



Colorimetric detection of Cd(II) ions based on di-(1H-pyrrol-2-yl)methanethione functionalized gold nanoparticles



Yi-Ming Sung, Shu-Pao Wu*

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan

ARTICLE INFO

Article history:

Received 26 February 2014

Received in revised form 21 April 2014

Accepted 22 April 2014

Available online 30 April 2014

Keywords:

Colorimetric sensor

Cd(II)

Gold nanoparticles

Di-(1H-pyrrol-2-yl)methanethione

ABSTRACT

A sensitive and selective colorimetric Cd²⁺ detection method was developed using di-(1H-pyrrol-2-yl)methanethione functionalized gold nanoparticles (DP-AuNPs). Aggregation of DP-AuNPs was induced immediately in the presence of Cd²⁺, yielding a color change from red to blue. This Cd²⁺-induced aggregation of DP-AuNPs was monitored using the naked eye and UV–vis spectroscopy. The SPR absorbance (635 nm) of the reaction between DP-AuNPs and Cd²⁺ shows a good linearity in the Cd²⁺ concentration range of 0.5–16 μM and a low detection limit 16.6 nM (S/N = 3). The DP-AuNPs showed excellent selectivity toward Cd²⁺ compared to other metal ions Ag⁺, Al³⁺, Ca²⁺, Cd²⁺, Co²⁺, Cr³⁺, Cu²⁺, Fe²⁺, Fe³⁺, Hg²⁺, Mg²⁺, Mn²⁺, Ni²⁺, Pb²⁺, and Zn²⁺. Optimal detection of Cd²⁺ was achieved over a pH range from 4 to 9.5. Furthermore, DP-AuNPs were applied to detect Cd²⁺ in lake water, showing low interference.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Cadmium (Cd) is one of the most toxic heavy metals, and is widely used in industry and agriculture in applications such as metal alloys, batteries, and phosphate fertilizers [1]. Cadmium is easily absorbed and accumulated by plants and organisms, subsequently going through the soil–plant–animal–human food chain [2]. Chronic cadmium exposure causes renal dysfunction, calcium metabolism disorders, and several serious diseases such as lung, prostate, and renal cancers [3–5]. The maximum limit of cadmium in drinking water set by the World Health Organization (WHO) is 3 μg/L [6]. In order to better detect and monitor the presence of Cd²⁺ ions, the demand for sensitive and selective Cd²⁺ detection has gained much attention.

For identifying and detecting cadmium ions, several analysis methods such as atomic absorption spectrometry [7], inductively coupled plasma mass spectrometry (ICP-MS) [8], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [9], and electrochemical methods have been developed. Recently, several fluorescent chemosensors for Cd²⁺ detection have been also reported [10–14]. However, because they are made of organic molecules, fluorescent chemosensors are not highly soluble in water and have photobleaching problem. On the other hand,

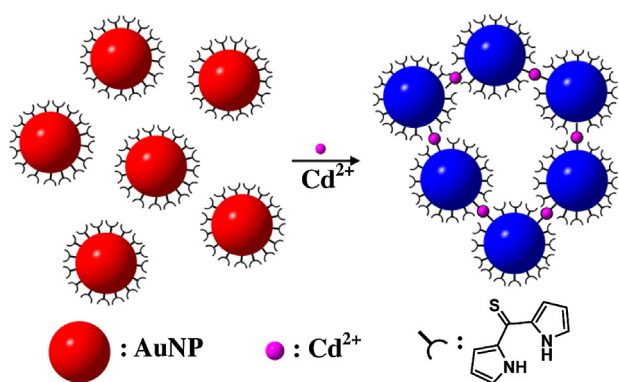
colorimetric methods based on functionalized gold nanoparticles (AuNPs) are simple and convenient, and can solve these limitations.

Gold nanoparticles have been widely applied as probes for metal ions [15–23], anions [24–27], small molecules [28], proteins [29,30], nucleic acids [31,32], and other analytes. Gold nanoparticles are easily modified by capping agents, possess excellent optical properties including high extinction coefficients, and distance-depend on plasmonic absorption [33,34]. Therefore, functionalized gold nanoparticles have been applied as colorimetric probes, and these have received great attention in visual sensing applications because of the plasmonic absorbance shift [35–37]. In these assays, analytes induce the aggregation of modified gold nanoparticles, resulting in color changes from red to blue, which are easily observed by the naked eye. The distance-dependent plasmonic absorbance shift of AuNPs has become a useful tool in the development of colorimetric sensing of various analytes.

