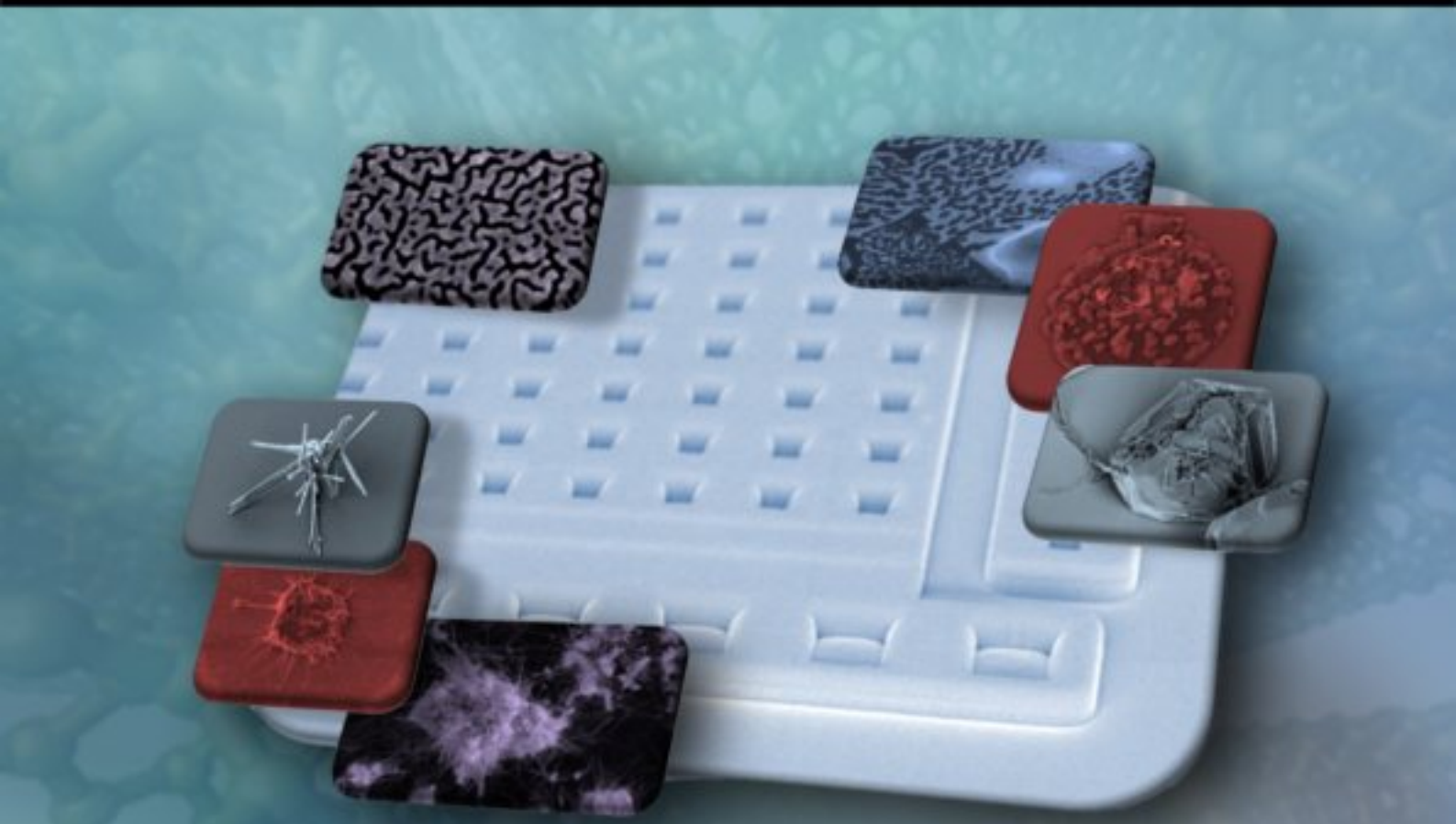
ISSN 1726-5749

SENSORS & TRANSDUCERS

vol. 12 Special 10/11



Nanomaterials and their Composites: from Fabrication to Applications

International Frequency Sensor Association Publishing

IFSA

Sensors & Transducers

Volume 12, Special Issue
October 2011

www.sensorsportal.com

ISSN 1726-5479

Sensors & Transducers Journal (ISSN 1726-5479) is a peer review international journal published monthly online by International Frequency Sensor Association (IFSA).
Available in electronic and on CD.

