

# Natural Dye Sensitizer for Grätzel Cells: Sepia Melanin

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**Abstract** The efficiency of Grätzel cell can be further improved by the anchoring groups, such as COOH to be adsorbed onto the TiO<sub>2</sub> surface with a large electronic coupling. Some of the most efficient sensitizers are synthetic dyes including transition metal coordination compounds such as Ruthenium polypyridyl complexes because of their highly efficient metal-to-ligand charge transfer, suitable ground and excited state energy levels with respect to titanium dioxide conduction band energy. They also have intense and wide range absorption in whole visible range. Even if they present such attractive features, their synthesis process is costly and complicated and they are not environment friendly because they contain heavy rare metals which are undesirable from the point of view of environmental conservation aspects. Natural dye can be the best alternative as they have acceptable efficiency in comparison to that one of transition coordination compounds and their extraction can be done by simple procedures from flowers, leaves, fruits, animals and other natural products. Melanin as the major component Sepia Officinalis ink pigment cause strong interactions with the hydroxyl groups of a TiO<sub>2</sub>. Melanin possesses a broad band absorbance in UV and visible range up to infrared. It also possesses the COOH and OH groups which would be free to bind to the surface of TiO<sub>2</sub>. Moreover, melanin polymer has interesting properties such as a considerable spectral absorbance width due to the high degree of conjugation of the molecule. This paper reports results from X-ray diffraction (XRD), UV-Vis as well as Raman spectroscopy of sepia melanin for Grätzel cell application.

**Keywords:** Grätzel cell, dye sensitizer, Sepia melanin, Sepia Officinalis, natural dye

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## 1. Introduction

The dye-sensitized solar cell (DSSC) also known as Grätzel solar cell from the name of its inventor Prof. Michael Grätzel [1] provides a technically and economically credible alternative concept to the present day p-n junction photovoltaic devices. DSSC are relatively new class of low-cost solar cells that belong to the group of thin film solar cells. They are very promising compared to silicon based solar cells because they are made from low-cost materials and do not need elaborate apparatus for their manufacture [2]. DSSC have received an increasing interest due to the simple fabrication process and relatively high conversion efficiency [3]. The developed state solid version of DSSC fabricated by a new two-process which raised their efficiency up to a record of 15% without sacrificing stability was recently published by Grätzel and co-workers at the Swiss Federal Institute of

Technology (EPFL) [4]. Figure 1 is a schematic diagram of Grätzel cell. DSSC contains several components: a transparent conducting oxide (TCO), a mesoporous semiconductor film, a dye sensitizer, and an electrolyte or mediator solution with a redox couple as well as counter electrode [1,5].

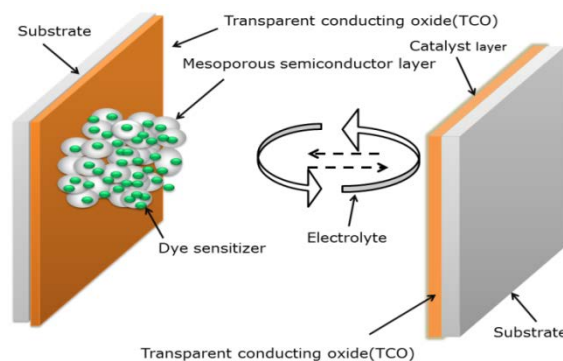


Figure 1. A schematic diagram of a dye-sensitized solar cell

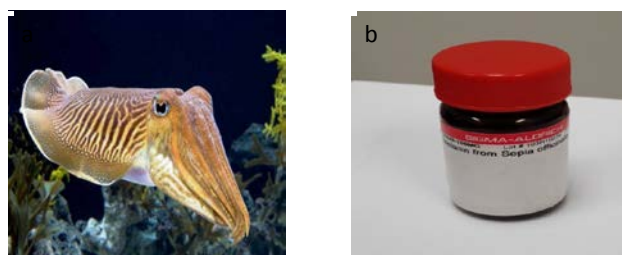
Since the role of the absorption of visible light and the conversion of photon energy into electricity is played by the dye, much attention should be paid in the analysis of effective sensitizer [6]. Due to their intense charge transfer absorption in the whole visible range, transition metal coordination compounds (ruthenium polypyridyl complexes) are generally used as the effective sensitizers [7,8]. Even if ruthenium polypyridyl complexes have been the best so far, their synthesis process is complicated and costly. In addition, they are environment pollutant, limited in amount and high in cost [9]. Therefore, natural dyes promises to be the best alternative as they can be used for the same purpose with acceptable efficiency [10,11,12].

