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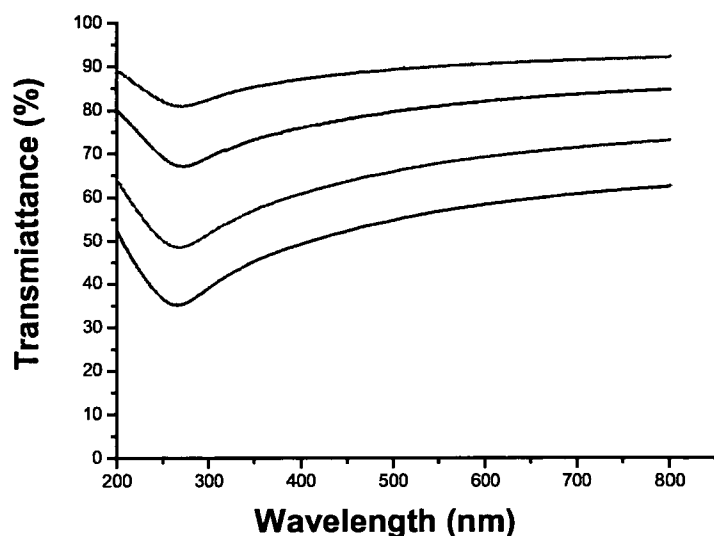
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(54) Title: HIGHLY CONDUCTIVE, TRANSPARENT CARBON FILMS AS ELECTRODE MATERIALS

Figure 1



(57) Abstract: The present invention relates to an optically transparent conductive carbon based film which is suitable for use as an electrode in optoelectronic devices etc. Further, the invention relates to a process for the production of the transparent conductive carbon film and the use thereof in electronic devices. Organic solar cells using transparent conductive carbon film as electrode display comparable performance with cells using ITO. These carbon films show high thermal and chemical stability, ultra-smooth surface, and good adhesion to substrates.

Highly conductive, transparent carbon films as electrode materials

5

Description

The present invention relates to an optically transparent conductive carbon-based film, a process for the production thereof and the application of the film as electrode in optoelectronic devices.

10 Optically transparent electrodes consisting of thin conductive films which are deposited on transparent substrates have been the subject of intense research. These film systems are of particular interest for use in for example flat panel displays, photovoltaic cells, electrochromic devices, electroluminescent lamps and a large number of further applications. For
15 these applications, transparent electrodes must exhibit three important qualities: high optical transparency, electrical conductivity and mechanical durability.

The most commonly used material in optically transparent conductive films is indium-tin oxide (ITO). However, due to the high cost and limited supply
20 of indium, alternatives are being sought for modern optoelectronic devices. So far, development of different inorganic and polymer layers as well as films of carbon nanotubes has been investigated. The use of carbon materials is particularly attractive since carbon is easily available, cheap and inert. The low electrical resistance and at the same time high optical
25 transparency are essential for good application properties of carbon films. These two properties, however, are oppositely influenced by the film thickness. Films had to be sufficiently thick to provide low electrical resistance for reasonable electrochemical properties, yet had to be sufficiently thin to maintain high optical transparency. The layer thickness
30 was chosen to obtain a compromise between the two desired properties.

Carbon has been used as an electrode material for a range of

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applications. The popularity can be traced to the versatility and availability of many types of carbon which can easily be fabricated into electrodes. Carbon materials also provide renewable and reproducible surfaces as well as low chemical reactivity.

5 Carbon-based optically transparent electrodes (OTEs) have been developed for spectroelectrochemical studies (Matthias Kummer and Jon R. Kirchhoff, *Anal. Chem.* (1993), 65, 3720-3725). Pyrolytic graphite-coated electrodes were prepared by vapor deposition of acetone as carbon precursor onto resistively heated metal mesh substrate, whereby a thin
10 layer of graphite was deposited on the heated metal mesh.

Another approach was the provision of reticulated vitreous carbon electrodes (Janet Weiss Sorrels and Howard D. Dewald, *Anal. Chem.* (1990), 62, 1640-1643). Reticulated vitreous carbon (RVC) is a porous, vitreous carbon foam material. For use as electrodes it is sliced to slides
15 having a thickness of about 0.5 to 3.5 mm.

