Preparation of graphene and its application in dye-sensitized solar cells

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Graphene sheets were prepared using electrochemical and chemical steps followed graphite electrochemical oxidation, graphite chemical oxidation, ultrasound expholiation and chemical reduction of carbon material. Films of graphene were electrophoretically deposited from aqueous dispersion on FTO electrode. These films were tested as cathode for a dye-sensitized solar cell. The morphology of the prepared products was imaged by scanning electron microscopy; the intermediate compound, graphene oxide was characterized by IR spectroscopy.

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1. Introduction

Graphene is a two dimensional material of a mono- or few layers of sp^2 hybridized carbon atoms (carbon atoms form a planar sheet) which has attracted wide interest owing to its electronic, thermal, mechanical, chemical, and optical performances [1-6]. Boehm et al.[7] referred for the first time to such single layers of graphite as graphene. Novel applications such as transparent electrodes [8], field-effect transistors (FETs) [9,10], ultrasensitive sensors [4,11], new nanocomposites [12] are based on this material. Transparent graphene was used as catalytic material [13] instead of an expensive one, platinum, for the preparation of the cathode of a dye-sensitized solar cell since it catalyzes the reduction of I_2 to I^- after electron injection.

Novoselov et al [1] produced graphenes of high quality by dry mechanical exfoliation of crystalline graphite, but, in principle this is not a scalable technique; large area graphene was prepared on copper and nickel substrates via chemical vapor deposition [14-18]. However, the integration of graphene into practical device systems, especially on plastic substrates is complicated by the necessity using of high temperature. Another preparation method of graphene is chemical exfoliation of graphite in which a process of graphite oxidation and/or thermal expansion of graphite oxide (GO)/expandable graphite is involved [19-22]. In the most cases, GO was chemically prepared from graphite powder using Hummers method [23] or a modified Hummers method [24], which involved the oxidation of natural graphite powder with various oxidants in acidic media. Graphene oxide is usually synthesized by exfoliation of GO and graphene is prepared by reduction of exfoliated graphene oxide using a chemical reducer, like hydrazine.

In this study, we present the synthesis of graphene sheets using electrochemical and chemical methods and fabrication of a counter electrode based on graphene film for dye-sensitized solar cells.

2. Experimental

2.1. Materials

Graphite plate was used as received. Sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2) hydrazine monohydrate ($N_2H_4\ H_2O$) are all pure chemicals.

Electrochemical behavior of the graphene/FTO cathode was observed in an electrolyte containing 0.5M KI. 0.03M I_2, 0.1M $LiClO_4$ in acetonitrile/ ethylene carbonate (v/v=1:4).

2.2. Electrochemical oxidation of graphite

Two electrodes, a graphite plate and a platinum foil another were employed as anode and cathode, respectively, in 96% sulfuric acid and a constant potential (dc, 10V) was applied on the electrodes at 0^0C temperature. After 3 minutes electrolysis, the graphite electrode was swollen and a powder was collected in a Berzelius glass beaker by a light touch of the electrode with a glass rod; the powder was washed, filtered and dried at 300 ^{0}C. Linear voltammetry measurements were performed using an Autolab PGSTAT 30 potentiostat controlled by computer in a cell with three electrodes, a graphite plate with 8 cm^2 surface area as working electrode, a platinum foil as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode.

2.3. Preparation of graphene oxide foils by a chemical way

Partial oxidized graphite powder obtained by an electrochemical method was supplementary oxidized using a chemical way based on Hummers method. 0.5 g partial oxidized graphite powder was mixed with 12 ml 96% H_2SO_4 in a flask, which was cooled to 0^0C (ice bath). 1.54g of $KMnO_4$ was gradually added and the mixture was stirred 2 h at a temperature lower than 35^0C. Further, the mixture was diluted with 24 ml of de-ionized water and, after 1 h of stirring 72 ml deionized water and 1.3 ml 30% hydrogen peroxide solution were added. The resulting yellow mixture was filtered and washed with 10% HCl solution (129 ml) to remove metal ions; the obtained solid was dispersed in water by a light stirring with a glass rod (2 h of stirring) and again filtered and washed with deionized water to remove the acid (neutral pH). The collected paste from filter paper was dispersed in 100 ml deionized water by ultrasonication. In order to remove the unexfoliated graphite oxide, the brown dispersion was subjected to 30 min of centrifugation at 4000 r.p.m. The remaining dispersion was heated at 60 ^{0}C in air and graphene oxide foils were deposited on the wall of the beaker.

