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Graphene oxide film as semi-transparent counter electrode for dye-sensitized solar cell

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ABSTRACT

Purpose: The aim of the paper is to fabricate semi-transparent graphene oxide counter electrodes for dye-sensitized solar cells.

Design/methodology/approach: A thermal reduction is applied to decreased the amount of surface oxygen functionalities on graphene sheets. For this purpose thermal treatments in oven in 250°C and 500°C were used. Graphene oxide materials were mixed with PEDOT:PSS and then deposited on FTO glass by spin coating method. PEDOT:PSS was added to graphene oxide to increase conductivity and enhance film forming ability.

Findings: Ultraviolet-visible spectroscopy measurement was carried out to monitor the degree of oxidation for the graphene samples. It has been found that annealing of graphene oxide counter electrodes under inert atmospheres enable a better ordering of graphene oxide films and also cause losing an oxygen functional groups, that makes layers become denser and smother, with a lower surface roughness, and thus less transparent.

Research limitations/implications: It has been found that due to development of the technology of dye-sensitized solar cells with graphene oxide counter electrode, it is possible to lowering a production costs by replacing a costly platinum. It is advisable to take into account in the further experiments application of counter electrode on different kinds of substrates in the selected process parameters, and research for using them in DSSC cells mass production.

Practical implications: DSSC cells are an interesting alternative to silicon solar cells. Presented in this paper results showed possibilities of modify dye-sensitized solar cells by replacing costly platinum.

Originality/value: It was shown that dye-sensitized solar cells with graphene oxide counter electrode can be used in building integrated photovoltaic.

Keywords: Dye-sensitized solar cells; Counter electrode; Graphene oxide

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MATERIALS

1. Introduction

In popular belief, fossil cells, which are currently the main but exhaustible resources, will be replaced by cleaner and cheaper renewable energy sources to meet environmental and economic challenges of the twenty-first century, including energy and environmental crisis. The development of new types of solar cells is driven by growing public awareness that oil reserves on Earth can be exhausted in that century.

Today's market is dominated by photovoltaic solar cells with a junction between inorganic materials with solid state, usually from a crystalline or amorphous silicon, using the experience and material availability resulting from the semiconductor industry [1-4]. In recent years, this dominance was disturbed by the appearance of a new generation of photovoltaic cells based on nanocrystalline materials and conductive polymer films. New generation of photovoltaic cells offers the prospect of low-cost manufacture of solar cells with a combination of various attractive features such as flexible or non-toxic of mainly used materials such as titanium oxide, which is used in paints, cosmetics and health care products. It is possible to complete separation of the semiconductor junction devices by replacing the contact phase of the semiconductor through the electrolyte-liquid or solid, resulting in a photo-electrochemical cell. Great progress in the preparation and characterization of nanocrystalline materials has opened new opportunities for these systems. One example of solar cells of this generation are dye-sensitized solar cells in which the optical absorption and charge separation process is achieved through the use of the dye as the material absorbing light and nanocrystalline semiconductor with a wide energy gap [5-12].

Dye-sensitized solar cells is consist of: photoanode, counter electrode and electrolyte. The counter electrode is one of the key elements of the dye-sensitized solar cells, which acts as a catalyst for the reduction reaction of the redox couple and is used as a mediator in the regeneration of the dye after electron injection or collection of holes in the hole conductive material. Fully obligation to transfer an electron from the external circuit to the electrolyte with a redox couple. Conductive glass coated with platinum is the most widely used counter electrode, but it is also one of the factors that significantly increase production costs due to the use of expensive platinum layers. It is important to search for new materials showing anti-corrosive, low cost, and allowing to produce a dye-sensitized solar cells with a relatively high efficiency [13-17].

An important issue is also the transparency of the counter electrode especially when used in Building Integrated Photovoltaics BIPV on glass and metal substrates. Transparency also allows the use in tandem cells.