Sensors & Transducers Journal

Contents

Volume 12
Special Issue
October 2011

www.sensorsportal.com

ISSN 1726-5479

Research Articles

Authors are encouraged to submit article in MS Word (doc) and Acrobat (pdf) formats by e-mail: editor@sensorsportal.com
Please visit journal's webpage with preparation instructions: http://www.sensorsportal.com/HTML/DIGEST/Submition.htm

Sensors & Transducers Journal, Vol. 12, Special Issue, October 2011, pp. 26-32

www.sensorsportal.com

Sensors & Transducers

ISSN 1726-5479

http://www.sensorsportal.com

Charge Transfer Properties of Surface-treated WS_2 Nanotubes and Fullerene-like Nanoparticles

[1] Tiziana DI LUCCIO, [1] Carmela BORRIELLO, [1, 2] Sumeet KUMAR, [1] Giuseppe NENNA

[1] ENEA, UTTP NANO, Centro Ricerche Portici, Portici (NA) I-80055 Italy
[2] DISTA, Università del Piemonte Orientale "A. Avogadro", Alessandria I-15121 Italy
Tel.: +39 081 7723244, fax: +39 081 7723344
E-mail: tiziana.diluccio@enea.it

Received: 15 June 2011 /Accepted: 18 July 2011 /Published: 31 October 2011

Abstract: We studied the effect of incorporation of inorganic fullerene like nanoparticles (IF) and inorganic nanotubes (INT) of WS_2 into device structures. In order to disperse in a uniform fashion the semiconducting INT/IF WS_2 nanoparticles were functionalized with dodecyltrichlorosilane (DTS). Poly-3(hexylthiophene) (P3HT) has been used along with WS_2 nanoparticles as an active layer for the solution processable material in the proposed OLED structure of the type: ITO/WS_2/P3HT/LiF-Al to test the electrical effect of the WS_2 and to obtain information on its energy levels. Based on the obtained results, we discuss the possibility to use the WS_2 nanoparticles in organic electronic devices.

Keywords: WS_2 nanotubes and nanoparticles, Band gap, Cyclic voltammetry, LED.

1. Introduction

Tungsten disulfide (WS_2) nanotubes (INT) and fullerene like nanoparticles (IF) belong to a family of chalcogenide materials [1] attracting much interest since their first synthesis in 1992 by Tenne and coworkers [2]. Since then the synthesis methods have been improved till the point to obtain pure materials that are already at commercial level of application as efficient lubricants or used as reinforcements in polymer nanocomposites (http://www.apnano.com). However possibilities of applications in other fields viz. e.g. as phototransistors [3] or absorption layers in thin film solar cells [4] have been investigated to a lesser extent in the past two decades. Nevertheless the electronic properties of INT/IF WS_2 nanostructures are extremely interesting. They behave electronically

differently when compared with carbon nanotubes (NTs). In fact they are not metallic but are majority n-type semiconductors [5] having a non-zero energy band gap depending on tube's diameter and type.

In this work we studied the feasibility of utilizing WS_2 nanoparticles into hybrid organic/inorganic electronic devices. Particularly interesting is the combination of WS_2 materials with conjugated electroluminescent polymers such as poly-3(hexylthiofene) (P3HT) that can be easily spin coated onto a variety of underlying layers. Whether used as a separate layer within a stacked structured device or in blends with polymers, the surface modification of WS_2 is always needed to obtain a uniform dispersion within the host matrix for an even deposition. Thus we functionalized WS_2 with diverse functional groups such as dodecyltrichlorosilane (DTS), and sodium dodecylsulphate (SDS). Dip coating technique was used to deposit WS_2 structures onto treated (Plasma O_2/CF_4) ITO patterned substrates both rigid (glass) and flexible (PET). Finally the P3HT layer was spin coated followed by the LiF-Al deposition as cathodic layer. A complete characterization including morphological, optical and electrochemical analyses of the WS_2 structures and P3HT in combination with the current-voltage (I-V) characteristic of the full stacked device has allowed finding important inputs to device designing and the possible role of WS_2 has been further explored.

