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Facile synthesis of chitosan-capped ZnS quantum dots as an eco-friendly fluorescence sensor for rapid determination of bisphenol A in water and plastic samples

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Abstract

The paper described a novel eco-friendly fluorescence sensor for determination of bisphenol A (BPA) based on chitosan-capped ZnS quantum dots (QDs). By using safe and inexpensive materials, nontoxic ZnS QDs were synthesized via an environment-friendly method using chitosan as capping agent. The as-prepared ZnS QDs exhibited characteristic absorption (absorbance edge at 310 nm) and emission (maxima at 430 nm) spectra with a relatively high fluorescence quantum yield of 11.8%. Quantitative detection of BPA was developed based on fluorescence quenching of chitosan-capped ZnS QDs with high sensitivity and selectivity. Under the optimal conditions, the fluorescence response of ZnS QDs was linearly proportional to BPA concentration in a wide range from 0.50 to 300 $\mu g \cdot L^{-1}$ with a detection limit of 0.08 $\mu g \cdot L^{-1}$. Most of potential coexisting substances did not interfere with the BPA-induced quenching effect. The proposed analytical method for BPA was successfully applied to water and plastic real samples, and the possible quenching mechanism was also discussed.

Key words: Bisphenol A, Zinc sulfide, Quantum dots, Sensor, Chitosan, Fluorescence quenching

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1. Introduction

Bisphenol A (BPA), 2,2-bis(4-hydroxyphenyl) propane, is one of the most important chemical raw materials in the world.[1] It is synthesized by phenol and acetone under catalysis of acid or base, and widely used for the production of polycarbonate (PC) and epoxy resins (EP), along with other applications. Among their uses, a wide variety of food contact materials are noticeable, such as tableware, storage container, water pipe, infant feeding bottle and protective lining for beverage cans.[2] Because of BPA's high volume production and widespread use in human life, however, there is far-ranging environmental contamination and human exposure to BPA.[3] Its presence in food has been paid great attention since it composes the principal pathway of human exposure.[4] Because of incomplete polymerization and degradation of the polymers under high temperature, BPA can migrate from food contact materials to food or water.[5] As an exogenous endocrine disrupting chemical (EDC), endocrine disrupting activity of BPA has a considerably negative impact on human health. Exposure to BPA might be an important factor in the decreasing sperm count in males, the increasing rates of mammary cancer, the increase in other diseases linked to endocrine dyscrasia, as well as the increase of neural and behavioral changes in infants and children.[6,7] Thus there is an urgent need to monitor the presence of BPA in daily water correlated to BPA-based food contact materials.

Traditional detection methods for BPA such as high performance liquid chromatography (HPLC),[8] liquid chromatography/mass spectrometry (LC/MS),[9] gas chromatography/mass spectrometry (GC/MS),[10] enzyme-linked immunosorbent assay (ELISA)[11] and capillary electrophoresis (CE),[12] require expensive instrumentation, considerable time, experienced technician and complex sample pretreatment, so their application in on-site rapid analysis is

extremely limited. Recently, different types of analytical methods including electrochemistry,[13] chemiluminescence,[14] quartz crystal microbalance (QCM),[15] aptasensor-based colorimetric method with Au nanoparticles,[16] surface plasmon resonance (SPR) biosensor,[17] liposome chromatography[18] *etc.*, have been developed to determine BPA, but most of them suffer from complex chemical synthesis, the use of volatile organic solvents, high cost or poor sensitivity. Therefore, developing rapid, simple, sensitive, low-cost and eco-friendly methods for BPA detection has become very essential.

Fluorescence assay is a promising analytical technique with the advantage of less sample, low cost, high sensitivity, quick-response and easy operation. Thus, in recent years, it is widely used in biochemical, food and environmental science. There have been several reports on fluorescence determination for BPA,[19-21] and the detection limits are comparable with those of HPLC,[8] LC/MS[9] and GC/MS,[10] and approximately 1-3 orders of magnitude lower than those reported by other methods such as ELISA,[11] CE,[12] electrochemistry[13] and chemiluminescence.[14] BPA can give a fluorescence signal by itself as its molecule possesses a conjugated cyclic structure, but in aqueous solution the signal is so weak that direct determination can only obtain a poor detection performance.[22] Some fluorescent probes are utilized for detection of BPA, such as fluorescent dyes,[19] CdSe[20] and CdTe[21] quantum dots (QDs). However, most of fluorescent dyes have disadvantages of low photobleaching threshold, poor chemical stability and biocompatibility, and Cd/Se/Te-based QDs have been confirmed to exhibit a strong cytotoxic activity.[23] Thus, Zn-based QDs may be regarded as a promising new choice of nanophosphors for detection of BPA, as they are a type of nontoxic (or low-toxic) QDs compared with traditional Cd/Se/Te-based QDs.[24] To the best of our knowledge, there is no report on fluorescence detection for BPA with

Zn-based QDs. Chitosan, β-(1,4)-2-amino-2-deoxy-D-glucose, is a unique cationic biocompatible polysaccharide built by repeated units of N-acetyl-D-glucosamine and D-glucosamine, derived from the partial deacetylation of chitin, a natural polysaccharide extracted from the crustacean shells. Chitosan exhibits a desirable chelating ability with transition metal ions due to its special structure, which makes it possible for its metal ion complexes to be used as precursors to synthesize QDs. Moreover, its high viscosity can effectively prevent the aggregation of QDs, which will greatly enhance the stability of QDs in aqueous solution.[25]

Herein, we present a novel eco-friendly fluorescence sensor for detection of BPA based on chitosan-capped ZnS QDs. Chitosan was used as modifier as well as stabilizer, and well-dispersed ZnS QDs with a uniform size were synthesized. By controlling the reaction conditions, the fluorescent properties of chitosan-capped ZnS QDs could be well regulated. The obtained water-soluble QDs were around 1.8 nm in diameter and displayed excellent fluorescent properties. We investigated the interaction between chitosan-capped ZnS QDs and BPA in aqueous solution. It was found that BPA dramatically quenched the fluorescence of chitosan-capped ZnS QDs, and the change of fluorescence intensity was proportional to the concentration of BPA. Based on this phenomenon, a sensitive, simple, rapid, low cost and environment-friendly fluorescence method has been established for detection of BPA. Interference tests showed that some potential co-existing substances, such as common inorganic ions and natural small molecules have little interference. The possible mechanism of the proposed sensing method for BPA is also discussed (Scheme 1). This green method has been applied to the determination of BPA content in water and plastic samples and satisfactory results were obtained.

