Synthesis, characterization and electrocatalytic properties of Delafossite CuGaO_2

Jahangeer Ahmed^{a,b} and Yuanbing Mao^{a†}

^aDepartment of Chemistry, University of Texas Rio Grande Valley, 1201 West University Drive, Edinburg, TX 78539, United States.

^bCurrent address: Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia

[†]To whom correspondence should be addressed: Phone: +1 956 665 2417; Fax: +1 956 665 5006; E-mail: yuanbing.mao@utrgv.edu.

Abstract

Delafossite CuGaO_2 has been employed as photocatalysts for solar cells, but their electrocatalytic properties have not been extensively studied, especially no comparison among samples made by different synthesis routes. Herein, we first reported the successful synthesis of delafossite CuGaO_2 particles with three different morphologies, i.e. nanocrystalline hexagons, sub-micron sized plates and micron-sized particles by a modified hydrothermal method at 190°C for 60 h,^{1,2,3} a sono-chemical method followed by firing at 850°C for 48 h, and a solid state route at 1150°C, respectively. Morphology, composition and phase purity of the synthesized samples was confirmed by powder X-ray diffraction and Raman spectroscopic studies, and then their electrocatalytic performance as active and cost effective electrode materials to the oxygen and hydrogen evolution reactions in 0.5 M KOH electrolyte versus Ag/AgCl was investigated and compared under the same conditions for the first time. The nanocrystalline CuGaO_2 hexagons show enhanced electrocatalytic activity than the counterpart sub-micron sized plates and micron-sized particles.

Keywords:

CuGaO_2 ; Delafossite; Oxygen evolution reaction; Hydrogen evolution reactions; Electrocatalytic activity

Graphical abstract

Introduction

Delafossite ternary oxides have an AMO_2 -type general structure, where 'A' is monovalent (1+ metals like Cu, Ag, etc.) and 'M' is trivalent (3+ metals like Al, Ga, In, Fe etc.). Delafossite CuMO_2 with monovalent Cu ion has closed packed plane with edge sharing of MO_6 octahedra.^{4,5} It belongs to a group of *p*-type transparent conducting oxides and has a band gap of 3.6 eV.^{6,7} The *p*-type conductivity in delafossite compounds was first discovered by Kawazoe et al in 1997.⁸ The conductivity and electronic structures of delafossite ($\text{CuM}^{\text{III}}\text{O}_2$) materials are reported in details elsewhere.^{1,9} Delafossite CuGaO_2 demonstrates very interesting properties including optical,^{9,10} electronic,^{7,9,10} and photovoltaic properties.^{2,3,11} CuGaO_2 nanoplates have been used as the photo-electrode materials in *p*-type dye sensitized solar cells to accelerate the photo-voltage and photocurrent.^{2,3} Sub-micron sized CuGaO_2 particles were also used as photo-electrode materials in the H_2 generation by splitting of hydrogen sulfide¹² and photochemical reduction of CO_2 to CO .¹³ Electrochemical impedance spectroscopy was employed to determine the hole conductivity and acceptor density of CuGaO_2 nanoparticles.¹⁴ Other than studies on CuGaO_2 , as the literature review points out, there were very few reports on the electro-catalysis of delafossite materials, e.g. PtCoO_2 ,¹⁵ PdCoO_2 ,¹⁵ PdRhO_2 ,¹⁵ CuRhO_2 ,^{16,17} CuAlO_2 ,^{17,18} but not extensively, nor comparatively among different morphologies. Hinogami et al have reported CuRhO_2 delafossite as active electrocatalysts for oxygen evolution reaction (OER) using 1.0 M KOH electrolyte and reversible hydrogen electrode as a reference electrode.¹⁷ Copper based nanostructures including oxides¹⁹ and intermetallic^{20,21} have also been used as the electro-catalysts in hydrogen evolution reaction (HER) and OER using 0.5 M KOH electrolyte versus Ag/AgCl as a reference electrode. Therefore, delafossites with copper at the A-site have demonstrated significant electronic properties but their electrochemical studies are still lacking,^{8,14} which motivates us to study delafossite CuGaO_2 with different morphologies on their electrochemical performance to OER and HER.

Delafossite CuGaO_2 nanostructures are of great interest in electrolysis of water for oxygen and hydrogen evolutions. Renewable and clean energy is the most important challenge for scientists due to the declining non-renewable energy sources (i.e. coal and oil). Hydrogen is an important form of energy carrier for next generation fuel to run the world's economy and has higher energy content. Electrolysis of water for hydrogen and oxygen evolution has an immense potential to supply sustainable energy via fuel cells, battery devices etc. Hydrogen is also a clean fuel which

can be used in the fuel cells by converting the chemical energy in to electrical energy. Hydrogen also combines with oxygen to produce electricity in a fuel cell. Oxygen could also be used in fuel cells in the generation of power by increasing the temperature of the reactor to complete the combustion of fuels. More specifically, the aim of the present work is to provide active and cost effective delafossite CuGaO_2 electro-catalysts for OER and HER. Oxygen and hydrogen are commonly used as fuels in power generations, automobile and aerospace industries. Here, we report that nanocrystalline CuGaO_2 hexagons show enhanced electro-catalytic activity as compared to the sub-micron sized and micron sized particles of CuGaO_2 counterparts for the OER and HER in 0.5 M KOH versus Ag/AgCl. The structural and morphological characterizations of the materials were investigated by powder x-ray diffraction (PXRD), Raman spectroscopy, thermo-gravimetric analysis, energy dispersive studies and electron microscopic studies. The electrochemical studies were successfully carried out using three electrode based electrochemical work station. The electrolysis of water by using the synthesized delafossite CuGaO_2 catalysts shows a clear feasibility of current generation in alkaline electrolyte. Besides, these delafossite CuGaO_2 materials could be useful to sustain the energy through fuel cells, battery devices, electrolyzer, solar water splitting, etc.