In recent times, the new carbon nanomaterials with two-dimensional lattice-like honeycomb called graphene aroused interest because of their special electronic properties like [18-25]:

- 0 eV energy gap, which makes that the valence band affects the conduction band (Fig. 1),
- a high electron mobility,
- high thermal stability,
- optimal mechanical properties.

Graphene is extremely durable and at the same time very flexible and transparent. By graphene electrons flow at high speed.

Like other carbon materials, graphene has excellent thermal and mechanical properties, so can be used in optoelectronics, electronics and photovoltaics.

Graphene as the thinnest material in the universe is a flat two-dimensional layer of carbon with a thickness of only 1 nm, forming a hexagonal network. Graphene structure resembles a honeycomb, and can be regarded as part of graphite, consisting of carbon atoms linked together with sp^2 bonds in a two-dimensional hexagonal crystal lattice (Fig. 2) [18,21]. The electronic structure of graphene evolves with the number of layers approaching the limit for graphite of approximately 10 layers. Electrical properties of graphene also depend on the number of layers of graphene. The various layers can be stacked on each other in the form of (Fig. 3):

- simple hexagonal (AAA)
- hexagonal arrangement called Bernel`s (ABA)
- rhomboedrical-trigonal network (ABC).

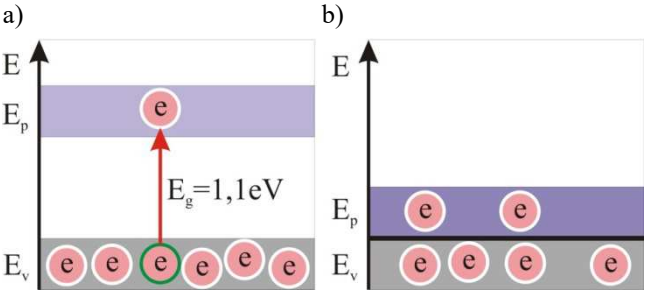

Fig. 1. Energy-band diagram for a) silicon, b) graphene, where E_p- conduction band, E_v-valence band, E_g-band gap [21]

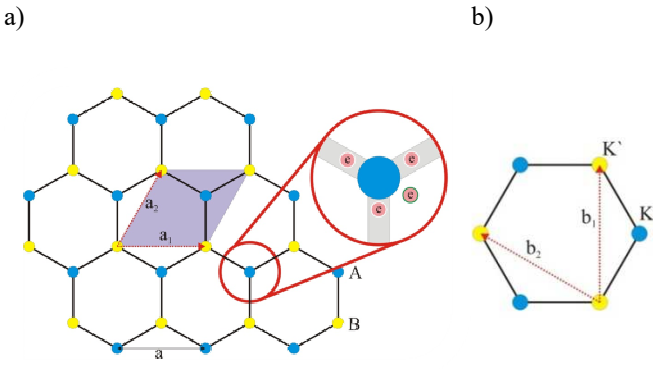

Fig. 2. Schematic of crystal structure of graphene forming a hexagonal structure from carbon atoms, a) real lattice, b) reciprocal lattice [18,21]

Methods for obtaining thin sheets of graphene substrates are [18-25]:

- micromechanical cleavage of highly oriented pyrolytic graphite
- chemical cleavage,
- chemical vapour deposition CVD.
- plasma enhanced chemical vapour deposition PECVD,
- reduction of graphite oxide,
- epitaxial growing/thermal decomposition of SiC substrate and other materials.

The reduction of graphite oxide (Fig. 4) is one of the easiest methods of obtaining derivatives of graphene like: graphene oxide GO or the reduced graphene oxide RGO. Reduced graphene oxide is a form of graphene which possesses some oxygen-containing functional group (-OH, =O) on the planes and –COOH carbonyl groups decorating the periphery of the planes. This defects produced during the oxidation of the graphene sheets, are believed to be responsible for the electrocatalystic activity. Taking this into consideration, using reduced graphene oxide as counter electrode materials is favoured in opposite to fully reduced and defect-free graphene [26-40].