2. Experimental

2.1 Chemicals, materials and apparatus

All chemicals were of analytical grade and used as received without further purification. High purity nitrogen (99.999%) and double deionized water (DDW) were used in all experiments. Zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$], sodium sulfide ($Na_2S \cdot 9H_2O$) and acetic acid were purchased from Xilong Chemical Co., Ltd (Shantou, Guangdong, China). Chitosan (high molecular weight, ≥ 75% deacetylated) and BPA were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). $CaCl_2$, NaCl, NH_4Cl, $MgCl_2$, $MnCl_2$, $CuCl_2$, $AlCl_3$, $FeCl_3$, $ZnCl_2$, $BaCl_2$, KNO_3, Na_3PO_4, Na_2SO_4, Na_2CO_3, $AgNO_3$, $Hg(NO_3)_2$, NaOH, CH_3COONa, HCl, glucose, lactose and glycine were purchased from Beijing Chemical Reagent Company (Beijing, China). Rhodamine 6G (Rh 6G) was obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Different brands of packaged drinking water, plastic cups, feeding bottles, microwave lunch boxes and epoxy resin-based bowls were procured from a local market. Besides, tap and rain water was also collected in our laboratory and campus, respectively.

The absorption spectra were recorded on a 2550 UV-vis spectrophotometer (Shimadzu, Tokyo, Japan). The fluorescence spectra were obtained on a RF-5301PC fluorescence spectrophotometer (Shimadzu, Tokyo, Japan) with both of the exciting and emission slits set at 5 nm. High resolution transmission electron microscopy (HRTEM) measurements were made on a TECNAI F20 (FEI Co., Eindhoven, Netherlands) operated at an accelerating voltage of 200 kV. A drop of the QDs solution was drop-cast on ultra-thin carbon film-supported copper grids and subsequently air-dried before HRTEM analysis. FT-IR spectra were recorded with an IRPrestige-21 FT-IR spectrometer (Shimadzu, Tokyo, Japan). Zeta potential was obtained on a Zetasizer Nano ZS90 particle size analyzer (Malvern, Worcestershire, UK). The ultrasonic

treatment was carried out on a 125 KQ-300DE ultrasonicator (Kunshan, Shanghai, China). The centrifugation was performed on a CR20B2 refrigerated centrifuge (Hitachi, Tokyo, Japan). Magnetic stirring was carried out on a GL-3250B magnetic stirrer (QILINBEIER, Haimen, China). All pH measurements were carried out with a Model pHS-3C pH meter (Chenghua, Shanghai, China). All optical measurements were performed at room temperature under ambient conditions.

2.2 Synthesis and purification of water-soluble chitosan-capped ZnS QDs

Chitosan is nearly insoluble in strong acidic and neutral media but soluble in weak acidic media, as amine group is protanated to NH_3^+,[26] thus we used 1% (*v/v*) acetic acid aqueous solution to dissolve chitosan. Water-soluble chitosan-capped ZnS QDs were synthesized according to the procedure described previously with some modification.[26,27] 0.22 g of $Zn(CH_3COO)_2{\cdot}2H_2O$ was firstly added to 99 mL of 0.05% (*w/v*) chitosan solution under constant stirring and heated at 80 °C for 20 min to facilitate a chelating balance. After the solution naturally cooled down to room temperature, 0.24 g of $Na_2S{\cdot}9H_2O$ was dissolved in 1 mL of ice water and thereupon added dropwise to the solution in an ice bath under continuous stirring and protection of N_2. The molar ratio of Zn^{2+}:S^{2-} is 1.5:1. The addition of Na_2S resulted in the formation of a milky white suspension immediately, and the solution was constantly stirred for 100 min. Then the solution containing chitosan-capped ZnS QDs was centrifuged at 12000 rpm for 10 min. The precipitated particles were washed 3 times using DDW and 0.1% (*v/v*) acetic acid aqueous solution respectively to remove the adhered impurities and excess chitosan. The washed chitosan-capped ZnS QDs were dried by a vacuum oven at 60 °C for 24 h. Finally, the prepared QDs were dispersed in 100 mL 1% (*v/v*) acetic acid aqueous solution again and stored in a refrigerator at 4 °C for further use. The QDs suspension can keep clear without any sedimentation for months.

To obtain high-quality chitosan-capped ZnS QDs, the influences of different synthesis conditions including the concentration of Zn^{2+} and chitosan, the molar ratio of Zn^{2+}:S^{2-} and the reaction time on the fluorescence intensity of ZnS QDs were investigated. According to the evaluation for the above conditions, the concentration of Zn^{2+} and chitosan, the molar ratio of Zn^{2+}:S^{2-} and the reaction time were optimized to be 1.0×10^{-4} mol·L^{-1}, 0.50 g·L^{-1}, 1.5:1 and 100 min, respectively. Under this synthesis condition, the as-prepared ZnS QDs can exhibit relatively high fluorescence emission intensity and good analytical performance for detection of BPA.

2.3 Analytical Procedure

Typically, in a 5 mL test tube, a certain volume of 500 μg·L^{-1} BPA aqueous solution was added and the solution was diluted to 2 mL with DDW. Then the solution was mixed with 1 mL of 3.5×10^{-6} mol·L^{-1} chitosan-capped ZnS QDs. After the mixture was homogenized thoroughly and equilibrated for 4.0 min at room temperature, the fluorescent intensity was recorded at excitation wavelength of 315 nm. The calibration curve for BPA was established according to the ratio of fluorescence intensity, that is, F_0/F, and F_0 and F are the maximum emission intensities of ZnS QDs in the absence and presence of certain concentrations of BPA, respectively.

2.4 Detection of BPA in real samples

Tap and packaged drinking water were directly determined for the presence of BPA without any pretreatment. Rain water was filtered with a 0.45 μm-filter membrane to remove particulate matter.

