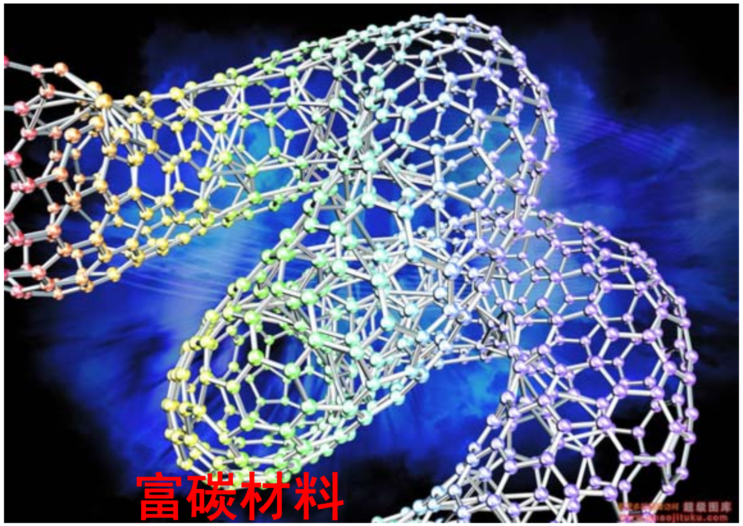
富碳及石墨炔材料的聚集态结构与性质

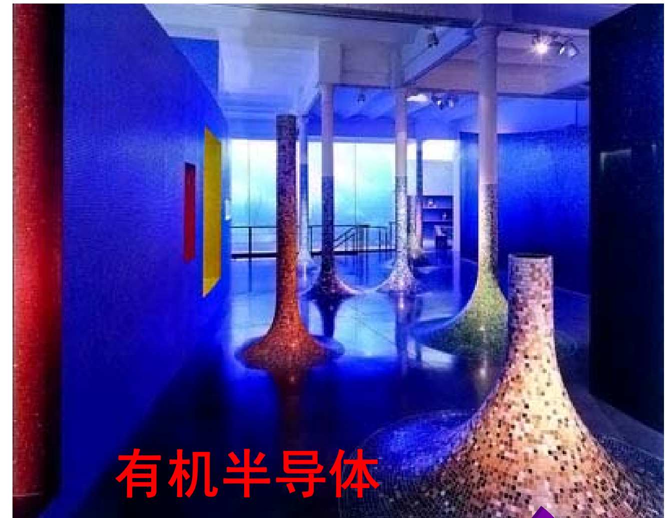
李玉良

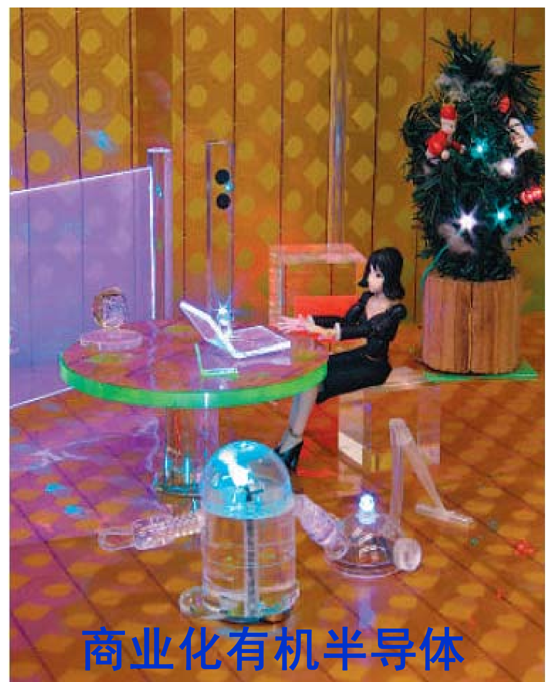
中国科学院化学研究所

2012.12.13

合成化学 → 新物质

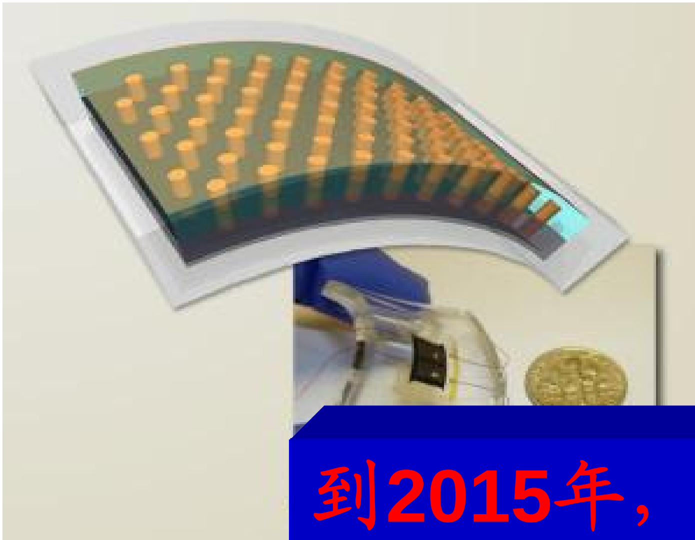

富碳材料


有机半导体

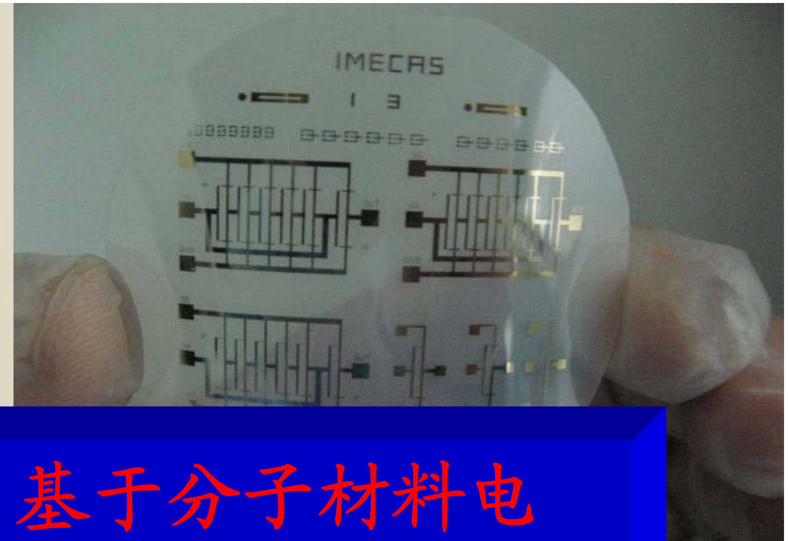

商业化有机半导体


Science
21 December 2001
Vol. 294 No. 5551
Pages 2417–2616 $9
Breakthrough of the Year
有机电子学
American Association for the Advancement of Science

可控自组装将成为21世纪新型分子材料发展的关键

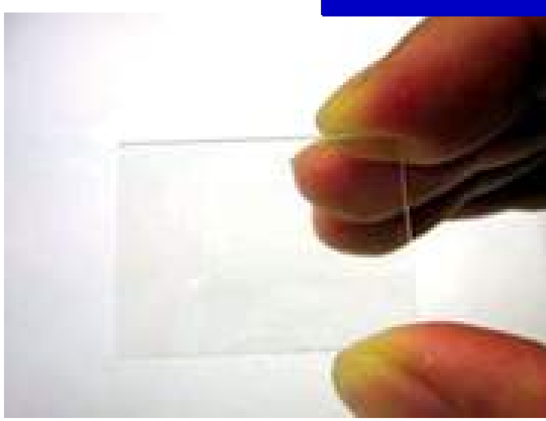


大面积阵列太阳

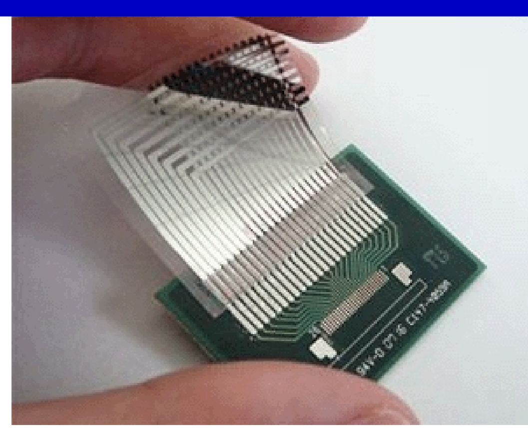


料电路

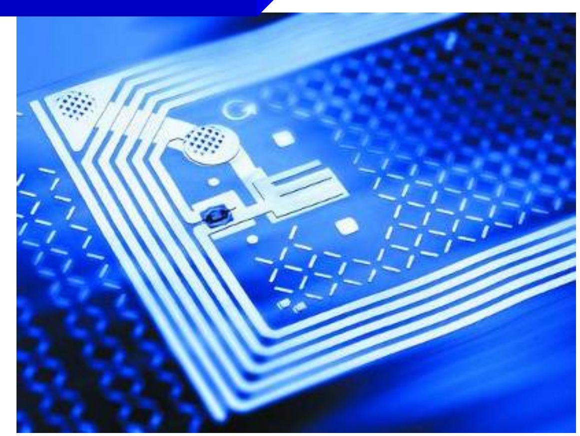
到2015年，基于分子材料电子器件的市场将达216亿美元



分子材料电存储器



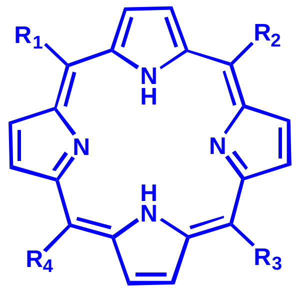
新型柔性分子材料记忆器



分子材料电子标签

有机电子学发展趋势

富碳材料



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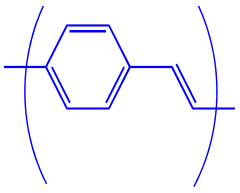

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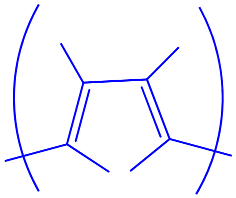

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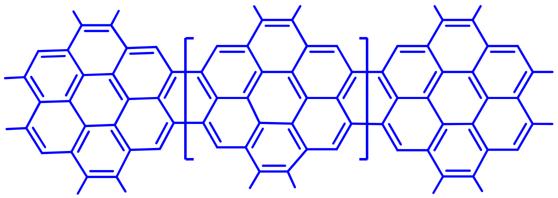

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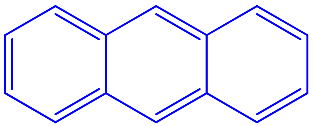

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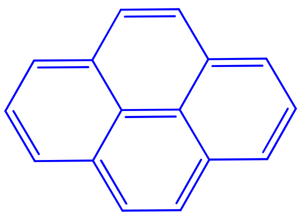

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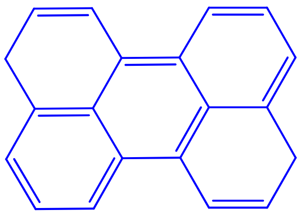

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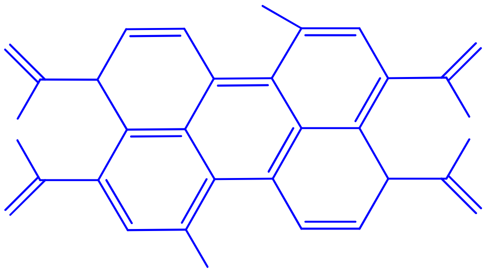

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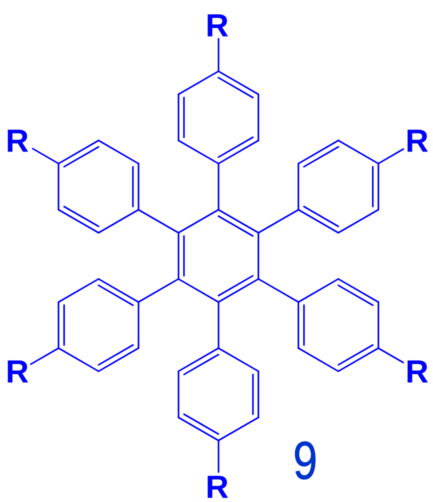