In this research, graphene oxide and thermally reduced graphene oxide deposited on glass coated with semi-transparent conductive oxide have been investigated. The use of graphene oxide semi-transparent films as counter electrode has been studied. In this regard, Raman spectroscopy and Spectrophotometer analysis (transmittance and absorbance) were utilized.

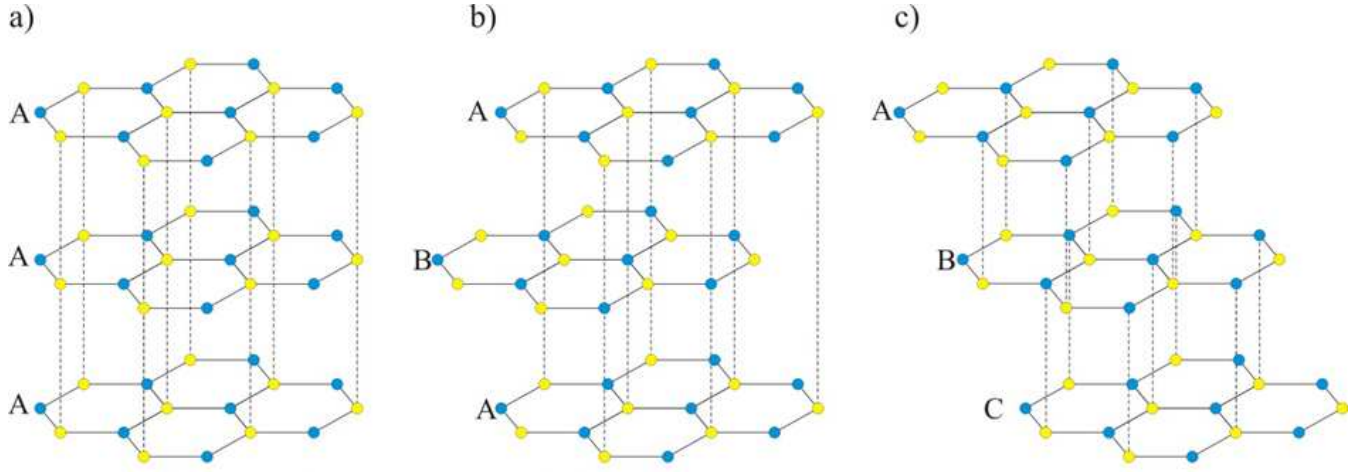

Fig. 3. Diagram of possibility alignment of several layers of graphene a) hexagonal (AAA), b) Bernal (ABA), c) rhombohedral (ABC) [17-20]

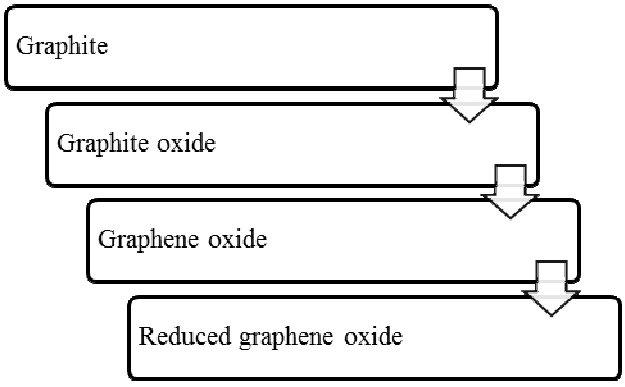

Fig. 4. Production steps of reduced graphene oxide

2. Materials and methods

2.1. Materials

The FTO (fluorine-doped tin oxide) glass substrates (10 Ω/ϒ, 3D nano, Cracow, Poland) were cut into pieces with size of 2,5×2,5 cm^2 and ultrasonically cleaned in distilled water, acetone and ethanol for 10 min, respectively. Few layer graphene oxide FLGO were purchased from Cheap Tubes (USA). In Table 1 basic properties of graphene oxide are shown. Because graphene oxide film has a poor quality and the relatively low conductivity [32] poly(3,4-ethylenedioxythiophene) polystyrene sulfonate PEDOT:PSS was used to increase conductivity and enhance film-forming ability. PEDOT:PSS was purchased from Sigma Aldrich.