Further, carbon optically transparent electrodes have been prepared by vapor deposition of a thin carbon film on a glass or quartz substrate (J. Mattson et al., *Anal. Chem.* (1995) Vol. 47 No. 7, 1122-1125; T.P. DeAngelis et al., *Anal. Chem.* (1977), Vol. 49, No. 9, 1395-1398). The
20 carbon was evaporated by an electron beam technique using a glassy carbon source and the evaporated carbon was then deposited as carbon film onto substrates.

Further, optically transparent carbon film electrodes were prepared by forming a carbon film on a quartz substrate by a vacuum pyrolysis of 3, 4,
25 9, 10-perylenetetracarboxylic dianhydride (D. Anjo et al., *Anal. Chem.* (1993), 65, 317-319). The carbon source 3, 4, 9, 10-perylenetetracarboxylic dianhydride was sublimed and then vapor-pyrolized at 800°C on the surface of a quartz substrate producing a mirror-like conductive coating.

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Donner et al., (Anal. Chem. (2006) Vol. 78, No. 8, 2816-2822) describe the preparation of carbon-based optically transparent electrodes fabricated by pyrolysis of thin films of photoresists. The photoresist AZ 4330 was spin coated onto quartz substrates and a carbon film was produced by pyrolysis
5 in a reducing atmosphere.

As we know, a compromise between electrical resistance and optical transparency had to be accepted with all known methods due to their dependence on the carbon film thickness. Generally, resistance of carbon films undergoes a dramatic increase as thickness decreases
10 below around 30 nm. Therefore, hitherto reported carbon films even in the thickness of ~13nm, with sheet resistance in the range of 1000~2000 ohm/sq, have transmittance lower than 55%. Since these reported carbon film electrodes were only used in spectroelectrochemical studies, such transparency was enough. However, such low transparency can not meet
15 demand of modern devices such as optoelectronic devices. Besides high transparency, modern devices require transparent electrodes with low resistance, smooth surface as well as suitable work function which depends strongly on the structure of carbon film. Obviously, the type of precursor and preparing methods are important for
20 fabrication of structure-controllable carbon films. Furthermore, most of the reported methods for preparing transparent carbon films are complicated.

The art therefore seeks suitable precursors and simple procedures
25 for making highly transparent, conductive and structure-controllable carbon films with smooth surface and appropriate work function for modern device application, in particular for use in optoelectronic devices.

30 The object of the present invention is therefore to provide a thin highly transparent and conducting carbon film which also has suitable work

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function for optoelectronic devices. A further object was to provide such a carbon film in an easy, cheap and reproducible way.

This object of the invention is solved by a method for the production of a transparent conductive carbon film comprising the steps (i) coating of a
5 solution of discotic precursors onto a substrate and (ii) heating the coated substrate under a protective gas to a temperature of from 400-2000°C.

The invention provides a simple, cheap and reliable method producing optically transparent conductive carbon films. In the inventive process, the thickness of the carbon film produced can easily be controlled by
10 concentration of the solution of discotic precursors or by the petition of the steps (i) and (ii). Further, the size of the film sheets is only limited by the size of the substrates used. Further, the carbon film obtained according to the inventive process has a higher thermal and chemical stability than
15 traditionally used ITO. Further, it has an extremely smooth surface, which can e.g. not be obtained with carbon nanotube films. With the inventive method, it is possible to provide conductive carbon films having both a high transparency and at the same time a low electrical resistance.

The transmittance of the carbon film produced is preferably at least 50%, more preferably at least 70%. Generally, the transmittance of the carbon
20 film is in the range of 60-95%. The transmittance of a material is dependent on the respective wave length. The transmittance values indicated herein refer to a wave length of 500-800 nm, particularly to a wave length of 600-700 nm, and particularly to a wave length of 700 nm, unless otherwise noted. Further, the transmittance is dependent on the film
25 thickness. The transmittance values indicated herein refer to a film thickness of ≤ 50 nm, particularly ≤ 30 nm and $5 \geq$ nm, in particular $10 \geq$ nm and in particular to a film thickness of 30 nm unless otherwise noted.

Unlike carbon-based films of the prior art, the sheet resistance of the carbon films of the invention is quite small, even if the thickness
30 decreases. For example, the sheet resistance of carbon films grown from

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discotic molecules on SiO₂/Si substrates was in the range of 1~20, 5~50, 10~500 and 10~800 ohm/sq, respectively, for 30 nm, 22nm, 12 nm and 4 nm thick films.

