2D Materials for Supercapacitors

Xiaodong Zhuang

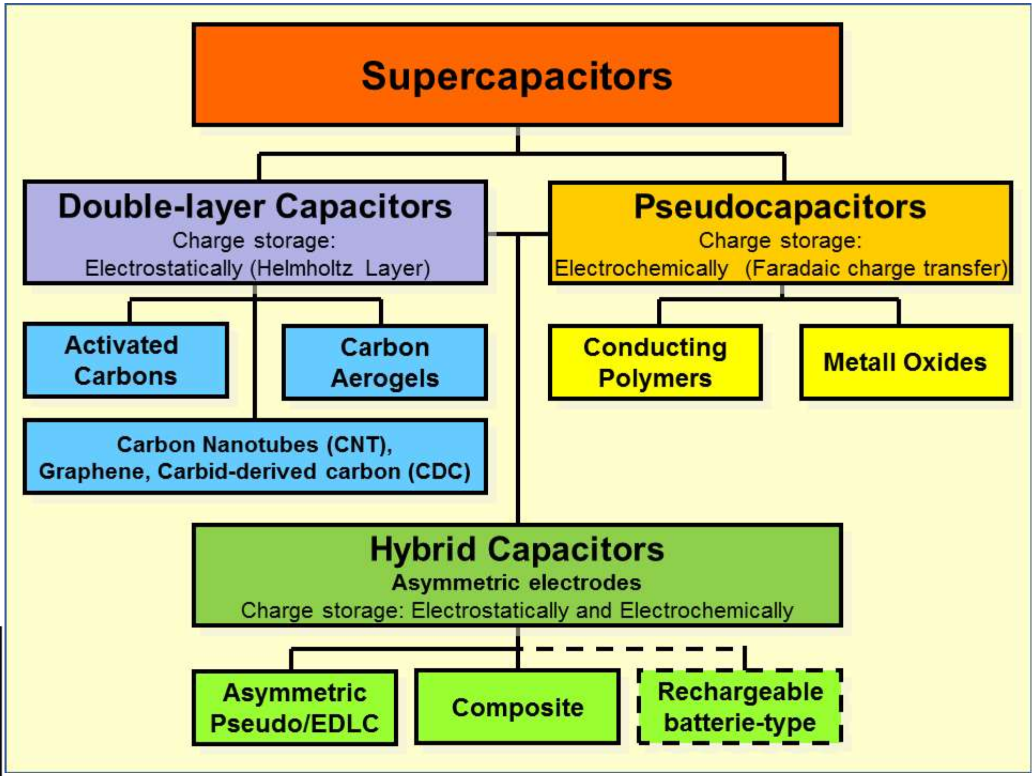
Dresden University of Technology
Dresden, Germany

Supercapacitors (SCs)

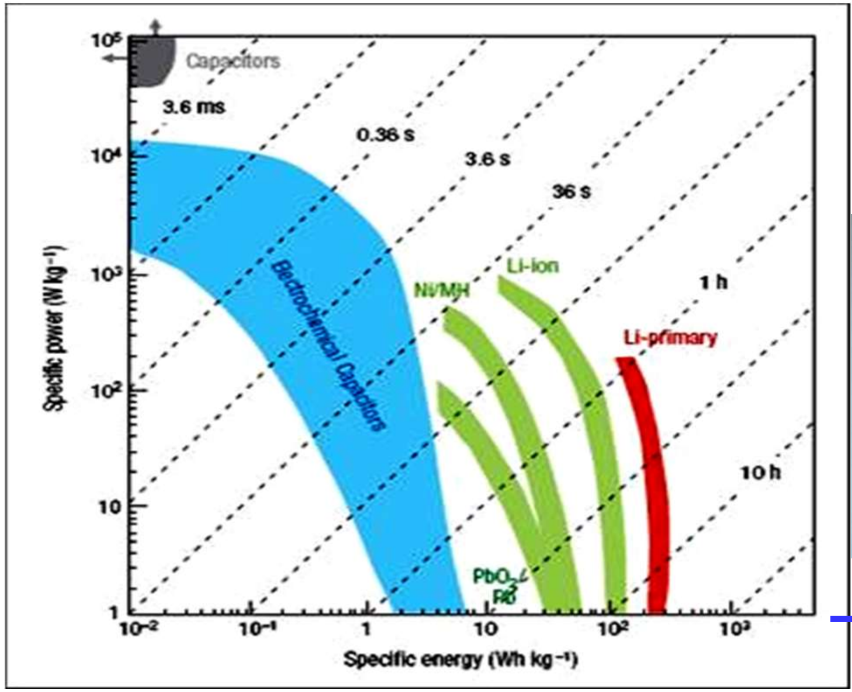
- Virtually unlimited cycle life
- High specific power
- Charge in seconds
- Safe
- Excellent low-temperature

charge and discharge performance

- Low (V) energy density
- Low potential window



https://en.wikipedia.org/wiki/Supercapacitor



Gogotsi et al,
Nat. Mater. **2008**, 7, 845.

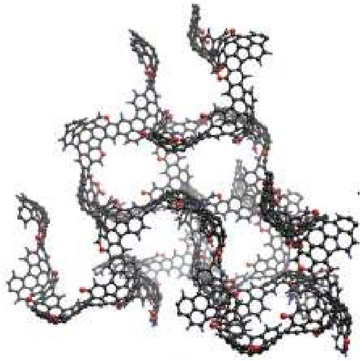
A bus driven by SCs, Shanghai, China

Porous carbons as electrode materials for supercapacitors (EDLC)

- Good conductivity
- High specific surface area
- Rich active sites

……

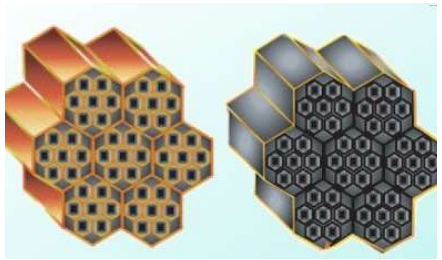
Activated Carbon



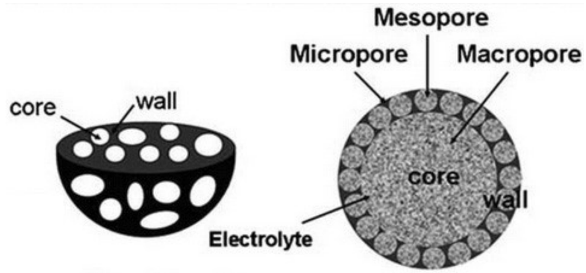
Porous Carbon

- Capacitance
- Energy/power densities
- Charge/discharge time
- AC line-filtering performance

……



Mesoporous Carbon



Hierarchical Porous Carbon

Porous polymers become new precursors for porous carbons

D. Wu, F. Xu, B. Sun, R. Fu, H. He, K. Matyjaszewski, *Chem. Rev.* 2012, *112*, 3959

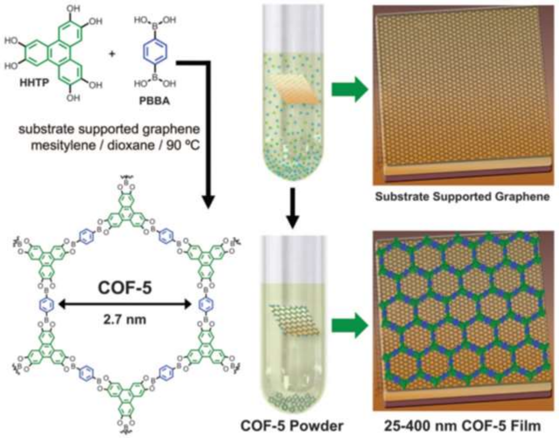
A. G. Slater, A. I. Cooper, *Science* 2015, *348*, aaa8075

2D morphology remains challenge

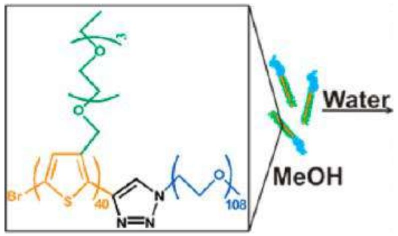
Long-distance conductivity; Anisotropy; Improved specific surface area;…

Solution I:
2D Template Approach

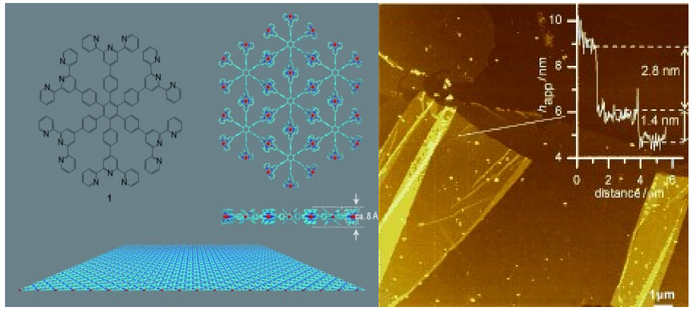
2D soft materials:



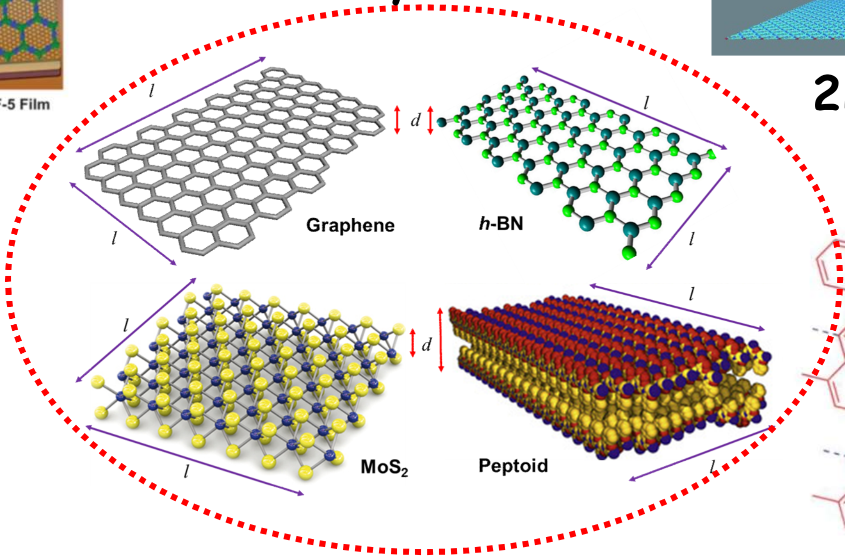
2D COFs

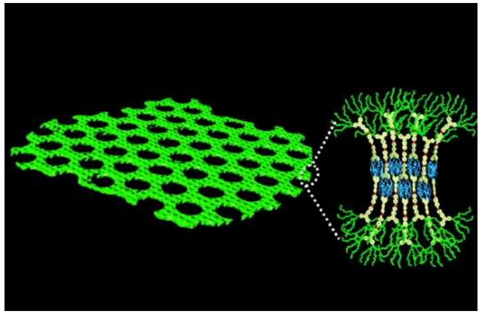


Assembly lamellar

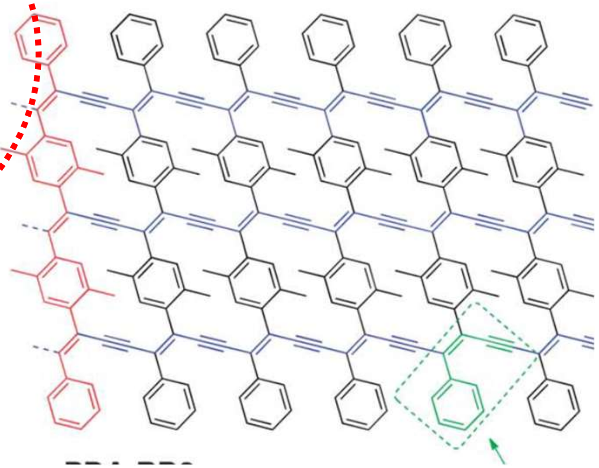


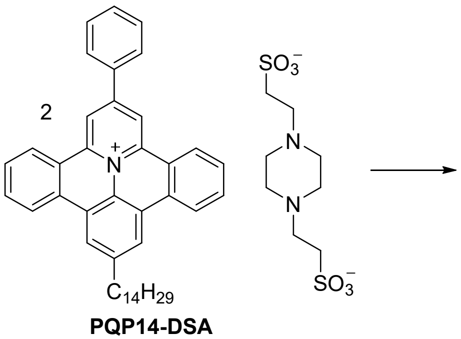
2D coordinated polymer

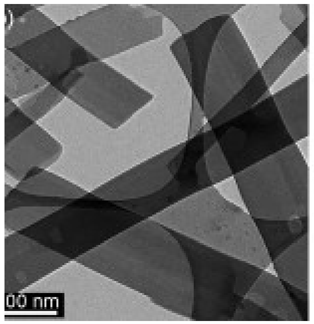




2D supramolecular





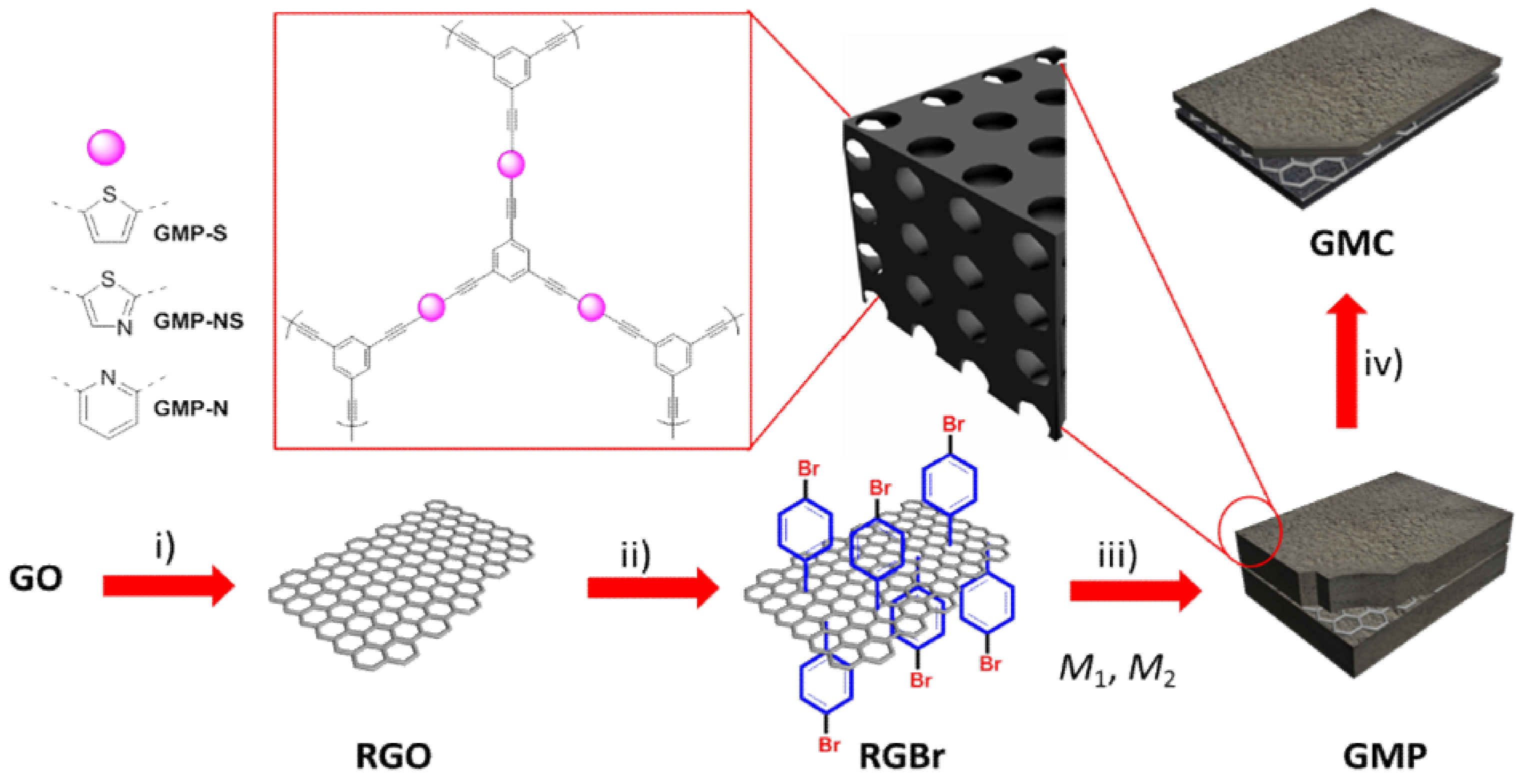


Assembly 2D crystal

- Most of them are not good carbon precursors due to the weak interaction and low carbon yield!