Table.
The basic properties of graphene oxide (from CheapTubes)

Thickness	<3 nm
Purity	< 99 wt%
Method	Modified Hummers
Concentration	2 mgs/ml
The number of graphene oxide layers	2-4
Solvent	Deionized water
Size	300-800 nm lateral dimensions
Elemental Analysis	C: 35-42%, O: 45-55%, H: 3-5%

2.2. Reduced graphene oxide film preparation

The production steps of graphene oxide counter electrodes were shown in Fig. 5. The graphene oxide GO thin films were mixed with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate PEDOT:PSS in a given volume ratio (95 wt.% active material and 5 wt.% PEDOT:PSS) by using ultrasonication, magnetic stirring and homogenization to form an electrode slurry. PEDOT:PSS was used to increase conductivity and enhance film forming ability. Then mixtures were directly deposited on FTO glass substrate by spin coating method. The two-stage spin coating were adopted: 500 rpm for 5 s and 3000 rpm for 10 s. The GO counter electrodes were then dried at 50°C in an oven for 12 h. Before the deposition, FTO glasses were cleaned from surface contamination by ultrasonic cleaning in deionized water, acetone, ethanol and isopropanol and holding in each liquids for 15 minutes.

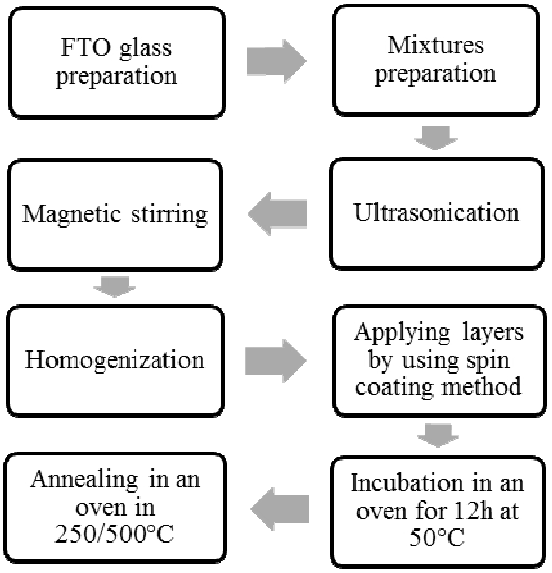

Fig. 5. Production steps of counter electrodes

The thermal treatment was performed to remove the surface oxides from GO sheets at different heat-treated temperatures. For this purpose, two from three samples after incubation in oven for 12 h at 50°C were heated and then kept at various temperatures under H_2 containing atmosphere. The thermal reduction was carried out in 250°C and 500°C for 30 min in a horizontal furnace. The graphene oxide thermally reduced in 500°C was designated as rGO (reduced graphene oxide). The graphene oxide

thermally reduced in 250°C and graphene oxide only incubated in an oven were designated as GO250 and GO respectively (Fig. 6).

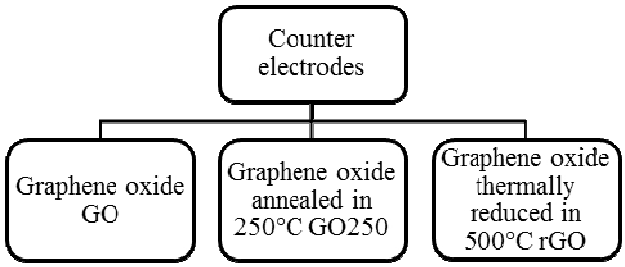

Fig. 6. Types of counter electrodes used in this work

2.3. Methodology

The studies of morphology and purity of the produced reduced graphene oxide as well as the layers of graphene oxide were made using a Renishaw inVia Raman microscope. Raman spectroscopy was performed at room temperature with 532 nm Nd-YAG excitation source.

