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# Novel Applications with Asphaltene Electronic Structure

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Eva M. Deemer and Russell R. Chianelli

Additional information is available at the end of the chapter

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## Abstract

Asphaltenes are the molecular components of Asphalts and have polyaromatic hydrocarbon (PAH) structures similar to nanographenes. Thus, organic-based dye sensitized solar cells can be produced from asphaltenes. In addition, graphene based structures doped with transition metals can be synthesized from asphaltenes. These materials are simple to synthesize and inexpensive relative to other methods for doping graphene. Thus, what is considered a “Waste Material - Tar” can now be utilized in several important applications. These novel materials from asphaltene are also termed Discotic Liquid Crystals (DLC) and now have great potential in many areas, because of novel and valuable properties, easy synthesis and low cost.

**Keywords:** synthetic asphaltene, organic photovoltaics (OPVs), polyaromatic hydrocarbons (PAHs), discotic liquid crystals (DLCs), dye sensitized solar cells (DSSC), light harvesting molecules, nanographene, doped graphene

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## 1. Introduction

Carbon-based systems including polymers, nanotubes, graphene and quantum dots are active materials in electronic, photonic or magnetic devices. Their properties depend on chemical structure and size and thus they can be chemically or physically tuned. Extended  $\pi$ -conjugated scaffolds that can be decorated with functional groups are the main feature related in these structures. Their functionalization can be optimized in order to facilitate their self-assembly into highly ordered supramolecular architectures, that are driven by non-covalent  $\pi - \pi$  stacking interaction, hydrogen bonding, etc. Small molecules which can be characterized by their  $\pi$ -conjugated networks (pyrenes, pentacenes, coronenes, polythiophenes, etc.) possess

| Device             | Area                               | Current density<br>(electrons/nm <sup>2</sup> -sec) |
|--------------------|------------------------------------|---|
|                    | Cross sectional (nm <sup>2</sup> ) |   |
| 1 mm copper wire   | 3 × 10 <sup>12</sup>               | 2 × 10 <sup>6</sup>                                 |
| Polyphenylene wire | 0.05                               | 4 × 10 <sup>12</sup>                                |
| Carbon nanotube    | 3                                  | 2 × 10 <sup>11</sup>                                |

**Table 1.** Current density of molecular wires expressed in nanoscale units compared to current density of macroscopic copper [14].

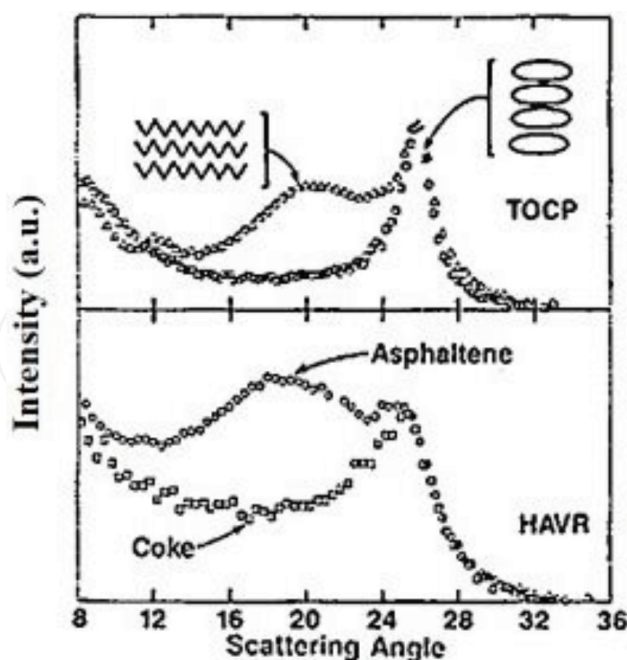
electronic bandgaps that are well defined and shapes such as fibers, nanocrystals or uniform monolayers which enable molecular self-assembly into highly ordered low-dimensional architectures. Conjugated molecules have been explored for use in organic electronics and vary widely, however conjugated discotic materials and their self-assembly have been of interest to researchers due to their unique liquid crystalline properties [1, 2].

Experiments done in the mid and late 1990s demonstrated individual molecules can possess physical phenomena which previously thought to have been limited to semiconductors and revolutionized the material science. In 1996, it was still questionable whether or not individual molecules could actually conduct electricity but experiments performed from 1995 to 1997 [3–8] determined that individual molecules can conduct and also switch small electrical currents [9–13]. These revolutionary works demonstrated the use and assembly of molecular electronic devices using aromatic organic molecules, nanotubes, biomolecules or nanowires (Table 1) but more importantly, they gave the promise of low cost, carbon-based electronics at the smallest of scales which could be printed onto plastic.

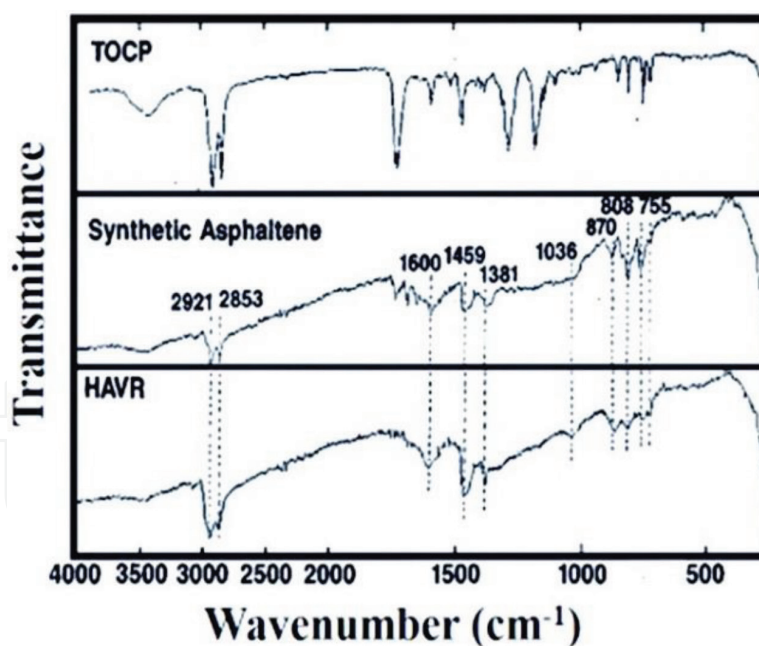
## 2. Asphaltene and synthetic asphaltene: the theoretical platform

