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Upconversion fluorescence metal-organic frameworks thermo-sensitive imprinted polymer for enrichment and sensing protein

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ABSTRACT

A novel fluorescence material with thermo-sensitive for the enrichment and sensing of protein was successfully prepared by combining molecular imprinting technology with upconversion nanoparticles (UCNPs) and metal-organic frameworks (MOFs). Herein, the UCNPs acted as signal reporter for composite materials because of its excellent fluorescence property and chemical stability. MOFs were introduced to molecularly imprinted polymer (MIP) due to its high specific surface area which increases the rate of mass transfer relative to that of traditional bulk MIP. The thermo-sensitive imprinted material which allows for swelling and shrinking with response to temperature changes was prepared by choosing Bovine hemoglobin (BHB) as the template, N-isopropyl acrylamide (NIPAAM) as the temperature-sensitive functional monomer and N,N-methylenebisacrylamide (MBA) as the cross-linker. The recognition characterizations of imprinted material-coated UCNPs/MOFs (UCNPs/MOFs/MIP) were evaluated, and the results showed that the fluorescence intensity of UCNPs/MOFs/MIP reduced gradually with the increase of BHB concentration. The fluorescence material was response to the temperature. The adsorption capacity was as much as 167.6 mg/g at 28 °C and 101.2 mg/g at 44 °C, which was higher than that of traditional MIP. Therefore, this new fluorescence material for enrichment and sensing protein is very promising for future applications.

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1. Introduction

Metal-organic frameworks (MOFs) are relatively new class of highly porous crystalline materials and are prepared by metal connected by various organic ligands such as carboxylates or phosphonates (Yaghi et al., 1995; Li et al., 1999; Eddaoudi et al., 2002; Furukawa et al., 2013; Deng et al., 2012). MOFs have attracted significant interest in adsorption and separation (Bloch et al., 2010), gas storage (Chen et al., 2005), drug delivery (Imaz et al., 2010) due to high specific surface area, high porosity and tenability of MOFs. Very recently, a variety of MOF composite materials has attracted dramatic increasing interest owing to potential in biomaterial and optics of these composite materials. A few pioneering synthetic studies on the MOF composite materials including MOF@SiO_2 (Rieter et al., 2008), MOF/GO (Petit et al., 2010, 2011a, 2011b), Fe_3O_4/MOF (Ke et al., 2012) have been reported. The MOF composite materials are widely used for adsorption and detection hazardous pollutants. A facile magnetization of MOF for enrichment polycyclic aromatic hydrocarbons was also prepared (Huo and Yan, 2012). Recently, dithizone functionalized magnetic MOF was prepared and used for the determination of trace levels of lead (Wang et al., 2013). Li et al. (2014a) successfully synthesized a magnetic sphere hybrid Fe_3O_4/$Cu_3(BTC)_2$/GO through a hydrothermal method for detecting methylene blue from water solution. However, these materials in application area were restricted due to lack of specificity.

Recently, Upconversion nanoparticles (UCNPs) have led to intense studies due to outstanding advantages in bioimaging, biological probe and optical amplifier (Cheng et al., 2013, 2011; Yang et al., 2012; Wang et al., 2009). UCNPs, compared with traditional fluorescent materials such as fluorescence dyes and semiconductor QDs, are low toxic, lack of auto-fluorescence, long lifetimes and low photobleaching. Furthermore, UCNPs are capable of converting NIR light to UV–visible light by multiple photon absorptions or energy transfers (Lu et al., 2014; Liu et al., 2011). The multifunctional nanoparticles based on UCNPs with combined magnetic and optical characterize were used for multimodal imaging and therapy (Cheng et al., 2011).

Molecular imprinting has been considered as a convenient

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technology that can create the materials with recognition sites which are spatially and chemically complementary to the template in materials (Ellen et al., 2011; Chen et al., 2011; Lofgreen et al., 2011). Compared with biological receptors, molecular imprinted polymer (MIP) possesses excellent mechanical and chemical stability and ease of preparation. However, traditional MIP bulks require crushed and sieved, leading to many limitations including irregularity in the shape of particles, low adsorption capacity and selectivity (Turner et al., 2006). The surface imprinting technology can overcome the above problem effectively. A novel surface-imprinted magnetic composite microsphere was successfully prepared for bovine serum albumin (BSA) recognition (Li et al., 2014b). Chen et al. (2014) prepared the molecularly imprinted nanoparticles by choosing the vinyl-modified silica nanoparticles as support material. Furthermore, quantum dots (QDs) also could be used as support material for surface imprinting (Tan et al., 2014; Yang et al., 2014; Li et al., 2015). Compared with traditional support materials, the advantages of MOFs include high specific surface area and porous structure, which increase the rate of mass transfer and adsorption capacity.

Based on the above considerations, we propose a novel strategy combined the high selectivity of molecular imprinting technology with the excellent fluorescence of UCNPs and the high specific surface area of MOFs to prepare a new type of composite materials for the enrichment and sensing of protein. Herein, $Cu_3(BTC)_2$ (known as HKUST-1) was chosen as the representative MOF. The HKUST-1 is water-stable and contains Cu^{2+} as the metal center linked to oxygen atoms from benzene tricarboxylate (H_3BTC). The UCNPs were synthesized by solvothermal reaction and modified with polyacrylic acid (PAA) through ligand exchange. The UCNPs/HKUST-1 were prepared by the reaction of copper nitrate ($Cu(NO_3)_2$) with H_3BTC after dispersing the PAA-modified UCNPs in ethanol through a solvothermal method. The thermo-sensitive imprinted layer was prepared by choosing Bovine hemoglobin (BHB) as the template, N-isopropyl acrylamide (NIPAAM) as the thermo-sensitive functional monomer which allowed for swelling and shrinking with response to temperature changes, and N,N-methylenebisacrylamide (MBA) as the cross-linker. The morphology and adsorption characterizations of the UCNPs/HKUST-1/MIP were investigated. Furthermore, the thermo-sensitive characterization of the composite material was discussed.