The carbon films produced according to the invention particularly show an electrical resistance of ≤ 30 kohm/sq, in particular ≤ 20 kohm/sq, ≤ 800 ohm/sq, preferably ≤ 500 ohm/sq, more preferably ≤ 200 ohm/sq, more preferably ≤ 100 ohm/sq, preferably ≤ 50 ohm/sq, and most preferably ≤ 15 ohm/sq. The electrical resistance is preferably at least 1 ohm/sq, more preferably ≥ 10 ohm/sq. The produced carbon films preferably have a sheet resistance of at most 30 kohm/sq, preferably 0.5-20 kohm/sq, 20-500 ohm/sq, 10-200 ohm/sq or 1-15 ohm/sq. Since the electrical resistance of the carbon films produced according to the invention in a certain way (even if to a smaller extent than the films of the prior art) depends on the thickness, the electrical resistance values indicated therein refer to, as far as not otherwise noted, carbon films having a thickness of ≤ 50 nm, preferably ≤ 30 nm, more preferably ≤ 20 nm and especially preferred to a film thickness of 30 nm.

As a carbon source, according to the invention, discotic precursors are used. It is thereby possible by means of the method of the invention to easily apply a solution of these discotic precursors to the substrate and subsequently heat them out to a carbon film. The use of technically more difficult methods, as for example vapor deposition or the like is not necessary. It was found out according to the invention that carbon film structures result from discotic precursors during heating, having excellent properties as shown herein. Thus, discotic precursors are particularly suitable for use in the fabrication of thin, highly transparent and conductive graphitic carbon films. Preferably, an optically transparent conductive carbon film is produced comprising a supermolecular assembly of discotic precursors.

Discotic precursors are any molecules or substances which have disc-like structures or subunits. In particular, discotic precursors have oligocyclic

aromatic units, in particular at least 2, more preferably at least 3 and most preferably at least 5 aromatic cycles, in particular annealed aromatic cycles. Preferably, the aromatic cycles are pure aromatic hydrocarbon cycles without any heteroatoms. However, it is also possible to employ discotic precursors having one or more heteroatoms, in particular O, N, S or P within their ring structures. Preferably, discotic precursors have planar, disc-like polyaromatic cores that can self assemble into a supermolecular assembly. Discotic precursors suitable for use in the present application are for example oligocyclic aromatic hydrocarbons, exfoliated graphites, pitches, heavy oils, discotic liquid crystals etc. Generally, all discotic precursors having units of polyaromatic structures can be employed. Particularly preferred are superphenalenes or hexa benzocoronenes (HBC) or derivatives thereof such as C₉₆-C₁₂ or HBC-PhC₁₂. Further preferred are pitches and heavy oils, particularly those from coal tar or petroleum tar or exfoliated graphites, particularly graphite sheets obtained by modification of physically exfoliated graphite or chemical oxidation of graphite particles.

The transparent film preferably has a thickness of at most 50 nm, preferably at most 20 nm, more preferably at most 13 nm. In a particularly embodiment, the thickness of the film is 3.5 nm or smaller.

A transparent substrate is preferably used according to the invention, especially a substrate having a transmittance of at least 50%, more preferably of at least 70% and most preferably of at least 90% of the interesting wave length, e.g. the wave length of from 500 to 800 nm, in particular from 600 to 700 nm and preferably at 700 nm and at a substrate thickness of $\geq 100 \mu\text{m}$, in particular of at least 1 mm. Suitable substrate materials are for example glass, quartz, sapphire or transparent polymers, in particular heat-resistant transparent polymers.

The film production process of the invention is extremely simple. In a first step, a solution of discotic precursors is provided. The solution is then coated onto a substrate, preferably, a transparent substrate such

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as glass, quartz or sapphire or transparent heat resistant polymers. Coating may be accomplished by any known process. It is preferred to apply for example spin coating, spray coating or zone casting processes. In the process, the thickness of carbon films can easily be controlled by the concentration of the discotic precursor solution and film size is only limited by the size of substrates.

In a second step, the coated substrate is heated to temperature of about 400-2000°C, in particular 500-1500°C, preferably 900-1100°C under an inert or reducing protective gas, preferably under inert gas. For example, noble gas such as argon or helium or another inert gas such as nitrogen or a reducing gas such as hydrogen or ammonia can be used as a protective gas. The heating is thereby preferably performed under a protective atmosphere, i.e. an atmosphere which consists only of the inert protective gas, or reducing gas or mixture of inert and reducing gas and does not contain any other substances. Steps (i) and (ii) can be repeated at least once in order to obtain the desired film thickness.

