Fabrication and characterisation of Cu_2O nanorods array by anodic oxidation method

Yanqun Lv[1], Baozhu Shi[1], Xiaofa Su[1], Yunhui Li[1], Jing Sun[1], Jing Shao[1], Lecheng Tian[1] ✉, Juan Ding[2]

[1]*Department of Chemistry and Chemical Engineering, Changchun University of Science and Technology, Changchun 130022, People's Republic of China*
[2]*Zhuhai College, Jilin University, Zhuhai 519041, People's Republic of China*
✉ *E-mail: tlc0915@126.com*

Published in Micro & Nano Letters; Received on 28th August 2017; Revised on 5th October 2017; Accepted on 25th October 2017

Cuprous oxide (Cu_2O) nanorods array was successfully fabricated on copper substrate by the anodic oxidation method. Field emission scanning electron microscopy images indicated that the fabricated Cu_2O nanorods grew vertically from the substrate. The Cu_2O nanorods had an approximately average diameter and length of 40 and 400 nm, respectively. Furthermore, the photoelectric output property of Cu_2O nanorods array as a photoanode was investigated.

1. Introduction: Cuprous oxide (Cu_2O) had attracted attention due to its excellent photocatalytic activity and photoelectric properties [1, 2]. Therefore, a great deal of effort had been made to synthesise Cu_2O nanomaterials for the past decade. Up to present, various shapes of Cu_2O nanomaterials had been prepared, including nanowire [3], nanorod [4], nanospheres [5], flower-like [6] and nano-cage [7]. There were many methods to synthesis Cu_2O nanomaterials including hydrothermal method [8], reflux method [9], thermal decomposition method [10], microemulsion method [11], solvothermal method [12] etc. The anodic oxidation method had been widely used in the fabrication of TiO_2 nanotube arrays with controllable morphology and ordered arrays [13]. However, there were few reports on the use of copper as a substrate for preparing Cu_2O nanorods array.

In this Letter, we used a simple one-step and template-free method to prepare Cu_2O nanorods array at room temperature. The field emission scanning electron microscopy images showed that the Cu_2O nanorods array had been prepared successfully. We also examined its photoelectrochemical characterisation. The experimental result showed that it will have potential applications in the field of photovoltaics in the future.

2. Experimental section

2.1. Chemical synthesis: Before performing the experiment, the copper substrate (1 cm × 3 cm, 0.5 mm thick, 99.99% purity) had been cleaned by an ultrasonic cleaner for 15 min in acetone, isopropanol, anhydrous ethanol and double-distilled water, respectively. In a standard experiment, anodic oxidation process was carried out using a two electrodes system with a graphite plate was used as the counter electrode and a Cu sheet as the working electrode. Direct current voltage stabilised power was supplied as voltage source driving anodic oxidation process. The distance between the two electrodes was 4 cm. Anodic oxidation operation was performed in 3.0 M KOH solution at 0.4 V for 1 h at room temperature. After that, these samples were annealed at 300°C for 1 h, and then used for characterisation analysis.

2.2. Characterisation: The crystal structure was identified by X-ray diffraction (XRD) analysis, which was performed using a Rigaku D/max-RA XRD diffractometer with Cu Kα radiation ($\lambda = 0.15418$ Å). X-ray-photoelectron spectroscopy (XPS) was obtained using an ESCLAB 250 spectrometer with a monochromatised Al Kα X-ray source. The composition of the sample was characterised by OXFORD ISIS-300 energy dispersive spectrometer (EDS). The morphologies of the sample were examined by field emission scanning electron microscopy (FESEM-JSM-7500F). High-resolution transmission electron microscopy (HRTEM) image was taken on a Hitachi H-7650. The CHI660E electrochemical workstation was used to do photoelectrochemical measurements at a scan rate of 100 mV/s in polysulphide electrolyte, which contains Na_2SO_3 (0.35 M) and Na_2S (0.25 M). The light source is a 500 W xenon arc lamp (light intensity 100 mW cm^{-2}, AM 1.5 G).

