, Hunan Province College Key Laboratory of QSAR/QSPR, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, 411201, PR China.
E-mail addresses: chenshumail@gmail.com (S. Chen), l_yunfei927@163.com (Y. Long).

http://dx.doi.org/10.1016/j.snb.2017.06.140
0925-4005/

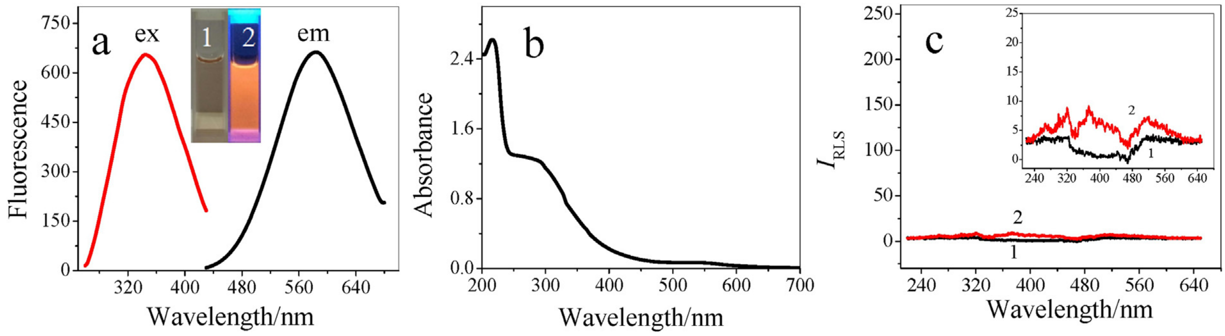

Fig. 1. (a) Fluorescent excitation spectrum and emission spectrum, (b) UV–vis absorption spectrum and (c) RLS spectrum of Au NCs as prepared. The inset in (a) shows photographs of Au NCs under (1) ambient light and (2) illuminated by an UV lamp of 365 nm. The line 1 in (c) is RLS spectrum of pure water.

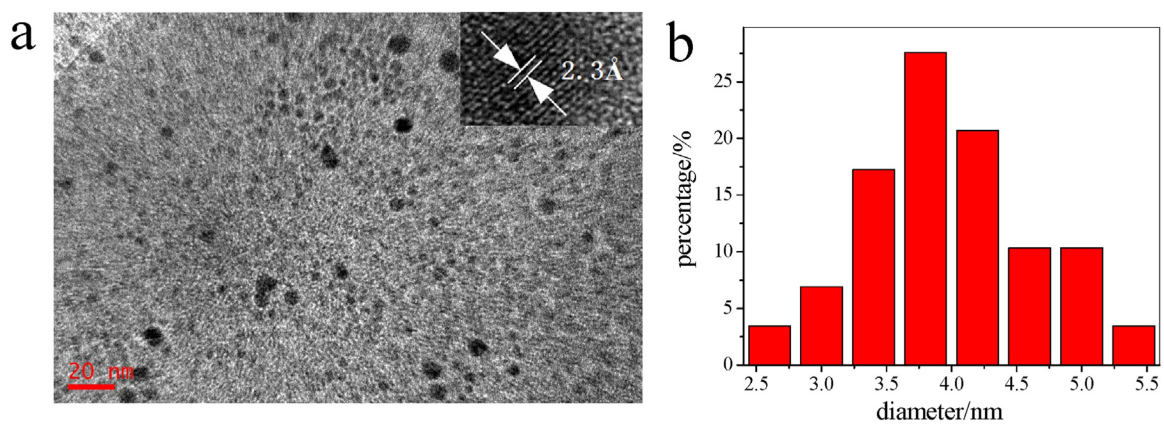

Fig. 2. (a) TEM image of Au NCs, the top inset is HRTEM of an individual nanocluster and (b) diameter distributions analysis of Au NCs.

have been received growing interest owing to their remarkable advances, such as ultra-small in size, large Stokes shift, good water dispersibility, strong fluorescence and excellent photostability [25]. It is reported that functional FM NCs have been used as fluorescence probes for various metal ions. In most cases, FM NCs (e.g. Au NCs, Ag NCs, Cu NCs) have been used in the independent determination of metal ions such as Hg^{2+} [26–31], Ag^{+} [32,33], Cu^{2+} [34], Fe^{3+} [35], Pb^{2+} [36], As^{3+} [37], Al^{3+} [38]. However, simultaneous detection of multiple metal ions using single NCs probe are still rare [39,40].

Herein, in this contribution, we report a dual-functional and label-free spectrum sensor for the detection of both Cu^{2+} and Hg^{2+} by using novel gold nanoclusters (Au NCs) prepared by citrate-stabilized stannous ions (Sn(II)-citrate) as reducing and capping agent. This new spectroscopic probe can be employed for the sensitive and selective detection of Cu^{2+} by fluorescence turn-off. Meanwhile, the Au NCs by contacting Hg^{2+} could produce enhanced resonance light scattering. Two different spectral responses appeared completely independent of each other. Thus, a single NCs probe can be applied for the selective determination of two different ions, Cu^{2+} and Hg^{2+}, in complex water samples.

2. Experimental

2.1. Materials and instruments

Stannous chloride ($SnCl_2$, Sigma-Aldrich, St. Louis, MO), trisodium citrate ($C_6H_5Na_3O_7{\cdot}2H_2O$), hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4{\cdot}4H_2O$, Sinopharm Chemical Reagent Co., Ltd.), hydrogen peroxide (H_2O_2), phosphoric acid (H_3PO_4), mercury nitrate ($Hg(NO_3)_2$), and copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) were of analytical grade and used as received without further purification. Double distilled water was used to prepare all solutions. Britton-Robinson buffer solution was used to control the acidity of the system.

Fluorescence (FL) and resonance light scattering (RLS) intensities study were conducted with a RF-5301PC fluorescent spectrophotometer (Shimadzu, Japan). The RLS spectra were obtained by scanning synchronously with the same excitation and emission wavelengths ($\lambda_{ex} = \lambda_{em}$) from 220 to 650 nm using fluorescence spectrophotometer [41]. The absorption spectra were obtained by a TU-1810 UV–vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd. China). The transmission electron microscopy (TEM) images were obtained using a Tecnai G20 transmission electron microscope (FEI Company, USA). A MM721NG1-PW microwave oven (GD Midea Holding Co., Ltd., China) was used to prepare gold nanoclusters (Au NCs). The dynamic light scattering (DLS) spectrogram was obtained using a Nano-ZS90 Zetasizer Nano ZS (Malvern Instrument Co., Ltd., UK). A ZF-7-type (black-box type) three-ultraviolet analyzer (Jia Peng, China) was used as the light source in semi-quantitative detection and Nikon coolpix-4500 digital camera was used to detect the images of the aqueous solutions upon excitation with three-ultraviolet analyzer at 365 nm.

2.2. Preparation of Au NCs

2.2.1. Sn(II)-citrate solution preparation

The Sn(II)-citrate stock solution was prepared by adding solid $SnCl_2$ into the trisodium citrate solution (1.7×10^{-2} mol L^{-1}) to get final concentration 1.2×10^{-2} mol L^{-1}. Herein, citrate acts as a complex ligand to avoid the hydrolysis of $SnCl_2$ and transparent solution are obtained. Sn(II)-citrate was used as reducing and capping agent in the following synthetic steps.