In this report, di-(1H-pyrrol-2-yl)methanethione (DP) functionalized gold nanoparticles (DP-AuNPs) were synthesized for detecting Cd²⁺. Gold nanoparticles were prepared through the citrate-mediated reduction of HAuCl₄. Di-(1H-pyrrol-2-yl)methanethione [38,39] was attached to the surface of AuNPs through the sulfur linkage, and the resulting DP-AuNPs can be used for metal ion detection (Scheme 1). Metal ions such as Ag⁺, Al³⁺, Ca²⁺, Cd²⁺, Co²⁺, Cu²⁺, Cr³⁺, Fe²⁺, Fe³⁺, Hg²⁺, Mg²⁺, Mn²⁺, Ni²⁺, Pb²⁺, and Zn²⁺ were tested for metal ion selectivity, but Cd²⁺ was the only metal ion that caused aggregation of DP-AuNPs. This caused the SPR absorption band of the DP-AuNPs to shift to a longer wavelength, leading to a color change from red to blue. This color change can be

* Corresponding author. Tel.: +886 3 5712121x56506.

E-mail addresses: spwu@mail.nctu.edu.tw, spwu@faculty.nctu.edu.tw (S.-P. Wu).



Scheme 1. Schematic depiction of the Cd^{2+} -triggered aggregation of DP-AuNPs for Cd^{2+} detection.

used to detect the presence of Cd^{2+} ions. The plasmonic absorbance shift at 650 nm directly indicates the degree of DP-AuNPs aggregation caused by the addition of Cd^{2+} ions.

2. Experimental

2.1. Materials

Hydrogen tetrachloroaurate(III) tetrahydrate and citric acid were purchased from Showa. Thiophosgene was purchased from ACROS ORGANICS. Pyrrole, $\text{Al}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cr}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ and trisodium citrate was purchased from Alfa Aesar. $\text{AgClO}_4 \cdot x\text{H}_2\text{O}$, $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cd}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$, $\text{Fe}(\text{BF}_4)_2$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Hg}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{O}_2\text{CCH}_3)_4 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Zn}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ were purchased from Sigma–Aldrich. $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was purchased from Riedel-de Haen. 4-(2-Hydroxyethyl)-1-piperazine-ethane-sulfonic acid (Hepes) and tris(hydroxymethyl) aminomethane (Tris) were purchased from Biobasic. 2-(N-morpholino)ethanesulfonic acid (Mes) was purchased from J.T. Baker. All the other materials were analytically pure and were used without further purification. All pure water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$ was provided by a Millipore Direct-Q 3 Ultrapure Water System (Billerica, Massachusetts, USA). The synthesis and characterization of di-(1H-pyrrol-2-yl)methanethione (DP) are described in the supporting information [40].

2.2. Instruments

NMR spectra were obtained on Bruker DRX-300 NMR (Billerica, Massachusetts, USA). UV–vis spectra were recorded on Agilent 8453 UV–vis spectrometer (Santa Clara, California, USA). TEM images were recorded from JEOL JEM-2010 Transmission Electron Microscope (Tokyo, Japan). IR spectra were recorded on Bomem DA8.3 Fourier transform spectrometer (Quebec, Canada). ICP-MS analysis was recorded on Perkin Elmer Sciex Elan 5000 inductively coupled plasma mass spectrometry (Waltham, Massachusetts, USA).

2.3. Preparation of DP-AuNPs

Gold nanoparticles were prepared by reducing HAuCl_4 with trisodium citrate in the aqueous solution [41]. All glassware was thoroughly cleaned with aqua regia (3:1 HCl/HNO_3) and rinsed with Millipore-Q water prior to use. Briefly, HAuCl_4 (40 mL, $195 \mu\text{M}$) was heated to 100°C . Trisodium citrate solution (540 μL , 0.1 M) was added rapidly to the solution and the mixture solution was heated for 2 h at the same temperature. In order to remove excess sodium

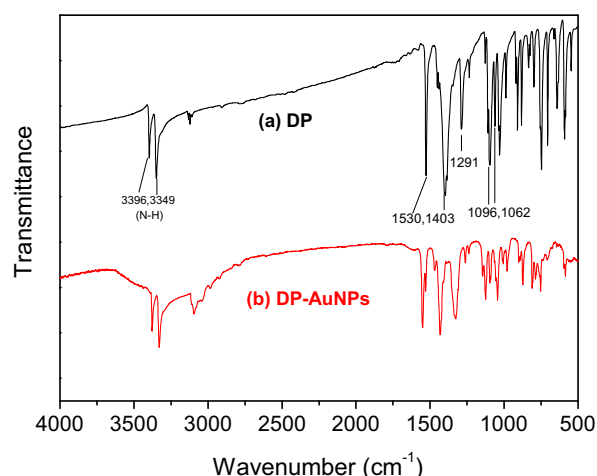


Fig. 1. FT-IR spectra of (a) DP and (b) DP-AuNPs.

citrate, the citrate-reduced Au nanoparticles were centrifuged for 15 min (12,000 rpm) and then dissolved with Millipore-Q water. Di-(1H-pyrrol-2-yl)methanethione (DP) solution (0.5 mL , 0.05 mM) was added into the AuNPs solution with sonication for ligand-exchange reaction. The excess ligands in the mixture were removed by centrifugation for 3 times. Finally, the DP-AuNPs were collected and stored at room temperature for further use.

