Large-Scale Synthesis of Few-Layer Graphene from Magnesium and Different Carbon Sources and its Application in Dye-Sensitized Solar Cells

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Graphical Abstract

Keywords:

Self-propagating high-temperature synthesis, Few-layer graphene, Dye-Sensitized Solar Cells.

Abstract

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A self-propagating high-temperature synthesis (SHS) method to synthesize few-layer graphene (FLG) from magnesium and different carbon sources is demonstrated. These carbon sources include CaCO_3 , $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, glucose, and polyvinyl alcohol (PVA). FLG produced by SHS method has a 3D porous structure with a special nanocrystallinity, and a low amount of defects. This fast, energy saving and low cost method is competitive as a candidate for industrial production of graphene for a wide range of applications. It is found that CaCO_3 are superior to others among these starting materials according to DSC properties. The dye-sensitized solar cell (DSC) with a FLG (produced from CaCO_3) counter electrode (CE) achieves a power conversion efficiency higher than that obtained with a reference DSC using a Pt counter electrode. The charge transfer resistance of FLG DSC is $0.13 \, \Omega \, \text{cm}^2$, which is more than thirty times lower than that of the DSC having a Pt counter electrode. SHS FLG has been demonstrated to be a promising alternative counter electrode in DSC.

1. Introduction

Graphene is a single planar layer of carbon atoms with many amazing properties such as giant intrinsic mobility [1], high thermal conductivity [2], super high strength [3], impermeability to gases [4] and high transparency [5]. All these unique features make graphene a promising and innovative material for many potential applications.

In order to meet the rapidly increasing demand of the graphene from the scientific research and industrial applications, both top-down and bottom-up strategies have been developed to produce graphene. Top-down strategies include such methods as micromechanical cleavage of graphite [6], liquid phase exfoliation of graphite [7, 8], laser exfoliation of highly ordered pyrolytic graphite [9], H_2O_2 plasma etching of graphite [10], unzipping of nanotubes [11], and chemical oxidation and reduction method [12-14]; examples of bottom-up methods are chemical vapor deposition (CVD) [15, 16], epitaxial growth on SiC [17], arc discharge [18], Shock-wave synthesis [19], conventional calcination from Mg and

CaCO₃ [20], and reduction of CO [21] and CO₂ (dry ice) [22].

However, most of those techniques suffer from several drawbacks. Firstly, the large amount of the heat or the electricity is needed during the synthesis process for most of these methods except for chemical oxidation and reduction method and CO₂ reduction method. Secondly, chemical oxidation and reduction method is efficient and inexpensive, however, strong oxidizing (e.g. H₂SO₄, HNO₃, KMnO₄) and reductive reagents are hazard and environment unfriendly; and a series of time consuming steps are also required [13]. Thirdly, the dry ice used in CO₂ reduction method is easy to sublime but hard to be stored and hard to control the synthesis process, which makes the method not convenient enough. Consequently, preparing graphene sheets with less energy consumption, simple and low cost process is always a huge challenge.

Self-propagating high-temperature synthesis (SHS) is a method of combustion synthesis, which denotes highly exothermic processes leading to solid-state products [23]. Since its discovery in the early 1970s [24, 25], SHS has attracted more and more attentions as an alternative method to the conventional furnace technology for the synthesis of a variety of advanced materials such as carbides, nitrides, borides and oxides [26-32]. SHS is characterized by the fact that the reaction is initiated at one end of the sample, and self-propagates through the reactants in the form of a combustion wave at a velocity which varies from 0.1 to 25 cm s⁻¹. The combustion wave driving force is the heat energy releasing from the exothermic combustion reactions; accordingly no further energy supply is needed after initialization. With these merits, SHS can provide an efficient way for the industrial production of ceramic powders. However, to the best of our knowledge, SHS has not been applied to synthesis graphene yet.

Here, we demonstrate a simple and facile SHS method to synthesize the few-layer graphene (FLG) by the reaction of magnesium (Mg) with various carbon sources. These carbon sources include inorganic substance (CaCO₃, 3MgCO₃·Mg(OH)₂·3H₂O), organic

small molecule (glucose), and polymer (polyvinyl alcohol) (PVA). Compared with other graphene preparation techniques, SHS method is commercially competitive because it is fast, scalable, and low cost.

