**SUPPORTING INFORMATION**

# Biomass-derived carbon electrodes for supercapacitors and hybrid solar cells: towards sustainable photo-supercapacitors

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## 1. EVALUATION METHODS OF SUPERCAPACITORS

Commonly used performance characteristics of SCs include specific capacitance ($C_{sp}$, F $g^{-1}$), resistance (R, Ω), cell voltage (V, V), specific energy (E, Wh $kg^{-1}$), power density (P, W $kg^{-1}$) and life cycles.[1] Several instruments and various test modes are carried out to assess and characterize the electrochemical performance of SCs. Cyclic voltammetry (CV) and constant current charge/discharge (CD) are two methods frequently used and, in general with these methods, the device response is analyzed with respect to voltage, current and time. At the same time, electrochemical impedance spectroscopy (EIS) analysis gives electrical impedance of the device as a function of frequency. Each instrument can evaluate its targeted performance characteristics by using above parameters. Furthermore, each test can be performed on both SCs materials (i.e. electrode material and electrolyte) or on complete SC device. However, there is a significant difference between the measurement setups. A two-electrode setup gives the device performance of complete SCs, while a three-electrode setup provides the electrochemical properties of the electrode material.[2] Formulas commonly used for the evaluation of the SC performances using different techniques are summarized in Table S1.

**Table S1** Evaluation of supercapacitors using different techniques.

| Techniques | Device specific capacitance ($C_D$), two electrodes system | Ref. | Single electrode specific capacitance ($C_S$), three electrodes system | Ref. |
|---|---|---|---|---|
| Cyclic voltammetry (CV) | $C_D = \frac{Q}{2 \times scan\,rate \times m_D \times \Delta V}$ | 3,4 | $C_S = \frac{Q}{2 \times scan\,rate \times m_S \times \Delta V}$ | 4,5 |
| Constant current charge/discharge (CD) method | $C_D = \frac{I}{m_D \times (\Delta V / \Delta t)}$ <br> Specific Energy ($E$): <br> $E = \frac{C_D \times (\Delta V)^2}{2 \times 3.6}$ <br> Power Density ($P$): <br> $P = \frac{E \times 3600}{\Delta t}$ | 6,7 | $C_S = \frac{I}{m_S \times (\Delta V / \Delta t)}$ | 6,8 |
| *Symmetric two electrodes SCs; <br> 1) Series connection capacitance: <br> $\frac{1}{C_D} = \frac{1}{C1} + \frac{1}{C2}$; $C_1 = C_2 = C_S$; $C_S = 2C_D$; <br> 2) Counting mass of both electrodes: <br> $m_D = 2m_s$; <br> 3) Theoretical relation of single and device capacitance: <br> $C_S = 4C_D$ <br> Multiplication by factor "4" is to adjust the capacitance considering series connection of two capacitors and mass of two electrodes. | | | | 2,4,5 |

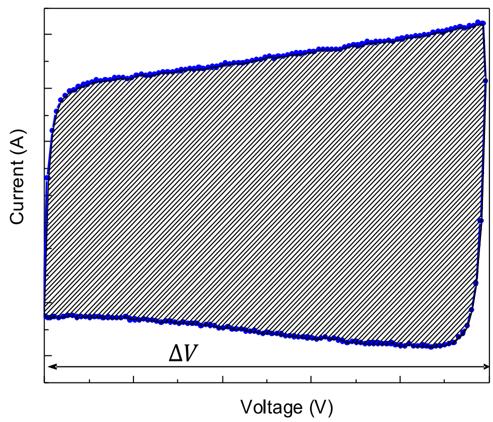
**Cyclic voltammetry (CV):**

$Q$ = Integrated area of the cyclic voltammetry curve

$\Delta V$ = Potential range

$m_D = $ *Total mass of active material for both electrodes*

$m_S = $ *Mass of active material for single electrode*



**Constant current charge/discharge (CD):**

I = Applied current

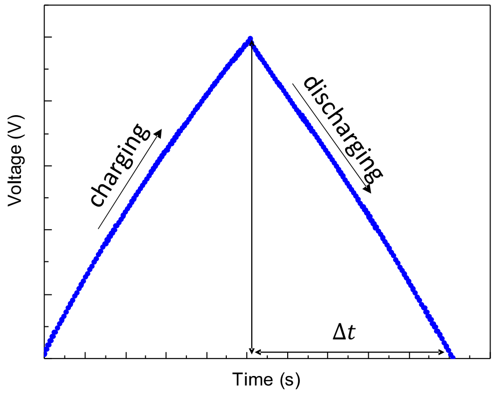
$m_D = Total\ mass\ of\ active\ material\ for\ both\ electrodes$