2.4. Colorimetric detection of Cd^{2+}

To a 1.0 mL of solution containing DP-AuNPs, different metal ions ($15 \mu\text{M}$) were added separately. The mixtures were maintained at room temperature for 20 min and then transferred separately into 1.5-mL quartz cuvette. Their SPR absorption bands were recorded by UV–vis spectrophotometer.

2.5. The influence of pH on Cd^{2+} induced aggregation of DP-AuNPs

AuNPs were added with Cd^{2+} ($15 \mu\text{M}$) in 1.0 mL aqueous solution (10 mM buffer). The buffers (10 mM) were: pH 3–4, sodium citrate/citric acid; pH 4.5–6, Mes; pH 6.5–10, Hepes; pH 10–12, Tris.

3. Results and discussion

3.1. Characterization of DP-AuNPs

Gold nanoparticles were prepared through the citrate-mediated reduction of HAuCl_4 . Di-(1H-pyrrol-2-yl)methanethione (DP) was added into the AuNPs solution as the capping agent. Transmission electron microscopy (TEM) images revealed that the average particle size of DP-AuNPs was around 13 nm . The maximum absorption of the surface plasma resonance (SPR) of the AuNPs was located at 520 nm by a UV–vis spectrophotometer. The presence of DP-AuNPs was also verified by infrared spectroscopy. As shown in Fig. 1a, the characteristic skeleton peaks of DP were 3396 , 3349 , 1530 , 1403 , 1291 , 1096 , 1062 , and 1025 cm^{-1} . In Fig. 1b, the peaks are similar to those of DP. These results indicate that DP was capped on the surface of the gold nanoparticles through the Au–S bond.

3.2. Interaction of DP-AuNPs with various metal ions

To evaluate the selectivity of DP-AuNPs toward various metal ions in an aqueous solution, the UV–vis spectra of the synthesized DP-AuNPs were measured in the presence of metal ions such as Ag^+ , Al^{3+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , Mg^{2+} , Mn^{2+} ,

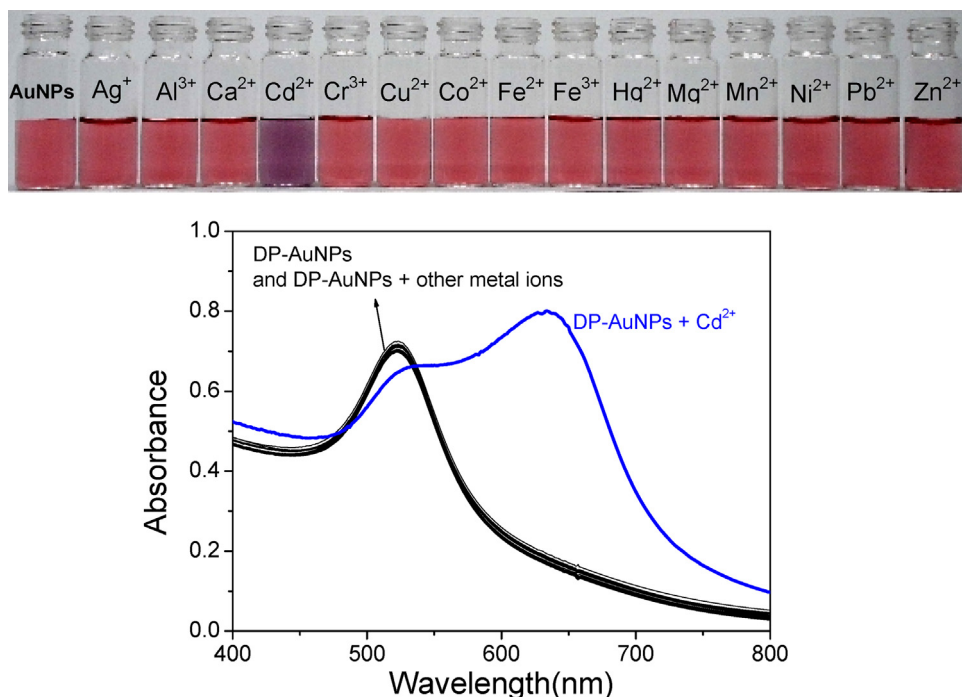


Fig. 2. (Top) Photographic image of DP-AuNPs in the presence of various metal ions (15 μM). (Bottom) UV-vis spectra of DP-AuNPs in the presence of different metal ions (15 μM). Buffer: 10 mM HEPES, pH 7.