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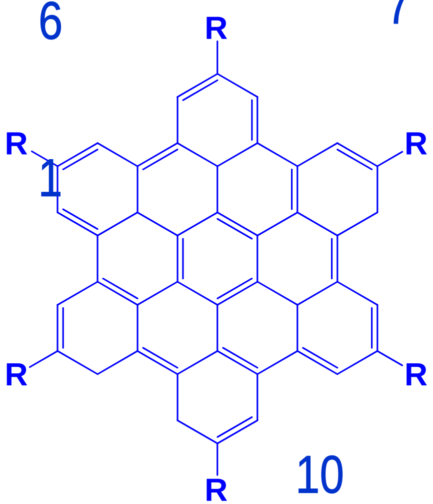

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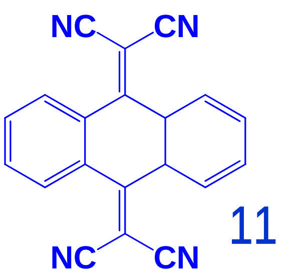

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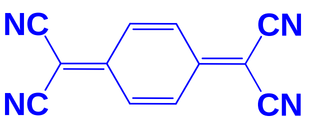

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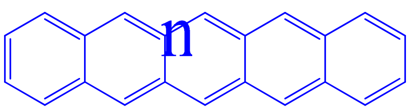

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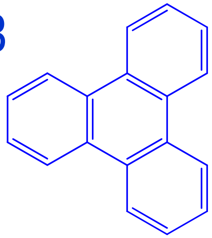
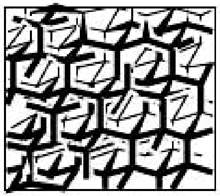
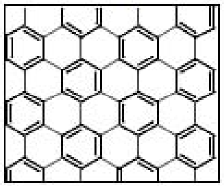


14

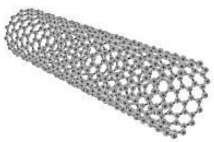
全碳材料



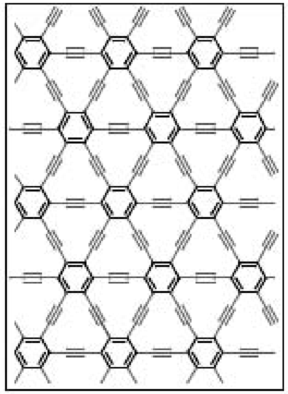
diamond



graphite



C_{60}



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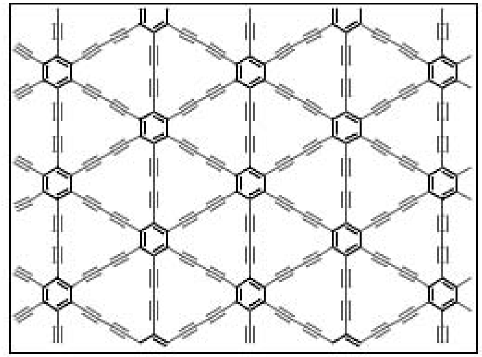

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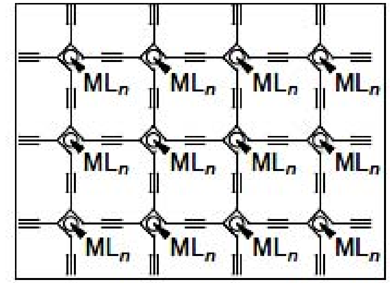

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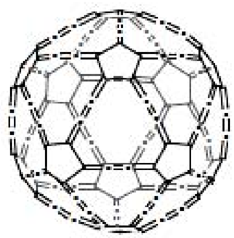

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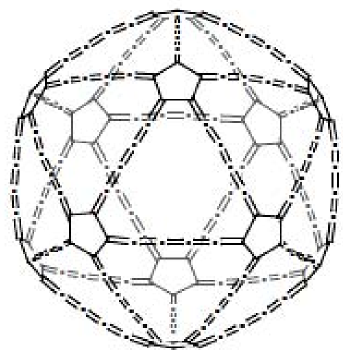

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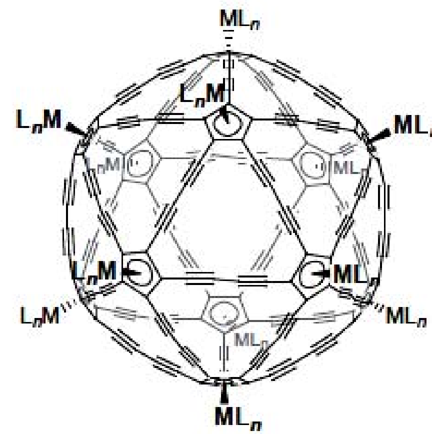

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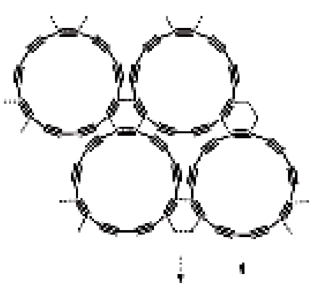
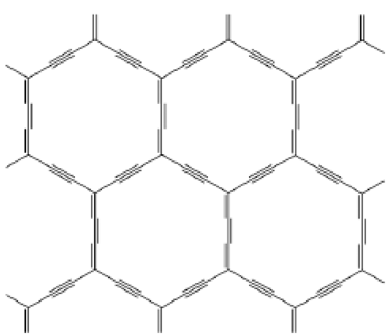
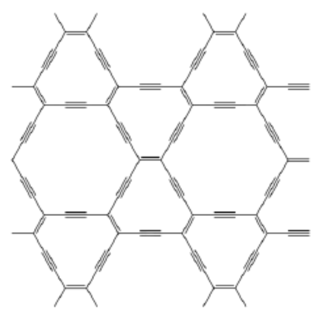
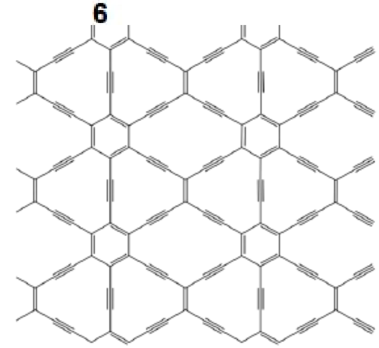
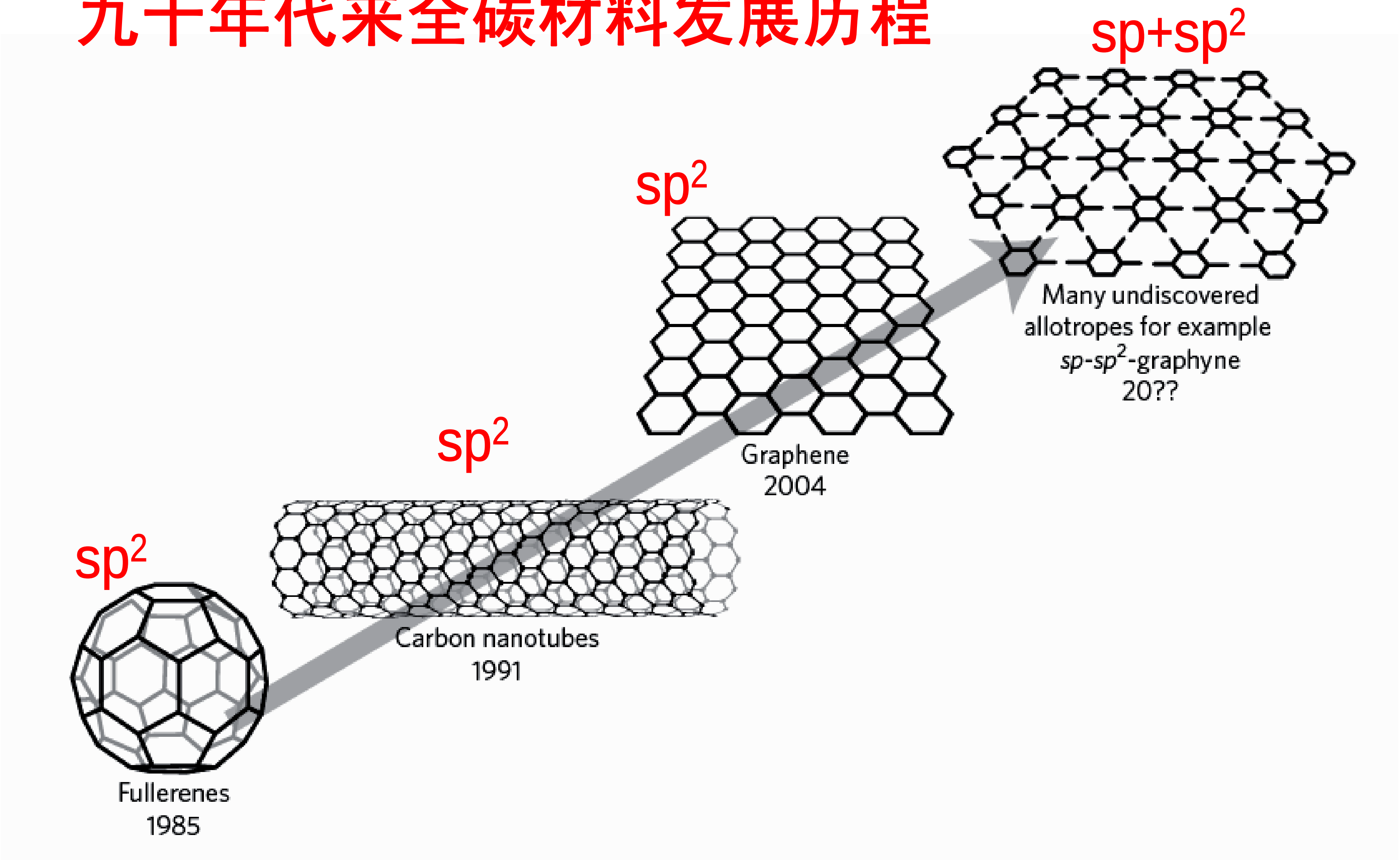