According to Chinese National Standard GB/T 23296.1-2009 (Materials and articles in contact with foodstuffs-Plastics substances subject to limitation-Guide to test methods for the specific migration of substances from plastics to foods and food simulants and the determination

of substances in plastics and the selection of conditions of exposure to food simulants), contacting temperature and time for the specific migrant test of BPA from plastic cup and feeding bottle to water-based food or food simulant should be chosen as 100 °C (or reflux temperature) and 240 min. In order to shorten the pretreatment time for rapid detection of these plastic samples, ultrasonic and microwave extraction were respectively chosen and applied in our experiments according to the actual usages of the samples. An ultrasonicator (220 V, 200 W) and a microwave oven (220 V, 500 W) were used in the extraction procedures. Plastic cups, feeding bottles, microwave lunch boxes and epoxy resin-based bowls were washed with DDW thoroughly, solarized and cut into small fragments about 5 mm × 5 mm size, respectively. Next, 10 g (± 0.0001 g) of each plastic sample was put into a conical beaker and 100 mL of DDW was added. The solutions containing plastic cup or feeding bottle fragments were ultrasonic-extracted for 90 min in a water bath (90 ± 0.5 °C). The solutions containing microwave lunch box or epoxy resin-based bowl fragments were microwave-heated for 10 min. Then all the sample leaching solutions were cooled to room temperature, filtered with a 0.45 μm-filter membrane and rediluted to 100 mL with DDW. Finally, 1 mL of the water or plastic leaching solution samples was used for BPA determination according to the proposed method in *Section 2.3*. In order to investigate the recoveries of these water and plastic leaching solution samples, a certain amount of BPA was doped into these samples, then pretreated and analyzed in accordance with the above procedure.

3. Results and Discussion

3.1 Characteristics of chitosan-capped ZnS QDs

Due to the protonation of $-NH_2$ group of chitosan in weak acidic condition, the surface of chitosan-capped ZnS QDs possesses positive charges, which is supported by the zeta potential

data of the QDs suspension (Fig. S1A). The zeta potential of ZnS QDs was measured to be 40.4 mV, which indicates that the surface of ZnS QDs is strongly positive-charged. The QDs suspension can be effectively stabilized against aggregation via electrostatic repulsion against van der Walls attraction.

In order to identify the conjugation mode between ZnS QDs and chitosan, FT-IR spectroscopy was applied to this study. The FT-IR spectra of pure chitosan (A) and chitosan-capped ZnS QDs (B) are shown in Fig. 1, and the major characteristic peaks observed in both spectra are shown in Table S1. The similarity in both spectral characteristics and major peak positions indicates that chitosan was well chemically bound onto the surface of the ZnS QDs. Moreover, by discerning the fine differences between the two spectra, the conjugation mode of chitosan and ZnS QDs can be confirmed. It is important to note that the peak around 3300-3500 cm^{-1} corresponding to stretching vibrations of hydroxyl, amino and amide groups, moved to lower wavenumber and became broader and stronger, which represents the strong interaction between these groups and ZnS QDs. The mechanism of this interaction may be mainly due to hydrogen and coordinate bonding, as the ZnS QDs growing in aqueous solution have a large amount of H_2O and excess Zn^{2+} bound to the surface of the nanocrystallite, which interact with −OH and $-NH_2$ of chitosan via hydrogen and coordinate bond. This interaction will result in some other fine spectral changes of covalent bonds in chitosan, especially for those corresponding to Zn^{2+}-bonded atoms. Generally, coordination to metallic ions will reduce the electron density of metallic ions-bonded atoms which makes stretching require less energy, and increase steric hindrance of covalent bonds corresponding to metallic ions-bonded atoms which makes bending require more energy. Therefore, the coordination between Zn^{2+} and chitosan caused the stretching vibration peaks of

198 covalent bonds corresponding to Zn^{2+}-bonded atoms shifting to lower wavenumber and their
199 bending vibration peaks moving to high wavenumber. In Fig. 1, the peaks located at 1264 and
200 1090 cm^{-1} respectively assigned to C_2−H and C_3−O stretching shifted to lower wavenumber 1261
201 and 1083 cm^{-1}, and the peak located at 1602 cm^{-1} assigned to N−H bending moved to a higher
202 wavenumber 1611 cm^{-1}, while the peak located at 1035 cm^{-1} attributed to C_6−O stretching
203 remained stable. These changes show that N_2 and O_3 of chitosan molecule are more responsible
204 for the interaction with ZnS QDs and O_6 takes little part in the interaction. Other peak changes in
205 Table S1 can also confirm the above inference. Since the growth of ZnS QDs is almost *in situ*, we
206 may deduce that the complex sites between chitosan and ZnS QDs are mainly located at C_2 and C_3
207 of the chitosan repeating units. The inferred formation process of chitosan-capped ZnS QDs was
208 shown in Scheme 1C.

209 The chitosan-capped ZnS QDs are optically characterized by UV-vis absorption spectroscopy
210 and fluorometry. The normalized absorption (a) and fluorescence emission (b) spectra are shown
211 in Fig. 2A. The absorption edge of ZnS QDs is around 310 nm with a considerable blue-shift
212 compared to that of bulk ZnS at 340 nm,[28] showing an apparent quantum confinement effect. The
213 emission maxima centered at 430 nm with the excitation of 315 nm. Photographs of the ZnS QDs
214 solution under daylight and a 308 nm UV lamp are respectively shown as c and d in Fig. 2A.
215 Under a 308 nm UV lamp, the QDs solution displayed bright blue fluorescence which was
216 attributed to the defect-related emission of ZnS. Besides, the fluorescence spectrum band is
217 relatively narrow and symmetric with full widths at half-maximum (FWHM) about 85 nm, which
218 reveals that the as-prepared QDs possess fairly uniform particle size due to their relatively low
219 size distribution. [29] The molar extinction coefficient (ε) of the chitosan-capped ZnS QDs at 315 nm

was estimated to be about 3.3×10^5 $M^{-1} \cdot cm^{-1}$, [27] thus the molar concentration of the ZnS QDs was calculated to be nearly 3.5×10^{-6} $mol \cdot L^{-1}$ according to Lambert Beer's law. TEM is also performed to study the morphology of the as-prepared chitosan-capped ZnS QDs. Fig. 2B shows a typical image of the obtained ZnS QDs. The shape of these nanoparticles is close to spherical and partly aggregated, with diameters ranging from 1.5 to 2.0 nm. The average particle size was about 1.8 nm.

