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A novel three-dimensional interconnected graphene–zinc oxide nanowall via one-step co-electrochemical deposition

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ABSTRACT

One-step co-electrodeposition was applied to prepare graphene–zinc oxide nanowalls (GZNWs) composite, where graphene oxide was electrochemically reduced and zinc oxide was electrodeposited simultaneously. The morphologies and the electrochemical properties of GZNWs were obviously influenced by the electrodeposition time. The contrast experiments illuminate that GZNWs presented superior electrochemical activity.

1. Introduction

As known, the nanostructure of zinc oxide (ZnO) could exist as nanobelts, nanosheets, nanowalls (NWs) and nanorods through chemical [1] and electrochemical preparations [2,3]. For instance, Bai et al. [4] realized the transition of ZnO nanorods to ZnO nanosheets by electrodeposition. Among them, aligned ZnO NWs with special growth direction and large surfaces have attracted great attention in solar cells, liquid crystal displays, optoelectronic devices, photocatalysts for water purification, sensor, and so on [5–8].

Electrochemical route [9–11] for reducing graphene oxide (GNO) has emerged as a mild, green, and fast technique, which does not result in contamination since no reducing agent was used [12,13]. In addition, in graphene-based nanocomposites, hybrids of metal oxide and graphene are widely investigated [14]. It should be noted that one-step co-electrodeposition could electrochemically reduce GNO to graphene, accompanied by the simultaneous deposition of metal oxide. One example is that Dong's group prepared graphene/MnO_2 nanowall hybrids (GMHs) via one-step electrochemical approach, which owns potential application for supercapacitor [15].

In this paper, graphene–zinc oxide nanowall (GZNWs) composite was fabricated by one-step co-electrodeposition. The morphologies and the electrochemical properties of GZNWs were obviously influenced by the electrodeposition time. The contrast experiments illuminate that GZNWs presented superior electrochemical activity.

2. Experimental

Apparatus and reagents: Electrochemical measurements were conducted on a CHI 660C workstation (Shanghai CH Instrument Company, China) with a conventional three-electrode system: a mirror-polished 3 mm glassy carbon electrode (GCE) or modified GCE, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE). The morphology of the samples was characterized via a JSM-6700F scanning electron microscope (JEOL, Tokyo, Japan).

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and Graphite powder (325 mesh, spectral pure) were purchased from Tianjin BASF Chemical Co., Ltd. and Sinopharm Chemical Reagent Co., China, respectively. Sodium sulfate anhydrous (Na_2SO_4) and other reagents were obtained from Shanghai Chemical Reagent Co. Ltd. And all aqueous solutions were prepared with ultrapure water (Aquaplus AWL-1002-P, Ever Young Enterprises Development Co., Ltd., China). Other reagents please see Supplementary material.

Preparation of the graphene oxide (*GNO*): The graphite oxide (GO) was synthesized by Hummers' method according to the literature [16]. (The detailed process please sees Supplementary material) Then a certain mass of resulted GO was dispersed in ultrapure water and exfoliated by ultrasonication for 30 min to fabricate a homogeneous solution of GNO [10,17].

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Preparation of the GZNWs modified electrode: 10 μL of GNO homogeneous solution was pipetted onto the polished GCE and dried naturally (GNO/GCE). Then GZNWs/GCE was obtained by electrodeposition for a given time (10, 20, 30 min). The details please see Supplementary material.

3. Results and discussion

The morphology characterization and possible formation mechanism of GZNWs: Just as shown in Fig. 1, after the GNO/GCE was deposited in 0.1 mol/L $Zn(NO_3)_2$ for 20 min, a large scale (Fig. 1A) and aligned nanowall (Fig. 1B, inclination angle: 30°) of cross-link GZNWs would be observed. The surface morphology of GZNWs was quite different from that of GNO (Fig. 1C), which presents rather smooth. If ZnO is directly processed on the bare GCE without GNO existence under the same conditions, the SEM micrograph of the obtained ZnO/GCE is shown in Fig. 1D. From it, there were only some inhomogeneously dispersed microrodes with unequal diameter formed on the surface of the GCE. It revealed that without GNO, even performed under the same experiments, ZnO nanowall would not formed [15]. Therefore, based on the comparison of SEM micrograph of the single component ZnO/GCE, we speculate that the existence of GNO provided an ideal platform for the formation of GZNWs [15]. Presumably, the oxygen-containing functional groups of GNO play a critical role as active sites in the preparation of ZnO NWs arrays due to the strong electrostatic interactions between the oxygen-containing functional groups and metal ions [18]. Instead of direct oxidation of Zn^{2+} to