Asphaltenes are a relatively exotic class of hydrocarbon component in crude oils [15, 51]. Naturally occurring crude oil contains an enormous range of compounds that spans hydrocarbon compositions from dry natural gas to tar. The density and viscosity increases dramatically and color changes from clear to deep brown as asphaltene content increases from 0 to nearly 20% across that range. Researchers agree that the asphaltene structure is comprised of some carbon and hydrogen atoms which are bound in ring-like, aromatic groups, and also contains the heteroatoms. Alkane chains and cyclic alkanes include the rest of the carbon and hydrogen atoms, linked to ring groups. Within this arrangement, asphaltenes exhibit a range of molecular weight and composition. These characteristics of asphaltenes are acceptable to nearly all researchers and specialists, but leaves sufficient room for discussion regarding the structure or size of individual asphaltene molecules.

Extensively studied by Chianelli et al., asphaltene structure has been shown to have a structure similar to that of the synthetic compound tetraoctyl carboxylate perylene (TOPC) [16]. X-ray diffraction (XRD) studies performed on TOPC (shown in Figure 1) differentiate two peaks



**Figure 1.** X-ray diffraction of asphaltene –high aromatic vacuum residue (HAVR) compared to synthetic molecule tetraoctyl carboxylate perylene (TOCP) [16].



**Figure 2.** Infrared spectra of the TOCP precursor, synthetic asphaltene and HAVR (heavy Arab vacuum residue) asphaltene showing the significant similarity between the synthetic and the HAVR asphaltene [16].

that can determine distinction between alkane chains and stacked aromatic cores. Using these synthetic structures as a model, the structure of asphaltene before and after thermal processing was explored using XRD and the results show that the production of coke is actually

| Chemical properties of synthetic asphaltene and HVAR |      |              |               |             |
|--|------|--------------|---------------|-------------|
|  | H/C  | % C Aromatic | % C Aliphatic | MW          |
| Synthetic asphaltene                                 | 1.06 | 58           | 42            | 2750        |
| HVAR asphaltene                                      | 1.10 | 33–45        | 55–65         | 1.000–10.00 |

**Table 2.** Comparison of some chemical properties of synthetic asphaltene and HVAR [16].

the self-assembly of stacked aromatic cores. This work helped researchers understand the fundamental physical characteristics and the process of coke formation through self-assembly using of synthetic asphaltene.

When the temperatures increased above 350°C during thermal processing, the aliphatic ester of TOCP becomes the weakest region for thermal cleavage. When temperature reaches above 420°C in the absence of oxygen, TOCP completely thermally converts into a sea of free radicals containing aromatic cores and long-chain alkyl fragments. After Chianelli et al. successfully prepared synthetic asphaltene, the Infrared (IR) spectrum of TOCP, synthetic asphaltene, and HVAR (Heavy Arab Vacuum Residuum) were compared (**Figure 2**) and it is clear that absorption bands of synthetic asphaltene match well with band position and intensity of the IR spectrum of HVAR [17]. The comparison in chemical properties between synthetic asphaltene and HVAR illustrated in **Table 2**.

### 3. Organic photovoltaics using asphaltenes

#### 3.1. Introduction to organic photovoltaics

The photovoltaic effect represents the generation of a potential difference at the junction of two different materials in response to various forms of radiation. The whole field of converting solar energy into electricity is the field of “photovoltaics” [18]. The photovoltaic process combines four stages which comprise the following: (1) light absorption, (2) charge generation, (3) charge transport, and (4) charge collection [19]. When the material has a semiconducting property that responds to incident waves, the first stage light absorption occurs. The absorption characteristic of the material is based on the intrinsic extinction coefficient and the band gap of the semiconducting material. Once light has absorbed by a material, the second stage occurs. As the incident photon hits electrons at the ground state, inorganic semiconductors generate free carriers (i.e. holes and electrons) and charge generation ensues. However, in organic semiconductors, excited electrons form an exciton, which is a bounded electron and hole pair. To make an efficient organic photovoltaic cell, the dissociation of excitons is an important matter as the binding energy of the exciton is relatively large (0.3 eV) [20].

Dye sensitized solar cells (DSSC) are low cost alternatives for the conventional solar cells, and commercially promising because of the promise of low-cost materials and roll-to-roll manufacturing. The DSSC can be classified as a photo electrochemical (PEC) solar cell because of its utilization of photons, charges, and electrolyte for its basic operation [21]. O'Regan and Grätzel built and demonstrated the first DSSC by 1991, [22] and attracted widespread academic and



industrial interest. Compared to conventional solar cells, DSSCs had the promise of easy fabrication at a low-cost in environment friendly and have high-energy conversion efficiency [23]. One more advantage of DSSCs is that changes in temperature do not affect the performance, while temperature changes can affect the performance of conventional silicon solar cells [24].