X.L. Feng, et al, *Adv. Mater.* 2015, ***27***, 403 (invited review

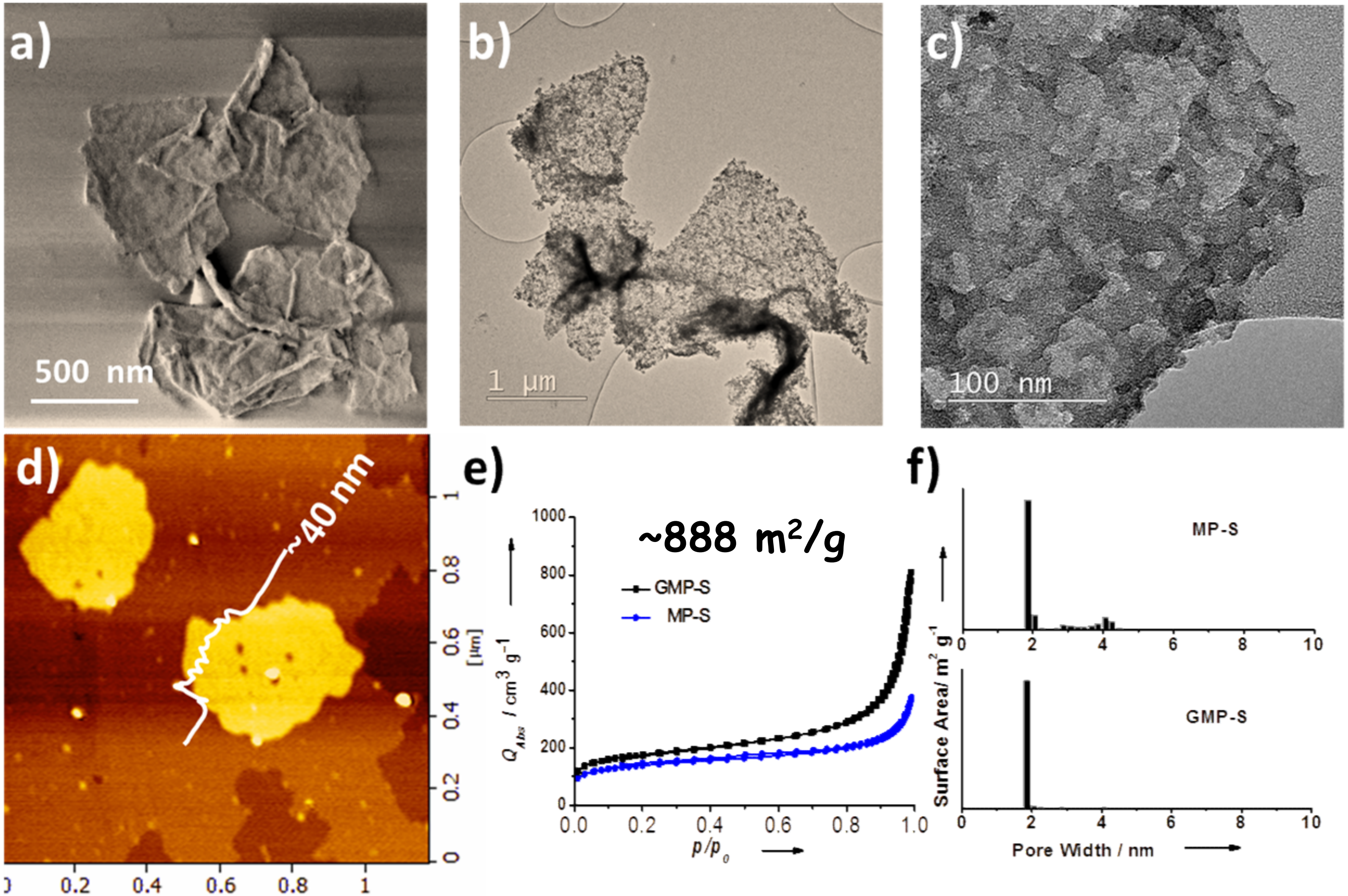
Case 1: Conjugated microporous polymer sandwiches



Synthesis of 2D conjugated porous polymers and 2D heteroatom-doped porous carbons

Angew. Chem. Int. Ed. **2013**, *52*, 9668
Adv. Mater. **2015**, *27*, 3789
Angew. Chem. Int. Ed. **2016**, *55*, 6858

Morphology and porosity



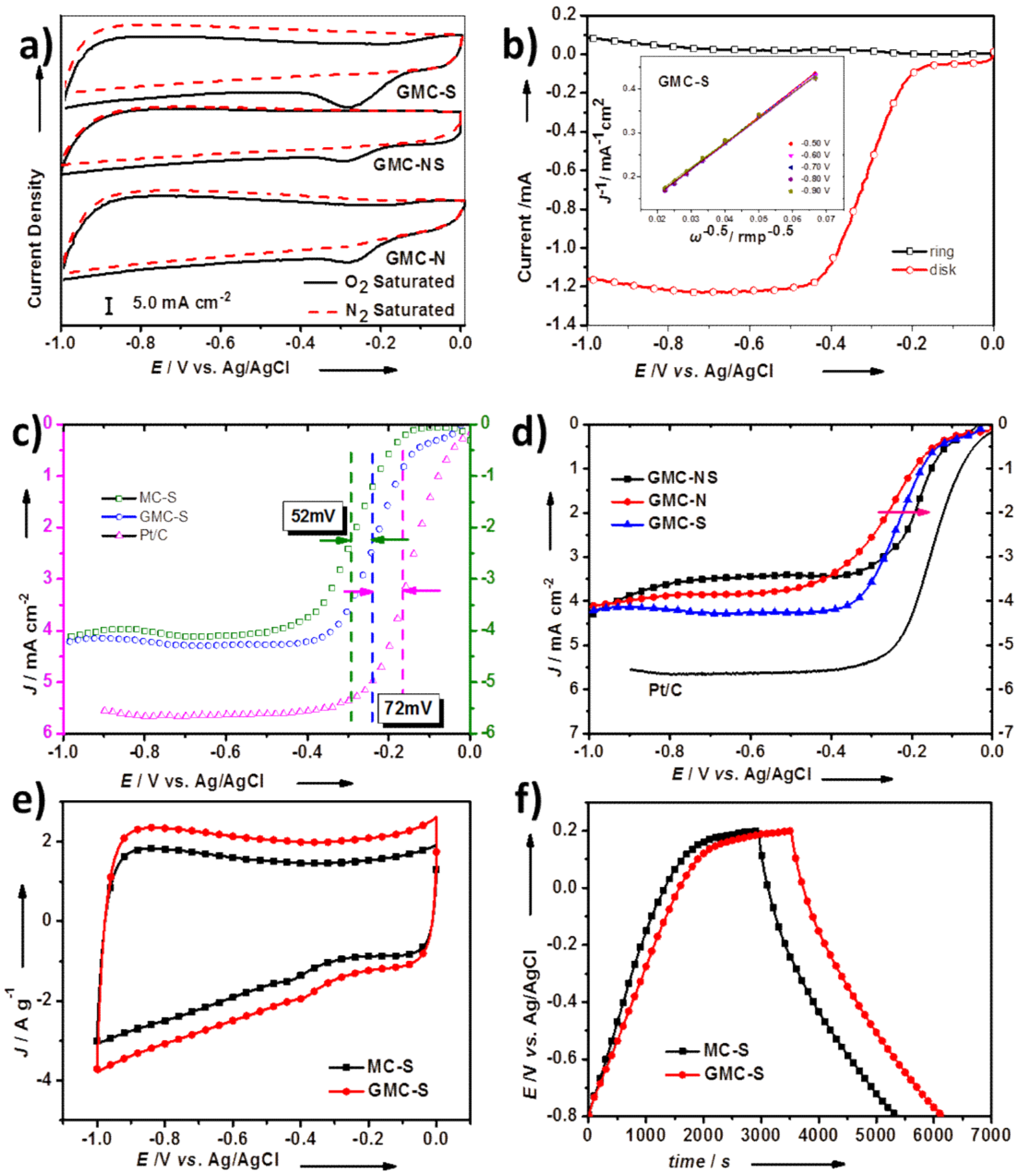
(a) Typical SEM, (b, c) TEM, and (d) AFM images of GMP-S.
(e) Nitrogen adsorption/desorption isotherms and (f) pore size distributions of CMP-S and GMP-S.

ACIE 2013, *52*, 9668

2D porous carbons for energy storage and conversion

DRESDEN concept

TECHNISCHE UNIVERSITÄT DRESDEN



As electrocatalysts for Oxygen reduction reaction

1. half-wave-potential (HWP) for GMC-S occurred at −0.23 V
2. kinetic-limiting current of GMC-S was calculated to be 27.0 mA cm^{-2}
3. Four electron transfer number
4. peroxide yield of about 5% at −0.50 V

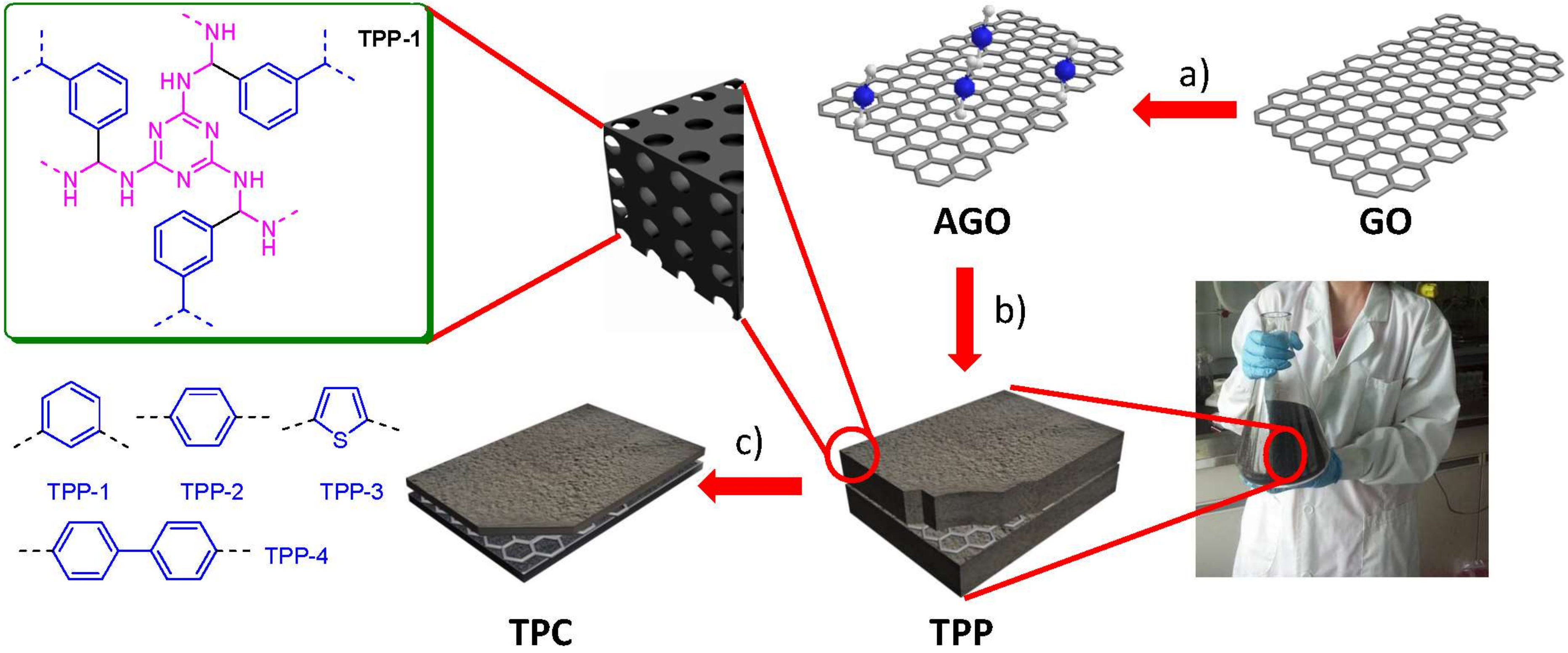
As electrodes for Supercapacitors

Specific capacitance of GMC-S was calculated to be 268 Fg^{-1} at 0.1 Ag^{-1}, which was 12% higher than that of MC-S (239 Fg^{-1}).

ACIE 2013, *52*, 9668

Case 2: Schiff base type 2D porous polymers

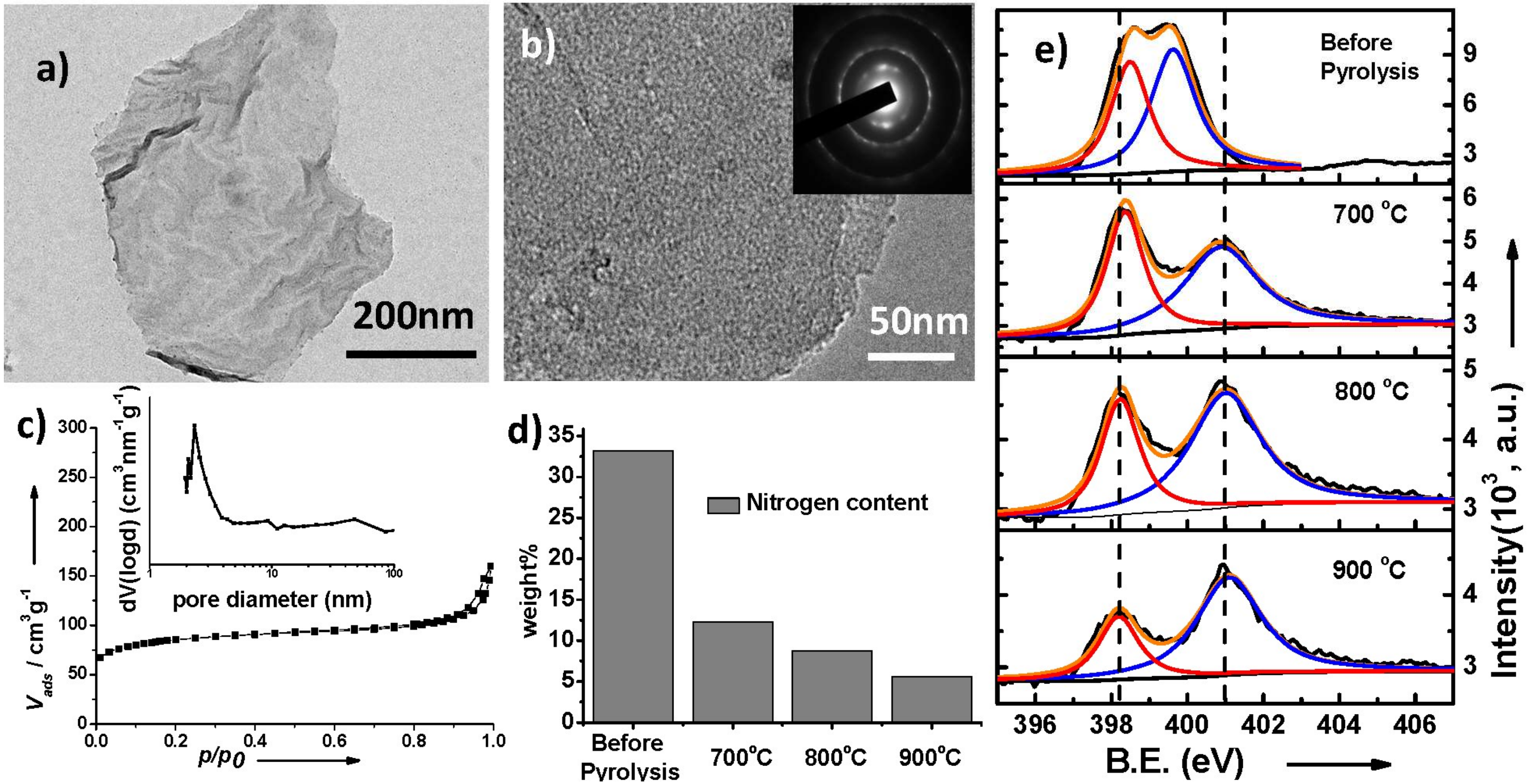
DRESDEN concept
TECHNISCHE UNIVERSITÄT DRESDEN



Synthesis of Schiff-base-type 2D porous polymers and heteroatom-doped porous carbon nanosheets

Adv. Mater. **2014**, *26*, 3081

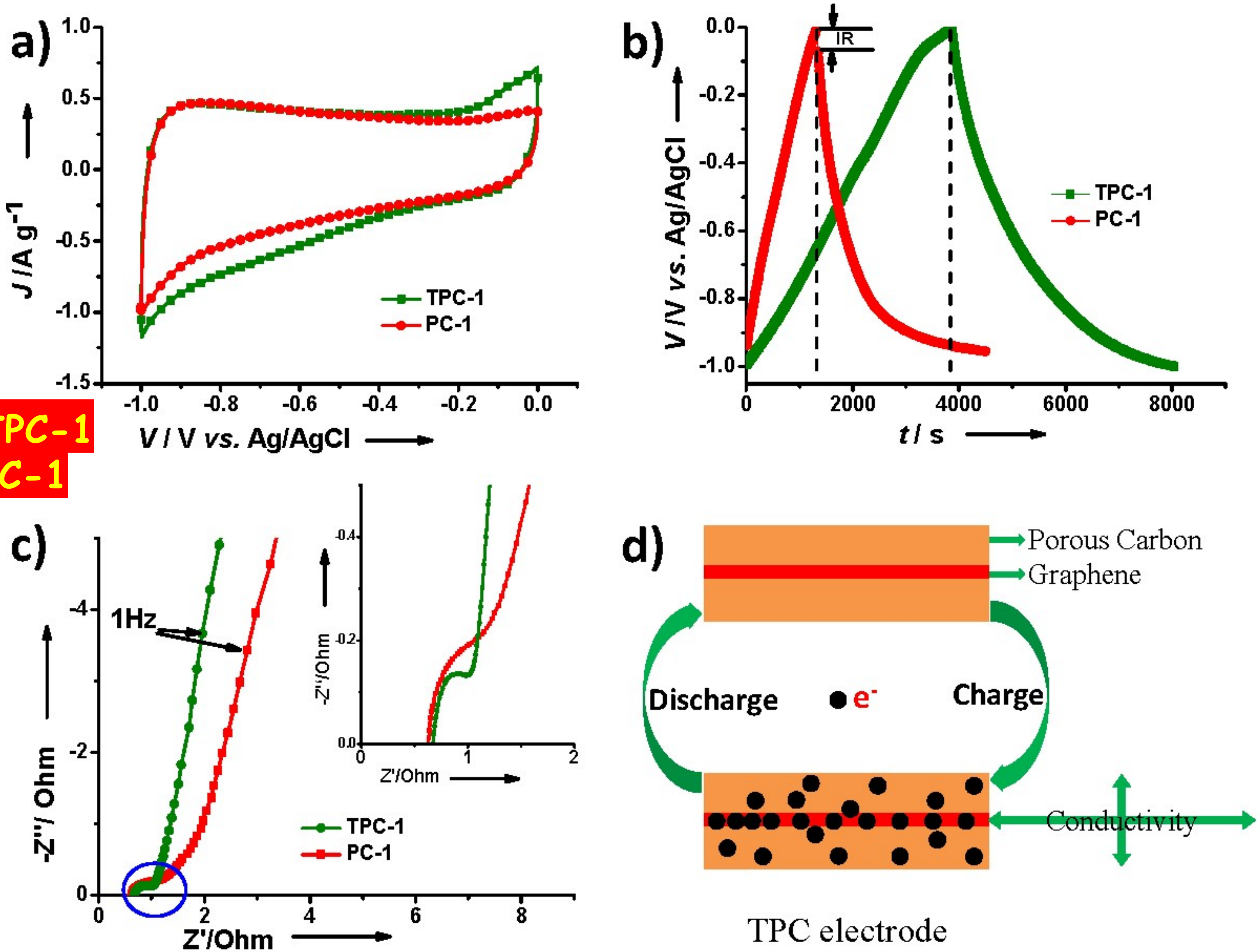
Nitrogen-doped carbon nanosheets



- Thin thickness (30~60 nm)
- Surface area up to 762 $m^2\ g^{-1}$
- Presence of mesopore and micropore
- High nitrogen-doping content (12.3%)

Adv. Mater. 2014, 26, 3081

Improved Electrochemical Capacity



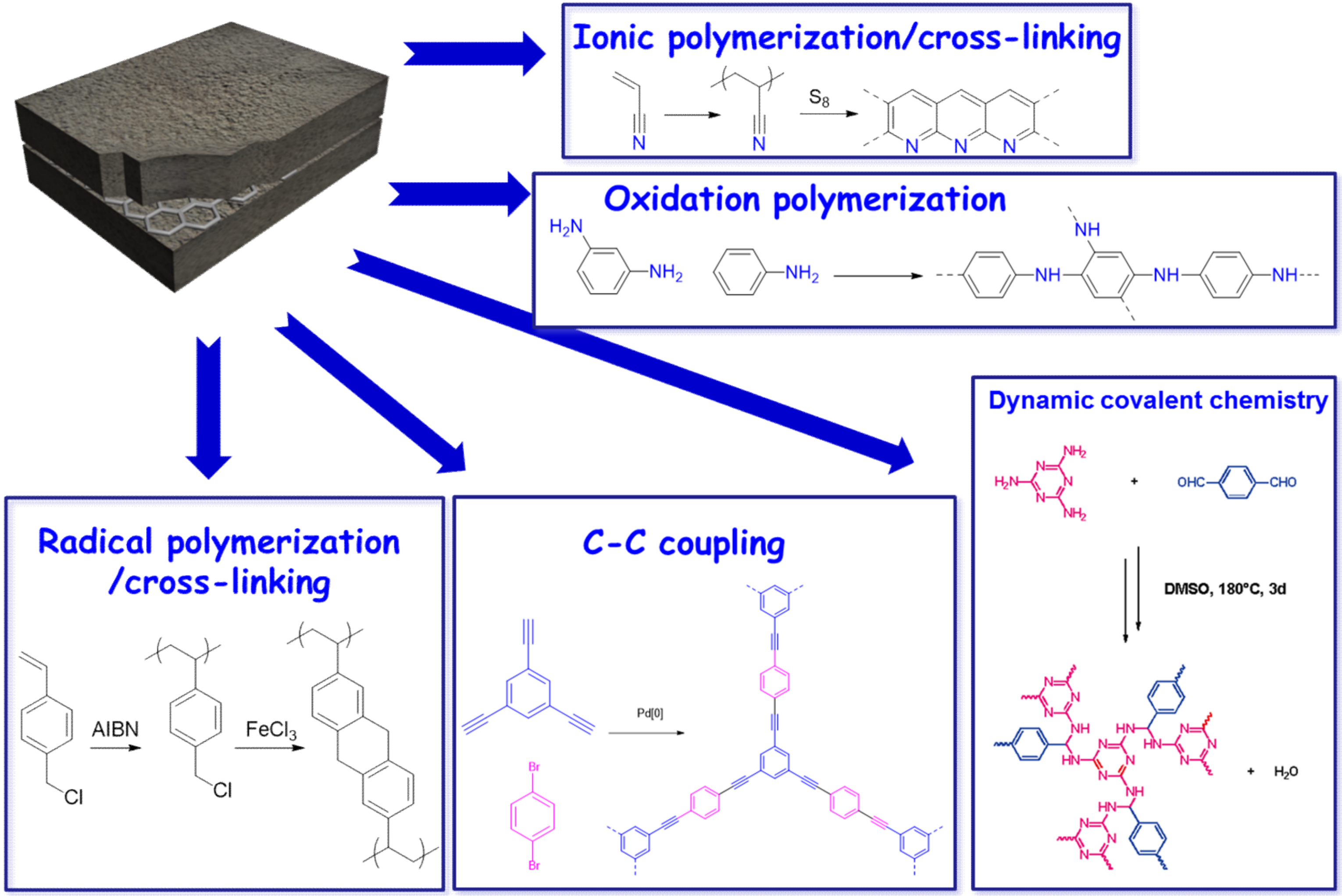
424 F/g for TPC-1
354 F/g for PC-1

- Graphene layer acts as both a mini-current collector and a long-distance in-plane charge transporter.
- Active surface of nanosheets can be efficiently exposed to the electrolyte.