$m_S = Mass\ of\ active\ material\ for\ single\ electrode$

$\Delta V/\Delta t = Slope\ of\ the\ discharge\ curve$

$\Delta t$ = Discharging time

$\Delta V$ = Potential change during the discharging




## 2. EVALUATION METHODS OF SOLAR CELLS

The common technique for solar cell evaluation is the current-voltage measurement where a voltage bias (V, V) is applied to the devices under illumination and a photo-current (I, mA $cm^{-2}$) is measured.[9] From the resulting curve, three important values are extracted: short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$, V) and fill factor (FF) as expressed in Equation 1. Using these parameters, the power conversion efficiency (PCE, %) is calculated following Equation 2.

$$FF = \frac{V_{mp} \times J_{mp}}{V_{oc} \times J_{sc}} \qquad \text{Equation 1}$$

$$PCE = \frac{V_{oc} \times J_{sc} \times FF}{P_{max}} \times 100\% \qquad \text{Equation 2}$$

with $V_{mp}$ and $J_{mp}$ are the voltage and the current density at the maximum power.

While the I-V curve measurement is a standard method for solar cell evaluation without hysteresis, this technique is no longer reliable to accurately calculate the PCEs of devices showing hysteresis such PSCs. In this case, several approaches have been proposed, reporting PCEs from I-V curves recorded at different scan speed, showing hysteresis index, steady-state efficiency, and more recently determining PCE at maximum power point (MPP).

[10,11] The MPP method, which consists in measuring the maximum power-output of the device over time until the device is stabilized, is widely used. MPP is performed using Perturb and Observe algorithms that continuously adjust the voltage to maximize the power output. This technique is recommended for PSCs showing hysteresis and is still being improved considering the unstable behavior of PSCs.

## 3. EVALUATION METHODS OF INTEGRATED DEVICES

In the evaluation of integrated device, solar cell PCE is separately evaluated using I-V curves and stored energy of the SC is calculated by photo-charging or discharging measurements. Complete charging and discharging cycles are performed to calculate the energy conversion and storage efficiency ($\eta_{ECSE}$) also called "overall efficiency" ($\eta_{overall}$) and "storage efficiency" ($\eta_{Storage}$).[12]

During the charging process, the output power of the solar cell varies during the course of the charging process. This modifies the conversion and storage efficiencies over time. Therefore, to evaluate the photo-charging time which gives maximum energy conversion and storage at constant incident light, several charge-discharge cycles should be performed. From this method, optimum charging time which gives maximum $\eta_{ECSE(C)}$ can be obtained. After charging, the SC is discharged with a constant current or known load under dark conditions.[12] The energy conversion and storage efficiency after discharging $\eta_{ECSE(D)}$ of the photo-capacitor is calculated by the ratio of total energy discharged over the energy falling on the solar cell during photo-charging time under light.[13] The storage efficiency $\eta_{Storage}$ of the integrated device is given by the ratio between $\eta_{ECSE(D)}$ and PCE of the solar cell or, in some cases, by the ratio between $E_{Discharge}$ and $E_{Charge}$ (Table S2).[13-17]

