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Colorimetric sensor for cysteine in human urine based on novel gold nanoparticles

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ABSTRACT

Herein, a novel, high sensitive, and specific colorimetric sensor for cysteine (Cys) based on pectinase protected gold nanoparticles (P@AuNPs) has been demonstrated for the first time. The P@AuNPs were synthesized by "MW-assisted heat method" and were characterized by UV–vis, TEM, FT-IR and zeta potential techniques. Cys could cause the aggregation of P@AuNPs due to formation of the strong covalent Au-S bond and electrostatic binding. As the Cys concentration increased, the color of the solutions gradually changed from wine-red to blue as well as the large absorption band shifted from 523 to 650 nm upon P@AuNPs aggregation. In addition, various experimental parameters such as pH, the amount of P@AuNPs and incubation time were investigated for the optimum sensing conditions. The concentration of Cys could be determined by monitoring with the naked eye or a UV–vis spectrometer. The proposed colorimetric sensor showed an extreme selectivity toward the determination of Cys in the presence of 20-fold all other different interferents. Under optimum conditions, this method exhibited two good linear ranges from 4.85×10^{-9} to 3.02×10^{-4} M ($R^2 = 0.996$) and 3.25×10^{-3} to 1.03×10^{-2} M ($R^2 = 0.999$), with a low detection limit of 4.6×10^{-9} M. Moreover, this colorimetric sensor was successfully applied to the detection of Cys in human urine samples, demonstrating its great value for practical application in biological systems.

1. Introduction

As an important amino acid containing thiol group, cysteine (Cys) plays a crucial role in biological systems and involves many biochemical pathways [1], such as protein synthesis, detoxification, and metabolism [2]. The altered level of Cys might lead to several clinical situations. Cys deficiency can result in lethargy, edema, muscle and fat loss, slowed growth, liver damage and skin lesion [3], while excessive levels of Cys will cause Alzheimer's disease, Parkinson's disease and autoimmune deficiency syndrome [4,5]. Meanwhile, Cys is also a potential neurotoxin [6,7], a biomarker for various medical conditions [8], and a disease-associated physiological regulator [9]. Thus, due to its biological importance, detection of Cys become more and more significant for human health.

Up to now, several methods have been established for the detection of Cys including high performance liquid chromatography (HPLC) [10], gas chromatography [11], capillary electrophoresis [12], electrochemical [13], flow injection analysis [14], and fluorescence methods [15]. Although these methods could be used to detect Cys with good selectivity and sensitivity, unfortunately, some inherent issues of these techniques still could not be avoided, such as expensive instrumentation, complex operations, costly polymerase and tedious sample pretreatments, which limit the scope of their practical applications. Therefore, it is essential to develop a simple, comparatively fast and cost-effective sensor for Cys to overcome most of such difficulties.

Recently, metallic nanoparticles have received significant interest as colorimetric sensors for selective and sensitive reorganization of wide variety analytes in environmental and biological samples [16–18]. The major advantages of metallic nanoparticles-based colorimetric assays were their excellent selectivity, easy operation with the naked eye, and low cost without the requirement of expensive and sophisticated instruments [19,20]. Among the various types of metallic nanoparticles, AuNPs have been extensively used as colorimetric probes for various analytes detection in complex samples, since AuNPs possess excellent optical properties including high molar extinction coefficient, high stability, and distance-depend on plasmonic absorption [21,22].

In particular, the optical properties of AuNPs are strongly dependent on the interparticle separation distances. When the

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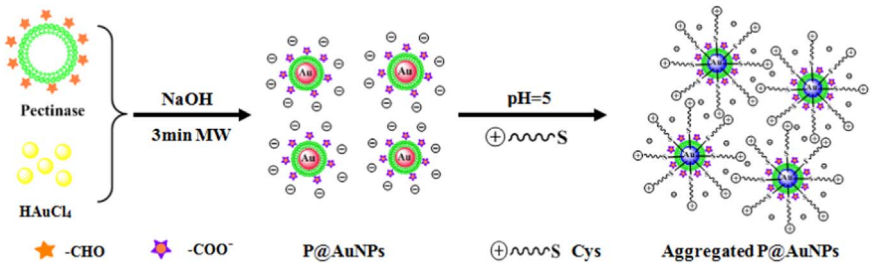

Scheme 1. Schematic representation of the synthesis of P@AuNPs and the colorimetric assay of Cys based on the proposed method.

