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Fabrication of copper nanowires by a solid-state ionics method and their surface enhanced Raman scattering effect

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ABSTRACT

Copper nanowires were prepared by a solid-state ionics method using fast ionic conductor $Rb_4Cu_{16}Cl_{13}I_7$ films under a direct current electric field (DCEF). The surface morphology of the copper nanowires was characterized by scanning electron microscopy (SEM). Rhodamine 6G (R6G) aqueous solutions were used as probe molecules to detect the Raman enhancement performance of the copper nanowires substrates. We found that the long-range disorder and short-range order copper nanowires were prepared by a solid-state ionics method. The diameters of nanowires ranged from 50 to 100 nm and the nanowires were bamboo-shaped. The limiting concentrations of R6G for the prepared copper nanowires SERS substrates is 10^{-11} mol/L.

1. Introduction

Nanowires have attracted widespread attention by scientists of condensed matter physics, chemistry and material science because of excellent optical properties, electrical properties and mechanical properties and so nanowires have become research hotspot of nanomaterials [1]. Metal nanowires assemble the characteristics of one-dimensional nanostructure materials and metal so they have unnegligible potential application prospect in the fields of optics, electricity and magnetics [2,3]. One-dimensional copper nanowires have potential application prospect in the fields of microelectronic devices, chemistry and biosensor because of high conductivity and so they have attracted wide attention at home and abroad [4].

Since surface enhanced Raman scattering (SERS) was discovered it has become a popular high surface-sensitivity research tool in surface science and in nanoscience. Along with the recent rapid development of nanotechnology, SERS is endowed with new developmental power [5]. SERS substrates are directly related to the enhancement effect of SERS. Active substrates with a high enhancement ability, reproducibility and high uniformity will receive significant attention. [6].

Currently, the liquid phase synthesis method is preferred for the synthesis of nanowires [7,8]. In this paper, we report a solid-state ionics method for the synthesis of copper nanowires for application as SERS substrates using fast ionic conductor films under a direct current electric field (DCEF) [2]. This method can be used to prepare copper nanowires in the solid state and the further integrated manufacturing can be made *in situ* after the preparation of the copper nanowires. The method has the characteristics of flexibility and diversity compared with more mature methods involving templates [9]. The micromorphology of the prepared copper nanowires was characterized and the SERS characteristics of Rhodamine 6G (R6G) were determined. A new type of nanometer SERS substrate was developed and the Raman enhancement mechanism of the copper nanowires was explored.

2. Experimental

Equipments and materials: For the experiments we used vacuum thermal evaporation plating equipment (type DM-450) made by the Beijing Instrument Factory. The vacuum extraction system comprised a mechanical pump (type XK-10A) and a molecular pump. A measuring Source-Meter (type Keithley 2400) was used to control the impressed current I. Thermionic field emission scanning electron microscopy (SEM, type LEO1530) was used to observe the morphology of the prepared copper nanowires. A confocal micro-Raman spectrometer (type RM2000) was used to measure the Raman spectra of the R6G solutions on the prepared copper nanowires SERS substrates.

Analytical reagent grade RbI ($\geq$99.0%), CuCl ($\geq$97.0%) and R6G ($\geq$99.5%), chemical reagent grade CuI ($\geq$99.0%) and copper powder ($\geq$99.5%) were used in the investigations. R6G solutions were prepared using deionized water.

Preparation of the fast ionic conductor films: Fast ionic conductor films were used to conduct metal ions for the preparation of the nanomaterials by the solid-state ionics method. Metal ions

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in the fast ionic conductor films are not bound within a fixed crystal lattice but travel in "ion channels" in the films under the DCEF [9,10]. The molar ratio of RbI, CuCl to CuI is 4:13:3 for the preparation of the $Rb_4Cu_{16}Cl_{13}I_7$ films in the experiment. The three materials are mixed, ground and evaporated to conduct cuprous ions, and the films have high cuprous ionic conductivity [11]. The evaporation conditions involved a vacuum of about 10^{-4} Pa and a substrate temperature of about 80 °C. The films were crystallized for 1 h at 120 °C to increase the cuprous ions conductivity.

Preparation of the copper nanowires: Fig. 1 shows that the process flow diagram for the preparation of the copper nanowires using the fast ionic conductor $Rb_4Cu_{16}Cl_{13}I_7$ film.

