

## GRAPHENE/CARBON BLACK COUNTER ELECTRODE FOR PEROVSKITE SOLAR CELL

*Nutsuda Bunyoo, Nuttapol Pootrakulchote\**

*Department of Chemical Technology, Faculty of Science, Chulalongkorn University*

*Center of Excellence on Petrochemical and Materials Technology*

Keywords: renewable energy; solar energy; perovskite solar cell; graphene; formamidinium lead iodide

### ABSTRACT

Counter electrodes (CEs) of perovskite solar cell (PSC) are usually prepared by thermal evaporation of noble metals such as Au or Ag under high vacuum condition. The replacement of costly metallic CEs by carbon material has attracted recent attentions aiming at the lower manufacturing cost of this kind of high-efficiency bulk heterojunction organometallic halide photovoltaic cell based on  $\text{NH}_2\text{CH}=\text{NH}_2\text{PbI}_3$  light harvester. This research has investigated the synthesis of graphene by electrolytic exfoliation method which was conducted by applying bias voltage in range of 0–8 V to the pure graphite electrodes submerged in the 0.5 M sulfuric solution. The graphene powder having surface resistance of 10.4 ohm/square was obtained with high carbon-content as confirmed by XRD and SEM results. PSC test devices were fabricated using FTO glass substrate by layering thin films of different materials in following order: compact layer / electron transport layer / insulating layer / hole transport medium / Graphene. A controlled amount of carbon black nanoparticles was added to graphene layer to enhance the interfacial contact. Formamidinium lead iodide ( $\text{FAPbI}_3$ ) perovskite was then synthesized using sequential step method and was penetrated through carbon electrode into inner layers to generate the bulk heterojunction. Finally, the devices have been tested and the photovoltaic characteristics including photo-conversion efficiency have been reported.

\*Corresponding author: [nuttapol.p@chula.ac.th](mailto:nuttapol.p@chula.ac.th)

### INTRODUCTION

The world currently depends heavily on coal, oil, and natural gas for its energy. Fossil fuels are non-renewable energy, becoming too expensive or too environmentally damaging to retrieve. In contrast, there are many types of renewable energy resources such as wind and solar energy that are constantly replenished and never run out. The solar energy converted to electricity by means of solar cells is believed to replace non-renewable energy in a near future. The main benefit of utilizing solar energy is that the process does not produce any pollutants. Perovskite material is favourable as the sunlight absorber in solar cell. It provides many advantages such as strong light absorption in the visible,

tunable band gap and high open circuit voltage close to band gap energy. For the past few years, perovskite thin film photovoltaic devices have been rapidly developed for their excellent photovoltaic performance[1].

Perovskite refers to any material sharing the crystal structure of calcium titanate ( $\text{CaTiO}_3$ ), based on the general formula  $\text{ABX}_3$ . When used in solar cells, A is typically a small molecular cation, B is a metal ion such as lead, and X is a halide such as iodide, bromide or chloride. The example of perovskite such as Methylammonium lead iodide ( $\text{MAPbI}_3$ ) and Formamidinium lead iodide ( $\text{FAPbI}_3$ ). The structure of perovskite solar cell contains FTO glass, compact layer, electron transport layer, insulating layer, hole transport medium and counter electrode. The counter electrode of perovskite solar cell is usually prepared by thermal evaporation of noble metals such as Au or Ag, which make PSC uncompetitive in price. Other materials have been studied to replace noble metals including conductive polymer[2] or carbon material which has been reported previously of the matching working function to that of gold ( $\sim 0.5$  eV compared to  $\sim 5.1$  eV of gold) [3]. This research studied the photoconversion efficiency of PSC using self-prepared graphene materials as counter electrode.