2.4. Synthesis of graphene

100 mg of graphene oxide were mixed with 100 ml deionized water in a 250-ml round-bottom flask, yielding an yellow- brown dispersion. The dispersion was sonicated 10 min using a Brasonic ultrasonic bath. At this dispersion 1.1 ml 98% hydrazine monohydrate was added and the mixture was heated at 100 ^{0}C, after a water-cooled condenser attaching to the flask. Graphene oxide was reduced in the course of 24 h and a black solid was gradually precipitated. The product was filtered on a fritted glass funnel, washed with deionized water (300 ml) and methanol (500 ml) and dried on the funnel [20].

2.5. Characterization

The morphologies of the prepared products were imaged by scanning electron microscopy (SEM), using Zeiss EVO 50 microscope. Graphene oxide was characterized by IR spectroscopy. The characterizations were performed on powders and films.

3. Results and discussion

During the electrochemical process with graphite as anode in concentrate sulfuric acid, the following reaction takes place:

$$C_m + 3H_2SO_4 \rightarrow [C_m^+ \cdot HSO_4^- \cdot 2\, H_2SO_4] + H^+ + e^- \qquad (1)$$

Where m is a function of quantity of electricity passed through the system; $HSO_4^- \cdot 2\, H_2SO_4$ groups are inserted between the carbon planes. Fig. 1 shows the response of current between the electrodes with respect to the applied potential when the insertion process carries on. Linear voltammogram points out that a potential more positive than 0.5V/SCE leads to the intercalation of anions acid and molecules between the carbon planes. The maximum quantity of absorbed H_2SO_4 into graphite corresponds to a product with m=24 [25]. The obtained product is stable only in the presence of concentrate acid; it is decomposed immediately by water, humid air, alcohol, ether, acetone, benzene regenerating graphite which always contains oxygen [23].

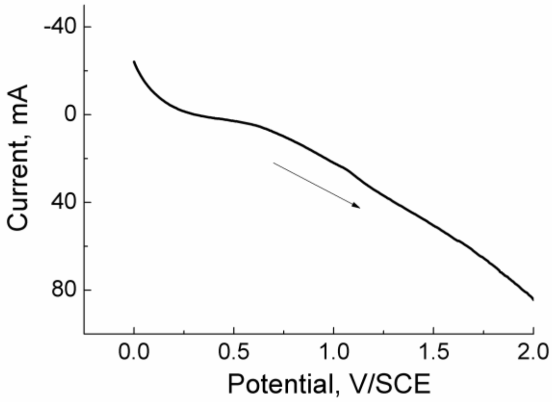

Fig. 1. Linear voltammogram recorded at the graphite working electrode in 96% sulfuric acid using a scan rate of 5mV/s.

The graphite partially oxidized by the electrochemical process was further oxidized and exfoliated by ultrasonication, in order to prepare graphene oxide. FT-IR spectrum of the product (Fig. 2) obtained in this step confirms the successful oxidation of the graphite.

The band at 3400 cm^{-1} can be assigned to O-H stretching vibrations, the sharp intense peak at 1730 cm^{-1} can be attributed to stretching of C=O groups and the peak at 1623 cm^{-1} was assigned to the vibrations of the adsorbed water molecules. The absorption bands at 1402, 1224 and 1051 cm^{-1} can be ascribed to O-H deformation, C-OH stretching and C-O stretching, respectively [26]. C-O of the epoxy groups in graphene oxide appear at 836 cm^{-1}.

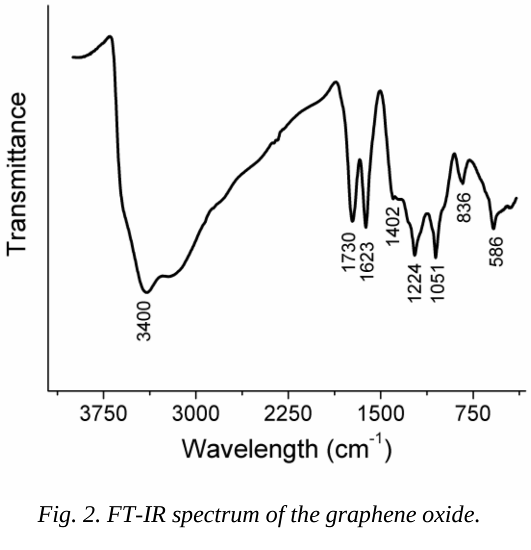

Fig. 2. FT-IR spectrum of the graphene oxide.