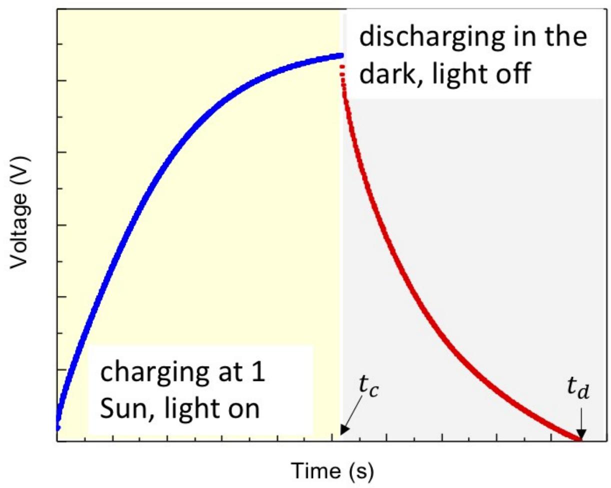
**Table S2** Evaluation of the photo-storage devices performances.

| Regime | Calculation of energy | Efficiencies | Ref. |
|---|---|---|---|
| Charging | $E_{Charge} = \int_{0}^{t_c} V_c \times I_c \times dt$ extracted from charging curves | $\eta_{ECSE(C)} = \frac{E_{Charge}}{P_{Light} \times \Delta t \times A_S} \times 100\%$ Plot of $\eta_{ECSE(C)}$ vs $\Delta t$ to find the maximum overall efficiency during photo-charging. | 12 |
| Discharging | $C = \frac{I}{\Delta V / \Delta t}$ $E_{Discharge} = \frac{1}{2} C \times (\Delta V)^2$ extracted from the discharge curves $E_{Discharge} = \int_{t_c}^{t_d} V_D \times I_D \times dt$ extracted from discharging curves | $\eta_{ECSE(D)} = \frac{E_{Discharge}}{P_{Light} \times \Delta t \times A_S} \times 100\%$ $\eta_{Storage} = \frac{\eta_{ECSE(D)}}{PCE} \times 100\%$ $\eta_{Storage} = \frac{E_{Discharge}}{E_{Charge}} \times 100\%$ | 12-14 |

**Evaluation of solar cell:**

$P_{Light}$ = Incident light intensity

PCE = Photo-conversion efficiency




**Evaluation of direct integrated device:**

$C$ = Capacitance of the supercacitor

$I$ = Discharging current

$E_{Charge}$ = Total energy during the charging

$E_{Discharge}$ = Total energy during the discharging

$\eta_{ECSE(C)}$ = Energy conversion storage efficiency during the charging

$\eta_{ECSE(D)}$ = Energy conversion storage efficiency during the discharging

$\eta_{Storage}$ = Storage efficiency

$A_S$ = Active area of the solar cell

$V_C$ = Instantaneous charging volatge

$V_D$ = Instantaneous discharging volatge

$I_C$ = Instantaneous charging current

$I_D$ = Instantaneous discharging current

$t_c$= time when the supercapacitor is completely charged by solar cell under 1Sun, light ON

$t_d$= time when the supercapacitor is completely discharged in the dark, light OFF

**Table S3** Abbreviations and full name of the materials cited on this review paper.

| Abbreviations | Full name |
|---|---|
| ADEKA-1 | Carbazole/hexyl-functionalized oligothiophene/trimethoxysilyl-anchor dye |
| LEG4 | 3-{6-{4-[bis(2′,4′-dibutyloxybiphenyl-4-yl)amino]phenyl}-4,4-dihexyl-cyclopenta-[2,1-b:3,4-*b*′]dithiophene-2-yl}-2-cyanoacrylic acid |
| BMIM $BF_4$ | 1-Butyl-3-methylimidazolium - tetrafluoroborate |
| EMIM $BF_4$ | 1-ethyl-3-methylimidazolium - tetrafluoroborate |
| TEMA $BF_4$ | Triehylmethylammonium - tetrafluoroborate |
| TEA $BF_4$ | Tetraethyl ammonium tetrafluoroborate |
| TEOS | Tetraethyl orthosilicate |
| MPPyFSI | 1-methyl-1-propy-pyrrolizinium bis(fluorosulfonyl)imide |
| AN | Acetonitrile |
| PC | Propylene carbonate |
| PVA | Polyvinylalcohol |
| spiro-OMeTAD | 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene |
| Y123 | 3-{6-{4-[bis(2′,4′-dihexyloxybiphenyl-4-yl)amino]phenyl}-4,4-dihexyl-cyclopenta-[2,1-b:3,4-*b*′]dithiophene-2-yl}-2-cyanoacrylic acid |
| N719 | Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) |
| N3 | cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) |
| SM-315 | Push-pull porphyrin dye |
| PVDF | Polyvinylidene fluoride |
| NMP | N-Methyl-2-pyrrolidone |
| $Pyr_{14}TFSI$ | 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide |
| EMII-PMII | 1-ethyl-3-methylimidazolium iodide<br>1-propyl-3-methylimidazolium iodide |

