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Intrinsically fluorescent polymer nanoparticles for sensing Cu^{2+} in aqueous media and constructing an IMPLICATION logic gate

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ABSTRACT

We have demonstrated a fluorescence approach for rapid, environment-friendly, and selective detection of Cu^{2+} in aqueous media using a kind of easily prepared and autofluorescent polymer nanoparticles (PNPs) as a sensor. The PNPs were synthesized by crosslinking hyperbranched polyethyleneimine (hPEI) with formaldehyde in water solution, and they emitted strong intrinsic fluorescence without the conjugation to any external fluorescent agent. The Cu^{2+} assay was on the basis of the principle that Cu^{2+} can be adsorbed on the surface of the PNPs, resulting in the fast and remarkable fluorescence quenching through electron transfer. The developed sensor was applied to the analysis of copper ions in environmental water samples with satisfactory results. Furthermore, the fluorescence of the PNPs-Cu^{2+} system can restore upon addition of cysteine (Cys) because of its ability to remove Cu^{2+} from the surface of PNPs. Based on the fluorescence "on-off-on" conversion, a reversible IMPLICATION logic gate was designed by using Cu^{2+} and Cys as the two inputs, and fluorescence intensity of the PNPs as the output signal.

1. Introduction

Fluorescent sensors possess such advantages as high sensitivity, easy operation, and capacity for rapid, real-time detection, resulting in an enormous demand in many areas such as clinical analysis, environmental monitoring, waste management, industrial and food processing, and biomedical technology [1,2]. Therefore, the development of fluorescent sensors is a field of immense interest. In particular, the study for sensing biologically important ions and molecules has captured great attention [3–6]. Copper, an essential element for organisms, plays a key role in human health [7,8]. It is necessary for bone formation, cellular respiration and connective tissue development. However, the exposure to high level of copper ions (Cu^{2+}) may cause disturbance of the cellular homeostasis and even damage of liver or kidney [9]. Some serious neurodegenerative diseases, such as Menkes disease, Alzheimer's disease, and Wilson disease, might also have a close relation with copper presented in excess [10]. Consequently, the maximum allowable level of copper in drinking water permitted by the United States Environmental Protection Agency (EPA) is 1.3 ppm (~20 μM) [11].

In view of the importance of copper for human health, the qualitative and quantitative detection of Cu^{2+} is very significant in environments, pharmaceutical industry, as well as biological fields. To date, considerable efforts have been devoted to developing optical sensing platforms for the detection of Cu^{2+}. For example, colorimetric sensors were created based on gold nanoparticles [12,13], dye-functionalized magnetic nanoparticles [14,15], et al., and also fluorescent sensors were developed based on various fluorescent species such as organic fluorophores [16,17], fluorescent carbon dots (CDs) [18,19], semiconductor quantum dots (QDs) [20,21], noble metal nanoclusters (NCs) [22,23], and other fluorescent materials [24–27]. Unfortunately, most of these optical sensors have some inherent drawbacks such as relatively complicated and costly synthesis, or even harmful systems, which hamper their practical applications. Therefore, the development of easily accessible and environment-friendly fluorescent sensors for Cu^{2+} detection is still in pursuit.

Recently, fluorescent polymer nanoparticles (PNPs) have attracted increasing interest in chemical and biological applications [28,29], because they are endowed with some intrinsic advantages including low toxicity, good biocompatibility, and flexibility of synthesis. Most reported fluorescent PNPs have been created by entrapment or covalent conjugation of fluorescent agents in polymeric matrixes [30,31]. But these preparation methods generally trend to be rather tedious and time-consuming. In addition, if the

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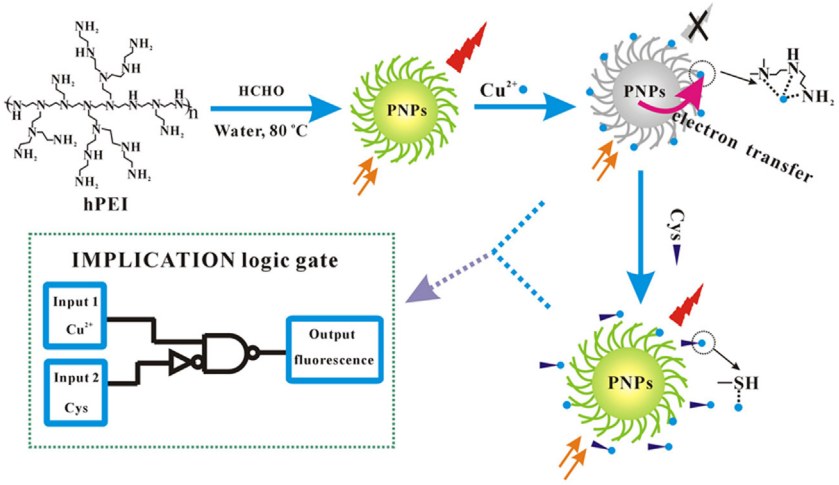

Scheme 1. Schematic illustration of the preparation of PNPs, Cu^{2+} detection and IMPLICATION logic gate operation based on the PNPs.