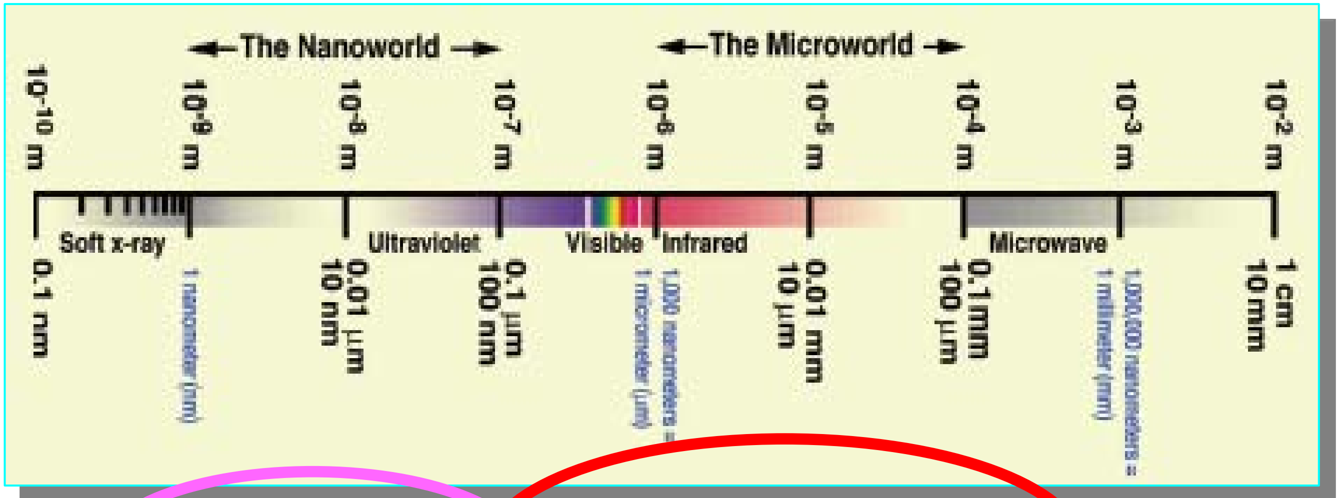


九十年代来全碳材料发展历程

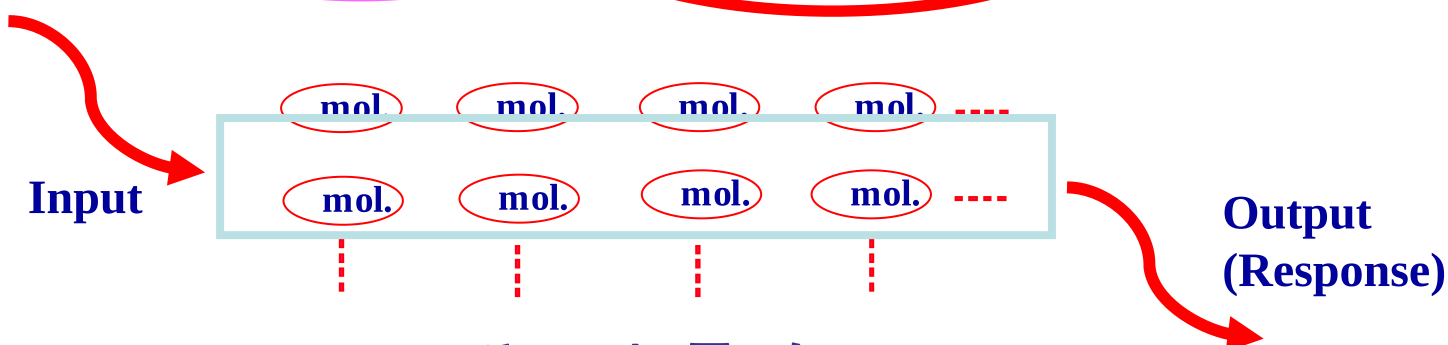


Andreas Hirsch, *Nature Materials* 2010, 9, 868

聚集态材料发展中的重要科学问题



单分子　　分子聚集体材料　　功能材料



分子凝聚态

富碳分子材料发展途径

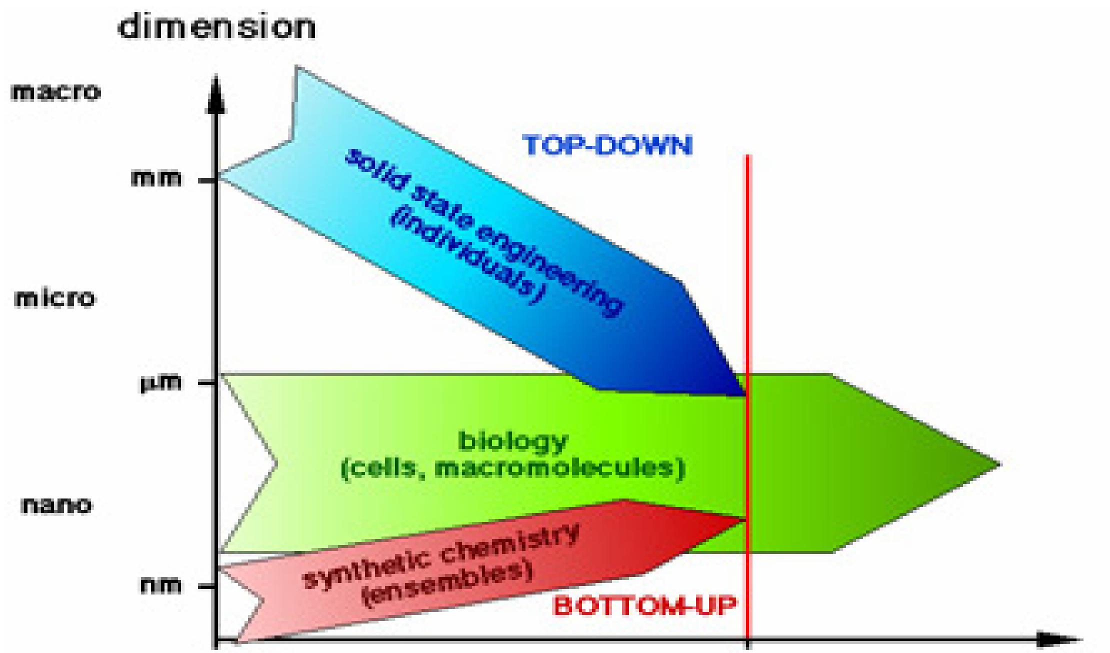
富碳分子材料设计；自组装方法学；表征技术建立；应用及器件。

自上而下

自组装

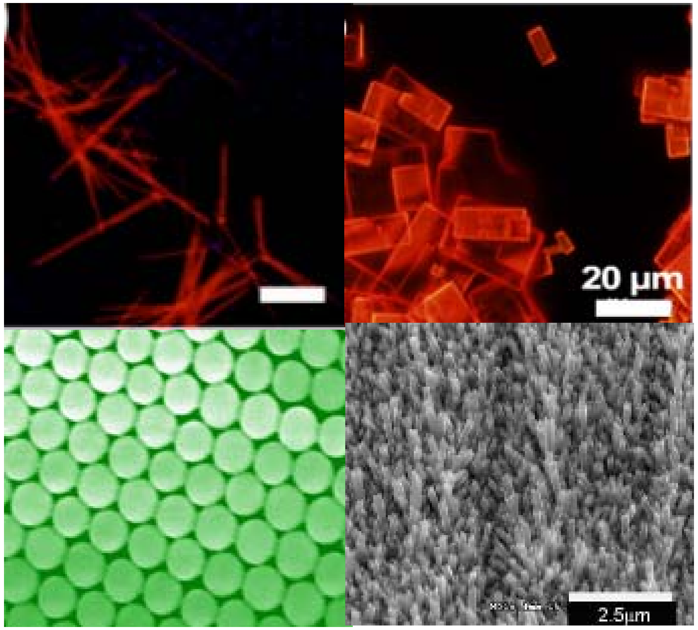
自下而上

核心科学之一：化学



Key Scientific Issues

- Rational Design of Molecules
- Molecular Aggregations
- Fundamental Properties of Molecular Aggregations
- Exhibit New Size-Based Properties
- Physical Measurable

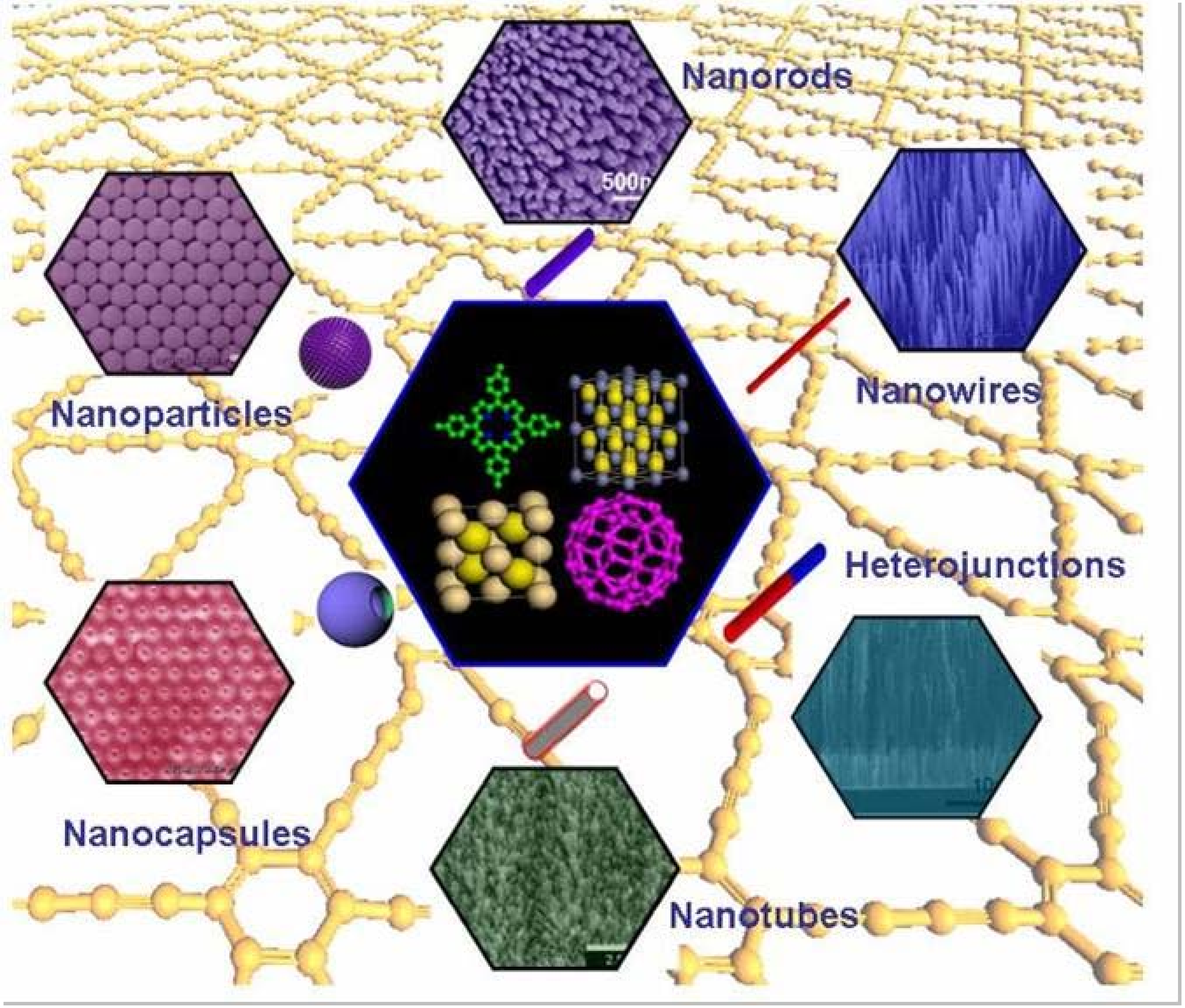


Molecular Aggregation

Function Performance

Supramolecular Electronics

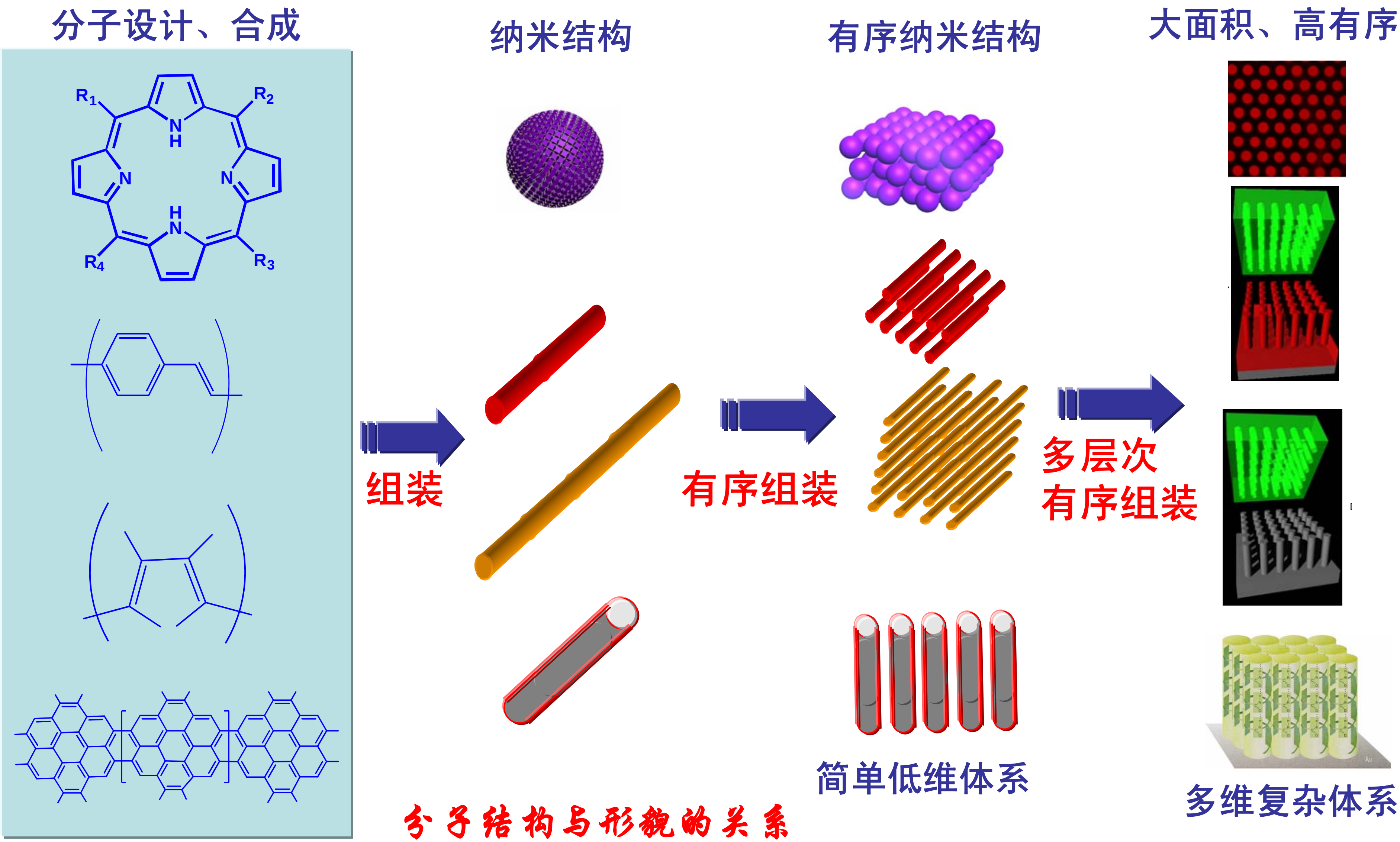
Aggregate Nanostructures of Organic Molecular Materials



