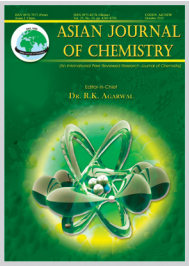
Asian Journal of Chemistry; Vol. 24, No. 6 (2012), 2671-2673

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Copper Oxalate Multilayer Micro-Sheet Film Grown Directly on Cu Substrate

HAINAN SONG[1,*], JUNCUI XU[2] and YANXIN WEI[2]

[1]Anhui Medical College, Hefei 230601, P.R. China
[2]Department of Chemical and Chemical Engineering, Hefei Normal University, Hefei 230061, Anhui, PR China

*Corresponding author: E-mail: shn_8288@163.com

(*Received*: 17 June 2011; *Accepted*: 17 January 2012) AJC-10970

A kind of copper oxalate film was prepared in aqueous acid solution at room temperature. During the preparation, a copper foil was used as substrate while $K_2S_2O_8$ was used as oxidizing agent. The film prepared was covered with micro-sheets which had polymer-like structure. This technique could be considered as an effective way to energy-retrenched, time-saving and environment friendly.

Key Words: Micro-sheet film, Oxidizing agent, Polymer-like structure.

INTRODUCTION

The synthesis of complex inorganic materials with dimensional, structural and morphological specificity is a key aspect in the development of new materials. Many considerable attention has been attracted to micro-scale inorganic materials with well-defined superstructures, for their structure characteristics endowing them with a very wide range of potential applications in diverse fields such as catalysts, medicine, electronics, ceramics, pigments and cosmetics[1-4]. Copper oxalate is a material with an unusual antiferromagnetic character, which are related to its polymer-like structure described as a stacking of …$Cu(C_2O_4)Cu(C_2O_4)$…ribbons[5] and copper oxalate is also a potential precursor material for the production of CuO and Cu particles[6]. As such, some of the material scientists published useful work on this material. For example, Bowen and co-workers[7] reported copper oxalate polycrystalline particles with cushion-and rod-liked shapes produced by a precipitation reaction in the presence of given amounts of a polymer additive (hydroxypropylmethylcellulose) and a rational self-organization mechanism for the formation of such polycrystalline particles was proposed. Haq and Haider[8] synthesized microsphere and micro-cube with pits on one face by mixing appropriate volumes of known concentration of oxalic acid and copper nitrate at different temperature. Zhao and co-workers[9] investigated the morphologies of copper oxalate polycrystalline pitted and patterned tablets between copper sulfate and oxalic acid solutions. However, to our best knowledge, there is no reports about the preparation of copper oxalate film.

Here, a kind of copper oxalate film with muti-layers was successfully fabricated without any surficants and at room temperature. Our synthetic method consisted of controlled surface oxidation on copper substrates in aqueous acid solution with $K_2S_2O_8$. The copper substrate was used not only as a source of copper but also as a support for the copper compound films. In present study, the synthesis, structure and morphology of the film was described and possible growth mechanism was discussed. This technique could be considered as an effective way to energy-retrenched, time-saving and environment friendly compared with the methods mentioned above.

EXPERIMENTAL

Hydrogen peoxide (30 %), potassium persulfate ($K_2S_2O_8$) and oxalic acid dihydrate ($H_2C_2O_4.2H_2O$) were analytical grade purity, obtained from Beijing Chemical Company. The above chemicals were used in the experiments without further purification. High-purity copper foils (99.99 %) were used.

A typical procedure was performed as follows: An aqueous acid solution was prepared in a 60 mL glass bottle by mixing 1 mL of $K_2S_2O_8$ solution (1 M), 1 mL of $H_2C_2O_4$ solution (1 M), 5 mL of H_2O_2 solution (30 %) and 13 mL of distilled water. The above mixed solution was stirred for 5 min. A piece of copper foil (15 × 15 × 0.25 mm^3, 99.99 %), which had been ultrasonically cleaned in acetone was immersed in this solution at room temperature. A few minutes later, the copper foil covered with a blue film was taken out of the solution, rinsed with distilled water and absolute ethanol and dried in air for about 6 h.

