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Carbon fiber cloth supported Au nano-textile fabrics as an efficient catalyst for hydrogen peroxide electroreduction in acid medium

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HIGHLIGHTS

- Textile-like Au particles are electrodeposited on CFC via electrodeposition.
- Au NTs/Ni foam electrode shows high catalytic activity for H_2O_2 electroreduction.
- The single Au particle is actually consisted of many interconnected nanospikes.

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ABSTRACT

The size-controlled hierarchical textile-like Au nanostructures supported carbon fiber cloth (Au NTs/CFC) is successfully fabricated through a simple low-cost electrochemical route. The electrodes are characterised by scanning electron microscopy equipped with an energy dispersive X-ray spectrometer, transmission electron microscopy and X-ray diffractometer. Without any conducting carbons and polymer binders, the 3D electrode with unique structure is directly used as the electrocatalyst for H_2O_2 reduction in acid solution and the catalytic performance is evaluated by voltammetry and chronoamperometry. The Au NTs/CFC electrode exhibits much higher catalytic activity and remarkably improved utilization of Au than Au nanoparticles (Au NPs/CFC) prepared by the same method owing to its unique structure. In the solution of 3.0 mol L^{-1} H_2SO_4 + 0.1 mol L^{-1} H_2O_2, with the reduction potential of 0 V, the current of −0.72 A cm^{-2} mg^{-1} can be obtained on Au NTs/CFC electrode and only a current of −0.09 A cm^{-2} mg^{-1} can be achieved on Au NPs/CFC electrode. All these results reveal that the novel Au NTs/CFC electrode exhibits excellent catalytic performance and superior stability for H_2O_2 electroreduction in acid medium, benefitting from the unique 3D structure which can ensure high utilization of catalyst.

1. Introduction

As the burgeoning development of nanotechnology, interest is rapidly emerging in the exploration of nanomaterials with special structure, shape, and morphology over the last two decades, because of their remarkable physicochemical properties and numerous applications [1–7]. Recently, hierarchical Au micro/nanostructures have attracted considerable research interests due to their important potential applications in the fields of catalysis, biological labeling, optics and electronics [8–10]. From the literature, a large variety of studies have been reported on the synthesis of Au nanomaterials [11–16], and it is not difficult to find that most of the syntheses are carried out in the presence of additional reagents like surfactants/polymers or templates which are required as shape-directing agents. However, this method commonly constructs special morphology by the addition of templates and surfactants which may suffer from many imperfections such as the introduction of impurities, and hierarchical materials thus formed in the process of preparation may be damaged during the progress of the template removal [17–19]. Also, the use of templates may complicate the synthetic procedure and limit the synthesis of nanostructured materials in large quantities [20,21]. Therefore,

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development of template- and surfactant-free method is of great importance. Moreover, a simple morphology-controllable and large-scale synthesis route continues to be highly expected.

Electrodeposition is a very powerful and low-cost technique for the one-step synthesis of micro/nanostructures on substrates [16,22–27]. The group of Wang [24] has successfully fabricated a simple low-cost electrochemical route to synthesis of size-controlled hierarchical flowerlike gold microstructures with "clean" surfaces using gold nanoplates or nanopricks as building blocks without introducing any template or surfactant. Bhargava et al. [23] have reported on a simple electrochemical route to produce uniformly sized Au nanospikes without the need for a capping agent or prior modification of the electrode surface. Li and co-workers [25] have also facilely prepared dendritic Au nanomaterials via a simple two-step electrodeposition method by treating a pure gold electrode.

In this work, we focus on the fabrication of Au nano-textile fabrics supported on carbon fiber cloth (Au NTs/CFC) through a one-step potentiostatic electrodeposition method. The novel electrode as the catalyst towards H_2O_2 electroreduction in acid medium is also examined in this report. H_2O_2 is used as the oxidant replacing O_2 for several types of low temperature liquid-based fuel cells [28–31], and it has be proved that the fuel cell with H_2O_2 as oxidant can greatly improve the performance than that with O_2 as oxidant. Some literature [32] have also pointed out that the fuel cell with H_2O_2 electroreduction in acid solution has higher open circuit potential (OCP) and improved power density than that in alkaline medium. So researches on the catalyst towards H_2O_2 electroreduction in acid solution have outstanding meanings for constructing high-performance fuel cells. Herein, CFC with open channels is applied as both the current collector for electron transfer and the substrate for Au deposits, owing to its high electrical conductivity and superior stability in strongly acidic solution. The as-prepared Au nanomaterials have unique properties with many secondary structures including small nano-scale kinks and the corrugated surface, greatly increasing the area of electrode surface and improving the utilization of noble metal. Results reveal that the obtained electrode (Au NTs/CFC) demonstrated high activity and good stability for H_2O_2 electroreduction in acid solution and can be a candidate for the application in H_2O_2-based fuel cells.