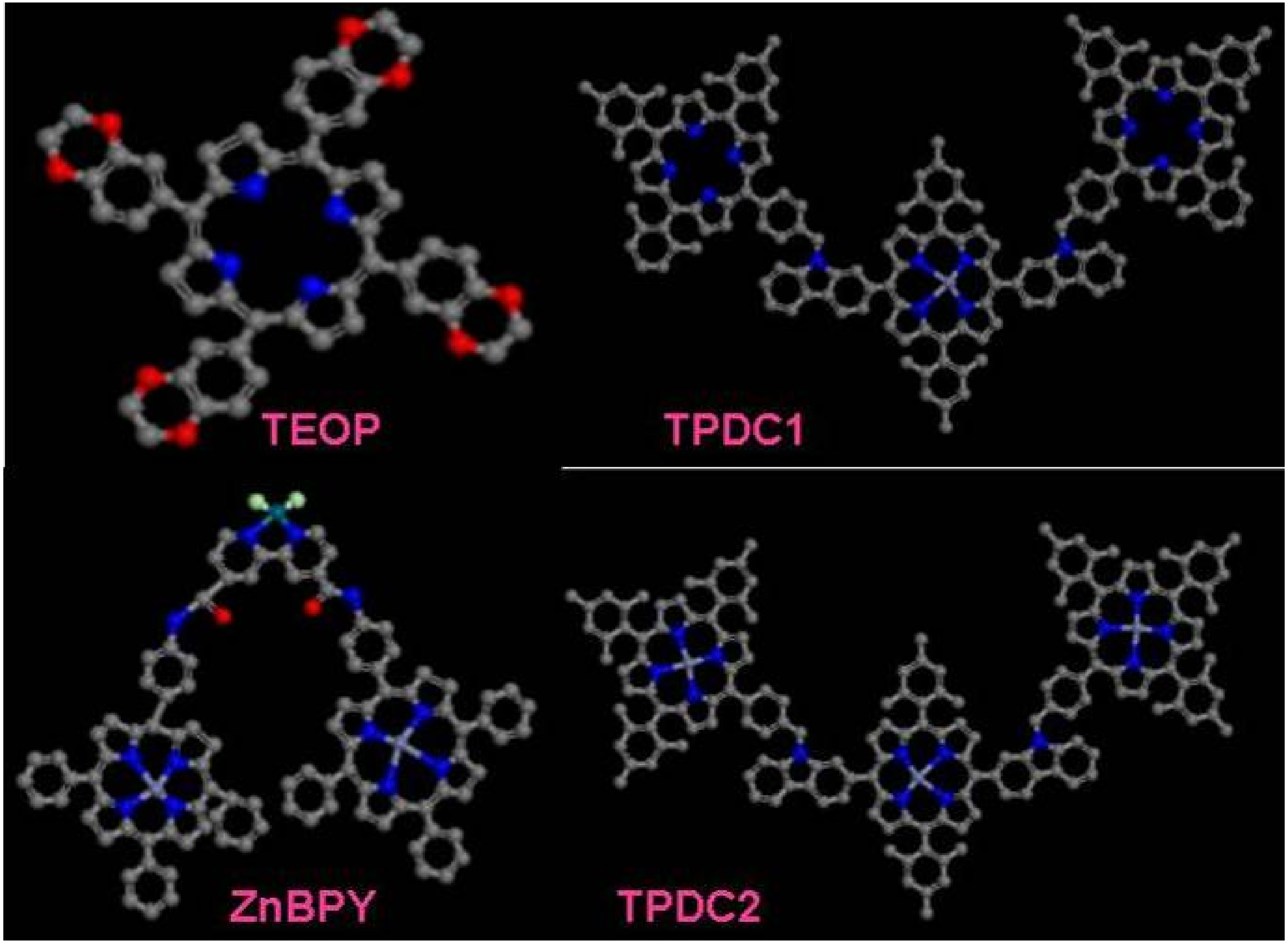
Acc. Chem. Res. 2010, 43, 1496-1508

富碳材料低维聚集态结构的可控组装

大面积、多层次有序纳米结构自组装的构建方法学

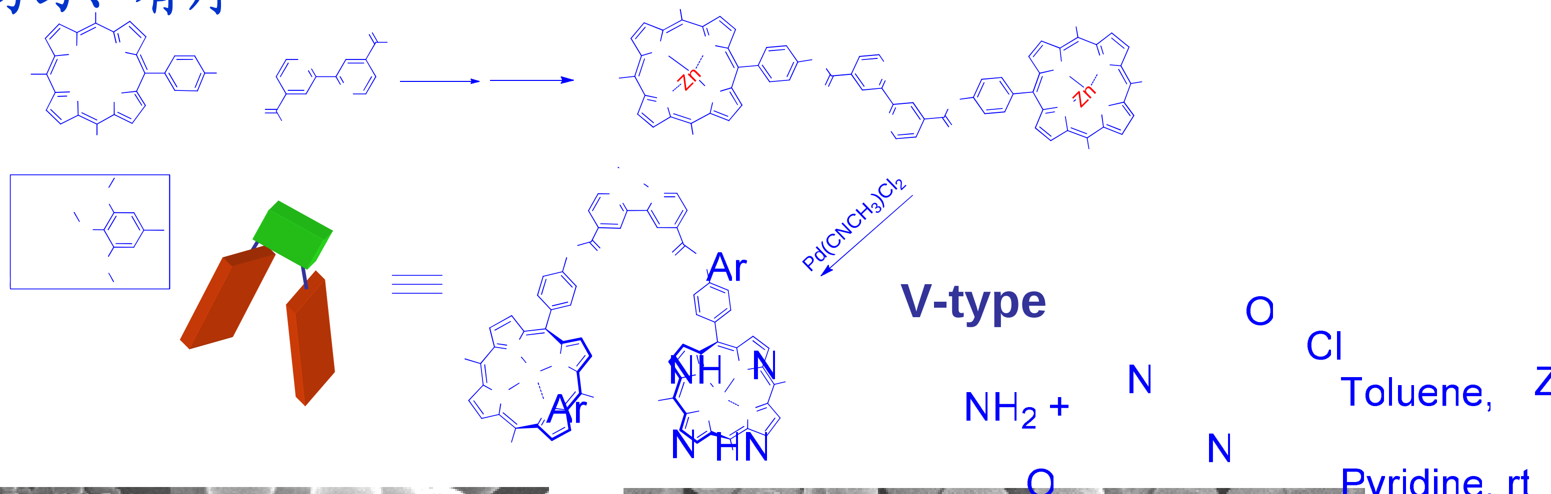


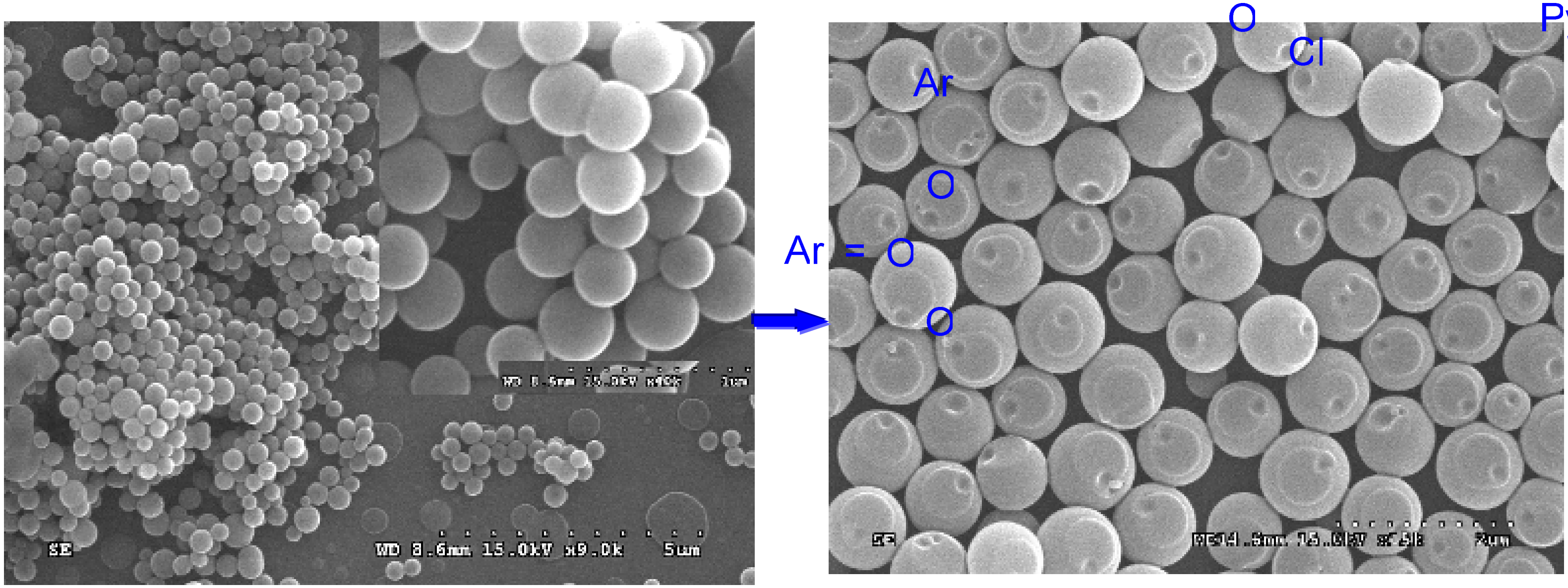
富碳功能分子聚集态结构的可控组装



新型卟啉分子体系的自组装聚集态

形貌的可控、均匀、有序

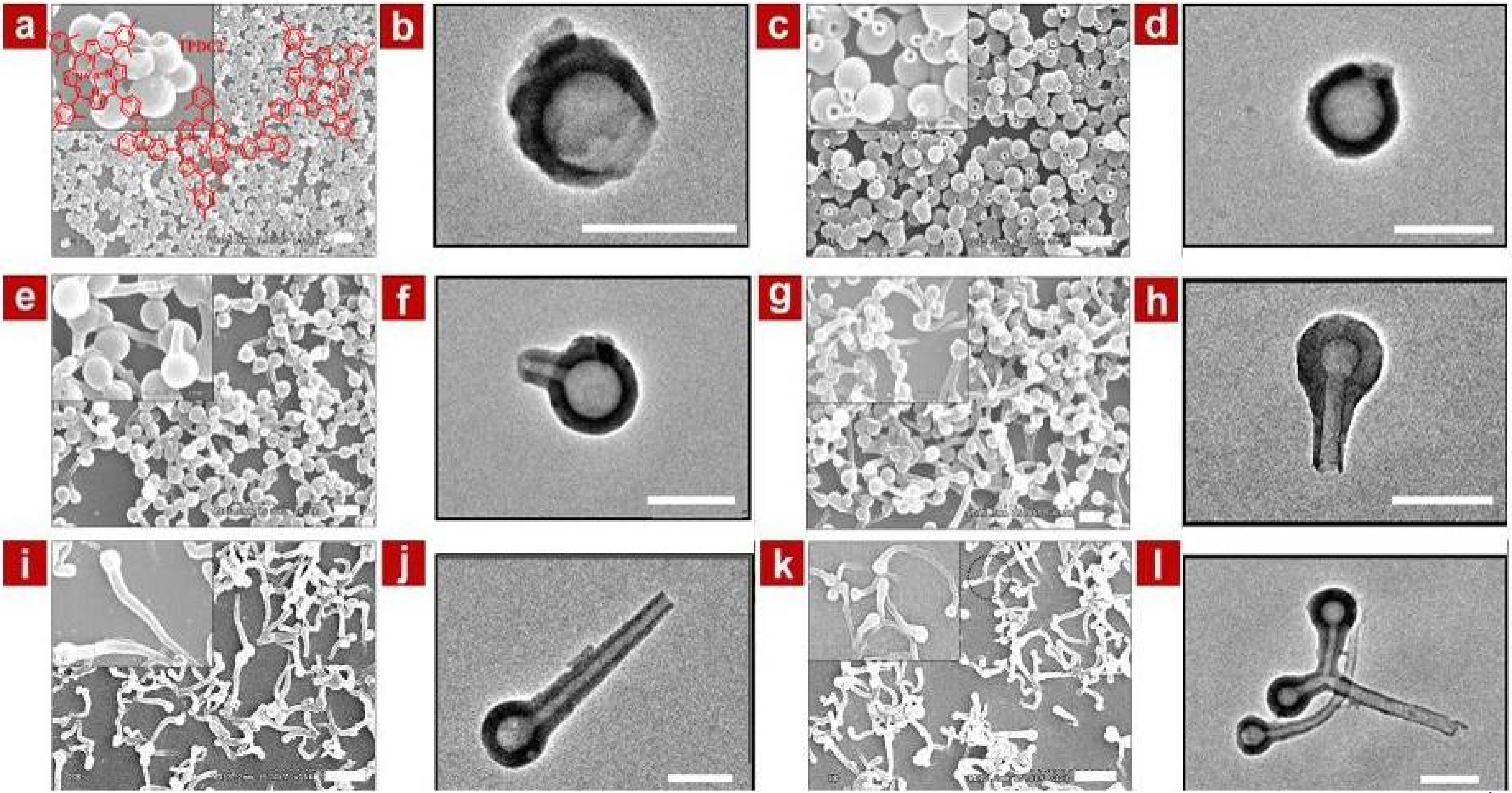




SEM images of BPY-ZnP in $CHCl_3/CH_3OH$(1/1)

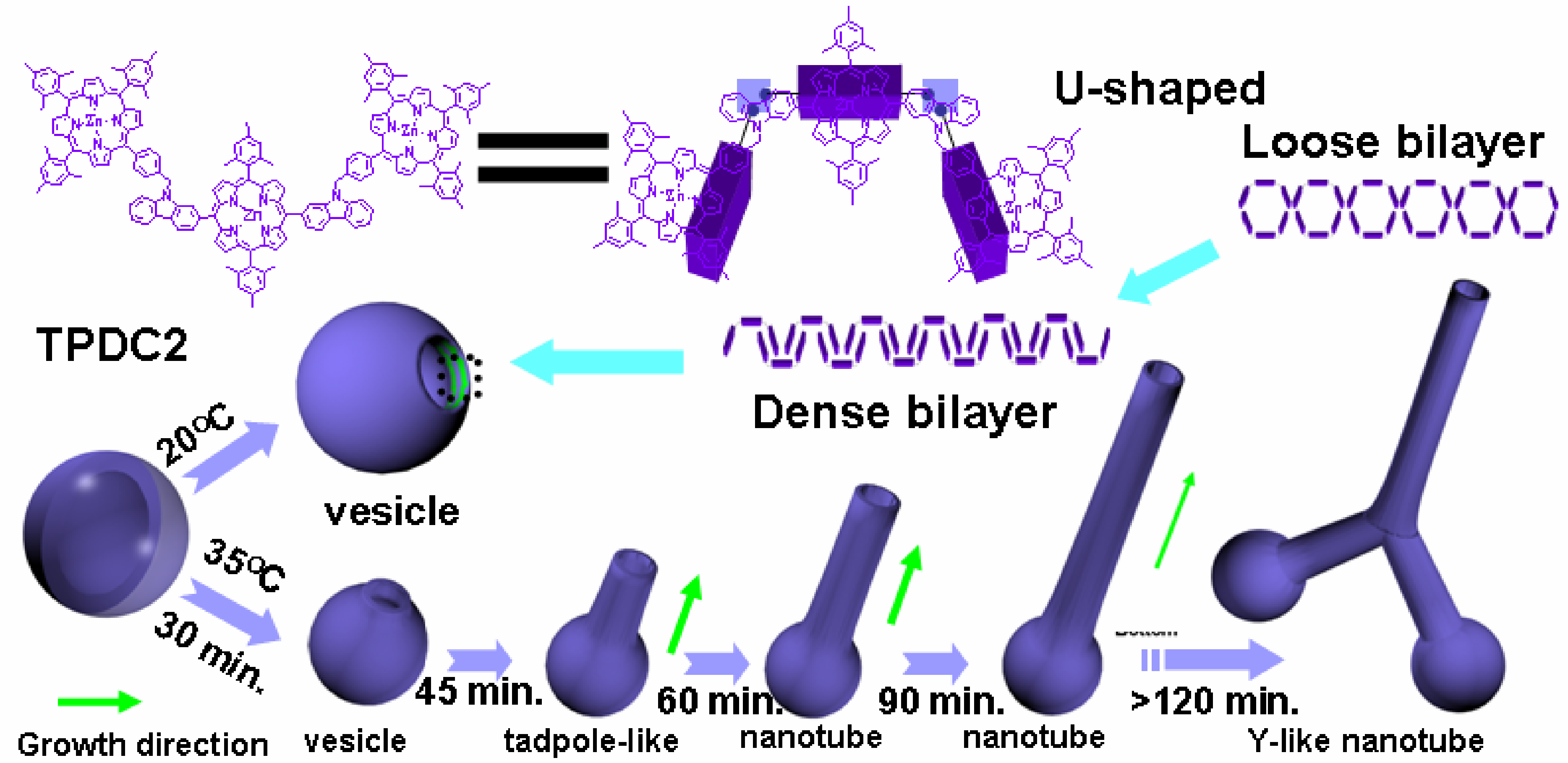
***Angew. Chem. Int. Ed.* 2006, 45, 3639**

卟啉三元体的控制自组装，从一维到多维的纳米结构的自然生长