## EXPERIMENTAL

### A. Synthesis of graphene.

Synthesis of graphene by electrolytic exfoliation [4]. High purity graphite rods (0.8 \* 0.8 cm.) were used as working and counter electrodes in the experimental setup. 0.5 M Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) dissolved in de-ionized (DI) water is used as electrolyte. Prior to the process of exfoliation, working electrode (WE) was given a cathodic pre-treatment (8 V) to remove any physically adsorbed impurities and to make the availability of surface pore for intercalation more efficient. Then the WE was subjected to a pre-treatment process at relatively sufficient bias. The anodic exfoliation was commenced at lower potentials of 0–5V at a ramping step of 1V per 600 sec. Then a ramping intercalating potential of 8V was given to the WE and the exfoliated black product was collected at the bottom of the bath. The dispersed product was then thoroughly washed in DI water and subjected to sonication for 4 h to further disintegrate the graphitic flakes. After that the homogeneously dispersed graphene colloidal was centrifuged at 8,000 rpm for 30min and decanted, then dried at  $60^\circ\text{C}$  after filtration.

### B. Preparation of carbon paste.

Graphene 2.4 grams, carbon black 0.6 grams,  $\text{ZrO}_2$  0.35 grams and Terpeneol 9 ml were added into ethanol solution. This solution was treated with ultrasonic probe for 5 min, followed by magnetic stirring for 10 min, and those processes were repeated for three times, followed by ball-milling for 6 hour, then adding 15 g ethyl cellulose (10%wt ethyl cellulose with ethanol). Final process is to evaporate ethanol by rotary evaporator.

### C. Device fabrication

A fluorine doped tin oxide (FTO) coated glass was etched with zinc powder and 2 M hydrochloric acid. Then, the FTO glass was cleaned by ultrasonic bath with detergent water, deionized water and ethanol respectively. These glass substrates were immersed in

50 mM of  $\text{TiCl}_4$  for 30 min at  $70^\circ\text{C}$ , followed by rinsing with DI water and calcined at  $500^\circ\text{C}$  for 30 min. Then compact  $\text{TiO}_2$  layer was screen-printed onto the substrate and calcined at  $500^\circ\text{C}$  for another 30 min. Finally, these substrates were immersed in 100 mM of  $\text{TiCl}_4$  solution for 30 min at  $70^\circ\text{C}$ , followed by rinsing with DI water. The final heat treatment at  $500^\circ\text{C}$  for 30 min was then followed to complete the formation of the blocking layer. After cooled down to room temperature, the mesoporous  $\text{TiO}_2$  nanocrystal film was deposited with screen printing, followed by  $\text{ZrO}_2$  insulating layer, then calcined at  $500^\circ\text{C}$  for 30 min. Then carbon paste was screen-printed onto the top and calcined at  $400^\circ\text{C}$  for 30 min. The structure of  $\text{TiO}_2/\text{ZrO}_2/\text{C}$  substrate show on Fig.1. The deposition of  $\text{FAPbI}_3$  onto the  $\text{TiO}_2/\text{ZrO}_2/\text{C}$  mesoscopic porous film was achieved by a two-step sequential method. A controlled amount of  $\text{PbI}_2$  solution in Dimethylformamide (DMF) was dropped on the composite films and heated at  $70^\circ\text{C}$  for 30 min. After cooled down the films were dipped into a FAI (Formamidinium iodide) solution dissolved in isopropanol (10 mg/mL) for 10-15 min to form perovskite. Finally, the whole substrates were heated at  $90^\circ\text{C}$  for 30 min.

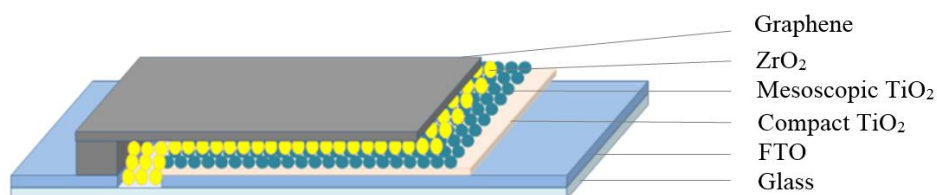


Fig. 1 A schemed structure of solar cells based on CCE (Carbon counter electrode)

