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Electrodepositing Ag nanodendrites on layered double hydroxides modified glassy carbon electrode: Novel hierarchical structure for hydrogen peroxide detection

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ABSTRACT

A novel hydrogen peroxide (H_2O_2) sensor has been fabricated by electrodepositing silver on glassy carbon electrode modified with layered double hydroxides (LDHs). Electrochemical characterizations demonstrate that the introduction of LDH substrate can enhance the electrocatalytic performance toward H_2O_2 of the sensor. Morphology characterization indicates that dendritic Ag nanostructure is present on the obtained electrodes by using LDHs as substrate. The growth mechanism of Ag nanodendrites is discussed using diffusion-limited aggregation model. After optimization of experimental conditions, a H_2O_2 sensor with a wide linear range (10 μM to 19.33 mM) and a low detection limit (2.2 μM) has been obtained. In addition, this sensor also exhibits good selectivity and reproducibility. This novel hierarchical structured sensor broadens the application of LDHs in electrochemical fields and provides a simple and feasible approach to meet the advanced application demand for H_2O_2 detection.

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1. Introduction

During the past few decades, a great deal of efforts have been devoted to the preparation and application of noble metals in catalysts, fuel cells, surface enhanced Raman scattering (SERS) and sensors [1–3]. Noble metal nanoparticles are considered to be one kind of attractive nanomaterials due to their extraordinary advantages which include stability, conductivity, biocompatibility, low cytotoxicity and catalytic property [4–7]. Because of these advantages, the application of noble metal nanomaterials in the field of electrochemical sensors has become a highly attractive topic.

Accurate determination of hydrogen peroxide (H_2O_2) is of great importance in the fields of clinical, food, pharmaceutical and environmental analysis. Among various noble metal nanomaterials used, silver nanostructure based sensors are being well-known for their low detection limit and fast response in detecting H_2O_2. Welch et al. proved that the electro-reduction of H_2O_2 occurred directly on the Ag nanoparticles (Ag NPs) [8]. It is also proved that the morphology of the metal nanomaterials plays a vital role on the catalytic reactivity of metal nanomaterials. A large number of research works have been carried out to investigate the relationship between the structure and morphology of Ag NPs as well as the electrocatalytic performance of Ag-based sensors. Cui et al. electrodeposited Ag NPs on DNA network modified glassy carbon (GC) electrode. The obtained electrode exhibited excellent catalytic ability toward H_2O_2, which is ascribed to the formation and the homogeneous distribution of small Ag NPs induced by DNA network [9]. Similarly, porous network of collagen and poly(o-phenylenediamine) was also found to be effective in the formation of small Ag NPs by electrodeposition method [10,11]. Wang et al. electrodeposited Ag NPs on zinc oxide film and found that relatively small particles could be formed, thus better sensitivity and stability could be reached [12]. Chen et al. found that attapulgite could facilitate the formation of homogeneously distributed small Ag NPs during electrodeposition [13]. Besides, dendritic Ag nanostructures were also investigated in previous articles. Qin et al. successfully synthesized Ag dendritic nanostructures by electrodeposition without using any template or surfactant. The density and the morphology of the Ag nanostructures can be easily controlled by changing the applied potential, precursor concentration and electrolysis time. They also discussed the possible formation mechanism of the dendritic morphology from the aspects of kinetics and thermodynamics. They found that the Ag dendrites exhibit favorable electro-reduction activity toward oxygen and H_2O_2 [14,15].

Layered double hydroxides (LDHs), also known as the anionic clays or hydrotalcite clays, can be expressed with the following general formula: $[M^{II}_{1-x}M^{III}_{x}(OH)_2]\cdot[A^{n-}_{x/n}\cdot mH_2O]$, where M^{II} and M^{III} represent divalent and trivalent metal ions within the brucite-like

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layers respectively, and A^{n-} is an interlayer anion [16–19]. LDHs have attracted great attention due to their compositional flexibility, anion exchangeability and biocompatibility [20–22]. Moreover, the morphology and size of LDHs can be controlled by applying different preparation conditions [23]. Owing to their excellent properties, LDHs have been proved to be promising building blocks for the design of high-performance and multi-functional materials in various applications [24–28]. Previously, Chen et al. developed facile hydrothermal processes to produce Ag NPs deposited layered double hydroxide nanoporous coatings with excellent antimicrobial activities [29]. In this study, due to the unique properties listed above, LDHs are being selected as the matrix for the electrodeposition of Ag, which turns out to provide a stable matrix for the formation of dendritic Ag nanostructure with high catalytic performance toward H_2O_2.

In this work, a new sensitive nonenzymatic H_2O_2 sensor has been fabricated by electrodepositing Ag onto LDH modified GC electrode. Our results show that this Ag/LDH based sensor exhibits noticeable catalytic ability toward H_2O_2, having a linear response range from 10 μM to 19.33 mM with the detection limit of 2.2 μM.

2. Experimental

2.1. Materials

$MgCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, NaOH, Na_2CO_3 and $AgNO_3$ (analytical purity) were supplied by Shanghai Chemical Reagent Company. H_2O_2 (30%, v/v aqueous solution) was obtained from Jiangsu Tongsheng Chemical Reagent Company. All other reagents were of analytical grade and used without further purification. Dilute solutions of H_2O_2 were freshly prepared daily. Phosphate buffer solutions (PBS, 0.2 M), used as supporting electrolyte, were prepared by mixing standard stock solutions of Na_2HPO_4 and NaH_2PO_4 and. All aqueous solutions were prepared with doubly distilled water.