3. Results and discussion: Fig. 1 shows XRD spectrum of the Cu_2O nanorods array. These XRD data were consistent with the index data in the JCPDS Card No. 77-199. They were indexed to the (110), (111), (200) and (220) plane of the cuprite structure. The diffraction peaks marked by an asterisk can be assigned to the copper substrate, which were consistent with the help of JCPDS Card No. 04-836. The prominent (111) diffraction peak showed that the Cu_2O nanorod grow along [111] direction. The corresponding EDS result showed that the prepared sample was mainly composed of oxygen and copper elements (Fig. 1, inset).

XPS measurement was presented in Fig. 2. There are two peaks in Fig. 2*c*, which were assigned to the Cu $2p_{1/2}$ and Cu $2p_{3/2}$ peaks at 951.8 and 932.0 eV, respectively. The two peaks correspond to Cu_2O, as previously reported [14, 15]. XPS spectra of Cu $2p_{3/2}$ measured part for the sample were displayed and the binding energies of different chemical species were marked in Fig. 2*a*. In this work, Cu $2p_{3/2}$ spectra can be fitted into two peaks. The binding energy at 932.0 eV measured in our sample agreed well with the reported value of the Cu_2O surface phase, and the binding energy at 934.3 eV was close to the literature data of CuO at 934.3 eV [16]. There may be a small amount of copper oxide phase. The Cu $2p_{3/2}$ binding energy of 932.0 eV and Cu L3VV kinetic energy (Fig. 2*d*) of 917.1 eV agreed well with the reported values of the Cu_2O phase. The O1s spectrum for the surface of the Cu_2O nanorods array film was shown in Fig. 2*b*. The original O1s profile can be fitted to four peaks (*a*, *b*, *c* and *d*, located at 531.3, 535.6, 532.5 and 530.0 eV, respectively). The four peaks, *a*, *b*, *c* and *d* arise from the O adsorbed on the surface of Cu_2O nanorods, oxygen of water vapor, oxygen of hydroxyl or carbonate and lattice oxygen of Cu_2O [15, 16], respectively. These data once again confirm that the sample was primarily in Cu_2O phase.

Figs. 3*a* and *b* show the surface and cross-sectional morphologies of the fabricated Cu_2O nanorods grown on the copper substrate.

