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Scalable synthesis of delafossite $CuAlO_2$ nanoparticles for p-type dye-sensitized solar cells applications

Jahangeer Ahmed [a], Colin K. Blakely [a], Jai Prakash [a], Shaun R. Bruno [a], Mingzhe Yu [b], Yiying Wu [b], Viktor V. Poltavets [a,*]

[a] Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA
[b] Department of Chemistry and Biochemistry, Ohio State University, Columbus, OH 43210, USA

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ABSTRACT

Delafossite $CuAlO_2$ nanoparticles were prepared using an easily scalable method under controlled partial oxygen pressure (pO_2) of 10^{-5} atm at 775 °C. Transmission electron microscopy showed a uniform particle size of 35 nm, agreeing well with the calculated particle size distribution obtained using the Whole Powder Pattern Method (WPPM) via the PM2K software package. Higher cathodic photocurrents ($J_{sc} = 0.954$ mA/cm^2 under AM1.5 sun) were observed in p-type dye sensitized solar cells (DSSCs) fabricated using these $CuAlO_2$ nanoparticles compared to the previous reports on delafossite $CuBO_2$ (B = Al, Ga) nanoparticles. Enhanced current efficiency in these solar cells is attributed to the nano-sized particles and narrow particle size distributions of nanocrystalline delafossite $CuAlO_2$.

1. Introduction

Delafossite $CuAlO_2$ belongs to a family of transparent conducting oxides (TCOs) – oxides with low electrical resistivity and high visual light transparency – that show promise in multiple applications including: liquid crystal displays, touch screens, gas sensors, thermoelectric devices, solar cells, dilute magnetic semiconductors, light-emitting diodes, etc. [1–6]. $CuAlO_2$ nanoparticles have also been used as thermo-catalysts in the thermal photo-catalytic reactions for the evolution of hydrogen gas from water splitting [5]. The most well-known TCOs, ZnO and In_2O_3, are n-type semiconductors; therefore, the synthesis of a p-type conducting oxide allows for the preparation of p–n junctions – the source of many interesting semiconductor properties in cutting edge technology [7,8]. Essentially, a p–n junction photovoltaic using $CuAlO_2$ and In_2O_3, respectively, would allow visible light to pass through the cell while producing electricity via the absorption of ultraviolet radiation [9].

$CuAlO_2$ has a layered crystal structure with Cu atoms between AlO_2 layers forming O–Cu–O pillars (Fig. 1) [10]. $CuAlO_2$ has indirect and direct band gaps of 1.2 and 3.6 eV respectively, high transparency (80%) in the visible region, and high light-to-electricity conversion efficiencies in solar cells [3,11]. Photocurrents ranging from 0.02 mA/cm^2 to 0.08 mA/cm^2 have been observed when $CuAlO_2$ nanoparticles (300 nm) were used as the photocathode materials in p-type DSSCs, while delafossite $CuGaO_2$ nanoplates produced comparatively high photocurrents (0.384 mA/cm^2) in the region of visible light using polypyridyl $Co^{3+/2+}$(dtb-bpy) as the electrolyte and the organic P1 dye [10,12].

Delafossite $CuAlO_2$ is thermodynamically unstable below 1000 °C in air, easily decomposing to the Cu^{2+} compounds CuO and $CuAl_2O_4$ under these conditions [13]. Synthesis of polycrystalline $CuAlO_2$ is typically achieved by firing a stoichiometric mixture of Al_2O_3 and Cu_2O at 1100 °C under argon or air atmosphere. Various techniques have been used to produce $CuAlO_2$ nanoparticles including: sol–gel, mechanical alloying, hydrothermal, field emission process, and electrospinning methods [4,14–16]. $CuAlO_2$ nanostructured semiconducting materials were synthesized by using boehmite (Υ-AlOOH) nanorods loaded with Cu(II) acetate as a nanoprecursor at 1150 °C in air [2]. $CuAlO_2$ nanowires (50 nm diameter) and nanoparticles (35 nm) were produced via a porous anodic alumina oxide (AAO) template at 900 °C and citrate route at 1000 °C, respectively [17]. Considering that most syntheses reported require very high reaction temperatures (>1000 °C) or complex instrumentation or templating, the production of bulk quantities of pure phase $CuAlO_2$ nanoparticles is still a serious challenge.

Herein, we report the synthesis of pure phase 35 nm diameter $CuAlO_2$ nanoparticles at 775 °C under a controlled oxygen partial pressure ($pO_2 = 10^{-5}$ atm) and at 800 °C under flowing ultrapure N_2 (99.999%) atmospheres. High photocurrent densities were observed when solar cells employing these nanoparticles were fabricated. The phase purity and morphology of the nanopowders

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[*] Corresponding author. Tel.: +1 517 355 9715x388.
E-mail address: poltavets@chemistry.msu.edu (V.V. Poltavets).

