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Protein-templated gold nanoclusters based sensor for off–on detection of ciprofloxacin with a high selectivity

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ABSTRACT

In this contribution, bovine serum albumin stabilized gold nanoclusters as novel fluorescent probes were successfully utilized for the detection of ciprofloxacin for the first time. Our prepared gold nanoclusters exhibited strong emission with peak maximum at 635 nm. Cu^{2+} was employed to quench the strong fluorescence of the gold nanoclusters, whereas the addition of ciprofloxacin caused the fluorescence intensity restoration of the Cu^{2+}–gold nanoclusters system. The increase in fluorescence intensity of Cu^{2+}–gold nanoclusters system caused by ciprofloxacin allows the sensitive detection of ciprofloxacin in the range of 0.4 ng mL^{-1} to 50 ng mL^{-1}. The detection limit for ciprofloxacin is 0.3 ng mL^{-1} at a signal-to-noise ratio of 3. The present sensor for ciprofloxacin detection possesses a low detection limit and wide linear range. In addition, the real samples were analyzed with satisfactory results.

1. Introduction

Few-atom noble-metal nanoclusters that exhibit strong, robust, and size-dependent fluorescence emission have been developed as a new class of fluorescent materials recently [1–4]. They typically consist of several to tens of atoms and are <1 nm in size. A variety of methods have been applied to the generation of noble metal clusters through the reduction of metal cations in different scaffolds such as thiolate, polymers, peptides and DNA that endowed these fluorophores with special properties [5–8]. Increasing interest has been focused on the application of fluorescent noble-metal nanoclusters in numerous fields especially bioanalytical fields due to their unique optical properties. Based on their unique optical properties, they are employed in copper(II) ion detection [9,10], mercury(II) ion detection [11], proteins detection [12], amino acids identification [13], single nucleotide mutation identification [14], drug–DNA interaction investigation [15], and so forth.

Ciprofloxacin is the third generation member of quinolone antibiotics that displays wide spectrum activity against both Gram positive and Gram negative bacteria. So far, ciprofloxacin has shown growth-inhibitory effects against human bladder cells, leukemic cell lines, human osteosarcoma cells, human prostate cancer cells, human colorectal carcinoma cells and human non-small cell lung cancer cell line [16]. In particular, ciprofloxacin is useful for the treatment of urinary tract infections, acute cystitis, lower respiratory tract infections, nosocomial pneumonia, skin and skin structure infections, intra abdominal infections, bone and joint infections and chronic bacterial infection [17–24]. However, ciprofloxacin has been reported to occur in aquatic and soil environments at concentrations that often exceed the suggested minimum inhibitory levels for various indicator species including many bacterial species [25]. Indeed after administration to humans, 50–90% of quinolone antibiotics are rapidly excreted into wastewater [26]. In recent years, public and scientific concern about the relevance of trace amounts of pharmaceuticals that occur in the environment has been continuously increasing.

Several analytical methods for ciprofloxacin have been developed so far, such as high-performance liquid chromatography [27], capillary electrophoresis [28], micellar liquid chromatographic [29], luminescence [30] and resonance light scattering [31]. However, these methods have their unavoidable drawbacks. For example, the high-performance liquid chromatography method is limited by the complex operation and expensive apparatus; the capillary electrophoresis method undergoes bad reproducibility and so on. Thus, a simple, rapid, reproducible and highly sensitive method for the determination of ciprofloxacin is highly desirable.

In the present study, novel luminescent gold nanoclusters (AuNCs) were synthesized by utilizing bovine serum albumin (BSA) as templates with a simple, rapid and one-pot procedure. Luminescence studies indicated that these BSA–AuNCs exhibited strong emission with peak maximum at 635 nm. Cu^{2+} is a well-known

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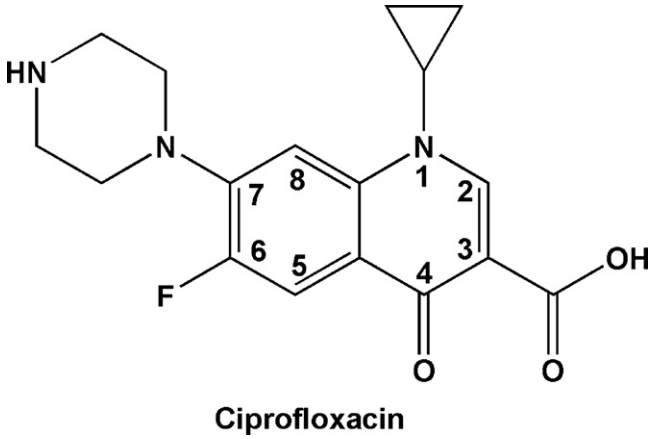