2. Experimental

The INT/IF WS_2 used in this work consisted of approximately 5% by weight of WS_2 nanotubes with respect to the fullerene like nanoparticles. In the paper we will shortly indicate INT/IF WS_2 with WS_2. They were kindly provided by Dr. Rita Rosentsveig, Weizmann Institute (Israel) within the COINAPO network (COST Action MP 0902). The powder mixture (25 mg) of WS_2 was transferred into $CHCl_3$ and sonicated for 180 min at 40 % power and 0.5 cycle, centrifuged (12000 rpm for 10 minutes) and dried at room temperature.

The WS_2 were further functionalized with DTS ($C_{12}H_{25}C_{l3}Si$; mW: 303.775; solvent: chloroform).

ITO covered glass substrates (CORNING 1737, DELTA TECHNOLOGIES Limited) and polyethylene terephtalate (PET, Diamond Coatings Limited) have been used as anode. The substrates were patterned through inverse photolithography and HCl-based etching in order to define the anodic area. Both Glass and PET substrates were surface treated (8 minutes) using a PECVD Multichamber MC5000 Elettrorava, according to the following conditions: Power =30 W, Pressure = 0.01 Torr, CF_4 and O_2 fluxes as 30 sccm.

The funzionalized WS_2 were deposited by a dip coater deposition system (Holmarc HO-TH-01) under the following conditions: dip speed = 50 μm/s, extraction speed = 50 μm/s , dip time = 10 s, extraction dip time = 5s, number of dips = 10.

Poly-3(hexylthiofene) (P3HT) (regioregular 99 %, Sigma-Aldrich) was dissolved at concentration of 25 mg in 10 ml chlorobenzene and spin coated in two steps onto the WS_2 structures: the first step at an rpm of 200 (acceleration 200) for 60 seconds; the second step at an rpm of 1000 (acceleration of 1000) for 20 seconds. The calibrated thickness of P3HT found under these conditions was approximately found out to be 80 nm, measured by profilometer (Tencor alpha step IQ).

The LiF(1 nm)-Al(100 nm) top electrode was successively deposited by thermal evaporation. The device area under consideration is 0.7 cm^2.

The morphology was investigated by a scanning electron microscope (SEM) Leo 1530 Gemini by Zeiss. Cyclic voltammetry (CV) was performed by using an instrument consisting of a potentiostat/galvanostat model 273A (Princeton Applied Research) and an electrochemical cell

provided with a Ag/AgCl Sat. KCl reference electrode, Pt tip electrode (0.28 mm^2 area), and Pt counter electrode. For CV measurements, we used an electrolytic solution having standard concentration of 0.1 M di tetrabutylammoniumhexafluorophosphate and a scan rate of 100 mV/s.

The I-V characteristics of devices have been measured in dark condition at room temperature using a Keithley 2400 Power Supply Source Meter in voltage mode in the range 0 – 10 V with constant increment steps and delay time of 1sec before each measurement point.

3. Results and Discussion

The functionalization of WS_2 by DTS has been explored by Energy dispersive spectroscopy (EDS) analysis performed on WS_2 layers obtained by drop casting the WS_2 and WS_2/DTS solutions in chloroform onto silicon substrates. The EDS analyses provided the stoichiometry ratio defined by the atomic % of tungsten and sulfur along with the carbon and sulfur molar ratios (see Table 1). The expected stoichiometry of W:S=1:2 is confirmed both in the non-functionalized and in the functionalized WS_2 samples. The strong increase of carbon moles with respect to sulfur moles after the functionalization indicates that the carbon content has greatly increased due to the presence of DTS molecules functionalizing the WS_2 nanostructures.

