



Vertically aligned single-crystalline ultra-thin CuO nanosheets: Low-temperature fabrication, growth mechanism, and excellent field emission



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ABSTRACT

An effective and one-step solvothermal process is developed to fabricate vertically aligned ultra-thin CuO nanosheets with high-quality single crystalline structure on Cu substrate at low temperature of 90 °C. The thickness and size of the prepared nanosheets can be tailored by changing reaction duration and temperature. On the basis of experimental results, a possible mechanism for the formation of the vertically aligned ultra-thin CuO nanosheets is speculated. Moreover, the prepared ultra-thin CuO nanosheets exhibit excellent field emission (FE) properties, a low turn-on electric field of 2.19 V/μm and a high current density of 4.5 mA/cm² at 8.23 V/μm can be realized from the optimized sample. More importantly, the optimized sample also shows excellent FE stability with fluctuations within 2%. Based on temperature-dependent FE measurement, the stable FE property can be attributed to the low local heating effects of sheet-like CuO emitters, originating from their superior heat dissipation ability and low Joule heating.

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1. Introduction

High-performance field emitters are of great technological promise as they serve as potential building blocks for microelectronic devices such as X-ray sources, microwave amplifiers, and flat panel displays [1–3]. CNTs have proven their candidature as charming field emitters owing to their low turn-on field and high emission current. Nevertheless, CNTs as field emitters can quickly degrade by oxidation and heating effects in the interface of CNTs film/conductive substrate, which have hindered their practical applications in FE [4,5]. Thus, a wide variety of metal oxide nanomaterials have been explored to expand the pool of candidates for FE owing to their superior antioxidation ability which can operate under unfavorable environment with relatively high oxygen partial pressure in their applications [6–10].

Cupric oxide (CuO), a typical p-type metal oxide, has emerged as an ideal candidate for FE [10–12], because of its lower work function (2.5–2.8 eV) compared with other extensively studied metal oxides such as ZnO (5.3 eV), SnO₂ (4.3 eV), Fe₂O₃ (5.6 eV), and TiO₂ (4.5 eV) [6–10]. Moreover, the narrow bandgap of CuO (1.2 eV) means a high electron high conductivity [13], which is conductive to make most injected electrons shuttle easily to

emission sites and diminish the voltage drop along the CuO emitters, resulting in the enhancement of the effective field at the emitter tip. Up this point, various CuO nanostructures including nanorods, nanofibers, nanowires and nanoparticles have been developed for FE and some significant progresses have been achieved [10–14]. However, the CuO field emitters in these works were all synthesized via thermal oxidation of Cu foil in air at high temperature, which is too energy consuming and hinders mass production. Moreover, the large stress between the CuO film and Cu substrate formed by the high-temperature heating usually leads to the poor adhesion of CuO film, which is also a common obstacle. Alternatively, solution methods have been explored to synthesize CuO field emitters because of their remarkable simplicity, cheapness, low-temperature process and flexibility to prepare various nanostructures [15–17]. For example, Jana et al. [18] synthesized uniform CuO nanostructures by a simple wet chemical route at room temperature, which showed turn-on fields in the range of 6–11.3 V/μm. Recently, CuO nanoknife arrays on flexible carbon fabric were successfully prepared at 80 °C and a maximum emission current density of 1.6 mA/cm² can be realized [19]. These works revealed the feasibility of solution methods to prepare CuO nanostructures for FE and shed light on their potential applications. Even so, the related research about solution-processed CuO field emitters is in its infancy. Their performances still cannot meet the requirement of practical application in FE, in particular

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the high turn-on electric field and the relatively low emission current density.

Additionally, long-term FE stability of field emitters is quite vital for their practical device applications. It has been demonstrated that the local heating effect is a major cause of the emission current instability for metal oxide emitters [20]. To weaken the local heating effect of CuO based field emitters; it is vital to construct a CuO nanostructure with a geometric shape similar to the heat release sheets, which possess superior heat dissipation ability and low Joule heating compared to other types of emitters such as nanowires or nanorods. More importantly, the sheet-like CuO field emitter also preserves the character of the large field enhancement factor, which is beneficial to lower turn-on field and enlarge FE current density. Taking these factors mentioned above into consideration, it is highly desirable to develop a low temperature method to synthesize sheet-like CuO field emitters for producing excellent FE properties with good stability.

In this work, a facile and effective solvothermal route is developed to controllable fabrication of vertically aligned ultra-thin CuO nanosheets on Cu substrate at a low temperature of 90 °C. The as-synthesized ultra-thin CuO nanosheets exhibit high purity single crystalline, and their thickness and size can be controlled by adjusting the reaction conditions such as temperature and reaction duration. On the basis of experimental results, a possible mechanism for the formation of this CuO nanostructure is speculated. Moreover, the as-formed ultra-thin CuO nanosheets are in effective contact with the Cu substrate and preserve the character of the large field enhancement factor. Therefore, a low turn-on electric field of 2.19 V/μm, and a high current density of 4.5 mA/cm² at 8.23 V/μm are realized from the optimized sample. Remarkably, due to its superior heat dissipation ability and low Joule heating, the optimized sample also shows excellent FE stability with fluctuations within 2%. Temperature-dependent FE measurements are also conducted to investigate the thermal effect on the emission process of the vertically aligned ultra-thin CuO nanosheets, which is conducive to understand the observed excellent FE stability from the regarded sample.

2. Experimental details

Cu foils (1 cm × 2 cm) with a thickness of 0.4 mm were cleaned by a consecutive ultrasonication in acetone, ethanol, deionized water and then in 1.0 M HCl solution for 15 min. After rinsing with ethanol and deionized water and drying in nitrogen stream, they were immersed in the mixture of 2.5 M NaOH and 0.25 M (NH₄)₂S₂O₈ and maintained at different temperatures 90 °C for different durations of 5–120 min. Then, the Cu substrates with black precipitate were rinsed extensively with ethanol and deionized water for several times and dried in nitrogen stream. For investigation the effect of temperature on the morphology of CuO nanosheet, the sample grown for 100 min at different reaction temperatures of 30, 50, and 70 °C were also prepared following the above process.

