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Molecularly imprinted polymer based on MWCNT-QDs as fluorescent biomimetic sensor for specific recognition of target protein

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ABSTRACT

A novel molecularly imprinted optosensing material based on multi-walled carbon nanotube-quantum dots (MWCNT-QDs) has been designed and synthesized for its high selectivity, sensitivity and specificity in the recognition of a target protein bovine serum albumin (BSA). Molecularly imprinted polymer coated MWCNT-QDs using BSA as the template (BMIP-coated MWCNT-QDs) exhibits a fast mass-transfer speed with a response time of 25 min. It is found that the BSA as a target protein can significantly quench the luminescence of BMIP-coated MWCNT-QDs in a concentration-dependent manner that is best described by a Stern–Volmer equation. The K_{SV} for BSA is much higher than bovine hemoglobin and lysozyme, implying a highly selective recognition of the BMIP-coated MWCNT-QDs to BSA. Under optimal conditions, the relative fluorescence intensity of BMIP-coated MWCNT-QDs decreases linearly with the increasing target protein BSA in the concentration range of 5.0×10^{-7}–35.0×10^{-7} M with a detection limit of 80 nM.

1. Introduction

With the rapid development of proteomics research, better understanding of the structure and function of living organisms at a molecular level through studying the function of newly discovered proteins in cells is highly significant [1,2]. Traditionally, it is very difficult to detect low abundance proteins that often have significant biological functions. The classical method of immunoassay employs antibodies which usually have several fundamental limitations including chemical and physical instability, complex preparation methods, and high manufacturing cost [3]. In this respect, alternative artificial biomimetic receptors, such as molecularly imprinted polymers (MIP), exhibit unique potential to apply in the field of protein recognition [4–6]. MIP, generally prepared by molecularly imprinted technique (MIT), is a synthetic material with an artificially generated three-dimensional network that can rebind to a specific target molecule [7–10]. Protein-imprinted materials have specific recognition sites formed through interaction with template proteins, which direct the positioning and orientation of the structural components of the materials [5,6]. While the imprinting of small molecules is straightforward, the preparation of MIP against biomacromolecules, such as proteins, still remains challenging due to the features of the protein such as large molecular size, flexible structure and many functional groups [2,11,12]. Therefore, it is vital to develop highly selective and efficient analytical approach for identifying and quantifying proteins through MIT. Protein-imprinting can be divided in several categories including bulk [13], particle [14,15], epitope partial [16], and surface imprinting [17–19]. Among the above approaches, surface imprinting offers unique potentials, which is achieved by attaching the protein template to the surface of a substrate (flat or spherical) with subsequent polymerization around it. This technique successfully places binding cavities on or near the substrate surfaces, solving the problems of restricted mass transfer and facilitating removal of the template, but the density of surface binding sites is still limited due to the small surface area to volume ratio of these conventional MIP [17,18].

Nanomaterials, which possess unique characteristics of large surface-to-volume ratio and size-related physical and chemical properties, are now among the most researched alternatives to overcome the drawbacks associated with conventional MIP. Recently, molecular imprinting of nanomaterial surfaces has been extended to imprinting of proteins. These nanostructured MIPs enable complete removal of templates, better site accessibility, reduction of effect of mass transfer resistance, and have a well-defined shape [20,21].

Quantum dots (QDs), also known as semiconductor nanocrystals, have found preliminary applications in optical and electronic devices [22,23], chemical sensors [24], light emitting diodes [25,26], photovoltaic devices [27,28] and biological imaging and sensing [29–35] due to the unique chemical, physical and optical properties. The combination of QDs with highly selective MIP has recently attracted considerable attention as the composite materials exhibiting both highly specific recognition from MIP and sensitive signal amplification and optical readout characteristic from QDs [36,37]. Although these materials have distinctive advantages, there are still some drawbacks such as long response time and poor fluorescence signal stability.