It is possible by means of the inventive method to obtain a unique carbon film with advantageous properties. A further subject-matter of the invention is therefore a transparent conductive carbon film. The transparent conductive carbon film according to the invention preferably has the herein given features.

Preferably used is the transparent conductive carbon film as an electrode. Especially preferred is the application as hole-collecting electrode in a solar cell.

Due to its improved characteristics, the transparent carbon film of the invention is particularly suitable for use in liquid crystal displays, flat panel displays, plasma displays, touch panels, electronic ink application, organic light emitting diodes and solar cells.

The invention further comprises optoelectronic devices having at least one electrode comprising a carbon film as described herein.

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The present invention relates to an optically transparent conductive carbon-based film which is suitable for use as an electrode in optoelectronic devices etc. Further, the invention relates to a process for the production of the transparent conductive carbon film and the use thereof in electronic devices. Organic solar cells using transparent conductive carbon film display comparable performance with cells using ITO. These carbon films show high thermal and chemical stability, ultra-smooth surface, and good adhesion to substrates. This unique combination of optical, electrical and chemical properties of these carbon films has great potential in various applications. In addition, the simple process for the fabrication of carbon films enables inexpensive and large-scale industrial manufacturing.

Thus, the invention also relates to an optoelectronic device comprising an electrode having a carbon film as described herein. The optoelectronic device preferably is a photodiode including solar cells, phototransistors, photomultipliers, integrated optical circuit (IOC) elements, photoresistors, injection laser diodes or light-emitting diodes.

The invention is further illustrated by the appended Figures and the following Examples.

Figure 1 shows the transmittance spectrum of carbon films produced according to the invention on quartz. The curve corresponds to 30 nm, 22 nm, 12 nm and 4 nm thick carbon films, respectively (from the bottom up).

Figure 2 shows AFM images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) of the surface of 4 nm (A) 12 nm (B) and 30 nm (C) thick carbon films produced according to the invention. Four sectional plots are given below each image.

Figure 3 shows a high-resolution transmission electron micrograph (HRTEM) image (A) and a Raman spectrum (B), proofing the graphitic structure of the carbon films.

Figure 4 shows a solar cell using a carbon film/quartz substrate as an anode.

Examples

1. Solutions of discotic precursors C₉₆-C₁₂, HBC-PhC₁₂, oxidized graphites and coal tar pitches, respectively, are coated onto a quartz substrate and the substrate is then heated to about 1100 °C under Ar protection.
- 5 2. The thickness of carbon films can be controlled by the concentration of solution; and the size of film is only limited by the size of substrates. Depending on the concentration of the solution applied transparent carbon-based films are obtained having a thickness of 50 nm, 30nm, 13 nm or 3.5 nm.
- 10 3. At a wavelength of ~700 nm, a carbon film having a thickness of 30 nm, 22 nm, 12 nm and 4 nm has a transmittance of 61%, 72%, 84% and 92%, respectively (Fig.1). In addition, at a given film thickness, transmittance was somewhat dependent upon wavelength with a minimum at ~260nm. This spectral feature is consistent with the carbon soot having a graphitic
15 structure.
4. The carbon films have a highly smooth surface, free of any large aggregates, pinholes and cracks, which is important for fabrication of optoelectronic devices in high quality. The average surface roughness (Ra) of carbon films with a thickness of 4nm, 12nm and 30nm over a 2 μm * 2 μm
20 area was around 0.4nm, 0.5nm and 0.7nm respectively (Fig. 2a, 2b and 2c).
5. The as-grown carbon films adhere strongly to substrates. These carbon films can keep intact even after long time bath sonication in ordinary organic solvents, and can pass laboratory Scotch-tape test. After immersing the carbon film/quartz into piranha solution (a mixture of concentrated sulfuric
25 acid and H₂O₂, V:V=7:3) for 48 hours, the conductivity of films keep almost the same, demonstrating the chemical stability of carbon films against strong acid and oxidative agent.
6. Structure of graphitic carbon films is confirmed by high-resolution transmission electron micrograph (HRTEM) (Fig. 3a) and Raman

spectroscopy (Fig. 3b). Carbon films show clearly graphitic domains distributed in the film. The layer-to-layer distance was around 0.35nm, close to the value of the (002) lattice spacing of graphite. Two typical bands at approximately 1598cm^{-1} (G band) and 1300cm^{-1} (D band) are observed, assigned to graphitic carbon and disordered carbon, respectively.