Ni^{2+} , Pb^{2+} , and Zn^{2+} . Fig. 2 shows the effect of the metal ions on the appearance of DP-AuNPs in solution. Cd^{2+} was the only ion that caused a plasmonic absorption peak to shift from 520 to 635 nm. This red shift was observed as a color change from red to blue. The other metal ions did not influence the absorption spectra, indicating that no aggregation occurred. The dipyrrole on DP-AuNPs functions as a metal ion chelator. Cd^{2+} binding between the dipyrrole on DP-AuNPs induced the aggregation of the DP-AuNPs (Scheme 1). Fig. 3 shows a TEM image of the Cd^{2+} -induced aggregation of DP-AuNPs.

The degree of aggregation of DP-AuNPs depended on the concentration of Cd^{2+} ions; Fig. 4 shows the plasmonic absorbance change on addition of different concentrations of Cd^{2+} . The absorbance at 520 nm decreased with increasing Cd^{2+} concentration. The absorbance at 635 nm rose during Cd^{2+} titration as a result of the Cd^{2+} -induced aggregation of AuNPs. A linear relationship between the absorbance and the Cd^{2+} concentration was found when the concentration of Cd^{2+} ions was between 0.5 and 16 μM . The limit of detection for Cd^{2+} was found to be 16.6 nM (see Figure S2 in the supplementary data), which is comparable with those of previously reported optical assays as shown in Table 1.

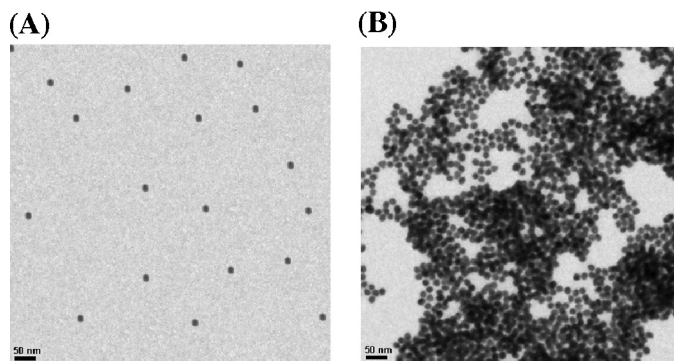


Fig. 3. (A) TEM images of DP-AuNPs. (B) TEM images of DP-AuNPs in the presence of Cd^{2+} . The scale bar is 50 nm.

Aggregated DP-AuNPs can be redispersed by removing Cd^{2+} ions with EDTA; this was confirmed by the consequent plasmonic absorption shift from 635 to 530 nm (Fig. 5). After removing the supernatant using a centrifuge and suspending the residue in an aqueous media, the dispersed DP-AuNPs can be reused to detect Cd^{2+} (see Figure S4 in the supporting information). Through this technique, the DP-AuNPs system can be used repeatedly for the detection of Cd^{2+} .

3.3. Interference studies

In order to study the influence of other metal ions on Cd^{2+} binding to DP-AuNPs, competitive experiments were carried out with Cd^{2+} (15 μM) in the presence of other metal ions, namely Ag^+ , Al^{3+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} at 150 μM each (Fig. 6). The plasmonic absorption shift caused by the mixture of Cd^{2+} with another metal ion

