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Preparing Co_3O_4 urchin-like hollow microspheres self-supporting architecture for improved glucose biosensing performance

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ABSTRACT

A new Co_3O_4 electrode material with self-supporting urchin-like hollow microspheres structure was fabricated via a self-assembly method. Incorporating the adsorption and entrapment, the high porosity and large surface area were favorable for the highly effective immobilization of glucose oxidases. Multiple responses, consisting of enzymatic and material catalysis, were subsequently employed and achieved on the microsphere surface. As the radially oriented nanowires array provided a vast number of catalytic active sites, which lowered the energy barrier of glucose redox and acted as a media to boost the electron transfer, the detection potential was largely decreased. Furthermore, numerous electron transport paths in a short distance were formed among the interconnected bridge-like nanowires, resulting in improved electron transfer efficiency. The prepared glucose biosensor exhibited extra high sensitivity (102.77 $\mu A\,mM^{-1}\,cm^{-2}$), fast response (3 s) and outstanding selectivity and stability at a lower applied potential (0.35 V).

1. Introduction

Fast and accurate detection of glucose is important in a vast range of application fields such as clinical diagnosis, diabetes management, biological analysis, beverage industry and environmental monitoring, numerous processes and methodologies have been developed for creating new glucose biosensors [1–9]. Among them, the amperometry acts as the typical representative of the electrochemical technique and is featured as its unbeaten sensitivity and selectivity by applying a constant bias potential. Therefore, intense attention has been paid to the amperometric glucose sensors during the last 40 years [10,11]. Generally speaking, a lower applied potential can weaken the interference of other coexistent, which is helpful to improve the selectivity. The realization of excellent sensing performance at a lower detection potential is thus really to be expected. Previous investigations have shown that the oxidation onset potential mainly depends on the energy barrier determined by the number of active sites [12]. Furthermore, the sensing performance is always influenced by the efficiency of electron transfer including the number of electron transmission paths and the distance of electron transport [13]. However, improving the efficiency of electron transfer and decreasing the detection potential simultaneously have been of great challenge. The specific recognitive glucose oxidase (GOx)-based glucose biosensors has been prevalently researched since the initial development of glucose enzyme electrodes in 1967 [14,15]. In the presence of oxygen, GOx converts glucose into gluconolactone following reduction of flavine adenine dinucleotide. The cofactor is then reoxidized, causing electrons transfer and yielding hydrogen peroxide. The formation of H_2O_2 can subsequently be detected to monitor the concentration of glucose [16,17]. Consequently, the key points of the biosensor could be elaborated from two aspects, one is the enzyme catalysis which is related to the oxidation of glucose, the other one is the material catalysis associated with electrochemical oxidation of the H_2O_2 at the detection potential.

The bioactivity and stability of enzyme molecule (10–20 nm) are the prerequisite of the enzyme-based systems. However, the denatured enzymes after immobilization are likely to result in the failure of enzyme catalysis [18,19]. It is well known that suitable pores can act as cells to offer desired room for enzyme immobilization. Holding enzymes through physical adsorption to keep their lifetime for ten weeks has been reported [20]. Meanwhile, entrapment with a 3D permeable polymer is an auxiliary method to avoid the leakage of immobilized enzymes [21]. Furthermore, nanostructured metal

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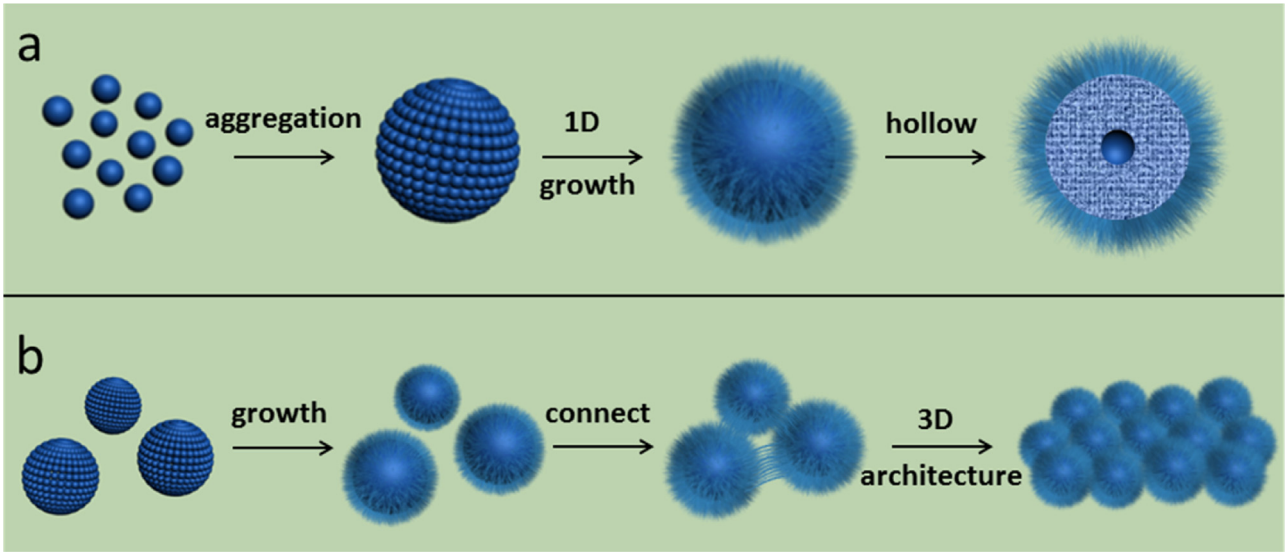

