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Colorimetric detection of bisphenol A based on unmodified aptamer and cationic polymer aggregated gold nanoparticles

Dongwei Zhang [a], Jiayi Yang [b, c], Jing Ye [a], Lurong Xu [b], Hanchu Xu [b], Shenshan Zhan [b], Bing Xia [a], Lumei Wang [a, b, *]

[a] School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China
[b] School of Agriculture and Biology and Key Laboratory of Urban Agriculture (South), Ministry of Agriculture, and Bor S. Luh Food Safety Research Center, Shanghai Jiao Tong University, Shanghai 200240, China
[c] Department of Management, Shanghai Sanda College, Shanghai 201209, China

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ABSTRACT

In this study, a colorimetric method was exploited to detect bisphenol A (BPA) based on BPA-specific aptamer and cationic polymer-induced aggregation of gold nanoparticles (AuNPs). The principle of this assay is very classical. The aggregation of AuNPs was induced by the concentration of cationic polymer, which is controlled by specific recognition of aptamer with BPA and the reaction of aptamer and cationic polymer forming "duplex" structure. This method enables colorimetric detection of BPA with selectivity and a detection limit of 1.50 nM. In addition, this colorimetric method was successfully used to determine spiked BPA in tap water and river water samples.

Bisphenol A (BPA, 2,2-bis(4-hydroxyphenyl) propane, CAS: 80-05-7) is a synthetic organic chemical primarily used in the manufacture of polymers (e.g., polycarbonate, epoxy resins, polysulfone, polyacrylate), polyvinyl chloride plastics, and flame-retardant tetrabromobisphenol A [1], which have been widely used in many fields. For example, polycarbonate is used as materials of reusable plastic bottles, baby bottles, and storage containers, and epoxy resins are used for internal coating of food and beverage cans. However, BPA is one of the endocrine-disrupting compounds that could mimic the action of hormone estrogen and disturb the estrogen–estrogen receptor binding process of humans and wildlife. Unfortunately, research has shown that BPA can migrate from reusable plastic bottles, feeding bottles, food packages, beverage cans, and other plastic products to food and water [2–4]. To make things even worse, research results indicate that BPA also exists in human bodies [5–8] that have increased cancer rates, decreased semen quality, and reduced immune functions [9–11]. Consequently, it is high on the agenda to detect BPA in the environment, food, and human bodies.

Until now, traditional methods such as high-performance liquid chromatography–ultraviolet absorption (HPLC–UV) [12], liquid chromatography/mass spectrometry (LC/MS) [13], and gas chromatography/mass spectrometry (GC/MS) [14] have been used for the quantification of BPA in environmental samples and human bodies. In addition, electrochemical sensors [15] and immunochemical methods [16] have been applied to the detection of BPA. Although the majority of these methods have good selectivity and low detection limits, complicated and expensive instruments, professional operators, complex pretreatments, and/or time-consuming detection processes are required. Therefore, a simple method for the detection of trace BPA in the environment is urgently needed.

Abbreviations: BPA, bisphenol A; HPLC, high-performance liquid chromatography; ssDNA, single-stranded DNA; AuNP, gold nanoparticle; PDDA, poly(-diallyldimethylammonium chloride); E2, 17β-estradiol; PRG, progesterone; THI, thiamphenicol; *o,p'*-DDT, *o,p'*-dichlorodiphenyltrichloroethane; DES, diethylstilbestrol; 7-ACA, 7-aminocephalosporanic acid; Kana, kanamycin; Gly, glycine; Cys, cysteine; Vc, L-ascorbic acid; $Na_3C_6H_5O_7 \cdot 2H_2O$, trisodium citrate dehydrate; DMSO, dimethyl sulfoxide; AMP, ampicillin; PBS, phosphate-buffered saline; PCS, photon correlation spectroscopy; CD, Circular dichroism; Mix. 1, mixture 1; Mix. 2, mixture 2.

* Corresponding author. School of Agriculture and Biology and Key Laboratory of Urban Agriculture (South), Ministry of Agriculture, and Bor S. Luh Food Safety Research Center, Shanghai Jiao Tong University, Shanghai 200240, China.
E-mail address: zjuwlm@163.com (L. Wang).