Fig. 1. The structure of CIP.

highly efficient fluorescent quencher due to its paramagnetic properties via electron or energy transfer [32]. Besides, Cu^{2+} can bind to the C3-carboxyl and C4-ketone groups of the quinolone antibiotics (Fig. 1 shows the structure of ciprofloxacin). Enlightened by the above facts, we think that a fluorescent assay for ciprofloxacin can be developed by utilizing the interaction between ciprofloxacin and Cu^{2+} to restore the fluorescence of Cu^{2+}–AuNCs systems. Herein, a simple, rapid and highly sensitive fluorescent method for the quantitative determination of ciprofloxacin has been presented by using the fluorescence restoration of Cu^{2+}–AuNCs after the addition of ciprofloxacin.

2. Experimental

2.1. Materials and reagents

Ciprofloxacin (CIP) was purchased from Huamei Biology Technology Co. Ltd. 0.1 g CIP was dissolved by 0.1 mol L^{-1} hydrochloric acid to prepare a 2.0 mg mL^{-1} stock solution. The subsequent concentrations of the needed working solutions were prepared by serial dilution of proper amounts of the stock solution. 0.0125 g $CuSO_4{\cdot}5H_2O$ was dissolved directly in 50 mL freshly obtained doubly distilled water to prepare a 1.0×10^{-3} mol L^{-1} stock solution.

The synthesis of protein–AuNCs was in accordance with the reported method [33] with minor modification. Briefly, 1.0 g $HAuCl_4{\cdot}4H_2O$ was dissolved in 100 mL doubly distilled water to prepare a 10 mg mL^{-1} stock solution. Then 4.1 mL aqueous $HAuCl_4$ solution was added to BSA solution (10 mL, 50 mg mL^{-1}, 37 °C) under vigorous stirring. Two minutes later, NaOH solution (1.0 mL, 1.0 mol L^{-1}) was introduced, and the mixture was incubated at 37 °C for 12 h.

All chemicals used were of analytical grade or the best grade commercially available, and doubly distilled water was used throughout.

2.2. Apparatus

The fluorescence spectra were recorded by an LS-55 spectrofluorometer (Perkin-Elmer, USA) equipped with a quartz cuvette (1.0 cm × 1.0 cm). DF-101S collection hot-like magnetic force heating mixer (Gongyi City Yuhua Instrument Co., Ltd, Henan, China) was employed to control the temperature. The circular dichroic (CD) spectra were recorded on a MOS450 spectropolarimeter (Bio-Logic, France) over the range of 200–270 nm, using 1.0 cm cells.

2.3. Fluorescence experiments

A 15 μL portion of the prepared gold nanoclusters was added into a 10 mL calibrated flask. Then a certain volume of Cu^{2+} and ciprofloxacin solutions were added into the gold nanoclusters. The final volume of the mixture was diluted to 5.0 mL by doubly distilled water. Under the excitation wavelength of 480 nm, the fluorescence spectra of gold nanoclusters were recorded.

3. Results and discussion

3.1. Characterization of the obtained gold nanoclusters

The as-prepared gold nanoclusters (BSA–AuNCs) are highly dispersed in aqueous solution and emit an intense red fluorescence under UV light (365 nm), as shown in Fig. 2A. They exhibit strong fluorescence and the maximum excitation and emission wavelengths of the predominant fluorescent emitters are 506 nm and 635 nm, respectively (Fig. 2B). To explore the structural change of BSA, CD spectra of BSA and BSA–AuNCs were measured. As displayed in Fig. 2C, BSA shows a strong minimum at 217 nm, and BSA–AuNCs reveals a decreased minimum, which is indicative of change in helicity of BSA in the synthesis processes of BSA–AuNCs. We also studied the effect of different excitation wavelengths on the fluorescence of BSA–AuNCs. With the increase of excitation wavelength, the fluorescence intensity increased, but the maximum emission wavelength remained at 635 nm, which indicates that the optical signal is real fluorescence from the BSA–AuNCs rather than mere light scattering (Fig. 2D) [34]. We selected 480 nm as the excitation wavelength. Therefore, the BSA–AuNCs have a large Stokes shift (more than 150 nm), which can prevent self-quenching of fluorescence and measurement errors caused by excitation light and scattering [35].