The ultraviolet-visible (UV-vis) absorbance and transmittance spectra of graphene oxide (with different thermal treatment) deposited on FTO glass were measured using spectrophotometer (Evolution 220, Thermo Scientific).

3. Results and discussion

Ultraviolet-visible spectroscopy measurement was carried out to monitor the degree of oxidation for the graphene samples. The UV-Vis absorption spectra for graphene oxide, graphene oxide annealing in 250°C and reduced graphene oxide are shown in Fig. 7. A general absorption peak was observed at 230 nm for GO, and 250 nm for GO250 and rGO corresponding to the $\pi \rightarrow \pi^*$ transition of the C=C bond. Compared with the main peak of GO, red-shift was observed for rGO and GO250 suggesting the conjugated structures within the graphene sheets were restored upon thermally reduction. These spectral results reflect that rGO sheets have a larger π-conjugated domains.

Also, there is a peak around 290 nm (for rGO and GO250) and 300 nm (for GO), which is attributed to $n \rightarrow \pi^*$ transition of C=O bond.

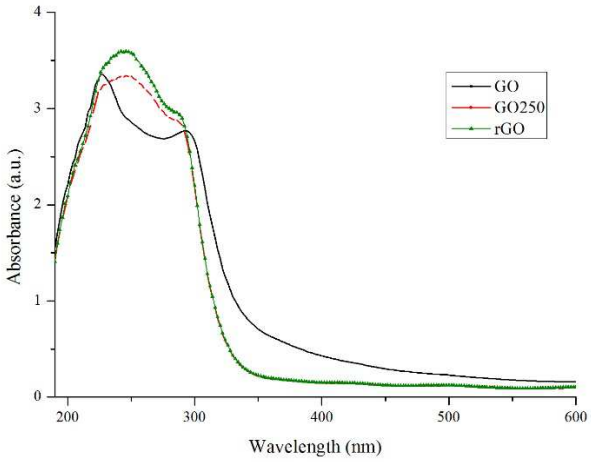

Fig. 7. Absorption spectra for graphene oxide and thermally reduced graphene oxide in 250°C and 500°C

Transmittance of the different counter electrodes was evaluated and the results are shown in Fig. 8. The transmittance of graphene oxide films coated on FTO glass was measured to be higher than 60% in the wavelength range 430-780 nm. The highest transmittance has GO because annealing of grapheneoxide counter electrodes under inert atmospheres enable a better ordering of graphene films and also cause losing an oxygen functional groups, that makes layers become denser and smother, with a lower surface roughness, and thus less transparent.

Raman spectroscopy was further applied to characterize the structures properties of GO, GO250 and rGO. Fig. 9 shows the Raman spectra of graphene oxide thin film substrates which was obtained using an excitation laser of 512 nm. All samples record two major Raman peak at ~1339 and ~1596 cm^{-1} corresponding to D (disorder) and G (graphitic) bands. The G band is usually assigned to the vibration of sp^2-bonded carbon atoms in a two dimensional hexagonal lattice. The D band is assigned to vibration of carbon atoms with dangling bonds in crystal lattice plane terminations of disordered graphite. These two bands can be observed in defective graphene materials. The original GO and thermally reduced GO250 and rGO samples display an identical position of G-band peak, what indicates on similar layer numbers through different thermal treatment.

The Raman I_D/I_G (disorder/order carbon) and I_{2D}/I_G intensity ratios correspond to the in-plane crystallinity dimension and are main feature of disorder in the graphitic material. I_{2D}/I_G intensity ratio is equal 2 in defect free single layer graphene.

I_D/I_G ratio for rGO (Table 2) increase in comparison with those for GO250 and GO, indicating an increase in the number of smaller graphitic domains upon reductions. I_{2D}/I_G ratio from Raman spectra suggesting that deposited GO, GO250 and rGO are a multilayered carbon nature. Size of graphene oxide (L_a) is proportional to the intensity of I_D/I_G as describe below:

$$I_D/I_G = C(\lambda)/L_a \quad (1)$$

where $C(\lambda)$ is 512 nm. From above equation, the average size of graphene oxide, thermally reduced graphene oxide in 250°C and in 500°C is calculated to be 575,28 nm, 556,52 nm and 492,31 nm respectively. It can be seen that, the reduction of the surface epoxy groups leads to the size decreasing of the graphene oxide.