2.2. Synthesis of layered double hydroxides

LDHs were prepared by coprecipitation and subsequent hydrothermal treatment method as reported by Xu et al. [30]. Typically, 10 mL salt solution mixture of 2.0 mM $MgCl_2$ and 1.0 mM $AlCl_3$ was quickly added (within 5 s) under vigorous stirring into 40 mL basic solution mixture containing 0.15 M NaOH and 0.013 M Na_2CO_3. After stirring for 20 min, the mixture was centrifuged and the precipitate was collected. After being washed twice with water, the precipitate was subsequently dispersed into 40 mL water. This aqueous suspension was then transferred into a Teflon-lined autoclave for hydrothermal treatment at 100 °C for 16 h. Finally, after air-cooling, a stable homogeneous LDH suspension with a concentration of 0.4 wt% was obtained. Suspensions with different LDH concentrations could be obtained by diluting the original LDH suspension. Some LDH crystallites were collected by centrifugation (14,000 rpm) for X-ray diffraction (XRD) and transmission electron microscopy (TEM) characterization. For TEM observation, the collected LDH nanoparticles were dispersed in ethanol and ultrasonicated for 5 min, then a droplet was dropped on a copper grid.

2.3. Preparation of the H_2O_2 sensor

GC electrodes (with a diameter of 3 mm) were prepared by a sequence of polishing with 1.0, 0.3 and 0.05 μm alumina slurry, followed by ultrasonication in a 1:1 ethanol/water mixture for 15 min to remove any traces of alumina. To prepare LDH/GC electrodes, 5 μL of LDH suspension was dropped onto bare GC electrode surface followed by subsequent drying the electrodes in a desiccator over silica gel. In order to obtain Ag/LDH/GC electrodes, the LDH/GC electrodes were immersed in 0.1 M KNO_3 solution containing 3.0 mM $AgNO_3$ and electrodeposited at −0.2 V for certain period of time. For the preparation of Ag/GC electrodes, similar procedures were used except that no LDH suspension was dropped onto the electrode surface prior to the electrodeposition process.

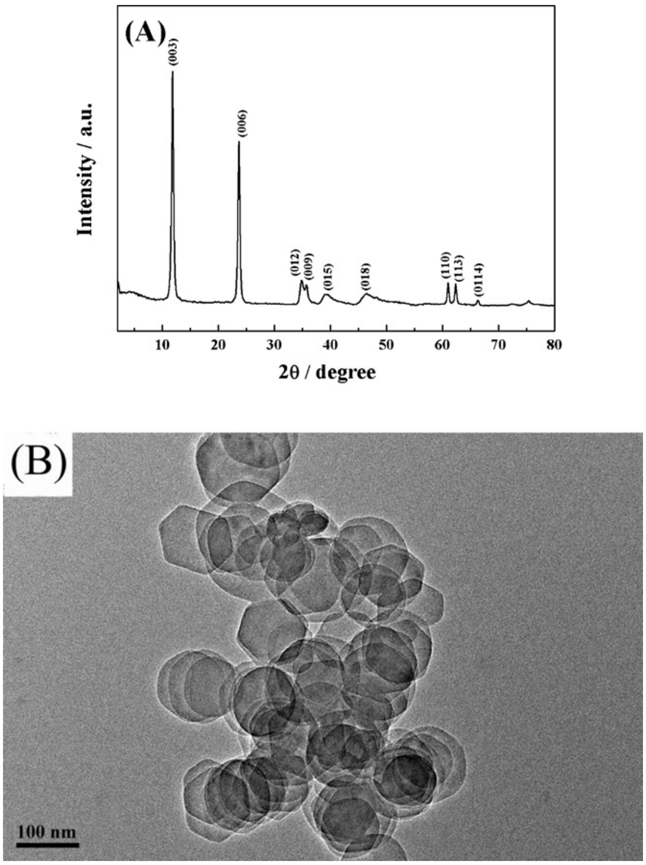

Fig. 1. (A) XRD pattern and (B) TEM image of LDHs.

2.4. Measurements and apparatus

All electrochemical measurements were performed using a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Co., China). A conventional three-electrode system was used, which consists of a modified electrode as the working electrode, a platinum wire as the auxiliary electrode, and an Ag/AgCl (3 M KCl) electrode as the reference electrode. The working solutions were purged with nitrogen for 20 min before measurements. All electrochemical measurements were performed at room temperature.

TEM observations were performed under an acceleration voltage of 200 kV with a JEOL JEM2100 TEM. X-ray diffraction patterns of the samples were conducted on a PANalytical X'Pro X-ray diffractometer with Cu Kα radiation ($\lambda = 0.1542$ nm) under a voltage of 40 kV and a current of 40 mA. Scanning electron microscopy (SEM) images were acquired using a JEOL JSM-7600F coupled with an energy-dispersive X-ray (EDX) detector. All samples were coated with a thin layer of gold prior to SEM observations.

3. Results and discussion

3.1. Characterization of LDH nanoparticles

Fig. 1(A) shows the XRD pattern of the as-prepared LDH nanoparticles. The result proves that the LDHs exhibited

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