ISSN 2229-5518

Synthesis of layered double hydroxide and their application in DSC

Kareem Jumaah AL-Salihi
University of Sulaimani Faculty of science /School of Science of Education Department of Chemistry
Karimjumaa69@yahoo.com
Kareem.jibrael@suluniv.ed.iq

Abstract: Mg-Al/CO3 layered double hydroxide (LDH) 5:1 ratio was synthesized by co-precipitation method from nitrate salt solutions. The LDH has been characterized by X-ray diffraction, FT-IR spectroscopy and TG thermal analysis. A paste of LDH and TiO2-P25 also have been prepared and used as photoande electrode in dye sensitized solar cell devices. The cells devices constructed by films of prepared composite materials TiO2-P25, Mg-Al/CO3 LDH, and mix of TiO2-P25 with Mg-Al/CO3 LDH using a N719 as sensitizer. The results showed that the device based on TiO2-P25 photoanode has the highest (Jsc=10.046 mAcm-2), (FF = 0.65) and (η =4.57%), compared to the devices based on the devices based on LDH and mix of TiO2- LDH which are gives 0.994 mAcm-2 and 1.624 mAcm-2 respectively.

Keywords: dye sensitized solar cells, photo-anode, layer double hydroxide, co-precipitation method.

Introduction

The demand for sustainable energy sources, dye sensitized solar cells (DSCs) have been considered as potential alternatives for the next generation solar cells due to low cost photovolataic technology, high solar energy to conversion efficiencies and friendly to environment"[1],[2]". Typically DSCs composed of dye adsorbed on semiconductor metal oxide electrode, electrolyte containing $I^{/}I_3^-$ redox couple and Pt- counter electrode" [3]".

The photo anode plays an important role on the photo injection of electron from sensitizers in DSC. In general, photo anode materials used which have high area to adsorb sufficient amount of dye, highly porous for effective mass transport by diffusion and a suitable band gap for effective electron injection and fast electron transport "[4]". Wide band gap metal oxide semiconductor such as TiO_2, ZnO, SnO_2 and Nb_2O_5 have been commonly used as photoanode materials due to their good stability, large surface area and good electronic properties "[5],[7]". As an alternative to band gap irradiation of metal oxides, Grätzel and coworkers have shown that solar responsiveness can be significantly improved when oxide surfaces are modified by adsorption or covalent attachment of dyes" [8]".

Layered double hydroxides (LDHs) are a group of anionic clay-like materials with unique layered structures "[9]". The structure of all LDH consists of positively charged mixed metal hydroxide layers separated by charge balancing anions and water molecules "[10]". The general chemical formula of these layered double hydroxides can be written as:

$$[M_{1-x}^{2+} M_x^{3+} (OH)_2](A^{n-})_{x/n} \cdot mH_2O$$

Where M^{2+} and $^{M3+}$ are divalent and trivalent cations respectively, and A^{n-} is an interlayer anion "[11]". The main properties of (LDHs) are their ability to substitute their interlayer anions with preservation of the layered structure "[12]". Type of materials are well known for their applications such or catalyst or as catalysts supports "[13]" ion exchangers "[14]" biosensors based on clay modified electrodes "[15]", and also is used as an adsorbent to remove dyes from effluents of textile, plastic and paper industries. Thermal treatment of LDH can lead to breakdown of the layered structure and the formation of the mixed metal oxides with high specific surface area "[16]". The mixed metal oxides interests as a promising for solar energy conversion and it also shows great potential in manufacture on a large scale because of the low cost, high purity and good quality control "[17]". This main aim of the present work was the preparation and photovoltaic application of the Mg-Al (LDH) as a photoanode electrode in dye sensitized solar cell, it will become a new approach for the preparation of anode materials for the DSSC by a

calcination method using the LDH as a photo anode electrode.

2. Experimental

2.1 Materials

All chemical reagents (puriss grade) were used without further purification, $Mg(NO_3)_2.6H_2O$, of $Al(NO_3)_3.9H_2O$, $NaHCO_3$, were purchased from Sigma Aldrich. LiI,4-tertbutylpyridin, iodine, and3-Methoxypropionitrile (Fluka) used as received. N-Methylbenzimidazole (NMBI) was purchased from Aldrich Cis-bis(isothiocyanato)bis(2,2'-bipyridyle-4,4'-discarboxylato)-ruthenium(II)-bis-tertabutylammonium, (coded as N719), was purchased from Dyesol company.