3.2. Quenching of gold nanoclusters by Cu^{2+}

The quenching effects of Cu^{2+} with different concentrations on the fluorescence emission of BSA–AuNCs were shown in Fig. 3A, and the quenching effect of Cu^{2+} on the fluorescence intensity was observed once Cu^{2+} was added into the gold nanoclusters solution. As shown in Fig. 3A, with addition of an increasing concentration of Cu^{2+} to BSA–AuNCs solution, an obvious decrease in the fluorescent peak at 635 nm was clearly detected, and 2.0×10^{-4} mol L^{-1} Cu^{2+} quenched the fluorescence intensity to ~26.99%. The surface of our prepared BSA–AuNCs was stabilized by a small amount of Au^{+}, and the fluorescence quenching of AuNCs was due to the interaction of Cu^{2+} with Au^{+}. As shown in Fig. 3B, upon addition of increasing concentrations of Cu^{2+}, a gradual decrease in the fluorescence of AuNCs was observed in the image characterized by a UV lamp with excitation at 365 nm.

3.3. Restoration of Cu^{2+}–gold nanoclusters by ciprofloxacin

Fig. 4A revealed that the addition of CIP caused the fluorescence intensity restoration of the Cu^{2+}–AuNCs system. As presented in Fig. 4B, increasing concentrations addition of CIP induced a gradual increase in the fluorescence of Cu^{2+}–AuNCs system in the image characterized by a UV lamp with excitation at 365 nm. Fig. 4C depicted the CD spectra of Cu^{2+}–AuNCs with and without CIP, which indicated that the surfaces of AuNCs had no obvious changes after the addition of CIP. Control experiments showed that there was no change in the gold nanoclusters fluorescence intensity in the presence of CIP. All the phenomena above were due to the facts that Cu^{2+} interacted with CIP and was thus unable to quench the fluorescence emission of the gold nanoclusters.

