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Protein-directed gold nanoparticles with excellent catalytic activity for 4-nitrophenol reduction

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ABSTRACT

To explore high-performance noble metal nanomaterials for the reduction of the biotoxin 4-nitrophenol (4-NP) in medicine, we developed a green synthesis strategy of bovine serum albumin-stabilized Au nanoparticles (Au@BSA NPs). The as-synthesized Au@BSA NPs were characterized by ultraviolet-visible absorption spectrum, fourier transformed infrared spectroscopy, transmission electron microscopy and dynamic light scattering. The functional bio-nanocomposites showed Au-protein core-shell structure and uniform distribution, and their sizes were dependent on the additive amount of $HAuCl_4$. Interestingly, Au@BSA NPs showed remarkable catalytic activity for the reduction of 4-NP into 4-aminophenol in the presence of sodium borohydride. Due to the introduction of Au@BSA NPs, the reduction reaction could be conducted at ambient temperature and pressure without any additional conditions. Moreover, the reduction rate was closely related to the sizes of NPs and reaction temperature, and the catalytic mechanism was verified to follow the pseudo-first-order kinetics. Due to the environmentally friendly synthesis process and green reduction strategy of 4-NP, Au@BSA NPs would show great potential in governance of the biotoxin in medicine.

1. Introduction

As a notorious biotoxin in medicine, 4-nitrophenol (4-NP) extensively and steadily exists within environment, and severely endangers human health. Therefore, various methods have been developed to remove 4-NP or reduce 4-NP into a harmless product [1–8]. Among these methods, the reduction of the nitro group catalyzed by noble metal nanomaterials in the presence of $NaBH_4$ has attracted much attention, because of high catalytic activity and mild catalytic reaction condition [9–11]. On the other hand, the reduction product, 4-aminophenol (4-AP) is a serviceable organic intermediate for the preparation of medicines, dyes and polymers [12–15]. Anyhow, it is still imperative to explore simple and mild reduction reaction based on high-performance noble metal nanomaterials.

Recently, gold nanoparticles (Au NPs) have received tremendous attention due to their high catalytic activity in some reactions, such as oxidation [16–19] and reduction [20–23] at low temperature. Generally, due to the high surface energy, Au NPs are easy to aggregate, reducing their catalytic activity and restricting their application [24]. Hence, it is very important to look for the synthesis method of Au NPs with good stability, long-term dispersity and high catalytic performance. In the past few decades, a variety of inorganic or organic substance have been used as supports or stabilizers, including carbon materials [25], metal oxides [26,27], polymers [26,28], which are helpful to protect Au NPs against aggregation and enhance their catalytic activities. However, these substances often meet with failure because of the weak interaction between gold and substances. Moreover, the addition of organic solvents such as *N*,*N*-dimethylformamide and glycol can lead to potential environmental hazards, impeding the application of Au NPs. Additionally, some reductants (such as sodium borohydride and hydrazine), which must be used to reduce Au ions, can bring latent danger to ecotope. Consequently, it is necessary to propose a green and environment friendly synthesis method of Au NPs to overcome these above problems.

With the growing interest in biomineralization [29–34], bovine serum albumin (BSA), a kind of abundant protein extracted from bovine serum, has been widely used as template to stabilize nanoclusters or nanoparticles and direct the growth of metal nanocrystals, because of the plentiful binding sites of metal ions [35–38]. In this work, BSA was selected as template to synthesize Au NPs by using chloroauric acid ($HAuCl_4$) as the precursor at room temperature. To ensure a green synthetic process, eco-friendly reductant ascorbic acid (AA) [39] was used instead of traditional reductants, such as sodium borohydride and hydrazine. In addition, the use of aqueous solution rather than organic solvents also satisfied the demands of green chemistry. Then, the simple

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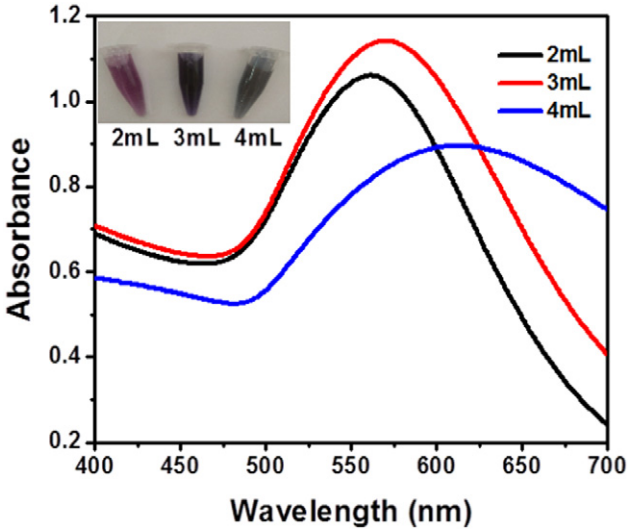

Fig. 1. UV–vis absorption spectrums of the Au@BSA NPs with different volume of $HAuCl_4$ (insert is the corresponding picture).

and mild reduction of 4-NP was established by using as-prepared Au NPs as catalysts. The influences of the size of Au NPs and reaction temperature on catalytic activities were also discussed.