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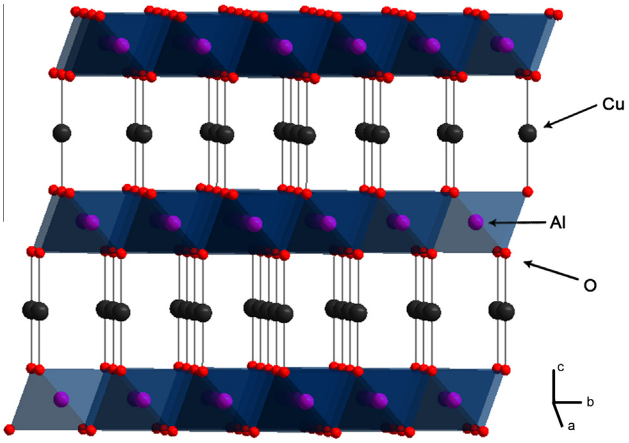

Fig. 1. Crystal structure (space group $R\bar{3}$, $a = 2.8585$ Å and $c = 16.958$ Å) of delafossite $CuAlO_2$ with AlO_6 polyhedra and O–Cu–O bonds highlighted for clarity.

were investigated by powder X-ray diffraction (PXD) and Transmission Electron Microscopy (TEM). The narrow size distribution of the nanoparticles was determined using the Whole Powder Pattern Modelling (WPPM) method via the PM2K software suite.

2. Experimental methods

The following reagents were used in the synthesis of $CuAlO_2$ nanoparticles via the sol–gel process: citric acid (99.5%, Sigma Aldrich), ethylene glycol (anhydrous, JADE scientific), $Cu(NO_3)_2{\cdot}2.5H_2O$ (99%, Sigma Aldrich), $Al(NO_3)_3{\cdot}9H_2O$ (99%, Alfa Aesar), HNO_3 (ACS Grade, Sigma Aldrich), and ultrapure nitrogen gas (99.999%, Airgas Ultra).

Aqueous solutions of 0.1 M $Cu(NO_3)_2{\cdot}2.5H_2O$ and 0.1 M $Al(NO_3)_3{\cdot}9H_2O$, were mixed in stoichiometric amounts and then transferred to a porcelain crucible containing citric acid (0.15 mol) and ethylene glycol (10 ml). Initially, a sky blue transparent solution was apparent. The solution was allowed to gel for three days at room temperature followed by a thermal treatment at 350 °C for 6 h in air to remove the chelating organics, resulting in a fine black powder of copper (II) oxide and an amorphous aluminum based compound as determined by PXD. The fine black powders were then fired at 775 °C for 12 h in air leading to the formation of CuO and $CuAl_2O_4$. This product was further treated at 800 °C in ultrapure N_2 for 48 h, affording pure $CuAlO_2$ nanoparticles.

Large quantities of $CuAlO_2$ nanoparticles were also synthesized in sealed silica tubes under a controlled partial oxygen pressure of $pO_2 = 10^{-5}$ atm. In the partial oxygen pressure controlled experiment, the starting material (precursor phases obtained at 350 °C in air) was pelleted, placed in an alumina boat, and closed in a quartz tube with a second boat containing an oxygen getter mixture – either Cu/Cu_2O or Ni/NiO. Many different metal/metal oxide buffer systems are available depending on the partial oxygen pressure desired [18–20]. The temperature of both the sample as well as the oxygen getter were controlled independently via a split-open two-zone furnace. Further information on the experimental setup for reactions under controlled pO_2 is available elsewhere [21]. A summary of experimental conditions for the synthesis of $CuAlO_2$ nanoparticles is presented in Table 1.

The samples were characterized by Powder X-ray diffraction (PXD) on a Bruker D8 Advanced with DAVINCI design diffractometer using Cu Kα radiation. Diffraction patterns were recorded at room temperature with a step size of 0.02° (2θ) on a zero background sample holder. The cell parameters were refined using the Bruker Topas software package. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a Netsch STA-449 F3 Jupiter at a heating rate of 5 °C per minute. TEM studies were carried out with a JEOL 2200FS transmission electron microscope operated at 200 kV. The specimens for TEM measurements were prepared by dispersing the nanoparticles in methanol via ultrasonic treatment for 20 min, placing a drop onto a porous carbon film supported on a copper grid, and then dried in air.

The p-type dye sensitized solar cells were made with $CuAlO_2$ nanoparticles - synthesized at 775 °C for 48 h – as the photocathode with a film thickness of 1.5 µm [10]. The film was calcined at 350 °C for 1 h and sensitized with O2 dye for 3 days. A 1.0 M LiI/0.1 M I_2 in acetonitrile solution was used as the electrolyte in the solar cells. The p-type DSSC's *J–V* curve and energy conversion efficiency were measured under 1 sun AM 1.5G simulated sunlight (Small-Area Class-B Solar Simulator, PV Measurements).