Fluorescence quantum yield (QY) represents the efficiency of a fluorescent material in converting the excitation into fluorescent emission. According to Williams' method,[30] by using Rh 6G (QY = 95%, in ethanol) as the reference and exciting all the samples at 315 nm, the QY of chitosan-capped ZnS QDs was calculated from the following equation:

$$QY_{ZnS} = QY_{Rh\,6G} \cdot \frac{m_{ZnS}}{m_{Rh\,6G}} \cdot \left(\frac{\eta_{water}}{\eta_{ethanol}}\right)^2 \quad (1)$$

where m and η are the slope of the integrated fluorescence intensity versus absorbance at 315 nm and refractive index of the solvent respectively. The integrated fluorescence intensity was obtained by integrating the emission intensity over the entire wavelength range under the emission peak, and the absorbance was kept between 0.01 and 0.1 to avoid the self-absorption effect. With the QY of Rh 6G taken as 95%, we obtained the QY of the ZnS QDs as 11.8%. Since it has been widely accepted that the QDs whose QY is more than 10% can be considered for practical applications, [31] it could be concluded that the obtained ZnS QDs can show a satisfactory fluorescent analytical performance in this assay.

3.2 Effects of BPA on the fluorescence of chitosan-capped ZnS QDs

According to the analytical procedure introduced in *Section 2.3*, the fluorescence emission spectra of the as-prepared chitosan-capped ZnS QDs (Fig. 3) in the absence (a) and presence (b) of

BPA were recorded. The fluorescence band of chitosan-capped ZnS QDs was centered at 430 nm. When BPA was added to the ZnS QDs solution, significant quenching of fluorescence intensity was observed. In order to identify the origins of the fluorescence quenching, control experiments were performed. Free $ZnCl_2$, chitosan and Zn^{2+}-chitosan complex with the same concentrations as those used in the synthesis of ZnS QDs were added into the mixture solution of ZnS QDs and BPA. The obtained results revealed that these substances had no contribution to the quenching effect of BPA on the fluorescence emission of ZnS QDs. Thus, the quenching effect was attributed to the interaction between BPA and chitosan-capped ZnS QDs. Considering this remarkable quenching of fluorescence intensity, the possibility of developing a simple and sensitive fluorescence chemosensor for rapid detection of BPA should be further studied.

3.3 Optimization of assay conditions

The influence of reaction time on the fluorescence intensity of the system was investigated at room temperature. The optimum incubation time for the reaction between ZnS QDs and BPA reaching equilibrium was examined by recording the fluorescence spectra every 0.5 min at real time (Fig. 4A). The results show that after addition of BPA into the ZnS QDs solution the fluorescence intensity decreased by prolonging the reaction time and the equilibrium was obtained within 4.0 min. F_0/F was nearly constant after 4.0 min and the fluorescence intensity of the BPA-ZnS QDs system could keep stable for at least 50 min. Thus the reaction time was fixed at 4.0 min.

It is well known that fluorescence intensity of QDs is greatly affected by medium pH. Using 0.1 $mol \cdot L^{-1}$ NaOH or 0.1 $mol \cdot L^{-1}$ HCl for pH adjustment, the effects of the solution pH on the fluorescence intensity of ZnS QDs in the absence and presence of BPA were investigated and the

results are shown in Fig. 4B and 3C respectively. In Fig. 4B, it can be seen that stable and high fluorescence intensity was obtained in the pH range of 4.0-4.5 and pH lower than 4.0 or higher than 4.5 resulted in a significant decrease of fluorescence intensity. Under the condition of pH < 4.0, the low fluorescence intensity is the result of dissociation of the QDs, as the interaction between chitosan and ZnS QDs was wrecked and the stability of the QDs dramatically decreased. With the increase of pH, the deprotonation of $-NH_2$ group in chitosan molecule occurred. The deprotonation could strengthen the interaction between chitosan and ZnS QDs in some degree, which brought about partly fluorescence enhancing. However, the fluorescence intensity began to decrease with the further increase of pH (pH > 4.5), as the solubility of chitosan decreased, which resulted in partly precipitation of the QDs. In the presence of BPA, as illustrated in Fig. 4C, F_0/F is also stable and high in the pH range of 4.0-4.5. Thus, the optimal pH was chosen to be 4.0 for further experiments.

To gain the widest linear range and the highest sensitivity of the calibration function, the effect of ZnS QDs concentration on the F_0/F of BPA-ZnS QDs system was further investigated. A relatively low concentration of ZnS QDs can only provide very weak fluorescence emission correspondingly, which is not beneficial for obtaining a wider linear range. With the increase of the ZnS QDs concentration, the fluorescence intensity of the system rises up gradually (not shown). A very high QDs concentration could enlarge the linear range but at the expense of sensitivity. As shown in Fig. 4D, the maximum F_0/F was achieved when the concentration was 1.2×10^{-6} mol·L^{-1}. Comprehensively considering high sensitivity and wide linear range, a QDs concentration of 1.2×10^{-6} mol·L^{-1} (in test sample) was recommended for further research.

3.4 Calibration and sensitivity

As shown in Fig. 5, under the optimal conditions mentioned above, the addition of BPA gradually decreased the fluorescence intensity of the ZnS QDs, so a quantitative determination of BPA based on fluorescence quenching was possible. The inset in Fig. 5 illustrates that F_0/F exhibits a good linear relationship with the concentration of BPA in a wide range from 0.05 to 300 μg·L^{-1}, which is well described by a Stern-Volmer (SV) equation with the correlation coefficient of 0.99531:

$$\frac{F_0}{F} = 0.97064 + 0.01431 c_{\mathrm{BPA}} \quad (2)$$

where c_{BPA} is the concentration of BPA (μg·L^{-1}). The limit of detection (LOD) for BPA in water is 0.08 μg·L^{-1} with the ratio of signal to noise of 3 (S/N = 3). The relative standard deviation (RSD) for 6 parallel determinations of a solution containing 25.0 μg·L^{-1} BPA was 1.2%. This indicates that the method can offer good precision for the detection of BPA. Compared with the existing methods (shown in Table S2), a relatively low detection limit was obtained and it was also greatly lower than 30.0 μg·L^{-1}, which is the LOD given by the HPLC method according to Chinese National Standard GB/T 23296.16-2009 (Food contact materials-Polymer-Determination of bisphenol A in food simulants-High performance liquid chromatography). Obvious advantages were reflected in the proposed method, such as easy sample pretreatment, short analysis time, low cost and nontoxicity.