Adv. Mater. 2014, 26, 3081

2D porous carbon based on graphene-coupled 2D porous polymers precursors

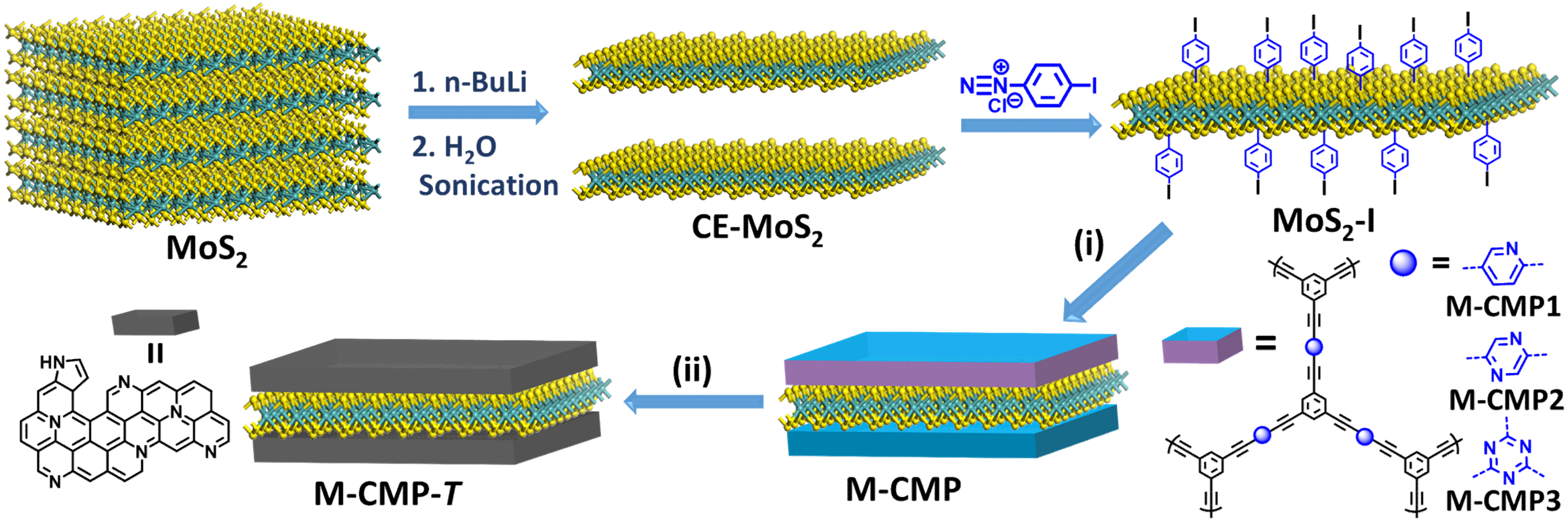
DRESDEN concept
TECHNISCHE UNIVERSITÄT DRESDEN



Angew. Chem. Int. Ed. **2013**, *52*, 9668; *J. Mater. Chem. A* **2014**, *2*, 7742; *Adv. Mater.* **2014**, *26*, 3081; *Polym. Chem.* **2015**, *6*, 1088; *Polym. Chem.* **2015**, *6*, 7171; *Adv. Mater.* **2015**, *27*, 3789; *Angew. Chem. Int. Ed.* **2015**, *54*, 1812; *Angew. Chem.* **2016**, *55*, 6858; *Adv. Funct. Mater.* **2016**, *26*, 8255

DRESDEN concept | TECHNISCHE UNIVERSITÄT DRESDEN

Case 3: What's more: beyond graphene

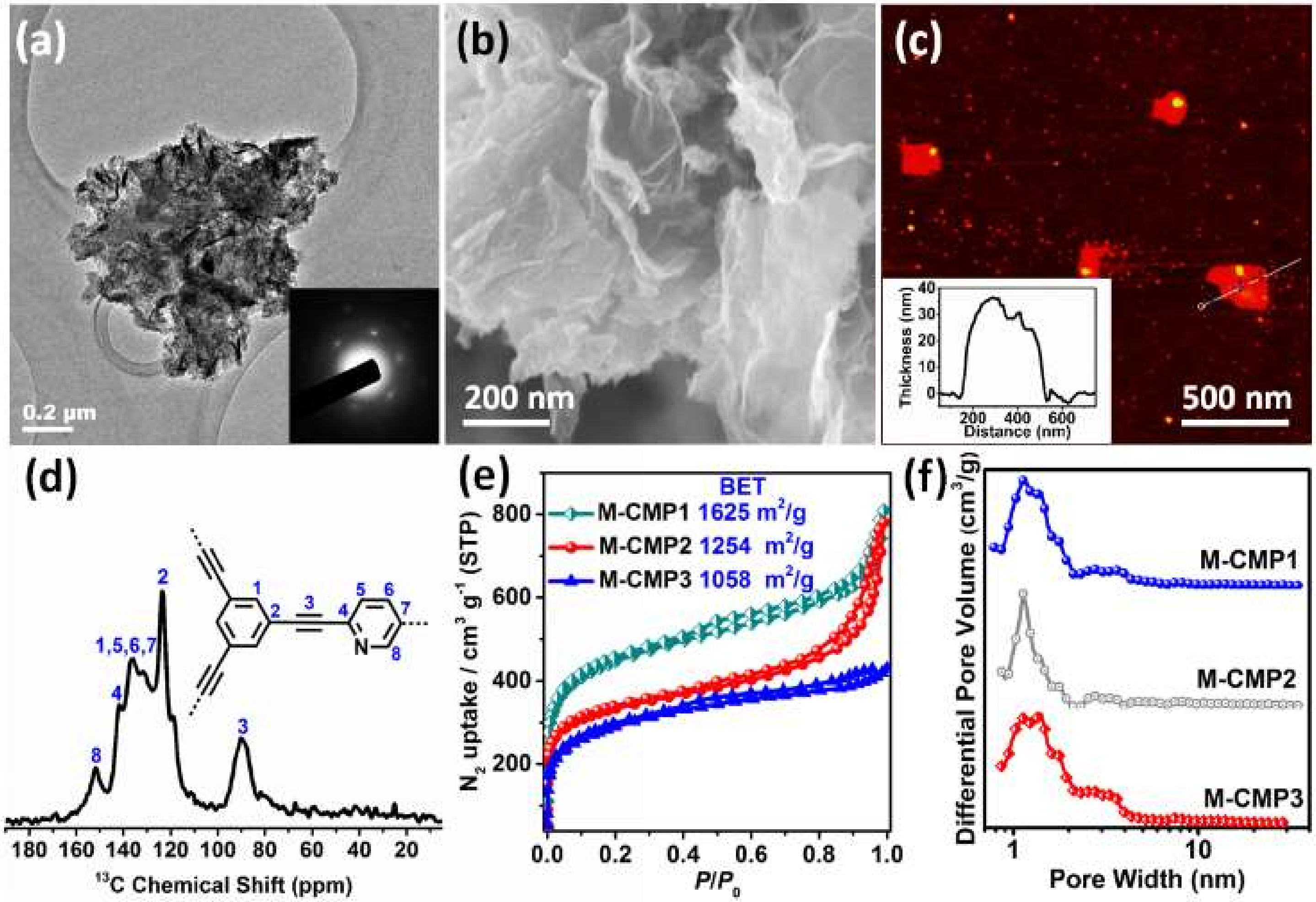


Scheme depicting the chemical exfoliation of bulk MoS_2 and subsequent functionalization with 4-iodophenyl substituents under formation of MoS_2-I as well as the preparation of MoS_2-templated conjugated microporous polymers (M-CMPs) and the corresponding MoS_2/nitrogen-doped porous carbon (M-CMPs-*T*) hybrids.

(i) monomers: 1,3,5-triethynylbenzene and 2,5-dibromopyridine, 2,5-dibromopyrazine, or 2,4,6-trichloro-1,3,5-triazine, argon, $Pd(PPh_3)_4$, CuI, Et_3N, DMF, 100 °C, 3 days;

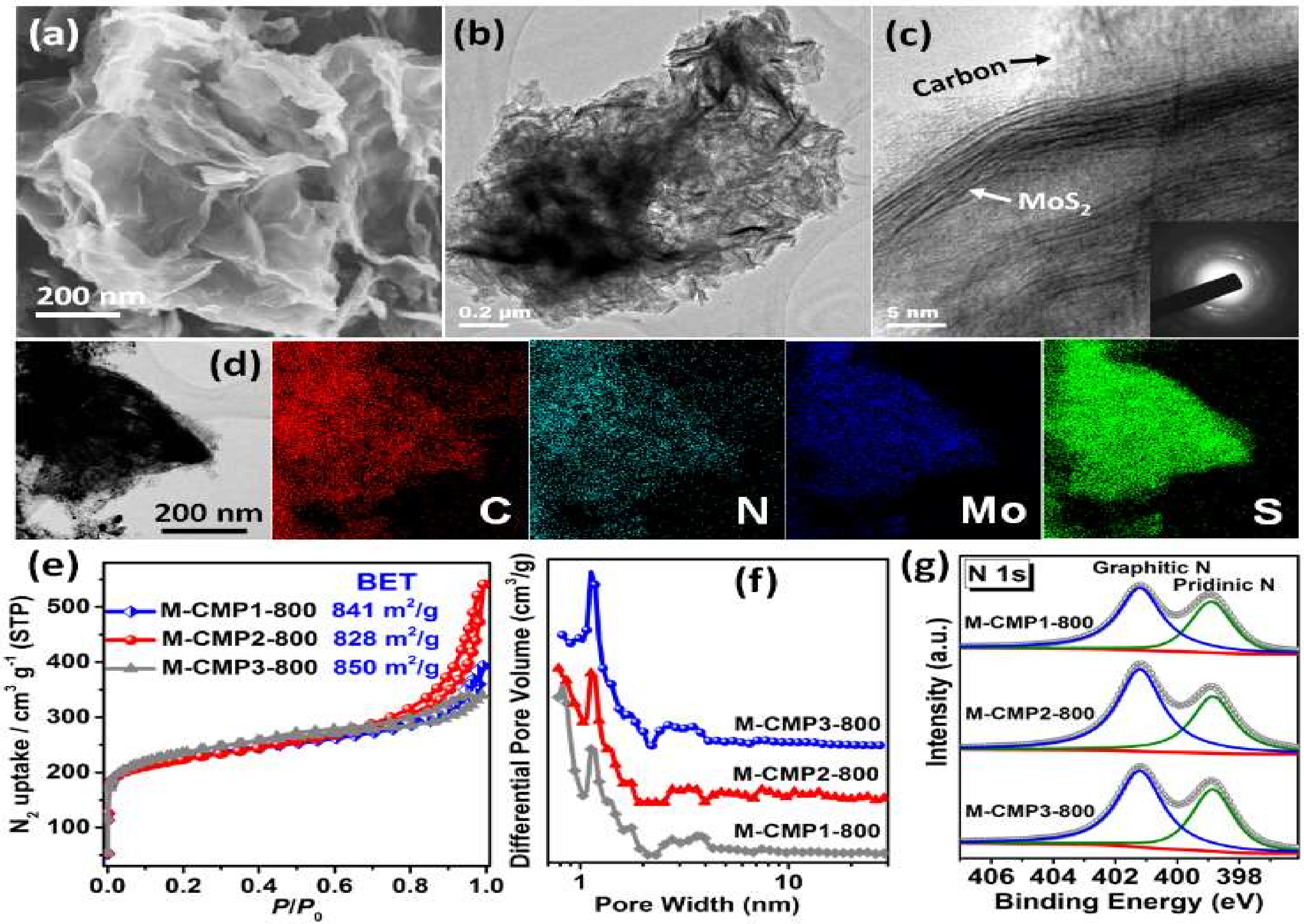
(ii) argon, heating rate: 10 °C min^{-1}, pyrolysis temperature: 700, 800, or 900 °C, 2 h.

Angew. Chem. Int. Ed. **2016**, 55, 6858



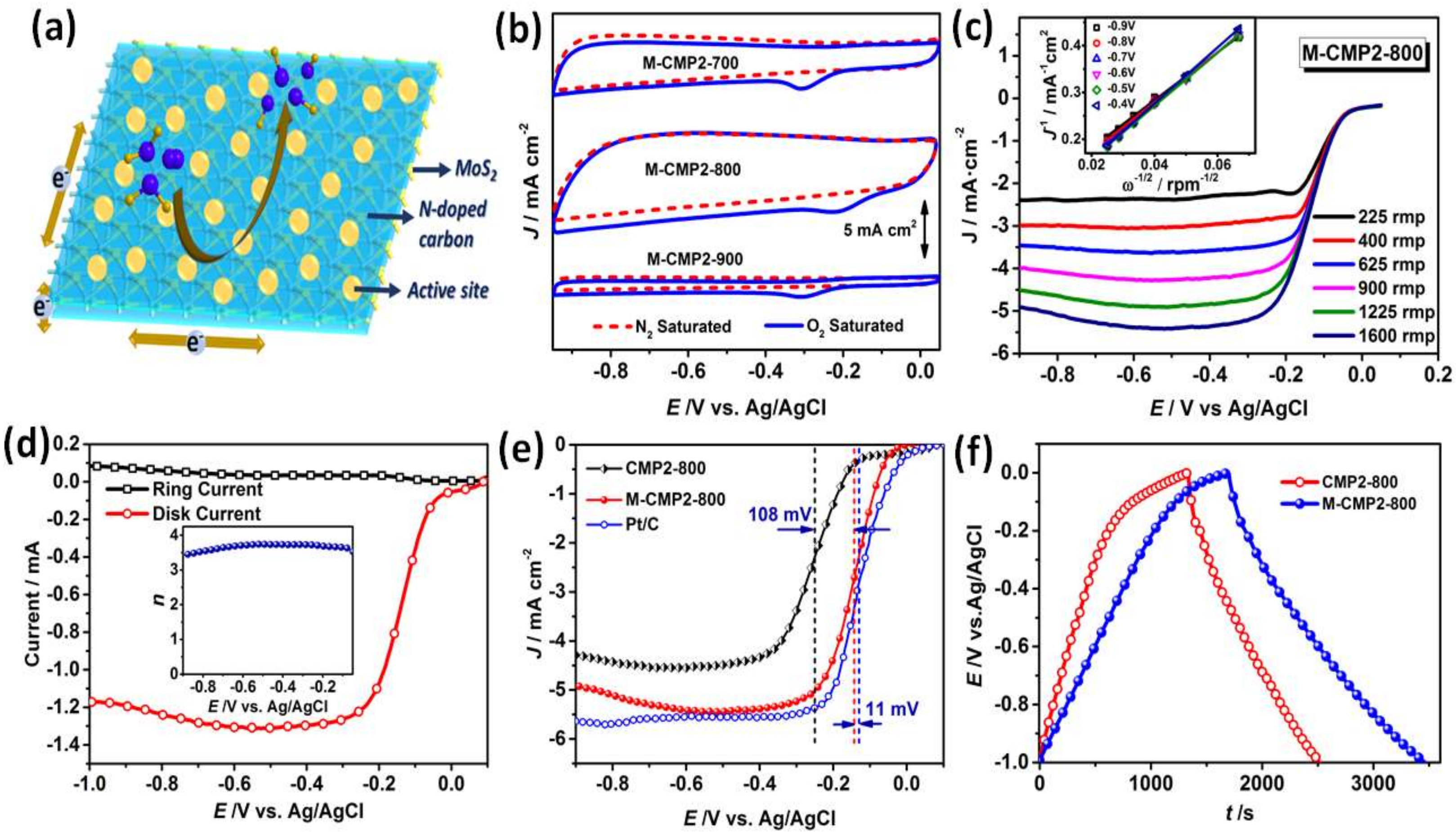
- 2D morphology
- Confirmed chemical structure by solid-state NMR
- High surface area up to 1625 m2/g
- Mainly micropore (<2nm)

Angew. Chem. Int. Ed. **2016**, 55, 6858



- MoS2/N-doped porous carbon hybrids
- High surface area up to 850m2/g
- Mainly micropore (<2nm)
- Graphitic and pyridinic N

Angew. Chem. Int. Ed. **2016**, 55, 6858



As electrocatalysts for ORR and as electrodes for supercapacitors:

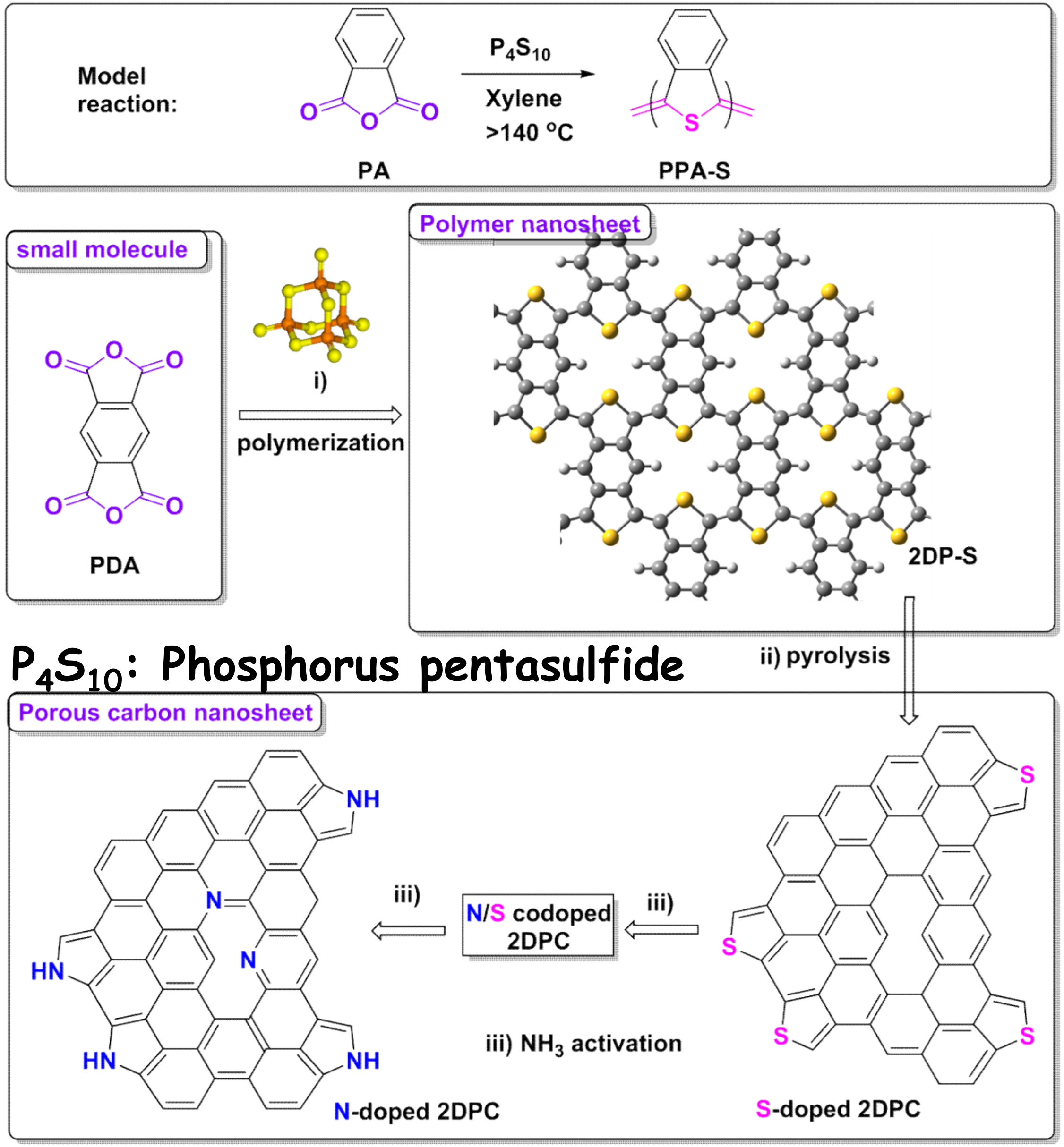
- 4e mechanism
- Low and much improved half-wave-poential
- Improved specific capacitance up to 344 F/g at 0.2 A/g, 45% higher than that of corresponding MoS2-free porous carbons

Angew. Chem. Int. Ed. **2016**, 55, 6858

Solution II:
2D-Template-Free?