Due to their cost, efficiency, availability, non-toxicity, complete biodegradation, natural dyes is a popular subject of research. The natural dyes found in flowers, vegetables, leaves and fruits that can be extracted by simple procedures have been extensively investigated as DSSC sensitizer [12,13]. Alhamed et al. reported homemade DSSC prepared using natural dyes extracted from raspberries, shami-berries, grapes, hibiscus, and chlorophyll [12]. Lai et al. applied rhoeo spathacea in DSSC as a dye sensitizer [14]. There are many examples of natural dyes that have been used as DSSC dye sensitizers and some of them are mentioned below. The natural dye extracted from pomegranate and punica granatum has been used as DSSC sensitizers [15]. The DSSC has been prepared using a combination of natural dyes (raspberries, hibiscus and chlorophyll) as photosensitizer [12]. The DSSC sensitization has been done by the dye from extracted bracts of bougainvillea glabra and spectabilis betalain pigments [13]. Zhou et al. reported DSSC fabricated using twenty natural dyes, extracted from natural materials such as flowers, leaves, fruits, traditional chinese medicines, and beverages [16]. DSSC using flame of the forest (*butea monosperma*) was fabricated [2]. The natural dyes extracted from black berry, black grapes, red spinach leaves; malabar spinach buds and aurum leaves were used as DSSC sensitizers [17]. Hemmatzadeh and Mohammadi fabricated a DSSC using a natural dye extracted from pastinaca sativa and beta vulgaris [18].

There are many other natural dye sensitizers used, among them are: pomegranate leaves and mulberry fruit [19,20]; red kola nut (*cola nitida*) [21]; hibiscus [22]; grapes [23]; lawsonia intermits leaves, sumac/rhus fruits, and curcuma longa roots [24]; the curcumin [25]; leaves of anethum graveolens, parsley, arugula, spinach oleracea, and green algae [3]; walnuts, rhubarb, and pomegranate [26]; red cabbage [27]; wormwood and purple cabbage [28] and natural dye extracted from rhododendron species flowers [29]. Even if dyes from plants have been used intensively as DSSC dye sensitizers, there are some challenges in their extraction such as the conservation; short life span; less stability as they degrade quickly, and their availability and possibly high variability because some appear according to the seasons. Despite the presence of carboxylic acid group in the structure of dye from plant; they do not have the broad absorption band because most of them absorb more in visible range only. To maximize the absorption of more photons from the sun light for DSSC; it is better to have a black dye sensitizer having extremely high broadband absorption. It should absorb not only in visible range but also in ultraviolet and

near-infrared regions. This challenge can be handled by using natural dyes from other sources such as fauna from which sepia melanin was obtained.

Melanins are well-known natural pigments used for the photoprotective role as a skin protector because of their strong UV absorbance and antioxidant properties. Sepia melanin is the melanin isolated from ink sac of the cuttlefish *Sepia Officinalis* and it has been proposed as a standard for natural eumelanin [30,31]. Sepia melanin is the melanin (Figure 2b) derived from the ink sack of various species of cephalopoda, more commonly from the cuttlefish *Sepia officinalis* [31] (Figure 2).



**Figure 2.** Sepia Officinalis (a) and the commercial sepia melanin from Sepia Officinalis (b)

This melanin is insoluble in organic solvents, acids, aqueous solutions, and only partially dissolves in alkaline solutions. Sepia ink from *Sepia Officinalis* contains  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$ , enzymes and other substances [30,32]. Purified sepia melanin is a black powder, hygroscopic that should be refrigerated at  $-20^\circ\text{C}$  to avoid decomposition. Sepia melanin is also sensitive to oxygen, pressure and pulses of radiation which produce a fragmentation of melanosomes similar to what happens in the skin [33].

The hydroxyl and carboxylic functional groups of melanin from *Sepia Officinalis* (Figure 2a) present the possibility that a purified extract of the squid ink pigment may induce strong interaction with the hydroxyl group of  $\text{TiO}_2$  surface [34]. Melanin possesses a broad band absorbance in UV and visible range up to infrared. It also possesses the COOH and OH groups which would be free to bind to the surface of  $\text{TiO}_2$  [32,35]. Moreover, melanin polymer has interesting properties such as a considerable spectral absorbance width due to the high degree of conjugation of the molecule [36]. Therefore sepia melanin can be an attractive alternative to Ruthenium polypyridyl complexes containing a heavy metal, which is undesirable from environmental point of view and for which the synthesis process is complicated and costly for DSSC sensitization [1,12]. The important feature that makes them to be attractive for Grätzel cell application is this: Sepia melanins have the capacity to absorb a wide range of electromagnetic radiation ranging from visible light (hence its colour is dark) and ultraviolet radiation up to near infrared [32]. Sepia melanin can also conduct electricity and is thus considered a semiconductor material [35]. This paper reports the obtained results from X-ray diffraction, UV-Vis as well as Raman spectroscopy.