3.5 Interference studies

The fluorescence titration of chitosan-capped ZnS QDs with various coexisting substances was performed to examine the detection selectivity. Table S3 described the influence of coexisting substances on the fluorescence intensity of ZnS QDs with BPA. For coexisting substances, K^+, Na^+, Al^{3+}, Ca^{2+}, Ba^{2+}, NH_4^+, Mg^{2+}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, CH_3COO^-, NO_3^-, Cl^-, Mn^{2+}, glucose,

lactose and glycine induced less than ± 5% change of the fluorescence intensity of ZnS QDs and the tolerance limits of these substances were more than 12500 $\mu g \cdot L^{-1}$, at least 500 times than the coexisting BPA concentration, which means these coexisting substances had no interference for detection of 25.0 $\mu g \cdot L^{-1}$ BPA. Zn^{2+} had a fluorescence enhancement effect at a relative higher concentration since they were adsorbed onto the surface of ZnS QDs and the increase of S surface vacancies improved the defect-related emission of ZnS QDs in some degree. Fe^{3+}, Cu^{2+}, Hg^{2+} and Ag^{+} exhibited effective quenching effect, which is attributed to their strong chemical adsorption onto the ZnS QDs surface. However, the tolerance limits of these ions were at least 5 times of the BPA concentration and greatly higher than their potential concentration present in real samples. Thus, the detecting system herein possessed a good selective fluorescence response toward BPA and it could be applied to determine BPA in real samples.

3.6 Detection of BPA in real samples

The proposed method was applied for the determination of BPA in tap, rain and packaged drinking water. Standard addition method was used to evaluate the analytical performance of the fluorescence sensor and the results were shown in Table 1. It can be clearly seen that the recoveries were in the range of 95.9-105.8% with RSD values between 1.5% and 4.0%, indicating that the fluorescence sensor might be sufficient and satisfactory for BPA detection in these water samples. No BPA was detected in the tap water sample. From one packaged drinking water sample, BPA was detected at a very low amount of 0.19 $\mu g \cdot L^{-1}$, and for the other, it was not detected. This very low amount of BPA in packaged drinking water may be caused by BPA migration from the packages under unreasonable storage conditions. 0.41 $\mu g \cdot L^{-1}$ BPA was detected in the rain water sample, which may be due to a very slow BPA migration from domestic

garbage and wastewater to the global water cycle.

Samples of plastic cups, feeding bottles, microwave lunch boxes and epoxy resin-based bowls with different brands were also inspected. Different ultrasonic and microwave extraction conditions had been investigated. The optimal conditions was selected as 90 °C and 90 min for ultrasonic extraction, and 10 min for microwave extraction since under these conditions the extraction periods were significantly shortened and the extraction effect were equivalent to those under the condition stipulated by GB/T 23296.1-2009. After extraction procedures under the above optimal conditions, leaching solutions of the plastic samples were respectively examined using the proposed method and the results were shown in Table 1. High recoveries from 96.4% to 104.3% were obtained for these plastic samples with RSD values between 1.0% and 4.4%. The result demonstrates that the proposed analytical method was also competent for BPA detection of plastic samples. It can be seen that no BPA was detected in the samples of the PP-made plastic products. However, in some PC-made or PC-containing materials, different amounts of BPA could be detected, which illuminates that the employed BPA extraction processes in this assay are very effective.

3.7 Quenching mechanism

Up to now, many quenching mechanisms including energy transfer, charge diverting and surface absorption have been proposed to explain the fluorescence quenching phenomena of QDs. To explore the possible mechanism involved in the interaction between chitosan-capped ZnS QDs and BPA, the UV-vis absorption spectra of BPA, ZnS QDs and ZnS QDs adding BPA were investigated. Shown as curve a in Fig. S2, BPA had no absorption in the wavelength range of 300-600 nm, so the quenching effect of BPA on the fluorescence of ZnS QDs is not due to inner

filter effect resulting from the absorption of the emission wavelength by BPA. No obvious change was observed from the ZnS QDs absorption spectra before and after adding BPA (curve b and c in Fig. S2) and no perceptible red shift on the maximum emission wavelength can be found in Fig. 5 with increasing concentration of BPA, which indicates that the presence of BPA mainly influences the surface status and not the size of the ZnS QDs. Generally, in alkaline environment, the process of complexation reaction between BPA and Zn^{2+} on ZnS QDs surface may occur. While the current ZnS QDs-BPA system is weak acidic, there is little probability of the complexation reaction. The zeta potential of BPA in the weak acidic solution was also measured to be 23.0 mV (Fig. S1B). Since both BPA and ZnS QDs possessed positive charges, there is no electrostatic attractive interaction between them. Thus, the quenching may be due to the hydrogen bonding between BPA and chitosan on the surface of the QDs (Scheme 1D). BPA could bind to the surface of chitosan-capped ZnS QDs like a cap through the hydrogen-bond interaction between –OH of BPA and $-NH_2$/–OH of chitosan.[32] The hydrogen bonds lead chitosan molecules to partly peel off from the surface of the ZnS QDs, then the surface changes induced the fluorescence quenching of the ZnS QDs.[21]

4. Conclusion

In summary, with chitosan as capping and stabilizing agent, water-soluble ZnS QDs were easily prepared. By using the nontoxic ZnS QDs as fluorescence probe, a novel and eco-friendly technique for rapid BPA detection with high sensitivity and selectivity was developed based on the quenching effect of BPA on the fluorescence emission of ZnS QDs. The possible quenching mechanism is due to the surface change of ZnS QDs, induced by hydrogen bonding between BPA and chitosan on the surface of ZnS QDs. The factors affecting both the synthesis of

chitosan-capped ZnS QDs and the fluorescence detection for BPA were also examined. Under the optimal assay conditions, a relatively wide linear range (from 0.50 to 300 $\mu g \cdot L^{-1}$) and low detection limit (0.08 $\mu g \cdot L^{-1}$) were obtained. Most common coexisting substances hardly interfered with the determination of BPA. The proposed method was successfully applied to the recognition of BPA in water and plastic samples, and simplicity, rapidity, high sensitivity and low cost was exhibited in detection process. Thus, it appears to be a promising candidate for on-site rapid screening of BPA contamination in water and plastic samples.