Experimental Section

Materials and methods:

The following reagents were used in the synthesis of CuGaO_2 delafossites: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Sigma Aldrich, 99%), $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Alfa Aesar, 99.9%), PEG 20,000 (Polyethylene glycol) (Alfa Aesar), ethylene glycol (Alfa Aesar, 99%), KOH (JT Baker Chemical Company), NaHCO_3 (Sigma Aldrich, 99.7%), and ethanol (Alfa Aesar, 96%). Thermal analysis of the commercial $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ produces a mass loss of ~74%, which corresponds to loss of six water molecules as reported.²² Therefore, we have used six water molecules of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ in our experiments to maintain the stoichiometric ratio of 1:1 of Cu:Ga.

Hydrothermal synthesis of nanocrystalline CuGaO_2 hexagons:

Nanocrystalline delafossites CuGaO_2 hexagons were synthesized using the modified hydrothermal method.^{1,2,3} An appropriate stoichiometric mixture of copper and gallium precursors in the molar ratio of 1:1, i.e. 0.002 mole of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and 0.002 mole of $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, was added into a 100 ml Teflon vessel. Subsequently, 10 ml of deionized

water, 10 ml of absolute ethanol, 5 ml of ethylene glycol and 100 mg of PEG 20,000 were added into the vessel. Then 15 ml of 0.5 M KOH solution was added to the autoclave containing the resulting mixture (pH ~ 8) and kept at 190°C for 60 h. A mixture of ethanol and water has been used as a solvent in the hydrothermal process. The surface tension of ethanol (22.39 mN/m) is lower than water (77.82 mN/m) at room temperature. High surface tension of the solvent would lead agglomeration of the particles. Addition of ethanol in water decreases the surface tension of the solvent that could help to increase the reaction kinetics of CuGaO₂ particles and decrease the agglomeration of the particles. The resulting products were washed with ammonia and dilute nitric acid followed by washing with deionized water. Finally a light yellow colored powder was collected and dried at 70°C for 4 h.

Sono-chemical synthesis of sub-micron sized CuGaO₂ plates:

The sono-chemical synthesis involved the mixing of parent materials (0.03 M Cu(NO₃)₂•3H₂O and 0.03 M Ga(NO₃)₃•xH₂O) followed by titration with 0.15 M NaHCO₃ solutions drop by drop at 25°C under ultrasonic process and kept for 3 h. The light green precipitates were collected by centrifugation and washed with deionized water three times. The resulting products were then dried at 60°C for 6 h and used as the precursor materials in the synthesis of the delafossite CuGaO₂ sub-micron sized plates by annealing the above precursor at 850°C for 48 h under ultra-pure nitrogen (99.999%) flow to form grey colored CuGaO₂ plates.

Solid state route of synthesis of micron-sized CuGaO₂ particles:

Micron-sized CuGaO₂ particles were synthesized via solid state route. Gallium oxide (Ga₂O₃, Sigma Aldrich, 98%) and copper oxide nanopowder (CuO, Sigma Aldrich, size ~50 nm) were taken in 1:2 molar ratio and ground together in an agate mortar pestle for 30 minutes. The resulting precursor was then annealed at 1150°C for 36 h under N₂ gas flow.

Characterizations:

All the resulting products were initially characterized by PXRD to determine the phase purity of the obtained delafossite CuGaO₂ samples using a Bruker D8 Advanced diffractometer with Ni-filtered Cu-K_α radiation at a scan speed of 1 second and scan step of 0.02 degree on a zero background sample holder. Raman scattering data was collected on a Bruker SENTERRA RAMAN microscope with an objective of 20X of optical microscope. The excitation line (785 nm) of an Ar⁺ laser beam was focused to a spot size of 5 μm with a laser power of 10 mW. The

spectral resolution range was used $3\text{--}5\text{ cm}^{-1}$ with the integration time of 100 s. Electron microscopic studies were carried out with a ZEISS SIGMA VP field emission scanning electron microscope (FESEM) operated at 5 kV. Transmission electron microscopic (TEM) studies were carried out with a ZEISS LEO 900 electron microscope operated at 80 kV. TEM specimens for the measurements were prepared by dispersing the delafossite CuGaO_2 powder samples in ethanol via ultra-sonication, a drop was put onto a porous carbon film supported by a copper grid, and then dried in air. Thermo-gravimetric analysis (TGA) was carried out using a Perkin-Elmer system with a heating rate of $5^\circ\text{C}/\text{min}$ in oxygen atmosphere.

Preparation of electrode materials and electrochemical measurements:

The electrochemical studies were carried out with a computer controlled potentiostat/galvanostat electrochemical work station (Metrohm Autolab B.V.) at room temperature. Three electrodes (Pt wire, Ag/AgCl , and glassy carbon electrodes as the counter electrode, reference electrode and working electrode, respectively) were used in the electrolysis of water to OER and HER. The working electrodes were prepared by pasting slurries of the CuGaO_2 powders mixed with carbon black and PVDF (weight fractions of CuGaO_2 :carbon black:PVDF of 75:15:10) on the surface of glassy carbon electrode. PVDF (polyvinylidene difluoride) was used as a binder with carbon black as conductive additive in the preparation of electrode materials. The prepared electrodes were then dried at 65°C for overnight in vacuum oven and used as a working electrode for the electrochemical measurements. Cyclic voltammetry (CV) was carried at the scan rate of 50 mV/s with a peak window between from -1.0 to 1.1 V versus Ag/AgCl electrode in 0.5 M KOH electrolyte. Electrolyte solution of 0.5 M KOH(aq) versus Ag/AgCl electrode (reference electrode) has been used in present electrochemical studies according to the literature.^{18,19,20,21} Chronoamperometric measurements were carried out for 200 s at 0.60 V and -1.2 V versus Ag/AgCl for OER and HER, respectively, in 0.5 M KOH electrolyte. Carbon corrosion at a high potential is largely responsible to ruin the OER performances. Therefore, to avoid the carbon corrosion, we have studied the oxygen evolution reactions (OER) at low potential (0.60 V) using chronoamperometry. Nitrogen gas was purged through the electrolyte for 5 minutes prior to the electrochemical measurements to remove dissolved air from the electrolyte toward the OER and HER. Also electrochemical measurements were run in O_2 -saturated 0.5 M KOH for OER. Note that freshly prepared electrodes and electrolytes were used in each measurement for the OER and