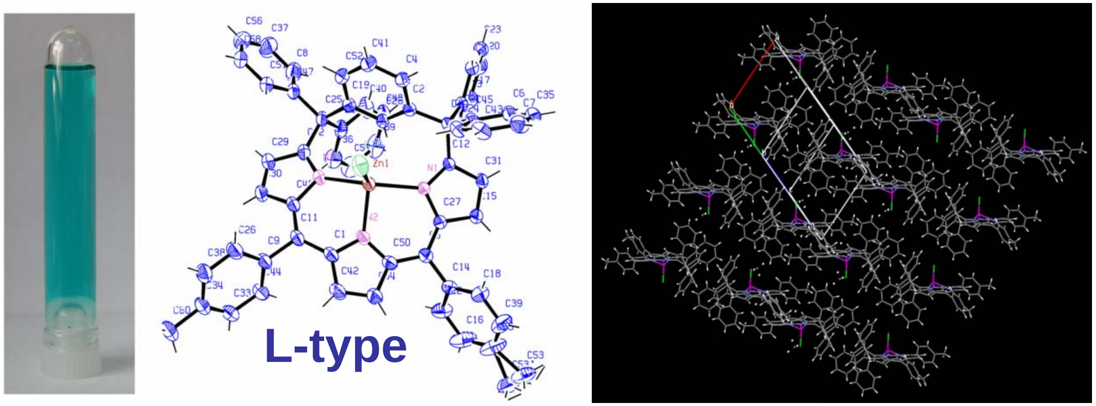
SEM and TEM images of the TPDC2 prepared in CH_2Cl_2/ CH_3OH (1:1) at the temperature of a) b) 20 ° C for 30 min, 35 ° C for c) d) 30 min, e) f) 45 min, g) h) 60 min, i) j) 90 min, and k) l) more than 120 min. The scale bar is 500 nm.

Adv. Mater. **2009, 21, 1721**

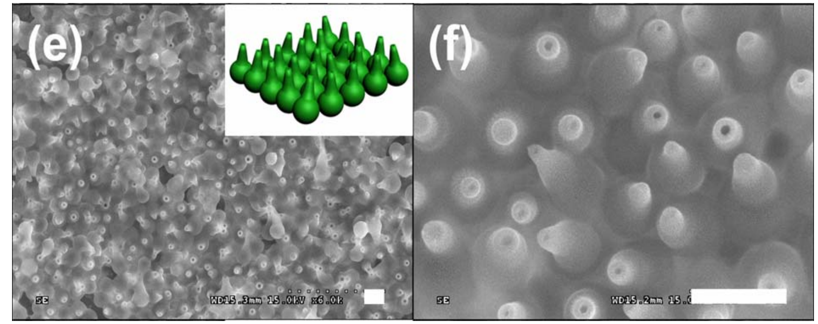


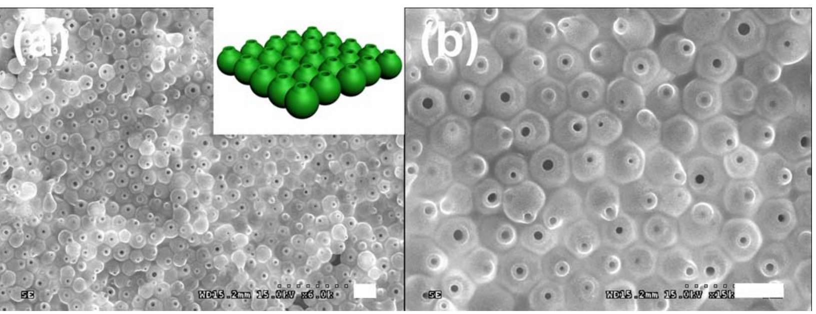
Schematic growth processes of the vesicles and their derivatives.

