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Analytical Methods

Detection of choline and hydrogen peroxide in infant formula milk powder with near infrared upconverting luminescent nanoparticles

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ABSTRACT

Choline is an essential nutrient for the growth and development of the baby, and therefore it is often added to infant formula. In this paper, a novel sensor for choline determination in infant formula is developed based on upconverting nanoparticles (UCNPs) with near infrared luminescence. UCNPs-based detection can avoid the interference of background fluorescence from complex samples, and thus provide high selectivity and sensitivity. It was observed that in the presence of Fe^{3+}, polyacrylic acid coated UCNPs were quenched to 3% of its original intensity. The degree of quenching was among the best for UCNPs. Hydrogen peroxide could oxidize Fe^{2+} to Fe^{3+}, which caused quenching of the upconversion luminescence. A new H_2O_2 detection method was thus established. In addition, choline could be hydrolyzed to betaine by choline oxidase, and at the same time produced H_2O_2, which also caused luminescence quenching through Fe^{2+} oxidation. Therefore, selective choline sensing was achieved.

1. Introduction

Hydrogen peroxide (H_2O_2) as a common disinfectant has extensive applications in the fields of food industry (Silva, Montes, Richter, & Munoz, 2012). H_2O_2 can kill harmful microorganism in food production and in packaging materials (Hsu, Chang, & Kuo, 2008; Zhang et al., 2011). However, the overuse of H_2O_2 is harmful. The residual of H_2O_2 in food can bring serious harm to the human body, such as accelerating the aging process and causing serious disease such as cancer (Liu et al., 2015). Therefore, the detection of H_2O_2 in food products is of vital significance.

Choline (trimethyl-beta-hydroxyethyl ammonium) is the component of lecithin and the precursor of acetylcholine (Zhao, Xiong, & Curtis, 2011). Choline has irreplaceable functions in human body. It is one of the key components of cell membrane, and can promote fat decomposition, avoid fatty liver, and transmit neural signals. Although the human body has the function of choline synthesis, dietary choline is also needed (Mitchell, 2004; Pati, Palmisano, Quinto, & Zambonin, 2005). For example, the amount of choline in the diet of infants and children can improve baby's ability to remember (Li, Huang, Shi, Li, & Su, 2013). It is very necessary that choline is added into baby food for critical brain development of infants. Proper choline content is required for the evaluation of infant formula milk powder (Hefni, McEntyre, Lever, & Slow, 2015). Thus quantitative measurement of choline in baby food is of great significance.

Various techniques have been utilized for the detection of choline including high performance liquid chromatography (HPLC) (Hefni et al., 2015), electrochemical (Thiagarajan, Madhurantakam, Sethuraman, Rayappan, & Krishnan, 2016), colorimetric (Khan, Khan, Wells, Maslin, & Connock, 1992), chemiluminescent (Pavel et al., 1997) and fluorescent detection (Chen et al., 2011; Wei et al., 2014). For example, Vignesh Thiagarajan and co-workers fabricated a nano-interfaced electrochemical biosensor for the rapid detection of choline (Thiagarajan et al., 2016). Sandra Pati and co-workers (Pati et al., 2005) developed an amperometric biosensor based on choline oxidase immobilized onto an electropolymerized polypyrrole film for flow injection detection of choline in dairy products. Zhenzhen Chen and co-workers constructed a choline detection method based on fluorescence quenching of QDs by H_2O_2, which was produced from the enzymatic reaction of choline (Chen et al., 2011). Jianfei Wei and co-workers fabricated a sensitive fluorescent biosensor for choline sensing based on the detection of choline and H_2O_2 using C-dots as probes (Wei et al.,

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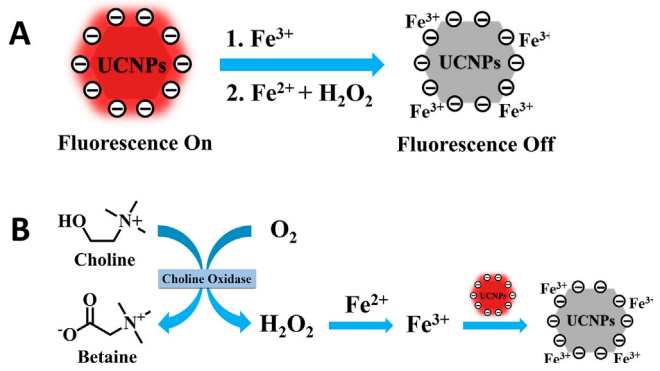

Fig. 1. Schematic illustration of the sensing strategy.

2014). Among the techniques, fluorescent method has several advantages comparing to the other methods, such as rapidity, specificity, sensitivity and real-time monitoring. However, background fluorescence interference from complex real samples and photo bleaching of traditional fluorescent materials limit the practical applications of these fluorescence-based sensing methods.

Lanthanide-doped upconverting nanoparticles (UCNPs) have the unique optical property that they can emit visible light upon excitation by NIR light rather than UV light (Cheng, Wang, & Liu, 2013; Feng, Han, & Li., 2013; Sun, Wang, & Yan, 2014; Wang & Liu, 2009; You et al., 2017). Compared to traditional fluorescence materials, UCNPs have the unique advantages of minimized background fluorescence, improved signal-to-noise ratio, and sensitive detection in real complex samples (Lin et al., 2012). These remarkable advantages make UCNPs applicable for wide variety of applications in the field of biology and medicine. However, UCNPs are rarely used in food analysis.