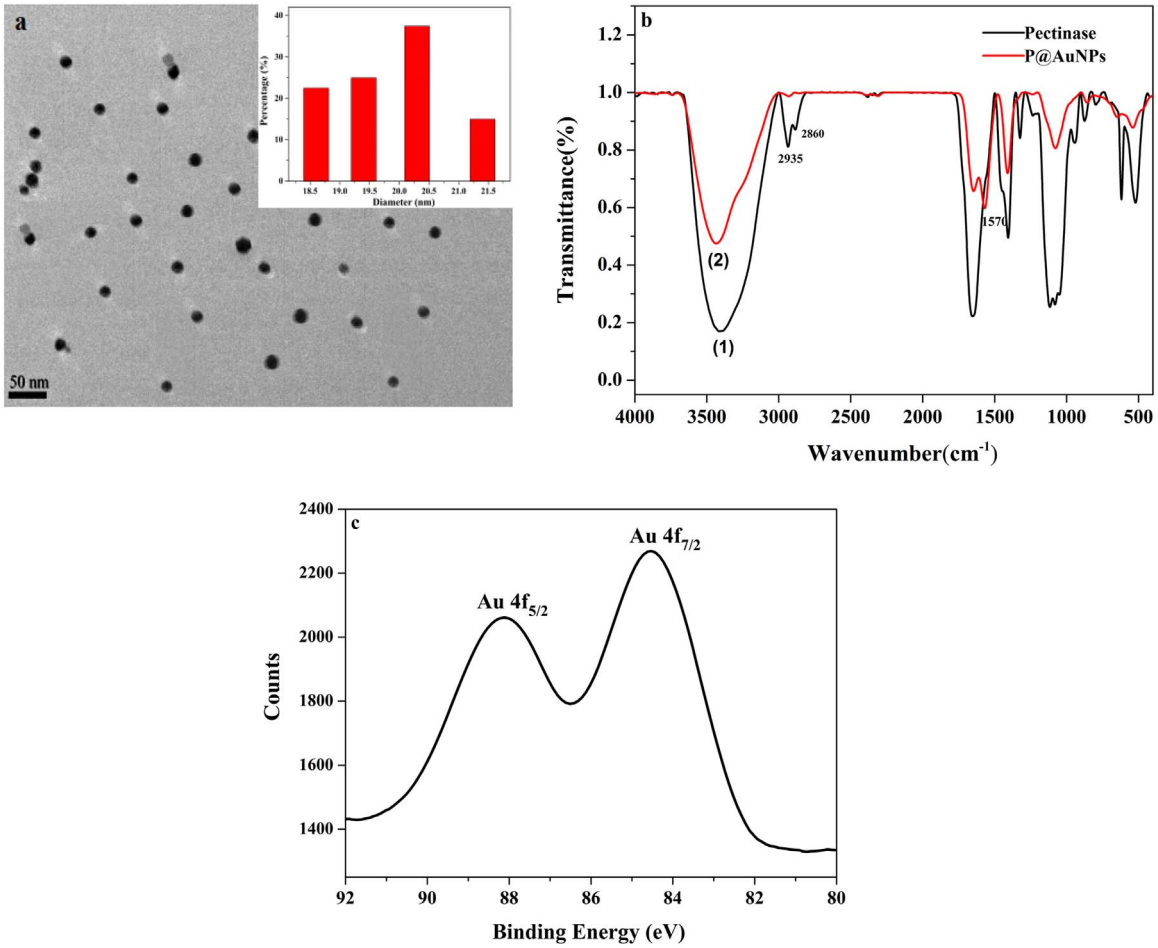

Fig. 1. (a) TEM image of P@AuNPs, the inset shows the particle size distribution of the P@AuNPs. (b) FT-IR spectra of pectinase (1-blank line) and P@AuNPs (2-red line). (c) XPS analysis of Au 4f orbitals of as-prepared P@AuNPs. (d) Zeta potential of P@AuNPs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)