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The hybrid nanostructure of vertically aligned cobalt sulfide nanoneedles on three-dimensional graphene decorated nickel foam for high performance methanol oxidation

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ABSTRACT

In this report, vertically aligned one-dimensional (1D) cobalt sulfide nanoneedles (CS-NNs) were directly synthesized onto the three-dimensional graphene (3DG) as the CS-NNs/3DG hybrid nanostructure and applied to methanol oxidation reaction (MOR). The 3DG and CS-NNs were prepared by chemical vapor deposition and two-step hydrothermal method, respectively. The 1D cobalt carbonate hydroxide nanoneedles (CCH-NNs) were initially synthesized onto the graphene surface of 3DG via the hydrothermal method (Step I). Finally, the CCH-NNs were converted into CS-NNs via the hydrothermal treatment using Na₂S as the sulfur source with the help of the Kirkendall effect (Step II). The structures and morphologies of 3DG, CCH-NNs/3DG, and CS-NNs/3DG were investigated by Raman spectroscopy, scanning electron microscopy and X-ray diffraction. The electrocatalytic performance was investigated by cyclic voltammetry measurements. The CS-NNs/3DG electrode showed higher electrocatalytic activity for MOR compared with CCH-NNs/3DG and 3DG. The excellent electrocatalytic performances of 3DG supported CS-NNs come from the unique 3D porous architecture, which can provide sufficient open spaces and shorter ion diffusion paths to facilitate rapid ionic transportation. Direct synthesis of 1D CS-NNs on graphene can result in a low resistance for fast electron transfer. The vertically aligned binder-free 1D CS-NNs not only avoid the aggregation to enhance the utilization efficiency of catalytic active sites but also serve as an electron highway in the axial direction for electron collection. The prepared CS-NNs/3DG is a promising non-platinum electrocatalyst for direct methanol fuel cells.

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1. Introduction

Renewable energy applications have been considered the important alternatives for fossil fuels, as a resolution to the global warming control by suppressing carbon dioxide emission. The development of high efficient electrochemical energy storage/conversion devices with inexpensive cost has administered the research way toward commercialization for renewable energy applications. In order to obtain the excellent electrochemical energy devices, the design and fabrication of electrode materials with excellent catalytic activities, large specific surface area, high porosity, and high conductivity is greatly wishful. To approach the requirements mentioned above, graphene is a wonderful strategy to synthesize the hybrid nanostructures for the renewable energy [1,2]. Recently, the three-dimensional graphene (3DG) have attracted a great deal of interest either for fundamental research or for the potential

applications in renewable energy [3,4], because of the unique and multifunctional properties of 3DG. The synthesis of three-dimensional graphene (3DG) on the Ni network can effectively overcome the strong π - π interaction and intersheet contact resistance between graphene sheets, and the perfect connection of graphene sheets in the 3D architecture gave the outstanding electrical conductivity, the porous 3DG also provided the large specific surface area [5,6]. Scaffolds of 3DG decorated with functional species lead to new hybrid nanostructures with a variety of renewable energy application opportunities, such as supercapacitor [6,7], batteries [8,9], and fuel cells [10,11]. The benefits of developing 3DG based hybrid nanostructures are the formation of a larger number and high uniformly distributed nanocatalysts, large specific surface area to enhance the reaction area, high porosity for the easily diffusion of electrolyte, and high conductivity for the fast charge transport rate to enhance the energy storage/conversion efficiency.

Recently, because of the nature abundance, low cost, low toxicity, and superior electrochemical redox activities, transition metal oxides and sulfides and their hybrids have been studied for high-performance and low-cost electrochemical energy storage/conversion devices, such

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as supercapacitors [12,13], dye-sensitized solar cells [14,15], and lithium batteries [16,17], and fuel cells [18–20]. The nanostructures of transition metal oxides and sulfides with various morphologies were synthesized for studying, such as three dimensional (3D) nanospheres [16,21,22], two dimensional (2D) nanosheets [12,23], and one dimensional (1D) nanorods and nanowires [14,24]. Among them, 1D nanostructure attracted wide interest because of its excellent advantage is known to be beneficial for electronic conduction. The electronic wavefunctions of 1D nanostructure are constrained by quantum effects in the nanoscale directions, resulting in the quantum confinement effect to allow electrons free movement through the 1D nanostructure to their substrate [25]. Therefore, 1D nanomaterials could play as an electron highway in the axial direction for fast electron transfer and collection in a shorter time.

Fuel cells based on methanol oxidation reaction (MOR) are electrochemical devices that can convert directly the chemical energy of fuels into electricity [26,27]. Direct methanol fuel cells (DMFCs) have attracted a great deal of attention as the promising next generation power sources, due to their high energy conversion efficiencies and power densities, simple handling and processing, and low pollution to the environment. Pt is the most common and effective electrocatalyst used in the DMFCs [28,29]. However, because the high cost and scarcity of Pt greatly limit the commercialization of DMFCs, the development of Pt-free and outstanding catalytic materials is highly desired to provide an economic solution for promoting practical commercial utilization of DMFCs. Consequently, the investigations of hybrid nanoarchitecture to develop the economic and excellent Pt-free catalytic materials for MOR have become the research focus in recent years in the fuel cell community. For instance, the hybrid materials of NiO nanoparticles dispersed on carbon nanotubes (CNTs) [18], the NiCo₂O₄ arrays grown on nickel foam [19], and the core-shell nanostructure of NiCo₂O₄ decorated CNTs [20].

In terms of the above considerations, in present work, the hybrid nanoarchitecture of vertically aligned 1D cobalt sulfide nanoneedles (CS-NNs) were synthesized on the 3DG to act as the promising alternative Pt-free catalytic electrode for DMFCs applications.