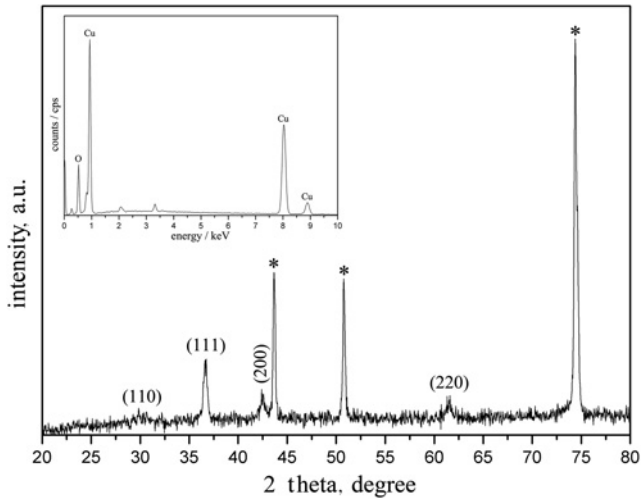

Fig. 1 *XRD and EDS patterns of Cu_2O nanorods array*

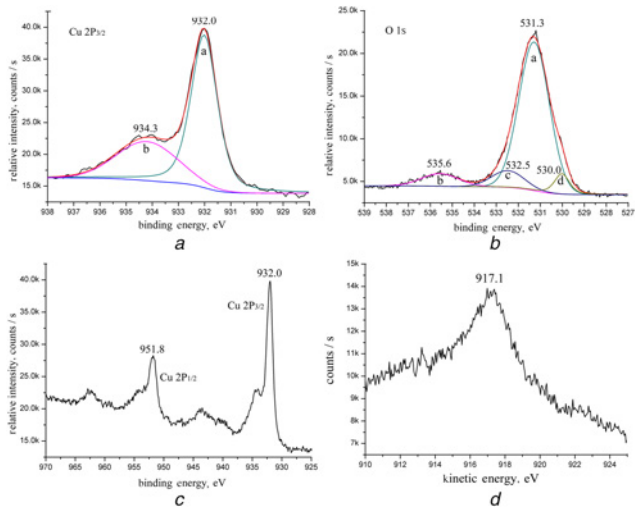

Fig. 2 *XPS spectra*
a Cu $2p_{3/2}$
b O 1s
c Cu 2p
d Cu L3VVspectra for Cu_2O nanorods array

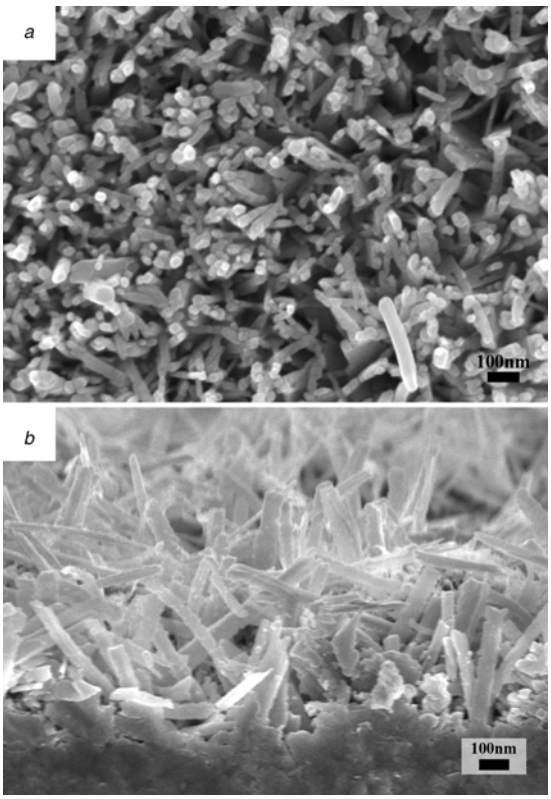

Fig. 3 *Top and side view of Cu_2O nanorods array*

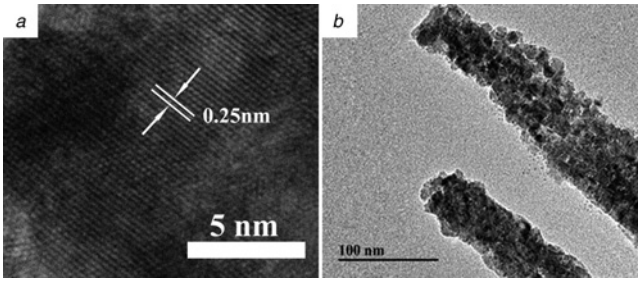

Fig. 4 *TEM image of the Cu_2O nanorod*
a HRTEM image of a Cu_2O nanorod
b Typical TEM image of of Cu_2O nanorods

It can be seen from Figs. 3*a* and *b* that the Cu_2O nanorods had an approximately average length of 400 nm and diameter of 40 nm. These nanorods were relatively straight and long, resulting in a large aspect ratio [17, 18]. Fig. 4*b* show a TEM image of Cu_2O nanorods. The diameter of the Cu_2O nanorod was ~40 nm. The HRTEM image of Cu_2O nanorod was shown in Fig. 4*a*. The interplanar spacing was ~0.25 nm, which was consistent with the (111) interplanar spacing of the cuprite structure Cu_2O. It was proved that the sample was preferentially grown along the [111] direction, which was consistent with the XRD result.