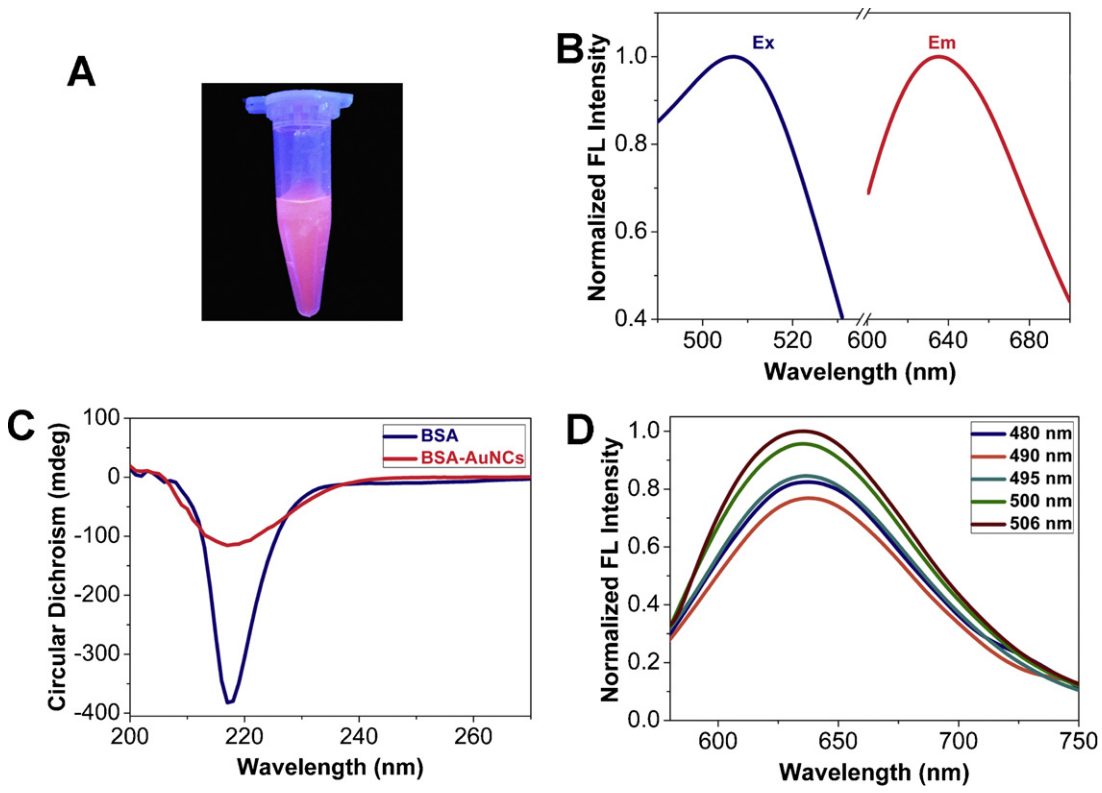


Fig. 2. (A) The photograph of AuNCs under UV light with excitation at 365 nm; (B) the maximum excitation and emission wavelengths of the prepared BSA–AuNCs; (C) CD spectra of BSA and BSA–AuNCs; (D) emission spectra of BSA–AuNCs at different excitation wavelengths.

The protocol of our strategy is displayed in Scheme 1. The sensitivity and selectivity of our assay depended on the interaction between Cu^{2+} and CIP which induced the fluorescence intensity of the Cu^{2+}–AuNCs system to restore.

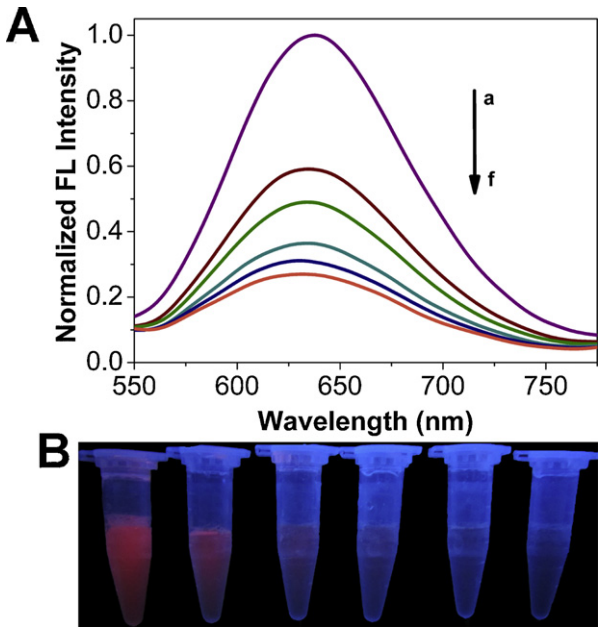
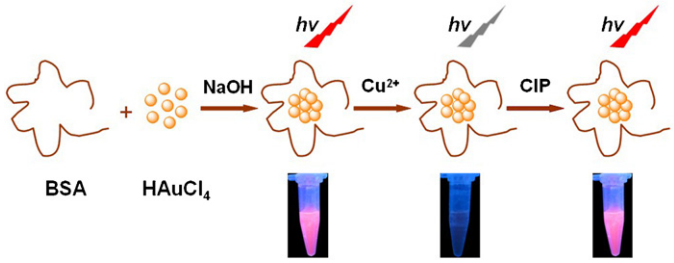


Fig. 3. (A) Emission spectra of BSA–AuNCs in the presence of different concentrations of Cu^{2+}, the concentrations of Cu^{2+} from a to f (10^{-5} mol L^{-1}): 0, 4.0, 8.0, 12, 16, 20; (B) photograph of BSA–AuNCs incubated with various concentrations of Cu^{2+} (from left to right (10^{-5} mol L^{-1}): 0, 4.0, 8.0, 12, 16, 20) illuminated by a UV lamp with excitation at 365 nm.

3.4. Fluorescence detection of ciprofloxacin

The influence of the concentration of BSA–AuNCs on fluorescence quenching by Cu^{2+} was also studied. The strong fluorescence quenching was observed at low BSA–AuNCs concentration in the presence of the same Cu^{2+} concentration, and this suggested that the detection limit can be reached with low BSA–AuNCs concentration. A 15 μL portion of our prepared BSA–AuNCs was the minimum gold nanoclusters concentration for CIP detection by the fluorescence instrument with reasonable signal-to-noise ratio (S/N > 3).