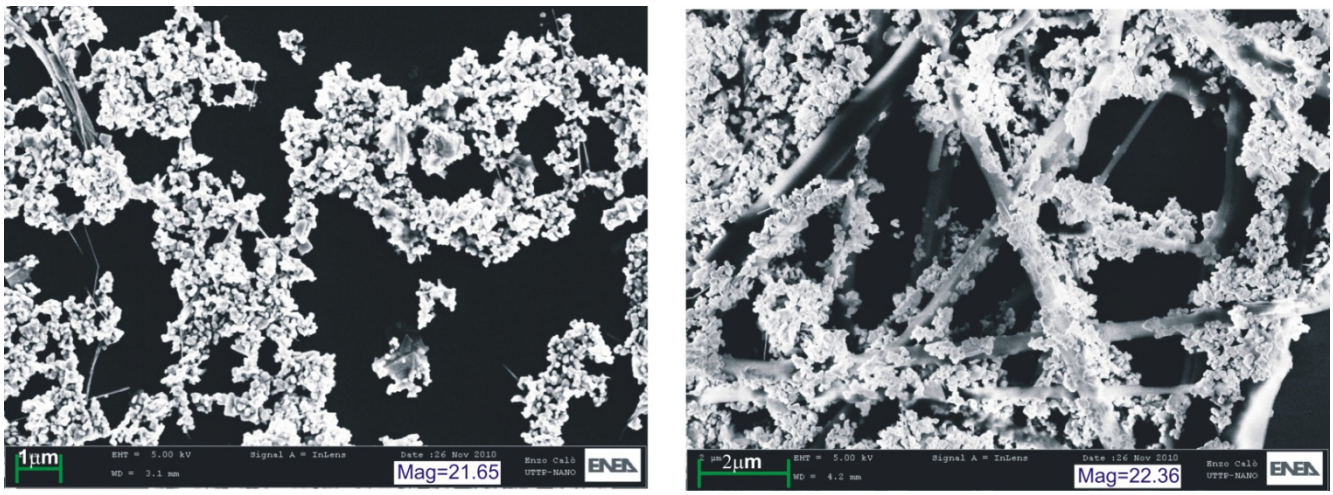
Table 1. Stoichiometric values as measured by energy dispersive spectroscopy (EDS)[1] of WS_2 before and after functionalization with DTS molecules. The samples were prepared by drop casting the WS_2 solution in $CHCl_3$ on silicon substrates.

Sample	WS_2	WS_2/DTS
(At % W) / (At % S)	0.51	0.52
Moles (C) / Moles (S)	2.91	57.14

In Fig. 1 we show the morphology of WS_2 before (a) and after (b) the functionalization. The two images have been recorded at almost the same magnification factor (21.65 KX in (a) and 22.36 KX in (b)). In both cases we observe the presence of the nanotubes along with the fullerene like nanoparticles that seem attached on the walls of the nanotubes. However a less agglomerated structure can be noticed after functionalization.