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During recent years, many studies have focused on the screening of nucleic acid aptamer through repeated rounds of in vitro selection, namely SELEX (systematic evolution of ligands by exponential enrichment), since it was reported in 1990 [17]. Aptamers are single-stranded DNA (ssDNA) or RNA oligonucleotides with unique conformations that can selectively bind to various targets. In addition, aptamers used as recognition elements for many novel biotechnological applications have the advantages of stabilization, cost-effectiveness, and high selectivity. BPA-specific aptamer has been used to detect BPA through colorimetric, electrochemical, and fluorescent assays [18–20]. In addition, the majority of them were labeled with FAM, biotin, or other groups at the 5′ end, which has increased the cost-to-use of the detection. Among the reported label-free aptamer-based biosensors, gold nanoparticles (AuNPs) have been extensively arousing scientific researchers' attention because of their controlled geometrical, optical, and surface chemical properties [21]. Quintessential examples can be cited to prove that AuNPs can serve as color indicators because their color can change from wine red to purple and even blue under conditions of appropriate concentration of salts [22], surfactant [23], or cationic polymers [24,25]. Therefore, a simple method for the detection of BPA based on label-free BPA-specific aptamer coupled with AuNPs and cationic polymer poly(diallyldimethylammonium chloride) (PDDA) was carried out in this study.

Materials and methods

Reagents and materials

BPA, 17β-estradiol (E2), progesterone (PRG), and thiamphenicol (THI) were purchased from Aladdin Industrial (Shanghai, China). *o*,*p*'-Dichlorodiphenyltrichloroethane (*o*,*p*'-DDT) was purchased from AccuStandard (New Haven, CT, USA). Diethylstilbestrol (DES), PDDA, and 7-aminocephalosporanic acid (7-ACA) were attained from Sigma–Aldrich (St. Louis, MO, USA). $HAuCl_4 \cdot 4H_2O$, kanamycin (Kana), glycine (Gly), cysteine (Cys), L-ascorbic acid (Vc), trisodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), $CuCl_2 \cdot 2H_2O$, $CdCl_2 \cdot 2.5H_2O$, and dimethyl sulfoxide (DMSO) were attained from Sinopharm Chemical Reagent (Shanghai, China). Ampicillin (AMP), $NaH_2PO_4 \cdot 2H_2O$, and $Na_2HPO_4 \cdot 12H_2O$ were obtained from Sangon Biotechnology (Shanghai, China). BPA-specific aptamer with a dissociation constant (K_d) of 8.3 nM (5′-CCG GTG GGT GGT CAG GTG GGA TAG CGT TCC GCG TAT GGC CCA GCG CAT CAC GGG TTC GCA CCA-3′, where C, G, T, and A represent cytosine, guanine, thymine, and adenine, respectively) [26] was synthesized by Sangon Biotechnology and purified by HPLC. The aptamer was dissolved in distilled water and kept at −20 °C for storage. Unless otherwise mentioned, all other reagents were of analytical grade and used without further purification or treatment. Buffer solutions of 10 mM phosphate-buffered saline (PBS) with different pH values were used for the experiments. Centrifuge tubes and 96-well microplates were purchased from Thermo Fisher Scientific (Nunclon, Denmark). Deionized water purified by a Milli-Q Advantage A10 System (Millipore, Bedford, MA, USA) was used throughout the experiment for aqueous solution preparation.

Preparation and characterization of AuNPs

AuNPs were prepared by sodium citrate reduction of $HAuCl_4$ solution [27]. First, the glassware used in this experiment was cleaned by freshly prepared 3:1 (v/v) HNO_3/HCl and rinsed with ultrapure water thoroughly. Then, 10.5 ml of 1% (w/v) trisodium citrate was added to the boiling solution of $HAuCl_4$ (100 ml, 0.03%, w/w) and stirred for 30 min to synthesize AuNPs. After that, the heater was turned off and the solution was stirred for another 20 min. Lastly, the resulting wine red solution was cooled to room temperature, filtered with 0.22μm filtration membranes, and stored in a brown glass bottle at 4 °C for further use.

Interactions among AuNPs, PDDA, aptamer, and BPA

To confirm the particle size of PDDA aggregated AuNPs, photon correlation spectroscopy (PCS; Nano S ZEN1600, Malvern Instruments, Malvern, UK) was used to evaluate the distribution of particle size of gradually aggregated AuNPs. In addition, a circular dichroism (CD) spectrometer (J-815, Jasco, Japan) was employed to characterize the structural changes of aptamer reacted with BPA or PDDA.