Ooyama and Harima [30] have done an extensive literature review on the main requirements for efficient organic molecule (dye) used so far for DSSCs. Their conclusions are summarized in the following four statements:

1. The organic molecule (dye) should have a minimum of one anchoring group like COOH,  $-\text{SO}_3\text{H}$ ,  $-\text{PO}_3\text{H}_2$ ,  $-\text{OH}$  for adsorption onto the  $\text{TiO}_2$  surface to provide a tightly held dye and suitable electron interaction between them.
2. To achieve efficient electron injection from the excited dye to the conduction band of the  $\text{TiO}_2$ , the dye has to have an energy level of the lowest unoccupied molecular orbital (LUMO) which is higher (more negative) than that of the conduction band of the  $\text{TiO}_2$  electrode. However, the energy level of the highest occupied molecular orbital (HOMO) of the dye must be lower (more positive) than the  $\text{I}_3^-/\text{I}^-$  redox potential in the electrolyte to achieve efficient regeneration of the oxidized state by electron transfer from  $\text{I}_3^-/\text{I}^-$  redox couple.
3. The organic molecule should have high molar absorption coefficients over the wide region of sunlight extending into near infra-red, to provide a large photocurrent to give the high light harvesting efficiency.
4. To achieve a stable DSSC, the organic molecule should have chemical stability in its photo excited state and the redox reactions throughout the reaction cycle.

Dye molecules (sensitizers) are the key component of a DSSC that increase efficiency through their abilities to absorb visible light photons. Despite the fact that the highest efficiency of a dye sensitized solar cells is achieved from a combined effect of numerous physiochemical nanoscale properties, the main focus in these studies is the dye sensitization of large band-gap semiconductor electrodes. In DSSCs, this is accomplished by coating the internal surfaces of porous  $\text{TiO}_2$  electrodes with dye molecules specifically tuned to absorb the incoming photons [23]. The dye is the light absorber and the photoreceptor sensitizing the semiconductor and so some conditions must be fulfilled. Without a doubt, a dye that absorbs nearly all the sunlight radiation incident on earth, like a black-body absorber, is highly desirable. Organic dyes consisting of natural pigments and synthetic organic dyes have a donor-acceptor structure called push-pull design, which improves the absorption in red and infrared region by increasing short circuit current density. Natural pigments, like chlorophyll, carotene, and anthocyanin, are available in plant leaves, flowers, and fruits and fulfill these requirements. Experimental results showing that natural-dye sensitized solar cells achieved the efficiency of 7.1% and high stability [24].

Co-sensitization, the use of two dyes combination that complements each other in their spectral features is another strategy to get a broad optical absorption expanding throughout the visible and near IR region. This strategy enhances photo-absorption through optical effects which allow the two sensitizers to be additive. In particular, there was no negative interference between co-adsorbed chromophores, making way for testing a multitude of other dye combinations [25].

To increase improvement of the performance of DSSC, different kinds of additives have been added into dye solutions. For example, Kay and Grätzel found that the addition of cholic acid (CA) with porphyrin derivatives improved both the photocurrent and photovoltage of the solar cell [26]. Additionally, other co-adsorbents such as hexadecylmalonic acid (HDMA) [27], deoxycholic acid (DCA) [28], and chenodeoxycholic acid (CDCA) [29] were also used in the dye solution when fabricating sensitized TiO<sub>2</sub> films into devices, among which CDCA is the most popular co-adsorbent.

Dye aggregation on the TiO<sub>2</sub> surface should be avoided. This aggregation leads to reduction in electron-injection yield from the dyes to the CB of the TiO<sub>2</sub> due to intermolecular energy transfer causing low conversion efficiency of the DSSC [30]. The main parts of the dye sensitized solar cell are illustrated schematically in **Figure 3**. The transparent and counter conducting electrodes, wide bandgap semiconducting nanostructured layer, the sensitizer, and the electrolyte are the main four elements of the cell. The transparent conducting electrode and counter-electrode are coated with a conductive and transparent thin film such as fluorine doped tin dioxide (SnO<sub>2</sub>) [31].

The photocurrent density calculated at short circuit ( $J_{sc}$ ) the open-circuit photovoltage ( $V_{oc}$ ) the fill factor (FF), and the power of the incident light ( $P_{in}$ ) are used to determine the total conversion efficiency ( $\eta$ ) of the dye-sensitized solar cell. These values can be taken from the photocurrent density-voltage characteristics (IV curves) under full sunlight ( $P_{in} = 100 \text{ mWcm}^{-2}$ ). The relationship between voltage (V) and current (I) is determined by varying the resistance of the outer circuit and considered  $J_{sc}$  when resistance of the outer circuit is zero (thus voltage is zero) and  $V_{oc}$  when resistance is maximum (thus photocurrent is zero). The power output of the device equals the product of J and V, and the fill factor states the efficiency of the device compared to that of an ideal cell.  $P_{max}$  relates to the maximum value that can reach the output power and is usually reported as the output power of the commercial device. The performance of DSSC can be projected using the following Equations [32]: (101)

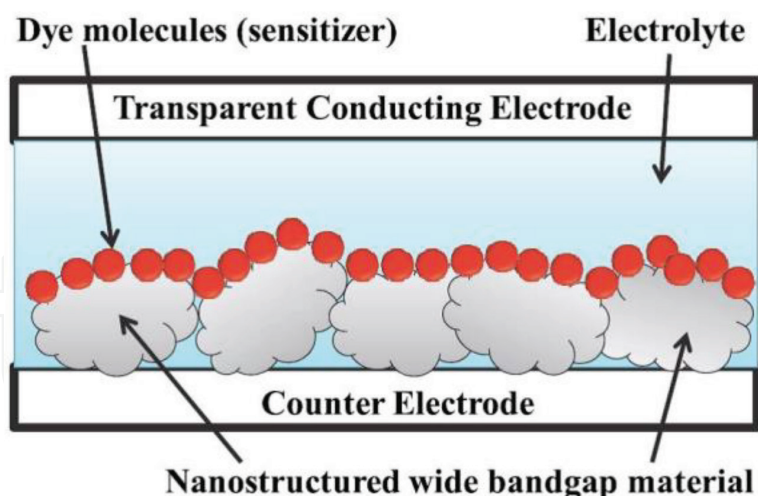
$$\eta (\%) = \frac{J_{sc} * V_{oc} * FF}{P_{in}} \quad (1)$$

where:

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}} \quad (2)$$

### 3.2. Results: The resurrection of an ancient leaf

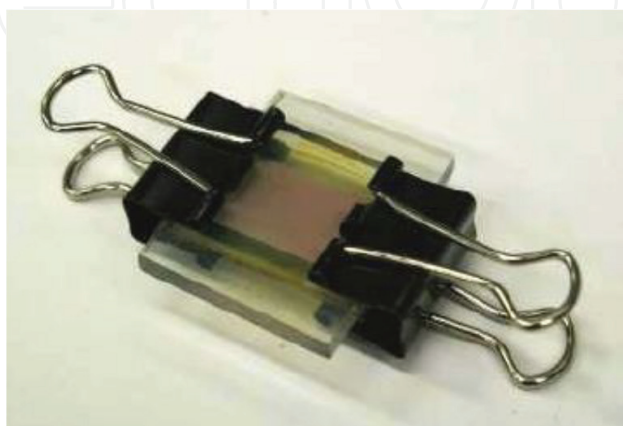
Dr. Rajab E. Abujnah built the first ever asphaltene DSSC (dye-sensitized solar cell) as a graduate student in the lab of Dr. Chianelli, which demonstrated a photo-conversion efficiency (PCE) of 1.8%. Four natural organic asphaltene fractions were extracted and tested as dyes using various parameters with TiO<sub>2</sub> based dye-sensitized solar cell DSSC. The photovoltaic performance of the cells was determined by parameters such as open-circuit voltage ( $V_{oc}$ ), short-circuit current ( $I_{sc}$ ), fill factor (FF), and series resistance. The overall energy conversion efficiency was also measured to correlate the different effects of asphaltene fraction as well as concentration and influence on the improvement of the solar cell parameters.



**Figure 3.** Schematic of the structure of the dye sensitized solar cell.

The sensitization of  $\text{TiO}_2$  electrode using asphaltene obtained with a 90/10 ratio of toluene to pentane ratio resulted in an energy conversion efficiency of 1.8%. Un-fractionated asphaltene was shown to produce comparable results as Fraction 3 as sensitizer in DSSC. A strategy to minimize series resistance, improve photo current and open circuit voltage was also studied. Purifying asphaltene using the RTV mask, employing the  $\text{TiO}_2$  compact layer, in addition to UV-Ozone cleaning treatment of the transparent electrode have been shown to improve the performance of asphaltene DSSCs [33].

The asphaltene dye covered  $\text{TiO}_2$  electrode and Pt-counter electrode were assembled into a sandwich type and assembled with using a binder clamps as shown in **Figure 4**. The clamps used to attach the two electrodes and to provide space for the electrolyte between two electrodes. Sealant also can be used to assemble the sandwich of electrodes. It is can be used to prevent leakage of electrolyte. For good results, sealant was put between two electrodes and put under the hot press machine. Temperature and pressure were adjusted and then the hot press was heated up to join both electrodes by using the sealant. A drop of the electrolyte solution was



**Figure 4.** Completed synthetic asphaltene DSSC.



injected into the hole in the back of the counter electrode and to prevent leakage of electrolyte, the hole was covered by tape. The electrolyte was introduced into the cell by using vacuum.

Synthetic asphaltene has shown experimental evidence and preliminary results to suggest it can fulfill the requirements of organic semiconductors due its ability to absorb visible light. It was also found that this material can be adsorbed easily on the surface of the nano-crystalline particles  $\text{TiO}_2$ , therefore synthetic asphaltene is an excellent candidate for use in DSSC. Dr. Hassan Sharif experimented with synthetic asphaltene samples subsequently to Dr. Abujnah and applied as-synthesized asphaltenes into various solar cells with different parameters in the  $\text{TiO}_2$  layer of the DSSC. DSSCs were fabricated using the synthetic asphaltene as dye.

To further research and optimize the cells, Porphyrin was added to the synthetic asphaltene to improve the efficiency of the cell. Porphyrin is already used as organic dye in DSSC. The new compound is prepared in the lab by dissolving the same ratio of synthetic asphaltene with free metal Porphyrin in Toluene for 24 hrs under heating; the mixture was kept under the hood to evaporate the Toluene. The final product was collected and used in this experiment. The table below shows the effects of mixing Porphyrin with synthetic asphaltene on the conversion efficiency of synthetic asphaltene dye. From the table it is clear that the new dye is increasing both current density  $J_{sc}$  and  $V_{oc}$ , and then increasing the performance efficiency.

Asphaltene has shown to be able to produce voltage, and according to the results outlined in **Table 3**, could be considered a good candidate in photovoltaic in part, due to its low cost [34]. New material was prepared by dissolving synthetic asphaltene and crude oil asphaltene. This asphaltene was extracted from crude oil asphaltene and purified by using Toluene. Real asphaltene was dissolved with synthetic asphaltene in Toluene in the ration of 1:1 and kept for 24 hours for dissolving under heating. The solvent kept under the hood until the Toluene completely evaporated, and the solid product was collected and used for the experiment.