$CuAlO_2$ films were fabricated with a $CuAlO_2$ "paste". A typical "paste" was made by adding 30 µL 0.6% (v/v) acetic acid and 30 µL 1% (v/v) Triton-100 polymer in isopropanol as surfactant into about 0.5 g $CuAlO_2$ aqueous colloid. The films were fabricated by dropping a certain amount of the "paste" on the central region of the FTO glass whose edges were covered by tape. After air drying, the films were sintered under 350 °C for 1 h. The dye sensitization was accomplished by immersing the films into a 0.3 mm O2 dye in dry acetonitrile (MeCN) solution under dark for 3 days. A typical solar cell was assembled by attaching a platinum-coated FTO glass with a drilled hole to the dye-sensitized film with a polymer spacer by heating under 120 °C for 1 min. The 1.0 M LiI/0.1 M I_2/MeCN electrolyte was injected into the cell through the drilled hole via vacuum back-filling technique. The hole was then sealed with a meltonix spacer. The dye sensitized solar cell performance was tested under 1 sun AM 1.5G simulated sunlight (Small-Area Class-B Solar Simulator, PV Measurements). A CV-50 W voltammetric analyzer was used here to record the solar cell's *J–V* curve.

Table 1
Details of the reactions conditions employed to synthesize $CuAlO_2$ nanoparticles.

Atmosphere	Temp (°C)	Time (h)	Phase composition
Air	350	6	CuO
Air	775	12	$CuAl_2O_4$,CuO
Air	900	48	$CuAl_2O_4$,CuO
Air	1000	48	$CuAl_2O_4$,CuO
Air	1100	24	**$CuAlO_2$**
Ultrapure N_2	800	48	**$CuAlO_2$**
Ultrapure N_2	800	60	$CuAlO_2$/$CuAl_2O_4$/CuO
Ultrapure N_2	850	60	$CuAlO_2$/$CuAl_2O_4$/CuO
Ultrapure N_2	900	60	$CuAlO_2$/$CuAl_2O_4$/CuO
Ultrapure N_2	950	48	$CuAlO_2$/CuO
$pO_2 = 10^{-5}$ atm	775	48	**$CuAlO_2$**

3. Results and discussion

CuO and an amorphous aluminum containing phase were present after firing the sol–gel mixture at 350 °C as evident by PXD. This sample was further treated at 775 °C in air for 12 h, resulting in the formation of CuO and $CuAl_2O_4$. This mixture was then pelletized and used as a precursor in the synthesis of the $CuAlO_2$ nanoparticles under various atmospheric conditions (Table 1).

High temperatures, above 1000 °C, used for $CuAlO_2$ preparation result in micron size particles. Lower synthesis temperature should lead to smaller particle size. There were some experimental [2,17] and theoretical [13] studies claiming the stability of $CuAlO_2$ at lower temperatures in air. For example, $CuAlO_2$ nanowires (50 nm diameter) and nanoparticles (35 nm from SAXS) were synthesized at 900 °C and 1000 °C in air, respectively [2,17]. Therefore we have reinvestigated the stability of $CuAlO_2$ in air. The decomposed sol–gel precursors were heated at 900 °C and 1000 °C in air for 48 h, resulting in the formation of CuO and $CuAl_2O_4$ (Fig. 2). In our case, the formation of $CuAlO_2$ did not occur until the reaction temperature was raised above 1000 °C in air. $CuAlO_2$ was finally crystallized by subsequent firing at 1100 °C for 24 h in air (Fig. 2). Since a high temperature is needed to lower O_2 activity and to prevent $CuAlO_2$ oxidation to Cu^{2+} phases, lower temperature reaction condition with low O_2 activity were investigated. Namely, an N_2 atmosphere and precisely controlled pO_2 conditions were employed.

Product phase composition of the reaction at 800 °C depended on the purity of N_2 used with irreproducible results for lower purity N_2, indicating sensitivity of the reaction to partial oxygen pressure. The reproducible synthesis of nanocrystalline $CuAlO_2$ particles was achieved by firing the pelletized precursor at 800 °C for 48 h in ultrapure N_2 (Table 1).

$CuAlO_2$ nanoparticles were also synthesized at 775 °C under a controlled pO_2 of 10^{-5} atm using a closed quartz tube. This methodology has the capability to make nanoparticles of $CuAlO_2$ using a lower partial oxygen pressure at low temperature compared to previous literature. The observed reflections of the PXD patterns were indexed on the basis of rhombohedral unit cell with the space group $R\bar{3}$ (JCPDS file # 01-075-2356). The refined lattice parameters of the $CuAlO_2$ nanoparticles were found to be $a = 2.8585(5)$ Å and $c = 16.958(1)$ Å (Fig. 3). $CuAlO_2$ did not form from the