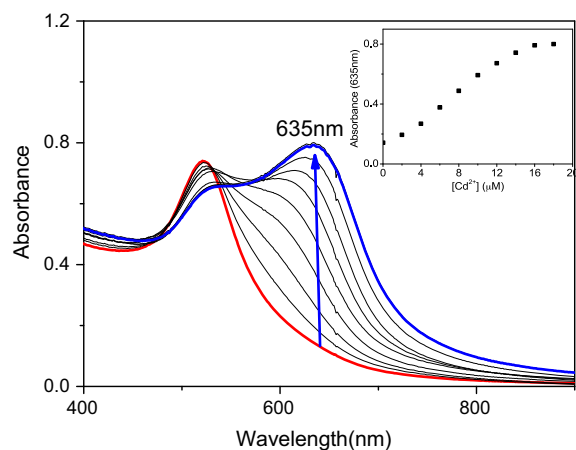


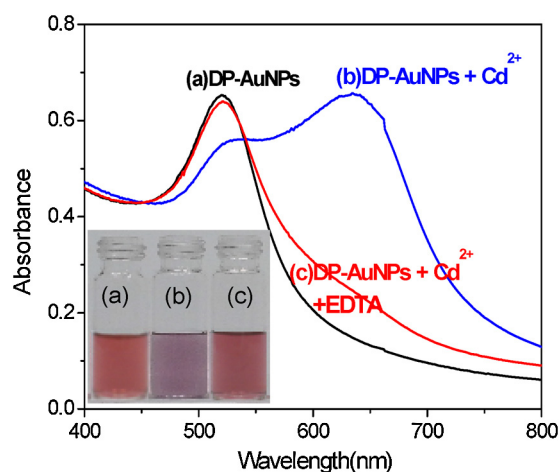
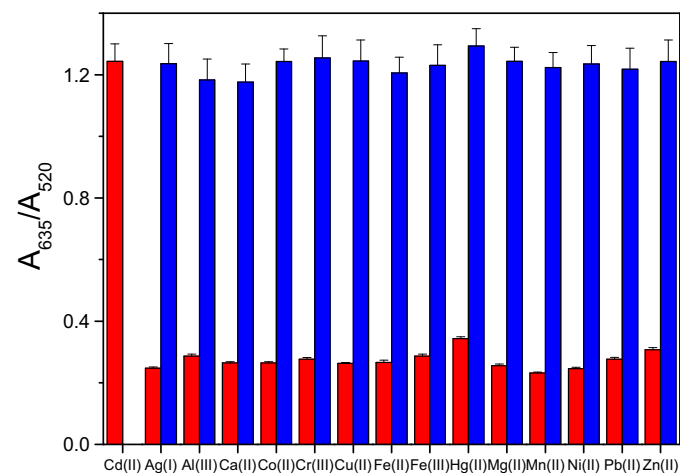
Fig. 4. SPR absorption changes of DP-AuNPs in the presence of various concentrations of Cd^{2+} (10 mM HEPES, pH 7).

Table 1
Comparison of this work with some methods for Cd²⁺ detection.

Detection method	Linear range (M)	Limit of detection (M)	Reference
AA	8.9×10^{-9} – 1.7×10^{-7}	1.8×10^{-9}	[7]
ICPMS	1.1×10^{-9} – 1.3×10^{-8}	7.1×10^{-10}	[8]
ICP-AES	4.5×10^{-8} – 8.9×10^{-7}	9.8×10^{-9}	[9]
Organic fluorescent probe	3.2×10^{-6} – 3.2×10^{-4}	1.2×10^{-9}	[11]
Organic fluorescent probe	0 – 5.0×10^{-5}	Not given	[12]
Organic fluorescent probe	Not given	1.0×10^{-9}	[13]
Organic fluorescent probe	8.0×10^{-6} – 4.0×10^{-4}	3.1×10^{-6}	[14]
This method	0.5×10^{-6} – 1.6×10^{-5}	1.7×10^{-8}	

Table 2
Determination of Cd²⁺ in lake water.

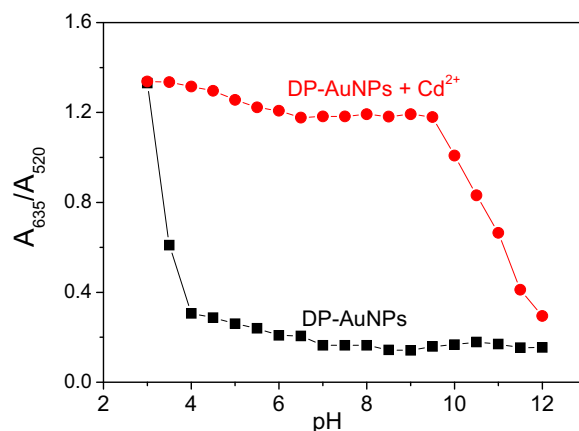
Sample	Added Cd ²⁺ (μM)	Proposed method ^a (μM)	Recovery (%)	RSD ^b (n = 3, %)	ICP-MS method (μM)
1	3.0	2.9	96.7	4.4	3.0
2	6.0	6.1	102.4	2.1	6.1
3	9.0	9.1	101.2	1.1	8.9

^a By using DP-AuNPs.^b RSD is the abbreviation of relative standard deviation.**Fig. 5.** Reversible binding of Cd²⁺ with DP-AuNPs in aqueous solutions (10 mM HEPES, pH 7.0). (a) The black line is the UV-vis spectrum of DP-AuNPs. (b) The blue line is the UV-vis spectrum of DP-AuNPs in the presence of Cd²⁺ (15 μM). (c) The red line is the UV-vis spectrum of DP-AuNPs in the presence of Cd²⁺ (15 μM) followed by addition of EDTA (1 mM). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)**Fig. 6.** Absorbance ratio (A_{635}/A_{520}) of DP-AuNPs in the presence of different metal ions. Black bars represent the addition of a single metal ion (150 μM); red bars represent a mixture of Cd²⁺ (15 μM) with another metal ion (150 μM).

was similar to that caused solely by Cd²⁺. This indicates that the other metal ions did not interfere in the binding of DP-AuNPs with Cd²⁺. This finding is consistent with previous studies suggesting that Cd²⁺ is the only metal ion that can induce the aggregation of DP-AuNPs.