7. Sheet resistance of carbon films is in the range of 5 ohm/sq-30 kohm/sq, dependent of film thickness, precursors, substrates type and heating condition etc. For example, sheet resistance of 30nm-thick carbon films grown from C₉₆-C₁₂ on SiO₂/Si substrates is in a range of 5~50 ohm/sq, and that of 10 nm-thick carbon films grown from oxidized graphite is in the range of 500-1500 ohm/sq.

8. A solar cell based on a blend of poly(3-hexyl)-thiophene (P3HT) (electron donor) and phenyl-C61-butyric acid methyl ester (PCBM) (electron acceptor) is fabricated using a carbon film/quartz as an anode (Fig. 4a, 4b). The highest external quantum efficiency (EQE) of around 43% is achieved at a wavelength of 520nm, comparable to the highest EQE value of 47% for a reference device, ITO/glass as anode, under similar condition (Figure 4c). The current-voltage (I-V) characteristic (Fig. 4d) of the carbon film based device under monochromatic light of 510nm shows a distinct diode behavior. A short-circuit photocurrent density (I_{sc}) of $0.052\text{mA}/\text{cm}^2$ is observed with open-circuit voltage (V_{oc}) of 0.13V, calculated filling factor (FF) of 0.23, and overall power conversion efficiency of 1.53%. When illuminated with simulated solar light, the cell gives I_{sc} of $0.36\text{mA}/\text{cm}^2$, V_{oc} of 0.38V, FF of 0.25 and an efficiency of 0.29%. Obviously, in comparison with ITO based cell, which shows V_{oc} of 0.41V, I_{sc} of $1.00\text{mA}/\text{cm}^2$, FF of 0.48, and an efficiency of 1.17%. The cell performance is comparable to the ITO based cell.

Claims

1. A method for the production of a transparent conductive carbon film
5 comprising the steps
(i) coating of a solution of discotic precursors onto a substrate and
(ii) heating the coated substrate under a protective gas to a
temperature of from 400-2000°C.
- 10 2. A method according to claim 1, wherein the produced transparent
carbon film has a transmittance in the range of 60-95%, for a carbon
film having a thickness of 30 nm- 4nm at a wave length of 700 nm.
3. The method according to claim 1 or 2 for the production of a
15 transparent conductive carbon film wherein the produced carbon
film has a sheet resistance at most 30 kohm/sq.
4. The method according to any of the preceding claims, wherein the
discotic precursors are selected from oligo- or polycyclic aromatic
20 hydrocarbons having at least two aromatic rings.
5. The method according to any of the preceding claims, wherein the
discotic precursors are selected from superphenalenes,
hexabenzochoronenes (HBC), ovalenes, coronenes, perylenes,
25 pyrenes, and their derivatives; pitches, heavy oils from coal or
petroleum; or exfoliated graphite from chemical or physical
exfoliation of any graphite.
6. The method according to any of the preceding claims, wherein the
30 produced carbon film has a thickness of ≤ 50 nm.
7. The method according to any of the preceding claims, wherein the
substrate is a transparent substrate.

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8. The method according to any of the preceding claims, wherein the substrate is composed of glass, quartz, sapphire or a polymer.
- 5 9. The method according to any of the preceding claims, wherein the coating of the discotic precursors onto the substrate is performed by spin coating, spray coating, dip coating, zone-casting, lifting deposition or Langmuir-Blodgett.
- 10 10. The method according to any of the preceding claims, wherein the inert gas is selected from nitrogen, or a noble gas, in particular Ar, or a reducing gas, in particular H₂.
- 15 11. The method according to any of the preceding claims, wherein the coated substrate is heated to a temperature of from 500-1500°C.
12. A transparent conductive carbon film obtainable by the method of any of claims 1-11.
- 20 13. An electrode comprising a carbon film according to claim 12.
14. Use of an electrode according to claim 13 for liquid crystal displays, flat-panel displays, plasma displays, touch panels, electronic ink applications, lasers, optical communication devices,
25 light-emitting diodes or solar cells.
15. Optoelectronic device comprising an electrode according to claim 13.
- 30 16. Optoelectronic device according to claim 15 being photodiodes, including solar cells, phototransistors, photomultipliers, integrated optical circuit (IOC) elements, photoresistors, injection laser diodes or light-emitting diodes.