## 2. Materials and Methods

### 2.1. Materials

Sepia melanin powder (standard) from *Sepia Officinalis* was obtained from Sigma-Aldrich (Chemie GmbH Kappelweg 1 D-91625 Schnellendorf, Germany). This purified sepia melanin is a black powder, hygroscopic that has been kept refrigerated at  $-20^{\circ}\text{C}$  to avoid any photo-chemical or photo-physical alterations. Methanol HPLC grade, acetone (99%) were used to clean substrates for X-ray diffraction (XRD) analysis sample preparation. Sodium hydroxide (ACS reagent,  $\geq 97.0\%$ , pellets from Sigma-Aldrich) was used to make the solution of 0.1 mole of sodium hydroxide. The solvent that was used in UV-Vis spectrometry was obtained using this solution drop by drop in deionized water in order to raise its pH up to 10.9354 and this pH was measured. Slides, microscope plain, size  $25\text{ mm} \times 75\text{ mm}$  have been used as substrates for XRD characterization; to prepare the thin films, the concentrated solution was drop-coated on them.

## 2.2. Characterisation Techniques

The crystallinity of sepia melanin was determined XRD. The UV-Vis characterisation shows the capacity of sepia to absorb electromagnetic waves as one of the very important criteria for a good dye sensitizer. The best dye sensitizer should absorb photons as much as possible; so that the excited dye molecules will inject many electrons in the conducting band of  $\text{TiO}_2$  to produce much electricity Raman was used in determining the group functions which are present in sepia melanin, and these function groups serve as the binding sites to  $\text{TiO}_2$  for DSSC application.

The sepia melanin was scanned using a Bruker AXS D8 Advance x-ray diffractometer with  $\text{Cu-K}\alpha$  radiation with wavelength,  $\lambda (K\alpha_1) = 1.5406\text{ \AA}$ . The x-ray tube was powered with a current of 40 mA and a voltage of 40 kV. The step size and the step time were  $0.027^{\circ}$  and 176 s respectively. The scanning rate was  $2^{\circ}/\text{min}$  x-ray beam at  $25^{\circ}\text{C}$ . The thin films samples used for XRD measurement were prepared by drop coating process. After preparing the solution to be coated, it was applied to the substrates. For effective coating, the substrate should be well cleaned and the solution to coat should be highly concentrated.

Sepia melanins are sparingly insoluble in water at neutral pH or in the organic solvent commonly used in UV-Vis spectroscopy; thus the solvent used here was ultrapure water at pH 10.93 adjusted by adding the amount of 0.1M NaOH drop by drop. To make sepia melanin solution, 10mg of sepia melanin were weighed and dissolved into 100 ml of water at pH 10.93. The sepia melanin solution was measured by UV-Vis Spectrometer (HP Office Jet Pro 8000). Typical Raman spectrum collected from sepia melanin powder at room temperature using a 532 nm Argon laser to excite the sample. It was recorded by a T64000 micro-Raman spectrometer from HORIBA scientific, Jobin Yvon Technology equipped with a triple monochromator system.

## 3. Results and Discussion

### 3.1. X-Ray Diffraction(XRD)

A typical XRD spectrum shows peaks at fixed  $2\theta$  angles. By the peaks position, it is possible to identify the

kind of crystals present on the sample. This is done by doing qualitative phase analysis (search match) using software like for example the PANalytical X'pert Highscore plus software employing the ICDD PDF database for comparison in order to identify the crystal phase. The observation of the results from sepia melanin sample was the lack of structure in the diffraction pattern corresponding to any significant crystallinity in this sepia melanin. The spectrum was dominated by a broad non-Bragg diffraction pattern. Figure 3 represents XRD spectra of a highly concentrated sepia melanin solution drop coated into  $2 \times 2\text{ cm}$  cleaned glass substrates.

