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Rapid synthesis of protein conjugated gold nanoclusters and their application in tea polyphenol sensing

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ABSTRACT

In this report, a rapid approach for the synthesis of protein conjugated gold nanoclusters under heating condition (AuNCs-protein(p)-heating(h)) was proposed. These AuNCs-p-h were synthesized within 3 min at approximately 100 °C and contain remarkable peroxidase-like activity. Notably, in the presence of tea polyphenols (TPs), the peroxidase-like activity of AuNCs-p-h is restrained, which is likely due to the TP-induced aggregation. A facile approach for TP sensing based on the inhibition effect of TPs towards the peroxidase mimic activity of AuNCs-p-h has been developed. Tea is one of the most popular and health beneficial beverages, the favourable effect of which attributes greatly to its key component, TPs. TP detection thus becomes an important task for various food and beverage companies. This novel TP colorimetric detecting method exhibits a linear response in the concentration range of 10 nM to 10 μM with detection limit of 10 nM as well as prominent selectivity towards various TP related molecules including tyrosol, protocatechuate, chlorogenic acid, theophylline, L-theanine, and L-norepinephrine hydrochloride. Comparing with the traditional tartaric acid colorimetric approach (Tac), this new system shows basically identical experimental results but with much higher sensitivity. AuNCs-p-h can be readily used for TP quantification from real tea samples.

1. Introduction

Tea is among the most popular and health beneficial drink. The favourable properties of tea attribute greatly to one of its major components, namely tea polyphenols (TPs). As secondary metabolites produced by tea plants, green TPs inhibit the growth of various cancers through inhibiting distinct cellular pathways and promote cell apoptosis [1]. Moreover, TPs also show anti-obesity effect through suppression of lipogenesis, down-regulation of fatty acid synthesis, increasing autophagy, and stimulation of cellular energy expenditure in mammalian mitochondria [2,3]. Furthermore, TPs also possess antibacterial, antiviral, and antifungal activities and therefore hold promise for the treatment of infection diseases [4]. In addition, TPs can react with reactive oxygen species (ROS), and thus serve as an antioxidant [5]. Recently, Ying et al. [6] developed a TP-based carrier for protein drug delivery and showed great perspective of TPs in material application.

Since their beneficial effects and multiple facets were recognized, TPs have been extensively studied. Therefore, setting up a highly selective, ultrasensitive, and cost-effective means for TP detection becomes an important task. Several TP sensing approaches have been lately proposed [7–17]. For instance, many electrochemical related systems [18] were well characterized, such as peroxidase-immobilized gold electrodes [7], carbon nanotubes–chitosan composite electrode [11], Zn/Al layered double hydroxide film modified glassy carbon [10], mesoporous Al-doped silica modified electrode [12], and gold nanoparticles/TiO_2 modified electrode [15]. Moreover, Thakur et al. [9] designed an amperometric principle-based biosensor containing immobilized enzyme tyrosinase, which showed a detection limit of 10 mM. Marty et al. [13] optimized the conditions of the system and reached a detection limit of 100 nM. Interestingly, Pundir et al. [14] developed a polyphenol biosensor based on laccase-gold electrode immobilized system, which showed good properties including larger determination range, faster response time, and higher stability. Very recently, Thakur et al. [17] proposed a smart polyphenol sensing system, which takes advantage of the interaction among four components including polyphenol, polyquinones, laccase, and quantum dots. Notably, a classical TP detective and

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visual method is also widely used by taking advantage of TPs and Folin–Ciocalteu reagent interaction [19]. Our report describes a facile approach for TP sensing based on the inhibition effect of TPs towards the peroxidase mimic activity of protein conjugated gold nanoclusters synthesized under heating condition (AuNCs-p-h).

During recent years, gold nanoclusters (AuNCs) emerged as attractive new nanomaterials with unique photoelectrical and photophysical properties and are widely used in analytical and bioimaging analysis [20–28]. The optical luminescence of AuNCs is tunable and frequently associated with the composition and aggregation states of Au(I) species on their surface [29,30]. Among these AuNCs based materials, protein conjugated AuNCs show high biocompatibility and thus frequently used in biology related research [31–35]. In addition to this, several other approaches for AuNCs synthesis are proposed, such as microwave irradiation (MWI) [36,37], sonochemical [38] and electrochemical synthesis [39]. In this work, we developed a new heating-based method for the rapid synthesis of protein conjugated AuNCs (AuNCs-protein(p)-heating(h)). AuNCs-p-h were synthesized within 3 min at 100 °C and contain remarkable peroxidase-like activity. Importantly, TPs show an inhibition effect towards the peroxidase mimic activity of AuNCs-p-h.