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In this study we aim to design and synthesize a novel molecularly imprinted optosensing material based on multi-walled carbon nanotube-QDs (MWCNT-QDs) attempting to overcome the above disadvantages. While the composites of MWCNT-QDs have exhibited enhanced photocatalysis and photocurrent in electrochemical sensing, very little attention has been paid to optosensing determination of analytes, especially for protein. MWCNTs have been extensively exploited for biomedical applications due to their unique intrinsic physical and chemical properties. Moreover, MWCNTs have been considered as an ideal matrix for the synthesis of MWCNT-based nanohybrids for biomedical

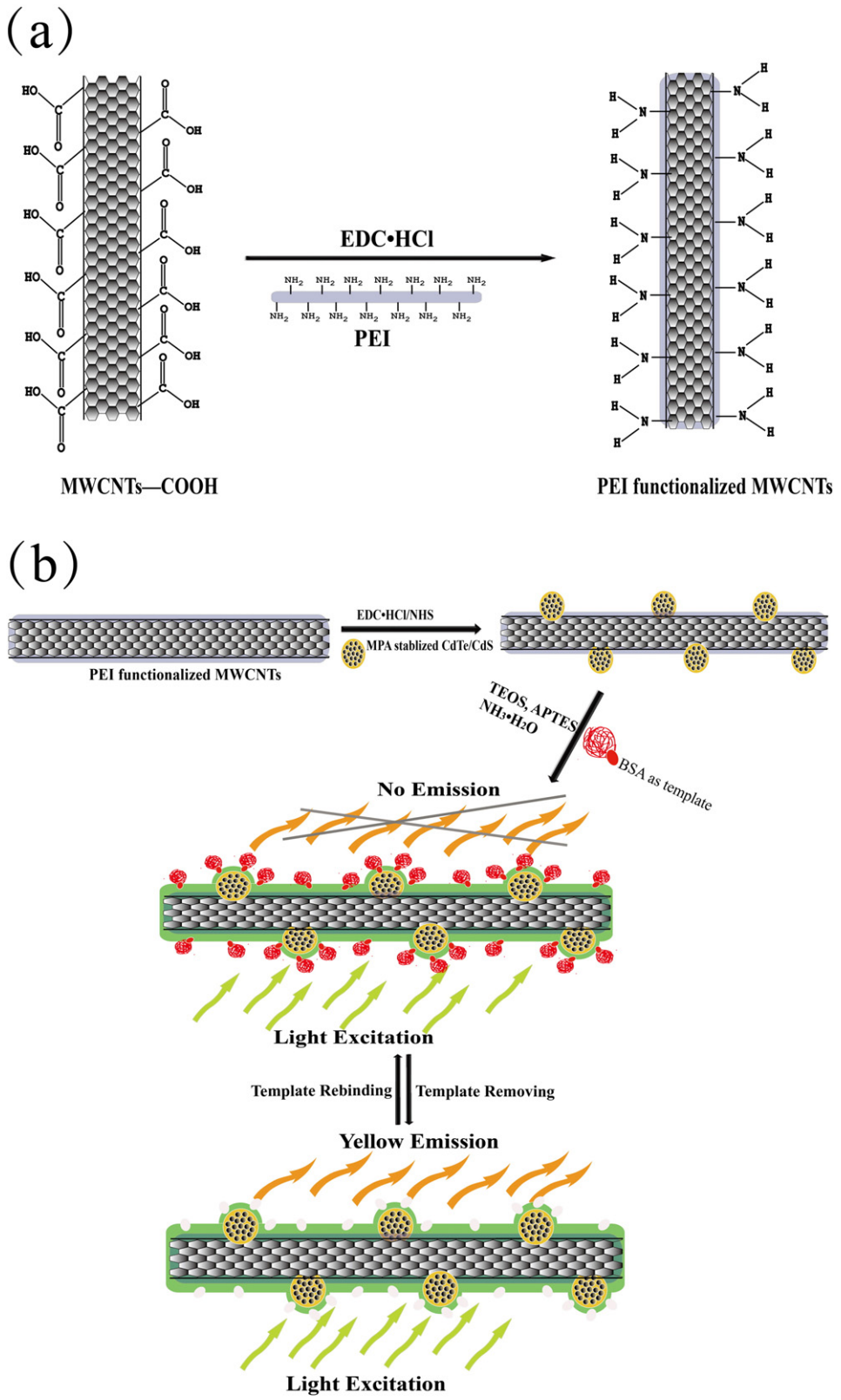

Fig. 1. Schematic illustration for the preparation of biomimetic sensor BMIP-coated MWCNT-QDs.