Measurement of absorbance

An Infinite M200 Pro microplate spectrophotometer (Tecan Austria, Salzburg, Austria) was used to record the absorbance of the reaction solutions from 400 to 800 nm. The absorbances at 520 nm (A_{520}) and 650 nm (A_{650}) were recorded because these two wavelengths represent the relative amounts of free and aggregated AuNPs. The values of A_{650}/A_{520} in sample solutions containing BPA (A) and the blank solutions without BPA (A_0) were calculated to reflect the aggregation degree of AuNPs. In addition, the values of ΔA ($\Delta A = A - A_0$) were calculated.

Optimization of detection conditions

First, the concentration of PDDA was optimized by adding different volumes of 500 nM PDDA solutions into the centrifugation tubes containing a certain amount of PBS buffer. Then, they were mixed thoroughly and followed by 100 μl of AuNPs to reach a total volume of 500 μl. After incubating for 15 min, the absorbance from 400 to 800 nm was measured by the M200 Pro microplate spectrophotometer. The optimized PDDA concentration that induced the maximum value of A_{650}/A_{520} was chosen. Second, the BPA-specific aptamer concentration was also optimized. Different amounts of 500 nM aptamer were incubated with 2000 nM BPA (including blank solutions without BPA) in PBS buffer for 30 min, and then the optimized concentration of PDDA was added into all the tubes and cultivated for 20 min, followed by 100 μl of AuNPs. What is more, the pH value and temperature of the reaction system were also optimized under the appropriate concentrations of PDDA and aptamer. Finally, A, A_0, and ΔA were calculated and the BPA-specific aptamer concentration, pH value, and temperature with maximum ΔA were selected.

Sensitivity and selectivity of sensing system

To investigate the sensitivity of the assay for BPA detection, the optimized concentration of BPA-specific aptamer was first added into 1.5-μl centrifugation tubes containing a certain amount of PBS buffer to react with BPA with different final concentrations (0, 50, 100, 150, 200, 250, 300, 400, 500, 600, 800, 1000, and 1500 nM). After incubating for 30 min, the optimal volume of PDDA was added to the reaction system, thoroughly mixed, and cultivated for 20 min, followed by 100 μl of AuNPs. In addition, A_{520} and A_{650} were recorded, and the values of A_{650}/A_{520} and ΔA were calculated 15 min later.

Furthermore, the selectivity study was performed by adding different nontarget chemicals to the reaction system instead of BPA in the sensitivity testing, including DES (1), *o*,*p*'-DDT (1), E2 (1), PRG (1), AMP (1), Cd^{2+} (1), 7-ACA (1), Cu^{2+} (1), THI (1), Kana (1), Gly (1), Cys (1), DMSO (1), Vc (1), mixture 1 [Mix. 1: BPA (1), E2 (1), PRG (1),