HER studies. The current density of the CuGaO₂ electro-catalysts was calculated using the surface area, amount of catalysts pasted on the glassy carbon and generated current.

Results and discussion

Using the sono-chemical method, crystalline sub-micron sized CuGaO₂ plates were synthesized after annealing the precursor materials prepared at 25°C in N₂ atmosphere at 850°C. Figure 1a shows the PXRD pattern of the green colored precursors obtained from the sono-chemical method showing the crystalline phases of basic copper carbonate (Cu₂(OH)₂CO₃) and gallium hydroxide (Ga(OH)₃). This green colored precursor was converted into grey colored CuGaO₂ powder with rhombohedral crystal structure (Figure 1b) after fired at 850°C for 48 h under N₂ gas flow. As reported in the literature, CuGaO₂ is thermodynamically unstable at or below 1100°C and 1200°C in nitrogen and air, respectively.^{23,24} Phase pure nanocrystalline CuGaO₂ hexagons in light yellow color were synthesized using the modified hydrothermal methods at 190°C (Figure 1c). All the observed reflections from the PXRD studies could be indexed with the peaks of (003), (006), (101), (012), (104), (015) and (018) on the basis of rhombohedral unit cell with the space group R-3m (JCPDS file # 00-035-1402). Figure 1 d shows the pure phase of micron-sized CuGaO₂ particles obtained at 1150°C for 36 h in N₂ via the solid state route. Figure 1d shows narrower XRD pattern of the CuGaO₂ particles obtained at 1150°C via solid state route as compared to the other two CuGaO₂ samples (Figures 1d vs 1c & 1b). This could be possible because the crystalline size of the three CuGaO₂ samples increases with processing temperatures. The temperature of the synthesis reaction, the nature of the reactants and the way of the preparation of materials play crucial roles in the formation of materials. Therefore, Bragg's reflections of the (hkl) depend on the crystallinity and size of the obtained samples.

Figure 1. PXRD patterns of (a) the as-synthesized precursor by the sono-chemical method; (b) the sub-micron sized CuGaO_2 plates obtained by firing the sono-chemical precursor at 850°C for 48 h in N_2 ; (c) the nanocrystalline CuGaO_2 hexagons obtained by the hydrothermal method at 190°C for 60 h; (d) the micron-sized CuGaO_2 particles obtained by solid state route at 1150°C for 36 h in N_2 .

Moreover, Raman spectra of these nanocrystalline hexagons, sub-micron sized plates and micron-sized particles of CuGaO_2 were collected by employing normal backscattering geometry as shown in Figure 2. For the sub-micron sized CuGaO_2 plate sample, three characteristic Raman bands are identified at 203 , 362 and 730 cm^{-1} , assigned to the A_g , E_g , and A_{1g} modes of rhombohedral structure, respectively, which agree well with that of the reported delafossite CuGaO_2 .^{25,26} All these three Raman bands of A_g , E_g , and A_{1g} also appear with nanocrystalline

CuGaO₂ hexagons and micron-sized particles at 204, 367 and 737 cm⁻¹, respectively. The A_g and A_{1g} phonon modes denote the atomic vibrations in the direction of c-axis along the O–Cu–O bonds while the E_g mode (double degenerate) describes the vibration in the perpendicular direction along the c-axis. A small shift in the Raman peak positions of E_g and A_{1g} phonon modes to the higher wavenumbers was observed when comparing the nanocrystalline CuGaO₂ hexagons and micron-sized particles with the sub-micron sized CuGaO₂ plates. This small shift in the E_g and A_{1g} phonon modes (Raman active mode) could be due to the surface effects or disorder in the powder with pressure.²⁶

Figure 2. Raman spectra of the nanocrystalline CuGaO₂ hexagons, sub-micron sized CuGaO₂ plates, and micron-sized CuGaO₂ particles.

The microscopic studies by FESEM show the formation of plate-like morphology of CuGaO₂ particles from the sono-chemical method followed by firing at 850°C with some agglomerations