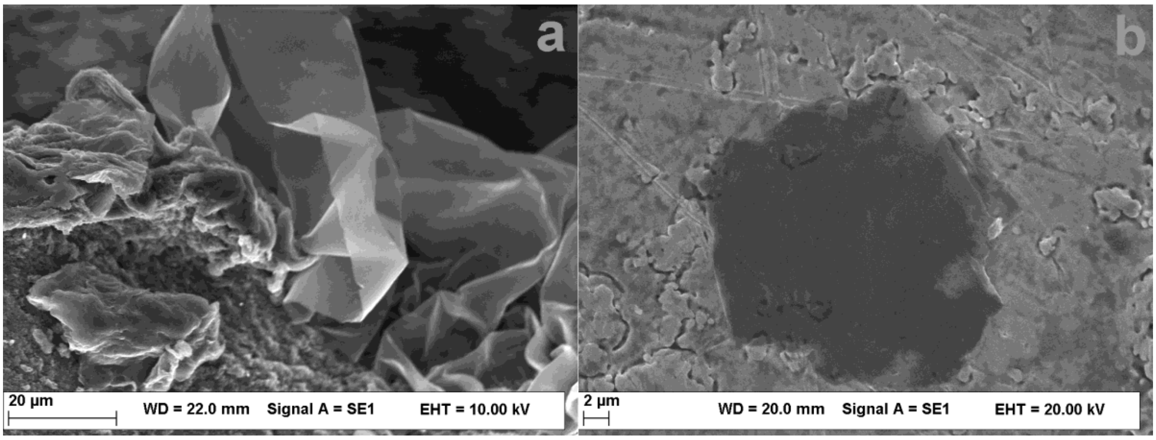

Fig. 3. SEM images of graphene powder a) transparent graphene sheet on microscope carbon double adhesive support; b) transparent graphene sheet deposited on platinum support by its immersion in 0.5mg graphene/1ml 1-methyl-2-pyrrolidone dispersion.

Reduction of the graphene oxide was carried out with aqueous N_2H_4; SEM images of the obtained black precipitate are presented in the Fig.3. The graphene sheets are transparent to electrons so that the morphological characteristics of the substrate are observed through them. However, due to incomplete exfoliation not many individual sheets are formed.

In another experiment, graphene oxide was chemically reduced to graphene in the presence of sodium lauricum sulfonicum: at 6 ml of graphene oxide aqueous dispersion (0.5 mg/ml) 0.03g sodium lauricum sulfonicum and 20 µl hydrazine monohydrate have been added. After 10 min heating at 90 ^{0}C a stable black dispersion was obtained. A graphene thin film was prepared using this dispersion in an electrophoretic experiment with FTO electrode as anode and a platinum foil as counter-electrode.

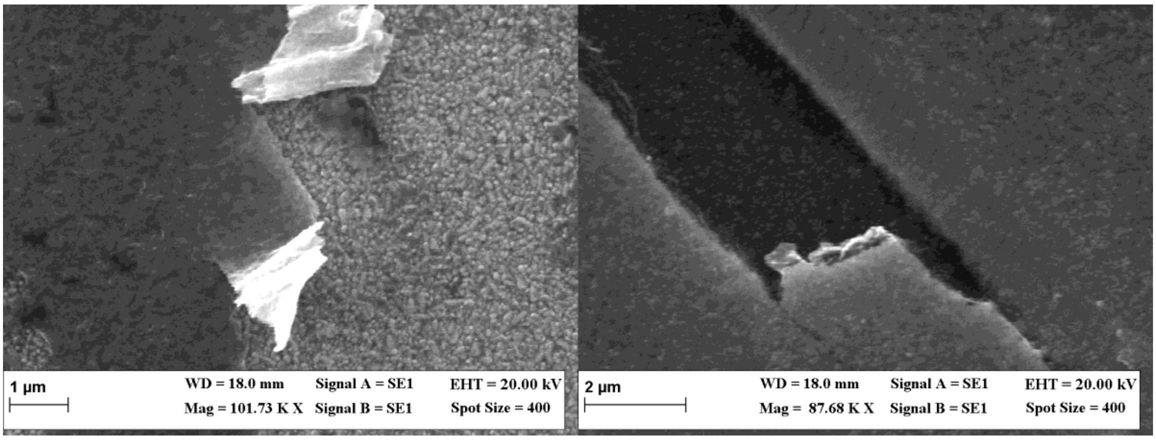

Fig. 4. SEM images of electrophoretically deposited graphene films at 3V on FTO.