Here we reported a simple and selective strategy for H_2O_2 and choline detection based on the near infrared luminescent UCNPs (Fig. 1). It was observed that, in the presence of Fe^{3+}, the upconversion luminescence of polyacrylic acid (PAA) coated UCNPs was effectively quenched to 3% of its original intensity. The quenching effect was among the best for UCNPs (Wang, Shen, Li, Wang, & Liu, 2012; Wu et al., 2012; Yuan, Wu, Shu, & Liu, 2014; Zhang et al., 2015). Hydrogen peroxide (H_2O_2) can oxidize Fe^{2+} to Fe^{3+}, which caused quenching of upconversion luminescence. A facile H_2O_2 detection method was thus established. Based on the H_2O_2 detection strategy, an upconversion luminescence sensor for the detection of choline was constructed. Through the catalysis of choline oxidase, choline was oxidized to betaine and H_2O_2 was generated, followed by oxidization of Fe^{2+} to Fe^{3+}, and luminescence quenching of UCNPs. The method is simple, selective and sensitive, and can be used for the analysis of choline and H_2O_2 in the infant formula milk powder.

2. Experimental section

2.1. Materials

Choline oxidase was purchased from Sigma-Aldrich (St Louis, MO). Horseradish peroxidase (HRP) was purchased from Sangon biotech. Choline chloride was obtained from Aladdin Co. (Shanghai, China). $FeCl_3{\cdot}6H_2O$, $FeCl_2{\cdot}4H_2O$ and rare earth oxides (Y_2O_3, Yb_2O_3 and Tm_2O_3) were obtained from Shanghai Chemical Industrial Co. (Shanghai, China). The rare earth trifluoroacetates were prepared by dissolving the rare earth oxides in trifluoroacetic acid. All chemicals were of analytical grade and used as received. All aqueous solutions were prepared with water of Milli-Q ultrapure grade.

2.2. Instrumentation

Transmission electron microscopy (TEM) measurements were made using a JEOL 1011 transmission electron microscope operated at 200 kV (Philips, The Netherlands). Fluorescence spectra were recorded with a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc., USA). The 980 nm diode laser was obtained from Hi-Tech Photoelectronics Co. (Beijing, China). The photoluminescence measurements were made in quartz cuvettes in the wavelength of 400–900 nm. The emission slit width was 8 nm.

2.3. Synthesis of the UCNPs

The UCNPs synthesis was carried out following a literature protocol with slight modifications (Cheng et al., 2011). 1 mmol of Re $(CF_3COO)_3$ (Y:Yb:Tm = 78%:20%:2%) and 2 mmol of CF_3COONa were added to a solvent mixture of 10 mL oleic acid and 10 mL 1-octadecene. The solution was degassed under vacuum at 100 °C for 1 h, rapidly heated to 320 °C under a nitrogen environment, and kept at this temperature for 1 h with constant stirring. The product was precipitated by the addition of ethanol after cooling down to room temperature, separated by centrifugation and washed with ethanol and water repeatedly.

Coating of polyacrylic acid (PAA) on the UCNPs was carried out following a literature protocol (Cheng et al., 2011). PAA was used to functionalize UCNPs via chelation between the carboxyl functional group of PAA and the surface Ln^{3+} of UCNPs. In a typical procedure, 300 mg of PAA and 30 mL of diethylene glycol were mixed and heated to 110 °C to form a clear solution. Under nitrogen protection, 100 mg of UCNPs in 5 mL toluene solution was added slowly. The mixture was heated to 240 °C for 1.5 h. The product was precipitated by the addition of ethanol after cooling down to room temperature, separated by centrifugation and washed with ethanol and water for several times.

2.4. H_2O_2 detection

Different concentrations of H_2O_2 were added to Fe^{2+} solution in Tris-HCl buffer (pH 7.0). After 10 min, UCNPs was added to the obtained mixture and the fluorescence spectra were recorded immediately. The final concentrations of the UCNPs, Fe^{2+}, and Tris-HCl buffer were 0.04 mg/mL, 0.5 mM and 20 mM, respectively.

2.5. Choline detection

Different concentrations of choline were added into choline oxidase solution in 25 mM Tris-HCl (pH 8.0) and maintained at 37 °C for 1 h. Then Fe^{2+} and UCNPs solution was added to the obtained mixture and the fluorescence spectra was recorded immediately. The final concentrations of the UCNPs, Fe^{2+}, and choline oxidase were 0.04 mg/mL, 0.5 mM and 0.05 U, respectively.

2.6. Choline detection in infant formula milk powder

The infant formula milk powder samples were pretreated using AOAC official method (Sanz-Vicentea, Lapieza, Cebolla, & Galba'n, 2015). Briefly, 5 g infant formula milk powder samples was added into 30 mL of 3 M HCl in a round bottom flask. The mixture was heated to 70 °C and maintained for 3 h. After cooling to room temperature, 50% NaOH solution was added to adjust the pH of the solution to 3.5–4.0. Then the solution was filtered through a 0.45 μm cellulose acetate membrane. The detection procedure for choline in infant formula milk powder was the same as those described in choline detection in buffer, except using the pretreated samples instead of choline standards.

3. Results and discussion

3.1. Fluorescence quenching of the UCNPs with Fe^{3+}

PAA protected Tm^{3+}-doped $NaYF_4$ UCNPs were synthesized following the previous protocol with slight modifications (Cheng et al.,