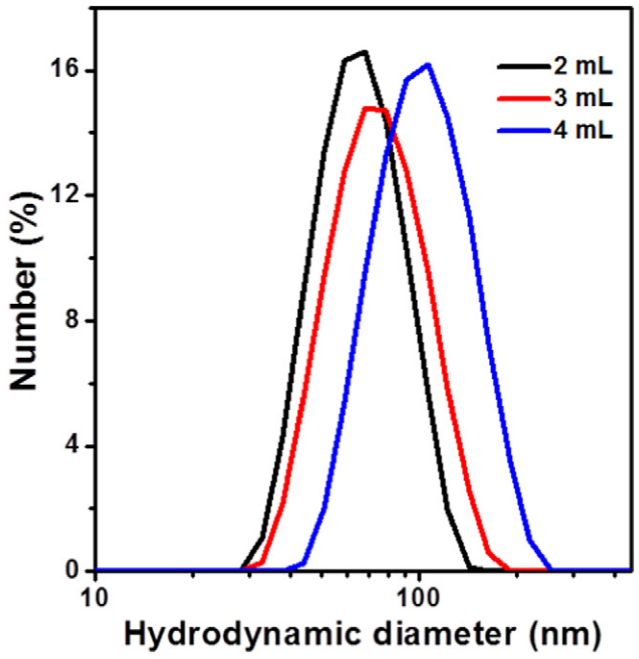

Fig. 3. Hydrodynamic diameter distributions of Au@BSA NPs measured by DLS.

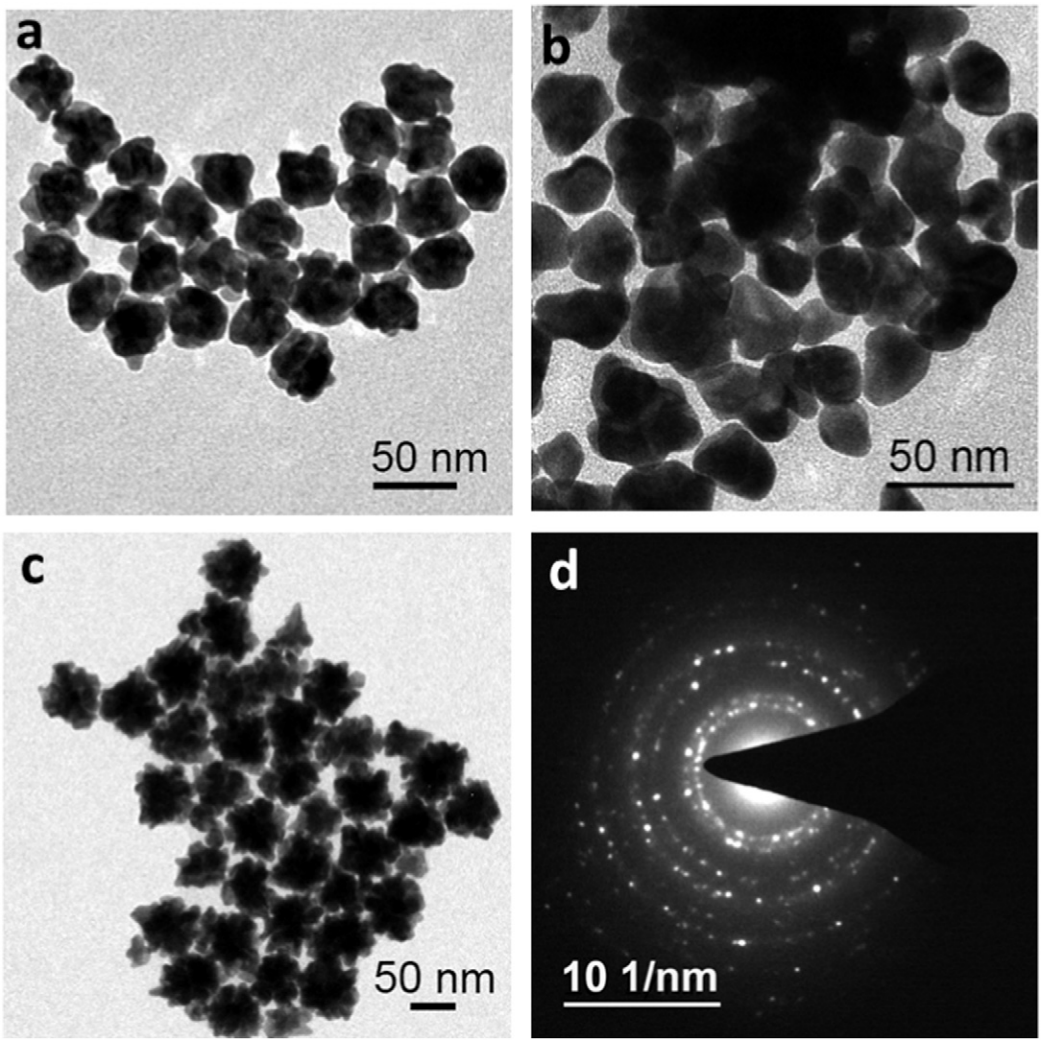

Fig. 2. TEM images of Au@BSA NPs with different volume of $HAuCl_4$ (a, 2 mL; b, 3 mL; c, 4 mL), and SAED pattern of Au@BSA NPs (d).