The dye-sensitized solar cells (DSC) is the third generation of solar cell, with the promising high conversion efficiency, simple manufacturing, low-cost, and also able to utilize the indoor light resource. It was first reported with the efficiency of 7.1 %-7.9 % in 1991 [33]. General procedures of preparing DSCs have been explored and developed to improve the control group to a reasonable high performance. The current world record is over 14 % [34], achieved by Hanaya's team in 2015. The highest efficiency of DSC with iodine electrolyte is 11.4% [35]. These solar cells utilize three main components: (1) Dye molecules will absorb the light. (2) The photo anode consists of the semiconducting material, i.e. TiO_2 , ZnO and WO_3 , with dye molecules attached onside. (3) To regenerate electrons for the dye molecules, the conductive counter electrode will catalyse the electrolyte redox reaction [35].

To achieve the low cost DSC with high efficiency, the proper material for cathode is one of the key factors. The conventional counter electrodes are the fluorine doped tin oxide (FTO) substrates with sputtered Pt thin film onside [36-38]. With the excellent catalytic activity, electrical conductivity, and corrosion resistance, Pt is a good candidate for high-efficiency DSC. Unfortunately Pt is also a relatively rare element and expensive material. To decrease DSC cost and further achieve practical large-scale production, an alternative cathode material with superior electrocatalytic activity as well as excellent high conductivity is highly desirable. Due to the low cost, excellent catalytic activity, high durability, and electrical conductivity, carbon based materials have been utilized as effective alternative counter electrode with low cost for many years [39-42]. Carbon nanohorns and nanotubes [39], carbon black [41] and graphite [42] have all been tested as potential counter electrodes. Graphene-based counter electrodes have been reported [43-48], recently. In the state-of-art Co-mediated DSC, the electrochemical performance of graphene-based DSC can also be improved dramatically

upon chemical reduction. [46] However, in general, the efficiencies of the DSC with graphene-based counter electrodes in iodine based electrolyte are still lower than that of the DSC with Pt. Therefore, it is still a challenge to develop materials with high performance and low cost as the counter electrode for DSCs. Here, we investigate the effect of SHS graphene synthesized by different carbon sources on the properties of DSC. FLG produced by SHS method has been demonstrated to be a good candidate for counter electrode in DSC.

2. Experimental

2.1 Synthesis of graphene

Magnesium powder (200 mesh, 99.0 %), polyvinyl alcohol powder (PVA, $M_n=1750$), AR grade carbonate salts (Calcium carbonate, CaCO_3 , basic magnesium carbonate, $3\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 3\text{H}_2\text{O}$) and AR grade glucose (99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd.. All materials were used as obtained without further purification.

Magnesium powder (16.8 g) was mixed with different carbon sources in a mortar with pestle, respectively; the carbon sources included 35.0 g of calcium carbonate, 127.8 g of magnesium carbonate, 21 g of glucose or 33.6 g of PVA. The mixture was added into a ceramic boat, which was put into a 21.2 L stainless-steel combustion chamber (30 cm in diameter and 30 cm in height) under an atmosphere of high purity carbon dioxide (99.9%) with a flow rate of 0.5 L s^{-1} in the synthesis system. The schematic illustration of the combustion synthesis system is shown in Figure 1. One end of the mixture was ignited by an electric ignition device composed of a DC power source and a resistant wire heater, the ignition current was 22 A. When the mixture was ignited the reaction was spontaneously propagating through the mixture in a form of a combustion wave from one side to another and the reaction finished when the combustion wave reached the other side of the mixture.

Figure 1. Schematic of the self-propagating high-temperature synthesis system.

As a contrast, Mg powder (16.8 g, 99.5 wt%) also burned in continuous CO_2 gas with a flow rate of 0.5 L s^{-1} in the synthesis system. In order to remove MgO, CaO and unreacted reactants in the raw product, the raw product was washed with dilute hydrochloric acid (20 wt%); Both the oxides in the raw product and the unreacted reactants can react with HCl to form soluble salts in water and thus they can be removed easily to get pure carbon material. The black product was washed with deionized water until the pH value of filtrate turned out to be neutral and then washed with alcohol and finally dried at 100°C in a vacuum drying chamber. At last, a black SHS product was obtained. The products synthesized by the reactions of Mg with CaCO_3 , $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, CO_2 , glucose and PVA are denoted as G_{CaCO_3} , G_{MgCO_3} and G_{CO_2} , G_{glucose} and G_{PVA} , respectively.