2.2 preparation of Mg-Al/CO_3 layered double hydroxide

Mg-Al/CO_3(LDHs) was prepared by co-precipitation a method adopted from the literature "[18],[19]". A solution containing (2M) $NaHCO_3$ and (0.2M) NaOH was added to 400 ml of distilled producing a solution of PH 10. Another solution was prepared containing a mixture of (46.15g) of $Mg(NO_3)_2.6H_2O$ and (22.5g) of $Al(NO_3)_3.9H_2O$ in 400 ml of distilled water with ratio Mg/Al (5:1), (all chemicals were used from Aldrich). Both solutions were heated to 70 ^oC and combined together through a Pyrex glass T-piece, adjusting the flow rate to maintain PH 10 with continuous stirring. Once addition was completed, the slurry was stirred at 70 ^oC for one hour then cooled to room temperature for 24 h. After cooling, the resulting precipitate was filtered and washed several times with distilled water and dried at 70 ^oC. The dry powder (LDHs) was analyzed by XRD, TGA and FT-IR

2.3 Preparation of TiO_2-p25 and Mg-Al/CO_3 (LDH) pastes

The TiO_2 paste has been prepared as per procedure for screen printing pastes described elsewhere "[20]". By dissolving ethyl cellulous in terpniol, the added TiO_2P 25 powder the mixture and stirring for 24 hr, finally the paste was homogenized by homogenizer for 30 minutes followed by sonification by sonifier for 15 minutes. A similar procedure was adapted to prepare LDH paste by dissolving 1 gm of ethyl cellulose in 2 ml of terpniol then added 2 gm of LDH powder to the mixture and stirring for 24hr, and then homogenized the mixture for 30 minutes.

2.4 Fabrication of photoanode electrode

For working electrode conductive glass (TEC- 15, Pilkington), (3 x 1.5 cm) was washed with isopropanol and dried under nitrogen. One layer of TiO_2-P25 paste was printed onto the conductive side of glass using doctor blade method "[21]". The layer thickness was defined by a scotch tap. The same procedure were applied with using LDH paste and also mix of LDH and TiO_2 paste .the resulting TiO_2-P25, LDH and mix of TiO_2-P25/ LDH (1:1) films were sintered at 450 ^oC for 30 min. After then the films were cooled to 30 ^oC then immersed in N719 dye (1 mM) for 24 hr for dyeing.

2.5 Preparation of Pt- electrode

To prepare the counter electrode, a hole was drilled on apart through conductive glass (TEC-15, Pilkington) (3 cm x 1.5 cm) and the glass was washed with isopropanol and dried in air. Then the conductive side of the glass was coated with an aqueous solution of H_2PtCl_6 (40 µL of 5mM, Aldrich) and the electrodes were sintered at 400^oC for 30 min.

2.6 Preparation of electrolyte

The composition of the electrolyte was as follows: 0.05 M I_2 and 0.7 M LiI in 3-methoxypropionitrile (3MPN), with 50 mM 4-tertbutylpyridinin a mixture of acetonitrile and valeronitrile (1:1) ratio.

2.7 Device manufacturing

Devices were then assembled by first placing a Surlyn™ (DuPont) gasket around the TiO_2 photo-electrode and then placing the platinized counter electrode on top of this and sealing at 120 ^oC with gentle pressure for 1 min. Finally, prior to the sensitization procedures described below, contacts were made onto the working and counter electrodes using conductive silver paint (Agar).

2.8 Characterization

The XRD pattern was recorded using a Rigaku D/MAX-rA Xray diffractometer with Cu Ka radiation (δ = 0.15418 nm). The samplewas scanned for 2Θ values ranging from 3° to 70° with a scan speed of 1/min. Thermogravimetric and differential thermal analysis (TG– DTA) were carried out in air using a SDTQ600 comprehensive thermal analyzer with a heating rate of 10^oC/min. IR spectra was obtained with KBr pellets using a FTIR spectrophotometer (Bruker RFS100/S FT). The current- voltage characteristics for all devices were measured using a keithley 2400 source meter, in a voltage range (0-1 V) at a maximum current 0.2 A.