2. Materials and methods

2.1. Materials and chemicals

Bovine serum albumin (BSA, molecular weight (MW) 67 kDa, isoelectric point (pI) 4.9), Bovine hemoglobin (BHB, MW 66 kDa, pI 6.7) and Cytochrome c (Cyt c MW 12.4 kDa, pI 10.2) were obtained from Sangon Biotech Co. Ltd. (Shanghai, China). $Y(CH_3COO)_3 \cdot 4H_2O$ (99.9%), $Yb(CH_3COO)_3 \cdot 4H_2O$ (99.9%), $Er(CH_3COO)_3 \cdot xH_2O$ (99.9%), PAA ($M = 1800$), $Cu(NO_3)_2 \cdot 3H_2O$, and diethylene glycol (DEG) were purchased from Sigma Aldrich (St Louis, USA). Oleic acid (OA, 90%), 1-octadecene (ODE, 90%), H_3BTC and NIPAAM were purchased from Alfa Aesar Co. Ltd. (Massachusetts, USA). MBA, ammonium perulfate (APS), N,N,N,N-tetramethylenebis (TEMED) were provided by Aladdin (Los Angeles, USA). All reagents were of the highest available purity and of analytical grade at least. Double distilled water (DDW, 18.2 $M\Omega\,cm^{-1}$) was prepared by a Water Pro water purification system (Labconco, Kansas City, USA).

2.2. Characterizations

Ultraviolet absorbance at a wavelength of 400 nm was recorded on a Cary 50-Bio Ultraviolet–visible (UV–vis) spectrometer (Victoria, Australia) in a quartz cuvette with 1 cm path length. Fluorescence measurements were performed on an F-2500 fluorescence spectrometer (Hitachi, Japan) connected with an external 980 nm diode laser (1 W, continuous wave with 1 m fiber, Beijing Viasho Technology Co.) as the excitation source. Scanning electron microscopy (SEM) images were obtained with a SU1510 microscope (Hitachi, Japan). X-ray powder diffraction (XRD) patterns were recorded on a D8 X-ray power diffractometer at a scanning rate of 1°/min in the 2θ range from 10° to 40° (Bruker, Germany). Energy-dispersive X-ray photoelectron spectroscopic (XPS) measurements were performed on PHI-5000 Versaprobe (PHI, Japan). Thermogravimetric analysis (TGA) was performed (Meteler, Switzerland) in the temperature range from room temperature to 1000 °C with a heating rate of 10 °C/min under nitrogen atmosphere. Nitrogen adsorption–desorption analysis was performed on an autosorb-1-mp (Quantachrome, USA) with a bath temperature of 77 K. Surface areas were determined using Brunauer–Emmett–Teller (BET) theory.

2.3. Preparation of UCNPs

UCNPs were synthesized according to the previous literature (Li and Zhang, 2008). To a 100 mL flask, $Y(CH_3COO)_3$ (0.78 mmol), $Yb(CH_3COO)_3$ (0.2 mmol) and $Er(CH_3COO)_3$ (0.02 mmol) were mixed with 6 mL OA and 17 mL ODE and heated to 160 °C, to form a transparent solution. The mixture solution cooled down to room temperature naturally. 10 mL methanol solution containing NaOH (2.5 mmol) and NH_4F (4 mmol) was slowly dropped into the flask and stirred for 30 min. Subsequently, the solution was slowly heated for removal of methanol, degassed at 100 °C for 10 min, and then heated to 300 °C and maintained for 1 h at argon atmosphere. After the resulted solution was cooled down naturally, UCNPs were precipitated via centrifugation, and washed with ethanol for three times.

PAA–UCNPs were synthesized according to the previous method with a modified procedure (Naccache, et al., 2009). PAA (300 mg) and 30 mL DEG were added into a 100 mL flask. The mixture was heated to 110 °C to form a transparent solution. 3 mL toluene solution containing 100 mg hydrophobic UCNPs was added, and kept at 110 °C for 1 h under argon protection. Then the mixed solution was heated to 240 °C and maintained for 1 h. The resulted solution was cooled down to room temperature naturally, and the PAA–UCNPs were obtained from the resulted solution with excess dilute hydrochloric aqueous solution, and washed three times with water.

2.4. Synthesis of the UCNPs/HKUST-1

UCNPs/HKUST-1 was synthesized according to the previous method with a modified procedure (Wang et al., 2013). To 250 mL round-bottomed flask, 0.5 g of H_3BTC was mixed with 40 mL DMF and 40 mL ethanol. 20 mL ethanol solution containing 100 mg PAA-modified UCNPs was added under vigorous stirring. The mixture was refluxed for 30 min at 75 °C, followed by the addition of 1.0 g $Cu(NO_3)_2 \cdot 3H_2O$ which was dissolved in 40 mL water. After refluxing for 4 h, the UCNPs/HKUST-1 was collected via centrifugation and washed with water and ethanol, then dried at 120 °C for 10 h.

2.5. Synthesis of the UCNPs/HKUST-1/MIP

10 mg of template protein, 50 mg of UCNPs/HKUST-1, and 10 mL of water were added in a 25 mL flask and stirred for 30 min. Then 100 mg of NIPAAM and 40 mg of MBA were added to the mixture and stirred for 1 h at room temperature. The oxygen was removed by nitrogen bubbling for 10 min. Subsequently, 10 mg of

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