During his work with synthetic asphaltene as new dye in the fabrication of DSSC, Dr. Sharif noticed some precipitates when synthetic asphaltene dissolved in Toluene. These precipitates prevent the good absorbance of synthetic asphaltene dye into the surface of  $\text{TiO}_2$ . So, synthetic asphaltene was filtrated to remove any impurities. The table below compares the

| Experiment   | Open current Voltage | Short Circuit Current (mA/cm <sup>2</sup> ) | Fill Factor % | PCE (%) |
|--|----------------------|---|---------------|---------|
| Synthetic asphaltene mixed with porphyrin and dissolved in toluene | 0.429                | 6.57  | 54            | 1.85    |
| Real Asph. mixed with synthetic asphaltene                         | 0.435                | 7.28  | 46            | 1.40    |
| Unpurified synthetic asphaltene                                    | 0.445                | 4.19  | 56            | 1.0     |
| Purified synthetic asphaltene                                      | 0.455                | 7.05  | 61            | 1.83    |
| Purified synthetic asphaltene with chenodeoxycholic acid (CDCA)    | 0.506                | 7.00  | 0.61          | 2.08    |

**Table 3.** The performance of synthetic asphaltenes in DSSCs using different parameters.

results before and after purifying the synthetic asphaltene. There is a high increase in the current density and also fill factor, but the small increase in the voltage. The efficiency was improved from 1.0 to 1.83% which illustrates the importance of processing parameters on devices performance and optimization.

The effects of chenodeoxycholic acid (CDCA) in a dye solution as a co-adsorbent on the photovoltaic performance of dye-sensitized solar cells (DSSCs) based organic dye containing purified synthetic asphaltene dye was also studied. It was observed that the co-adsorption of CDCA can eliminate and reduce the formation of dye aggregates and improve electron injection yield and thus, the short-circuit current ( $J_{sc}$ ). This has also led to a rise in photovoltage, which is attributed to the decrease of charge recombination. The DSSC, based on synthetic asphaltene dye with CDCA, overall conversion efficiency was further improved to 2.0% ( $J_{sc} = 7.00 \text{ mA/cm}^2$ ,  $V_{oc} = 0.506 \text{ V}$ ,  $FF = 0.61$ ) upon addition of 1:1 ratio of CDCA to the dye solution.

### 3.3. Summary and discussion

In general, we can conclude from these studies that asphaltene was successfully prepared in the lab and the characterization results were similar as in the literatures. Even primary results show that synthetic asphaltene has good ability to absorb sunlight, but the results of the first use of synthetic asphaltene in DSSC were not satisfied. More work was carried during the study to increase the performance efficiency from 0.4 to 2.0%. We conclude also synthetic asphaltene can give good results by adding some additives, but it also can improve the conversion efficiency just by purifying process which increase efficiency from 1.0 up to 1.83%. Instead of additives, there is another parameters can increase the efficiency of synthetic asphaltene as dye in DSSC for example, the number of layers of the paste and using UV-O treatment. Therefore, a total overall efficiency of 3.5–5.0% could be easily attained with good engineering design and material process.

The first result obtained with using synthetic asphaltene as dye was 0.4%. The maximum PCE obtained using synthetic asphaltene as dye after adjusting some variables and adding some additives reached 2.0%. The benefit to this study and in using synthetic material will help researchers to find new and inexpensive dyes as well as to understand better the characterization of crude oil asphaltene [35].

## 4. Doped graphene from asphaltene

### 4.1. Introduction to doped graphene applications

The electronic and magnetic properties of graphene can be modified through combined transition-metal (TM) and nitrogen decoration of vacancies. Additional modes of functionalization that are currently being explored for a wide range of applications in nanoelectronics [36–38], spintronics [39] and electrocatalysts [40]. Researchers previously discovered that TMs bind to graphene strongly in a porphyrin ring coordinated by four nitrogens [41]. The stability in the presence of the defects associated with TMs can be attributed to the reduced

electrostatic repulsion between nitrogen lone-pair electrons due to the hybridization between N and TM. Results from DTF studies have predicted these types of structures to be particularly promising candidates for graphene-based ferromagnets, which could find applications in nanoelectronics and nanomagnetism.

Graphene-type molecules, typically large polycyclic aromatic hydrocarbons (PAHs), have gained enormous interest because of their unique self-organization behavior and promising electronic properties for applications in organic electronics [42]. Asphaltene is a part of crude oils that contain a large number of structures, specifically high molecular weight bonded aromatic hydrocarbons components with hetero-atoms. Several metals (e.g., Ni, V, Fe, Al, Na, Ca, and Mg) shown to accumulate in the asphaltenes fraction of crude oil, typically in concentrations less than 1% w/w [43–45]. Vanadium and nickel, the most abundant of the trace metals, present mainly as chelated porphyrin compounds, and they linked to catalyst poisoning during upgrading of heavy oils [46, 47]. The concentrations of other trace metals not bound in porphyrin structures (e.g., Fe, Al, Na, Ca, and Mg) indicated to change in deposits as a function of well depth [48], and among sub fractions of asphaltene.

Graphene produced from chemical vapor deposition is viable for use in technologies such as touch screens, sensors, transistors, novel optical/electronic/photonic devices such as IR cameras, radiation shielding and camera lenses. Because they are expected to induce novel magnetic and superconducting behavior, TM adatoms and graphene are a topic of great interest are expected to induce novel magnetic and superconducting behavior. Because of this interest, there have been extensive theoretical studies but the experimental exploration of TM/graphene systems is very limited. Graphene with Boron and Nitrogen (BCN) is a sought after material due to the fact that graphene has no band gap [49]. Graphene in its single crystal form is a conductor, not a semi-conductor, so while it has amazing properties sought after by so many researchers, it has yet to make a significant impact on electronic industries for this reason. BCN is currently the subject of doped graphene research because it can be introduced by vapor. In contrast, TMs cannot be introduced by vapor. Even if they could be introduced at high temperatures, it has been determined that they would not be stable in an in-plan configuration due to the high differences in energy between TMs and carbon. Boron and Nitrogen both neighbor carbon on the periodic table and do not have a large differences in electron structure. As a carbon source, asphaltene is generated from waste crude oils and remains unsuitable for hydrocracking because of the presence of TMs. This study attempts to utilize that waste as a valuable source of metalloporphyrins for placing TMs doping graphene materials.