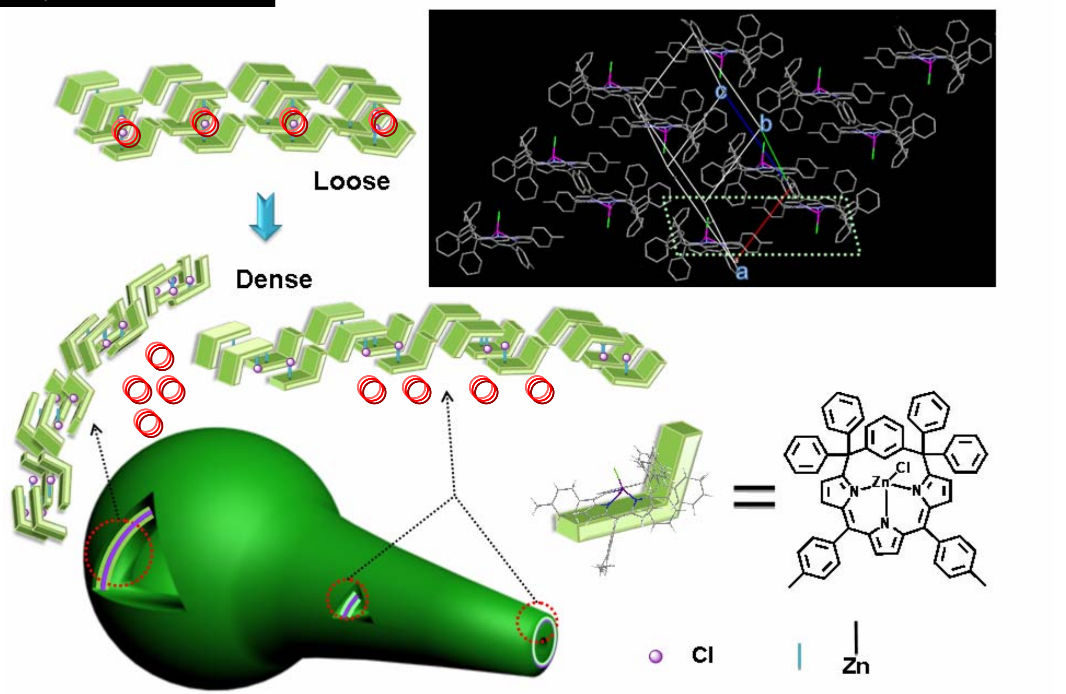
TMBPZnCl的自组装



TMBPZnCl晶体结构



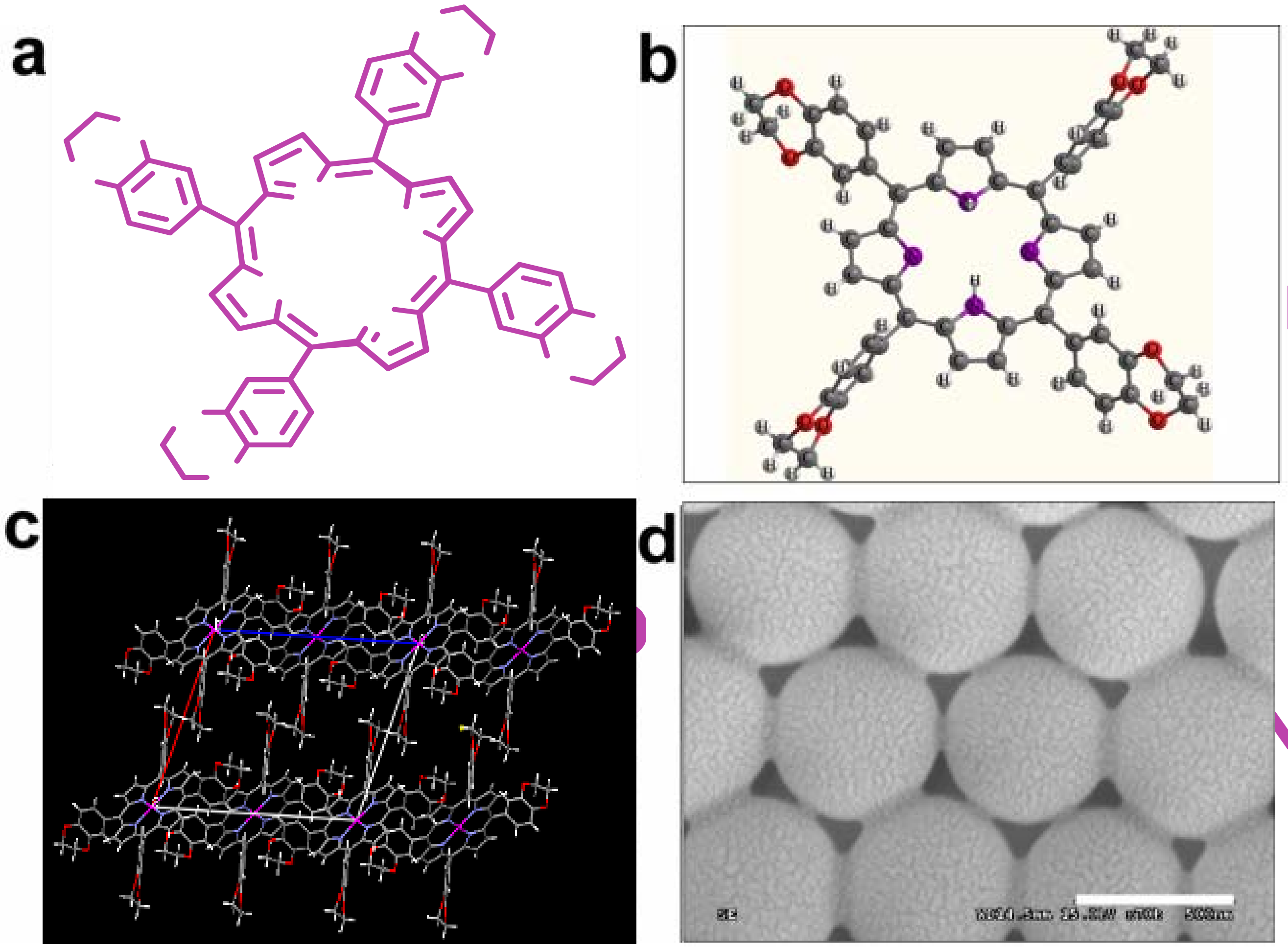




TMBPZnCl 纳米胶囊的自组装过程

Chem. Commun. 2010, 46, 3161

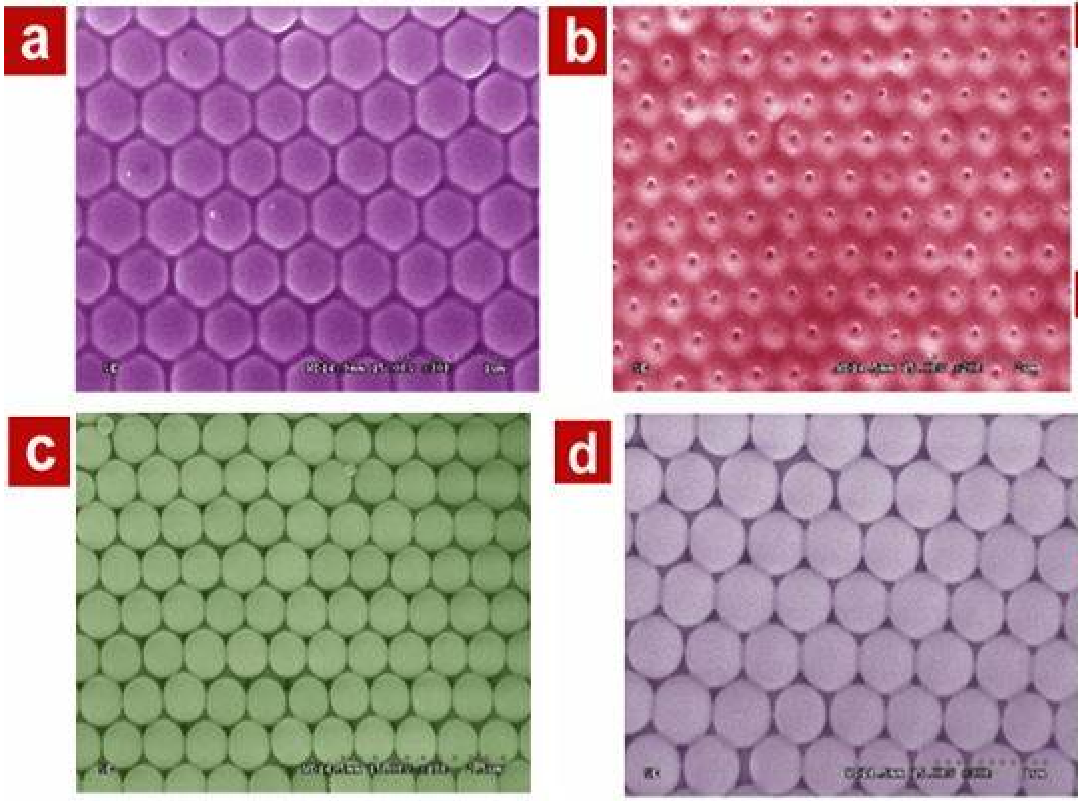
大面积、高有序的卟啉纳米阵列可控组装的构筑



(a) molecular structure of TEOP, (b-c) Crystal structure, (d) SEM images of TEOP pattern with well-ordered morphologies. Scale bars: 500 nm.

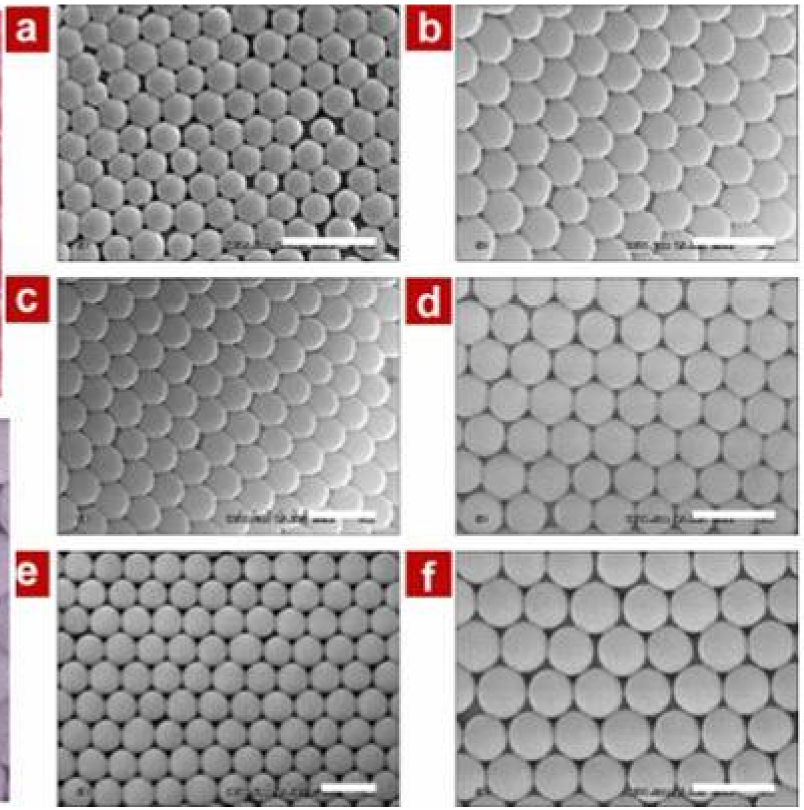
Adv. Mater. 2010, 22, 3532, Acc. Chem. Res. 2010, 43, 1496

形貌可控的有序阵列



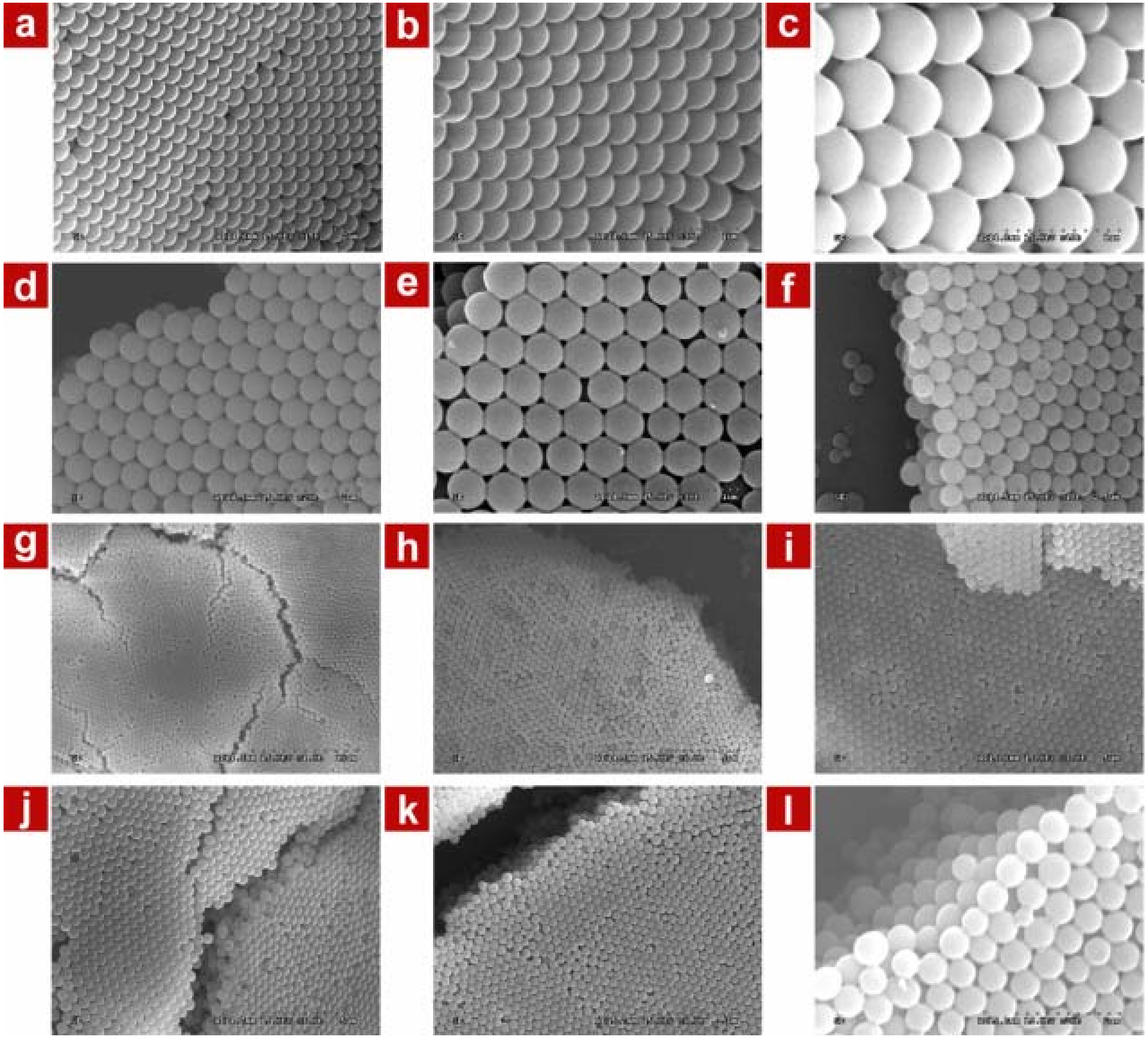
SEM images of TEOP film pattern with different well-ordered morphologies (a) from 30 to 40 ° C, chloroform: isopropanol: water =10:10:2, (b) from 20 to 40 ° C, (c) 30 ° C, chloroform and isopropanol, (d) 30 ° C, chloroform: isopropanol: water = 10:10:0.5. Scale bars: 1 μm.