The fluorescence intensity of Cu^{2+}–AuNCs increased with the increasing concentration of CIP, as displayed in Fig. 4A. Meanwhile, the maximum fluorescence wavelength was constant with the addition of increasing ciprofloxacin concentrations, indicating that the surface state of the BSA–AuNCs had no change. Consequently, it was the interaction between Cu^{2+} and CIP that caused the fluorescence intensity restoration of the Cu^{2+}–AuNCs system. As Fig. 4D showed, there existed linear correlation between the expression F/F_0 and the concentration of ciprofloxacin over the range of 0.4 ng mL^{-1} to 50 ng mL^{-1}, which could be expressed as $F/F_0 = 0.34 + 0.014C_{CIP}$ (C_{CIP} is the concentration of CIP) with the



Scheme 1. Schematic illustration of the fluorescent BSA–AuNCs for CIP detection.

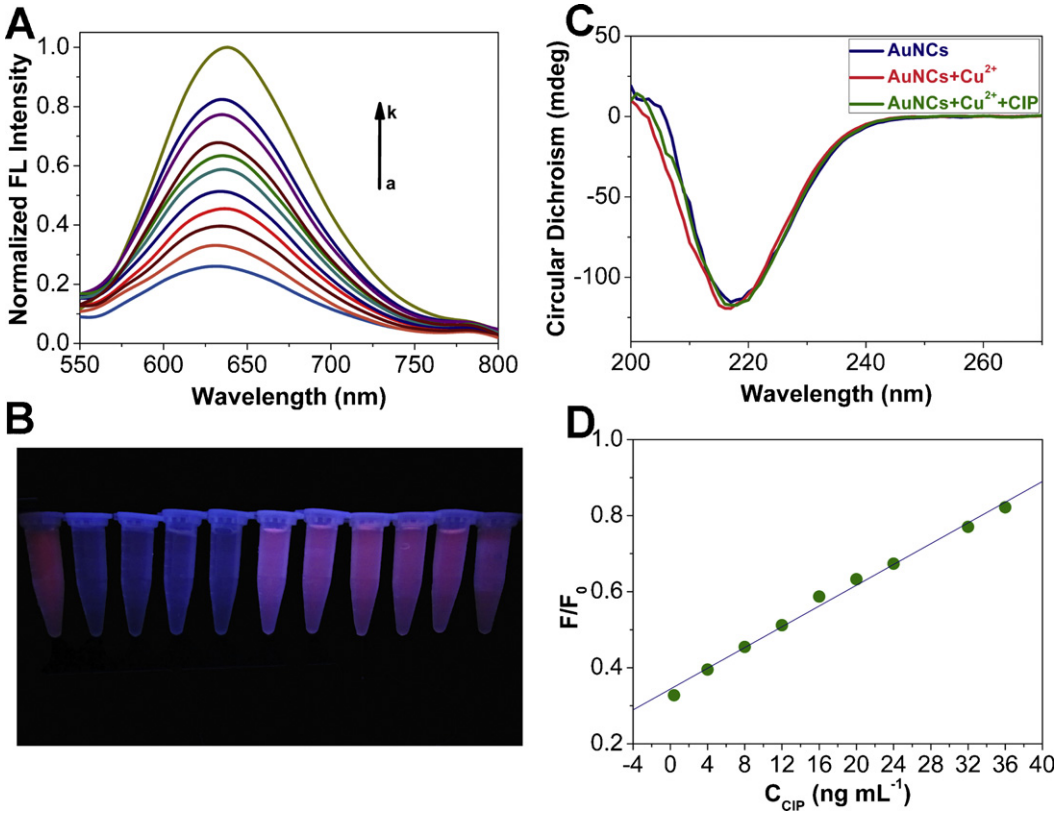


Fig. 4. (A) Emission spectra representing the fluorescence intensity restoration of Cu^{2+}–AuNCs by the addition of CIP with concentrations a–j: 0, 0.4, 4.0, 8.0, 12, 16, 20, 24, 32 and 36 ng mL^{-1}; k: fluorescent spectra of AuNCs; (B) from left to right: the photograph of AuNCs and photograph of Cu^{2+}–AuNCs incubated with different concentrations of CIP (0, 0.04, 0.1, 0.2, 12, 16, 20, 24, 32, 36 ng mL^{-1}) under a UV lamp with excitation at 365 nm; (C) CD spectra of AuNCs, Cu^{2+}–AuNCs and Cu^{2+}–AuNCs–CIP; (D) the relationship between F/F_0 and the concentration of CIP.

Table 1
Comparison with the results of the determination of CIP by other assays.