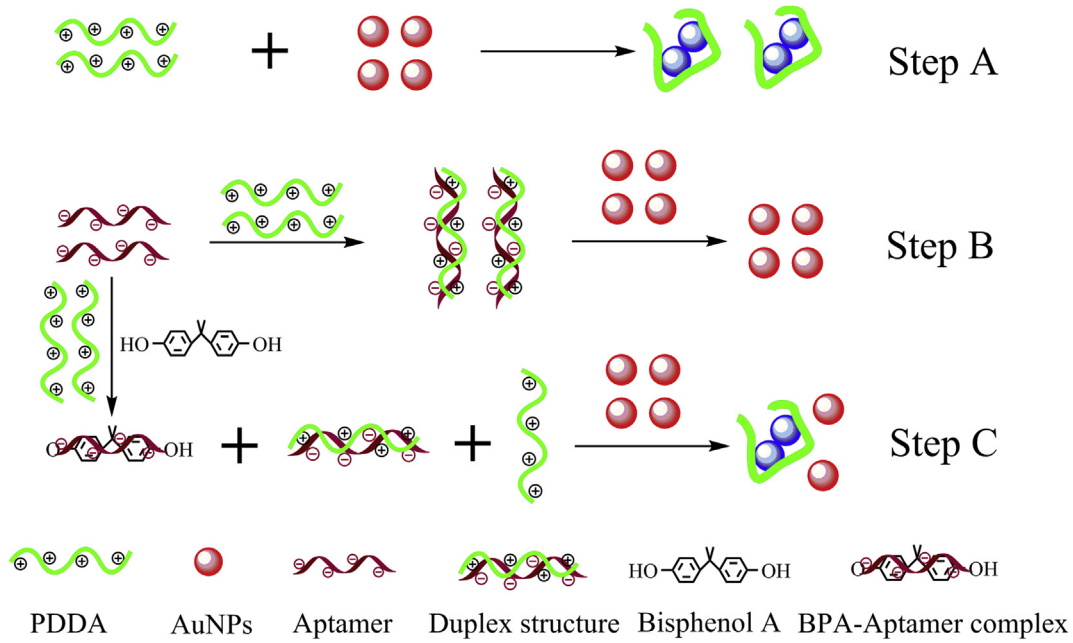

Fig.1. Schematic representation of the colorimetric detection of bisphenol A.

and DES (1)], and mixture 2 [Mix. 2: BPA (1), E2 (10), PRG (10), and DES (10)]. The numbers in parentheses were the final concentrations (μM) of the chemicals in the selectivity detection. The absorbances at 520 and 650 nm were measured, and the values of A_{650}/A_{520} and ΔA were calculated.

Application in water samples

To investigate the practicability of this biosensor, two concentrations of BPA (50 and 300 nM in the final detection system) were spiked to tap water of our laboratory and river water taken from Shanghai Jiao Tong University (Shanghai, China). Tap water was used without any pretreatment. In contrast, river water was centrifuged at 6000 rpm for 5 min and filtrated with a 0.22μm filter membrane to remove the suspended solids and microorganisms. In addition, the samples were detected according to the determination procedures of sensitivity and selectivity of the sensing system mentioned above. Three replicates were performed for all samples.

Results and discussion

Principle of biosensor for BPA detection

The colorimetric sensing for BPA is based on the specific reaction among PDDA, AuNPs, BPA-specific aptamer, and BPA. As shown in Fig. 1, step A indicates that PDDA could break the electrostatic equilibrium of AuNPs and promote the aggregation of them. Step B proves that BPA-specific aptamer can hybridize with PDDA, forming a "duplex" structure through electrostatic attraction, and the following addition of AuNPs would maintain wine red due to the exhaustion of PDDA. In contrast, step C makes clear that aptamer would specifically integrate with BPA to form the BPA–aptamer complex at first. Then, the redundant aptamer reacts with PDDA, and lastly the remaining PDDA induces the aggregation of AuNPs and the color of the solution changes from wine red to purple or even blue.

Interactions among aptamer, BPA, PDDA, and AuNPs

For the purpose of certifying the experimental principle of this assay, the absorption spectrum and PCS characterization of pure and PDDA-induced aggregation of AuNPs were conducted. Fig. 2A shows that the absorbance of A_{650} increased and the colors of AuNPs changed from red to purple and blue with the increasing concentrations of PDDA. Fig. 2B shows the diameter distribution of pure AuNPs and AuNPs with different concentrations of PDDA. The average size of pure AuNPs was 17.5 nm, it increased to 85.4 nm when the concentration of PDDA was 12 nM, and the consequences are shown in Fig. 2B (graphs 1–4). These results demonstrate the feasibility of step A in Fig. 1.

Furthermore, to confirm the interactions of aptamer with BPA and PDDA, CD spectroscopy was used to characterize the structural conformation changes of BPA-specific aptamer. Fig. 3 shows that pure BPA-specific aptamer had a negative peak at 240–250 nm and a positive peak at 270–280 nm, which can be attributed to the helicity and base stacking interactions of natural DNA, respectively [28,29]. When BPA was added into the system and reacted with aptamer, the positive peak increased and the negative peak maintained almost the same due to the structure changes of the aptamer, which is consistent with previous reports [20]. Unlike the reaction of BPA with aptamer, cationic polymer PDDA hybridizes with the phosphate backbone of aptamer to form a "duplex" structure, which has altered the helicity of aptamer and causes the decrease of the negative peak [30].