2.2 Chemical analysis and textural characterization

The microstructure of the SHS product was observed in a scanning electron microscope (SEM, Helios Nanolab 600i), and a transmission electron microscope (JEM-2100). Raman spectra were obtained using a Raman Station (B&WTEK, BWS435-532SY) with a laser operating at 532 nm. Powder X-ray diffraction (XRD) analyses were performed on a Philips X'Pert diffractometer with Cu-K_a radiation ($\lambda=1.54 \text{ \AA}$). The X-ray photoelectron spectroscopy (XPS) measurements were conducted with a K-alpha (Thermo Fisher) system.

2.3 Electrochemical characteristics

A 12 μm diffusion TiO₂ layer (DSL 18NR-T, Dyesol) and 8 μm scattering layer (WER4-O, Dyesol) were screen-printed onto the FTO (Pilkington FTO glass Tec 15) glass. The photo-electrode was sintered at 500 °C for 30 min in air. The sintered photo-electrode was immersed in the N719 ([RuL₂(NCS)₂]:2 TBA (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA = tetra-n-butylammonium), N719, Dyesol) solution ($3 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$) for 2 h at 50 °C. The anode and cathode were packaged with the sealant (1170 Series, 60 μm , Solaronix) at 125 °C. The electrolyte solution was made of 0.05 M I₂, 0.5 M N-methylbenzimidazole (NMBI), 1.0 M 1-propyl-3-methyl-imidazolium iodide (PMII), and 0.1 M guanidinium thiocyanate (GNCS) in 2-methoxypropionitrile (MPN) as the solvent.

3. Results and Discussion

The microstructures of FLG samples are shown by the SEM in Figure 2. It can be observed that G_{CaCO₃} has a porous, almost continuous 3D structure as shown in Figure 2(a); the 3D structure of G_{CaCO₃} is composed of thin corrugated sheets with irregular shapes. Compared with G_{CaCO₃}, G_{MgCO₃} shows 3D pore structures without corrugated sheets as shown in Figure 2(b). The microstructure of G_{glucose} in Figure 2(c) is similar to G_{MgCO₃} but it has a small number of corrugated graphene sheets. Compared with G_{CaCO₃}, G_{MgCO₃} and G_{glucose}, it is very interesting to observe that the G_{PVA} sheets display novel sphere shape, and the diameter of sphere graphene can range from 20-100 nm as shown in the Figure 2(d). And this sphere

graphene may be attributed to a large amount of gases released during thermal decomposition of polymer PVA in SHS reaction. MgO was a by-product in all the SHS processes and could act as a template for the preparation of graphene since graphene sheets can be grown on the MgO [49, 50]. MgO could contribute to the shape construction of the graphene sheets and be removed by HCl.

Figure 2. SEM images of the few-layer graphene samples produced from different carbon sources: (a) G_{CaCO_3} ; (b) G_{MgCO_3} ; (c) $G_{glucose}$; (d) G_{PVA} .

Figure 3. TEM images of the few-layer graphene: (a) TEM image of G_{CaCO_3} ; (b) HRTEM of G_{CaCO_3} sheets; (inset image: selected area electron diffraction patterns (SADP) of G_{CaCO_3} sheets); (c) HRTEM image of $G_{glucose}$; (d) HRTEM image of G_{PVA} .

Transmission electron microscopy (TEM) study was further used to investigate the morphology and crystalline structure of G_{CaCO_3} , $G_{Glucose}$ and G_{PVA} . A representative TEM image of G_{CaCO_3} in Figure 3(a) clearly shows the nanostructure with a diameter ~ 50 nm. A high-resolution transmission electron microscopy (HRTEM) image of G_{CaCO_3} in Figure 3(b) shows abundant edges of the graphene sheets. Generally the number of the layers of these edges approximately ranges from 3 to 8. The typical interplanar spacing of the sheets is ~ 0.34 nm which is similar to the interplanar spacing of graphite (002) (0.335 nm). A corresponding SADPs of G_{CaCO_3} has also been inserted in Figure 3(b). A clear continuous sharp Debye ring can be found which arises from nanocrystalline structure with a interplanar spacing of $1.21 \text{ \AA}$

related to graphene (110). As shown in Figure 3(c), the HRTEM image of G_{Glucose} indicates that the number of the layers is 2-4. The sphere-shaped graphene (G_{PVA}) is clearly displayed in Figure 3(d). The number of the layers of G_{PVA} is about 2-5. The TEM results prove that the SHS products are FLG with special nanocrystalline structure. Both the nanostructure and the abundant thin edges of the SHS graphene may endow SHS graphene with special catalytic and electrochemical properties.