Quinolone antibiotics	Methods	Linear range (ng mL^{-1})	Detection limit (ng mL^{-1})	References
CIP	HPLC	20–12,500	20	25
CIP	CE	170–170,000	78	26
CIP	MLC	100–5000	24	27
CIP	Luminescence	30–1500	9.0	28
CIP	RLS	8000–20,000	6000	29
CIP	Fluorescence	0.4–50	0.3	This work

correlation coefficient R of 0.9958 and the limit of detection (3σ) around 0.3 ng mL^{-1}.

Comparisons with other determination methods of CIP were shown in Table 1. As listed in the table, our developed assay was demonstrated to be superior to that of other assays for the quantification of CIP, which had the advantages of low detection limit and wide linear range.

3.5. Incubation time and stability of the systems

The effects of time on the fluorescence intensities of Cu^{2+}–AuNCs and Cu^{2+}–AuNCs–CIP systems were tested. The incubation time and stability were studied by determining the fluorescence intensities of the two systems every 2 min for 2 h immediately after mixing. The results showed that the reaction between Cu^{2+} and CIP occurred rapidly at room temperature and the fluorescence intensity of the assay system reached the maximum in 5 min. Moreover, the intensity remained constant for at least 100 min. Thus, this assay did not require crucial timing.

3.6. Effect of ionic strength

There exists a high concentration of sodium chloride in ciprofloxacin injections and tablets. In this work, the effect of ionic strength on the fluorescence intensity of the assay system was controlled by NaCl. The experimental results showed that the fluorescence intensities of Cu^{2+}–AuNCs and Cu^{2+}–AuNCs–CIP systems hardly changed with the changing concentration of added sodium chloride. Therefore, the system can be allowed in solutions with high ionic strength such as injections and tablets.

3.7. Tolerance of potentially interfering substances

Some cationic and anionic species normally found in ciprofloxacin injections and tablets are studied by the addition of potentially interfering substances. The results reveal that metal ions such as Na^+, K^+, Mg^{2+}, Cu^{2+}, Pb^{2+}, Al^{3+}, Ba^{2+}, Fe^{3+}, Ca^{2+}, Ag^+, Zn^{2+}, Cl^-, HCO_3^- and Fe^{2+} can be tolerated at high concentrations. However, Co^{2+} and Hg^{2+} can be tolerated at relatively low concentrations, but the concentrations of them were low in real analysis of samples, so they did not interfere with

Table 2
Determination results of CIP in injections and tablets.

No.	Samples[a]	Labeled amount ($\mu g\,mL^{-1}$)	Found amount ($\mu g\,mL^{-1}$)	Recovery ($n=6$, %)
1	Injection	2000	2025.41	101.27
2	Injection	2000	1995.78	99.79
3	Injection	2000	2013.09	100.65
4	Tablet	2500	2519.01	100.76
5	Tablet	2500	2490.74	99.63
6	Tablet	2500	2503.58	100.14

[a] Samples were diluted 1000–10,000-fold with doubly distilled water.

the real determination. Other studied ions have nearly no effect on the determination when their concentration is the same or greater than CIP. The organic molecules such as amino acids and aminothiols can be tolerated at high concentrations. Due to the good selectivity of this method, assays can be performed without removing other coexisting ions.

4. Analytical application

With the purpose of testing the applicability of the investigated assay, the analysis of different kinds of real samples was performed.

4.1. Detection of ciprofloxacin in injections and tablets

The developed assay was applied to determine the concentration of CIP in injections and tablets. Weigh accurately a quantity of the mixed contents of 10 powdered tablets (0.25 g/tablet), equivalent to 2.5 g of CIP, transfer into a 1000 mL calibrated flask, and dilute to volume with fresh doubly distilled water to prepare a 2.5 mg mL^{-1} stock solution. The CIP injections (0.1 g/injection) were dissolved in 50 mL fresh doubly distilled water in a flask to prepare a 2.0 mg mL^{-1} stock solution. Suitable amounts of the solution were measured by the developed assay. As Table 2 showed, the results were satisfactory.

4.2. Detection of ciprofloxacin in human urine

To evaluate whether the Cu^{2+}–AuNCs fluorescent sensor for CIP is applicable to real samples, human urine was analyzed by this assay. One milliliter of fresh urine sample (healthy people) and the other sample after oral administration of CIP tablets were pipetted into 10 mL of calibrated flasks after filtration, respectively. The experimental results showed that this sensing system gave no obvious fluorescence response to the blank urine sample of a healthy person, suggesting that human urine had little interference in the performance of this sensing system. The analytical results were given in Table 3. In the table, the found amount was the CIP concentration in the detected sample without the addition of standard, while the found value was the total CIP concentration with the addition of standard. The recoveries of CIP in spiked human urine were in the range of 98.69–99.55%.