(Figure 3a). The average size of the sub-micron sized plates was found to be in the range from 500 to 800 nm. Figure 3b and 3c show the FESEM images of the hydrothermally synthesized nanocrystalline CuGaO₂ hexagons. The low and high magnification FESEM images reveal that the hydrothermally synthesized nanocrystalline CuGaO₂ particles have regular hexagonal shape with the average thickness of ~40 nm. TEM studies also show the formation of the polygons with six edges and six vertices with diameter of ~500 nm (Figure 3d). With more careful visualization by TEM studies, these nanocrystalline CuGaO₂ hexagons appear to be composed of tiny nanoparticles with the average particle size of ~10 nm. Similar type of nanoparticle aggregations to sub-micron sized hexagonal plates from other materials have also been reported by micro-emulsion method.²⁷ Figure 3e shows the formation of micron-sized spherical shaped particles of CuGaO₂ by the solid state method. Energy-dispersive X-ray spectroscopic (EDS) studies confirmed that these delafossite CuGaO₂ samples contained only copper, gallium and oxygen elements without any impurity which clearly support the PXRD patterns of these delafossite CuGaO₂ samples (Figures 3f & 1). The elemental composition of the copper and gallium was found according to the initial 1:1 loading stoichiometry. The appearance of carbon content in the EDS studies is mainly due to the surface of carbon tape on sample holder (Figures 3f). From the BET surface area measurements, the specific surface area of the nanocrystalline CuGaO₂ hexagons, sub-micron sized CuGaO₂ plates and micron-sized CuGaO₂ particles were found to be 2.63, 2.33 and 0.42 m²/g, respectively. So the specific surface area per unit volume of CuGaO₂ particles decreases with increasing of particle size of CuGaO₂ as expected.

Figure 3. (a) FESEM image of the sub-micron sized CuGaO_2 plates; (b) Low- and (c) high-magnification FESEM; (d) TEM images of the nanocrystalline CuGaO_2 hexagons; (e) FESEM image of the micron-sized CuGaO_2 particles; (f) EDS spectra of the nanocrystalline CuGaO_2 hexagons, sub-micron sized CuGaO_2 plates and micron-sized CuGaO_2 particles.

Thermal properties of all three delafossite CuGaO_2 samples, i.e. sub-micron sized plates, nanocrystalline hexagons and micro-sized particles, were investigated in oxygen atmosphere with the heating rate of $5^\circ\text{C}/\text{min}$ up to 800°C using the Perkin-Elmer TGA analyzer. As shown in Figure 4, a very small weight loss was initially observed that could be due to the adsorbed moisture, and then the thermal studies of the delafossite CuGaO_2 samples showed no weight loss/gain up to 350°C in oxygen, which indicates the existence/absence of oxygen deficiency in the CuGaO_2 samples. The weight increase above 350°C was attributed the decomposition of the CuGaO_2 sample. The weight gain was saturated to $\sim 4.9\%$ at 700°C , which indicated that the decomposition of CuGaO_2 was completed to CuO and CuGa_2O_4 as also reported in the literature.^{23,24}

Figure 4. TGA studies of the delafossite CuGaO_2 samples (nanocrystalline hexagons and sub-micron sized plates) in oxygen.

Cyclic voltammetry (CV) and chrono-amperometric (CA) measurements were carried out to test the OER and HER performance of these delafossite CuGaO_2 samples with different morphologies. For the electro-catalytic measurements, 0.5 M KOH and Ag/AgCl were used as the electrolyte and reference electrode, respectively, and N_2 gas was passed through the electrolyte for 5 min before the tests. Figure 5a shows the CV curves of the nanocrystalline

hexagons, sub-micron sized plates and micron-sized particles of delafossite CuGaO₂ from –1.0 to 1.1 V versus Ag/ AgCl with the scan rate of 50 mV/s. Cyclic voltammograms demonstrate redox behavior around –0.2 V. A sharp peak was observed around –0.18 V, which is due to the oxidation of Cu⁺ to Cu²⁺, as reported in the literature.¹⁹ This is noteworthy that the electro-catalytic oxidation current was observed in CV beyond the potential of 0.5 V to OER in 0.5 M KOH according to the following reaction occurs at anode: $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{O}_2 + 4\text{e}^-$. From the CV curves, the nanocrystalline CuGaO₂ hexagons generate higher current than the sub-micron sized CuGaO₂ plates and micron-sized CuGaO₂ particles.

Chrono-amperometry (CA) is a potentiostatic true quantitative measurement to investigate the electro-catalytic behavior of the nanomaterials at the fixed potential with time. Figure 5b shows the chrono-amperometric measurements of the nanocrystalline hexagons, sub-micron sized plates and micron-sized particles of CuGaO₂ at the fixed potential of 0.60 V for 250 seconds for OER. By comparing the catalytic activity of all four electrodes with CA, it is clearly observed that the nanocrystalline CuGaO₂ hexagons generate higher current than the sub-micron sized plates and micron-sized particles of CuGaO₂. It means that the nanocrystalline CuGaO₂ hexagons show higher electro-catalytic activity than the sub-micron and micron sized particles toward OER. No current is generated when we use an electrode without any electro-catalyst. The electrode without catalytic materials contains only carbon black and PVDF. A careful visualization shows that the current decreases with time using the sub-micron sized CuGaO₂ plates obtained via sono-chemical process as the catalysts while the generated current was more stable with time when the nanocrystalline CuGaO₂ hexagons obtained via hydrothermal process were used as the catalysts. This could be possible because of the degradation of the CuGaO₂ plates as the catalysts on oxidation. Therefore, the CuGaO₂ hexagons are more stable electro-catalytic materials compared to the other two samples.

The current density for the nanocrystalline CuGaO₂ hexagons, sub-micron sized plates and micron-sized particles was calculated by using the electro-active surface area of the electrode. The geometric electro-active surface area of electrodes for OER was calculated by using Randles–Sevcik equation^{28,29,30} as that of the nanocrystalline hexagons is equal to 0.21 cm², that of the sub-micron sized plates to 0.19 cm², and that of the micron-sized particles to 0.12 cm². Commonly, the current densities of the materials were calculated using the resulting currents obtained from the electrochemical measurements divided by the geometric electroactive surface