2. Materials and methods

2.1. Reagents

Bovine serum albumin (BSA), gold (III) chloride trihydrate ($HAuCl_4{\cdot}3H_2O$), TPs (≥98%) (Fig. S1), glycine, histidine, alanine and dimethyl sulfoxide (DMSO) were obtained from DingGuo Changsheng Biotechnology (Beijing, China). 3,3′,5,5′-Tetramethyl-benzidine(TMB), and L-norepinephrine hydrochloride were ordered from Sinopharm Chemical Reagent (Shanghai, China). Theophylline, L-theanine, chlorogenic acid, tyrosol, and 2,2′-azino-bis(3-ethyl-benzothiazoline-6-sulphonic acid) (ABTS) were obtained from Aladdin Industrial Corporation (Shanghai, China). Protocatechuate were purchased from Shanghai Ryon Biological Technology (Shanghai, China), Catechin, gallic acid and EGCG were obtained from Yuanye Biological Technology (Shanghai, China). Hydrogen peroxide, Sodium hydroxide glucose, sucrose and all the other chemicals were purchased from Beijing Chemical Reagent Company (Beijing, China). Tea samples were purchased from local supermarkets (Changchun, China). All the reagents were of analytical reagent grade. Double distilled water (dH_2O) (18.25 mΩ) by a Milli-Q system (Millipore, Bedford, USA) was used throughout the experiments.

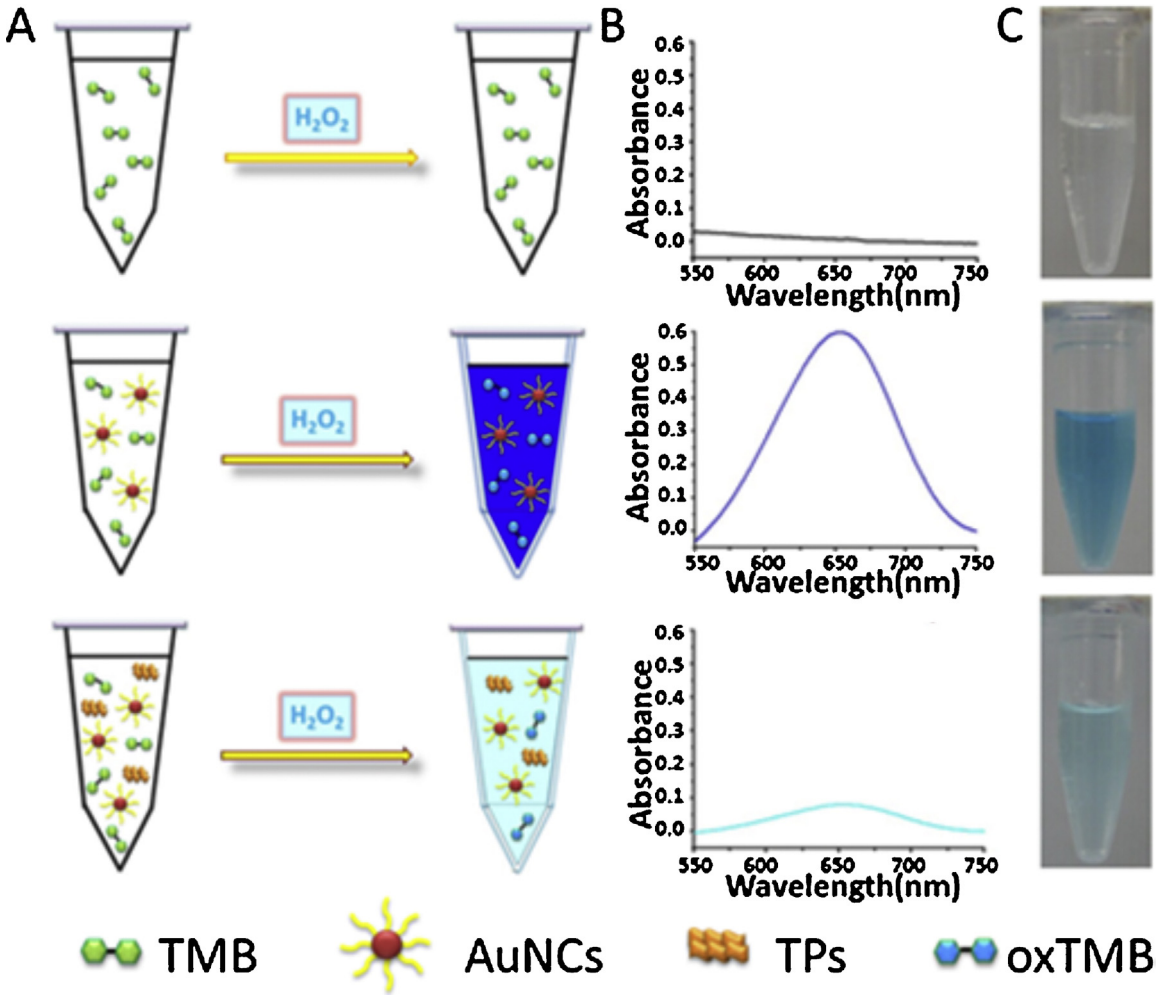

Fig. 1. Schematic presentation of AuNCs-p-h sensing system towards TPs. (A) In the absence of AuNCs-p-h, TMB cannot be converted to oxidized form (oxTMB) (upper panel); in the presence of AuNCs-p-h, TMB can be converted to oxTMB completely (middle panel); in the presence of both AuNCs-p-h and TPs (40 μM), TMB cannot be efficiently converted to oxTMB (lower panel). (B) UV–vis absorption spectra of (A). (C) Images of (A) taken under visible light.