XPS spectra of FLG are shown in Figure 4. The samples were etched by Ar for 120 seconds before XPS measurement. The peaks at 1303.7 eV and 350.14 eV are corresponding to Mg (1s) and Ca (2p), respectively, which illustrate the presence of a small amount of Mg and Ca in G_{CaCO_3} . The quantified contents of the elements C, O, Mg and Ca found in G_{CaCO_3} determined by XPS are shown in Table 1. From Table 1, the main element in G_{CaCO_3} is carbon (94.18 at%), while the contents of Mg (1.11 at%), Ca (1.01 at%) and O (3.70 at%) are much less. Element O could come from MgO and CaO, absorbed oxygen and oxygen-containing groups in G_{CaCO_3} . Since Mg and Ca can exist in a state of oxides as MgO and CaO, which means that the element O in oxides could be 2.12 at%, and O content for the absorbed oxygen and the oxygen-containing groups in G_{CaCO_3} could be less than 1.58 at%. As a result, only a small quantity of carbon in G_{CaCO_3} is in oxidization state. Compared with reactants of inorganic substance, when organic small molecule (glucose) and polymer (polyvinyl alcohol) were used as reactants, the contents of carbon were decreased to 82.56 at% (G_{Glucose}) and 89.90 at% (G_{PVA}) (See Table 1). This result indicates that the contents of oxygenic groups in FLG tend to be increased when the organic reactants were used in the SHS reactions.

Figure 4. XPS spectra of few-layer graphene: (a) survey spectrum of G_{CaCO_3} ; (b) C_{1s} spectrum of G_{CaCO_3} ; (c) C_{1s} spectrum of G_{MgCO_3} ; (d) C_{1s} spectrum of $G_{glucose}$; (e) C_{1s} spectrum of G_{PVA} .

Table 1. XPS analysis of C, O, Mg, Ca contents in few-layer graphene sample.

Sample	Atomic Concentration (at%)			
	C	O	Mg	Ca
G_{CaCO_3}	94.18	3.70	1.11	1.01
G_{MgCO_3}	93.68	5.63	0.68	
$G_{Glucose}$	82.56	13.1	4.43	
G_{PVA}	89.90	9.30	0.80	

Figure 4 (b) shows the XPS spectrum of C_{1s} of G_{CaCO_3} . The peak located at 284.4 eV

originates from the sp^2 -hybridized carbon [51], the higher relative intensity of peak at 284.4 eV suggests that the sp^2 carbon is the main state of carbon in FLG. The small peaks at 285.5 eV, 287.4 eV, and 289.6 eV correspond to C-OH, C-O-C and O=C-O structure, respectively [52, 53], which indicate the existence of a small quantity of oxygen-containing groups.

Figure 5. (a) Raman spectra of samples produced by different starting materials ; (b) histogram of I_{2D}/I_G corresponding to curves in (a) and FLG^{20} ; (c) histogram of I_D/I_G corresponding to curves in (a), FLG^{20} and reduction graphene oxide (RGO)⁶⁵.

Raman spectroscopy is one of the most widely used techniques to characterize the structural and electronic properties of graphene including the number of layer, disorder and defect structures, defect concentration, and doping levels [54-56]. Figure 5(a) gives the Raman spectra of SHS products synthesized from different raw materials, and as a comparison Raman spectrum of graphite is also demonstrated. The spectra were recorded under the same experimental conditions. The Raman spectra of the SHS products in Figure

5(a) show three peaks. The G band at 1570 cm^{-1} represents the in-plane bond-stretching motion of the pairs of sp^2 hybridized C atoms (the E_{2g} phonons); while the D band at 1341 cm^{-1} corresponds to breathing mode of rings or K-point phonons of A_{1g} symmetry; the second-order D (2D) band at 2678 cm^{-1} originates from a two phonon double resonance process [54, 57]. From Figure 5(a) it can be found that the 2D peaks of all SHS products (2678 cm^{-1}) are greatly shift to lower wavenumber compared with that of graphite (2714 cm^{-1}), which is a typical feature of FLG.