Figure 1

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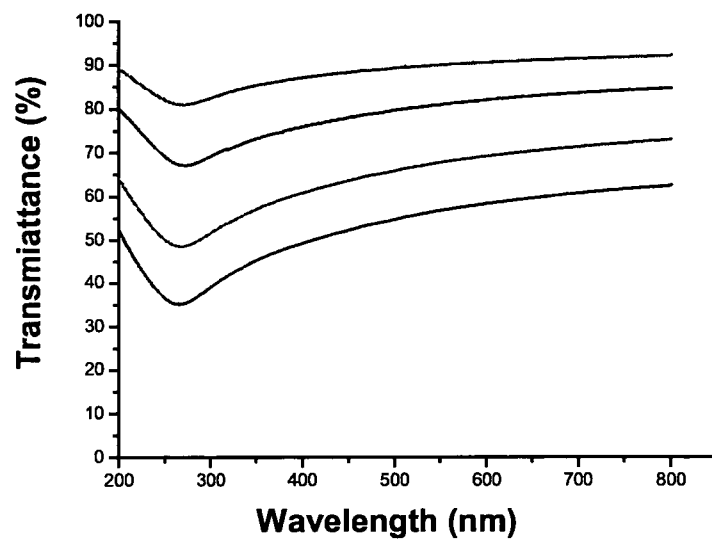
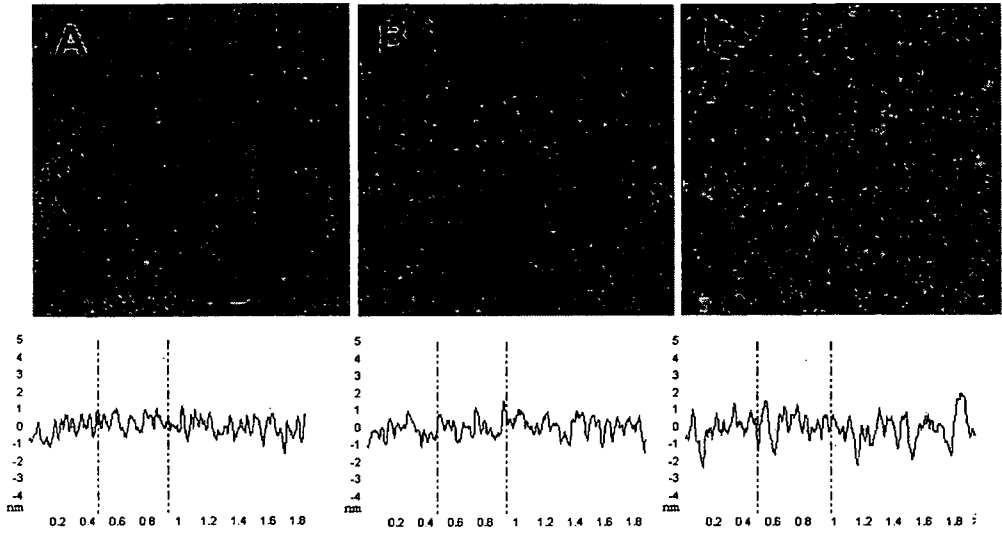