Case 3-1. Conjugated Polymer Nanosheets

DRESDEN concept
TECHNISCHE UNIVERSITÄT DRESDEN



P_4S_{10}: Phosphorus pentasulfide

Key concept

Small molecules

↓

Polymer nanosheets

↓

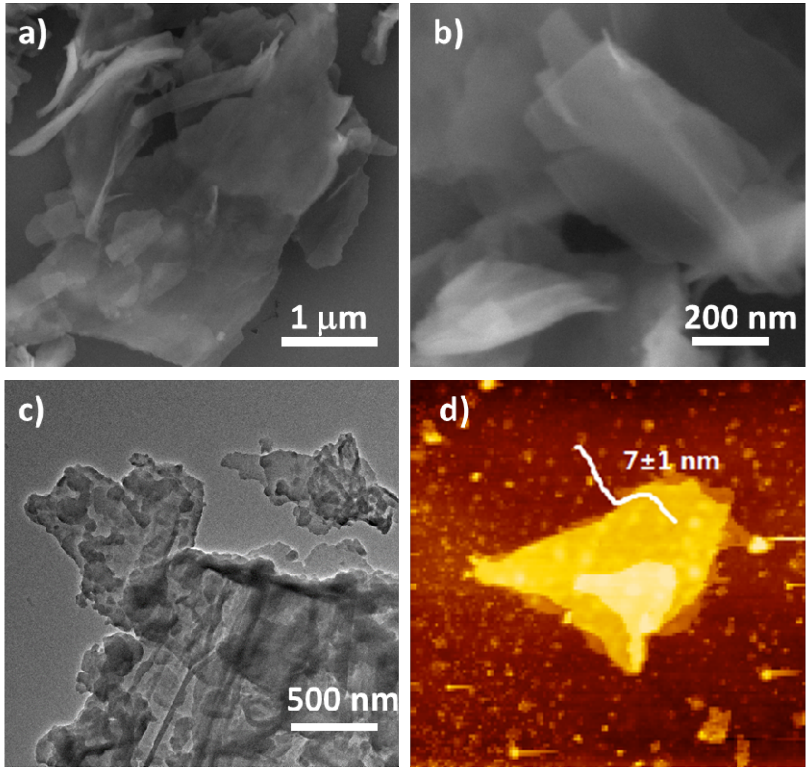
Carbon nanosheets

Key novelty

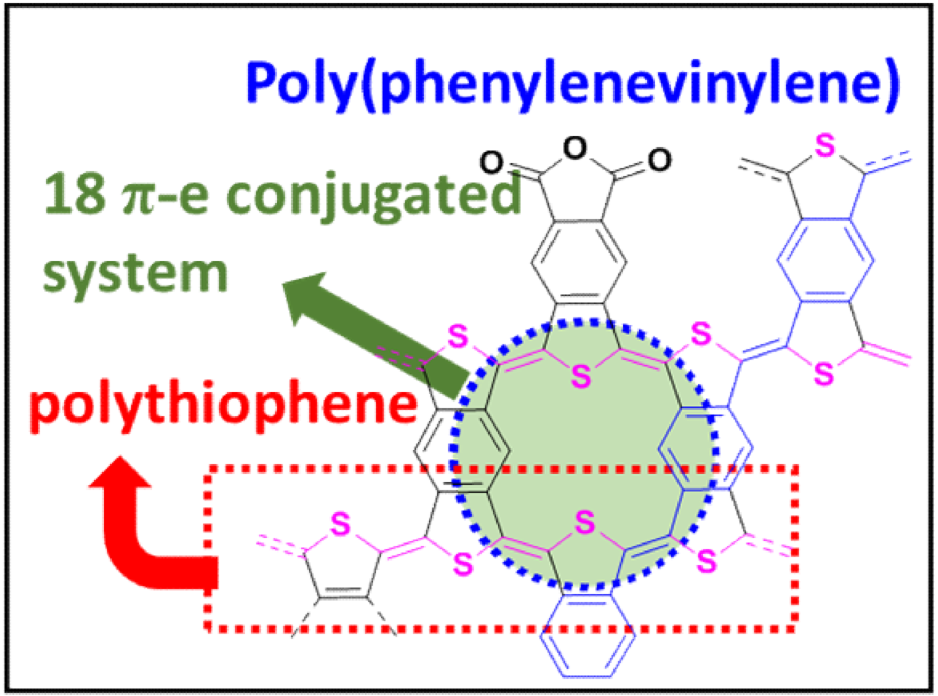
- ✓ Template-free
- ✓ N/S co-doping
- ✓ N/S ratio rational controllable

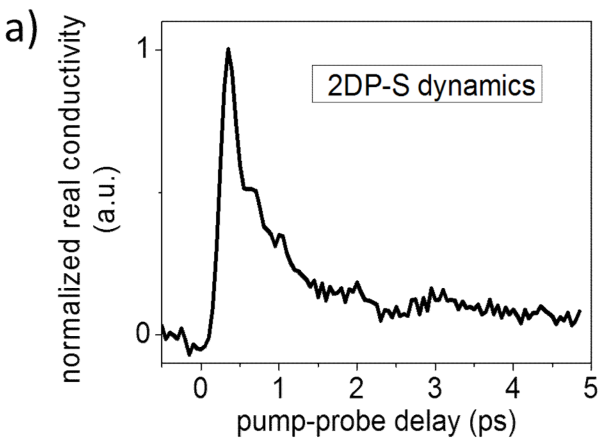
Adv. Funct. Mater. **2016**, *26*, 5893

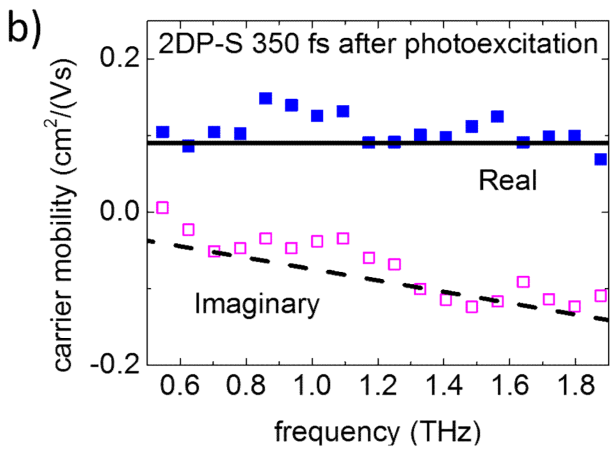
Polymer nanosheets



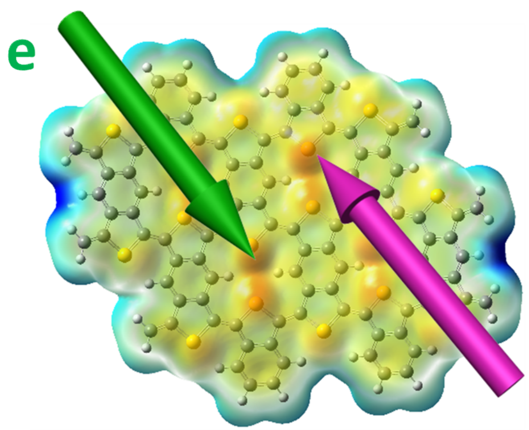
Proposed chemical structure



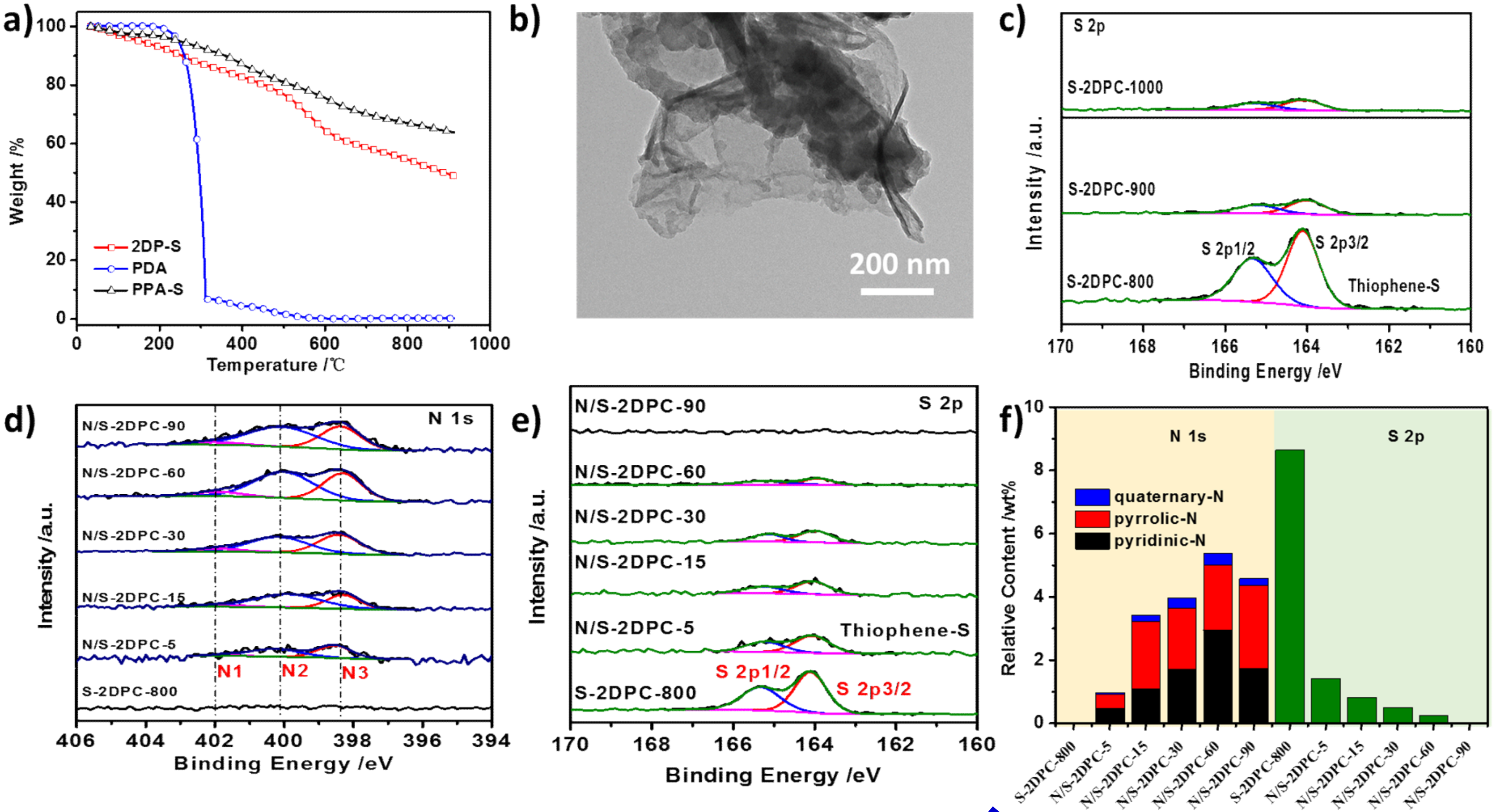




$0.1 \pm 0.05\ cm^2V^{-1}s^{-1}$



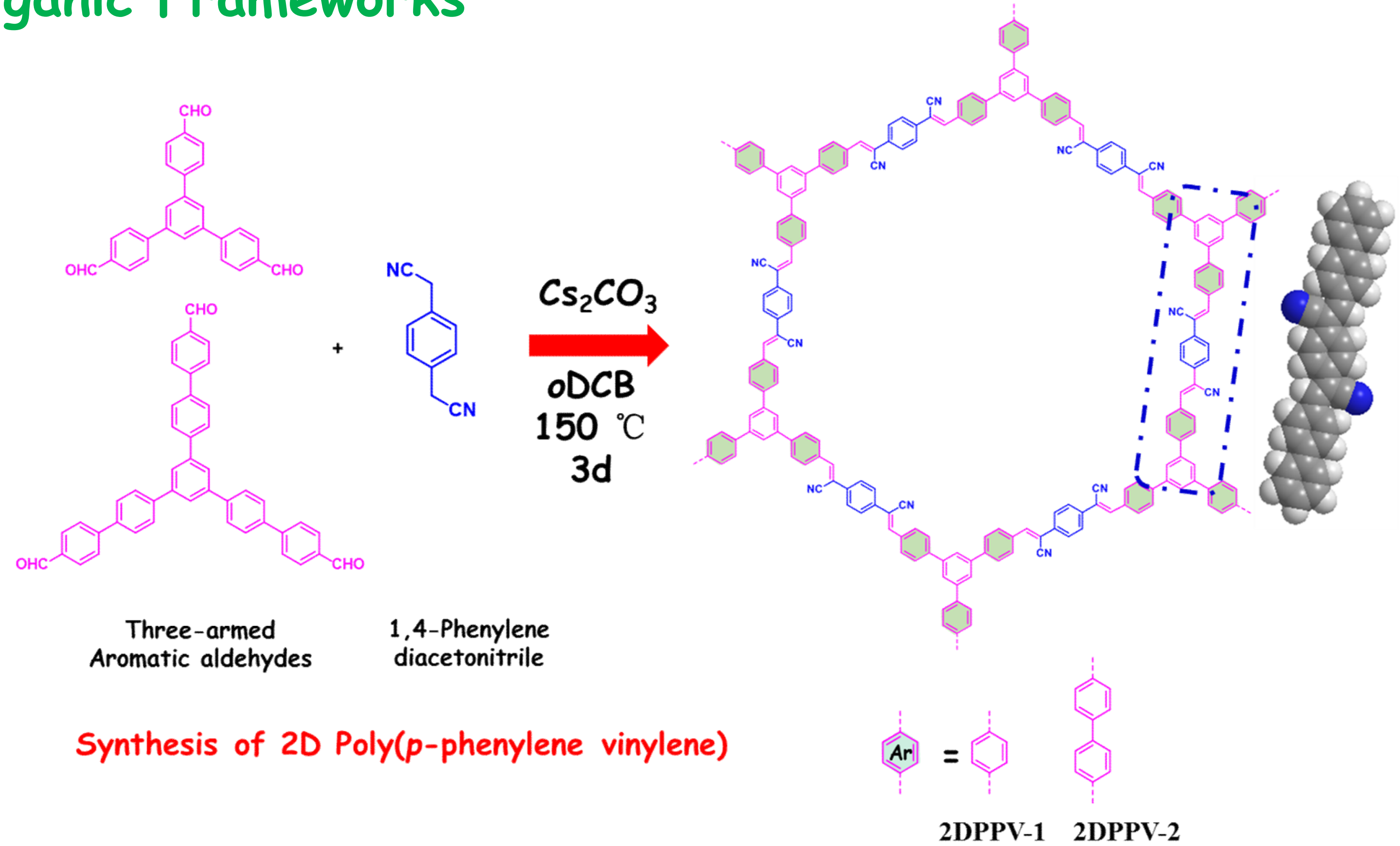
N/S doped porous carbon nanosheets



N/S ratio can be rational controlled

Supercapacitor performance is under measurement

Case 3-2. Olefin-Linked 2D Covalent Organic Frameworks



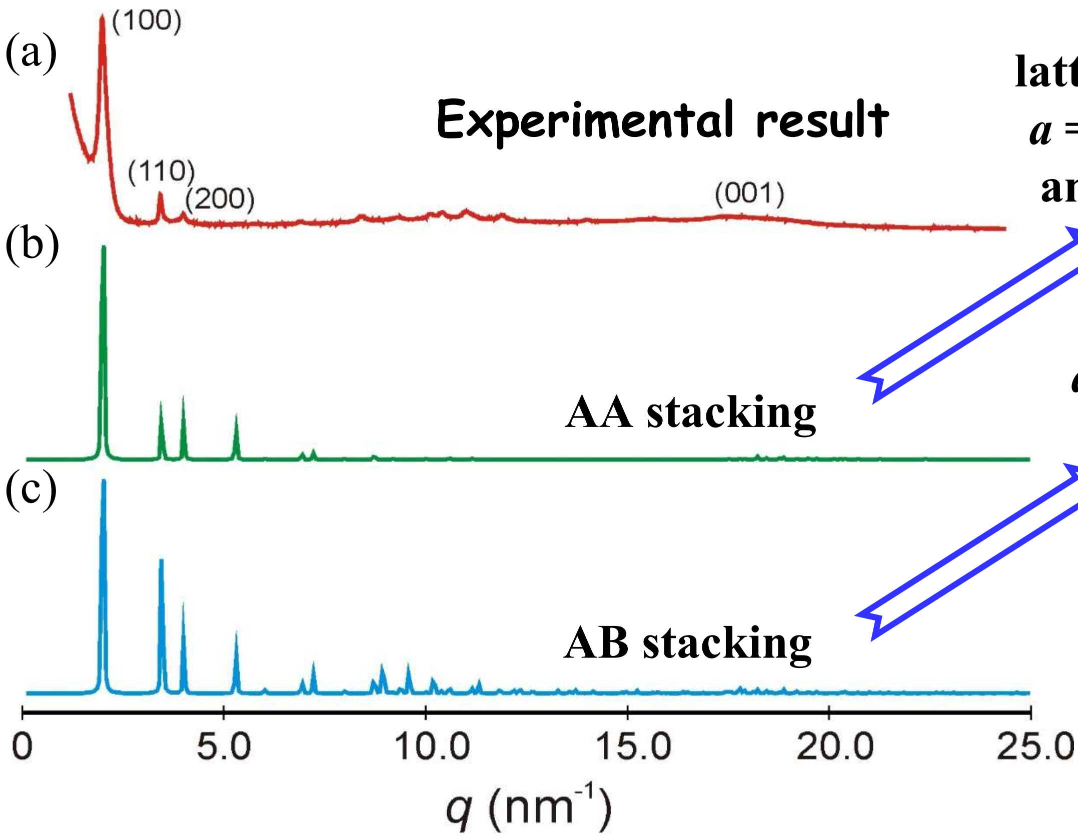
Polym. Chem. **2016,** *7* (25), 4176-4181. (**The first and the only C=C linked COFs**)

Highlight by:
M. Ebrahimi, F. Rosei, *Nature* **2017**, 542, 423-424.
Most-read 4 Full Papers published in *Polym. Chem.* in **2016**.