Scheme 1. Schematic illustration: (a) the formation of the urchin-like hollow microspheres and (b) the self-assembly process of the microspheres to form an integrated 3D architecture.

oxides, such as ZnO [22], CuO [23], MnO_2 [24], NiO [25] and so on, have been successfully used for immobilizing enzymes due to their desirable biocompatibility. Especially, Co_3O_4 (IEP ~ 8), a versatile transition metal oxide, has been demonstrated as a good matrix for GOx (IEP ~ 4.2) immobilization through electrostatic interaction [26]. Additionally, it continues to attract considerable interest mainly due to its excellent electrocatalytic activity, non-toxicity and easy fabrication [27,28].

As we all known, the electro-active center of the enzymes is embedded in the protein shell and the surface charges distribute on protein molecule unevenly [29]. The electron communication between the enzymes and electrode is so inaccessible that the number of electron transmission paths or the distance of electron transport is not easy to optimize directly. Therefore, improving the active surface area of electrode materials has been noticed to solve this problem, which facilitates the incorporation of the enzyme into the nanostructured materials [30]. Recently, Co_3O_4 microspheres with novel interior geometry and surface functionality have been prepared and its improved electrochemical properties and catalytic activity have also been verified [31]. Nevertheless, the isolated microspheres are easily damaged during the process of electrode modifying, leading to no well-constructed transport channels and largely decreased catalytic activity. With the help of branches, the microspheres connect to each other to form the sturdy and solid integrated architecture, which is favorable to preserve the intrinsic structure. In addition, the electron can be further transferred by the branches via a short distance, leading to an enhanced sensing performance [32]. Considering the above factors, the interconnected Co_3O_4 microsphere architecture with high porosity and large active surface area is desired to be synthesized.

Herein, we report an improved glucose biosensor based on the Co_3O_4 urchin-like hollow microspheres self-supporting architecture (UHMSA). The self-assembly structure with three dimensional (3D) self-supporting architecture, great mechanical stability, and large active surface area is fabricated by nanoparticles aggregation, outer nanowires growth and supporting branches formation.

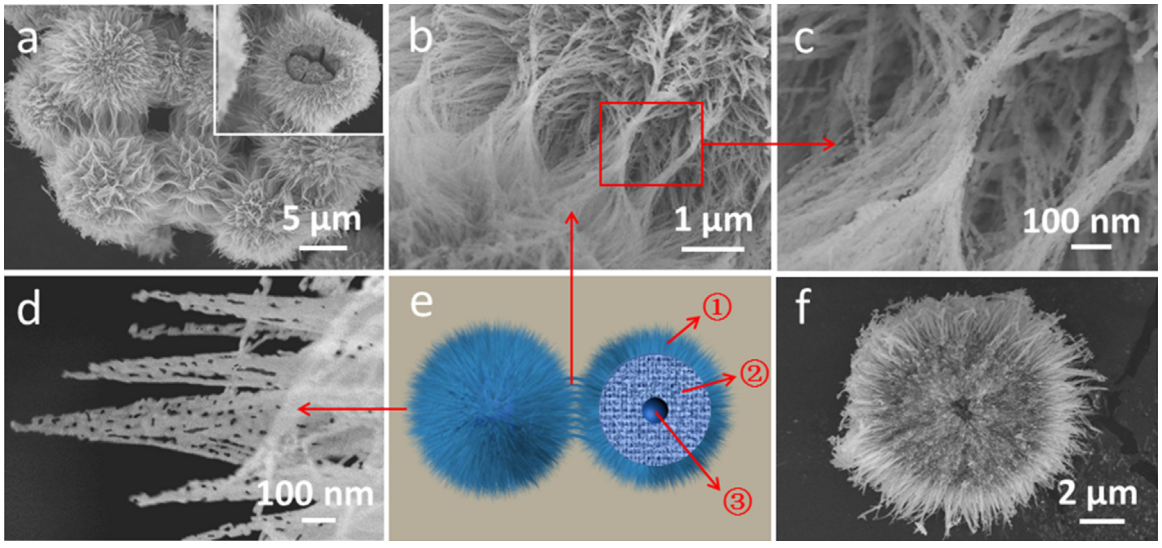

Fig. 1. Scanning electron microscopy (SEM) images (a–c) and schematic diagram (e) of the self-supporting Co_3O_4 microspheres. High magnification SEM image (d) of the Co_3O_4 nanowires grown on the microsphere surface. SEM image (f) of the broken structure of an isolated microsphere.