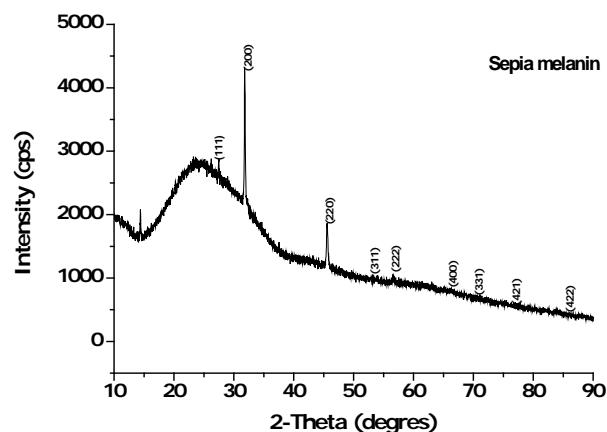


Figure 3. The XRD spectrum plotted from low data collected by x-ray diffractometer in measuring sepia melanin.

The produced sharp peaks in diffraction spectrum by the scattering of X-rays by crystalline structures serve as a signature for the crystal that is analysed. However, broad features in a diffraction spectrum, known as non-Bragg features as a result of the absence of coherent scattering from regular and repeating structures as observed in crystals are produced by amorphous compound such as sepia melanin [37,38].

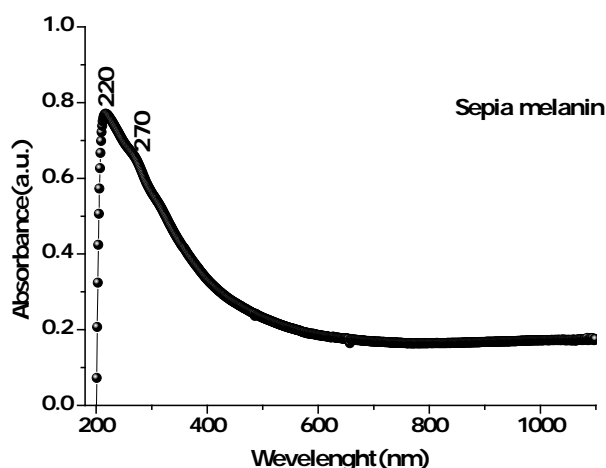
The sharp diffraction peaks appearing on the spectrum (except the first peak that the used software was not able to identify) are due to NaCl molecules which have been confirmed to be the component of sepia melanin by EDS. From the peaks position of the XRD spectra shown in Figure 3, it can be observed that the sepia melanin crystallographic patterns showed peaks at  $2\theta = 27.33, 31.69, 45.45, 53.85, 56.47, 66.22, 73.06, 75.30$  and  $83.97$  which have the corresponding reflections (111), (200), (220), (311), (222), (400), (331), (420) and (422) respectively. The lattice parameter corresponding to this crystallographic structure is about  $a = 5.64020$  (PDF 00-005-0628).

A broad diffraction peak ( $2\theta=10-90^{\circ}$ ) observed on the XRD spectra of sepia melanin is showing its amorphous nature. Because of amorphous, insoluble as well as heterogeneous nature of melanins, their structures are uncertain [38]. The utility of XRD techniques for the analysis of the structure of amorphous materials such as sepia melanin is limited. This same overall structure of sepia melanin was obtained in the literature [38,39].

### 3.2. UV-VIS-NIR Spectrum

The UV-Vis measurement shows the UV-VIS-NIR absorbance in the optical range of 190 - 1100 nm (1.12 -

6.652 eV). One can distinguish 2 spectral regions; 190 - 300 nm and 300 - 1100 nm. The UV-visible wavelength scan showed the absorption was highest at the UV region of 200 to 300 nm, but diminished towards the visible region. It has one sharp peak centered approximately at 220 nm and a shoulder hump at 270 nm. It was found that the maximum absorption was at the value of 78% and the minimum intensity of absorption was about 16.4%. The overall UV-Vis structure is similar to the UV-Vis spectrum of synthesized melanin nanoparticles [40]. The UV-Vis spectra of the melanin samples are given in Figure 4. Huang et al. reported that melanin has no distinctive absorption peaks to distinguish itself from other cutaneous chromophores. Instead, melanin absorption decreases monotonically with increasing wavelengths from 300 to 1100 nm [41].