Optimization of experimental conditions

The good balance among AuNPs, PDDA, and BPA-specific aptamer is essential for the sensitive and selective detection of BPA. What is more, the reaction pH and temperature also play significant roles in this study for BPA detection. Thus, the following parameters were optimized one by one: (i) the concentration of the cationic polymer PDDA, (ii) the concentration of BPA-specific aptamer, (iii) the pH of the reaction system, and (iv) the reaction temperature of the system. The results are shown in Fig. S1A–D of

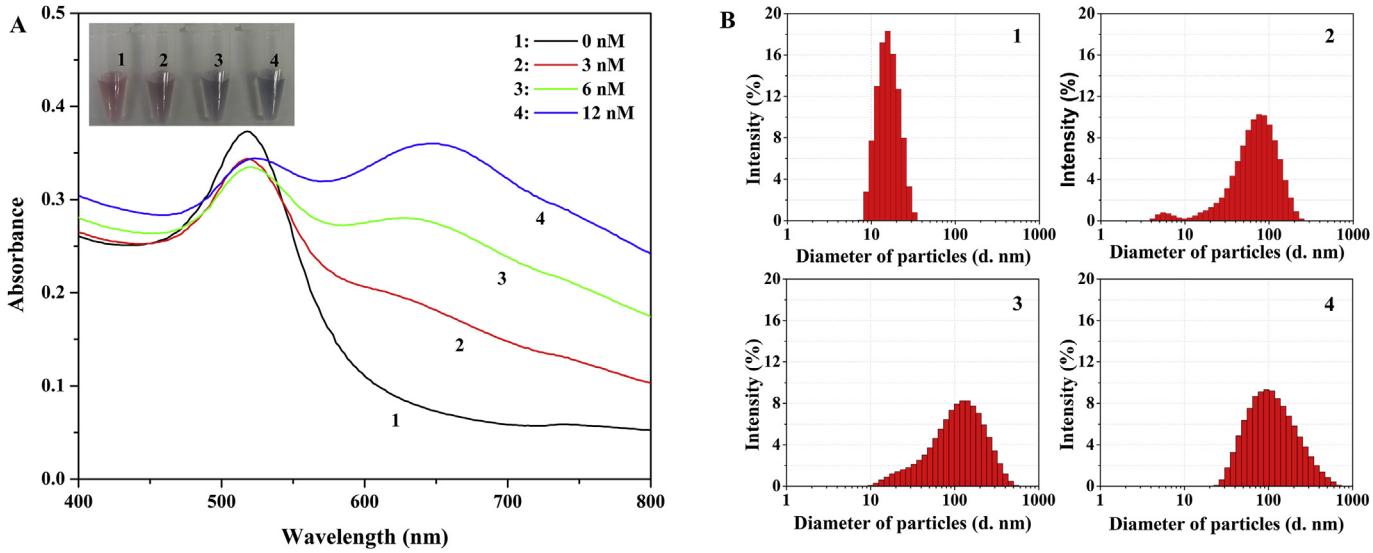

Fig.2. (A) Absorption spectra and corresponding visual color changes of AuNPs with different concentrations of PDDA. (B) Particle size changes of AuNPs with different concentrations of PDDA. Experimental conditions: (1) AuNPs + 0 nM PDDA; (2) AuNPs + 3 nM PDDA; (3) AuNPs + 6 nM PDDA; (4) AuNPs + 12 nM PDDA. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the online supplementary material. Fig. S1A suggests that the optimized concentration of PDDA is 12 nM because the value of A_{650}/A_{520} attained the maximum. Fig. S1B indicates that $\Delta A_{650}/A_{520}$ between the BPA group and the blank group is approximately 0.35 when the concentration of aptamer is 4 nM. Compared with similar experiments done on thrombin, it could be found that the ratio of the base number to the concentration of PDDA in these two methods is 1:1 [25]. However, compared with similar experiments done on other targets [24,31], the same conclusion could not be reached. In addition, Fig. S1C and D demonstrate that the optimal pH is 8.0 and the range of optimal temperature is from 20 to 30 °C. It could be assumed that BPA-specific aptamer that is also ssDNA would be degenerated by acid, strong alkali, and relatively low temperature and that high temperature would influence the activity of the aptamer, according to the results of Fig. S1C and S1D.