Table 3
Determination results of CIP in human urine.

No.	Samples	Found amount ($ng\,mL^{-1}$)	Standard added ($ng\,mL^{-1}$)	Found value ($ng\,mL^{-1}$)	Recovery ($n=6$, %)
1	Urine	ND	16	15.79	98.69
2	Urine	ND	20	19.91	99.55
3	Urine[a]	20	–	20	–

ND: not detected.
[a] Urine sample was taken from healthy people after oral administration CIP tablets.

Table 4
Determination results of CIP in human serum.

No.	Samples	Found amount ($ng\,mL^{-1}$)	Standard added ($ng\,mL^{-1}$)	Found value ($ng\,mL^{-1}$)	Recovery ($n=6$, %)
1	Serum	ND	16	15.92	99.50
2	Serum	ND	20	19.83	99.15
3	Serum	ND	24	24.17	100.71

ND: not detected.

4.3. Detection of ciprofloxacin in human serum

The developed method was also applied to the analysis of human serum samples. 10 mL blood sample was kept at 37 °C in a water bath for about 0.5 h and the blood coagulation was preconditioned. The sample without blood clot was deproteinized by adding approximate 10 mL acetonitrile and centrifuging (40 min at 4000 rpm) at the room temperature. Then the acetonitrile was removed under reduced pressure on a rotary evaporator in a 60 °C water bath. The human serum without proteins was dissolved by 100 mL doubly distilled water and stored at 4 °C [36]. A suitable volume of the solution appropriately spiked with the standard CIP solution was taken and three different samples with different CIP concentrations were obtained for analysis. The results were summarized in Table 4. In all cases quantitative recoveries between 99.15 and 100.71% were obtained. These results showed that this sensing system has great potential for quantitative determination of CIP in human serum samples.

5. Conclusion

In summary, a novel methodology for the detection of ciprofloxacin has been developed based on the fluorescence intensity restoration of the Cu^{2+}–AuNCs system by ciprofloxacin. In contrast to the previously reported detection methods for ciprofloxacin, this new fluorescent assay exhibits high sensitivity and selectivity. With the developed assay, ciprofloxacin injections, ciprofloxacin tablets, human urine and human serum were analyzed with satisfactory results. More importantly, the gold nanoclusters functionalized by Cu^{2+} can provide a variety of specific recognition which can result in the fluorescence intensity restoration of the Cu^{2+}–AuNCs system. Consequently, the developed assay would be expected to be extended for the quantitative determination of other drugs only if there are interactions between Cu^{2+} and the drugs.

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References

[1] C.I. Richards, S. Choi, J.C. Hsiang, Y. Antoku, T. Vosch, A. Bongiorno, Y.L. Tzeng, R.M. Dickson, J. Am. Chem. Soc. 130 (2008) 5038–5039.
[2] L.A. Peyser, A.E. Vinson, A.P. Bartko, R.M. Dickson, Science 291 (2001) 103–106.
[3] Y. Tao, Y.H. Lin, Z.Z. Huang, J.S. Ren, X.G. Qu, Talanta 88 (2012) 290–294.
[4] J. Ai, W.W. Guo, B.L. Li, T. Li, D. Li, E.K. Wang, Talanta 88 (2012) 450–455.
[5] J.P. Wilcoxon, B.L. Abrams, Chem. Soc. Rev. 35 (2006) 1162–1194.
[6] H. Duan, S. Nie, J. Am. Chem. Soc. 129 (2007) 2412–2413.
[7] J.H. Yu, S.A. Patel, R.M. Dickson, Angew. Chem. Int. Ed. Engl. 46 (2007) 2028–2030.
[8] P.R. O'Neill, L.R. Velazquez, D.G. Dunn, E.G. Gwinn, D.K. Fygenson, J. Phys. Chem. C 113 (2009) 4229–4233.
[9] M. Zhang, B.C. Ye, Analyst 136 (2011) 5139–5142.
[10] C.V. Durgadas, C.P. Sharma, K. Sreenivasan, Analyst 136 (2011) 933–940.
[11] J.L. Chen, Y.C. Gao, Z.B. Xu, G.H. Wu, Y.C. Chen, C.Q. Zhu, Anal. Chim. Acta 577 (2006) 77–84.