**Figure 4.** UV-Vis spectra of sepia melanin. The UV-Vis wavelength scan showed the absorption was highest at the UV region of 200 to 300 nm, but diminished towards the visible region

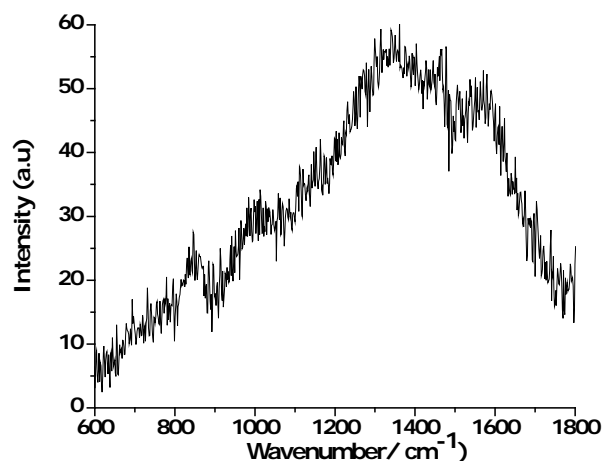
The UV-Vis spectrum obtained showed the typical absorption profile of melanin that is characterized by a strong absorption in the UV-Vis spectral range, with a nearly featureless line shape and absorbance values monotonically decreasing from UV-Vis to NIR spectral region [32,41,42]. The spectrum shows a strong UV absorption in the 200 - 300 nm region that can be attributed to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  of the amino, carboxylic and aromatic moieties [32]. The UV-Blue energy transitions corresponds to the transition from the nonbonding orbital  $n$  to the antibonding orbital  $\pi^*$  ( $n \rightarrow \pi^*$ ), which occurs predominantly in carbonyl ( $C=O$ ) bonds that are very abundant in the melanin. Region 2 (300 - 1100nm) displays a quasi-constant and large absorbance which certainly is the source of the black color of the sepia melanin itself. This broad and large spectral absorption is attributed to strong absorption transitions involving the orbital energy of the antibonding  $\pi^*$  and the bonding  $\pi$  ( $\pi \rightarrow \pi^*$ ). This later occurs in the aromatic-unsaturated C bonds [32,33]. The movement of delocalized electron in the sepia melanin structure and the high degree of conjugation facilitate the transitions to the antibonding  $\pi^*$  orbitals. A strong absorption of sepia melanin in the red part of visible sepia melanin is mainly due to many carbonyl groups present in its indolic groups [32]. This is the source of the black color of sepia melanin.

One of the criteria for a good dye sensitizer for Grätzel cell is that the dye should be “black” in the UV-Vis-NIR

spectral region, with extremely high broadband absorption, preferably all the way into the near-IR in order to harvest as many incident photons as possible [43]. Therefore, the obtained UV-Vis results showed that sepia melanin exhibits a high absorption throughout UV-Vis-NIR range and this lead it to an effective candidate dye for DSSC.

### 3.3. Raman Spectroscopy

Two broad bands centered at about  $1344\text{ cm}^{-1}$  and  $1551\text{ cm}^{-1}$  were observed in such Raman spectrum. The two broad bands were observed by Perna et al., and were centered at about  $1400\text{ cm}^{-1}$  and  $1590\text{ cm}^{-1}$  [42]. The melanin Raman spectrum was reported to be dominated by two intense and broad peaks at about  $1580\text{ cm}^{-1}$  and  $1380\text{ cm}^{-1}$  [41]. The observed bands were in agreement with two broad bands that were observed in the Raman spectrum of the commercial sepia melanin at about  $1590\text{ cm}^{-1}$  and  $1360\text{ cm}^{-1}$ . The confirmation of the origin of two prominent peaks in melanin; as inelastic Raman scattering was done by measuring variety of melanin sources using multiple wavelengths [41].



**Figure 5.** Typical Raman spectrum of sepia melanin.

The observed broad bands on Raman spectrum are related to Raman active vibrational modes involving different atoms, as carbon, oxygen, hydrogen and nitrogen, which are the main constituent of melanin. They are from the overlapping of several vibrational mode mainly; the  $C=C$ ,  $C=N$  and  $C=N$  ring stretching mode of pyrrole structure as well as the  $C-O$  stretching mode and combination bands due to  $C-O$  stretching and  $O-H$  deformation of carboxylic acid [42].

The sepia melanin atoms are organized according to an indolic structure having several functional groups bonded to it. The main functional groups are hydroxyl groups  $OH$ , carbonyl groups  $C=O$ , carboxylic acid  $COOH$  as well as  $NH$  groups. This melanin complexes formation results to the challenge in assigning precisely the observed Raman features of melanin to the large amount of different vibrational modes involving the many functional groups inside this biopolymer. The overall shape of the found sepia melanin Raman spectrum is similar to those reported for melanin samples about the vibration mode of melanin monomer units; and this confirms the presence of such units inside the analyzed sepia melanin sample [31,41,42].