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Figure Captions

Scheme 1. (A) The molecular structure of BPA. (B) The molecular structure of chitosan. (C) Formation process of chitosan-capped ZnS QDs. (D) The proposed mechanism for the quenching effect of BPA on the fluorescence of chitosan-capped ZnS QDs.

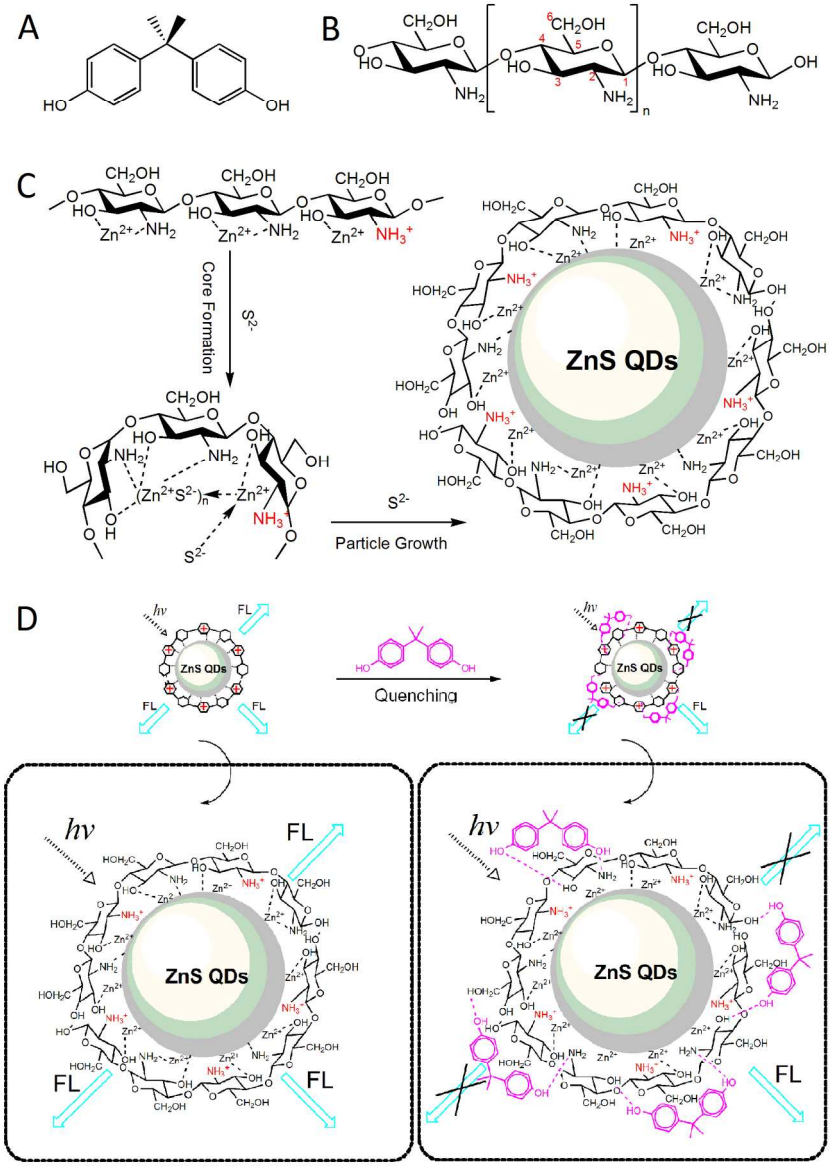
Fig. 1. FT-IR spectra of pure chitosan (A) and chitosan-capped ZnS QDs (B).

Fig. 2. (A) The absorption spectrum (a) and fluorescence emission spectrum (b) of the as-prepared ZnS QDs, and the digital photographs of the ZnS QDs solution under daylight (c) and a 308 nm UV lamp (d). (B) HRTEM images of the ZnS QDs.

Fig. 3. The fluorescence emission spectra of 1.2×10^{-6} mol·L^{-1} ZnS QDs in the absence (a) and presence (b) of 150 μg·L^{-1} BPA.

Fig. 4. (A) Variation of F_0/F versus the reaction time for ZnS QDs after addition of BPA. (B) Effect of pH on the fluorescence intensity of ZnS QDs. (C) Effect of pH on F_0/F with the presence of BPA. (D) Effect of ZnS QDs concentration on F_0/F with the presence of BPA. ZnS QDs for A, B and C, 1.2×10^{-6} mol·L^{-1}; BPA for A and C, 150 μg·L^{-1}, for D, 50 μg·L^{-1}.

Fig. 5. Fluorescence emission spectra of ZnS QDs in the presence of increasing concentrations of BPA. The concentration of BPA in samples (a)-(o) is 0, 0.50, 0.83, 1.66, 3.33, 8.33, 13.3, 16.6, 25.0, 33.3, 50.0, 100, 150, 200 and 300 μg·L^{-1}, respectively. ZnS QDs, 1.2×10^{-6} mol·L^{-1}. The inset shows the calibration curve of F_0/F versus the concentration of BPA.