The surface morphologies of as-prepared samples were examined by a field emission scanning electron microscopy (FESEM, JSM-6701F, operated at 5 kV). The structure of the samples was analyzed by X-ray diffraction (XRD) using a Rigaku D/max-2400 diffractometer (with Cu Kα1 0.154056 nm radiation at 40 kV and 150 mA). Micro-Raman measurements were carried out using a Horiba HR800 Raman system at room temperature, and a 632.8 nm line from a He-Ne laser was utilized as the excitation laser. A high resolution transmission electron microscope (HRTEM, Tecnai-G2-F30, operated at 300 kV) was used to study the structure with corresponding selected area electron diffraction (SAED) pattern. The FE properties of as-prepared samples were measured with a diode structure in a vacuum chamber with a base pressure of 5.2 × 10⁻⁹ Pa. The vacuum system was consisted of a vacuum chamber, a compound molecular pump with the ultimate pressure of 6.0 × 10⁻⁶ Pa, and a mechanical pump. The cathode consisted of the samples and a polished copper rod served as the anode that was kept 50 μm away from the samples by a mica spacer containing a hole (~1 mm²) in the center. To guarantee the outgassing in the small space, we employ a two-layer mica spacer. The bottom one contains a circular hole (~1 mm²) in the center and the top one contains a rectangle hole (1 mm in width and 5 mm in length) in the center. The emission current was measured under varying applied voltage (up to 3500 V) and a multiple number of samples were tested to ensure the repeatability and reliability of the obtained results.

3. Results and discussion

Fig. 1 illuminates the representative FESEM images of the CuO nanosheets synthesized in the mixture of 2.5 M NaOH and 0.25 M (NH₄)₂S₂O₈ at 90 °C with different reaction times. As exhibited in Fig. 1(a–d), the films are uniform in a large-scale and the surface rough gradually increase with the prolonging of growth time, indicating the growing of the CuO film with the increase of reaction time. To further reveal the details of the CuO film, high-resolution FESEM images are given in Fig. 1(e–h). It is obvious that the CuO film is composed of CuO nanosheets with maple-like shape. Meanwhile, the morphologies of the CuO nanosheets show some differences depending on the reaction time. At a short reaction time of 60 min, dense and small CuO nanosheets with thicknesses of ~10–16 nm are formed (Fig. 1(e)). And most of nanosheets are randomly accumbent. With an increase in reaction time to 80 min, larger CuO nanosheets with similar thicknesses are obtained. Moreover, more vertical aligned CuO nanosheets emerge on the surface (Fig. 1(f)). By increasing the reaction time to 100 min, high-quantity, smooth, and ultra-thin CuO nanosheets with thicknesses of ~10–13 nm grow on the substrate, as expressed in Fig. 1(g). More importantly, even though the CuO nanosheets get more slender and relatively sparse, most of the CuO nanosheets turn into vertically aligned, which is beneficial to FE. When the temperature is prolonged to 120 min, the CuO nanosheets become dense and thicker. The thickness is ~25–30 nm. In addition, some larger CuO nanosheets bundled together homogeneously embed into underlied layer comprised of small CuO nanosheets, tending to form a hierarchical structure (as shown in Fig. 1(d)). Thus, the reaction time plays a key role in determining morphologies of the CuO nanosheets.

XRD was employed as a bulk analysis technique to reveal the compositional homogeneity across the nanosheet samples. A resultant XRD diffractogram of the ultra-thin CuO nanosheets grown for 100 min (Fig. 2(a)) shows major reflections of a monoclinic CuO structure with C2/c symmetry matching well with the literature data (JCPDS Card, No. 05-0661) [10,14], except for the existence of typical diffraction peaks of metallic copper. The sharp diffraction peaks indicate the good crystallinity of the product. The relative intensities of the peaks differ from the standard pattern of a bulk material because of the preferred orientation and distribution of ultra-thin CuO nanosheets. To further investigate the surface structure of the ultra-thin CuO nanosheets, Raman scattering was conducted. As illustrated in Fig. 2(b), there are three Raman peaks at 287.3, 335.7 and 627.1 cm⁻¹, with the second one being the weakest and the third being broad. In comparison with the vibrational spectrum of a CuO single crystal, the peak at 287.3 cm⁻¹ to the A_g mode and the peaks at 335.7 and 627.1 cm⁻¹ to the B_g modes, which are comparable to the reported data for nanocrystal CuO [21]. It is noticeable that there are no additional peaks related to other phases such as Cu₂O and Cu(OH)₂, which confirms the single phase of the ultra-thin CuO nanosheets. A high-resolution transmission electron microscopy (HRTEM) image of the single nanosheet is shown in Fig. 2(c). The fringe spacing of 0.273 nm matches well the distance between the (–1 1 0) planes of monoclinic-phase CuO. The corresponding SAED pattern (Fig. 2(d)) reveals that the nanosheet is high-quality single-crystalline structure and grows in the [0 1 0] crystallographic direction of the monoclinic CuO [22]. The results of the HRTEM and electron diffraction analysis confirm the presence of high-quality single-crystalline ultra-thin CuO nanosheets oriented along the [0 1 0] direction.

The oxidation of copper in air or under humid conditions is a well-known phenomenon and the reaction proceeds very slowly due to the passivation of the surface by the formation of an oxide layer [23]. In the presence of NaOH and (NH₄)₂S₂O₈ as an oxidizing

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