3. Results and discussions

Mg-Al/CO_3 has been synthesized by co-precipitin method as shown from the XRD pattern Fig. (1) The hydrotalcite type phase was characterized in synthesized layered double hydroxide, more intensive and sharper reflections of the (003) and (006) planes low 2Ø value (11°) and (23°) respectively, and broad asymmetric reflections at higher 2Ø (34 - 66°) can be observed in the XRD patterns. The (009) reflection overlaps with the (102) resulting abroad signal.

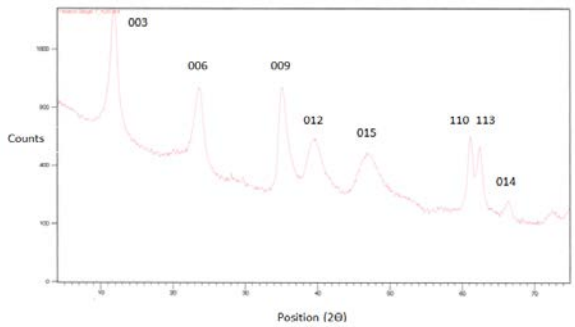

Figure (1): XRD pattern of Mg-Al/CO_3 LDH synthesised by co-precipitation method at PH 12.

Fig (1) shows the FT-IR spectrum of Mg-Al/CO_3 LDH, Abroad band which has located at 3450 cm^{-1} is the stretching vibration both of hydroxide group layers and interlayer water molecules. The strong band at 1383 cm^{-1} is characteristic of the intercalated carbonate group. A sharp band located at 790 cm^{-1} is assigned to the Mg-O vibration "[19]".

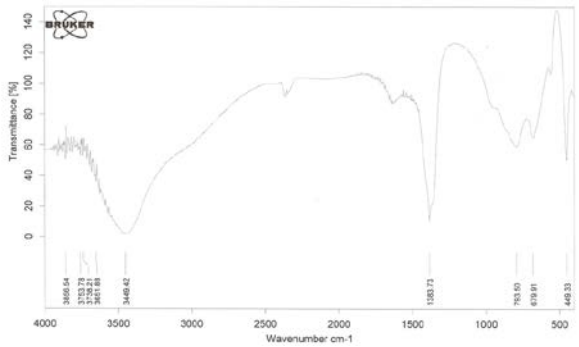

Figure (2): FT-IR spectra of Mg-Al/CO_3 LDH

Thermogravimetric (TG) analysis in figure (2) shows the thermal change of the hydrotalcite like layered Mg-Al/CO_3 LDH. Using a heating rate of 10 ^{o}C min^{-1} in air atmosphere and the temperature range from 30 ^{o}C 850 ^{o}C with ceramic sample holder has been used. Mg-Al/CO_3 LDH undergo thermal decomposition at higher temperatures shows that the mass changes up to 200 ^{o}C is due to the removal of interlayer and adsorbed water

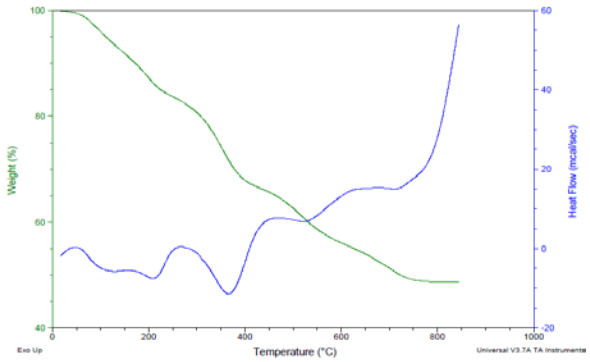

Figure (3): TGA analysis of Mg-Al/CO_3 LDH synthesised at PH 12.