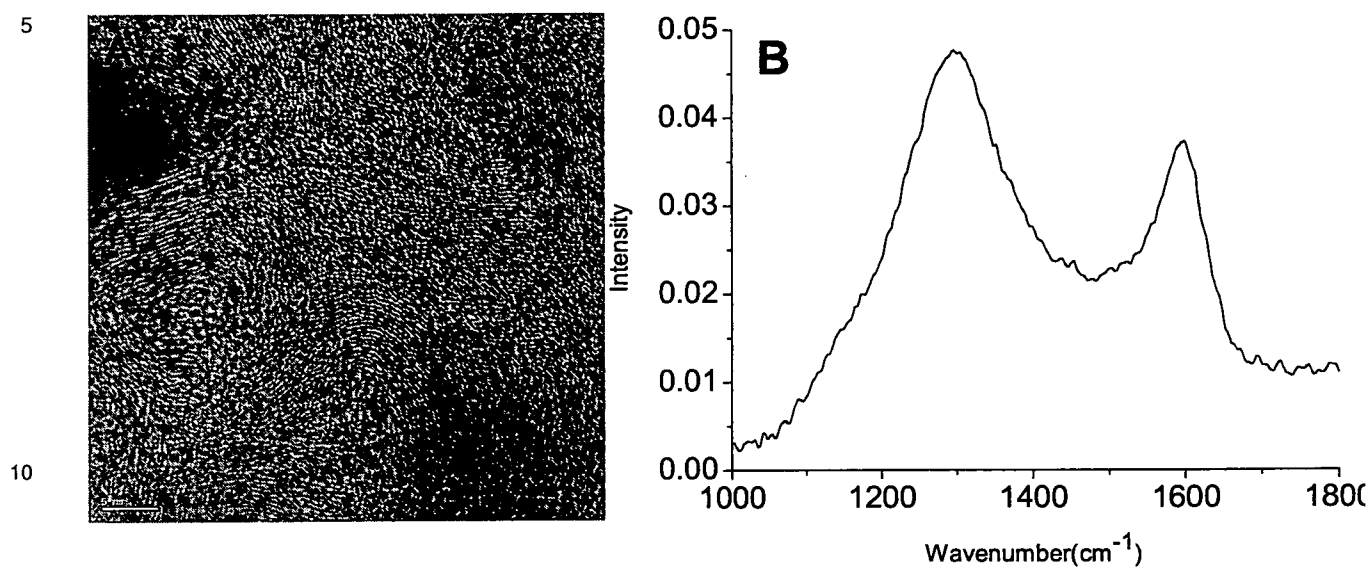
Figure 2

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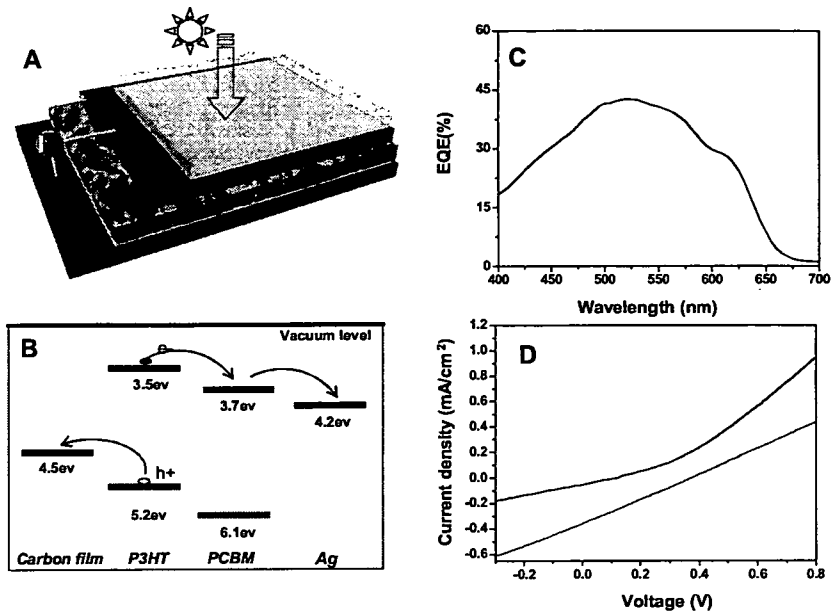
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Figure 3



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Figure 4



INTERNATIONAL SEARCH REPORT

International application No

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A. CLASSIFICATION OF SUBJECT MATTER

INV. C09D5/24 C01B31/00 H01L51/52 G01N27/30 H01L31/0224

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09D C01B H01L G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 063 196 A (SONY CORP [JP]; RES INST INNOVATIVE TECH EARTH [JP]) 27 December 2000 (2000-12-27) paragraph [0029] - paragraph [0033] example 15	1,4-8, 10-16
X	DONNER S: "Fabrication of Optically Transparent Carbon Electrodes by the Pyrolysis of Photoresist Films: Approach to Single-Molecule Spectroelectrochemistry" ANALYTICAL CHEMISTRY, vol. 78, no. 8, 15 April 2006 (2006-04-15), pages 2816-2822, XP002463388 cited in the application the whole document	1-4,6-16



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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MATTHIJSEN, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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Patent document cited in search report		Publication date		Patent family member(s)		Publication date
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