Asphaltene materials were extracted from crude using different n-alkanes and dissolved in toluene for deposition. Asphaltene/toluene (1 mg/ml) solutions were then deposited using drop coating onto previously prepared copper foil and experiments proceeded according to **Table 4**. Experiment 1 deposited asphaltene onto copper using spin coating. A 4 inch tube furnace was used to anneal the material under a reducing environment ( $H_2$ ). The system was equipped with a turbo pump with a direct line-of-sight to the sample and the substrate and allowed for base pressures below  $10^{-8}$  Torr. A turbo pump was used and all the flanges on the high vacuum side of the system were constructed with conflat flanges; capable of achieving ultra-high vacuum (UHV). Reaching low background pressures allowed the removal of residual gasses like water

| Experiment | Temperature [°C] | Time [min] | Material       | Gas        |
|------------|------------------|------------|----------------|------------|
| 1          | 1050             | 5          | C7-spin coated | H (10 ccm) |
| 2          | 1050             | 5          | C7-drop coated | H (10 ccm) |
| 3          | 1050             | 5          | Synthetic      | H (10 ccm) |

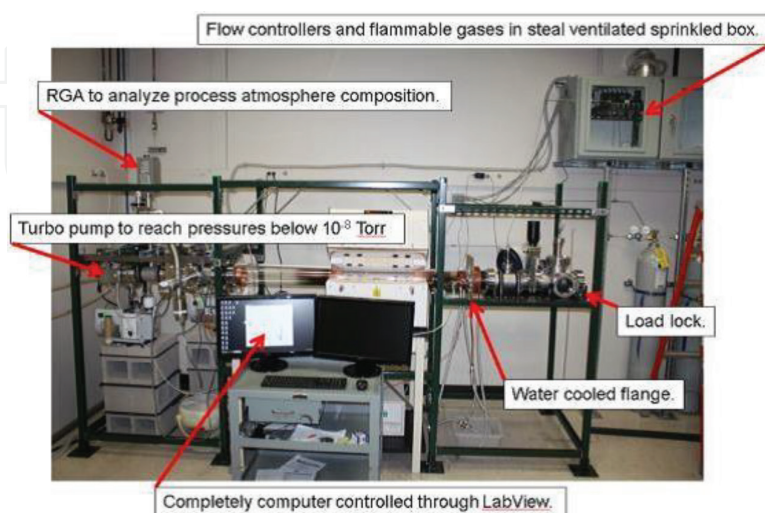
**Table 4.** Experimental conditions and parameters and (above) figure of furnace used in experiment.

and oxygen from the system before growth. The use of a turbo pump also allowed for the system to reach pressures low enough (below  $10^{-5}$  Torr) to operate a residual gas analyzer (RGA) instrument. In a typical growth, the sample was loaded into the furnace and allowed to pump down using the turbo pump for 2 hours prior to heating and gas flow (**Figure 5**).

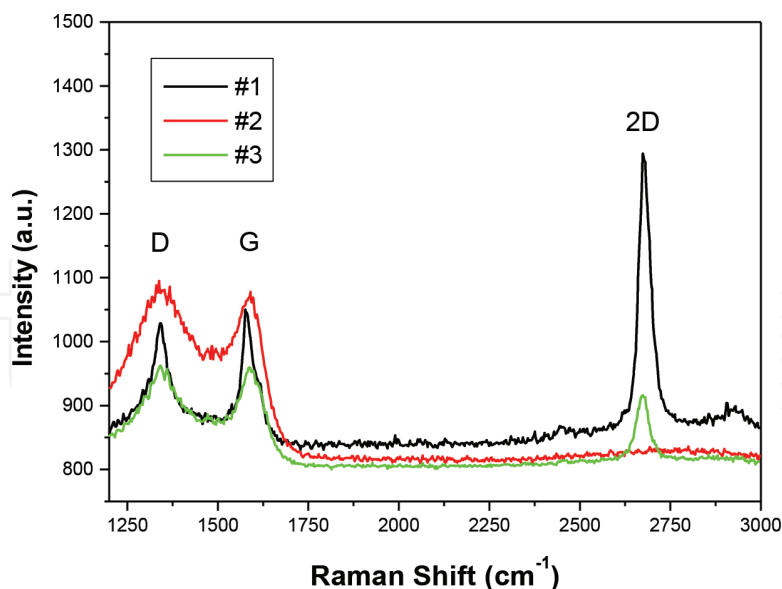
Raman was taken using Witec Alpha 300 micro-Raman confocal microscope after graphene had been transferred to  $\text{SiO}_2/\text{Si}$  wafers. Scanning Electron Microscope (SEM) Images were taken using a FEI Quanta 650 SEM equipped with Bruker EDX system for chemical analysis. Optical Microscope images of asphaltenes were taken on copper foils before and after growth. Transfers were performed by spin coating polymer, dissolving copper foil and transferring graphene to  $\text{SiO}_2/\text{Si}$  wafers. Zeiss Axiovert 100A Light Microscope was used to take images of asphaltenes before and after growth.