area of the electrode. Therefore, the current densities of the nanocrystalline CuGaO₂ hexagons, sub-micron sized plates and micron-sized particles at 0.60 V were found to be 26, 23 and 5 mA/cm², respectively. So the current density of the nanocrystalline CuGaO₂ hexagons was found to be more than 5 times higher than the micron-sized CuGaO₂ particles while close to that of the sub-micron sized CuGaO₂ plates. To the best of our knowledge, there were very few reports in the literature on delafossite CuRhO₂, CuGaO₂, CuFeO₂, and CuAlO₂ micron-sized particles as the electro-catalysts for OER using 1.0 M KOH electrolyte and reversible hydrogen electrode as a reference electrode by applying the potential of 1.6 V.¹⁷ Moreover, the nanocrystalline delafossite CuGaO₂ hexagons are an efficient electro-catalyst to OER at much lower potentials compared to the reported delafossite compounds.¹⁷ Previously, the current density of CuGaO₂ particles for OER was reported to be ~8 mA/cm² at the applied potential of 1.6 V,¹⁷ while our results here showed that nanocrystalline CuGaO₂ hexagons and submicron sized plates generate much higher current densities of ~26 and ~23 mA/cm², respectively, at much lower applied potential, i.e. 0.60 V. Table 1 shows the comparison of the electro-catalytic performances of the as-synthesized delafossite CuGaO₂ nanostructures with those of previously reported delafossite compounds. These nanocrystalline hexagons and sub-micron sized plates of delafossite CuGaO₂ show higher current density than metallic copper nanoparticles (15 mA/cm² with Pt as a working electrode),¹⁹ and copper (I) oxide nanostructures (20 mA/cm² with glassy carbon as a working electrode and 35.5 mA/cm² with Pt as a working electrode) versus Ag/AgCl.¹⁹ Several other materials like IrO₂, RhO₂ are the important electro-catalysts for OER, but it is always prominent to find less expensive catalysts as alternates. The nanocrystalline CuGaO₂ hexagons also show much higher electro-catalytic activity than IrO₂ (~4 μA/cm² in acidic and ~2 μA/cm² in alkaline medium) and RuO₂ (~10 μA/cm² in acidic and ~3 μA/cm² in alkaline medium) at 1.48 V versus RHE.³¹ The current density of IrO₂ nanoflowers was reported to be of 0.5 mA/cm² in 0.1 M buffer solution using glassy carbon electrode versus Ag/AgCl.³²

The current densities of the nanocrystalline CuGaO₂ hexagons, sub-micron sized plates and micron-sized particles were also calculated using the amount of materials pasted on electrode, observed current and BET surface area of the materials. The current densities for OER were found to be 0.099, 0.062 and 0.015 mA/cm² of nanocrystalline hexagons, sub-micron sized plates and micron-sized particles of CuGaO₂, respectively, at 0.60 V. The electro-catalytic performance of nanocrystalline CuGaO₂ hexagons for OER was found much higher (1.5 and 6 times) than the

performances observed with sub-micron sized CuGaO₂ plates and micron-sized CuGaO₂ particles.

These delafossite CuGaO₂ samples have also been used as electro-catalysts for HER. CV curves show that the hydrogen evolution begins from -0.9 V versus Ag/AgCl electrode according to the following reaction: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (Figure 5a). During the electro-catalysis process, electrons transfer from the delafossite CuGaO₂ electrode materials to water molecules to generate H₂ and OH⁻. Nanocrystalline CuGaO₂ hexagons perform better electro-catalytic activity compared to the sub-micron sized CuGaO₂ plates and micron-sized particles to HER. CA studies of the delafossite CuGaO₂ particles were carried out to confirm the catalytic activity toward the evolution of hydrogen in 0.5 M KOH at -1.2 V for 250 seconds (Figure 5c). By comparing the current density of all three electrode materials from CA, we clearly observe that the nanocrystalline hexagons generate higher current compared to the sub-micron sized plates and the micron-sized particles with time. The current densities of the nanocrystalline hexagons, sub-micron sized plates and micron-sized particles were found to be about 65, 45, and 35 mA/cm², respectively. The current density is directly proportional to the generation of oxygen or hydrogen which depends on both the surface area and the morphology of the catalysts. By using the BET surface area to compare the catalytic activities of all three electrodes, we examined that the nanocrystalline hexagons (0.25 mA/cm²) show higher efficiency compared to the sub-micron sized plates (0.122 mA/cm²) and the micron-sized particles (0.105 mA/cm²). The current density obtained could be a function of both the faradaic and non-faradaic processes. The faradic process is the only one that contributes to either OER or HER by the illustration of charge being transferred with these CuGaO₂ particles while the non-faradic process stimulates the formation of the electrical double layer. Note that here we reported that delafossite CuGaO₂ is also an efficient electro-catalyst for HER for the first time. The investigation of CuGaO₂ electrocatalysts for the generation of hydrogen is highly admirable as the next generation fuel.

Figure 5. (a) Cyclic voltammograms of the nanocrystalline CuGaO₂ hexagons, sub-micron sized CuGaO₂ plates and micron-sized CuGaO₂ particles in 0.5 M KOH by applying the potential range from -1.0 to 1.1 V vs Ag/AgCl with scan rate of 50 mV/s; (b) chronoamperometric voltammograms of the nanocrystalline CuGaO₂ hexagons, sub-micron sized CuGaO₂ plates and micron-sized CuGaO₂ particles for OER at 0.6 V for 250 seconds; (c) Chronoamperometric voltammograms of the nanocrystalline CuGaO₂ hexagons, sub-micron sized CuGaO₂ plates and micron-sized CuGaO₂ particles for HER at -1.2 V for 250 seconds. Note that N₂ gas was purged through the electrolyte for 5 minutes prior to the electrochemical measurements to remove dissolved air from the electrolyte.

