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The effect of microstructure and crystal defect on electrochemical performances of MgO nanobelts

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ABSTRACT

The electrochemical properties of one-dimensional (1-D) nanomaterials are highly sensitive to their surface microstructure and crystal defects. MgO nanobelts were obtained by magnesium nitrate decomposition using the direct arc plasma jet chemical vapor deposition technique, with a molybdenum substrate at 950°C for 5 min. The structural details, defects, and electrochemical properties of MgO nanobelts were determined. From high-resolution transmission electron microscopy, the nanobelts contain numerous contacts, rough edges, vacancies, and doping defects. Nanobelts with large surface area and oxide ions in low coordination (with O_{5C}^{2-} and O_{4C}^{2-}, for terrace and edge sites, and O_{3C}^{2-} for corner and kink sites) were seen by various analytical studies. The electrochemical performances of the MgO nanobelts-modified electrode were investigated using standard techniques. The unique nanostructural features and crystal defects endow MgO nanobelt with excellent electrochemical performance as demonstrated in their application in the selective determination of hydroquinone (HQ) and catechol (CC); both can be oxidized at the MgO nanobelt-modified electrode. This nanomaterial allows the sensitive determination of HQ and CC without cross-interference. The MgO nanobelts/glassy-carbon electrode exhibited high sensitivity in the selective determination of HQ and CC, with detection limits of 1×10^{-8} M.

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1. Introduction

Since the discovery of metallic oxide nanobelts, a variety of inorganic materials of nanobelts/ribbons have been synthesized and characterized because of their distinctive geometries, novel physical and chemical properties, and potential applications in electronics,[1] optoelectronics,[2,3] sensor devices,[4] and the biological sciences.[5] One-dimensional (1-D) nanocrystallines possess high aspect ratios, long segments of crystal planes, and a low number of surface defect sites. Attention has focused on the relationship between coordination, electronic properties, and reactivity of ions belonging to the different $Mg^{2+}_{LC}O^{2-}_{LC}$ pairs. The electronic transport can exhibit surprising variations that depend on the type of defects and edge structure.[6] Crystalline defects such as grain boundaries, interfaces, dislocations, and point defects are sources of many interesting properties that are not normally found in perfect crystalline structures.[7,8] Grain boundaries, interfaces, surfaces, and hidden defects are very attractive areas from the viewpoint of lattice discontinuity.[9,10] The electronic

transport through edge-roughened crystalline retains quasi-ballistic transport characteristics of the pristine crystalline. Grain growth, electron transport, and boundary structures are closely related to atomic configurations at grain boundaries and interfaces that are induced by small amounts of dopant and point defects. The electrochemical properties are dependent on the electrical properties of the electrode and modified materials.

Magnesium oxide (MgO) is an important metallic oxide that has potential applications such as catalysts, refractory additives, paint, and superconductor products. Because of its high specific surface area and unique biocompatible properties, MgO nano-/microstructures can also be used to fabricate highly sensitive amperometric biosensors; for example, the MgO nanoparticle-based H_2O_2 biosensor,[11] the MgO polyhedral nanocage- and nanocrystal-based glucose biosensors,[12] and the tubular tetrapod MgO-based H_2O_2 biosensor.[13] However, in most of these biosensors, the MgO nanostructures can serve as high-sorbing material for enzyme immobilization, which can help to achieve higher sensitivities for MgO-based biosensors. The MgO (111) nanobelts with zigzag edges show metallic behavior, whereas the MgO (111) nanobelts with armchair edges and MgO (100) nanobelts exhibit semiconductive properties.[14] The electronic structures of the corresponding nanobelts are revealed to be dependent on facets, edge

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features, and width of the nanobelts. Oxide ions in low coordination (O_{LC}^{2-}) play a major role in adsorption and catalysis properties of MgO powders.[15]

We report the synthesis of MgO nanobelts by direct current (DC) arc plasma jet chemical vapor deposition (CVD) chamber and analysis of electrochemical performances; results show that the MgO nanobelts possess the strongest electrocatalytic properties towards electro-oxidation of phenolic compounds. In addition, the MgO nanobelt has been applied to the simultaneous determination of hydroquinone (HQ) and catechol (CC) with high selectivity.

2. Experimental procedures

2.1. Preparation of the MgO nanobelts

MgO nanobelts were prepared by using direct current (DC) rc plasma jet chemical vapor deposition (CVD) method, and the details were described in earlier studies.[16,17] The MgO nanobelts prepared at 950 °C for 5 min.

2.2. Materials characterization

The morphology and microstructure of the samples were characterized by field emission scanning electron microscopy (SEM) (JEOL JSM-6700F), and transmission electron microscopy (TEM), (Philips Tecnai F20, 200 kV). Phase identification was done by the powder X-ray diffraction (XRD), (Rigaku D/max-2500/PC, CuK$_\alpha$, λ = 0.15406 nm). The 2θ is ranged from 10 ° to 90 °. Functional groups on the samples were analyzed by fourier transform infrared spectroscopy (FT-IR) (Bruker VERTEX 70). The photoluminescence spectrum (PL) was characterized in the range of 300–700 nm by a fluorescence photoluminescence spectrophotometry (Hitachi F-4500, 150 W xenon lamp). The thermal decomposition behavior of the sample was detected by a thermo-gravimetric analyzer (TGA), (Netzsch STA 409 C, Germany), carried out in dynamic air with a heating rate of 10 °C/min.