Figure (4) shows the photocurrent density-voltage curves obtained under AM 1.5 simulated sunlight (100 mW cm^{-2}) for DSCs devices prepared with The devices of various photoanode materials of TiO_2-P25, Mg-Al/CO_3 LDH and mix of TiO_2-P25 and Mg-Al/CO_3 LDH (1:1) were sensitized with N719 dye (1 mM) in association with electrolyte I_3^-/I^- and Pt. counter electrode [5]. The performance parameters of the DSCs devices are summarized in Table1. As compared with the photoanode electrodes a high energy conversion efficiency of 4.57% was achieved with the device of TiO_2-P25 which was higher than the devices of LDH and mix of TiO_2-P25 and Mg-Al/CO_3 LDH that of (0.62%) and (0.38%), respectively

Table (1): I-V data of 1 cm^2 TiO_2-P25, LDH and mix of TiO_2-P25/LDH (1:1) devices dyed with 1 mM N719

Photoanode material	η %	*V*oc (V)	*J*sc (mA/cm^2)	FF
TiO_2	4.57	0.70	10.046	0.650
LDH	0.38	0.75	0.944	0.548
TiO_2- LDH	0.62	0.59	1.624	0.646

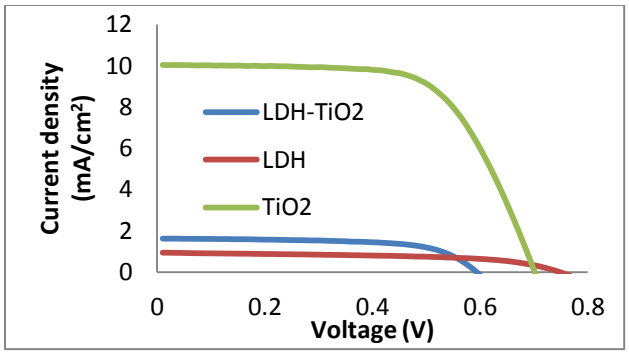

Figure (4): Current density-voltage characteristics of DSCs for the comparing photoanode electrodes under illumination of a simulated solar light (AM 1.5,100 mV cm^{-2})

The device based on TiO_2-P25 photoanode has the highest (*J*sc=10.046 $mAcm^{-2}$), (FF = 0.65) and (η =4.57%), compared to the devices based on the devices based on LDH and mix of TiO_2- LDH which are gives 0.994 $mAcm^{-2}$ and 1.624 $mAcm^{-2}$ respectively. Higher short circuit current density (*J*sc) value means better electron transfer to the redox mediator for the TiO_2-P25 device [22]. Thus the device based on a layer of LDH shows low (*J*sc=0.994 $mAcm^{-2}$), (FF = 0.548) and (η =0.38%). Upon mixing TiO_2-P25 paste with LDH paste by the ratio (1:1 w/w) to prepare photoanode electrode the device displayed enhancement, i.e., (*J*sc=1.624 $mAcm^{-2}$), (*V*oc=0.59 V), (FF = 0.646) and (η =0.62%).

Conclusion

Layered double hydroxide, a type of anionic clay materials, was developed as an effective metal oxide for photoanode in DSCs. Mg-Al/CO_3 LDH was prepared by co-precipitation method and used as photoanode electrode in DSC device. Different kinds of photoanode materials of (TiO_2-P25, Mg-Al/CO_3 LDH and mix of TiO_2-P25 and Mg-Al/CO_3 LDH (1:1)) were sensitized with N719 dye (1 mM) in association with electrolyte I_3^- /I^- and Pt. counter electrode. The results shows that the device based on TiO_2-P25 photoanode has the highest (*J*sc=10.046 $mAcm^{-2}$), (*V*oc=0.7 V), (FF = 0.65) and (η =4.57%), as compared to the devices based on the devices based on LDH and mix of TiO_2- LDH which are gives 0.994 $mAcm^{-2}$ and 1.624 $mAcm^{-2}$ respectively.

References

[1].O'Reagan, B., Grätzel, M. "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films", *Nature*, **Vol. 353**, (1991), 737-740.

[2]. Chiba Y., Islam A., Watanabe Y., Komiya R., Koide, N., and Han L., "Dye sensitized solar cells with conversion efficiency of 11.1% ", *Japanese Journal of Applied physics, part 2: letters*, **Vol. 45**, (2006), 638-640.

[3]. Grätzel M. "Photo electrochemical cells", *Nature*, **Vol. 414**, (2001), 338-344.