Table 1. Comparison of the electro-catalytic activities of the as-synthesized delafossite CuGaO₂ nanostructures for OER with previous reports in the literature

Samples	Applied Potential	Current Density	Ref. #
Nanocrystalline CuGaO ₂ hexagons	0.60 V	26 mA/cm ²	Present study
CuGaO ₂ sub-micron sized plates	0.60 V	23 mA/cm ²	Present study
CuGaO ₂ micron-sized particles	0.60 V	5 mA/cm ²	Present study
CuGaO ₂ micron-sized particles	1.6 V	6 mA/cm ²	17

CuRhO ₂ micron-sized particles	1.6 V	8 mA/cm ²	17
CuGaO ₂ micron-sized particles	2.0 V	30 mA/cm ²	17
CuAlO ₂ micron-sized particles	2.0 V	10 mA/cm ²	17
CuFeO ₂ micron-sized particles	2.0 V	8 mA/cm ²	17
CuYO ₂ micron-sized particles	2.0 V	5 mA/cm ²	17

By using the cyclic voltammetry, the freshly prepared electrodes of the nanocrystalline CuGaO₂ hexagons (Figure 6a), sub-micron sized CuGaO₂ plates (Figure 6b) and micron-sized CuGaO₂ particles (Figure 6c) were also used to investigate the OER in O₂ saturated 0.5 M KOH by applying potential ranging from -0.60 to 0.80 V versus Ag/AgCl electrode. All the measurements were carried out at various scan rates of 10, 25, 50 mV/s. These delafossite CuGaO₂ samples start the current generation from 0.55 V and act as electro-catalysts for OER beyond this potential. From the CV curves, we observed that the peak current is higher for the nanocrystalline hexagons than the sub-micron sized plates and micron-sized particles at 0.8 V versus Ag/AgCl (Figure 6a, 6b and 6c). The peak current is directly proportional to the amount of oxygen evolved during the electrolysis which depends on the surface area and morphology of the electro-catalysts.

The electro-catalytic activities of these nanocrystalline hexagons, sub-micron sized plates and micron-sized particles of delafossite CuGaO₂ were also investigated by chrono-amperometric measurements in O₂ saturated 0.5 M KOH at 0.60 V for 200 seconds (Figure 6d). In the chrono-amperometric experiments, the chemical reaction occurred on the surface of working electrode to generate the current during the electrolysis at the applied voltage of 0.60 V versus Ag/AgCl and the electrochemical reaction stops when the potential is switched off and hence current drops to zero. Calculated by using the Randles–Sevcik equation, the geometric electro-active surface area of the electrodes was found to be 0.09, 0.126 and 0.085 cm² of the nanocrystalline CuGaO₂ hexagons, sub-micron sized CuGaO₂ plates and micron-sized CuGaO₂ particles, respectively.^{28,29,30} By comparing the electro-catalytic activity of the nanocrystalline CuGaO₂ hexagons, sub-micron sized plates, and micron-sized particles for OER, it was clearly observed again that the nanocrystalline hexagons (20 mA/cm²) possess better catalytic activity than the sub-micron sized plates (12 mA/cm²) and micron-sized particles (5 mA/cm²) at 0.6 V versus Ag/AgCl. Recently, Stoerzinger *et al.* have reported the orientation dependent oxygen evolution

activity of IrO₂ nanocrystals (3 $\mu\text{A}/\text{cm}^2$ for $\langle 100 \rangle$ and 0.5 $\mu\text{A}/\text{cm}^2$ for $\langle 110 \rangle$) in O₂-saturated 0.1 M KOH at 1.2 V versus RHE.³³ Hence, the nanocrystalline CuGaO₂ hexagons show enhanced electro-catalytic behavior than the most active IrO₂ electrode materials in oxygen saturated electrolyte at 0.6 V versus Ag/AgCl. For OER, the current densities were also calculated using the BET surface area. The current densities were found to be 0.033, 0.021 and 0.011 of the nanocrystalline CuGaO₂ hexagons, sub-micron sized CuGaO₂ plates and micron-sized CuGaO₂ particles, respectively. Therefore, oxygen evolution efficiency of the nanocrystalline CuGaO₂ hexagons is much better than the sub-micron sized CuGaO₂ plates and micron-sized CuGaO₂ particles. The observed current is proportional to the amount of oxygen or hydrogen generated during the electrolysis of water. The amount of current generation is a function of surface area, size and morphology of nanomaterials. The specific surface area (from BET) of the nanocrystalline CuGaO₂ hexagons was found to be higher (2.63 m²/g) compared to the sub-micron sized CuGaO₂ plates (2.33 m²/g) and micron-sized CuGaO₂ particles (0.42 m²/g), which also support the observed electrolysis of water to OER and HER.

Figure 6. Cyclic voltammograms of the (a) nanocrystalline CuGaO₂ hexagons; (b) sub-micron sized CuGaO₂ plates; (c) micron-sized CuGaO₂ particles for OER in saturated O₂ and 0.5 M KOH using various scan rates, i.e. 10, 25, and 50 mV/s;. (d) Chronoamperometric voltammograms of the nanocrystalline CuGaO₂ hexagons, sub-micron sized CuGaO₂ plates and micron-sized CuGaO₂ particles for OER in saturated O₂ and 0.5 M KOH.

Conclusions

In the present study, we tested and compared a type of active and cost effective electrode material, i.e. delafossite CuGaO₂ with three different morphologies, for the electrolysis of water to sustain the efficiency in fuel generation technology. The phase purity and morphology of the synthesized materials were confirmed from the PXRD, Raman spectroscopy, and electron microscopic studies. The nanocrystalline CuGaO₂ hexagons

show superior electro-catalytic activity than the sub-micron sized plates and micron sized particles of CuGaO₂ toward oxygen and hydrogen evolution reactions in both nitrogen- and oxygen-saturated 0.5 M KOH electrolyte versus Ag/AgCl. Therefore, it is expected that these delafossite CuGaO₂ particles could be useful for sustainable energy conversion applications.