[12] H.Q. Chen, L. Wang, L.Y. Wang, G.F. Wang, L. Li, F.G. Xu, Anal. Chim. Acta 521 (2004) 9–15.
[13] M. Wang, Q.S. Mei, K. Zhang, Z.P. Zhang, Analyst 137 (2012) 1618–1623.
[14] W.W. Guo, J.P. Yuan, Q.Z. Dong, E.K. Wang, J. Am. Chem. Soc. 132 (2010) 932–934.
[15] J.P. Yuan, W.W. Guo, E.K. Wang, Anal. Chim. Acta 706 (2011) 338–342.
[16] T. Kloskowski, N. Gurtowska, T. Drewa, Pulm. Pharmacol. Ther. 23 (2010) 373–375.
[17] B. Dybowski, O. Jabłońska, P. Radziszewski, J. Gromadzka-Ostrowska, A. Borkowski, Int. J. Antimicrob. Agents 31 (2008) 130–134.
[18] J.X. Fu, H.J. Wang, Y.Q. Zhou, J.Y. Wang, Mater. Sci. Eng. C 29 (2009) 1161–1166.
[19] S.H. Jeong, Y.K. Song, J.H. Cho, Regul. Toxicol. Pharm. 53 (2009) 209–216.
[20] B.P. Rossi, C. García, M. Calenda, C. Vay, M. Franco, Int. J. Antimicrob. Agents 34 (2009) 260–264.
[21] D.W. Sohn, C.H. Han, Y.S. Jung, S.I. Kim, S.W. Kim, Y.H. Cho, Int. J. Antimicrob. Agents 34 (2009) 215–219.
[22] W.C. Tsai, C.C. Hsu, H.C. Chen, Y.H. Hsu, M.S. Lin, C.W. Wu, J.H.S. Pang, Eur. J. Pharmacol. 607 (2009) 23–26.
[23] D. Wojnicz, A. Cisowska, Int. J. Antimicrob. Agents 33 (2009) 579–582.
[24] D.R. Xiao, E.B. Wang, H.Y. An, Y.G. Li, L. Xu, Cryst. Growth Des. 7 (2007) 506–512.
[25] B. DeWitte, J. Dewulf, K. Demeestere, V.V. Vyvere, P. Wispelaere, H.V. Langenhove, Environ. Sci. Technol. 42 (2008) 4889–4895.
[26] A. Khadra, E. Pinelli, M.Z. Lacroix, A. Bousquet-Melou, H. Hamdi, G. Merlina, M. Guiresse, M. Hafidi, Ecotoxicol. Environ. Saf. 76 (2012) 187–192.
[27] U. Neckel, C. Joukhadar, M. Frossard, W. Jäger, M. Müller, B.X. Mayer, Anal. Chim. Acta 463 (2002) 199–206.
[28] Y.M. Liu, Y.X. Jia, W. Tian, J. Sep. Sci. 31 (2008) 3765–3771.
[29] J.L. Vílchez, L. Araujo, A. Prieto, A. Navalón, Anal. Chim. Acta 516 (2004) 135–140.
[30] R.C. Rodríguez-Díaz, M.P. Aguilar-Caballos, A. Gómez-Hens, Anal. Chim. Acta 494 (2003) 55–62.
[31] J.B. Xiao, C.S. Yang, F.L. Ren, X.Y. Jiang, M. Xu, Meas. Sci. Technol. 18 (2007) 859–866.
[32] A.W. Varners, R.B. Dodson, E.L. Wehry, J. Am. Chem. Soc. 94 (1972) 946–950.
[33] J.P. Xie, Y.G. Zheng, J.Y. Ying, J. Am. Chem. Soc. 131 (2009) 888–889.
[34] Y.M. Guo, Z. Wang, H.W. Shao, X.Y. Jiang, Analyst 137 (2012) 301–304.
[35] H.H. Lin, Y.C. Chan, J.W. Chen, C.C. Chang, J. Mater. Chem. 21 (2011) 3170–3177.
[36] Z.G. Chen, Y.R. Peng, S.B. Wang, X. Chen, T.H. Song, S.H. Qian, M.Z. Chen, Q.R. Wang, Talanta 82 (2010) 885–891.