2. Experimental

2.1. Preparation and characterization of Au NPs/CFC and Au NTs/CFC electrodes

The Au NTs/CFC electrode was fabricated by a one-step potentiostatic electrodeposition of textile-like Au arrays directly grown on CFC. The electrodeposition was carried out in a three-electrode electrochemical cell controlled by computerized potentiostat (Autolab PGSTAT302, Eco Chemie). The CFC (1.0 × 1.0 cm) served as the working electrode, which was placed between two pieces of platinum foil (1.0 × 1.0 cm) in parallel as the counter electrodes. A saturated Ag/AgCl ($KCl_{sat.}$) electrode was used as the reference electrode, and all potentials in this work were referred to this reference electrode. The solution contains 10 mmol L^{-1} $HAuCl_4$, 1.25 mol L^{-1} N-methylimdazole and 0.5 mol L^{-1} H_2SO_4. The constant reduction potential of 0.4 V is applied for 600s to the CFC.

The Au NTs/CFC electrode was characterized by scanning electron microscopy equipped with an energy dispersive X-ray spectrometer and transmission electron microscopy. The structure was analyzed using an X-ray diffractometer (Rigaku TTR III) with Cu Kα radiation (λ = 0.1514178 nm). The Au loading was measured using an inductive coupled plasma emission spectrometer (ICP, Xseries II, Thermo Scientific). Au in the 1.0 cm^2 electrode was first dissolved in aqua regia solution and then diluted to 1 L solution for the ICP measurement. For comparative study, CFC supported Au particles (Au NPs/CFC) were also prepared by the same method as that for Au NTs/CFC except the electrolysis solution only containing 10 mmol L^{-1} $HAuCl_4$.

2.2. Electrochemical measurements

Cyclic voltammetry (CV), chronoamperometry and electrochemical impedance (EIS) experiments were performed in a conventional three-electrode electrochemical cell using a computerized potentiostat (Autolab PGSTAT302, Eco Chemie) controlled by GPES software. Differing from the configuration for Au and Pd electrodeposition, two Pt foils were placed behind D-porosity glass frits to serve as the counter electrode in order to minimize the effect of H_2O_2 decomposition. The electrolyte for H_2O_2 electroreduction was H_2SO_4 solution. The reported current densities were calculated using the geometrical area of the electrode. All solutions were made with analytical grade chemical reagents and ultra-pure water (Milli-Q 18 MΩ cm). All measurements were performed at ambient temperature (20 ± 2 °C) under N_2 atmosphere. EIS measurements were performed by applying an AC voltage with 10 mV amplitude in a frequency range from 0.01 to 100 kHz.

3. Results and discussion

3.1. Characterization of Au NTs/CFC electrode

The low- and high-magnification SEM images of Au NTs/CFC electrode are shown in Fig. 1. As can be seen that CFC is composed of cross-oriented carbon fiber bundles weaving together (Fig. 1A). There exist void spaces between carbon fibers, which allow electrolytes to access the full electrode surface. Besides, the high electrical conductivity and the flexibility of CFC make it a desirable support for Au catalysts and much easier to prepare the membrane electrolyte assembly of fuel cell. After the progress of electrodeposition, Au deposits are uniformly covered on the surface of carbon fibers with even size distribution (Fig. 1B and C). To get insight into the details of Au particles, high magnification SEM image of Au NTs/CFC electrode is also examined, displaying in Fig. 1D. A variety of tiny nanothorns or nanospikes are interconnected to making up the Au textile-like structures which are vertically standing on the substrate. TEM analysis is also examined in order to get more information on the details of Au nanostructures and the results are displayed in Fig. 2. Fig. 2A exhibits the low-magnification TEM image of the whole textile-like Au particle which has the size of several micrometers. Moreover, there exist many secondary structures such as sharp edges or tips, as well as nanoscale junctions with the size down to around 20 nm (Fig. 2B and C). These features of structure endow Au nano-textile unique properties and excellent catalytic performance, which can be demonstrated in the subsequent testing of this report.

The structure and composition of Au nanostructures is investigated by XRD, and the results are shown in Fig. 3. In order to eliminate the influence of the substrate, XRD pattern of CFC is also analyzed, and there only displayed three broad peaks centered at about 23°, 43° and 80°, which can be associated with carbon. For Au NTs/CFC electrode, the observed peaks at 38.2°, 44.4°, 64.5°, 77.5° and 81.7° corresponding to the (111), (200), (220), (311), and (222) facets demonstrate that the electrodeposited Au is composed of pure crystalline Au with the face-centered cubic (fcc) structure. In addition, the diffraction peaks is very sharp, indicating that Au nanostructures have high crystallinity. The ratios of the peak intensities from Au NTs/CFC electrode due to the (111) planes relative