PNPs are prepared just by physical entrapment, there is a risk that fluorescent agent may leak out of the nanoparticles in practical applications. Thus, ideal fluorescent PNPs should be intrinsically fluorescent without the need of embedding an external fluorochrome. In this respect, conjugated polymer nanoparticles (CPNs) are autofluorescent because they contain large π-conjugated backbones and delocalized electronic structure [32]. Furthermore, when conjugated polymers serve as fluorescent sensors, the excitation energy along the whole backbone of the polymers can transfer to a lower energy electron or energy acceptor quickly, leading to the amplification of fluorescence response signal and the high sensitivity [33,34]. However, the preparation of conjugated polymer nanoparticles requires sophisticated multistep synthetic pathways in organic solvents, which is a significant disadvantage to their applications. In our latest researches [35,36], we reported the synthesis of a kind of non-conjugated PNPs with intrinsic fluorescence emission which was prepared from hyperbranched polyethyleneimine (hPEI) and aldehydes, and also the intrinsic fluorescence mechanism was investigated in detail.

In this work, we used the new kind of fluorescent PNPs constructed by crosslinking of commercial hPEI with formaldehyde to develop a fluorescent sensor for detecting Cu^{2+}. On the one hand, similar to conjugated polymer nanoparticles, the PNPs in this work can emit strong intrinsic fluorescence without the conjugation to any external fluorescent agent, and the developed sensor shows high sensitivity to Cu^{2+}. On the other hand, the preparation of the PNPs is very facile and environment-friendly (one-pot reaction in water solution), which is an obvious merit compared to those of conjugated polymer nanoparticles or most other fluorescent materials. The fluorescence of the PNPs can be selectively quenched by Cu^{2+} in the pH 4.0 HAc-NaAc buffer, and it is hardly influenced by other metal ions. This is because Cu^{2+} can interact with the functional groups on the PNPs surface, leading to an electron transfer from the PNPs to Cu^{2+}. The Cu^{2+}-induced fluorescence quenching makes it possible to probe Cu^{2+} in aqueous media. Molecular logic gates have received much attention over the past decades because they own high potential in the field of molecular-scale computers and electronics [37,38]. Interestingly, we found that the fluorescence of the PNPs-Cu^{2+} system could be recovered upon addition of cysteine (Cys), which was attributed to the strong binding affinity of Cys to Cu^{2+}. Based on the fluorescence "on-off-on" conversion, a reversible IMPLICATION logic gate was successfully designed. The schematic illustration of Cu^{2+} sensing and logic gate operation is shown in Scheme 1.

2. Materials and methods

2.1. Materials

Hyperbranched polyethyleneimine (hPEI, M_w = 10 000, 99%) and formaldehyde (35 wt%) were obtained from Aladdin Ltd., Shanghai, China. Sodium hydroxide, NaCl, KCl, $LiNO_3$, $AgNO_3$, $MgCl_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Mn(Ac)_2$, $Zn(NO_3)_2{\cdot}6H_2O$, $BaCl_2{\cdot}2H_2O$, $CdCl_2$, $Cr(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Hg(NO_3)_2{\cdot}H_2O$, $NiSO_4{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Pb(NO_3)_2$, and $CaCl_2{\cdot}2H_2O$ were supplied by Chengdu Kelong Chemical Reagent Plant (Sichuan, China). Cysteine (Cys), and other 19 amino acids including arginine (Arg), alanine (Ala), aspartic acid (Asp), asparagines (Asn), glutamine (Gln), glutamic acid (Glu), glycine (Gly), histidine (His), isoleucine (Ile), leucine (Leu), lysine (Lys), methionine (Met), proline (Pro), phenylalanine (Phe), serine (Ser), tyrosine (Tyr), threonine (Thr), tryptophane (Trp), and valine (Val) were purchased from Sigma-Aldrich (USA). Other reagents were of analytical reagent grade and used as received. Ultrapure water with a resistivity of 18.2 MΩ cm was used throughout the experiment. Buffer solutions were prepared in accordance with standard protocols, and the pH values were measured with a PHS-3C pH meter (Leici, China). The concentrations of Britton-Robinson (BR) buffer and HAc-NaAc buffer solutions are 0.04 M and 0.1 M, respectively.

2.2. Instruments

UV-vis absorption spectra were collected by using a UV–vis 2450 spectrophotometer (Shimadzu, Japan). The fluorescent emission spectra were recorded with an F-2700 spectrofluorometer (Hitachi, Japan) equipped with a 150-W xenon lamp. A 1 cm path quartz cell was used for the measurement of both UV–vis absorption and fluorescence spectra. Transmission electron microscopy (TEM) measurements were performed with a JEM 1200EX transmission electron microscope at an accelerating voltage of 120 kV (JEOL, Japan). Scanning electron microscopy (SEM) characterization was carried out on a JSM-6510 LV scanning electron microscope (JEOL, Japan). For SEM measurement, the sample was pasted on the holder with a conductive adhesive tape and then sputtered with a layer of platinum. The Fourier transform infrared (FT-IR) spectra were tested using a Bruker IFS 113 v spectrometer (Bruker, Germany). For the preparation of FT-IR samples, the PNPs solution was lyophilized to collect dry product, and then the fine powder