It was found that under alkaline conditions [19], Cu would lose one electron and produce Cu^+ in the interface between the copper sheet and KOH solution. Cu^+ and OH^- were able to formation $Cu(OH)_2^-$ thin film [20]. Therefore, the electric field would induce OH^- and K^+ to migrate in electrolyte. The Cu_2O nanorods were produced by the following reactions:

Anode reaction:

$$2Cu + 4OH^- - 2e^- \rightarrow 2Cu(OH)_2^- \quad (1)$$

$$2Cu(OH)_2^- \rightarrow Cu_2O + H_2O + 2OH^- \quad (2)$$

Cathode reaction:

$$2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^- \quad (3)$$

Fig. 5 shows the photovoltaic current density versus voltage of the Cu_2O nanorods array film electrode. As can be seen from Fig. 5, the short-circuit current density (J_{sc}) was 33.38 mA/cm^2. The photocurrent density we obtained was much larger than previously reported in [21]. The photocurrent density of the samples was very large, which indicated that the Cu_2O nanorods array can obtain higher conductivity. In addition, the high aspect ratio of Cu_2O nanorod also had an important contribution to its high current density. Therefore, it may have a good application prospect in the field of photovoltaic.

4. Conclusion: In summary, Cu_2O nanorods array with a rod length of about 400 nm was successfully fabricated by anodic oxidation method. The Cu_2O nanorods array was characterised by XRD, XPS, FESEM, HRTEM and EDS. Our experimental results demonstrate that this simple route can produce high-quality

doi: 10.1049/mnl.2017.0643

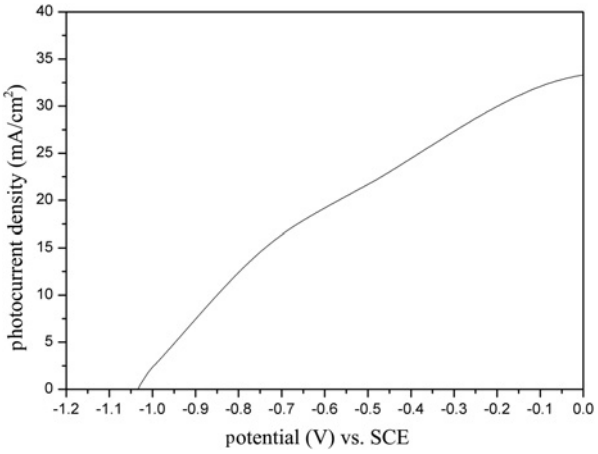

Fig. 5 *Trace of current density against applied voltage for Cu_2O nanorods array film electrode*

crystalline Cu_2O nanorods array. FESEM results demonstrated that these Cu_2O nanorods have a nearly uniform length and diameter. This work further demonstrated that anodic oxidation is a simple, feasible and efficient method to produce Cu_2O nanorods array. For the result of the photoelectrochemical characteristics studies, Cu_2O nanorods array will have more potential applications in photovoltaics in the future.

5. Acknowledgements: This work was financially supported by the Youth Foundation of Changchun University of Science and Technology (grant no. XQNJJ-2015-09).

6 References

[1] Pan L., Li L., Chen Y.H.: 'Synthesis of Ag/Cu_2O hybrids and their photocatalytic degradation treatment of p-nitrophenol', *Micro Nano Lett.*, 2011, **6**, (12), pp. 1019–1022

[2] Zheng H.Y., Li Q., Zhang Y.P., *ET AL.*: 'Convenient and green soft chemical route to cuprous oxide films and their visible-light photocatalytic properties', *Micro Nano Lett.*, 2015, **10**, (10), pp. 554–557

[3] Hacialioglu S., Meng F., Jin S., *ET AL.*: 'Facile and mild solution synthesis of Cu_2O nanowires and nanotubes driven by screw dislocations', *Chem. Commun.*, 2012, **48**, (8), pp. 1174–1176

[4] Ju H.K., Lee J.K., Lee J., *ET AL.*: 'Fast and selective Cu_2O nanorod growth into anodic alumina templates via electrodeposition', *Curr. Appl. Phys.*, 2012, **12**, (1), pp. 60–64

[5] Sun S., You H.J., Kong C.C., *ET AL.*: 'Etching-limited branching growth of cuprous oxide during ethanol-assisted solution synthesis', *CrystEngComm*, 2011, **13**, (8), pp. 2837–2840