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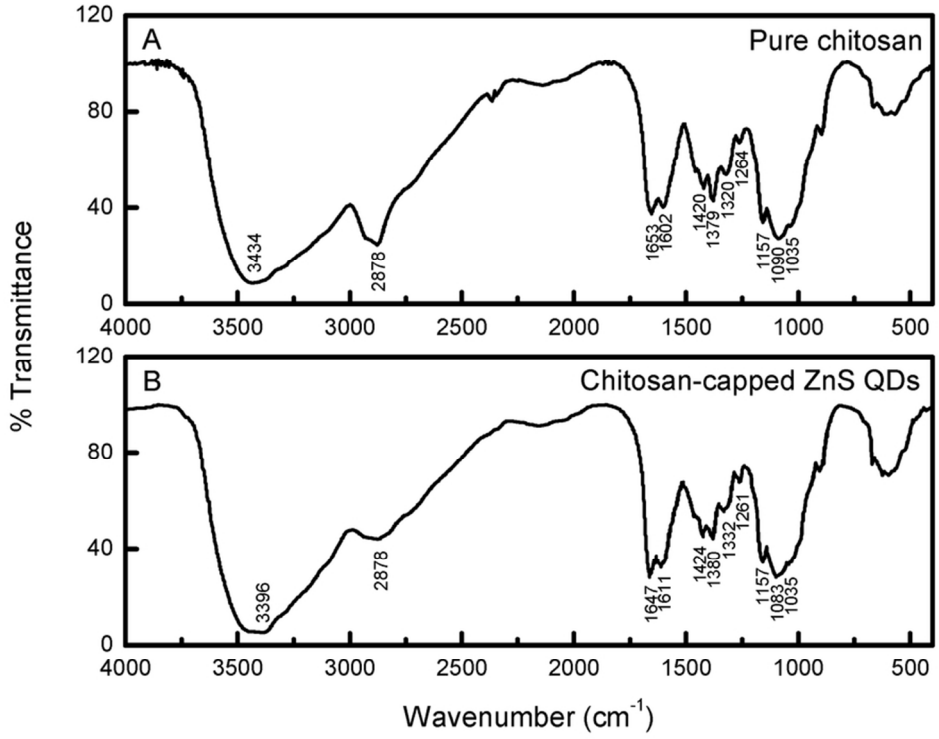

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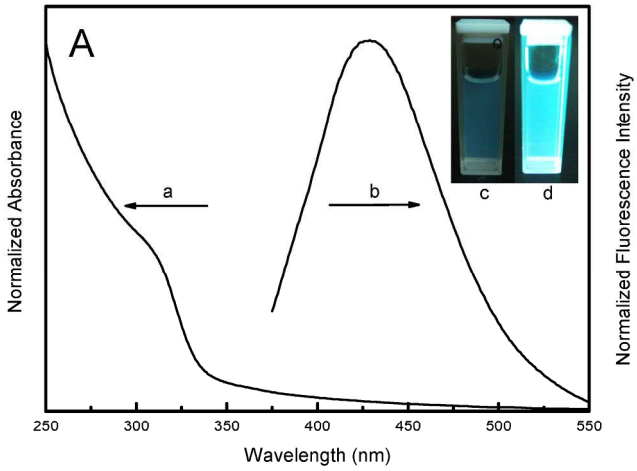

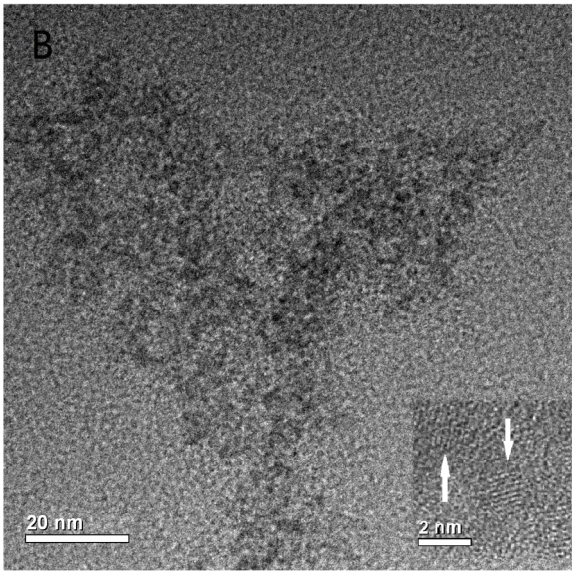

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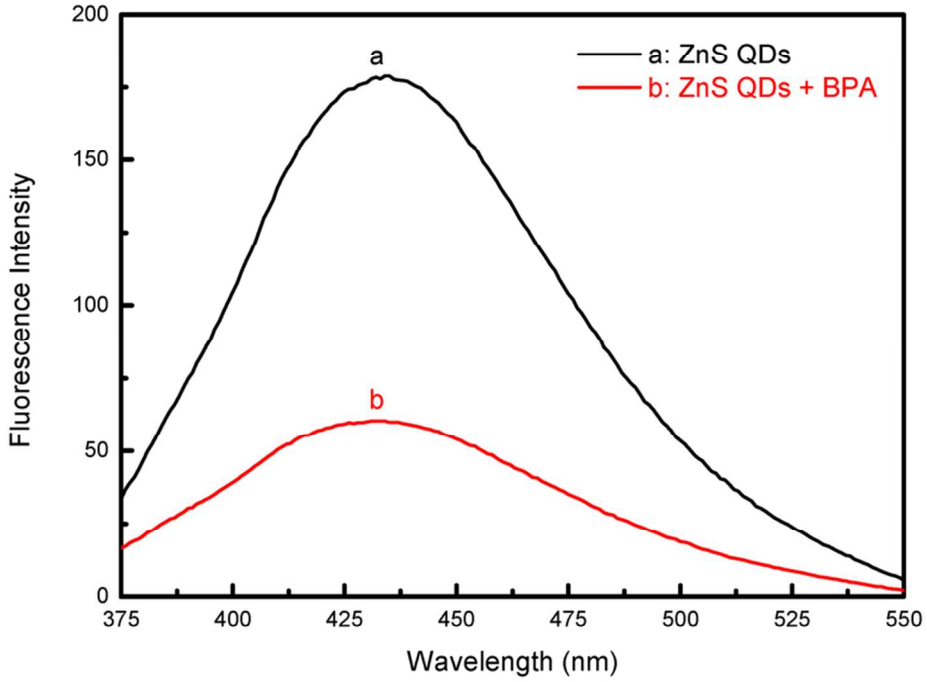