3.4. Influence of pH on Cd²⁺-induced aggregation of DP-AuNPs

To investigate the pH range over which DP-AuNPs can effectively detect Cd²⁺, a pH titration of DP-AuNPs was carried out. In Fig. 7, the absorbance ratio (A_{635}/A_{520}) of DP-AuNPs was low and constant over the pH range of 4–12. This indicates that the DP-AuNPs were stable in the pH range of 4 to 12. When the pH was lower than 4, the absorbance ratio (A_{635}/A_{520}) of DP-AuNPs increased. Under acidic conditions (pH 3), protonation on DP resulted in the aggregation of AuNPs. The influence of pH on the Cd²⁺-induced aggregation of DP-AuNPs is also shown in Fig. 7; addition of Cd²⁺ resulted in a high absorbance ratio (A_{635}/A_{520}) over a pH range of 4–9.5. At pH > 10, the absorbance ratio (A_{635}/A_{520}) decreased due to the formation of colloidal Cd(OH)₂ [42]. Therefore, the optimal pH range for detecting Cd²⁺ by DP-AuNPs is 4–9.5.

**Fig. 7.** Influence of pH on the UV-vis spectra of DP-AuNPs in the absence and presence of Cd²⁺ (15 μM).

3.5. Application to the analysis of lake samples

To verify the practical application of DP-AuNPs, water samples from different lakes in Hsinchu, Taiwan were collected. All the water samples were filtered through a 0.2 μm membrane and then spiked with different amounts of a Cd^{2+} standard solution. A calibration curve of DP-AuNPs plasmonic absorption shifts in the presence of different Cd^{2+} concentrations was prepared (see Figure S5 in the supplementary data). The analytical results are shown in Table 2. The recovery values ranged from 96.7% to 102.4%, with the relative standard deviation (RSD) lower than 4.4%. The results obtained by DP-AuNPs are in good agreement with those obtained by ICP-MS. As a result, DP-AuNPs could be applied to detect Cd^{2+} ions in complex aqueous solutions. Compared with other methods for Cd^{2+} ion detection, this probe showed a lower cost and better performance.

4. Conclusion

This report demonstrated that DP-AuNPs can be used to detect Cd^{2+} ions effectively. Cd^{2+} was the only metal ion that induced aggregation of DP-AuNPs, resulting in a color change from red to blue and a corresponding plasmonic absorption shift from 520 to 635 nm. The optimal pH range for Cd^{2+} detection using DP-AuNPs was determined to be from 4 to 9.5. In addition, DP-AuNPs can be used to detect Cd^{2+} in environmental samples.

Acknowledgements

We gratefully acknowledge the financial support of Ministry of Science and Technology (Taiwan, 101-2113-M-009-016-MY2) and National Chiao Tung University.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2014.04.069>.