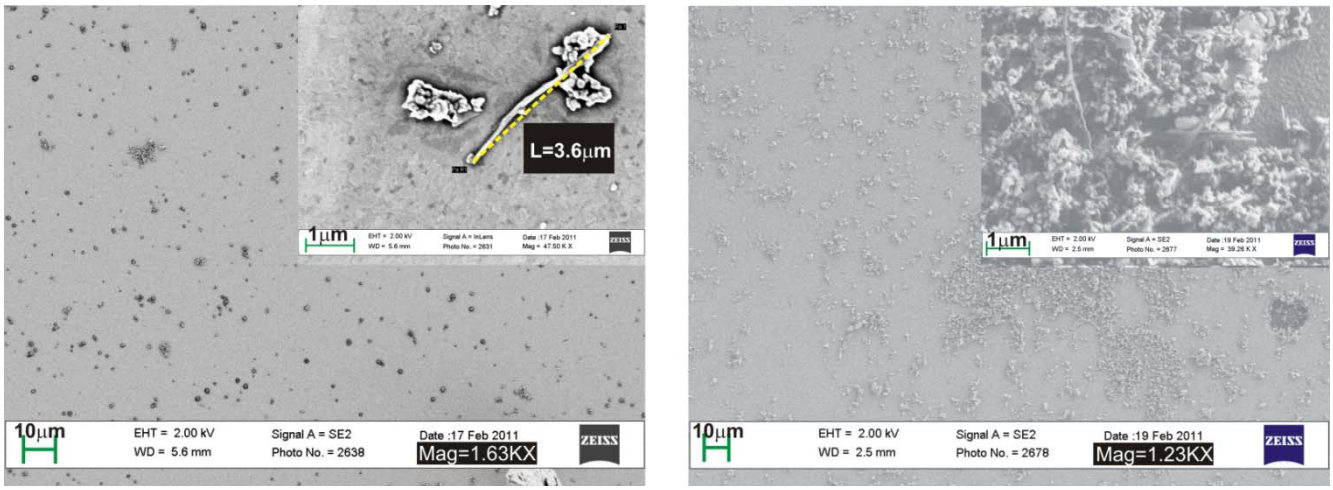
The WS_2 were deposited from solution phase to patterned ITO/glass and ITO/PET by dip coating technique. The morphology of the WS_2 structures is shown in Fig. 2 on glass (a) and PET (b), respectively. Both images are reported on 10μm scale, with a magnified inset view at 1 μm scale. The ITO coverage by WS_2 structure is more efficient in the case of PET due to higher surface roughness of the ITO covering such substrate. On the other hand, in the case of PET the contrast is bad with respect to ITO on glass substrate rendering it hard to focus the WS_2 structures at higher magnification. One of the few images on a magnified scale (See inset of Fig. 2b) shows the usual nanotube/fullerene aspect. Some peculiar shape can be also found, see for example the “leaf” like shape in the inset of Fig. 2a having a length around 3.6 μm.

[1] Courtesy of dr. A. Vecchione, Dep. Physics, University of Salerno.



(a) (b)

Fig. 1. SEM micrographs of WS_2 before (a) and after (b) surface modifications.



(a) (b)

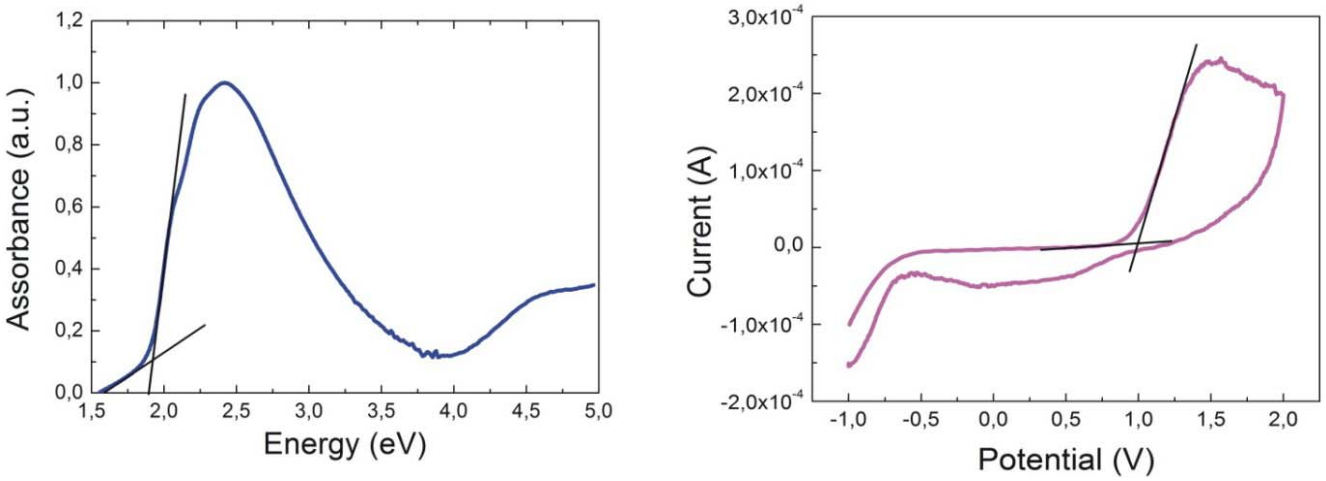
Fig. 2. SEM micrograph of WS_2 structures deposited onto glass/ITO (a) and PET/ITO (b).