| | |
|---|---|
| ITO-PEN | Indium doped tin oxide-polyethylene naphthalate |
| FTO | Fluorine doped tin oxide |
| Polyurethane:RTIL | Polyurethane:<br><br>1-butyl-2,3-di-methylimidazolium bis(trifluoromethanesulfonyl)imide |
| PEM | Poly(ethyl methacrylate) |
| PEG | Poly(ethylene glycol) |
| PEO | Poly(ethylene oxide) |
| PEDOT:PSS | Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate |
| $PC_{61}BM$ | [6,6]-Phenyl-C61-butyric acid methyl ester |
| PANI | Polyaniline |
| PMMA | Polymethyl methacrylate |
| PPy | Polypyrrole |
| PI | Polyimide |
| $CH_3NH_3PbI_3$ ($MAPbI_3$) | Methylammonium lead triiodide |
| $CH_3NH_3PbBr_3$ ($MAPbBr_3$) | Methylammonium lead tribromide |
| $FAPbI_3$ | Formamidinium lead triiodide |
| $Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$ | Mixed cation lead halide perovskite |
| $CH_3NH_3I$ | Methylammonium iodide |
| $CH_3O(CH_2)_2CN$ | Methoxypropionitrile |

**Table S4** Integrated devices with information about the structure, efficiencies of individual solar cell and areal capacitance of storage devices.

| ***DSCs structure:*** | *Inter-layer* | *PCE (%), (active area, $cm^2$)* | *Storage device structure* | *Areal capacitance $mF\ cm^{-2}$)* | *Ref.* |
|---|---|---|---|---|---|
| FTO/mp-$TiO_2$/N719/PVDF:I-:$I_3^-$/ MWCNT | MWCNT | 6.10 (0.36) | MWCNT/PVA-$H_3PO_4$/MWCNT | 262.3 (calculated) | 15 |
| Ti/mp-$TiO_2$/N719/$I^-$:$I_3^-$/Pt | Pt | 1.38 (0.22) | G/NaCl/G | 25.7 (calculated) | 16 |
| Ti/mp-$TiO_2$/N719/$I^-$:$I_3^-$/Pt | Pt | 4.33 (2.5) | AC/NaCl/AC | 36.4 (calculated) | 17 |
| ITO-PEN/mp-$TiO_2$/N719/$I^-$:$I_3^-$/Pt | Pt | 2.8 (0.16) | rGO/Polyurethane:RTIL/rGO | 0.14 | 18 |
| ***PSCs structure:*** | | | *Storage device structure:* | | |
| FTO/c-$TiO_2$/mp-$TiO_2$/ $MAPbI_3$/spiro-OMeTAD/Au | Au | 12.6 (0.06) | MWCNT/PPy/ MWCNT | 572 | 16 |
| FTO/c-$TiO_2$/mp-$TiO_2$/$ZrO_2$/$MAPbI_3$/ PEDOT:C | PEDOT:C | 6.37 (0.07) | PEDOT:C/$LiClO_4$/PEDOT:C | 12-8.5 | 19 |
| FTO/c-$TiO_2$/MWCNT/$MAPbI_3$/PMMA | PANI:CNTs | 2.476 (1.0) | PANI-CNT/PVA:$H_2SO_4$/PANI-CNT | 422 | 20 |
| FTO/c-$TiO_2$/mp-$TiO_2$/$MAPbI_3$/C | C | 7.79 (0.071) | $MnO_2$:C/PVA-LiCl/C | 61.01 | 21 |
| FTO/c-$TiO_2$/ mp-$TiO_2$/$CsPbBr_3$ /nano-C | nano-C | 6.1 (0.1) | nano-C/Silica gel/nano-C | 33.8 | 22 |