Structure analysis

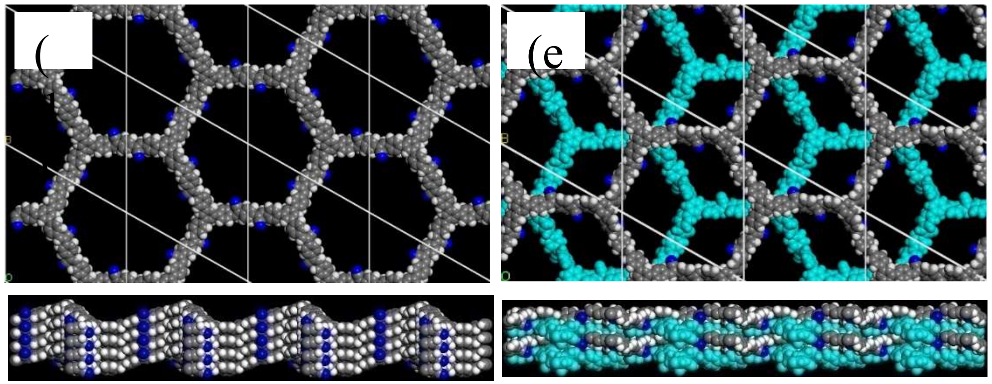
DRESDEN concept

TECHNISCHE UNIVERSITÄT DRESDEN

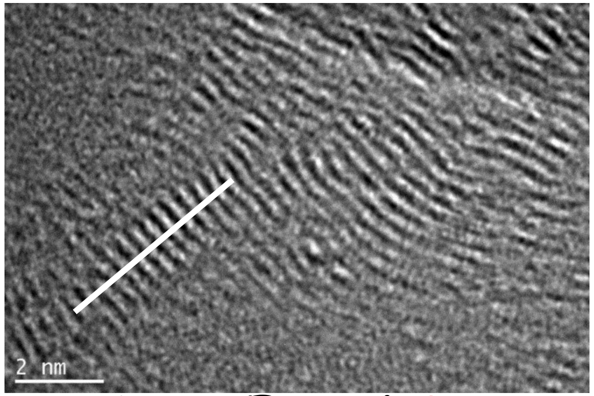


lattice parameter $\alpha = \beta = 90^o$, $\gamma = 120^o$, $a = b = 3.62$ nm and c = 0.35 nm, gave an XRD pattern in good agreement with the experimental result

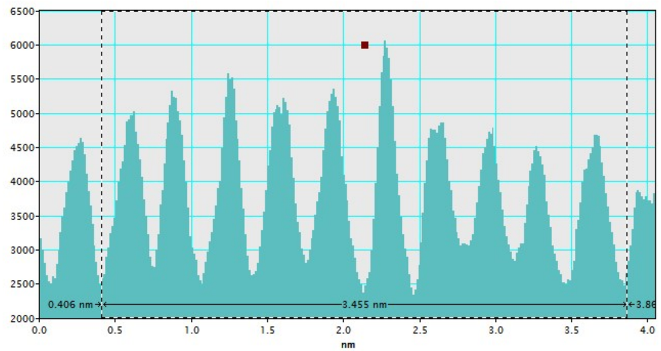
$a/2$ and $b/2$ and c = 0.70 nm could not reproduce the experimental XRD

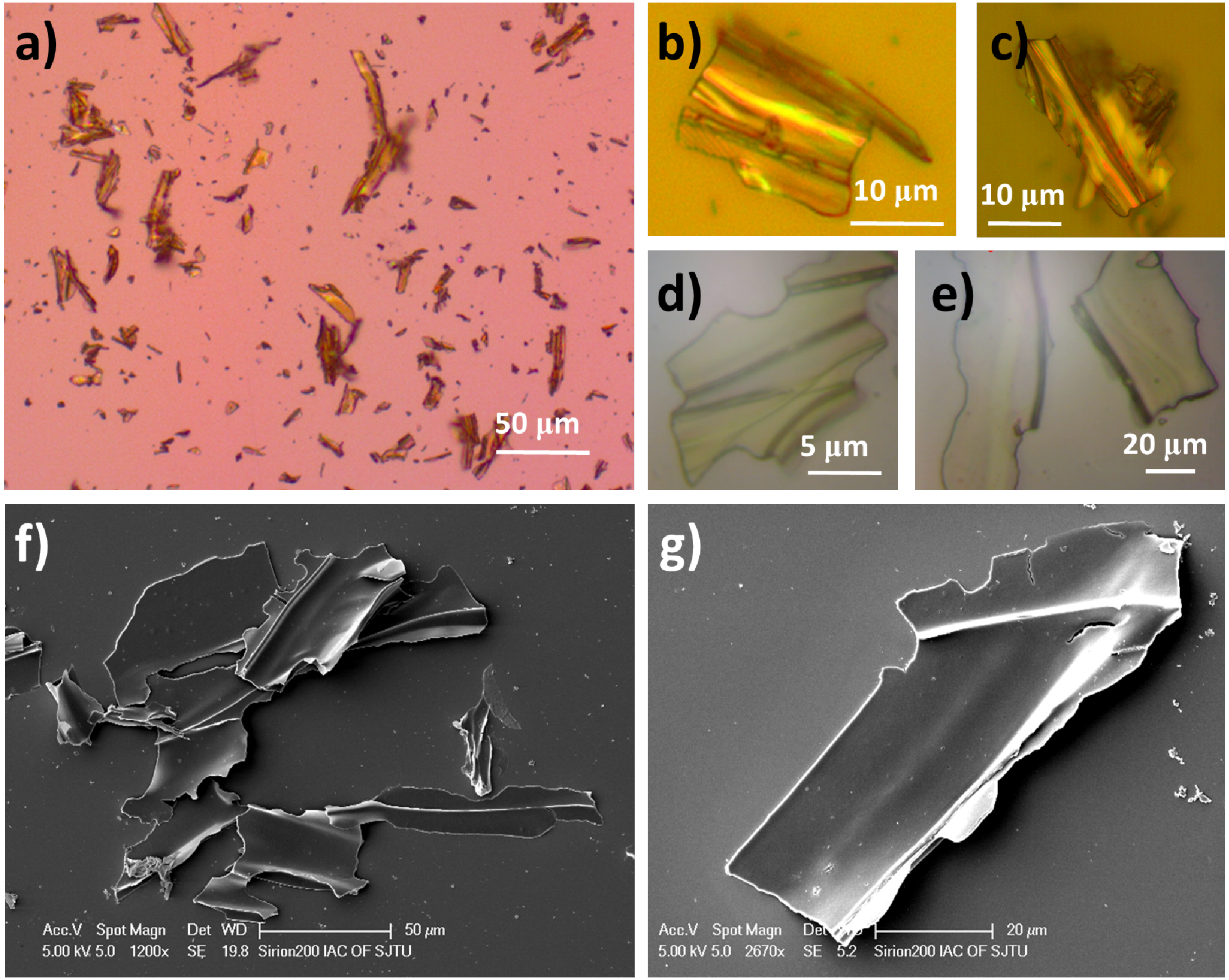


(d) AA stacking mode **(e) AB stacking mode**

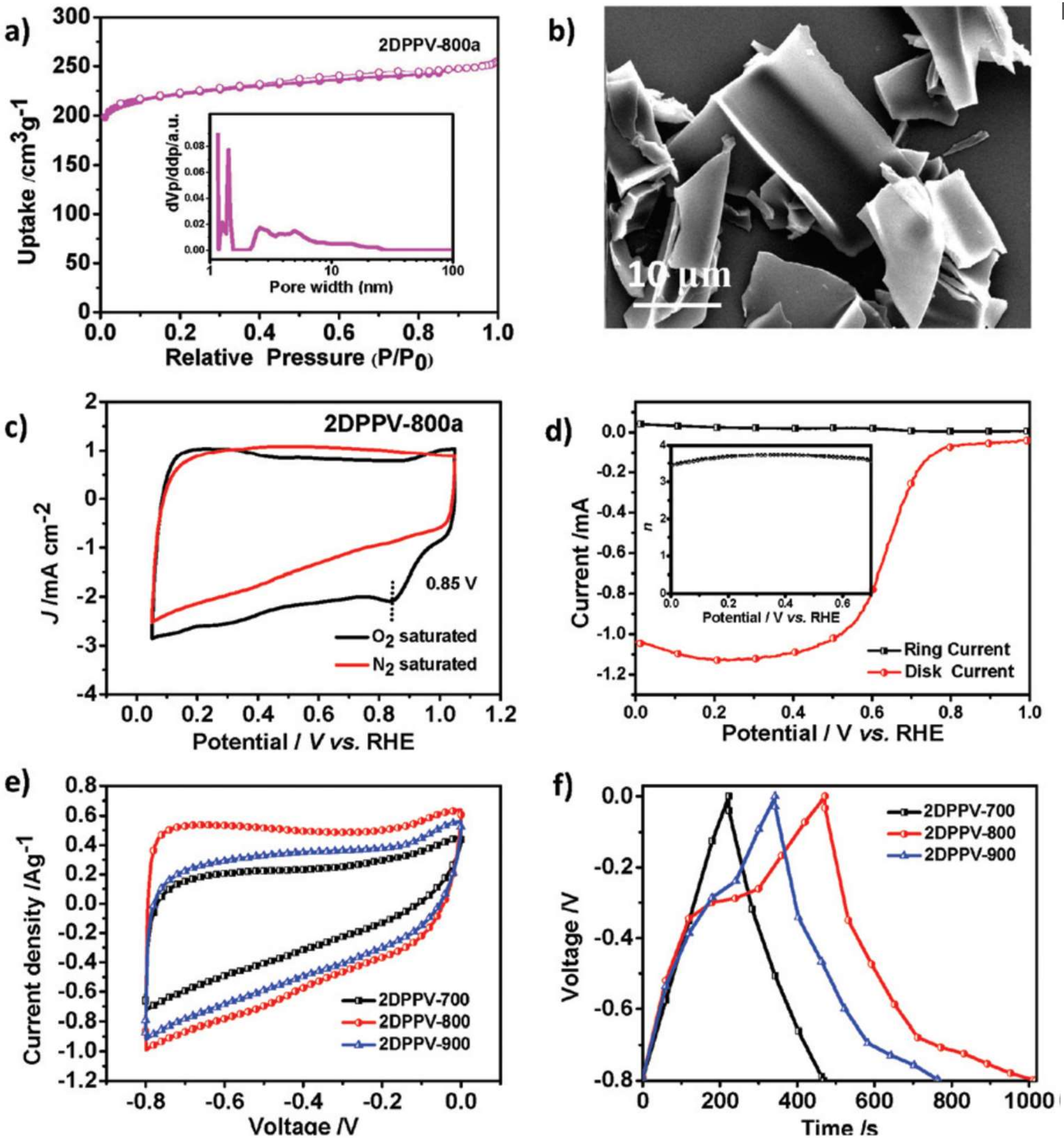


From HR-TEM: d=0.355 nm





Semi-transparent flakes, large size (>100 µm), thickness (50-300 nm)

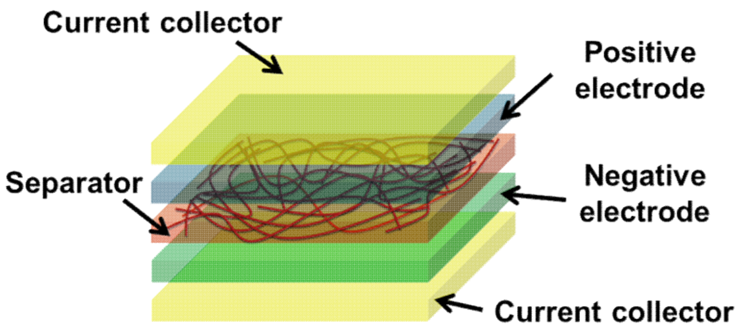


- ☐ Surface area up to 880 m2/g
- ☐ 2D morphology
- ☐ Highly activity for ORR (onset: 0.85V, 4e mechanism)
- ☐ High capacitance up to 334 Fg−1 at 0.5 Ag−1 for 2DPPV-800

Solution II:
Beyond 2D Porous Carbons

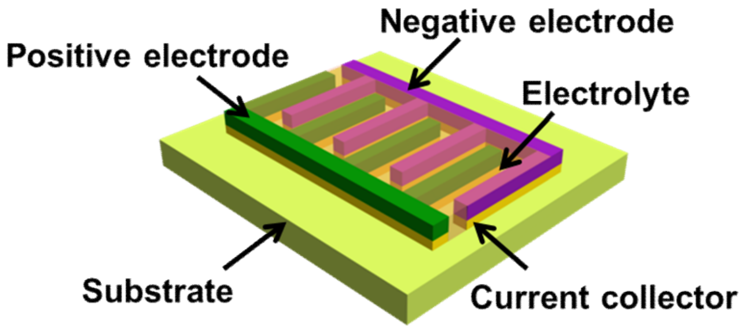
Supercapacitor

Vertical sandwich structure



In-Plane Micro-supercapacitor

In-plane interdigitated structure



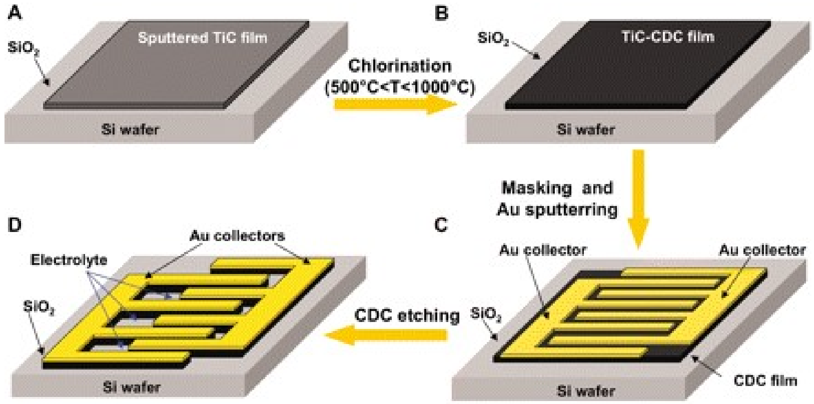
MSC (in-plane) is one kind of supercapacitors which possesses miniaturized in-plane configuration and can acts as power source or energy backup storage unit for micro-devices, e.g. portable and implantable electronic devices

Features/Advantages:

1. Thin, separator-free, large-area, flexible and Si-technology compatible, etc.;
2. Fast ion transport, possible AC-line filtering performance, low relaxation time constant, etc.

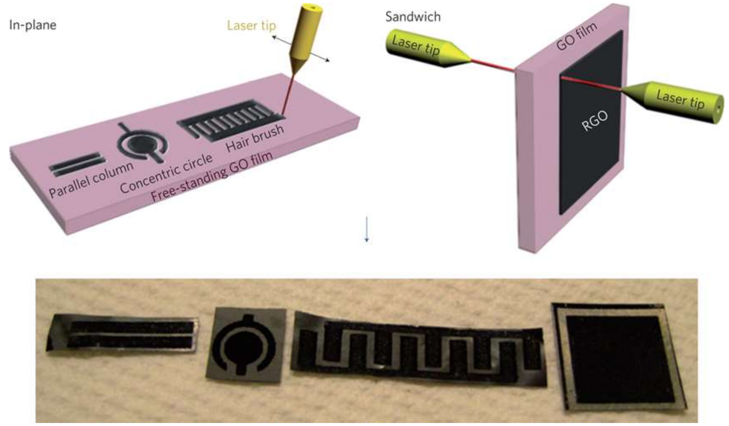
In-plane micro-supercapacitors (MSCs)

Monolithic Carbide-Derived Carbon Films

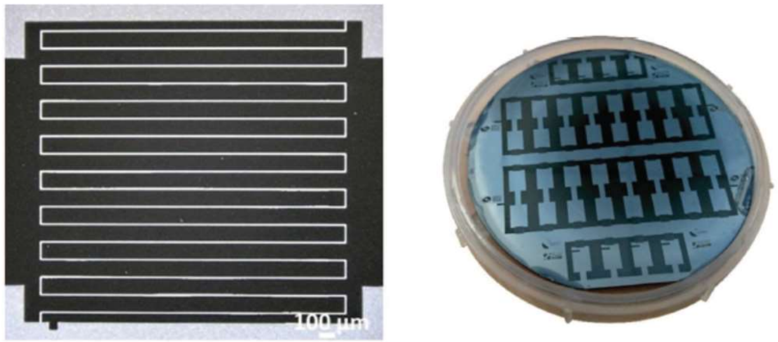


Y. Gogotsi, et al. *Science* **2010**, *328*, 480

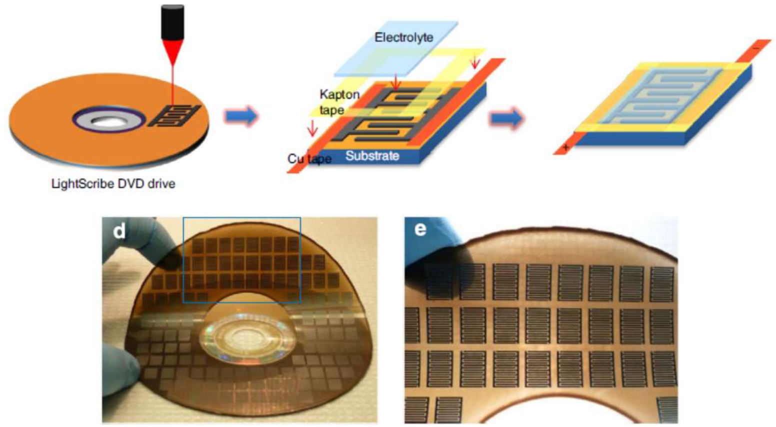
Graphene (or reduced graphene oxide) film