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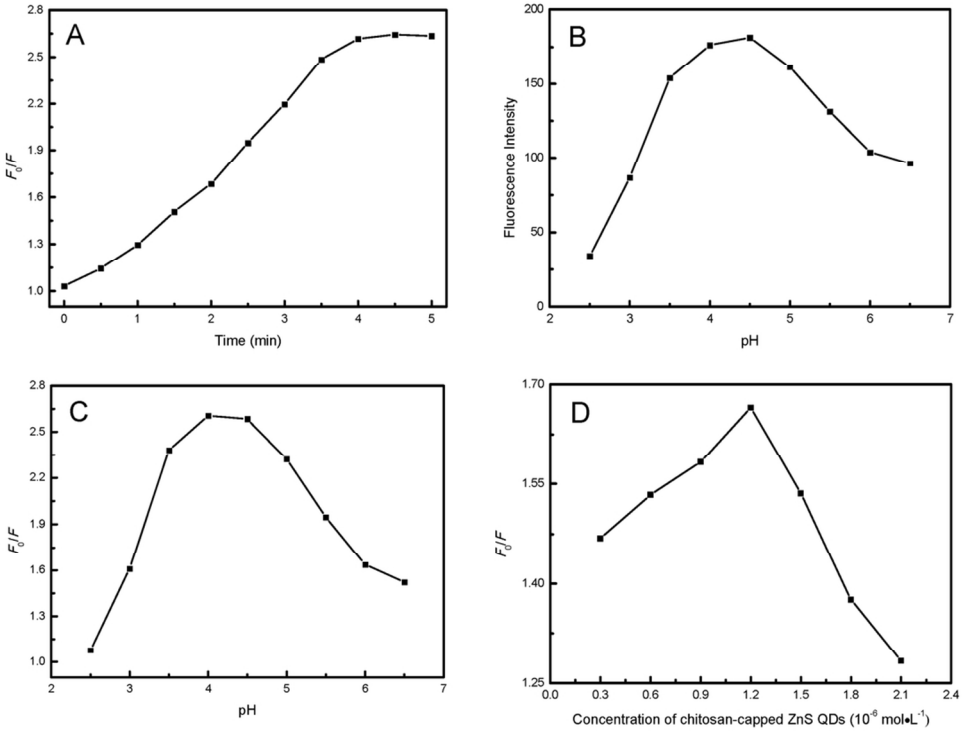

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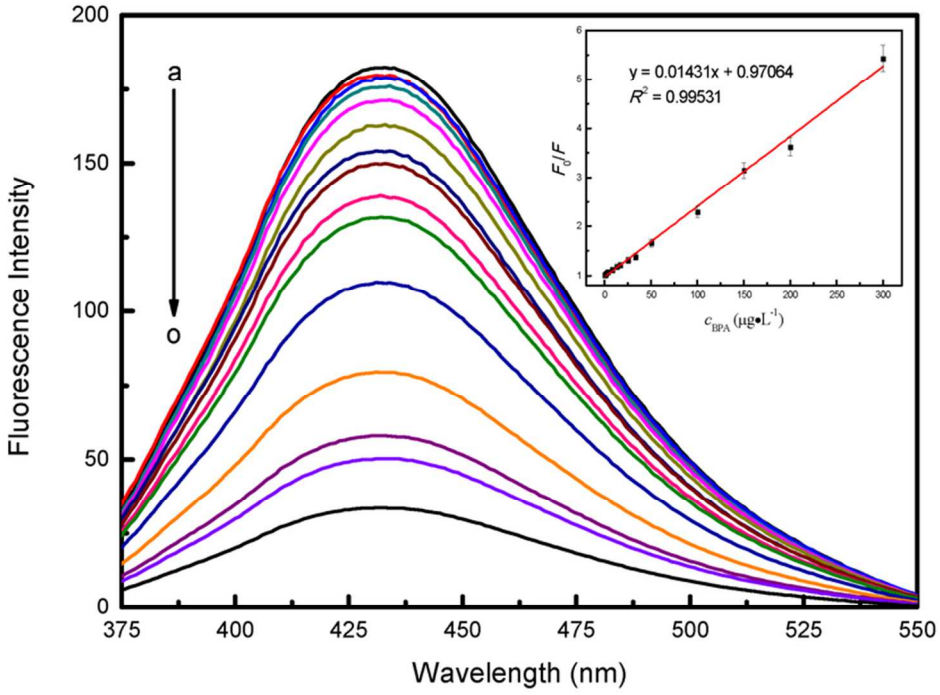

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Table 1 Concentrations and recoveries of BPA in various water samples and plastic leaching solutions

Sample	Background ($\mu g \cdot L^{-1}$)[a]	Spiked ($\mu g \cdot L^{-1}$)	Found ($\mu g \cdot L^{-1}$)[a]	Recovery (%)	RSD (%, $n = 6$)
Tap water	ND[b]	2	1.98	99.0	2.5
		10	10.17	101.7	2.2
		50	49.36	98.7	3.0
Rain water	0.41	2	2.55	105.8	4.0
		10	10.79	103.7	2.6
		50	51.72	102.6	3.1
Packaged drinking water 1	ND	2	2.07	103.5	1.6
		10	9.90	99.0	2.1
		50	50.99	102.0	1.9
Packaged drinking water 2	0.19	2	2.10	95.9	2.3
		10	10.34	101.5	1.5
		50	51.46	102.5	3.3
Leaching solution:	10.46	2	12.15	97.5	3.6
plastic cup 1 (PC)		10	20.86	102.0	2.3
		50	61.70	102.1	2.0
Leaching solution:	ND	2	2.07	103.5	2.6
plastic cup 2 (PP[c])		10	9.83	98.3	1.8
		50	48.93	97.9	3.2
Leaching solution:	22.55	2	24.13	98.3	2.0
feeding bottle 1 (PC)		10	32.92	101.1	2.4
		50	72.10	99.4	3.2
Leaching solution:	ND	2	1.97	98.5	4.1
feeding bottle 2 (PP)		10	10.36	103.6	3.0
		50	52.14	104.3	2.7
Leaching solution:	ND	2	2.04	102.0	3.7
microwave lunch box 1		10	9.89	98.9	1.7
(PP)		50	51.24	102.5	1.9
Leaching solution:	1.58	2	3.55	98.1	2.2
microwave lunch box 2		10	11.64	103.8	2.4
(PET[d] + PC)		50	51.61	101.9	1.0
Leaching solution:	39.21	2	41.99	102.0	2.8
epoxy resin-based bowl 1		10	50.28	102.7	3.8
		50	90.47	103.2	2.3
Leaching solution:	3.05	2	5.02	99.0	1.9
epoxy resin-based bowl 2		10	13.12	102.3	3.2
		50	52.94	96.4	4.4

[a] Mean of six measurements.

[b] Not detected.

[c] PP: polypropylene.

[d] PET: polyethylene terephthalate.

Table of Contents Entry

Quantitative detection of BPA in water and plastic samples was developed based on fluorescence quenching of eco-friendly chitosan-capped ZnS QDs.