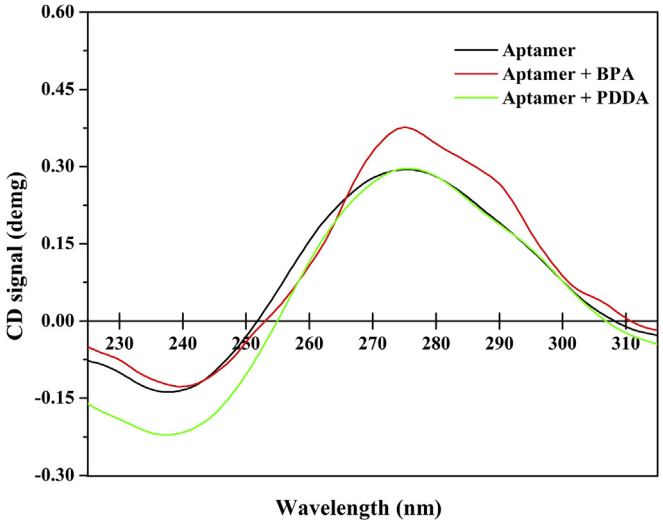

Fig.3. Circular dichroism (CD) spectra of BPA-specific aptamer solutions treated with BPA or PDDA. Experimental conditions: 500 nM aptamer, 50 μM BPA, and 100 nM PDDA.

Sensitivity and selectivity of biosensor for BPA detection

For the sake of quantitatively assessing the sensitivity of the biosensor, BPA solutions with varying concentrations from 0 to 1500 nM were measured under the conditions of optimized PDDA concentration, BPA-specific aptamer concentration, pH, and temperature. The results are shown in Fig. 4A. The colors of the solutions changed gradually from red to blue, indicating the gradual aggregation of AuNPs with the increasing concentrations of BPA. In addition, the inset illustrates that the values of ΔA at low concentrations of BPA were fitted to a linear plot with a regression equation of $\Delta A = 4.05 \times 10^{-4}\, C_{BPA} + 0.003$ and an R^2 of 0.996. Based on previous reports, 3σ/slope was used to determine the detection limit of the biosensor [31]. The standard deviation (σ) of the instrument was calculated from the results of the blank sample containing 100 ml of AuNPs and 400 ml of PBS buffer, as shown in Table S1 of the supplementary material. Thus, the detection limit was calculated as 1.50 nM, which is much lower than Chinese standards for drinking water (~43.8 nM) and the standards of the U.S. Federal Drug Administration (FDA) (~219 nM) [18]. Compared with BPA-specific aptamer detection methods reported before (Table 1), the current method has both advantages and disadvantages. First, although the detection limit of this method is only a little lower than a few of the previous reports [19,32,33], the aptamer used in this study does not need labeling fluorescence groups or modifying other special functional groups on the 5′ side of the aptamer, which distinctly decreases the cost of the detection. Second, it is a colorimetric assay for the detection of BPA, so we can determine the extent of BPA pollution in water samples by optical color changes of AuNPs when the BPA concentration is more than 150 nM. Furthermore, sophisticated and expensive detection instruments are not needed with this method, so this assay can realize the detection of BPA on-site.

Selectivity, as well as sensitivity, is an important parameter of the biosensor for the detection of BPA. To investigate the selectivity of this biosensor, estrogens such as DES and *o,p'*-DDT were chosen because they have similar structures as BPA. What is more, several other chemicals and the mixture solutions [Mix. 1 including BPA (1), E2 (1), PRG (1) and DES (1); Mix. 2 including BPA (1), E2 (10),