P. M. Ajayan, et al. *Nat. Nanotech.* **2011**, *6*, 496



P. Simon, et al. *Science* **2016**, *351*, 691

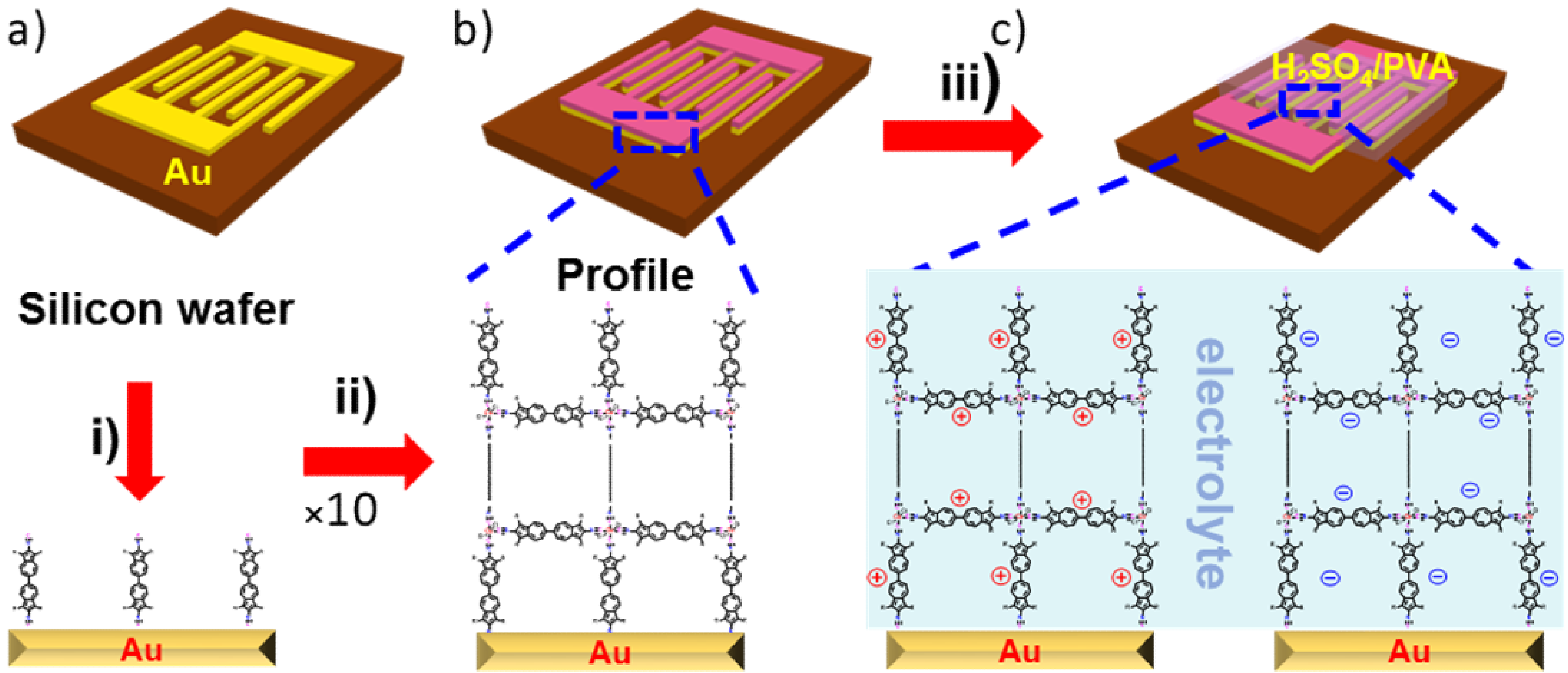


X. Zhuang, X. Feng, *ACIE* **2016**, *55*, 6136 (highlight) R. B. Kaner, et al. *Nat. Commun.* **2013**, *4*, 1475.

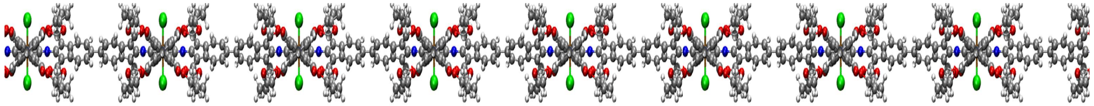
- Porous Carbons suffer from uniform film fabrication due to high temperature procedure, especially on Si wafer substrate.
- Complicate photolithography procedures

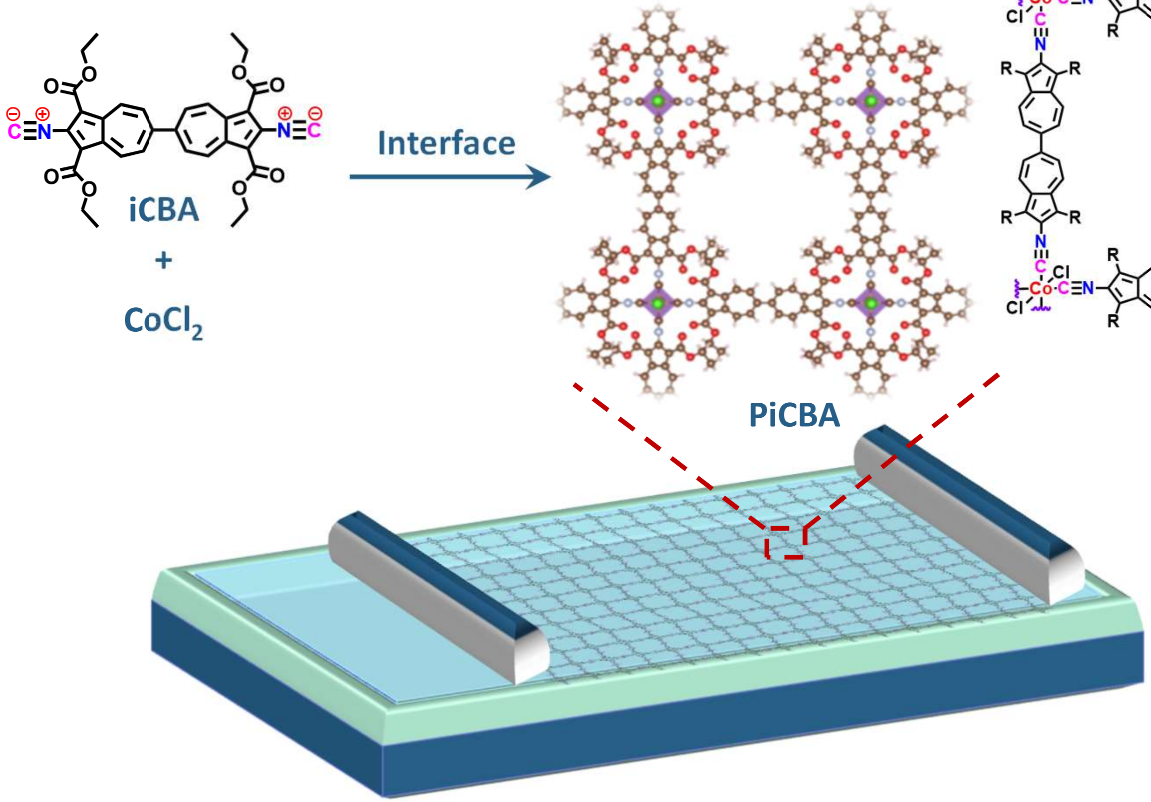
Case 4. Coordination Polymer Framework for On-Chip MSCs

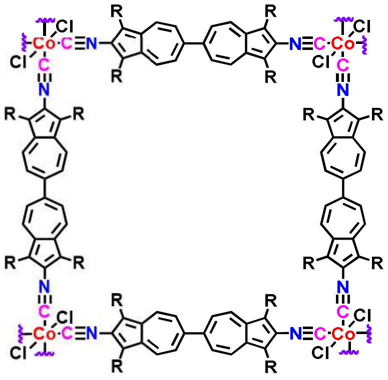
Solid-state PiCBA-Au MSC with an in-plane geometry

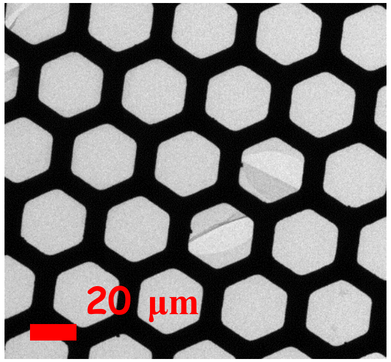


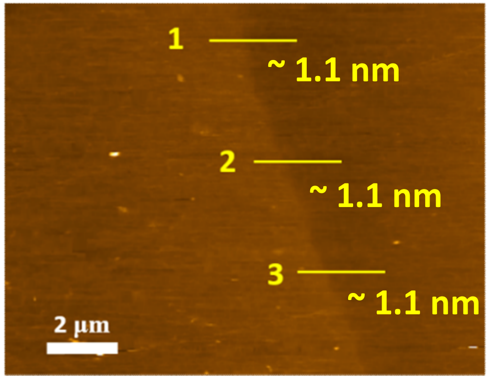
- Layer-by-layer (LBL) fabrication of a 10 layer PiCBA film on Au interdigital electrodes
- H_2SO_4-polyvinyl alcohol (H_2SO_4-PVA) acts as gel electrolyte









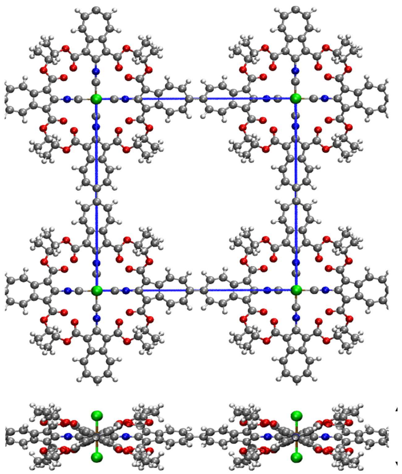


Targets:

- **Simple synthesis of large-area, free-standing azulene-bridged single-layer nanosheet coordination polymer framework with permanent dipole moment**
- **Potentially up-scalable method for the room temperature fabrication of on-chip MSCs**

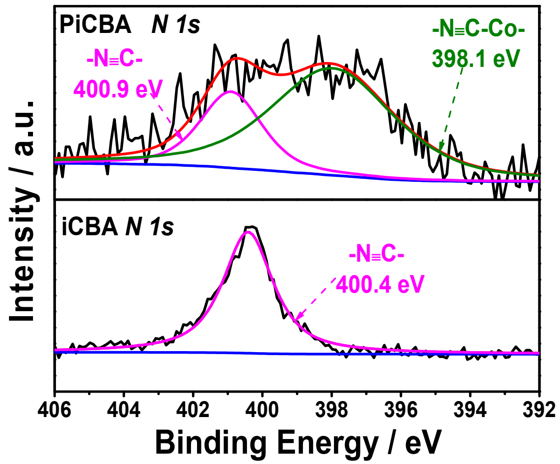
Angew. Chem. Int. Ed. **2017**, 56, 3920 (VIP).

Structural characterization of PiCBA single-layer nanosheet

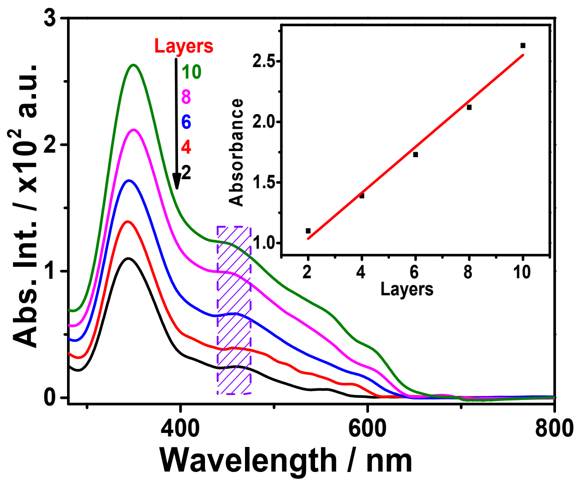


generation of quasi-free e-h pairs subsequently condensing into localized states

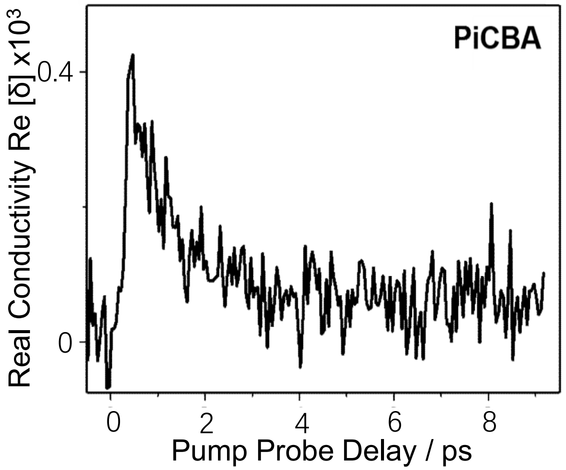
XPS

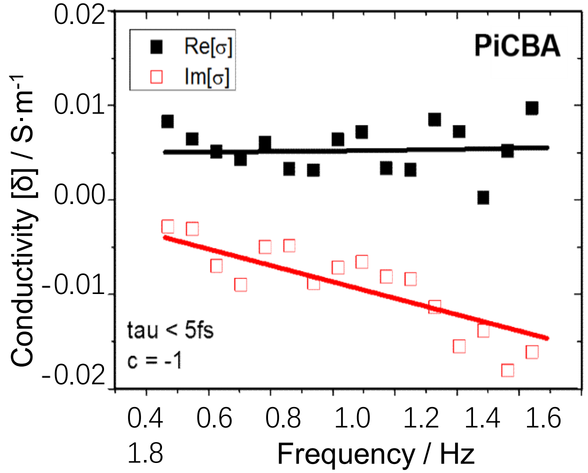


UV-vis



Time-resolved terahertz spectroscopy

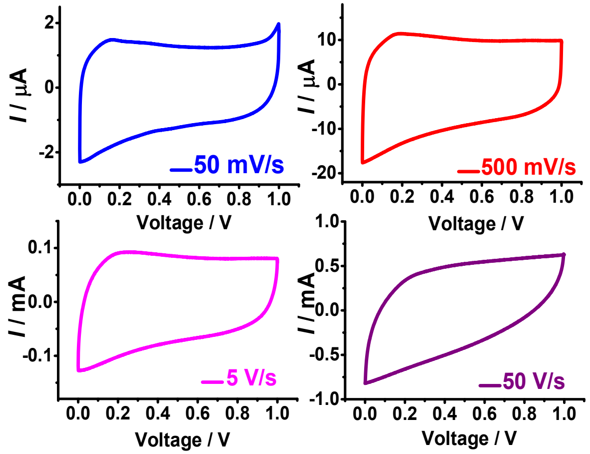




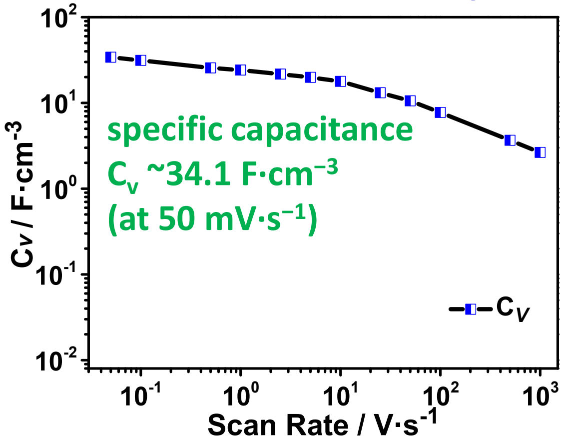
- **carrier mobility μ(PiCBA) = 5 × 10^{-3} $cm^2 \cdot V^{-1} \cdot s^{-1}$; conductivity of bilayer PiCBA (thickness: ~2.0 nm) σ = 2.4 × 10^{-4} $S \cdot cm^{-1}$**
- **all absorbed photons generate quasi-free charges immediately after pump excitation**

Electrochemical Performance of Solid-state PiCBA-Au MSC

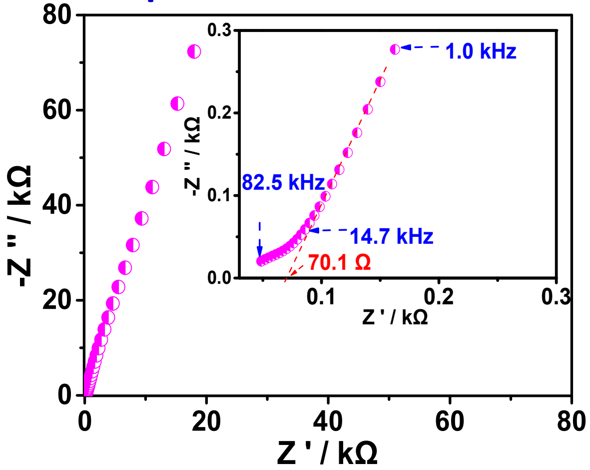
CV



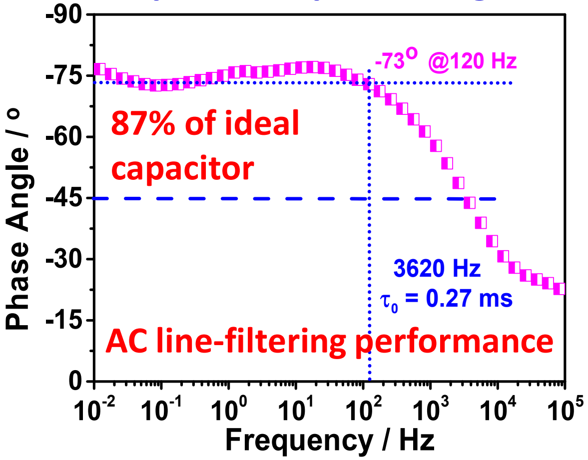
stack capacitance (C_v)