Acknowledgements

The authors thank the support from the American Chemical Society – Petroleum Research Fund #51497, the Air Force Office of Scientific Research (award # FA9550-12-1-0159), and the National Science Foundation under DMR grant # 0934157 (PREM-UTPA/UMN-Science and Engineering of Polymeric and Nanoparticle-based Materials for Electronic and Structural Applications). J.A. is gratefully acknowledged “The Deanship of Scientific Research, Research Center, College of Science, King Saud University, Kingdom of Saudi Arabia. The authors also thank Mr. Q. Li for taking SEM images, Ms. T. Olmedo for taking TEM images, Dr. M. Pokhrel for EDX studies, and Ms. J. Cruz for performing BET measurements.

References

- 1 Srinivasan, R.; Chavillon, B.; Doussier-Brochard, C.; Cario, L.; Paris, M.; Gautron, E.; Deniard, P.; Odobel, F.; Jobic, S., Tuning the size and color of the *p*-type wide band gap delafossite semiconductor CuGaO₂ with ethylene glycol assisted hydrothermal synthesis. *Journal of Materials Chemistry* 2008, 18 (46), 5647-5653.
- 2 Yu, M.; Natu, G.; Ji, Z.; Wu, Y., *p*-type dye-sensitized solar cells based on delafossite CuGaO₂ nanoplates with saturation photovoltages exceeding 460 mV. *The Journal of Physical Chemistry Letters* 2012, 3 (9), 1074-1078.
- 3 Xu, Z.; Xiong, D.; Wang, H.; Zhang, W.; Zeng, X.; Ming, L.; Chen, W.; Xu, X.; Cui, J.; Wang, M.; Powar, S.; Bach, U.; Cheng, Y.-B., Remarkable photocurrent of *p*-type dye-sensitized solar cell achieved by size controlled CuGaO₂ nanoplates. *Journal of Materials Chemistry A* 2014, 2 (9), 2968-2976.

- 4 Li, J.; Sleight, A. W.; Jones, C. Y.; Toby, B. H., Trends in negative thermal expansion behavior for AMO_2 (A = Cu or Ag; M = Al, Sc, In, or La) compounds with the delafossite structure. *Journal of Solid State Chemistry* 2005, 178 (1), 285-294.
- 5 John, M.; Heuss-Aßbichler, S.; Park, S.; Ullrich, A.; Benka, G.; Petersen, N.; Rettenwander, D.; Horn, S. R., Low-temperature synthesis of CuFeO_2 (delafossite) at 70°C : A new process solely by precipitation and ageing. *Journal of Solid State Chemistry* 2016, 233, 390-396.
- 6 Nie, X.; Wei, S.-H.; Zhang, S. B., Bipolar doping and band-gap anomalies in delafossite transparent conductive oxides. *Physical Review Letters* 2002, 88 (6), 066405.
- 7 Robertson, J.; Peacock, P. W.; Towler, M. D.; Needs, R., Electronic structure of *p*-type conducting transparent oxides. *Thin Solid Films* 2002, 411 (1), 96-100.
- 8 Kawazoe, H.; Yasukawa, M.; Hyodo, H.; Kurita, M.; Yanagi, H.; Hosono, H., *P*-type electrical conduction in transparent thin films of CuAlO_2 . *Nature* 1997, 389 (6654), 939-942.
- 9 Han, M.J.; Huang, T.; Zhang, J.Z.; Li, Y.W.; Hu, .G., Structural, optical and electrical properties of delafossite CuGaO_2 films grown by sol-gel method. *Proceedings of SPIE* 2013, 906809. doi:10.1117/12.2053125.
- 10 Omata, T.; Nagatani, H.; Suzuki, I.; Kita, M.; Yanagi, H.; Ohashi, N., Wurtzite CuGaO_2 : a new direct and narrow band gap oxide semiconductor applicable as a solar cell absorber. *Journal of the American Chemical Society* 2014, 136 (9), 3378-3381.
- 11 Renaud, A.; Chavillon, B.; Le Pleux, L.; Pellegrin, Y.; Blart, E.; Boujtita, M.; Pauporte, T.; Cario, L.; Jobic, S.; Odobel, F., CuGaO_2 : a promising alternative for NiO in *p*-type dye solar cells. *Journal of Materials Chemistry* 2012, 22 (29), 14353-14356.
- 12 Gurunathan, K.; Baeg, J.-O.; Lee, S. M.; Subramanian, E.; Moon, S.-J.; Kong, K.-J., Visible light assisted highly efficient hydrogen production from H_2S decomposition by CuGaO_2 and $\text{CuGa}_{1-x}\text{In}_x\text{O}_2$ delafossite oxides bearing nanostructured co-catalysts. *Catalysis Communications* 2008, 9 (3), 395-402.
- 13 Lekse, J. W.; Underwood, M. K.; Lewis, J. P.; Matranga, C., Synthesis, characterization, electronic structure, and photocatalytic behavior of CuGaO_2 and $\text{CuGa}_{1-x}\text{Fe}_x\text{O}_2$ ($x = 0.05, 0.10, 0.15, 0.20$) delafossites. *The Journal of Physical Chemistry C* 2011, 116 (2), 1865-1872.

