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Single crystal cupric oxide nanowires: Length- and density-controlled growth and gas-sensing characteristics

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HIGHLIGHTS

- Large-scale CuO nanowires were controllably synthesized by a simple method.
- The CuO nanowires were clearly exhibited as p-type gas sensors.
- The CuO nanowires sensors have good response to C_2H_5OH and H_2 gases.
- Novel gas sensors based on hetero-junction of p-type and n-type NWs can be developed.

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ABSTRACT

Nanowire structured p-type CuO semiconductor is a promising material for gas-sensing applications because of its unique electrical and optical properties. In this study, we demonstrate the length and density controlled synthesis of single crystal CuO nanowires (CuO NWs) by a simple and convenient thermal oxidation of high-purity copper foils in ambient atmosphere. The density and length of the CuO NWs are controlled by varying the oxidation temperature and heating duration to investigate their growth mechanism. As-synthesized materials are characterized by different techniques, such as X-ray diffraction, field emission-scanning electron microscopy, and high-resolution transmission electron microscopy. The gas-sensing characteristics of the CuO NWs are tested using hydrogen and ethanol gases. The results show that the CuO NWs could potentially sense hydrogen and ethanol gases given a working temperature of 400 °C.

1. Introduction

The development of a low-cost and scalable gas sensor for the detection of toxic, combustible, explosive and flammable gases with fast response and high sensitivity is extremely important because of its huge potential applications in various fields such as environmental monitoring and disease diagnosis [1]. For instance, receiving early warning of explosive gas leakage could potentially prevent disaster, and the ability to trace VOCs at low concentrations can help diagnose early state of lung cancer [2]. In the early 1960s, Seiyama, and Taguchi introduced a sensor that operated based on the variations in the resulting electrical resistance (conductance) of a chemical reaction and/or the absorption of the analytical species and the surface of metal oxide semiconducting layers [3]. Since then, research on resistive gas sensors has received enormous attention [4]. Up until now, minimization of production cost and the improvement of sensor performance still garner massive interest in the field of gas sensor technology.

On the other hand, nanowire-structured cupric oxide material has also received a lot of attention because of its facile and low cost synthesis and potential applications in various fields, such as heterogeneous catalysts, electrochemical capacitors, photovoltaic cells, field emission nano-devices and gas sensors [5]. Cupric oxide is known as an environment-friendly and thermally stable p-type semiconductor with a bandgap of ~1.2 eV; thus, it is believed to be an excellent candidate for long-term stable and low-power consumption sensing devices. Indeed, the particles, plates [6], thin film [7], nanosheets [8], and nanowires of CuO were fabricated for CO, NO_2, H_2, and H_2S sensing applications [9,10]. According to the gas-sensing mechanism, the gas adsorption/desorption processes take place on the surface of sensing materials which lead to the expansion or reduction of the electron depletion (n-type) or accommodation (p-type) regions and result in varying the sensing conductance, thus large sensing sites are advantages for enhancement of sensor performances. In addition, small size compatible with the Debye length of the sensing crystals was believed to significantly enhance the sensitivity of devices [11]. Therefore, the

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nanowire structures exhibit significant advantages, such as high length-to-diameter ratio and small-diameter compatibility with Debye length [12]. These characteristics promise excellent sensitivity as well as cost efficiency with regards to device fabrication. Reports on the synthesis and application of CuO NWs for detecting toxic and flammable gases are increasing, where the CuO NWs could be grown by various methods, such as chemical routes [13], template ways [14] and eletrospinning techniques [15]. CuO NWs were also grown by simply heating the copper foil/wire in ambient atmosphere [16]. This method is one of the most convenient and simple ways to synthesize CuO NWs with high-quality single crystals [17]. However, large quantities of NWs are needed for mass production and the cost of producing these sensing devices must be lowered. Therefore, controlling the length and density towards the scalable synthesis of high-quality CuO NWs is still an interesting undertaking. In addition, the proper application of CuO NWs for gas sensors is also important.

In this study, we demonstrate the density- and length-controlled synthesis of the CuO NWs by varying the oxidation temperatures and heating times. The growth mechanism of the CuO NWs is obtained by directly heating Cu foils in ambient atmosphere and is also clarified by comparing the surface morphology of the Cu foil and the Cu thin film after growth. The growth of CuO NWs is believed to obey the vapor solid (VS) model, where a higher surface roughness is preferred for the growth of the CuO NWs. The CuO NWs obtained by directly heating Cu foils are then used for low-concentration ethanol and hydrogen sensor applications.