#### 4.2. Single-layer asphaltene

Conditions for graphene growth were applied for all experiments. The resulting averaged Raman from all experiments show heavy carbonization and some graphitization of the solid carbon source. We were able to find metals in more than one sample of the post growth heptane extracted asphaltene. When drop coating was used for application before the growth process, the Raman from **Figure 6** indicates mostly carbon with some graphitization. Only



**Figure 5.** CVD set-up at the J.J. Pickle Research Center Austin, TX [50].



**Figure 6.** Raman summary of experiment 1, 2 & 3.

experiment 1 exhibited the ratio of ( $> 2:1$ ) 2D to G and D peaks that would indicate the presence of quality graphene rather than  $sp^2$  hybridized carbon.

Metals identified in post growth samples from experiment 1 and 2 included Al, Fe, Zr and adatoms included sulfur. Electron Diffraction X-ray (EDX) analysis was taken of the copper foil before any etching in **Figure 7** and foil which had been sonicated in acetone before applying asphaltenes shows no metals or adatoms present before growth indicating that metals and adatoms indeed came from asphaltene samples. After growth, EDX spectra taken of sample from Experiment 1 show the presence of Aluminum and Iron.

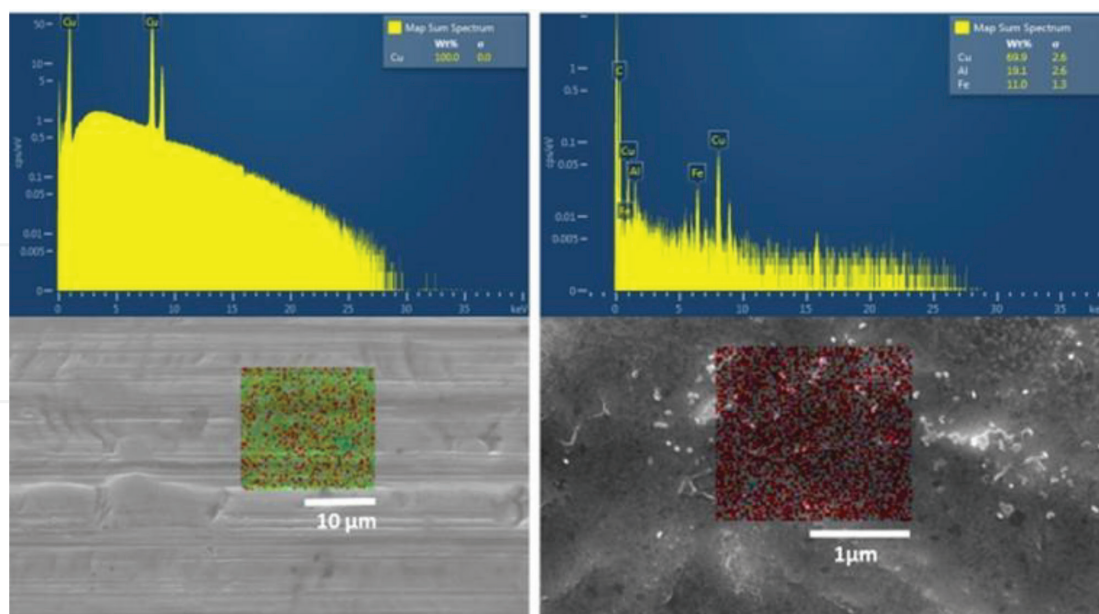
To further study asphaltene adatoms, EDX elemental analysis was taken of synthetic asphaltene containing no metals applied to copper foil. Needless to say from data in **Figure 8** no TM or adatoms could be found present after growth.

Images taken using optical microscope **Figure 9** show copper coated with heptane extracted asphaltenes before and after Experiment 1 growth. There are clustered discotic structures before growth and curiously there are areas after growth that show clearly more than a few layers graphitized **Figure 10**. There are areas that can be seen where copper can be seen as clear orange from underneath sheets of graphitized carbon in **Figure 9(c)** and **(d)**.

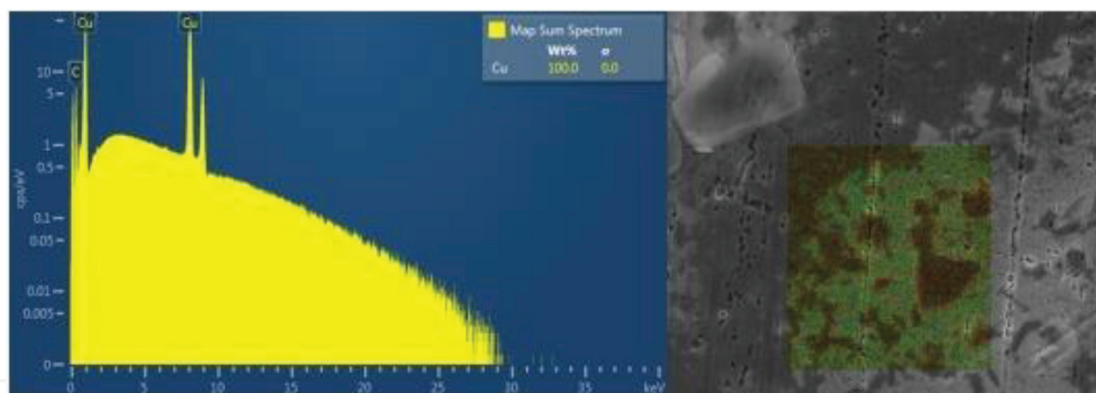
### 4.3. Summary

Because they are expected to induce novel magnetic and superconducting behavior, TM adatoms and graphene are a topic of great interest. There have been extensive theoretical studies because of these interesting properties but the experimental exploration of TM/graphene systems is very limited. Graphene with Boron and Nitrogen (BCN) is a sought after material due to the fact that graphene has no band gap. Graphene in its single crystal