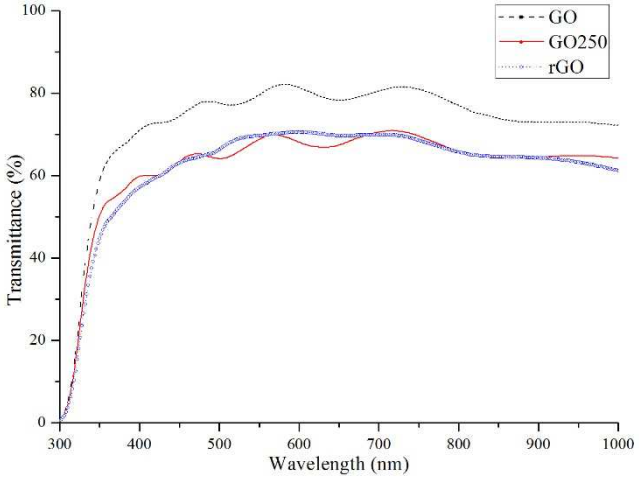

Fig. 8. Transmission UV-visible spectrum of the graphene oxide films coated on FTO substrates

The small broader 2D band at ~2700 cm^{-1} correspond to second order D peak due to fourth order phonon momentum exchange double resonance process. The Raman peak at ~2900 cm^{-1} correspond to D+D` band which is related to two disorder-induced competing mechanism contributing to Raman D band.

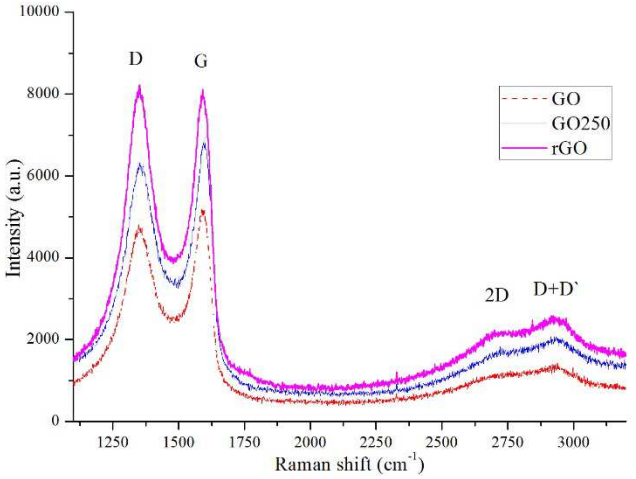

Fig. 9. Raman spectra of graphene oxide counter electrode

Table 2.
Basic properties determined from Raman spectra

	I_D/I_G	L_a [nm]	I_{2D}/I_G
GO	0.89	575.28	0.27
GO250	0.92	556.52	0.24
rGO	1.04	492.31	0.21

4. Conclusions

We have demonstrated a dye-sensitized solar cells with a semi-transparent graphene oxide counter electrodes which can be successfully applied in building integrated photovoltaic. The different thermal treatment of graphene oxide mixed with PEDOT:PSS were shown. The successful synthesis of reduced graphene was confirmed by UV-Vis spectroscopy. The absorbance was found to increase with thermally reduction. The transmittance of graphene oxide films coated on FTO glass was measured to be higher than 60% in the wavelength range 430-780 nm. It was found that, transmittance is depend of ordering of graphene and amount of oxygen functional groups.

The nature of the graphene oxide counter electrode has been confirmed by the Raman scattering spectroscopy. The increased intensity ratio I_D/I_G for rGO defines the quantitative disorder in graphene is a consequence of a high number of defects in materials resulting from the heat treatment after oxidation and reduction process. From Raman spectroscopy it can be also found the used graphene oxide sheets have a multilayered carbon nature.

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