In order to observe the Raman spectra more clearly, we have separated the Raman spectra in Figure 5 (a) into 5 images as shown in Figure S1 (a) - (e). As shown in Figure S1 (a) - (d), the 2D peaks of G_{CaCO_3} , G_{MgCO_3} , G_{CO_2} and $\text{G}_{\text{glucose}}$ can be fitted according to Lorentzian equation, shown as the red lines. These results indicate that the materials produced by SHS method belong to turbostratic carbon.[57, 58]

On the other hand, as reported in a recent study on the structure of graphene, the position of the 2D peak in the Raman spectrum can identify the presence of few-layer graphene.[22, 59] The 2D peak of few-layer graphene is distinguishable from graphite, downshift from 2730 to $\sim 2675\text{ cm}^{-1}$. [54, 58] As shown in Figure S1, the 2D peaks of G_{CaCO_3} , G_{MgCO_3} , G_{CO_2} and $\text{G}_{\text{glucose}}$ are 2678, 2679, 2676 and 2679 cm^{-1} , which are in agreement with the raman spectra of few-layer graphene produced by similar methods in literatures. [20, 22, 60] The features of our Raman spectra indicate that the SHS products are turbostratic few-layer graphene. In addition, the 2D peak of G_{PVA} is almost disappeared as shown in Figure S1 (e), which is similar with the 2D peak of reduced graphene oxide, [61] indicating that the structure of G_{PVA} is different from other products.

The position of the 2D band and the ratio of the peak intensity of 2D and G (I_{2D}/I_G) have been used for the identification of the number of graphene layers [62, 63]. The values of I_{2D}/I_G obtained from Figure 5(a) for samples produced from different raw materials are shown in Figure 5(b). It can be found that the I_{2D}/I_G values of G_{MgCO_3} (0.54) and G_{CaCO_3} (0.81) are much

larger than that of graphite (0.33) but also than that of FLG produced by conventional calcination from Mg and CaCO_3 (0.36) [20]. Since the higher the value of I_{2D}/I_G it is, the fewer the layer number of graphene will be.⁴¹ Both of these results clearly indicate that the SHS products produced from CaCO_3 and basic MgCO_3 are FLG.

Furthermore, it is generally accepted that the intensity ratio of the D to G bond (I_D/I_G) can reflect the defect concentration of carbonaceous materials; the lower the ratio, the less the defect concentration [64]. As shown in Figure 5(c), the minimum value of I_D/I_G of the SHS products is 0.32 and 0.49 corresponding to G_{CaCO_3} and G_{MgCO_3} , while the values corresponding to G_{CO_2} , G_{Glucose} and G_{PVA} are 0.94, 0.97 and 0.96 separately. In comparison with G_{CaCO_3} and G_{MgCO_3} , which were synthesized by inorganic matters, the values of I_D/I_G of the G_{Glucose} (micromolecule) and G_{PVA} (macromolecule) are closed to RGO [65] and graphene synthesized by CO_2 . The results indicates that SHS graphene synthesized by inorganic matters has higher quality and that SHS graphene synthesized by organic matters has more defects comparable with RGO and graphene synthesized by CO_2 .

Figure 6. XRD patterns of: (a) raw G_{CaCO_3} and (b) G_{CaCO_3} , G_{MgCO_3} and G_{CO_2} purified by HCl.