[4]. Wang, Z, Kawauchi, H, Kashima, T, Arakawa, H, "Significant influence of TiO_2 photoelectrode morphology on the energy conversion efficiency of N719 dye-sensitized solar cell", *Coordination Chemistry Reviews*, **Vol. 248**, (2004), 1381-1389

[5].Ito S., Chen P., Comte P., Nazeeruddin M. K., Pechy P., and Grätzel M, "Fabrication of screen printing pastes from TiO_2 powders for dye sensitised solar cells", *progress in Photovoltaics: Research and applications*, **Vol. 15**, (2007), 603-612.

[6]. Saito M., and Fujihara S., "Large photocurrent generation in dye-sensitized ZnO solar cells", *Energy & Environmental Science*, **Vol. 1**, (2008) pp. 280-283.

[7].Onwona-Agyeman B., Kaneko S., Kumara A., Okuya M., Murakami K., Konno A., and Tennakone K., "Sensitization of nanocrystalline SnO_2 films with indoline dyes", *Japanese Journal of Applied Physics, Part 2: Letters*, **Vol. 44**, (2005) pp. L731-L733.

[8].Guo P., and Aegerter M. A., "RU (II) sensitized Nb_2O_5 solar cell made by the sol-gel process", *Thin Solid Films*, **Vol. 351**, (1999), pp. 290-294.

[9].Cavani, F., Trifir`o, F., and Vaccari, A. "Hydrotalcite-type anionic clays: preparation, properties and applications". *Catalysis Today*, **Vol. 11,** (1991), 173–301.

[10].Mascolo G., Marino O., "A new synthesis and characterization of magnesium-aluminium hydroxides", *Mineralogical Magazine*, 1980, **Vol. 43**, 619-621.

[11]. Wang Q., and O'Hare D., "Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets", *Chemical Reviews*, **Vol. 112**, (2012), 4124-4155.

[12]. Mascolo G., and Marino O., "A new synthesis and characterization of magnesium-aluminum hydroxides", *Mineralogical Magazine*, **Vol. 43**, (1980), 619-621

[13]. Bouraada M.,Belhalfaoui F., and Quali M. S., "Sorption study of an acid dye from an aqueous solution on modified Mg-Al layered double

hydroxides", *Journal of Hazardous Materials* , **Vol. 163**, (2009), pp 463-467.

[14].Shigeo M., "Anion-Exchange properties of hydrotalcite-like compounds", *Clays and clay Minerals* **Vol. 31**, (1998), pp 305-311.

[15]. Christine M., "Sensors and biosensors based on clay modified electrodes new trends", *Applied Clay Science*, **Vol. 27**, (2007), 159- 177.

[16]. Gago S., Pillinger M., Santos T. M., Gonçalves I. S. "Zn-Al Layered double hydroxide pillared by different carboxylate anions", *Ceramics – Silikáty*, **Vol. 48**, (2004), 155-158.

[17]. Zheming N., Fangfang X. , Ping W. and Genting C., "Synthesis ,characterization and release of curcumin –intercalated Mg-Al-layered double hydroxides", *Applied Clay Science* ,**Vol. 40**, (2008), pp 72-80.

[18]. Guimaraes, J. L., Marangoni, R., Ramos, L. P., Wypych, F. "Covalent Grafting of Ethylene Glycol into the Zn−Al−CO_3 Layered Double Hydroxide". *J. Colloid Interface Science*, **Vol. 227**,(2000), 445−451.

[19]. Seron A., Delorme F., "Synthesis of layered double hydroxides (LDHs) with varying pH: A valuable contribution to the study of Mg/Al LDH formation mechanism", *Journal of Physics and Chemistry of Solids*, **Vol. 69**, (2008), 1088–1090.

[20]. Wang, Z, Kawauchi, H, Kashima, T, Arakawa, H, "Significant influence of TiO_2 photoelectrode morphology on the energy conversion efficiency of N719 dye-sensitized solar cell", *Coordination Chemistry Reviews*, **Vol. 248**, (2004), 1381-1389

[21]. Hagfeldt, A., Baschloo, G., Sun, L., Pettersson, H., "dye sensitized solar cells", *Chemical review*, **Vol. 110**, (2010), 6595-6663.

[22].Pavol G., Milan M., "efficiency of full screen printed dye sensitized solar cells with conductive polymer PEDOT:PSS counter electrode", *Chem. Listy*, **Vol. 107**, (2013), s101-s202