尺寸可控



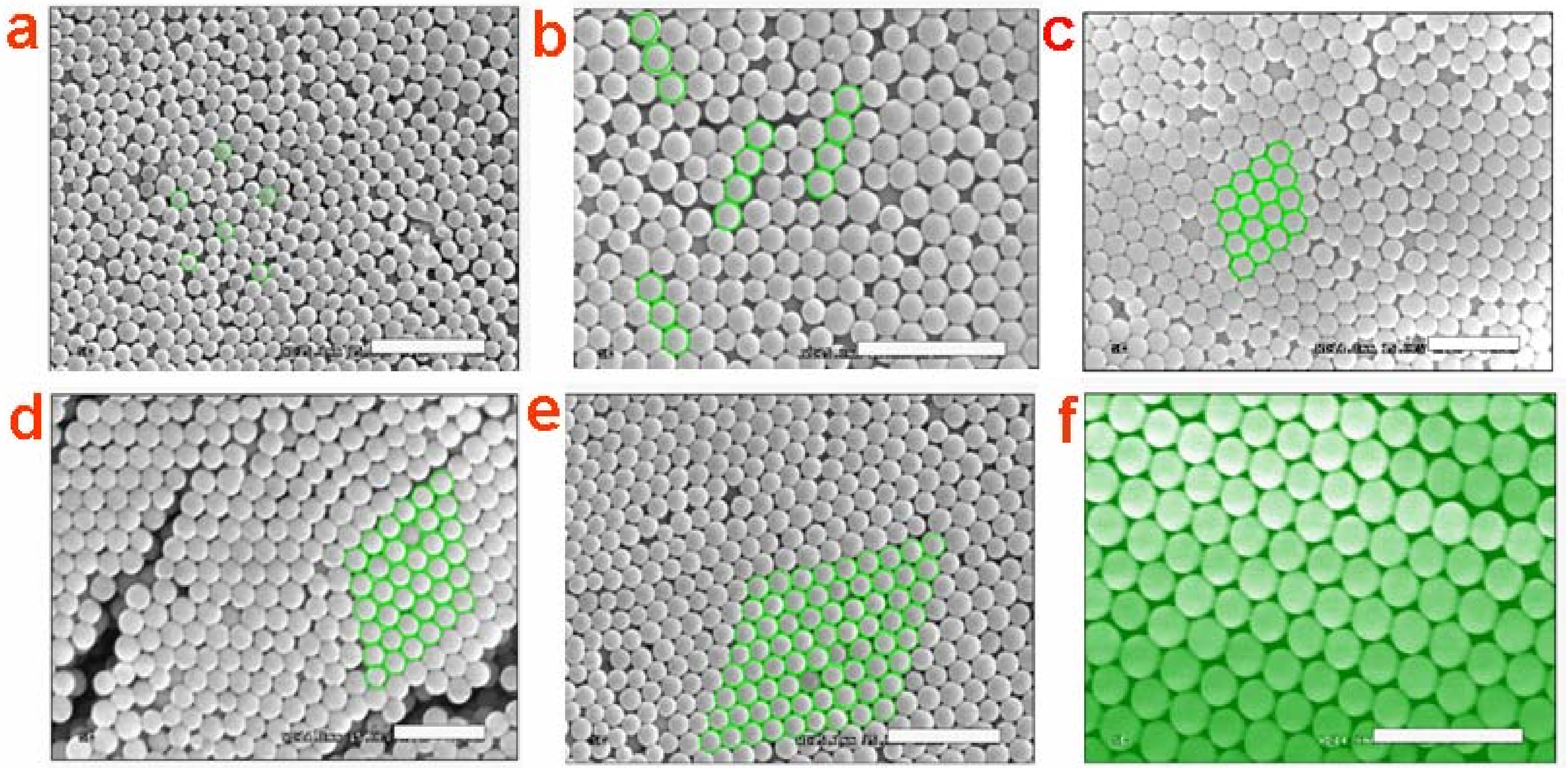
SEM surface images of TEOP ordered pattern film.

维数可控



SEM images of TEOP nanoparticles film (a-c) single layer, (d) bilayer assembly, (e) tetralayer assembly (f) trilayer assembly, (g) top surface, (h) cleaved edges, (i) layer by layer, (j-l) multilayer. chloroform: isopropanol: water =10:10:1

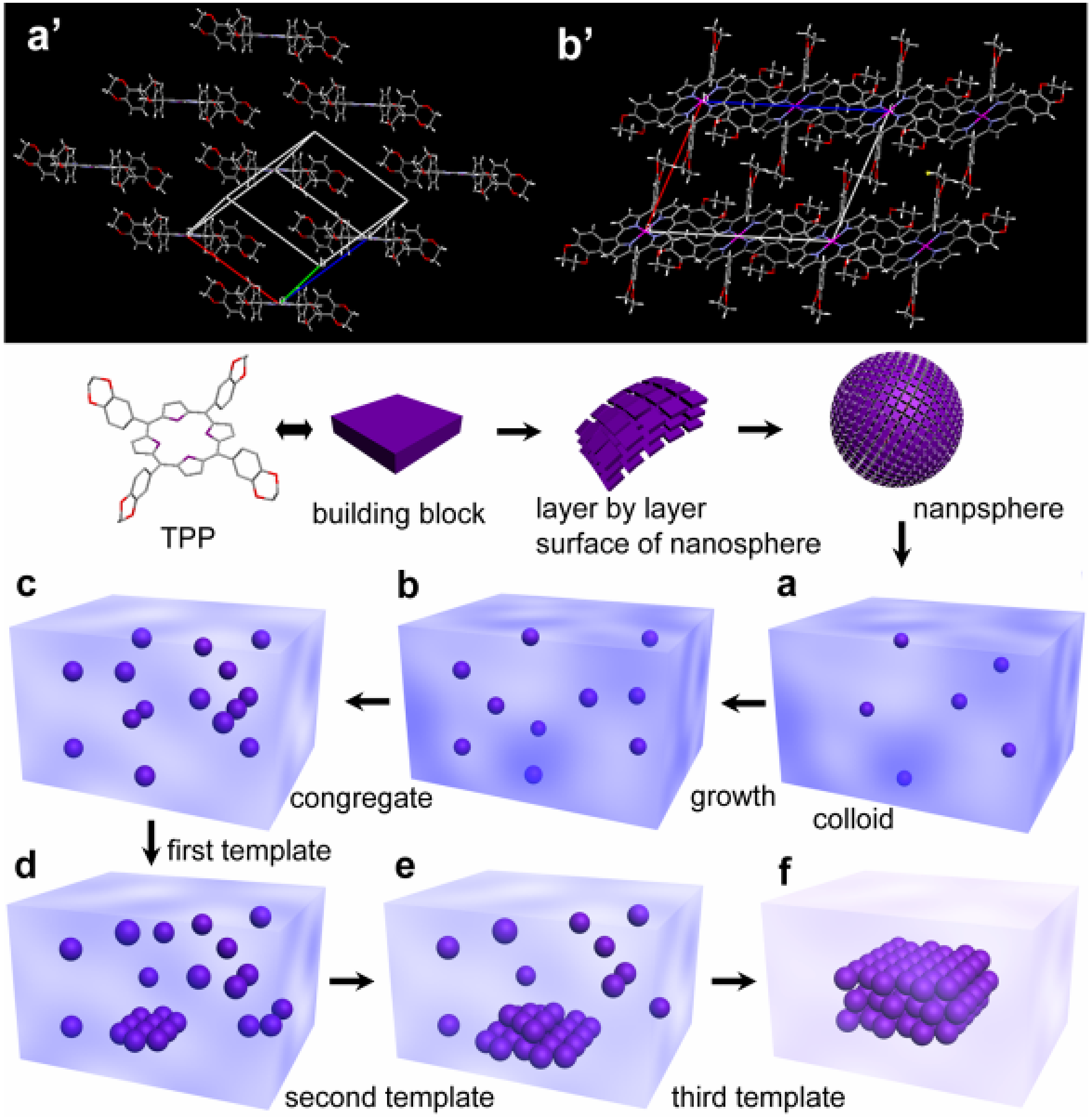
组装有序性可控



SEM images of TEOP pattern prepared by thermal treatment mode Ⅰ in (a) 5 min, (b) 6 min, (c) 7 min, (d) 8 min, (e) 9 min, (f) 10 minScale bars: 2 μm.

Adv. Mater. 2010, 22, 3532

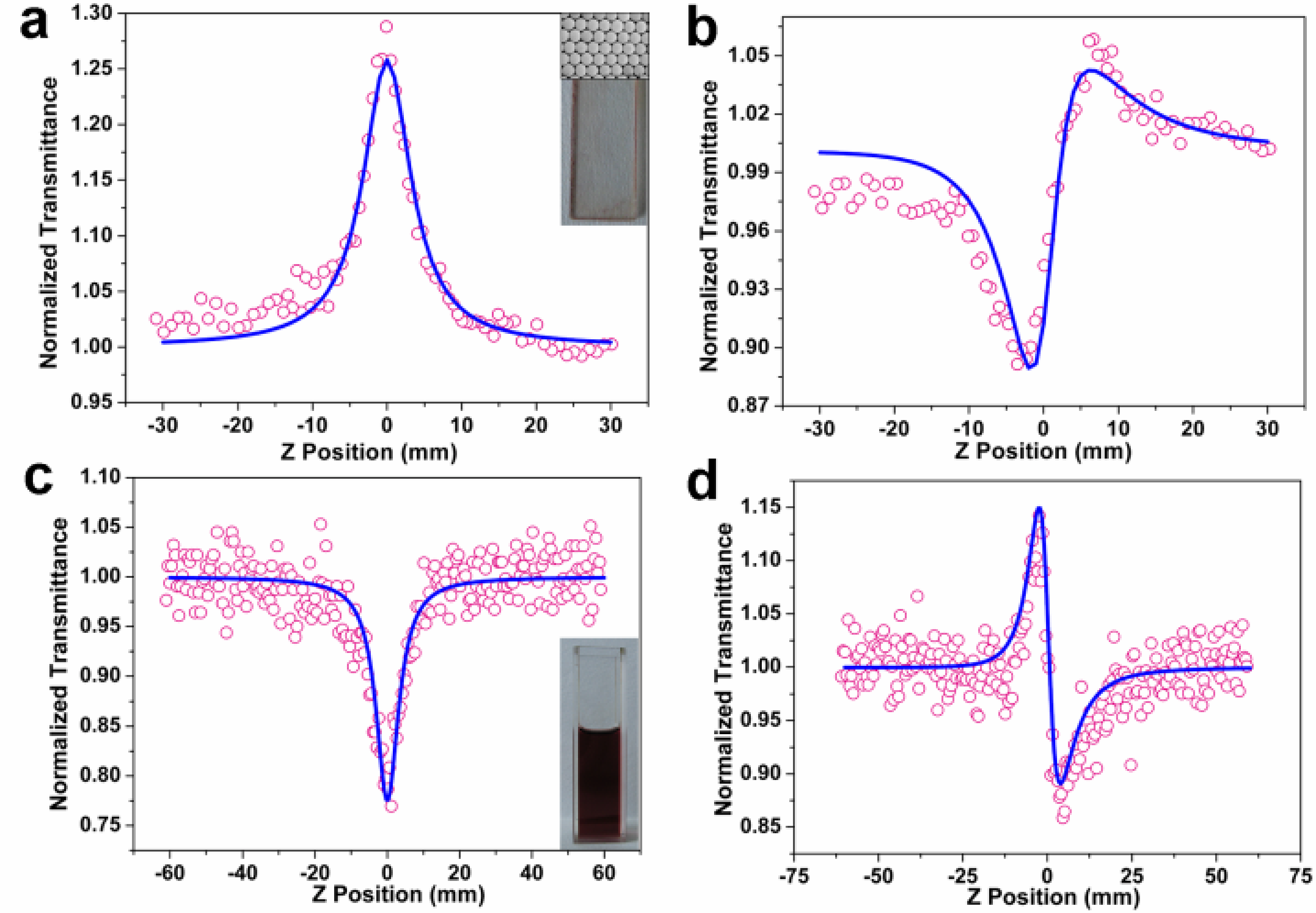
组装机理



Schematic outline of the growth and assembly procedure of TEOP film with ordered pattern. The inset depicts the crystal structure of ZnTEOP