[6] Liang Z.H., Zhu Y.J.: 'Synthesis of uniformly sized Cu_2O crystals with star-like and flower-like morphologies', *Mater. Lett.*, 2005, **59**, (19), pp. 2423–2425

[7] Jiang X.S., Zhang M., Shi S.W., *ET AL.*: 'Microstructure and optical properties of nanocrystalline Cu_2O thin films prepared by electrodeposition', *Nanoscale Res. Lett.*, 2014, **9**, (1), pp. 219–324

[8] Wei M.Z., Huo J.Z.: 'Preparation of Cu_2O nanorods by a simple solvothermal method', *Mater. Chem. Phys.*, 2010, **121**, (2), pp. 291–294

[9] Luo J.S., Steier L., Son M.K., *ET AL.*: 'Cu_2O nanowire photocathodes for efficient and durable solar water splitting', *Nano Lett..*, 2016, **16**, (3), pp. 1848–1852

[10] Ma G.F., Liu S., Wang P., *ET AL.*: 'Synthesis of pod-like Cu_2O nanowire arrays on Cu substrate', *Mater. Lett.*, 2014, **120**, (4), pp. 212–215

[11] Wijesunderan R.P., Gunawardhana L.K.A.D.D.S., Siripala W.: 'Electrodeposited Cu_2O homojunction solar cells: fabrication of a cell of high shortcircuit photocurrent', *Sol. Energy Mater Sol. C*, 2016, **157**, (2), pp. 881–886

[12] Brown K.E.R., Choi K.S.: 'Electrochemical synthesis and characterization of transparent nanocrystalline Cu_2O films and their conversion to CuO films', *Chem. Commun.*, 2006, **31**, (31), pp. 3311–3313

[13] Xiang L.J., Li J.A., He Z.K., *ET AL.*: 'Design and construction of TiO_2 nanotubes in microarray using two-step anodic oxidation for application of cardiovascular implanted devices', *Micro Nano Lett.*, 2015, **10**, (6), pp. 287–291

[14] Cheng Z.P., Xu J.M., Zhong H., *ET AL.*: 'Repeatable synthesis of Cu_2O nanorods by a simple and novel reduction route', *Mater. Lett.*, 2011, **65**, (12), pp. 1871–1874

[15] Ji R., Sun W.D., Chu Y.: 'One-step hydrothermal synthesis of a porous Cu_2O film and its photoelectrochemical properties', *Chem. Phys. Chem.*, 2013, **14**, (17), pp. 3971–3976

[16] Teo J.J., Chang Y., Zen H.C.: 'Fabrications of hollow nanocubes of Cu_2O and Cu via reductive self-assembly of CuO nanocrystals', *Langmuir*, 2006, **22**, (17), pp. 7369–7377

[17] Zhang Z.H., Dua R., Zhang L.B., *ET AL.*: 'Carbon-layer-protected cuprous oxide nanowire arrays for efficient water reduction', *ACS Nano*, 2013, **7**, (3), pp. 1709–1717

[18] Wang W.Z., Wang G.H., Wang X.S., *ET AL.*: 'Synthesis and characterization of Cu_2O nanowires by a novel reduction route', *Adv. Mater.*, 2002, **14**, (1), pp. 67–69

[19] Poulston S., Parlett P.M., Stone P., *ET AL.*: 'Surface oxidation and reduction of CuO and Cu_2O studied using XPS and XAES', *Surf. Interface Anal.*, 1996, **24**, (12), pp. 811–820

[20] Marchiano S.L., Elsner C.I., Arvia A.J.: 'The anodic formation oxide films on copper and cathodic reduction of cuprous in sodium hydroxide solutions', *J. Appl. Electrochem.*, 1980, **10**, (3), pp. 365–377

[21] Shooshtari L., Mohammadpour R., Zad A.I., *ET AL.*: 'Enhanced photoelectrochemical processes by interface engineering, using Cu_2O nanorods', *Mater. Lett.*, 2016, **163**, (1), pp. 81–84