We were able to estimate the HOMO and LUMO levels of WS_2 structures and P3HT by combination of UV-Vis absorption and CV techniques. The UV-Vis absorption allowed us to determine the energy band gap E_g. The CV provided with much accuracy the onset of the oxidation energy peak positions E_{ox} which are related to the ionization potential I_p through the formula given by equation (1) [6]:

$$I_p = -(E_{ox}+4.22)\ eV\,, \tag{1}$$

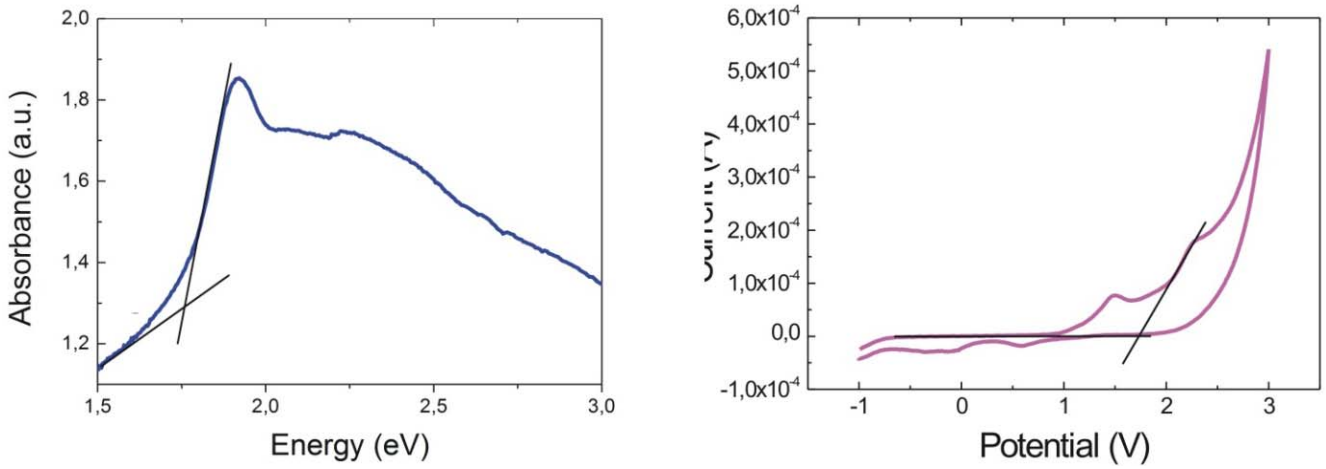
where 4.22 is the ionization potential of the normal hydrogen electrode (NHE) w.r.t. vacuum added to the potential of the Ag|AgCl working electrode respect to NHE. The HOMO level is approximated by I_p, and the LUMO is calculated by adding the E_g value known from the absorption data. The results of the UV-Vis absorption and CV experiments of P3HT are reported in Figs. 3a and 3b, respectively. The P3HT used in the experiment absorbs in the blue-yellow wavelength range between 375 and 550 nm, corresponding to an energy interval from 1.75 to 3.75 eV. The value of the E_g by UV-Vis measurements is found out to be 1.92 eV. CV measurements of P3HT show an oxidation peak around 1.25 eV, with a value of E_{ox} = 0.96 eV (taken at the onset). With these values, the HOMO level of

P3HT is found out to be -5.18 eV and the LUMO is calculated as -3.26 eV. Following the same procedures, for WS_2 structures the E_g measured from UV-Vis absorption data (Fig. 4a) was 1.76 eV, while the HOMO measured from CV (Fig. 4b) was -5.95 eV and finally the calculated LUMO level was equal to -4.19 eV.



(a) (b)

Fig. 3. UV-Vis absorption (a) and cyclic voltammetry (CV) (b) of P3HT.



(a) (b)

Fig. 4. UV-Vis absorption (a) and cyclic voltammetry (CV) (b) of WS_2 structures.