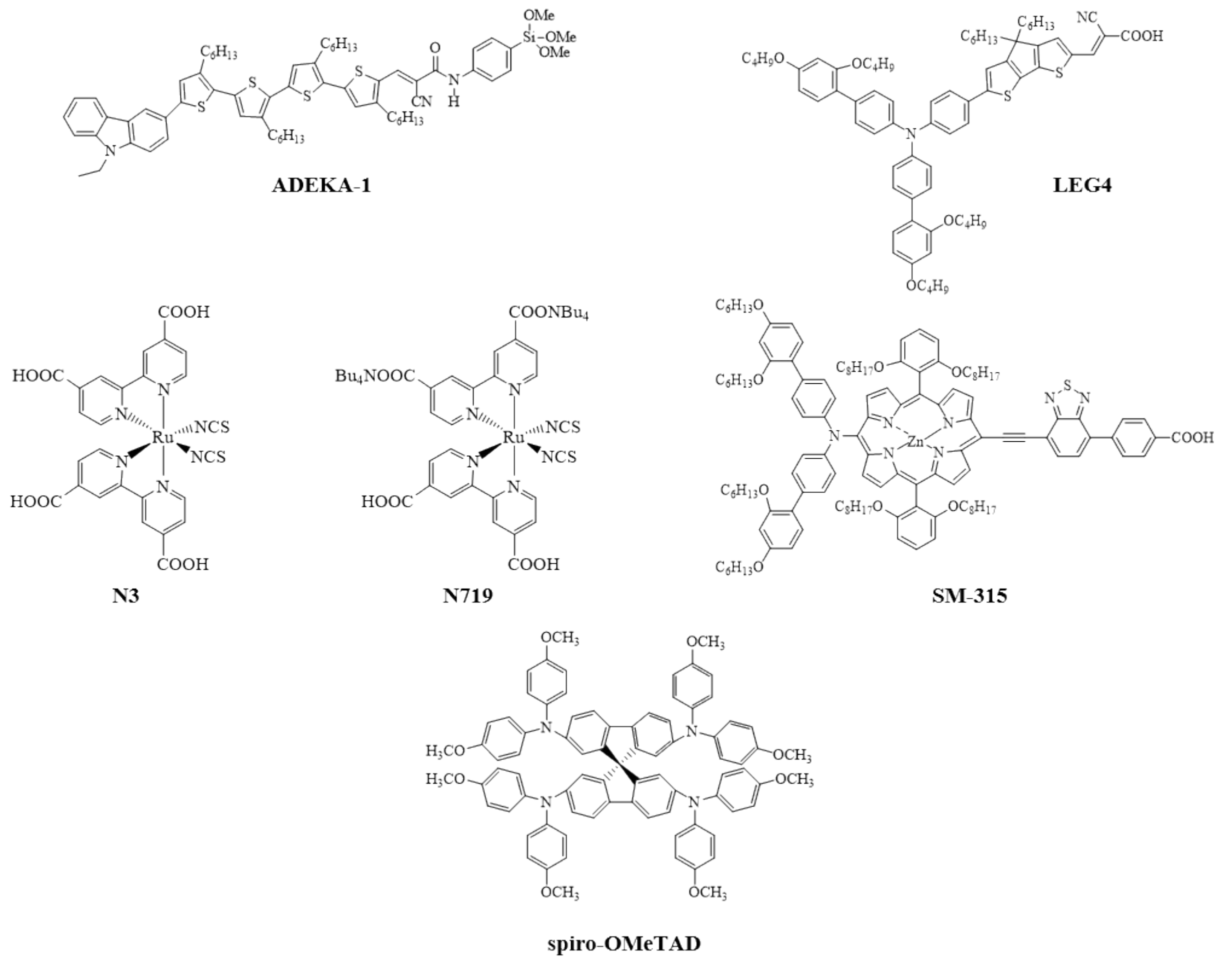



**Figure S1.** Chemical structure of the dyes (ADEKA-1, LEG-4, N3, N719, SM-315) and hole transport material (spiro-OMeTAD) cited in this review paper.

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