References

- [1] A. Mendes, G. Duda, C. do Nascimento, M. Silva, Bioavailability of cadmium and lead in a soil amended with phosphorus fertilizers, *Sci. Agric.* 63 (2006) 328–332.
- [2] L. Lu, I. Chang, T. Hsiao, Y. Yu, H. Ma, Identification of pollution source of cadmium in soil. Application of material flow analysis and a case study in Taiwan, *Environ. Sci. Pollut. Res.* 14 (2007) 49–59.
- [3] G. Jiang, L. Xu, S. Song, C. Zhu, Q. Wu, L. Zhang, L. Wu, Effects of long-term low-dose cadmium exposure on genomic DNA methylation in human embryo lung fibroblast cells, *Toxicology* 244 (2008) 49–55.
- [4] R. Goyer, J. Liu, M. Waalkes, Cadmium and cancer of prostate and testis, *BioMetals* 17 (2004) 555–558.
- [5] J. Godt, F. Scheidig, C. Grosse-Siestrup, V. Esche, P. Brandenburg, A. Reich, D.A. Groneberg, The toxicity of cadmium and resulting hazards for human health, *J. Occup. Med. Toxicol.* 1 (2006) 1–6.
- [6] WHO, Cadmium, in: *Guidelines for Drinking-Water Quality*, 3rd ed, 2008, pp. 317–319.
- [7] H. Parham, N. Pourreza, N. Rahbar, Solid phase extraction of lead and cadmium using solid sulfur as a new metal extractor prior to determination by flame atomic absorption spectrometry, *J. Hazard. Mater.* 163 (2009) 588–592.
- [8] S. D'Ilio, F. Petrucci, M. D'Amato, M. Di Gregorio, O. Senofonte, N. Violante, Method validation for determination of arsenic, cadmium, chromium and lead in milk by means of dynamic reaction cell inductively coupled plasma mass spectrometry, *Anal. Chim. Acta* 624 (2008) 59–67.
- [9] M. Zougagh, A.G. de Torres, J.M. Cano Paven, Determination of cadmium in water by ICP-AES with on-line adsorption preconcentration using DPTH-gel and TS-gel microcolumns, *Talanta* 56 (2002) 753–761.
- [10] T.Y. Cheng, T. Wang, W.P. Zhu, X.L. Chen, Y.J. Yang, Y.F. Xu, X.H. Qin, Red-emission fluorescent probe sensing cadmium and pyrophosphate selectively in aqueous solution, *Org. Lett.* 13 (2011) 3656–3659.
- [11] H.-Y. Luo, J.-H. Jiang, X.-B. Zhang, C.-Y. Li, G.-L. Shen, R.-Q. Yu, Synthesis of porphyrin-appended terpyridine as a chemosensor for cadmium based on fluorescent enhancement, *Talanta* 72 (2007) 575–581.
- [12] T. Cheng, Y. Xu, S. Zhang, W. Zhu, X. Qian, L. Duan, A highly sensitive and selective OFF-ON fluorescent sensor for cadmium in aqueous solution and living cell, *J. Am. Chem. Soc.* 130 (2008) 16160–16161.
- [13] G.M. Cockrell, G. Zhang, D.G. VanDerveer, R.P. Thummel, R.D. Hancock, Enhanced metal ion selectivity of 2,9-di-(pyrid-2-yl)-1,10-phenanthroline and its use as a fluorescent sensor for cadmium(II), *J. Am. Chem. Soc.* 130 (2008) 1420–1430.
- [14] Y. Yang, T. Cheng, W. Zhu, Y. Xu, X. Qian, Highly selective and sensitive near-infrared fluorescent sensors for cadmium in aqueous solution, *Org. Lett.* 13 (2010) 264–267.
- [15] S.-P. Wu, Y.-P. Chen, Y.-M. Sung, Colorimetric detection of Fe^{3+} ions using pyrophosphate functionalized gold nanoparticles, *Analyst* 136 (2011) 1887–1891.
- [16] Y. Kim, R.C. Johnson, J.T. Hupp, Gold nanoparticle-based sensing of spectroscopically silent heavy metal ions, *Nano Lett.* 1 (2001) 165–167.
- [17] Y. Xue, H. Zhao, Z. Wu, X. Li, Y. He, Z. Yuan, Colorimetric detection of Cd^{2+} using gold nanoparticles cofunctionalized with 6-mercaptopicolinic acid and L-cysteine, *Analyst* 136 (2011) 3725–3730.
- [18] J. Yin, T. Wu, J. Song, Q. Zhang, S. Liu, R. Xu, H. Duan, SERS-active nanoparticles for sensitive and selective detection of cadmium ion (Cd^{2+}), *Chem. Mater.* 23 (2011) 4756–4764.
- [19] A.-J. Wang, H. Guo, M. Zhang, D.-L. Zhou, R.-Z. Wang, J.-J. Feng, Sensitive and selective colorimetric detection of cadmium(II) using gold nanoparticles modified with 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole, *Microchim. Acta* 180 (2013) 1051–1057.
- [20] V.V. Kumar, S.P. Anthony, Silver nanoparticles based selective colorimetric sensor for Cd^{2+} , Hg^{2+} and Pb^{2+} ions: tuning sensitivity and selectivity using co-stabilizing agents, *Sens. Actuators B* 191 (2014) 31–36.
- [21] S.K. Tripathy, J.Y. Woo, C. Han, Colorimetric detection of $\text{Fe}(\text{III})$ ions using label-free gold nanoparticles and acidic thiourea mixture, *Sens. Actuators B* 181 (2013) 114–118.
- [22] Y. Chen, I. Lee, Y. Sung, S. Wu, Triazole functionalized gold nanoparticles for colorimetric Cr^{3+} sensing, *Sens. Actuators B* 188 (2013) 354–359.
- [23] D. Maity, R. Gupta, R. Gunupuru, D.N. Srivastava, P. Paul, Calix[4] arene functionalized gold nanoparticles: application in colorimetric and electrochemical sensing of cobalt ion in organic and aqueous medium, *Sens. Actuators B* 191 (2014) 757–764.
- [24] K.S. Youk, K.M. Kim, A. Chatterjee, K.H. Ahn, Selective recognition of fumarate from maleate with a gold nanoparticle-based colorimetric sensing system, *Tetrahedron Lett.* 49 (2008) 3652–3655.
- [25] W.L. Daniel, M.S. Han, J.S. Lee, C.A. Mirkin, Colorimetric nitrite and nitrate detection with gold nanoparticle probes and kinetic end points, *J. Am. Chem. Soc.* 131 (2009) 6362–6363.
- [26] L. Chen, W. Lu, X. Wang, L. Chen, A highly selective and sensitive colorimetric sensor for iodide detection based on anti-aggregation of gold nanoparticles, *Sens. Actuators B* 182 (2013) 482–488.
- [27] H. Deng, C. Wu, A. Liu, G. Li, W. Chen, X. Lin, Colorimetric sensor for thiocyanate based on anti-aggregation of citrate-capped gold nanoparticles, *Sens. Actuators B* 191 (2014) 479–484.
- [28] Z. Sun, Z. Cui, H. Li, p-Amino benzenesulfonic acid functionalized gold nanoparticles: synthesis, colorimetric detection of carbaryl and mechanism study by zeta potential assays, *Sens. Actuators B* 183 (2013) 297–302.
- [29] C.S. Tsai, T.B. Yu, C.T. Chen, Gold nanoparticle-based competitive colorimetric assay for detection of protein–protein interactions, *Chem. Commun.* 427 (2005) 4273–4275.
- [30] A. Laromaine, L. Koh, M. Murugesan, R.V. Ulijn, M.M. Stevens, Protease-triggered dispersion of nanoparticle assemblies, *J. Am. Chem. Soc.* 129 (2007) 4156–4157.
- [31] H. Li, L. Rothberg, Colorimetric detection of DNA sequences based on electrostatic interactions with unmodified gold nanoparticles, *Proc. Natl. Acad. Sci. U.S.A.* 101 (2004) 14036–14039.
- [32] C.A. Mirkin, R.L. Letsinger, R.C. Mucic, J.J. Storhoff, A DNA-based method for rationally assembling nanoparticles into macroscopic materials, *Nature* 382 (1996) 607–609.
- [33] M.-C. Daniel, D. Astruc, Gold nanoparticles: assembly supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology, *Chem. Rev.* 104 (2004) 293–346.
- [34] C. Burda, X. Chen, R. Narayanan, M.A. El-Sayed, Chemistry and properties of nanocrystals of different shapes, *Chem. Rev.* 105 (2005) 1025–1102.
- [35] A. Majzik, L. Fülöp, E. Csapó, D. Sebök, T. Martinek, F. Bogár, B. Penke, Imre Dékány, Functionalization of gold nanoparticles with amino acid, β -amyloid peptides and fragment, *Colloids Surf. B* 81 (2010) 235–241.
- [36] E. Csapó, R. Patakválvi, V. Hornok, Á. Sipos, A. Szalai, M. Csete, I. Dékány, Effect of pH on stability and plasmonic properties of cysteine-functionalized silver nanoparticle dispersions, *Colloids Surf. B* 98 (2012) 43–49.
- [37] A. Szalai, Á. Sipos, E. Csapó, L. Tóth, M. Csete, I. Dékány, Comparative study of plasmonic properties of cysteine functionalized gold and silver nanoparticle aggregates, *Plasmonics* 8 (2013) 53–62.
- [38] C. Bruckner, S.J. Rettig, D. Dolphin, 2-Pyrrolylthiones as monoanionic bidentate N,S-chelators: synthesis and molecular structure of 2-pyrrolylthionato complexes of nickel(II), cobalt(III), and mercury(II), *Inorg. Chem.* 39 (2000) 6100–6106.