Particle morphology of the powders was inspected with scanning electron microscope (SEM; JEOL, JSM-5910) at the accelerating voltage of 20 keV. Before examination, the powder sample was sputtered with gold. The crystallinity of the solids was assessed from the XRD patterns, obtained with a Rigaku D_{max}-λB X-ray diffractometer (XRD, JEOL JDX-3532) using CuK_α radiations (k = 1.5418 Å). The XRD was operated with 40 kV voltage and 20 mA current. The sample was scanned in the 2θ range 10-70º.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of the the as-prepared copper oxalate micro-sheets on the copper substrate was illustrated in Fig. 1 and the diffraction lines were attributed to (110), (120), (011), (111), (220) and (211) planes of copper oxalate, respectively. The product could be indexed as orthorhombic crystalline structure with the cell parameters determined are a = 5.403 Å, b = 5.571 Å and c = 2.546 Å, in agreement with the literature value of copper oxalate crystal (JCPDS file no. 21-0297). No diffraction line of other inorganic impurities was observed.

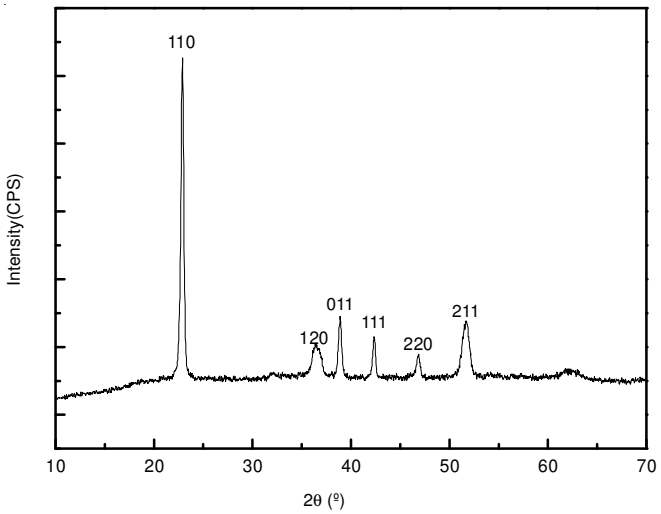


Fig. 1. XRD pattern of the product

Surface morphological study: Scanning electron micrographs of copper oxalate thin films at two different magnifications were presented in Fig. 2a and b. The micrographs revealed the formation of hierarchical multilayer microsheets clusters. Those microsheets stacked layer by layer. This was similar with the internal structure of the polymer. It is clearly seen that these microsheets clusters were well covered to substrate surface. These microsheets' surface was very smooth. At the same time, they looked like many big pills, whose arounds were thin and whose middles were thick. At low magnification (Fig. 2a) a few balls could be seen, possibly some microsheets stood on end. It was worth mentioning that at higher magnification (×5500) the cross secion of voluminous mirocsheets took the form of fusiform viewed from the side and one end of the minority fusiforms had a divarication. The formation of the muti-layer stucture is to be further studied. Moreover, the thickness of each microsheet was about 1 μm, but the area of each them couldn't be defined.