With the HOMO and LUMO of P3HT and WS_2 structures we have constructed a band diagram as shown in Fig. 5 explaining a possible working mechanism of the LED device. The electrons can go from the LiF-Al cathode (work function = -4.3 eV) to the LUMO of P3HT but also to the LUMO of WS_2. Owing to the large difference between the energy levels, few holes might transfer from the ITO anode (work function = -4.7 eV) to the HOMO level of WS_2 structures and since these holes are the majority carriers, their blocking at the ITO/WS_2 interface limits the current and the eventual recombination with electrons at the WS_2/P3HT interface. Thus the radiative recombination of holes and electrons at the WS_2/P3HT interface is inhibited resulting into no light emission, confirmed by the electroluminescence measurements.

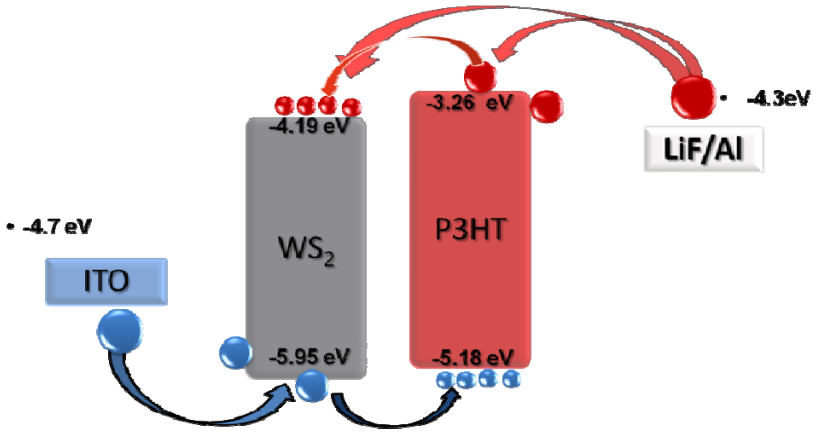


Fig. 5. Schematic band diagram scheme of a WS_2/P3HT based LED device.

The IV curves measured on two devices, i.e. ITO/P3HT/LiF-Al (reference device) and ITO/ WS_2/P3HT/LiF-Al are reported in Fig. 6. The current flowing into the reference device is found out to be higher than the current in the WS_2/P3HT device, in agreement with the band diagram of Fig. 5. These data confirm that the conductivity of WS_2 is low because the absolute value of the HOMO level of WS_2 is too low respect to the anode. A possible solution is to realize an inverted structure depositing P3HT close to the ITO electrode and WS_2 structures as hole blocking layer close to the LiF-Al cathode, thus rendering the device much more efficient. The expected complications are that the WS_2 structures functionalized by DTS are dip coated from their chloroformic solution, which can destroy the P3HT layer already deposited. We thus, propose to dip coat the WS_2 functionalized with SDS into aqueous solution, thus avoiding such complications. Further work into this direction is in progress to confirm the band diagrams realizing the device structures based on the HOMO/LUMO values obtained by CV measurements.

Finally work is also under progress under the COINAPO project, in utilizing luminescent (functionalized) CdSe quantum dots into the active layer, along with the P3HT as electron transferring matrix and WS_2 structures as hole blocking layer together with PEDOT:PSS as hole transfer layer over all, constituting the following device structure: ITO/PEDOT:PSS/CdSe/P3HT/WS_2/LiF-Al. The WS_2 structure will be dip coated close to the cathode by a suitable choice of the solvent to avoid damages of the P3HT layer.

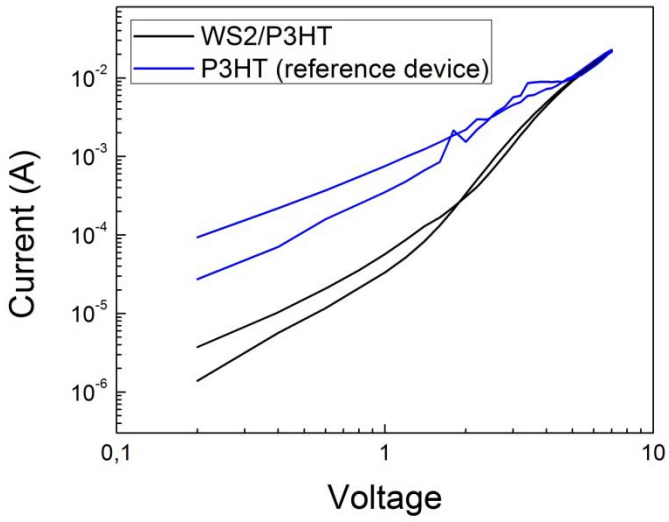


Fig. 6. Current-Voltage characteristics of two devices, ITO/P3HT/LiF-Al and ITO/WS_2/P3HT/LiF-Al.