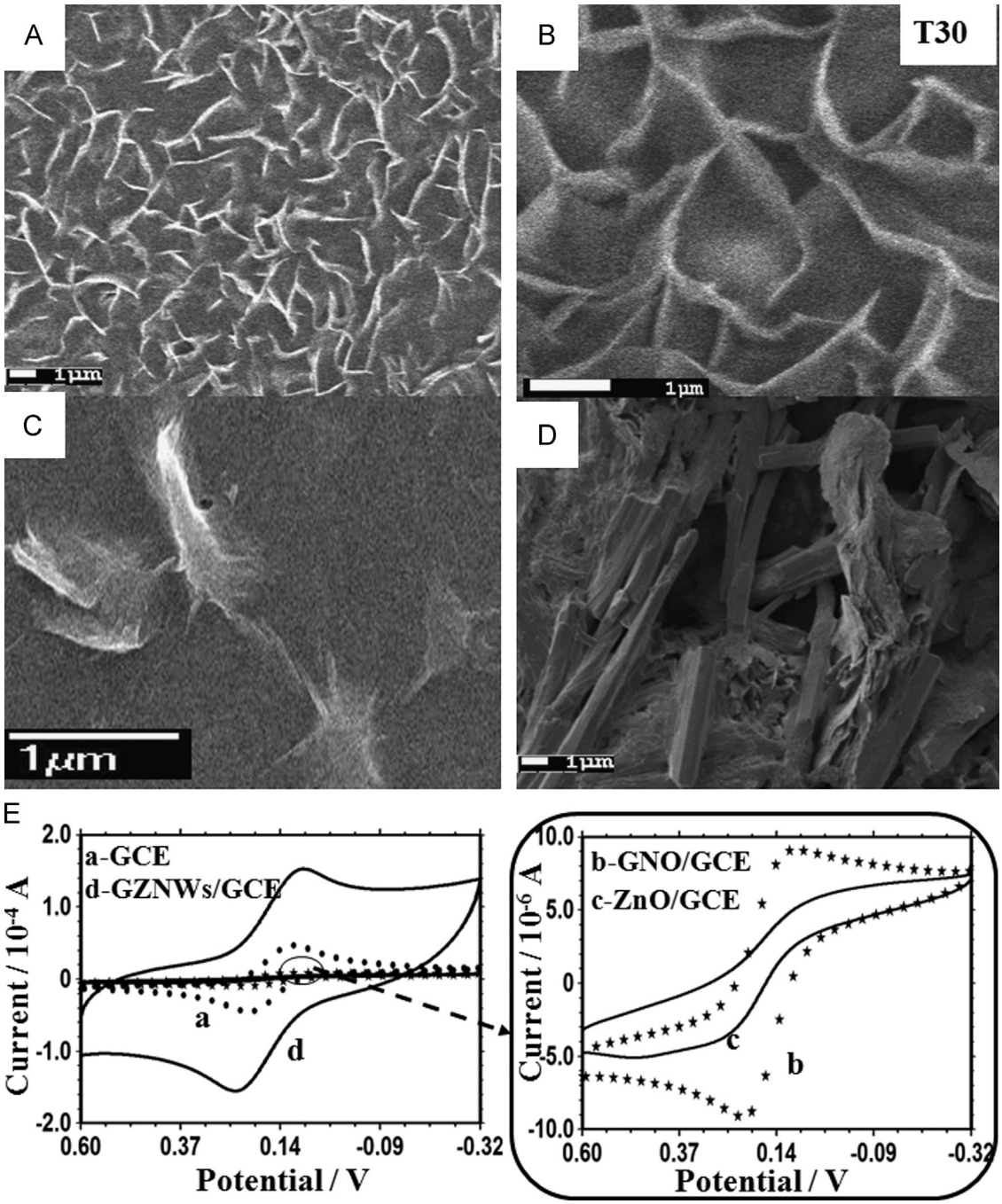

Fig. 1. SEM micrographs of the GZNWs-20 min ((A) top view), GZNWs-20 min ((B) tilted with an inclination angle of 30°), (C) GNO, (D) ZnO without GNO support, and (E) cyclic voltammograms of 2 mmol/L $[Fe(CN)_6]^{3-/4-}$ (1:1) at bare GCE (a), GNO/GCE (b), ZnO/GCE (c) and GZNWs/GCE (d).