2. Experimental

CuO NWs were synthesized by directly heating Cu foils in ambient atmosphere with humidity of about 60–90% [20]. In a general synthesis process, the commercial Cu foils were cut into small pieces (1×1 cm^2), washed with acetone for 15 min, and then rinsed in distilled water to remove all organic contamination. The small Cu-foil pieces were dipped in hydrochloric acid solution (1 M) solution for a few minutes to clean the unwanted oxide layer on the surface. The samples were then rinsed once more with distilled water and blown with clean, compressed gas to dry. Thereafter, the Cu foils were loaded into the center of a quartz tube to grow the CuO NWs. The CuO NWs were grown by increasing the temperature of the quartz tube to 400 °C, 500 °C, or 600 °C and maintained for various time periods. The furnace temperature was

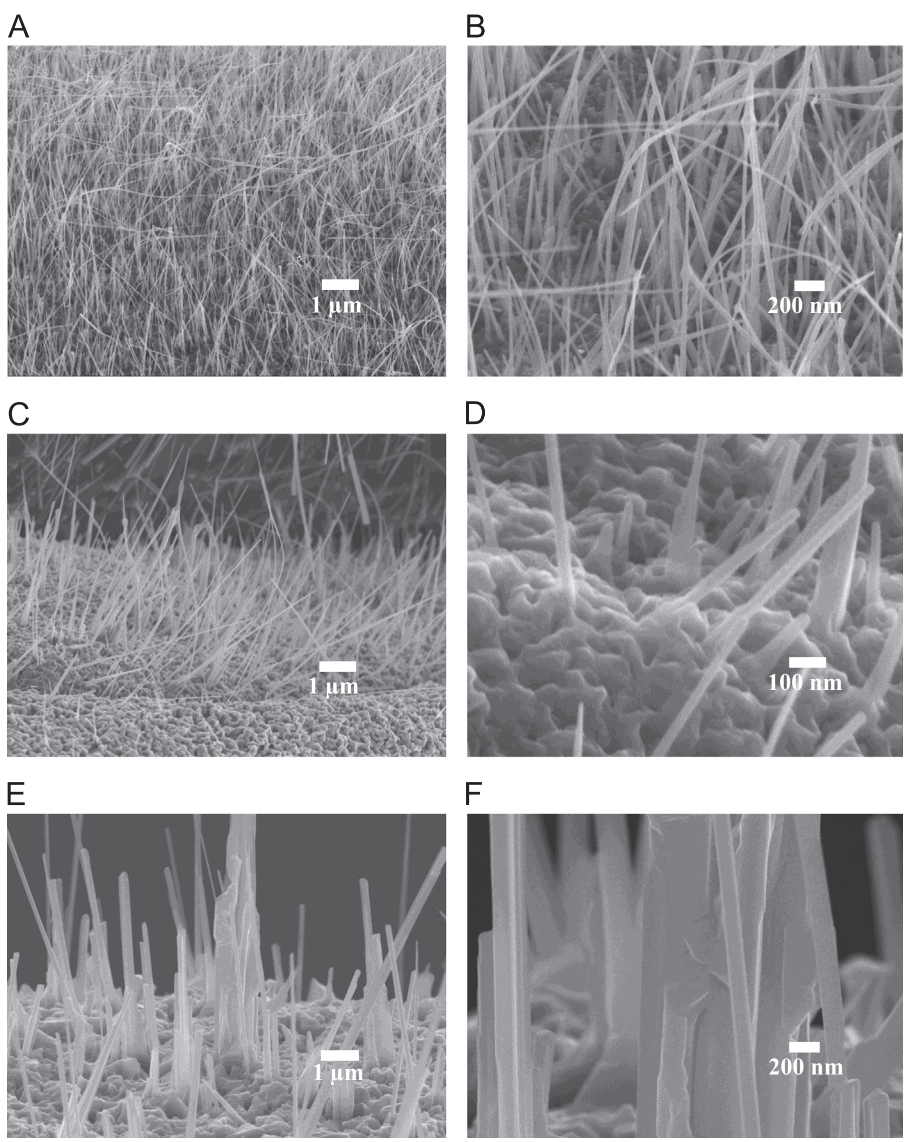

Fig. 1. CuO NWs grown by heat-treated Cu foils in ambient atmosphere for 2 h at different temperatures: ((A), (B)) 400 °C, ((C), (D)) 500 °C, and ((E), (F)) 600 °C.