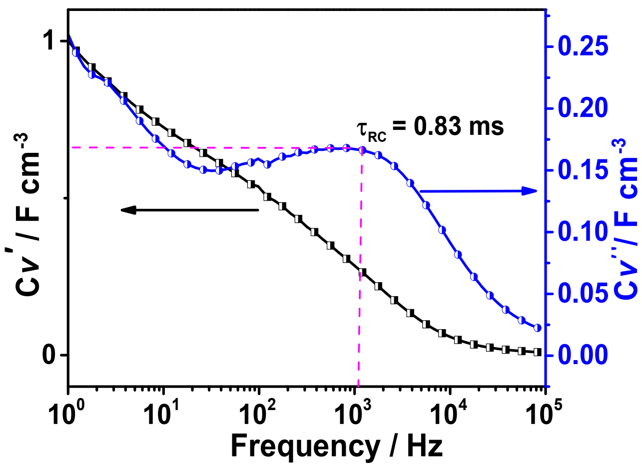


Complex plane plot of the impedance

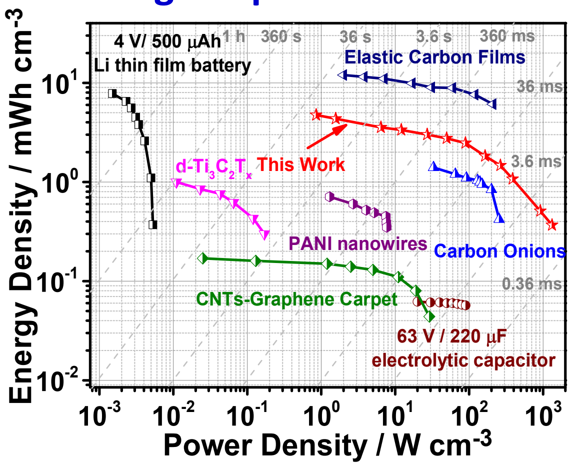


Impedance phase angle





Ragone plot

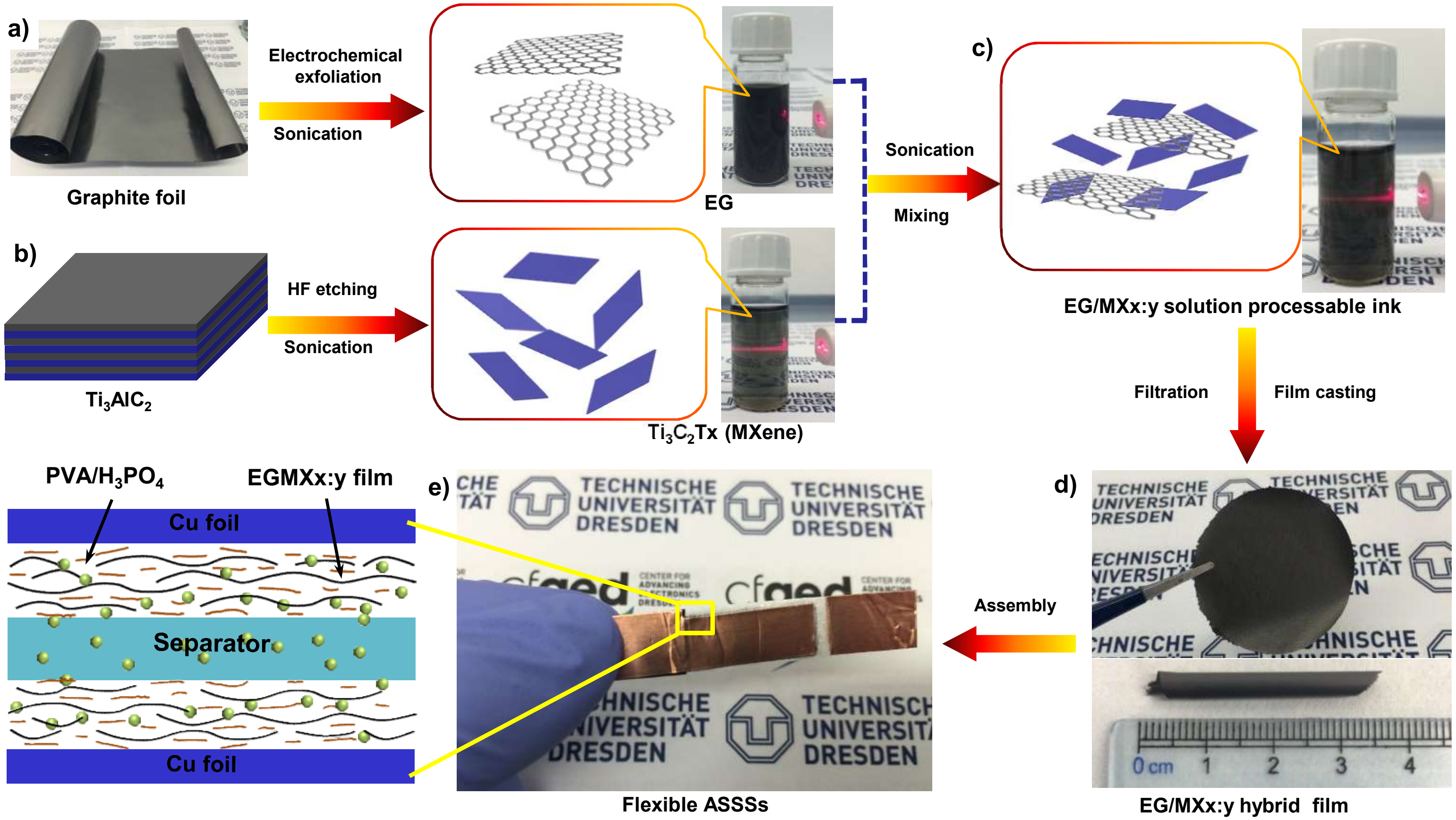


- typical double-layer capacitive behavior (under high rate)
- high capacitance and rate performance

- Energy density: 4.7 $mWh\cdot cm^{-3}$
- Power density: 1323 $W\cdot cm^{-3}$

Solution IV:
2D Composites

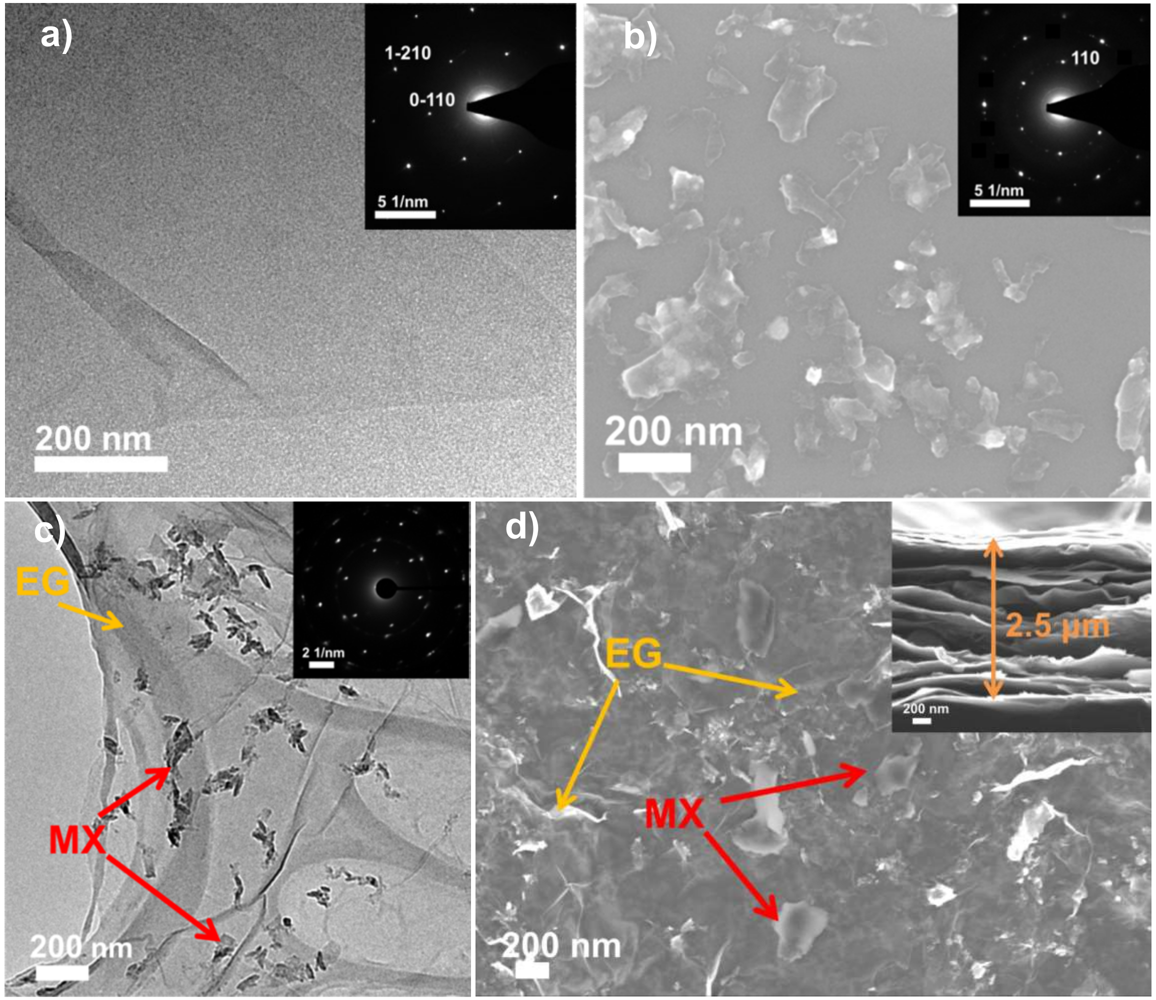
Case 5-1: Mxene/EG-based SCs



- ✓ The small size of MXene incorporate among the graphene interlayer can create an ideal "buffer layer" and increase the interlayer spacing.
- ✓ The larger size of graphene layers in the hybrid structures can function as a mechanical backbone sandwiched between the MXene nanoflakes and further enhanced the long distance conductivity of nanohybrid.

Adv. Energy Mater. 2017, 7, 1601847

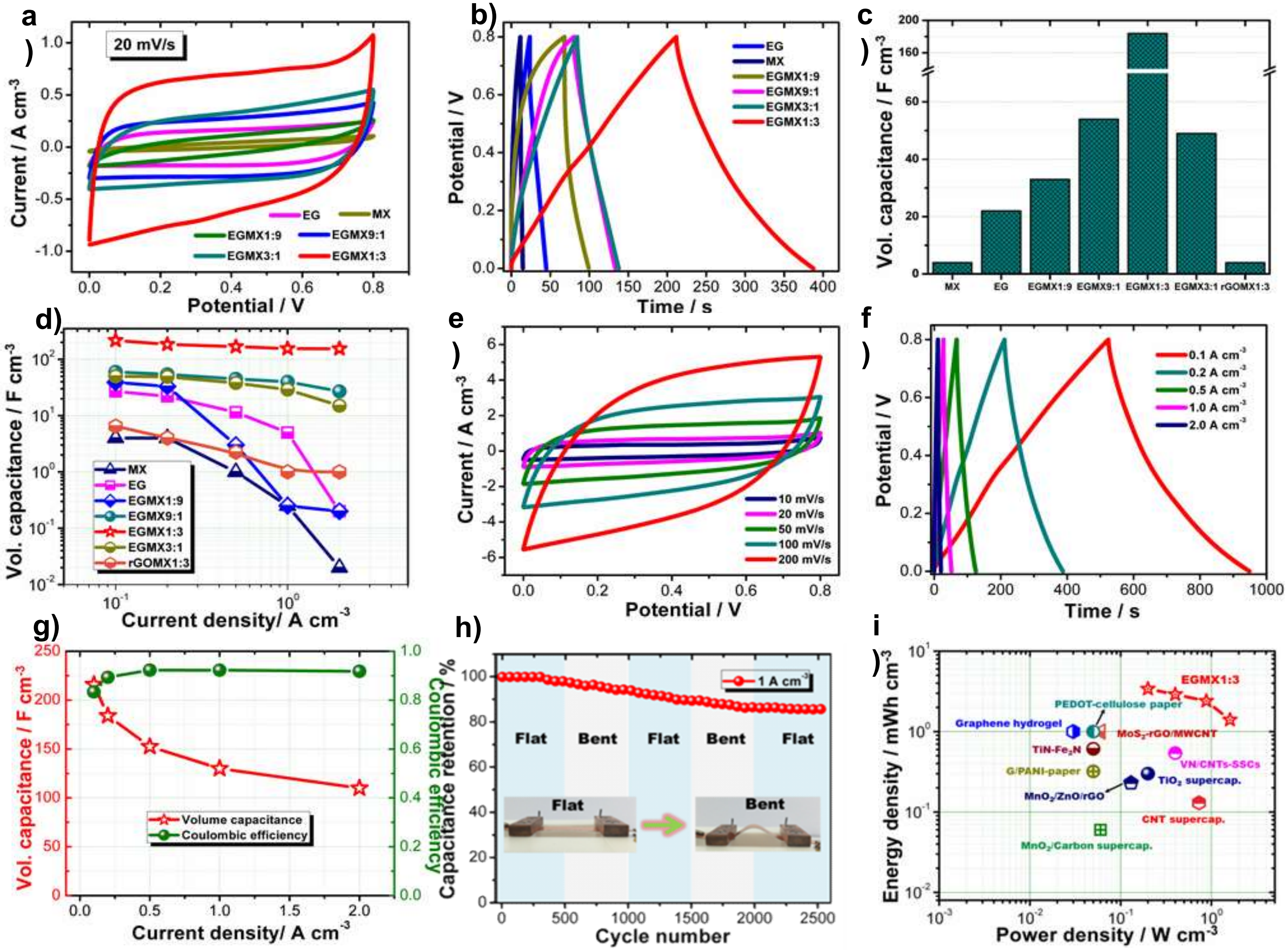
Morphology characterization:



Typical TEM images of EG (a) and EGMX1:3 nanohybrid (c). Field emission SEM images of MXene (b) and EGMX1:3 hybrid film (d). The insets in a), b) and c) are selected area electron diffraction (SAED) patterns of EG, MXene, and EGMX1:3, respectively; the inset in d) is the cross-section SEM image of EGMX1:3 film.

Adv. Energy Mater. **2017, 7, 1601847**

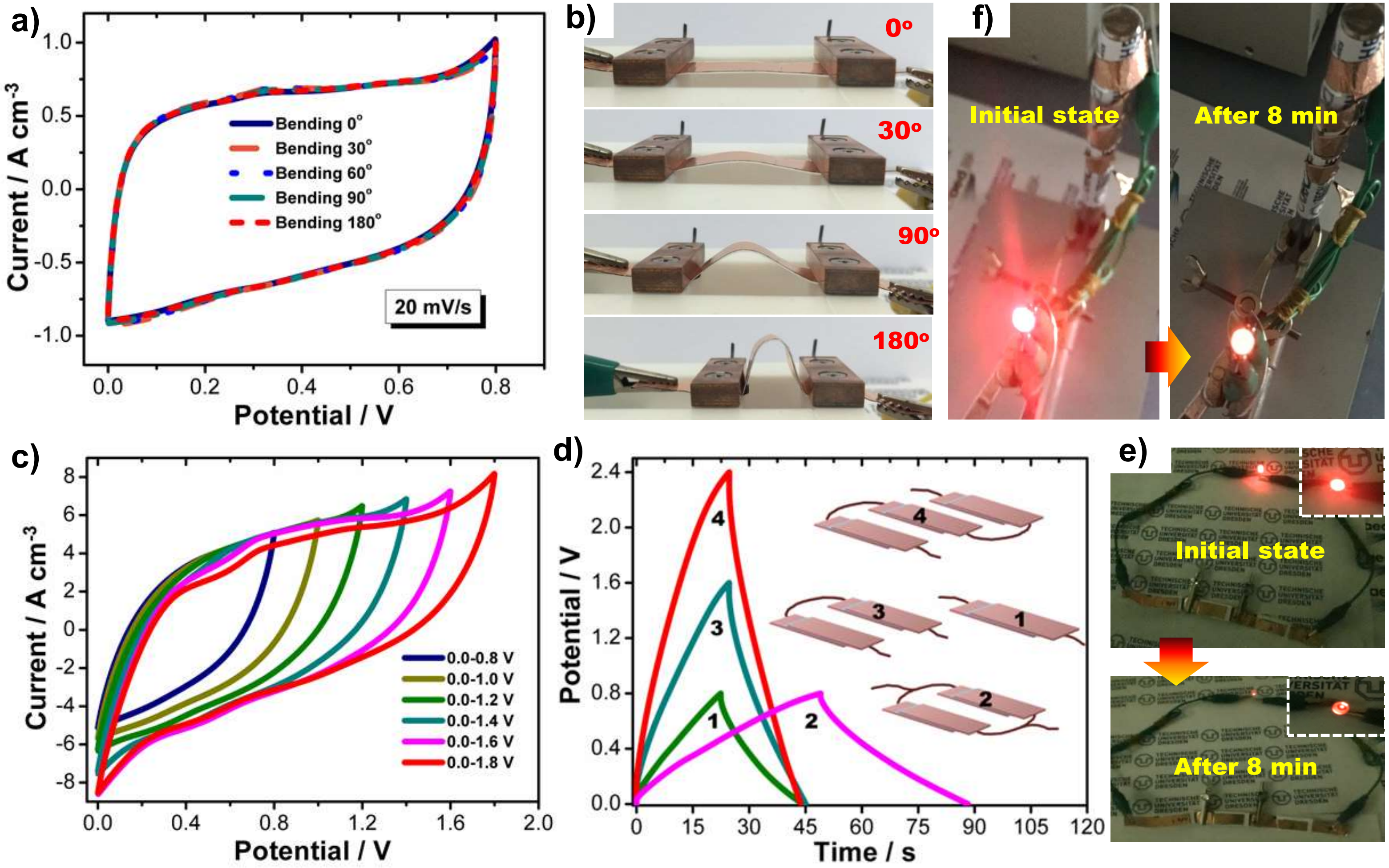
Electrochemical performance of the ASSSs.



- ✓ **Volumetric capacitances of EGMX1:3 based ASSS were determined to be 216 F cm^{-3} at 0.1 A cm^{-3}.**
- ✓ **The smallest charge transport resistance Rct of EGMX1:3 (4.76 Ω) was observed in contrast to pristine EG (22.07 Ω) and MXene (42.79 Ω).**

Adv. Energy Mater. 2017, 7, 1601847

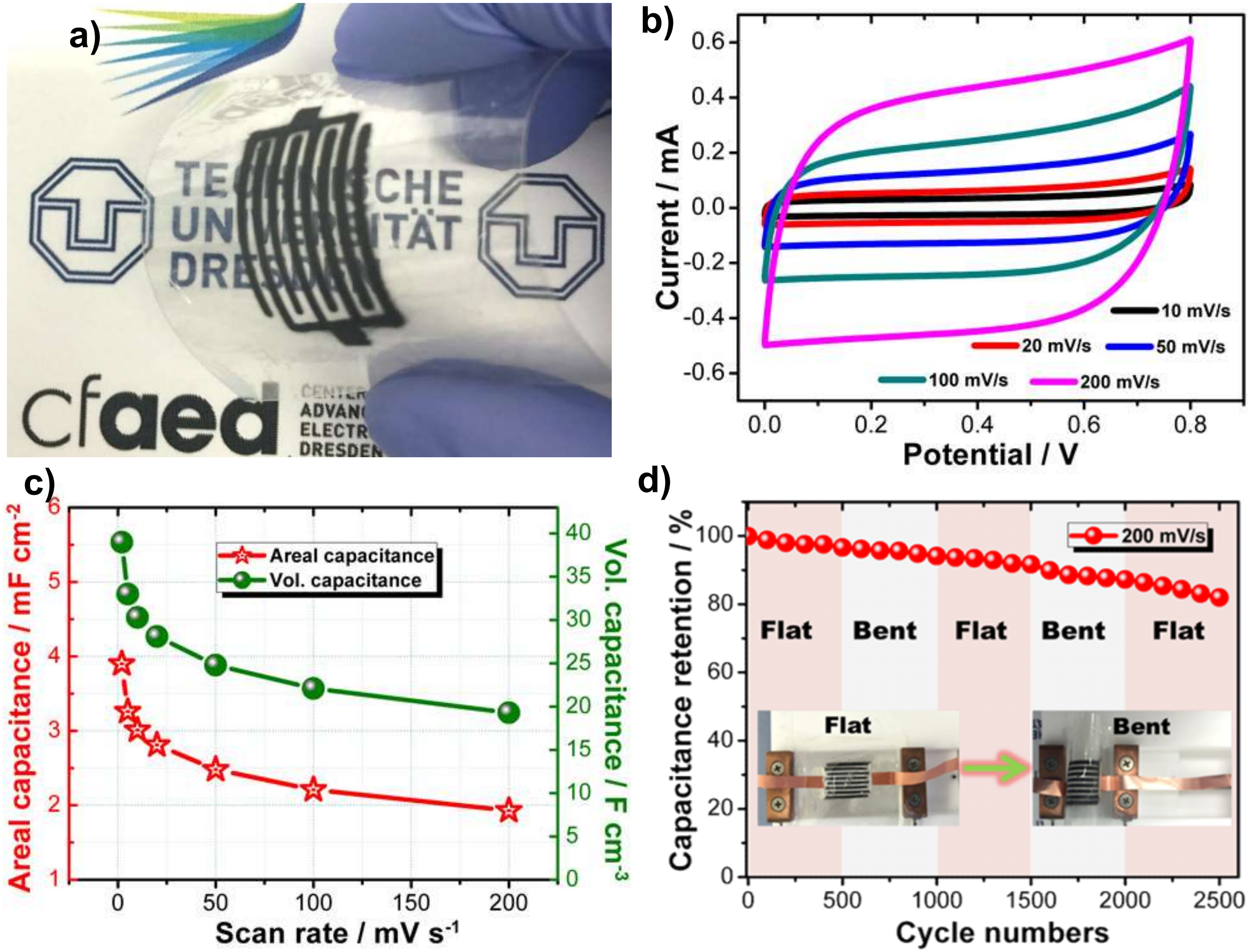
Flexibility and voltage window control of the ASSSs.