## RESULTS AND DISCUSSION

### A. Graphene synthesis process

Graphene was synthesized by electrolytic exfoliation technique. Sulfuric acid is a suitable media for electrochemical intercalation as well as the exfoliation of graphite precursors because: 1) the ionic size of sulfate ion ( $\text{SO}_4^{2-}$ ) (0.46 nm) is larger than the graphite interlayer spacing (0.335 nm) and the intercalated  $\text{SO}_4^{2-}$  ion has weak bonds between the graphitic layers, so that leads to the exfoliation of graphite into separate graphene layers; 2) the electrolysis of sulfate ions and the co-intercalated water lead to the generation of gaseous species such as  $\text{SO}_2$ ,  $\text{O}_2$  and  $\text{H}_2$ . The efficient intercalation as well as gas eruption promote the separation of graphene sheets from neighboring graphene layers. [5] The graphene prepared by electrolytic exfoliation of graphite rods was analyzed for elemental content. It was found that graphite has pure carbon element but the graphene product consists of carbon 72.43%, oxygen 25.64%, hydrogen 1.34% and sulfur 0.61% by weight. The sulfur element clearly comes from sulfate ion of sulfuric acid (electrolyte) attached on surface of graphene. Figure 2 shows XRD analysis of synthesized graphene in comparison with that of graphite powder. The XRD pattern of graphite shows significant peaks at  $2\theta = 26.36^\circ$ ,  $42.37^\circ$ ,  $44.55^\circ$  and  $54.30^\circ$  which are indexed to the planes (002), (100), (101) and (004) respectively, corresponding to those of graphite powder. However, the peak at  $2\theta = 26.16^\circ$  in XRD pattern of the synthesis graphene appears broader and shifted towards lower angles compared to that of graphite powder. This peak broadening and shifting towards the lower angle may be attributed to its corrugated structure and the increase of

interlayer spacing within graphitic structures. The graphene powder having surface resistance of 10.4 ohm/square was obtained with high carbon-content.

Table 1. CHN elemental composition of each component

Sample	Elements (%wt.)				
	C	O	H	S	N
Graphite	99.53	0.00	0.00	0.00	0.00
Synthesized Graphene	72.43	25.64	1.34	0.61	0.00

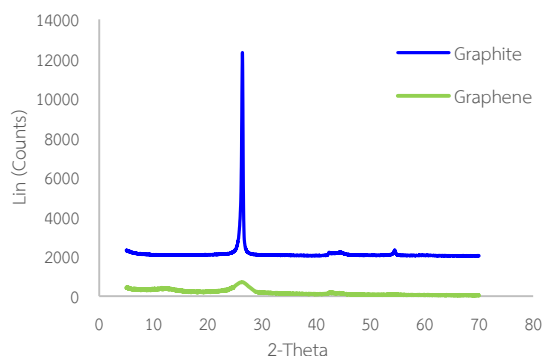


Fig. 2 XRD patterns of graphite and synthesized graphene

### B. Perovskite Characterization

Formamidinium lead iodide (FAPbI<sub>3</sub>) is one type of perovskite, as its crystalline structure was confirmed by XRD technique shown in Fig 3. , For the FAPbI<sub>3</sub> based cell, XRD reflections at 24.32°, 28.17°, 31.55°, 40.20° and 42.76° are indexed to (202), (220), (222), (400), and (330) reflections, corresponding to the black polymorph of FAPbI<sub>3</sub>[6]. Absorption spectrum of FAPbI<sub>3</sub> (Fig.4) covers a broad range of wavelength from 450 nm to 800 nm as shown in Fig 4.