- [39] S.V. Selivanova, D. Dolphin, C. Bruckner, J.E. van Lier, S. Kudrevich, The synthesis and properties of new 2-pyrrolylthiones as chelating agents for transition metals and technetium, *Bioorg. Med. Chem. Lett.* 11 (2001) 2697–2699.
- [40] T.V. Goud, A. Tutar, J.-F. Biellmann, Synthesis of 8-heteroatom-substituted 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene dyes (BODIPY), *Tetrahedron* 62 (2006) 5084–5091.
- [41] G. Frens, Controlled nucleation for the regulation of particle size in monodisperse gold suspensions, *Nature* 241 (1973) 20–22.
- [42] I. Ichinose, K. Kurashima, T. Kunitake, Spontaneous formation of cadmium hydroxide nanostrands in water, *J. Am. Chem. Soc.* 126 (2004) 7162–7163.

Biographies

Yi-Ming Sung is studying for Ph.D. in the Department of Applied Chemistry at National Chiao Tung University.

Dr. Shu-Pao Wu had Ph.D. in 2004, Department of Chemistry, The Ohio State University, USA. Currently, he is working as an Associate Professor in Department of Applied Chemistry National Chiao Tung University, Taiwan, Republic of China. Current interests: metal ion chemosensors and AlkB.