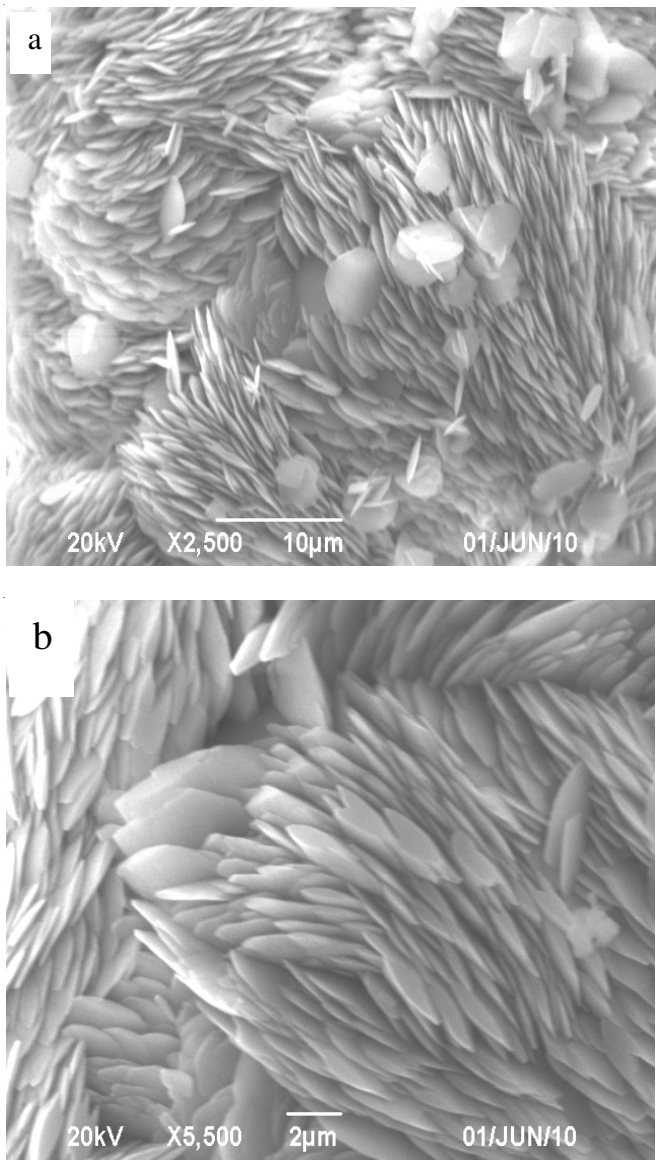


Fig. 2. SEM images of copper oxalate thin film at (a) × 2500 and (b) × 5500 magnifications.

Film formation and reaction mechanism: The blue copper oxalate film was uniform and well adherent to the substrates. In general, the film was produced as follows. The ionic product (IP) of the solution exceeded the solubility product (SP) for some kind of film and the solution reached a maximum degree of supersaturation (S = degree of supersaturation = IP/SP), which consequently led to the growth of nuclei and deposition of the film. For deposition of copper oxalate film, copper foil was used as source of copper ions (Cu^{2+}). In acidic medium, the precipitation reactions are redox reactions. The calculated emf (E^θ = 1.655 V) is positive by using half-cell potentials (E^θ (Cu^{2+}/Cu) = 0.345 V, E^θ ($S_2O_8^{2-}/S_2O_4^{2-}$) = 2.0v. In acidic solution, $K_2S_2O_8$ oxidizes and dissolves copper continuously, preventing films from being formed on the copper surface. The concentration of Cu^{2+} in the solution was enhanced with the prolonging of oxdizing time. The Cu^{2+} ions resulting from copper oxidation react with $C_2O_4^{2-}$ ions. When the product of the copper ionic concentration and oxalate concentration is higher than solubility product for CuC_2O_4($c(C_2O_4^{2})$. $c(Cu^{2+}) > Ksp$), the blue CuC_2O_4 precipitation occurred on the

substrate and thus well adherent and uniform CuC_2O_4 film formed. This could be represented by the following reactions:

$$S_2O_8^{2-} + 2e^- \rightleftharpoons 2S_2O_4^{2-} \quad E^\theta (S_2O_8^{2-}/S_2O_4^{2-}) = 2.0v \quad (1)$$

$$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad E^\theta (Cu^{2+}/ Cu) = 0.345\ v \quad (2)$$

$$2Cu + S_2O_8^{2-} + C_2O_4^{2-} \rightarrow CuC_2O_4 + 2SO_4^{2-} \quad (3)$$

In summary, copper oxalate multilayer microsheets had been suceessfully synthesized *via* a simple and efficient approach. The formation and reaction mechanism of microsheets film was discussed. The XRD pattern revealed the amorphous nature of copper oxalate thin films. The SEM images revealed the development of hierarchical multilayer nanosheets, which are well covered with the substrate surface. The formation process of the multi-layer structure is to be further studied in detail.

REFERENCES

1. P. Jiang, J.F. Bertone and V.L. Colvin, *Science,* **291**, 453 (2001).
2. Y. Huang, X. Duan, Y. Cui, L. Lauhon, K. Kim and C.M. Lieber, *Science*, **294**, 1313 (2001).
3. R. Jin, Y.W. Cao, C.A. Mirkin, K.L. Kelly, G.C. Schatz and J.G. Zheng, *Science*, **294**, 1901 (2001).
4. Y. Sun and Y. Xia, *Science*, **298**, 2176 (2002).
5. A. Michalowicz, J.J. Girerd and Goulon, *J. Inorg. Chem.*, **18**, 3004 (1979).
6. X. Zhang, D. Zhang, X. Nia and H. Zheng, *Solid-State Electron*, **52**, 245 (2008).
7. L.C. Soare, P. Bowen, J. Lemaitre and H. Hofmann, *Mater. Res. Soc. Symp. Proc.*, Vol. 788 (2004).
8. I. ul Haq and F. Haider, *Mater. Lett.,* **63**, 2355 (2009).
9. X. Zhao and J. Yu, *J. Cryst. Growth*, **306**, 366 (2007).