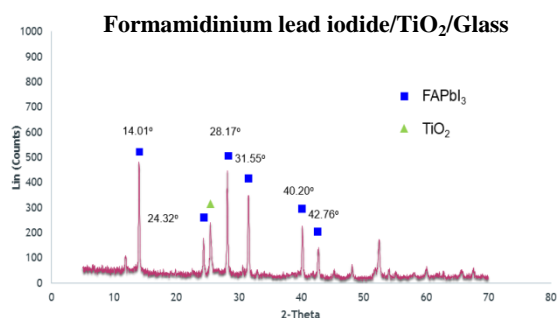


Fig.3 XRD pattern of Formamidinium lead iodide/TiO<sub>2</sub>/Glass

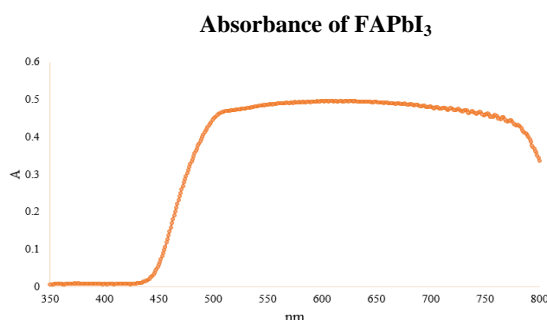


Fig.4 Absorbance of Formamidinium lead iodide

### C. Characterization of devices

Fig 5 shows the preliminary current–voltage (J–V) characteristics of PSC device based on Graphene/Carbon black counter electrode. The result exhibits  $V_{oc}$  0.76 V,  $J_{sc}$  8.09 mA/cm<sup>2</sup>, Fill Factor(FF) 41.13% and photoconversion efficiency (PCE) of 2.52%. Low values of the characteristic current density and the fill factor are probably resulting from boundary resistance arising from an improper contact between CE and FTO glass, causing low efficiency of the test cell.

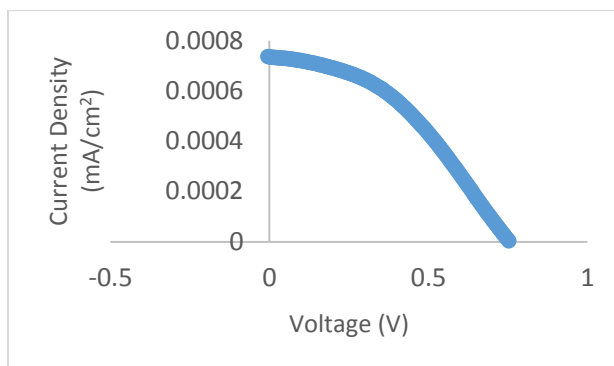


Fig.5 Current density vs. voltage curve under AM 1.5G illumination( $100 \text{ mW /cm}^2$ ) of Graphene/Carbon black counter electrode solar cell device (active area  $0.3 * 0.3 \text{ cm}^2$ )

## CONCLUSIONS

High carbon-content graphene was successfully prepared by electrolytic exfoliation method and can be applied for counter electrode on perovskite solar cell by mixing with carbon black by graphene:carbon black = 4:1 weight ratio. The perovskite was synthesized by two-step sequential method, and its formation was confirmed using XRD and UV-Visible spectroscopy techniques. The importance of carbon counter electrode in the determination of the efficient device is the homogeneity of carbon paste that has a strong interfacial effect when brought into contact with the FTO glass.

## ACKNOWLEDGEMENTS

Authors would like to thanks the Department of Chemical Technology, Chulalongkorn University and Center of Excellence on Petrochemical and Materials Technology for financial support.

## REFERENCES

- Liu, D., et al.**, Controlling  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  Film Morphology with Two-Step Annealing Method for Efficient Hybrid Perovskite Solar Cells, *ACS Appl Mater Interfaces*, 2015. **7**(30): p. 16330-7.
- Jiang, F., et al.**, Metal electrode-free perovskite solar cells with transfer-laminated conducting polymer electrode, *Optics Express*. **23**(3): p. A83-A91.
- Ku, Z., et al.**, Full printable processed mesoscopic  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$  heterojunction solar cells with carbon counter electrode, *Sci Rep*, 2013. **3**: p. 3132.
- Kumar, S.S. and Archana, M.**, Simple, Fast and Cost-Effective Electrochemical Synthesis of Few Layer Graphene Nanosheets, *Nano*, 2015. **10**(02): p. 1550019.

**Yang, S., et al.**, New-Generation Graphene from Electrochemical Approaches: Production and Applications, *Adv Mater*, 2016. **28**(29): p. 6213-21.

**Min, H., et al.**, Efficient hole-conductor-free, fully printable mesoscopic perovskite solar cells with a broad light harvester  $\text{NH}_2\text{CH}=\text{NH}_2\text{PbI}_3$ , *J. Mater. Chem. A*, 2014. **2**(40): p. 17115-17121.