Figure 6(a) shows XRD pattern of raw G_{CaCO_3} . The peaks in Figure 6(a) can be identified as CaO (JCPDS No. 48-1467), MgO (JCPDS No. 45-0946) and CaCO_3 (JCPDS No. 47-1743), separately. XRD patterns of FLG samples produced by Mg with CaCO_3 , $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ and CO_2 are similar as shown in Figure 6(b). The most intense peak in Figure 6(b) is at 25.9° corresponding to the (002) plane of FLG, and the peak at 43.2° is

assigned to (100) plane of graphene, which is another characteristic peak of graphene structure. The results are in close agreement with the literature [20, 22]. According to the analysis of FLG XRD patterns, it can be concluded that most of the Mg and CaCO_3 have participated the reaction, and the products are CaO, MgO and graphene. Small sum of residual CaCO_3 may exist near the wall of the ceramic boat where the reaction heat is easy to be distributed and the temperature near the wall is not high enough for the reaction. Compared with G_{CaCO_3} , G_{MgCO_3} and G_{CO_2} , the (002) peaks corresponding to G_{PVA} and G_{Glucose} are obviously broad and almost disappeared as shown in Figure 6(b), which indicates thinner or amorphous carbon exists in G_{PVA} and G_{Glucose} . The peaks corresponding to CaCO_3 , CaO or MgO almost disappear in Figure 6(b) as compared to Figure 6(a), indicating the good purification effect of HCl.

There are several advantages of the SHS method for graphene. Firstly, SHS method for graphene is fast and energy efficient. It only needs several minutes to finish the reactions, and it utilizes the energy released by the exothermic combustion reactions. From this aspect, it is much better than the conventional calcination method which needs heating at high temperature for several hours. Because SHS processes can produce very high temperature instantly, the volatile impurity in the reactants can be eliminated (“self-cleaning” effect) during the reaction, thus SHS graphene has low defect density and high purity.

Secondly, magnesium powder and all of the carbon sources used are abundantly available with low price, which makes the price of SHS graphene cheap enough for most of the applications. Moreover, since both the reagents and main products are solid materials, the SHS process is easy to be implemented compared to CO_2 reduction method using dry ice.

Thirdly, it is a great obstacle to keep the graphene sheets individually separated during their preparation, storage and application since flat graphene sheets are generally prone to agglomerate spontaneously and even restack to form graphite as a result of strong van der Waals forces [66]. The 3D structure of SHS graphene could offer an effective solution for the

challenge, which is useful to prevent the sheets from recombination and very useful for practical applications.

These unique advantages make SHS method a more competitive candidate toward the industrially production of 3D graphene with low price, large scale and high quality. The SHS graphene with novel 3D structure may contribute to a wide range of potential applications in nanocomposites, catalysts, energy generation and storage.

As an application of SHS graphene, the SHS graphene samples are initially used as a counter electrode in DSCs. 0.5 wt% polyvinylidene fluoride (PVDF) in N, N-dimethylacetamide was used as binder to paint FLG sheets onto FTO-glass. The novel counter electrodes were shown in the inset image in Figure 7(b). We tested one group of reference DSCs with Pt counter electrode and DSCs with FLG samples. Figure 7(a) shows the normalized efficiency values of samples produced by different starting materials compared with Pt. The normalized efficiency values of G_{CaCO_3} , G_{PVA} , G_{CO_2} , $G_{Glucose}$ and G_{MgCO_3} are 107%, 100%, 90%, 88% and 69%, respectively. The normalized efficiency of G_{CaCO_3} is the highest among the five samples. This result may be caused by the unique 3D structure composed of thin corrugated sheets and lower defect concentration of G_{CaCO_3} . The characteristic J - V plots of the devices were shown in Figure 7(b); the detailed photovoltaic parameters are summarized in Table 2. For the DSCs with G_{CaCO_3} , the short-circuit current density (J_{sc}) is measured to be 13.83 mA cm^{-2} yielding a total conversion efficiency of 5.4 %, with an open-circuit voltage (V_{oc}) and fill factor (FF) of 0.72 V and 54 %, respectively. The efficiency of 5.4 % is also higher than that of 5.0 % for the reference DSC with evaporated Pt as counter electrode. The values of V_{oc} and J_{sc} of DSCs with hybrid structure are slightly higher than that of DSCs with Pt.