4. Conclusions

In this paper we characterized the morphology of tungsten disulfide (WS_2) structures constituted of nanotubes (INT) and inorganic fullerene-like (IF) nanoparticles. We conducted cyclic voltammetry obtaining respectively a HOMO level around -5.95 eV and a LUMO level around -4.19 eV with respect to vacuum for the hybrid WS_2 functionalized structures. The current-voltage (I-V) characteristic of the proposed device structure: ITO/WS_2/P3HT/LiF-Al gave a further understanding about the energy levels that confirm the data obtained by CV and gave us an important clue for improving the efficiency of the device structure ITO/PEDOT:PSS/CdSe/P3HT/WS_2/LiF-Al.

Acknowledgements

We would like to acknowledge G. Pandolfi (ENEA, Portici) for his assistance in surface treating the substrates with Plasma O_2/CF_4 and Dr. P. Morvillo (ENEA, Portici) is aknowledged for the use of CV instrumentation. Dr. A. De Girolamo Del Mauro and E. Calò are kindly acknowledged for their assistance during the SEM analyses. Finally Dr. Rita Rosentsveig (Weizmann Institute, Israel) is kindly acknowledged for providing the WS_2 materials.

References

[1]. R. Tenne and G. Seifert. Recent Progress in the Study of Inorganic Nanotubes and Fullerene-Like Structures, *Annu. Rev. Mater. Res.*, Vol. 39, 2009, pp. 387-413.

[2]. R. Tenne, L. Margulis, M. Genut, G. Hodes. Polyhedral and cylindrical structures of WS_2, *Nature*, Vol. 360, 1992, pp. 444-445.

[3]. H. U. Unalan, Y. Yang, Y. Zhang, P. Hiralal, D. Kuo, S. Dalal, Tim Butler et al. ZnO Nanowire and WS_2 Nanotube Electronics, *IEE Transactions on Electron Devices*, Vol. 55, No. 11, 2008, pp. 2988-3000.

[4]. E. Gourmelon, O. Lignier, H. Hadouda, G. Couturier, J. C. Bernède, J. Tedd, J. Pouzet and J. Salardenne. MS_2 (M = W, Mo) photosensitive thin films for solar cells, *Energy Mater. Col. Cells*, Vol. 46, Issue 4, 1997, pp. 115-121.

[5]. G. Seifert, H. Terrones, M. Terrones, G. Jungnickel, T. Frauenheim, On the electronic properties of WS_2 nanotubes, *Solid State Comm.*, Vol. 114, Issue 5, 2000, pp. 245-248.

[6]. E. Kucur, J. Riegler, G. A. Urban, and T. Nann, Determination of quantum confinement in CdSe nanocrystals by cyclic voltammetry, *J. Chem. Phys.*, Vol. 119, Issue 4, 2003, pp. 2333-2337.

Sensors & Transducers Journal

Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because of it is a peer reviewed international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per year by International Frequency Sensor Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc. Since 2011 the journal is covered and indexed (including a Scopus, Embase, Engineering Village and Reaxys) in Elsevier products.

Topics Covered

Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

Submission of papers

Articles should be written in English. Authors are invited to submit by e-mail editor@sensorsportal.com 8-14 pages article (including abstract, illustrations (color or grayscale), photos and references) in both: MS Word (doc) and Acrobat (pdf) formats. Detailed preparation instructions, paper example and template of manuscript are available from the journal's webpage: http://www.sensorsportal.com/HTML/DIGEST/Submition.htm Authors must follow the instructions strictly when submitting their manuscripts.

Advertising Information

Advertising orders and enquires may be sent to sales@sensorsportal.com Please download also our media kit: http://www.sensorsportal.com/DOWNLOADS/Media_Kit_2011.pdf