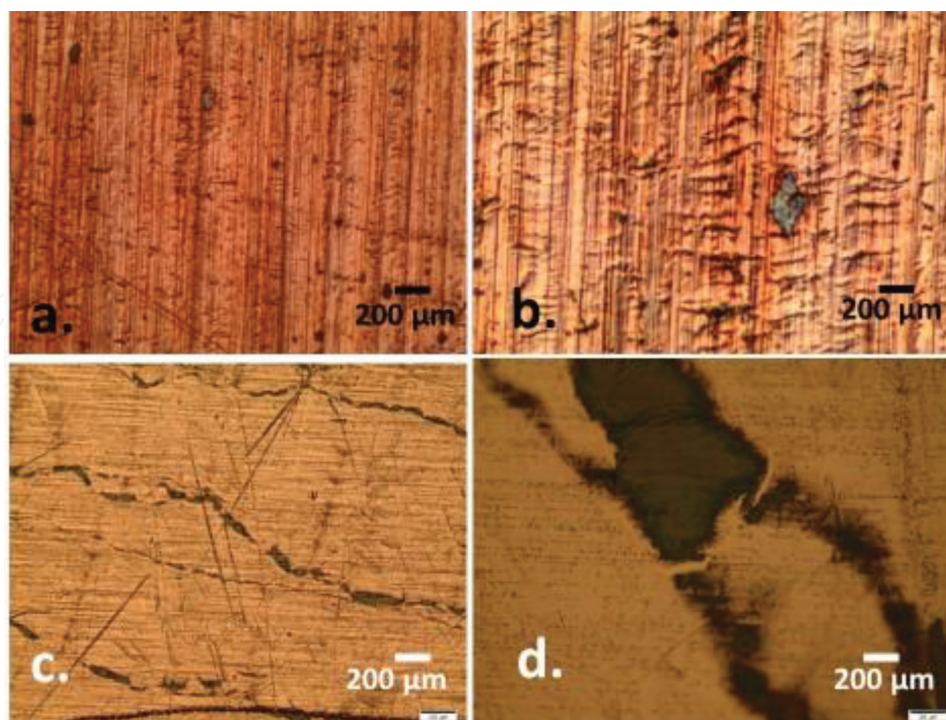


**Figure 7.** EDX analysis (top left) of copper foil sonicated in acetone before application of solid carbon source with corresponding SEM image (bottom left) EDX elemental analysis respectively (top right) from SEM section (bottom right) from asphaltene extracted using heptane in Experiment 1.

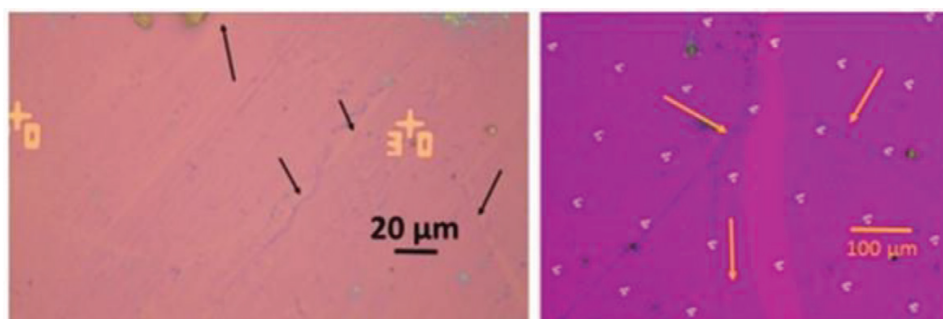


**Figure 8.** EDX (left) copper with drop coated synthetic asphaltene (right) after growth.

form is a conductor, not a semi-conductor, so while it has amazing properties sought after by so many researchers, it has yet to make a significant impact on electronic industries for this reason. BCN is currently being researched because it can be introduced by vapor. In contrast, TMs cannot be introduced by vapor. Even if they could be introduced at high temperatures, it has been determined that they would not be stable in an in-plan configuration due to the high differences in energy between TMs and carbon. Boron and Nitrogen both neighbor carbon on the periodic table and do not have a large difference in electron structure. Our carbon source generated from waste crude oils is unsuitable for hydrocracking because of the presence of TMs. We were able to utilize that waste as a valuable source of metalloporphyrins for placing TMs directly inside the graphene lattice.



**Figure 9.** Optical microscope images of heptane asphaltene on copper foil from experiments before (a,b) and after growth (c,d).



**Figure 10.** Optical microscope image of experiment 1 transferred to SiO<sub>2</sub>/Si wafer with rips and wrinkles (left) compared to OM image of a graphene sheet (purple) on SiO<sub>2</sub>/Si wafer (pink). Arrows show wrinkles and tears in the material (right). (graphene provided courtesy Ruoff group at UT).

## 5. Conclusions

All electronic processes in nature occur using carbon-based molecular structures; from signal transduction in the brain all the way to photosynthesis in a leaf. Carbon Molecular Electronics (CMEs) as a field is the result of developments in an interdisciplinary field with increasing numbers of synthetic and quantum chemists, physicists and engineers. New devices have been designed and investigated for the exciting realization of CMEs for photovoltaics, transistors, switches and other non-linear electronic components.

The results demonstrated in these works illustrate the use of asphaltene as a light-harvesting active molecular dye effectively in dye sensitized solar cells for application in the field of organic photovoltaics. Higher-power conversion efficiencies can be achieved by further optimizing the device structure. In addition, they also show asphaltene as a promising candidate for doping multi-layer and potentially single layer graphene for future novel nanoscale magnetic or optoelectronic uses.

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