- 14 Herraiz-Cardona, I.; Fabregat-Santiago, F.; Renaud, A.; Julián-López, B.; Odobel, F.; Cario, L.; Jobic, S.; Giménez, S., Hole conductivity and acceptor density of *p*-type CuGaO₂ nanoparticles determined by impedance spectroscopy: The effect of Mg doping. *Electrochimica Acta* 2013, 113, 570-574.
- 15 Carcia, P. F.; Shannon, R. D.; Bierstedt, P. E.; Flippen, R. B. O₂ electrocatalysis on thin film metallic oxide electrodes with the delafossite structure. *Journal of the Electrochemical Society* 1980, 127 (9), 1974-1978.
- 16 Hinogami, R.; Toyoda, K.; Aizawa, M.; Kawasaki, T.; Gyoten, H., Copper delafossite anode for water electrolysis. *ECS Transactions* 2013, 58 (2), 27-31.
- 17 Hinogami, R.; Toyoda, K.; Aizawa, M.; Yoshii, S.; Kawasaki, T.; Gyoten, H., Active copper delafossite anode for oxygen evolution reaction. *Electrochemistry Communications* 2013, 35, 142-145.
- 18 Ahmed, J., Mao, Y., Delafossite CuAlO₂ nanoparticles with electrocatalytic activity toward oxygen and hydrogen evolution reactions, in *Nanomaterials for Sustainable Energy*, ed. Jingbo Louise Liu and Sajid Bashir, American Chemical Society, Washington DC, 2015, Chapter 4, 57-72.
- 19 Kumar, B.; Saha, S.; Ganguly, A.; Ganguli, A. K., A facile low temperature (350°C) synthesis of Cu₂O nanoparticles and their electrocatalytic and photocatalytic properties. *RSC Advances* 2014, 4 (23), 12043-12049.
- 20 Ahmed, J.; Trinh, P.; Mugweru, A. M.; Ganguli, A. K., Self-assembly of copper nanoparticles (cubes, rods and spherical nanostructures): Significant role of morphology on hydrogen and oxygen evolution efficiencies. *Solid State Sciences* 2011, 13 (5), 855-861.
- 21 Ahmed, J.; Ganguly, A.; Saha, S.; Gupta, G.; Trinh, P.; Mugweru, A. M.; Lofland, S. E.; Ramanujachary, K. V.; Ganguli, A. K., Enhanced electrocatalytic activity of copper-cobalt nanostructures. *The Journal of Physical Chemistry C* 2011, 115 (30), 14526-14533.
- 22 Melnikov, P.; Nascimento, V. A.; Zanon Consolo, L. Z., Thermal decomposition of gallium nitrate hydrate and modeling of thermolysis products. *Journal of Thermal Analysis and Calorimetry* 2012, 107 (3), 1117-1121.

- 23 KumeKawa, Y.; Hirai, M.; Kobayashi, Y.; Endoh, S.; Oikawa, E.; Hashimoto, T., Evaluation of thermodynamic and kinetic stability of CuAlO₂ and CuGaO₂. *Journal of Thermal Analysis and Calorimetry* 2010, 99 (1), 57-63.
- 24 Amrute, A. P.; Łodziana, Z.; Mondelli, C.; Krumeich, F.; Pérez-Ramírez, J., Solid-state chemistry of cuprous delafossites: synthesis and stability aspects. *Chemistry of Materials* 2013, 25 (21), 4423-4435.
- 25 Han, M.; Jiang, K.; Zhang, J.; Yu, W.; Li, Y.; Hu, Z.; Chu, J., Structural, electronic band transition and optoelectronic properties of delafossite CuGa_{1-x}Cr_xO₂ (0 ≤ x ≤ 1) solid solution films grown by the sol-gel method. *Journal of Materials Chemistry* 2012, 22 (35), 18463-18470.
- 26 Pellicer-Porres, J.; Segura, A.; Martínez, E.; Saitta, A. M.; Polian, A.; Chervin, J. C.; Canny, B., Vibrational properties of delafossite CuGaO₂ at ambient and high pressures. *Physical Review B* 2005, 72 (6), 064301.
- 27 Ahmed, J.; Menaka; Ganguli, A. K., Controlled growth of nanocrystalline rods, hexagonal plates and spherical particles of the vaterite form of calcium carbonate. *CrystEngComm* 2009, 11 (5), 927-932.
- 28 Taurino, I.; Carrara, S.; Giorcelli, M.; Tagliaferro, A.; De Micheli, G., Comparison of two different carbon nanotube-based surfaces with respect to potassium ferricyanide electrochemistry. *Surface Science* 2012, 606 (3–4), 156-160.
- 29 Min-Jung, S.; Dong-Hwa, Y.; Joon-Hyung, J.; Nam-Ki, M.; Suk-In, H., Comparison of effective working electrode areas on planar and porous silicon substrates for cholesterol biosensor. *Japanese Journal of Applied Physics* 2006, 45 (9R), 7197.
- 30 Aljabali, A. A. A.; Barclay, J. E.; Butt, J. N.; Lomonossoff, G. P.; Evans, D. J., Redox-active ferrocene-modified Cowpea mosaic virus nanoparticles. *Dalton Transactions* 2010, 39 (32), 7569-7574.
- 31 Lee, Y.; Suntivich, J.; May, K. J.; Perry, E. E.; Shao-Horn, Y., Synthesis and activities of rutile IrO₂ and RuO₂ nanoparticles for oxygen evolution in acid and alkaline solutions. *The Journal of Physical Chemistry Letters* 2012, 3 (3), 399-404.
- 32 Zhao, C.; E, Y.; Fan, L., Enhanced electrochemical evolution of oxygen by using nanoflowers made from a gold and iridium oxide composite. *Microchimica Acta* 2012, 178 (1-2), 107-114.

33 Stoerzinger, K. A.; Qiao, L.; Biegalski, M. D.; Shao-Horn, Y., Orientation-dependent oxygen evolution activities of rutile IrO_2 and RuO_2 . *The Journal of Physical Chemistry Letters* 2014, 5 (10), 1636-1641.