The typical Raman spectrum has been analyzed by mean of Gaussian function for better analysis of the

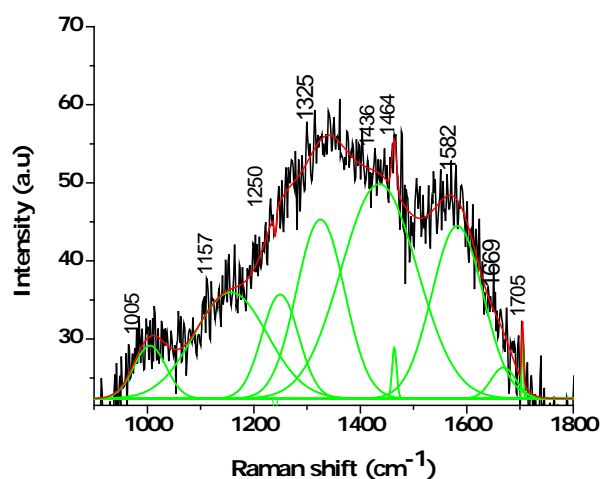
functional groups characteristic of the sepia melanin structure and to point out some spectral features which may be hidden in the experimental spectra.

The results of this fitting procedure are shown as red dashed lines in Figure 6 and the spectral position of

Raman peaks are listed in Table 1. It is clearly evident that the sum of Gaussian functions (red continuous line) is well fitted to the experimental spectrum (black continuous line).

**Table 1. Spectral Positions of Raman Peaks Obtained by Gaussian Function Fitting with their Respective Center Positions, Areas, Widths, Height, and their Corresponding Assignments (Figure 6)**

Peak (cm <sup>-1</sup> )	Center	Area	Width	Height	Assignments
1	1004.95	515	60.69	6.78	C-H in plane deformation
2	1156.66	2343.01	137.24	13.62	pyrrole NH in-plane deformation/ring Breathing
3	1249.60	1159.05	69.34	13.33	C-O stretching; combination of C-O stretching and O-H deformation in carboxylic acid
4	1325.26	2586.54	89.97	22.93	C-H in-plane deformation
5	1435.63	4909.71	142.53	27.48	C=C, C=N in plane vibration in pyrrole
6	1463.99	68.85	8.42	6.52	pyrrole ring stretching vibration
7	1582.41	2670.77	96.36	22.11	C=C aromatic/pyrrole ring stretching vibration
8	1668.98	234.68	46.75	4	C=C in plane vibration in pyrrole
9	1704.71	55.52	3.63	7.74	C=O stretching in COOH/Indole ring vibration



**Figure 6.** Fitting analysis of the experimental average Raman spectrum (black continuous line) obtained by means of Gaussian functions (green continuous lines): the sum of the Gaussian bands (red continuous line) is in good agreement with the experimental spectrum.

## 4. Conclusion

The performance of DSSC depends mainly on the dye sensitizer that absorbs the light and converts it into electrical energy. Natural dyes were found to be the best alternative DSSC dye sensitizer comparing to synthetic dyes because their synthesis process is complicated and costly. In addition, they are environment pollutant, limited in amount and high in cost. The natural dyes from plant have been used intensively as DSSC dye sensitizers but they present some challenges in their extraction such as the conservation; short life span; less stability as they degrade quickly, and their availability and possibly high variability because some appear according to the seasons. In addition, these dyes do not absorb in a wide range of electromagnetic radiation. This challenge can be handled by using natural dyes from other sources such as fauna from which sepia melanin was obtained.

The characterization of Sepia melanin by XRD shows that sepia melanin is amorphous in structure. The high

absorbance capacity of Sepia melanin has been measured by UV-Vis and it was found that sepia melanin absorbs in a wide range of electromagnetic waves from UV-Vis till Near-IR. Raman spectroscopy was used to identify COOH and OH group in sepia melanin that are responsible for the binding of sepia melanin to TiO<sub>2</sub>. Sepia melanin that can be easily extracted from Sepia Officinalis by simple techniques possesses a broad band absorbance in UV and visible range up to infrared. It also possesses the COOH and OH groups which would be free to bind to the surface of TiO<sub>2</sub>. Moreover, melanin polymer has interesting properties such as a considerable spectral absorbance width due to the high degree of conjugation of the molecules. All these are important features that make sepia melanin to be attractive for Grätzel cell application.

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