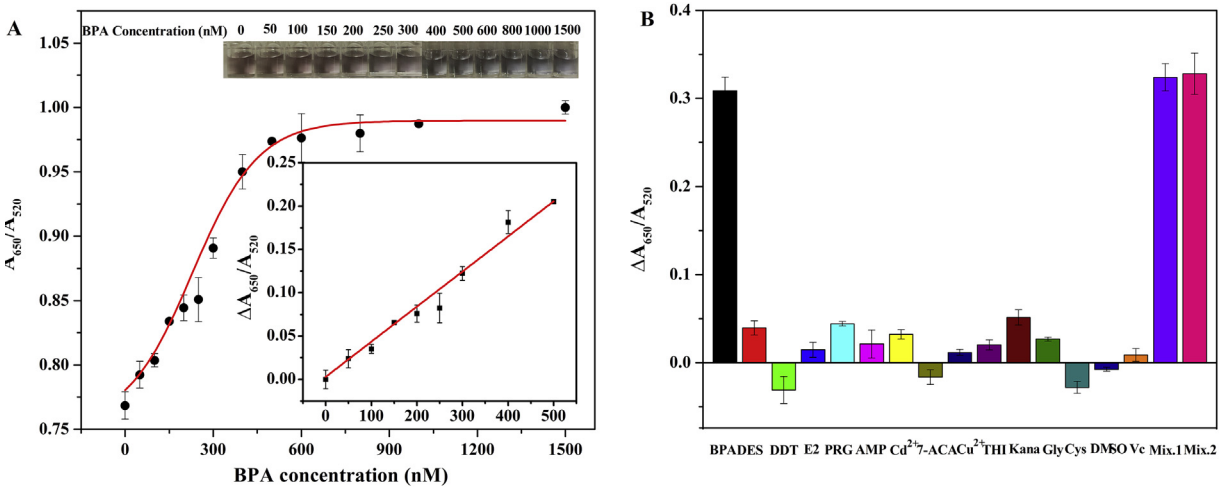

Fig.4. (A) Sensitivity of the label-free biosensor for bisphenol A (BPA) detection. The inserted picture shows the visual color changes of the AuNP solutions treated with different concentrations of BPA. The inset shows the values of $\Delta A_{650}/A_{520}$ of BPA concentrations from 0 to 500 nM. Experimental conditions: 4 nM aptamer + different concentrations of BPA + 12 nM PDDA + 100 μl of AuNPs. (B) Selectivity of BPA A toward DES, *o*,*p*'-DDT, E2, PRG, AMP, Cd^{2+}, 7-ACA, Cu^{2+}, THI, Kana, Gly, Cys, DMSO, Vc, Mix. 1, and Mix. 2. Experimental conditions: 4 nM aptamer + different chemicals with the concentration of 1 μM + 12 nM PDDA + 100 μl of AuNPs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Comparison of different methods for detection of BPA based on BPA-specific aptamer.

Method	Labeled group	Linear range (nM)	LOD (nM)	Reference
Electrochemical aptasensor	Thiol	4.38×10^{-4}–0.438	1.24×10^{-3}	[34]
Functionalized aptamer	FAM/BHQ-1	4.38×10^{-4}–43.8	4.38×10^{-5}	[35]
Resonance Rayleigh scattering	\	$14.6–14.6 \times 10^{2}$	0.36	[36]
Surface-enhanced Raman scattering	Cy5	3–300	3	[32]
Portable optic fiber aptasensor	Cy5.5	2–100	1.86	[19]
Electrochemical aptasensor	$SH-(CH_2)_6$	$10–1 \times 10^{4}$	5	[33]
Fluorescence resonance energy transfer	FAM	0.438–43.8	0.22	[20]
Colorimetric biosensor	\	1.50–500	1.50	This assay

Note. LOD, limit of detection; FAM, fluorescein amidite; BHQ: black hole quencher; \, BPA-specific aptamer was not labeled functional groups.

PRG (10) and DES (10)] were also tested. The numbers in parentheses represent the final concentrations (μM) of the chemicals in the mixtures. Fig. 4B shows that this developed biosensor has good specificity toward BPA, with much lower values of $\Delta A_{650}/A_{520}$ when all other Endocrine Disrupting Chemicals (EDCs) and chemicals were tested. The results indicate that the aptamer used in this study has specificity toward BPA and further confirm the selectivity of the aptamer-based biosensor.

Application in water samples

Finally, the analytical utility of the developed biosensor for practical application was explored. In this study, tap water and river water were chosen for spiked BPA analysis. A series of known concentrations of BPA were added to the water samples and measured with the developed method. As shown in Table 2, the mean recoveries of the spiked BPA samples were between 100.9 and 112.7% and the relative standard deviations (RSDs) were in the range of 6.72–13.10%. These results indicate the potentiality of the developed aptamer sensor for further detection of BPA in water samples.

Table 2
Determination of spiked BPA in tap water and river water ($n = 3$).

Sample	Spiked BPA (nM)	Mean found (nM)	Mean recovery (%)	RSD (%)
Tap water	50	56.35	112.7	5.33
	300	302.8	100.9	13.1
River water	50	55.50	111.0	6.72
	300	312.0	104.0	7.90

Note. RSD, relative standard deviation.

Conclusions

In this study, a label-free colorimetric method for the detection of BPA has been carried out. The principle of the sensitivity and selectivity for BPA detection is based on the gradual aggregation of AuNPs controlled by the specific interactions among aptamer, BPA, and cationic polymer PDDA. This biosensor can detect higher concentrations of BPA than 150 nM through the distinct color change of the aggregated AuNPs. What is more, the biosensor enables the sensitive and selective detection of BPA with a linear range of 1.50–500 nM and a detection limit of 1.50 nM.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ab.2016.01.011.

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