Fig. 1 shows that the substrate selected a clean quartz glass (Fig. 1a) and two parallel copper films with a thickness of about 1 μm that was deposited by vacuum thermal evaporation on the

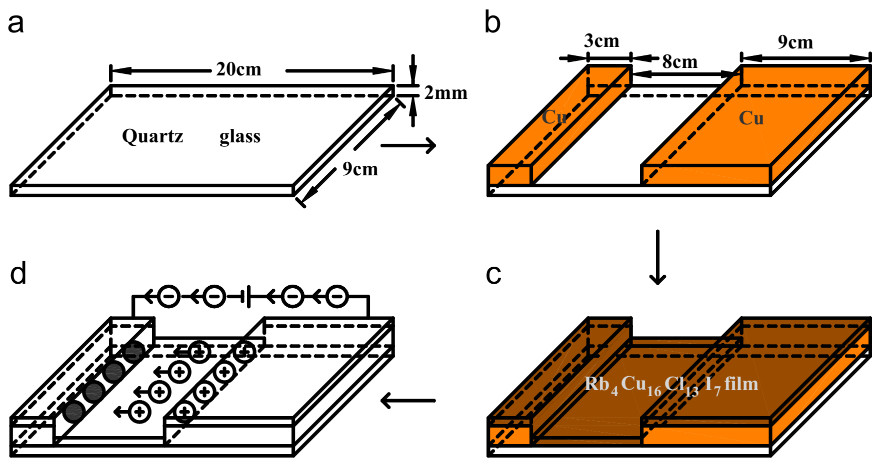

Fig. 1. Process flow diagram for the preparation of the copper nanowires using the fast ionic conductor $Rb_4Cu_{16}Cl_{13}I_7$ films: (a) clean quartz glass substrate; (b) the deposited copper electrodes on the two ends of the substrate; (c) the $Rb_4Cu_{16}Cl_{13}I_7$ films deposited over the whole substrate and (d) applying a direct current electric field.

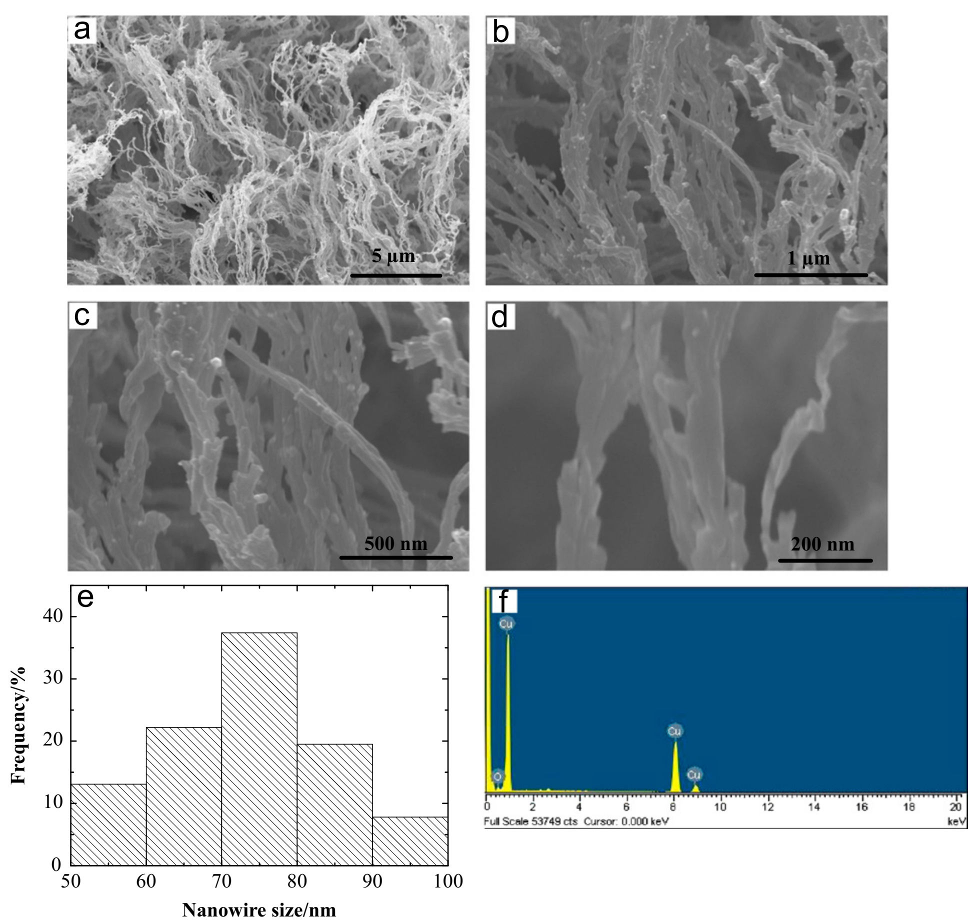

Fig. 2. SEM micrographs (a,b,c,d), size distribution diagram (e) and EDS graph (f) of the grown copper nanowires when the impressed current *I* between the two ends of the electrodes was 12 μA.