A dc voltage of 3V was applied to the electrophoretic cell for 60 s; the deposition of carbon film was observed on the positive electrode. The samples were immersed in distilled water, dried by argon blowing and heated at 200 ^{0}C for five minutes. In the Fig. 4 are presented SEM images of these films on FTO electrode.

Graphene/FTO electrode was investigated as cathode for dye-sensitized solar cells. Pt, which is now used for the preparation of those cathodes, exhibits high electrocatalytic activity toward the iodide/triiodide redox couple, which is the common redox relay for most DSSC. Although the necessary amount of Pt on the cathode is very low, there is a challenge for substituting platinum with a cheaper material.

Fig. 5 presents the electrochemical behavior of graphene/FTO electrode in a cell with a platinum auxiliary electrode and an Ag/AgCl electrode as reference. The electrolyte 0.5M KI, 0.03M I_2, 0.1M $LiClO_4$ in acetonitrile/ethylene carbonate (v/v=1:4) closes the electrical circuit of the cell. The graphene/FTO electrode was prepared as above, by electrophoretic deposition. Comparatively, there are presented the electrochemical behaviors of a platinum electrode (Fig. 5,a) and a pure FTO electrode (Fig. 5,b curve1) in a similar cell.

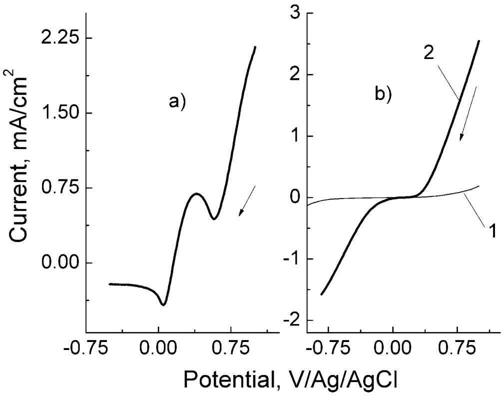

Fig. 5. Linear voltammograms of platinum (a) and graphene/FTO (b, curve 2) electrodes in the solution: 0.5M KI. 0.03M I_2, 0.1M $LiClO_4$ in acetonitrile/ ethylene carbonate (v/v=1:4). Comparatively is presented a linear voltammogram of FTO electrode (b, curve 1) in the same solution; scan rate 50 mV/s; auxiliary electrode was a platinum foil.

At the cathode of a dye-sensitized cell the following processes take place:

$$3I_2 + 2e^- \rightarrow 2I_3^- \qquad (2)$$

$$I_3^- + 2e^- \rightarrow 3I^- \qquad (3)$$

The two reducing processes are observed on the voltammogram of platinum electrode (Fig. 5,a); in the case of the graphene/FTO electrode the two processes do not appear separately and one can observe a cathodic shift of the reducing potential for I_2/I^-. However the current increases significantly in comparison with the case of the pure FTO electrode.

4. Conclusions

Graphene nanoplates were prepared by electrochemical and chemical processes; during the electrochemical process in concentrated sulfuric acid a partial oxidation takes place followed by exholiation of graphite plate. These processes are continued by subsequent chemical treatments. An oxidized form of graphite was obtained which was exfoliated by ultrasonication, with the formation of graphene sheets. However, due to incomplete exfoliation not many individual sheets are formed. FT-IR spectrum of this product confirmed the successful oxidation of the graphite. By reducing of graphene oxide dispersion with hydrazine was obtained graphene powder; SEM measurements showed formation of transparent graphene sheets. A graphene/FTO electrode prepared in an electrophoretical process was tested as cathode for a dye-sensitized solar cell. It was found that the iodine reduction processes occur at higher cathodical potential than the case of platinum electrode.

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