- ✓ **Good flexibility and stability**
- ✓ **Flexible ASSS can be operated in different working voltage ranging from 0.0-0.8 V to 0.0-1.8 V with quasi-rectangular shape at a scan rate of 200 mV s^{-1}**

Adv. Energy Mater. 2017, 7, 1601847

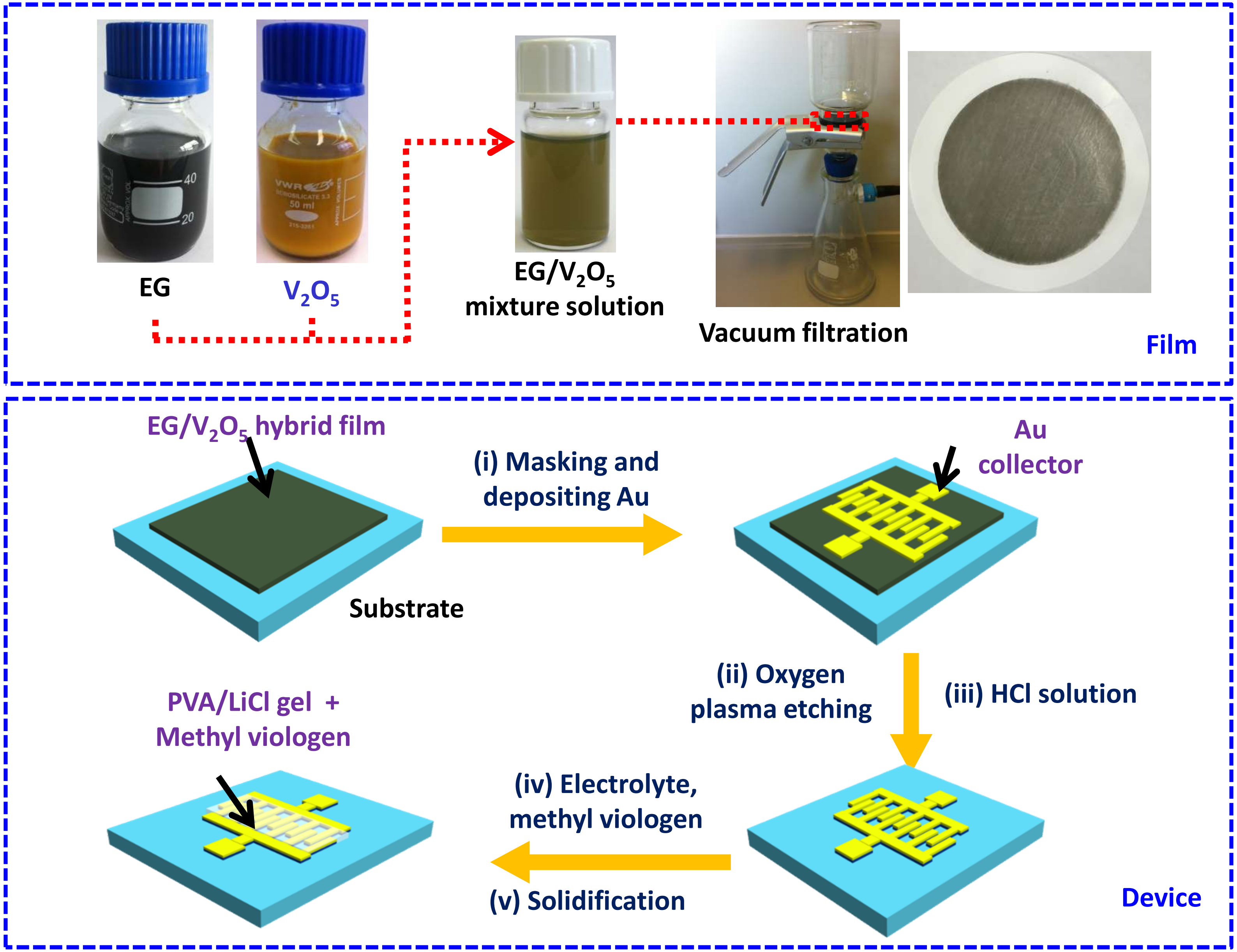
Electrochemical performance and flexibility studies of the fabricated MSCs.



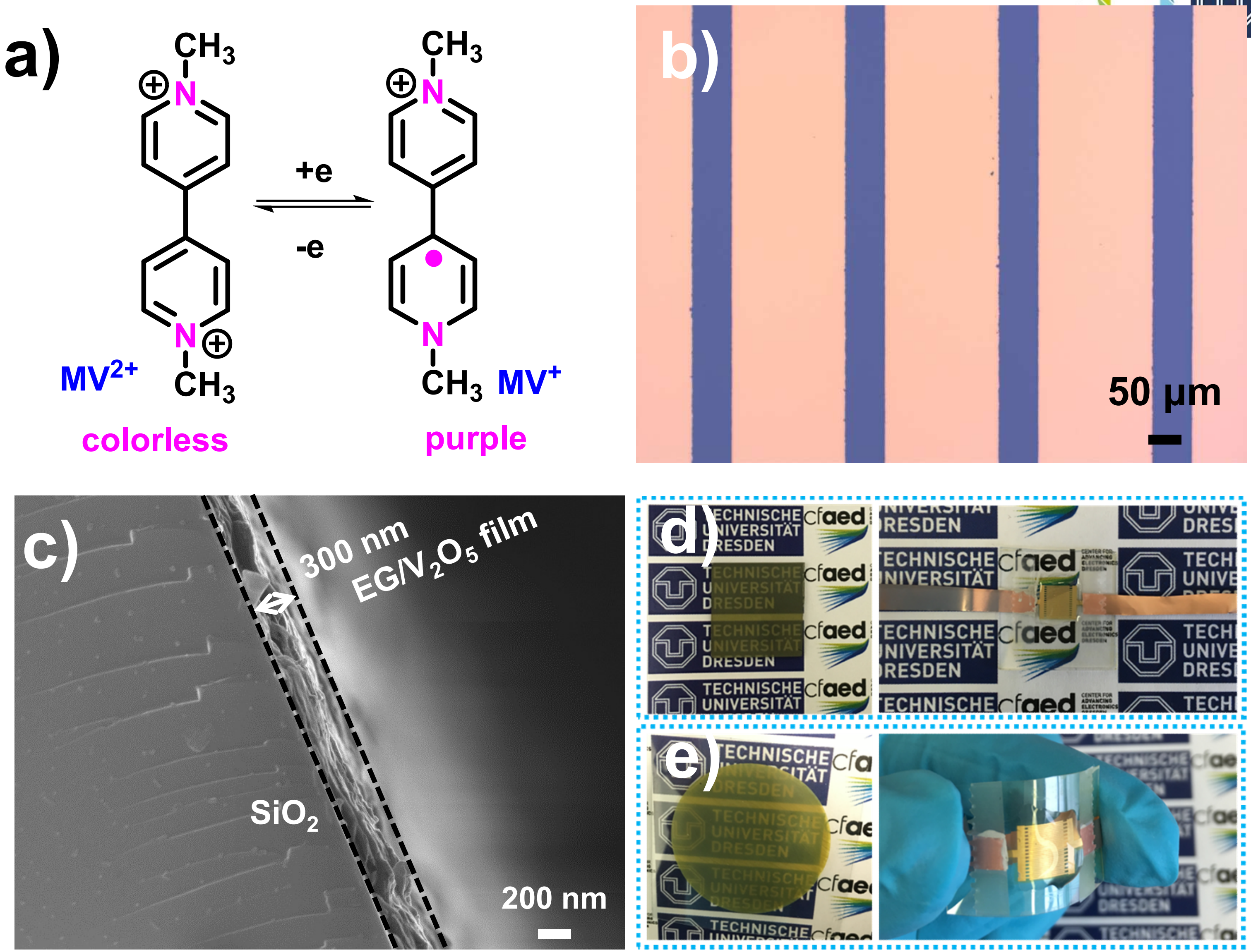
- ✓ EGMX1:3 based MSC presented a ultrahigh areal capacitance of 3.26 mF cm^{-2} and a volumetric capacitance of 33 F cm^{-3} at 5 mV s^{-1}
- ✓ Long term stability with 82% of capacitance retention after 2500 cycles

Adv. Energy Mater. 2017, 7, 1601847

Case 5-2: Stimulus-responsive MSCs

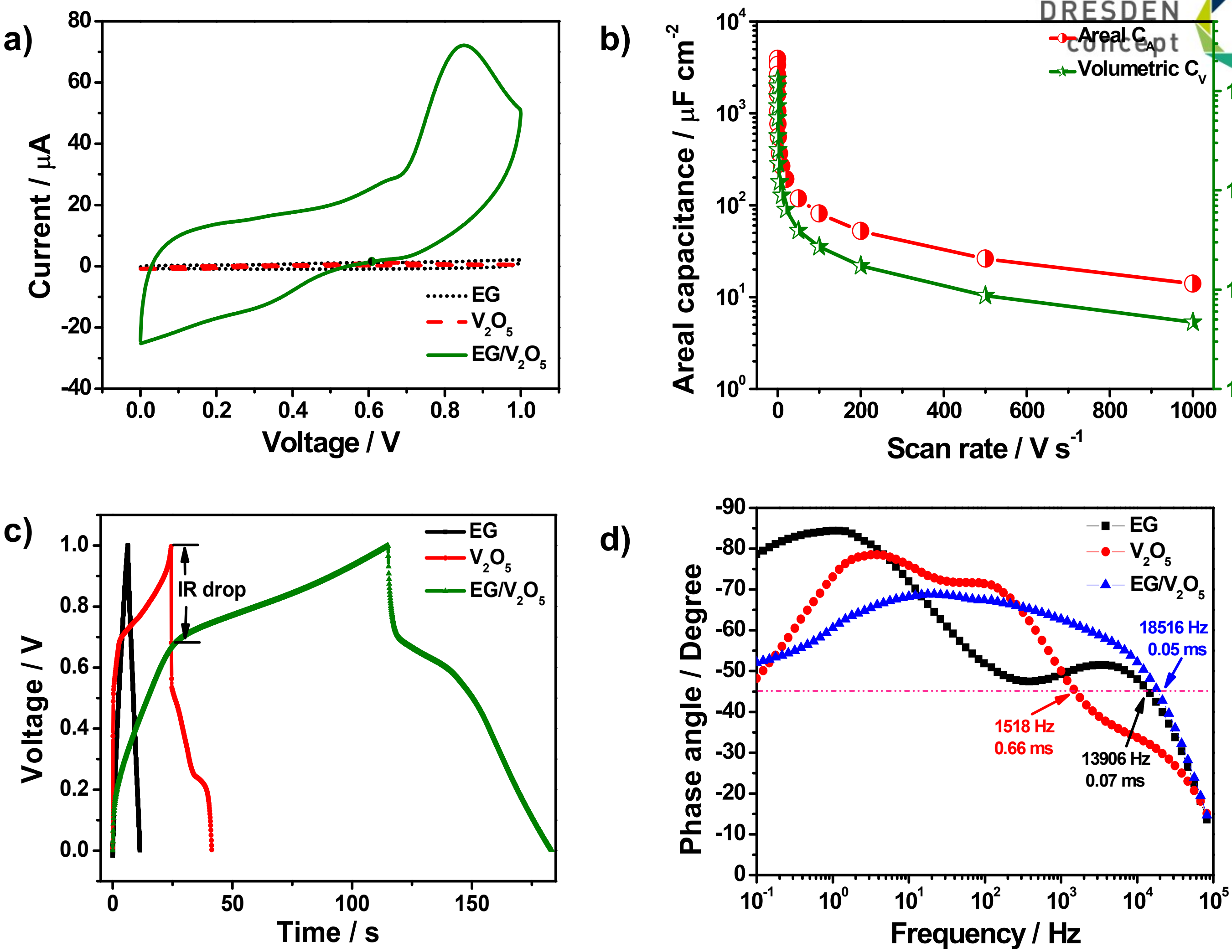


Adv. Mater. **2017**, 29 (7), 1604491.



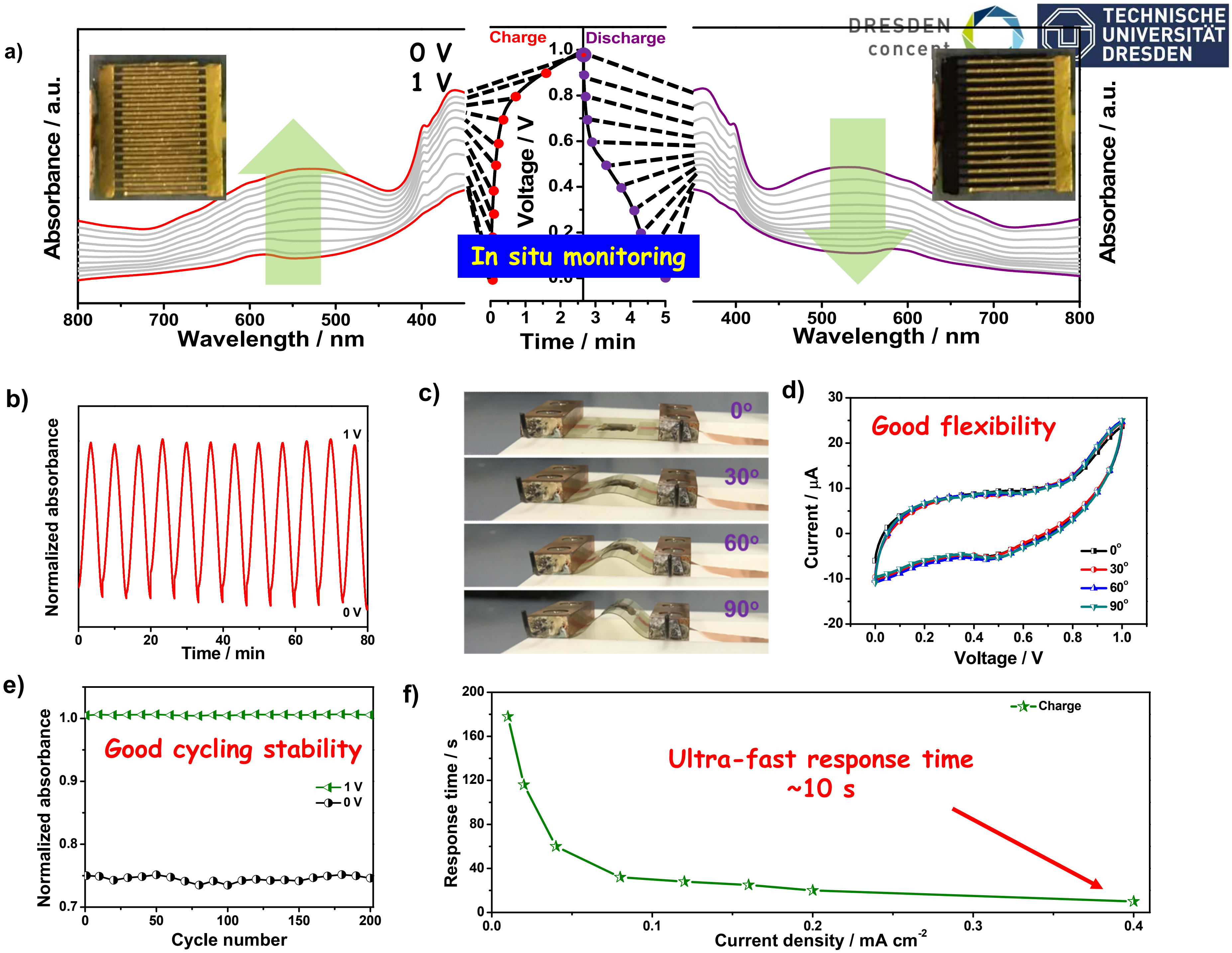
- ✓ Viologen (a) was added to electrolyte and acted as electrochromic materials
- ✓ The thickness of EG/V2O5 nanofilm is 300 nm (c)
- ✓ Transparent (d, e) and flexible (e) substrates were used

Adv. Mater. **2017**, 29 (7), 1604491.



- ✓ Based on CV, C_V for EG/V_2O_5-MSC reached 130.7 F cm^{-3} at the rate of 10 mV s^{-1};
- ✓ No IR drop was observed for EG/V_2O_5-MSC;
- ✓ Based on GCD, 2.3 mF cm^{-2} and 76.7 F cm^{-3} at 0.02 mA cm^{-2} was found;
- ✓ EG/V_2O_5-MSC exhibited lower charge transfer resistance (13.2 Ω) than that for V_2O_5-MSC (18.3 Ω), suggesting rapid ion transport for EG/V_2O_5-MSC.

Adv. Mater. **2017**, 29 (7), 1604491.



DRESDEN concept
TECHNISCHE UNIVERSITÄT DRESDEN
a)
Absorbance / a.u.
0 V
1 V
Charge
Discharge
Voltage / V
In situ monitoring
Wavelength / nm
Time / min
b)
Normalized absorbance
1 V
0 V
Time / min
c)
0°
30°
60°
90°
d)
Good flexibility
Current / μA
Voltage / V
e)
Normalized absorbance
Good cycling stability
1 V
0 V
Cycle number
f)
Charge
Response time / s
Ultra-fast response time
~10 s
Current density / mA cm-2

DRESDEN concept TECHNISCHE UNIVERSITÄT DRESDEN

Conclusion and Outlook:

- **2D materials have show obvious advantages for thin-films based ASSSs and MSCs.**
- **Call for development of new capacitive 2D materials**
- **New nano-processing methods for MSCs.**
- **New functions, e.g. stimulus-responsive properties, are the trend.**

Acknowledgement

Panpan Zhang
Chongqing Yang
Hongyan Li
Zhaoquan Yao
Yafei He
Chenbao Lu
Wenbei Zhang
Dr. Feng Zhu
Dr. Kai Yuan
Dr. Wuxue Zhao
Dr. F. Ortmann

Prof. Xinliang Feng (TUD)
Prof. Fan Zhang (SJTU)
Prof. K. Müllen (Mainz)
Prof. M. Bonn (Mainz)
Prof. Oliver G. Schmidt
Prof. Ullrich Scherf (Wuppertal)
Prof. M.R. Hansen (Münster)
Prof. F. Laquai (KAUST)
Prof. G. Cuniberti (Dresden)
Prof. G. Seifert (Dresden)

Funding Supports

DFG, BMBF, BASF, UPGRADE, Insolcell, ERC NANOGRAPH, ERC 2DMATER, Graphene Flagship, Cfaed Cluster, Talga, ESF

Thank You for Your Attention!

TECHNISCHE UNIVERSITÄT DRESDEN

Founded in 1828
Excellence University
Center for Advancing Electronics Dresden