To further understand the important parameters in the operation of the DSCs, electrochemical impedance spectroscopy (EIS) analysis employing the ZView software were carefully conducted. The EIS experiment was conducted under the dark conditions. The

applied bias voltage is the open-circuit voltage, V_{oc} . In the impedance measurements, the frequency range is from 100 mHz to 1 MHz; while the amplitude of alternating current is 10 mV. As clearly shown in Figure 7(c), there are two semi-circles in the Nyquist plots. Upper inset is the zoomed-in EIS result, which clearly reflects the first semi-circle of the DSC. After the plots have been fitted with the equivalent circuit shown in the lower inset of the Figure 7c, the charge transfer resistance (R_{pt}) of G_{CaCO_3} was found to be $0.13 \Omega \text{ cm}^2$. This value is more than thirty times lower compared to that of the DSC having a Pt counter electrode, which is $\sim 4 \Omega \text{ cm}^2$. This proves that G_{CaCO_3} offer lower interface resistance between the electrolyte and counter electrode, compared to the reference DSCs. The electrocatalytic activity of G_{CaCO_3} electrode was compared to Pt electrode by measuring the cyclic voltammetry (CV) in a three-electrode system (Figure 7d). The typical CV curves for both G_{CaCO_3} and Pt counter electrodes state the reactions indicative of the iodide (I^-)/triiodide (I_3^-) complex redox peaks. For the G_{CaCO_3} electrode, the peak potential for I^- oxidation shifts more cathodically while the peak potential for I_3^- reduction shifts more anodically as compared to Pt electrode. In addition, the cathodic peak current density for I_3^- reduction on G_{CaCO_3} electrode is larger than that on Pt electrode. The comparison of CV results indicates G_{CaCO_3} catalyzes I^-/I_3^- redox reaction more efficiently than Pt counterpart, which is consistent with the results of full DSC performance.

Moreover, though the efficiency of the DSC with SHS graphene on non-conductive flexible substrate is only 1.8 %, which is not as high as some other reported FTO-free DSC [44, 67], we believe further work about this paintable process of preparing counter electrodes offers a much wider applications on many flexible surfaces in the future.

Figure 7. Photovoltaic parameters of DSCs: (a) Normalized efficiency of samples produced by different starting materials; (b) J - V curves of the reference and the DSCs with G_{CaCO_3} ; Inset image represents the novel counter electrodes for DSCs. (c) Nyquist plots of the DSCs with G_{CaCO_3} . Upper inset is the zoomed-in EIS result, clearly reflecting the first semi-circle of the DSC with G_{CaCO_3} . Lower inset shows the equivalent circuit used in the fitting process. (d) Cyclic Voltammetry of G_{CaCO_3} and Pt in a three-electrode setup.

Table 2. J - V parameters of DSC with G_{CaCO_3}

Counter Electrode	V_{oc} [V] ^{a)}	J_{sc} [$mA\ cm^{-2}$] ^{b)}	FF ^{c)}	PCE ^{d)}
SHS Graphene on FTO glass	0.72	13.83	0.54	5.4%
SHS Graphene on non-conductive flexible substrate	0.69	9.98	0.26	1.8%
Pt on FTO glass	0.68	13.04	0.56	5.0%

a) V_{oc} =open-circuit voltage; b) J_{sc} =short-circuit photocurrent density; c) FF=fill factor; d) PCE=power conversion efficiency.

4. Conclusions

In conclusion, $CaCO_3$, $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$, glucose, and polyvinyl alcohol (PVA) can be used to synthesize FLG by SHS method, which is a fast, energy efficient, highly productive and low cost method. Compared with conventional methods of fabrication of

graphene, the SHS method has advantage of wide raw material sources such as inorganic substance (CaCO_3 , $3\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 3\text{H}_2\text{O}$), organic small molecule (glucose), and polymer (polyvinyl alcohol) (PVA), which endows SHS method with potential commercial applications of graphene. FLG samples have different microstructure by changing of raw materials. G_{CaCO_3} produced by SHS method has a porous structure composed of thin corrugated sheets with lower defect concentration, high purity and a nanocrystalline structure mainly made up of sp^2 carbon atoms. The porous structure is beneficial to prevent the graphene sheets from recombination, which makes it more useful in many applications. The DSCs with G_{CaCO_3} achieved an efficiency of 5.4 %, higher than 5.0 % obtained with a reference DSCs with Pt. EIS results found the R_{pt} of G_{CaCO_3} to be $0.13 \Omega \text{ cm}^2$ which is more than thirty times lower than that of the DSC having a Pt counter electrode. G_{CaCO_3} has been demonstrated to be an alternative counter electrode in DSC. In the future, SHS method is also very promising to be designed to produce doped graphene or graphene based composites by choosing different reagents.

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