2.3. Electrochemical measurement

The measurements of electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and differential pulse voltammetry (DPV) were carried out using an electrochemical workstation (Zennium/IM6, Zahner-Electrik, Germany). A three-electrode configuration, consisting of an Ag/AgCl (3 M KCl) electrode as the reference electrode, a platinum wire as the counter electrode, and a glassy-carbon electrode (GCE) with the active material deposited on it as the working electrode, was used for the measurements. Prior to modification, the GCE (3 mm in diameter) was first polished with alumina powder, then rinsed ultrasonically with dilute nitric acid, ethanol, and deionized water, and dried under an infrared heat lamp. Five microliters of the MgO nanobelts/chitosan composite (2 mg/L) was dropped on a well-polished GCE, and dried slowly; this yielded the MgO nanobelt/CS/GCE. All measurements were performed at room temperature.

3. Results and discussion

The morphology and size of the products were investigated by SEM and TEM. Fig. 1a and b shows typical SEM and TEM images of the as-prepared MgO nanobelts. The SEM image (Fig. 1a) indicates the as-obtained MgO consists of a large number of 1-D nanobelts with length in the range of 100 nanometers to several micrometers and width ranging from 20 to 50 nm. A lower magnification TEM (Fig. 1b) image is consistent with the SEM image in width and length of nanobelts. The micrographs in Figure 1 show that the nanobelts

contain numerous contacts. The phase and structure of as-prepared MgO nanobelts were studied by X-ray powder diffraction (Fig. 1c). Five main peaks located at 36.78, 42.76, 62.14, 74.54, and 78.46° can be indexed to the (111), (200), (220), (311), and (222) diffraction peaks of cubic MgO phase (JCPDS# 45-0946, a = 0.421 nm). Moreover, the XRD pattern shows diffraction peaks of the cubic Mo (JCPDS# 89-5023 a = 0.3145 nm) phase. The growth of MgO nanobelts is initiated by Mo catalyst nanoparticles via a catalyst-assisted vapor-liquid-solid (VLS) process, and a side growth along the belt width direction via a VS process is also suggested.[18]

The MgO nanobelts contain diverse surface defects as revealed from the FTIR, PL emission, and TGA studies. The FTIR spectrum (Fig. 1d) of MgO nanobelts shows many absorption bands. The peak centered at 3610 cm^{-1} indicates the presence of hydroxyl groups (-OH) on the crystal face at low-coordinate or defects sites.[19] The broad peak at 3471 cm^{-1} indicates the presence of four-coordinate hydroxyl groups interacting with surface O_{LC}^{2-} ions.[20,21] The broad vibration peak at 3191 cm^{-1} is assigned to the stretching mode of the hydroxyl group in the water molecules, whereas those at around 1654 cm^{-1} are assigned to bending modes. In addition, a sharp peak corresponding to the adsorption of gas-phase CO_2 is visible at around 2360 and 2337 cm^{-1}, and bands at 860, 1082, and 1481 cm^{-1} are attributed to the CO_3^{2-} absorption bands.[21] These carbonates are absorbed on the MgO surface exposed to the atmosphere. The absorption peak centered at 974 cm^{-1} indicates the presence of H$^-$ ions.[19] Hydrogen gas was used in the synthesis of MgO nanobelts. The H$^-$ group formed by the heterolytic splitting of H$_2$ is located at anionic-type vacancies present at inverse corner sites. The PL spectra (Fig. 1e) of MgO nanobelts were measured at an excitation wavelength of 292 nm. The spectrum de-convolutes into eight emission bands, including six UV emission bands at *ca.* 309 (4.01), 330 (3.76), 344 (3.60), 358 (3.46), 372 (3.33), and 394 nm (3.15 eV), and two blue bands at *ca.* 415 (2.98) and 460 nm (2.70 eV). These bands are not band-gap emissions, so the emission was attributed to various structural defects. The emission bands at 309 (4.01), 330 (3.76), 344 (3.60), and 358 nm (3.46 eV) were attributed to oxide ions in low coordination (O_{5C}^{2-}) present in terrace sites.[15,22] The emission band at 372 nm (3.33 eV) is reported to correspond to the near-band-edge peak, attributed to oxide ions in low coordination (O_{4C}^{2-}) present at edge sites.[23,24] The energy level at 394 nm (3.15 eV) is attributed to oxide ions in low coordination present in corner and kink sites (O_{3C}^{2-}).[22,24–26] Energy levels at 415 (2.98) and 460 nm (2.70 eV) were attributed to F centers. [23,27,28] F centers are oxygen vacancies with electrons. The excited-state F (2p) energy levels are at about 3 eV and about 2.7 eV [27]. Therefore, the UV emission is thought to be associated with oxide ions present with low coordination, and the blue emission related to F color centers.[29] A typical TG-DTG plot is shown in Fig. 1f. The weight loss below 100 °C is due to the release of the humidity adsorbed during storage in ambient air. The dehydration of magnesium carbonate occurred over the temperature range 100–200 °C. The mass loss from 200 to 393 °C is assigned to the evolution of CO_2. The dehydration of Mg(OH)$_2$ occurred in temperatures ranging from 393 to 500 °C. The DTG data showed a sharp peak within the temperature range 500–612 °C, which might be connected with the elimination of the structural water. Thus, Figs. 1d-f indicates the presence of surface-absorbed carbonate species, bound and free hydroxyl groups, and various O_{LC}^{2-} ions on the MgO nanobelts.

Fig. 2 shows various structural aspects of MgO nanobelts that were investigated. In particular, Fig. 2a shows an HRTEM image and the corresponding fast Fourier transform (FFT) pattern of a single nanobelt. The nanobelt had a single-crystal structure. The fringe spacing was 0.21 nm, which coincided with the {200} interplanar spacing. This suggested the nanobelt had growth directions along the <100> axes, and that the nanobelt surface is the {100}