2. Experimental methods

2.1. Fabrication of the hybrid nanomaterials of CS-NNs/3DG

In this study, the commercial Ni foam (Innovation Materials Co., Ltd., purity >99%) was used as a 3D framework for the CVD growth of 3DG. A simple method based on a home-made thermal CVD system with the acetylene (C₂H₂) as a supplemental carbon source was used to synthesize the 3DG. The Ni foam was loaded into a quartz tubular furnace for CVD process. The Ni foam was heated to 900 °C under an H₂ atmosphere and annealed for 20 min to eliminate the surface oxide layer. A C₂H₂/H₂ gaseous mixture (8 and 16 sccm, respectively) was then introduced into the quartz tube for 20 min, and subsequently cooled to room temperature under an H₂ atmosphere. The furnace pressure throughout the process was maintained at 93.33 Pa by using an advanced pressure control system (APC, MKS Instruments). Then, a two-step hydrothermal method was used to synthesize the vertically aligned CS-NNs onto the graphene surface of 3DG. Firstly, a 3DG substrate was suspended in an aqueous solution containing 0.075 M of cobalt chloride 6-hydrate (CoCl₂·6H₂O, 98%, ACS reagent) and 6.25 wt% urea (Co(NH₂)₂, 99%, ACS reagent) at 150 °C for 3 h, to obtain the vertically aligned 1D cobalt carbonate hydroxide (Co(CO₃)_{0.5}(OH)_x·6H₂O) nanoneedles (CCH-NNs) synthesized onto the graphene surface of 3DG. The obtained specimen was then rinsed with deionized water, and dried at 60 °C in air. Subsequently, the specimen was suspended in an aqueous solution containing 0.25 M of sodium sulfide nonahydrate (Na₂S·9H₂O, 98%, ACS reagent) at 90 °C for 6 h, to perform an ionic-exchange process for the CCH-NNs converted to CS-NNs with the help of the Kirkendall effect.

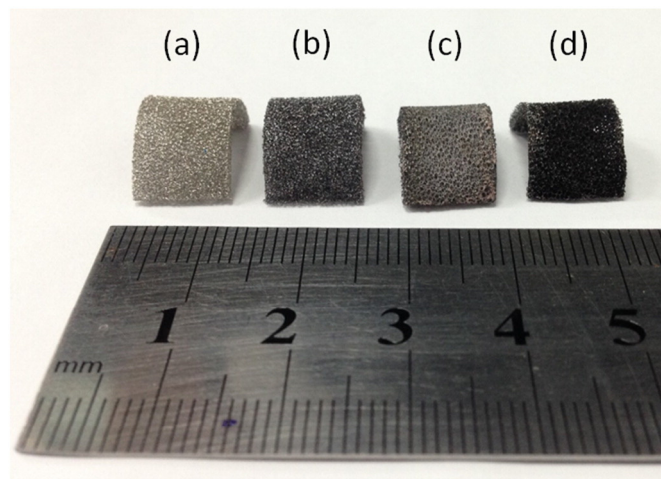


Fig. 1. Photographs of (a) nickel foam, (b) 3DG, (c) CCH-NNs/3DG, and (d) CS-NNs/3DG.

Fig. 1 showed the photographs of the nickel foam, 3DG, CCH-NNs/3DG, and CS-NNs/3DG, respectively.

2.2. Characterization

Raman spectra was performed with a confocal micro-Raman spectroscopy (LABRAM HR 800 UV, Japan) using a He-Ne laser source (632.8 nm, 17 mW) with a spot size of approximately 1 μm to character the features of 3DG. The surface morphologies and the microstructures of the specimens were examined by scanning electron microscopy (SEM, JEOL JSM-6330F) at the acceleration voltage of 10–15 kV. X-ray diffraction (XRD, PANalytical-X'Pert PRO MPD) using monochromatic high-intensity CuKα radiation ($\lambda = 0.1541$ nm) was used to determine the crystallinities of the specimens; the scanning angle ranged from a 2θ of 10° to 80° with a scanning rate of 1.6° min⁻¹.

2.3. Electrochemical measurements

The cyclic voltammetry (CV) was carried out to determine the electrochemical properties by using a potentiostat/galvanostat in a three-electrode electrochemical cell, which was using a saturated calomel electrode (SCE) as the reference electrode, a platinum wire as the counter electrode and the specimens as the working electrode. The electrocatalytic measurements were carried out in 1.0 M aqueous KOH with and without 0.5 M methanol. The CV analyses for evaluating the MOR efficiency of the specimens were conducted at a scan rate of 10 mV s⁻¹ in the potential range between 0 and 0.6 V. An Autolab PGSTAT302N potentiostat (Eco Chemie, Netherlands) was used for all of the electrochemical measurements. All potentials of electrochemical measurements were quoted with regard to the SCE electrode.

3. Results and discussion

3.1. Material characterization

Raman spectroscopy was used to examine the quality of the CVD-grown 3DG. As shown in Fig. 2, the three graphene characteristic peaks at 1353 cm⁻¹, 1586 cm⁻¹, and 2692 cm⁻¹ corresponded to D, G and 2D bands, respectively [30,31]. The peak of D band at 1353 cm⁻¹ corresponded to the disorderly carbon and defects, the small peak of D band indicated the high quality of graphene. The peak of G band at 1586 cm⁻¹ corresponded to the graphitization of the sp²-bonded carbon atoms in the two-dimensional ordered hexagonal graphene. The peak of 2D band at 2692 cm⁻¹ was related to the intervalley double resonant Raman scattering. The Raman intensity of the

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