$\beta = -4.3\times10^{-6}$ m/W $\quad$ $n_2 = 2.8\times10^{-13}$ m^2/W

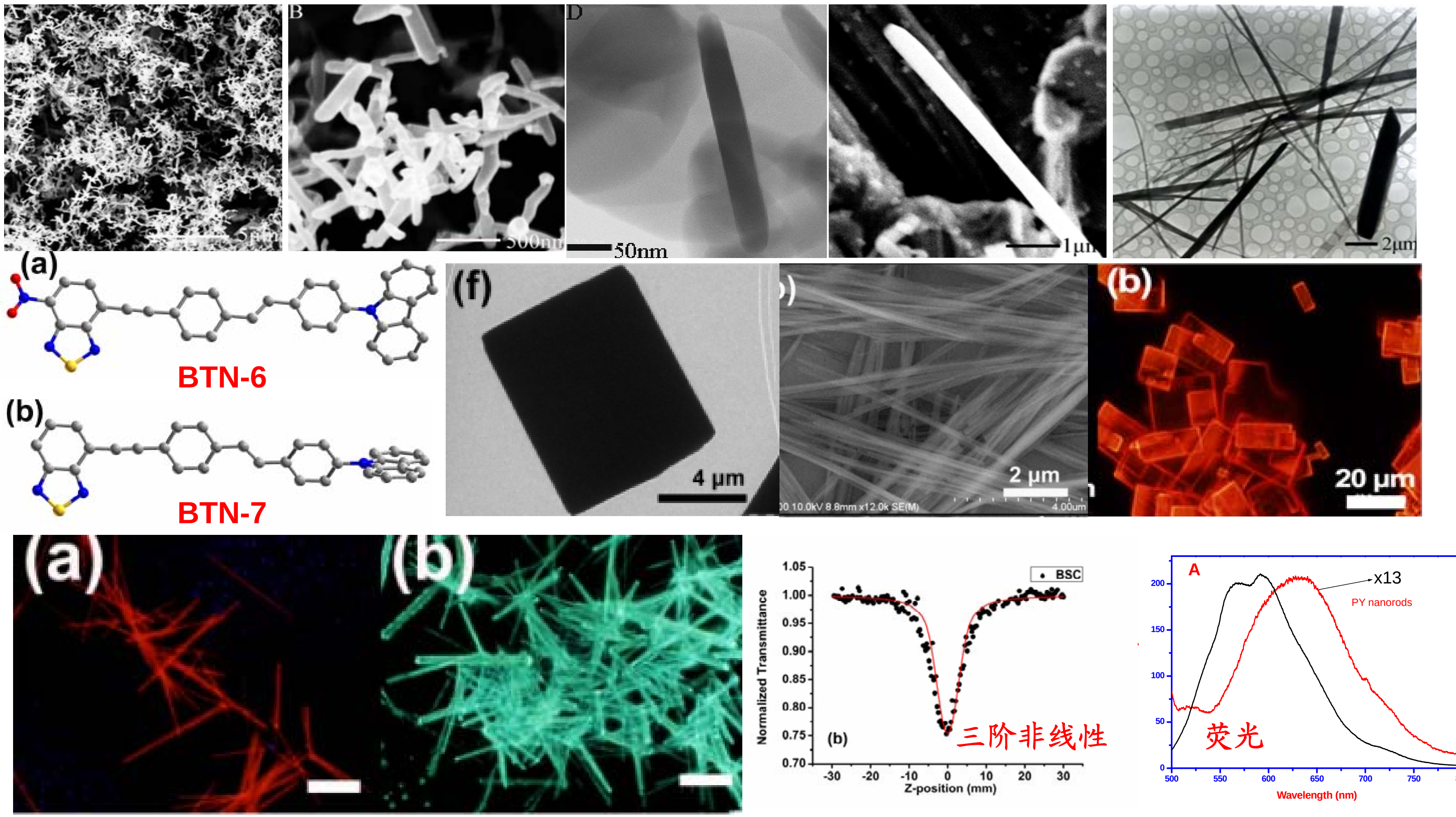
性能可控



$\beta = 1.5\times10^{-9}$ m/W $\quad$ $n_2 = -2.53\times10^{-16}$ m^2/W

Nonlinear optical properties of TPP (a) NLO absorptive properties of the TPP well-ordered film under an open-aperture configuration and (b) the closed-aperture configuration, (c) NLO absorptive properties of the TPP solution under an open-aperture configuration and (d) the closed-aperture configuration.

富碳分子聚集态纳米结构的可控生长及其性质



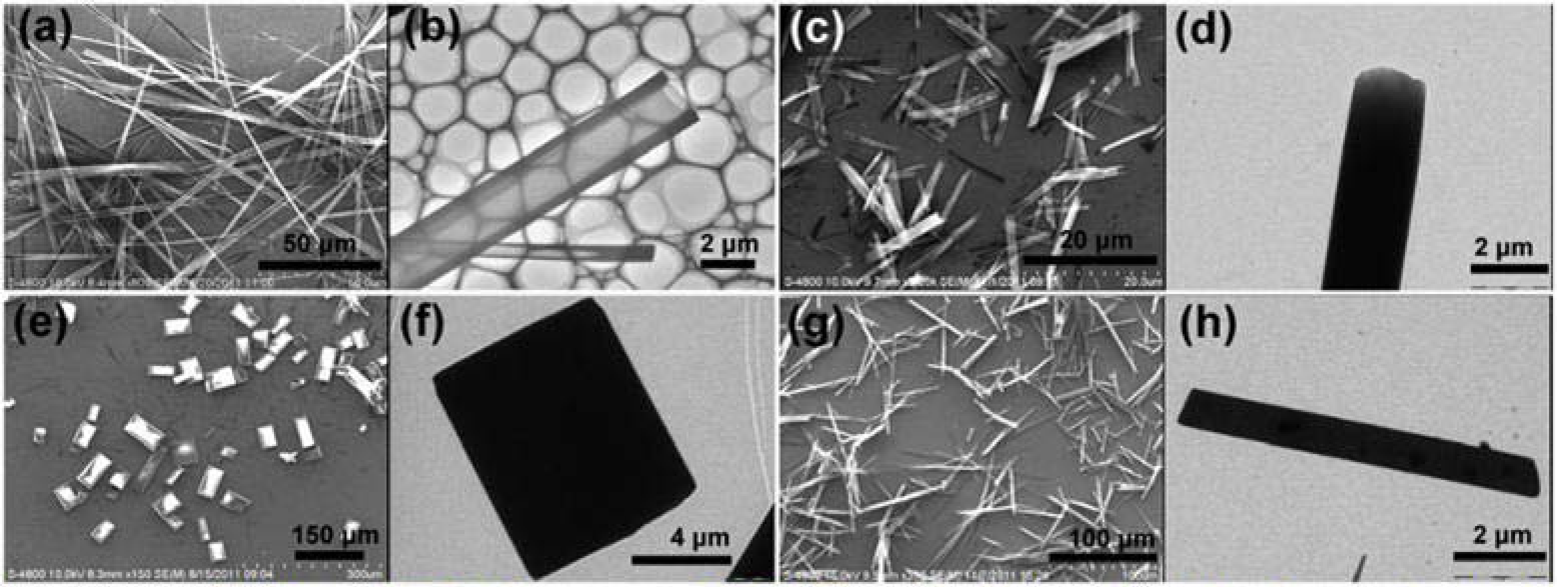
分子材料聚集态纳米结构的调控与光学性质的维数效应

J. Am. Chem. Soc. 2005, 127, 12452

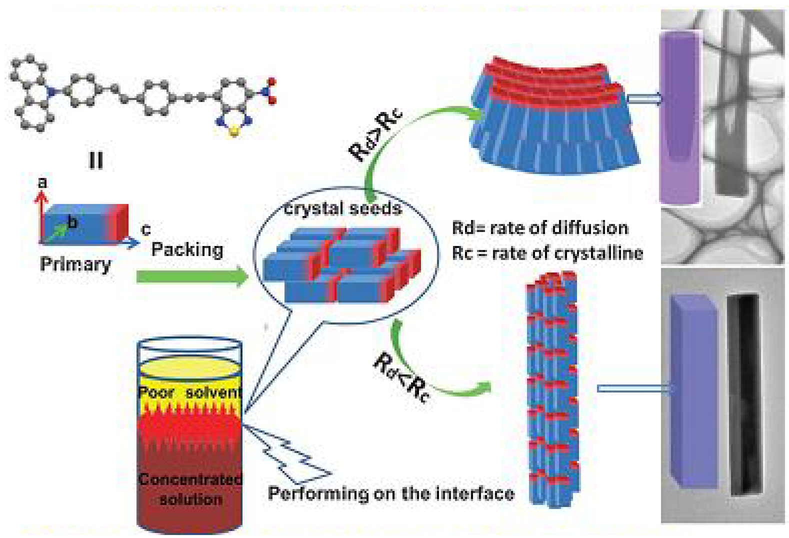
Chem Commun. 2012，48, 9011

J. Am. Chem. Soc. 2003，125, 10794

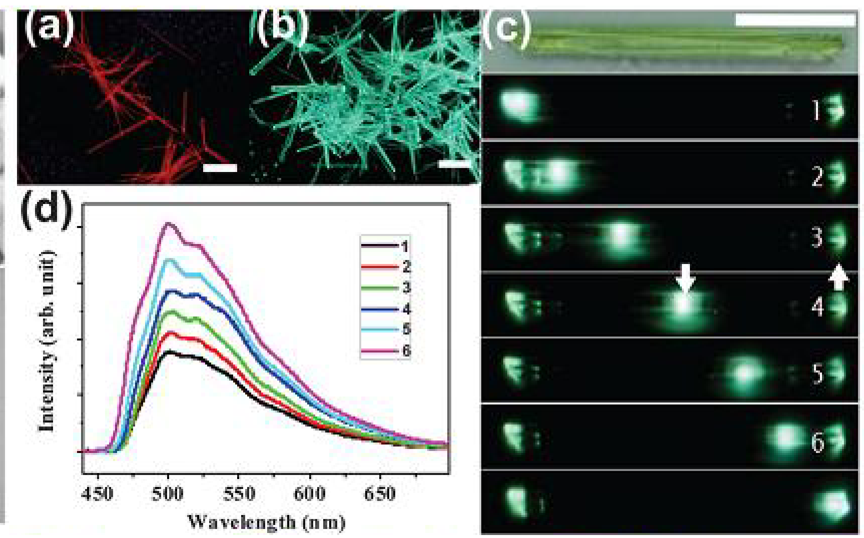
J. Am. Chem. Soc. 2002,124, 13370



Large-area SEM and TEM images of BTN-6: microtubes (a–b), microrods (c–d), microcrystals (e–f). Microrod structure of BTN-7 (g–h).



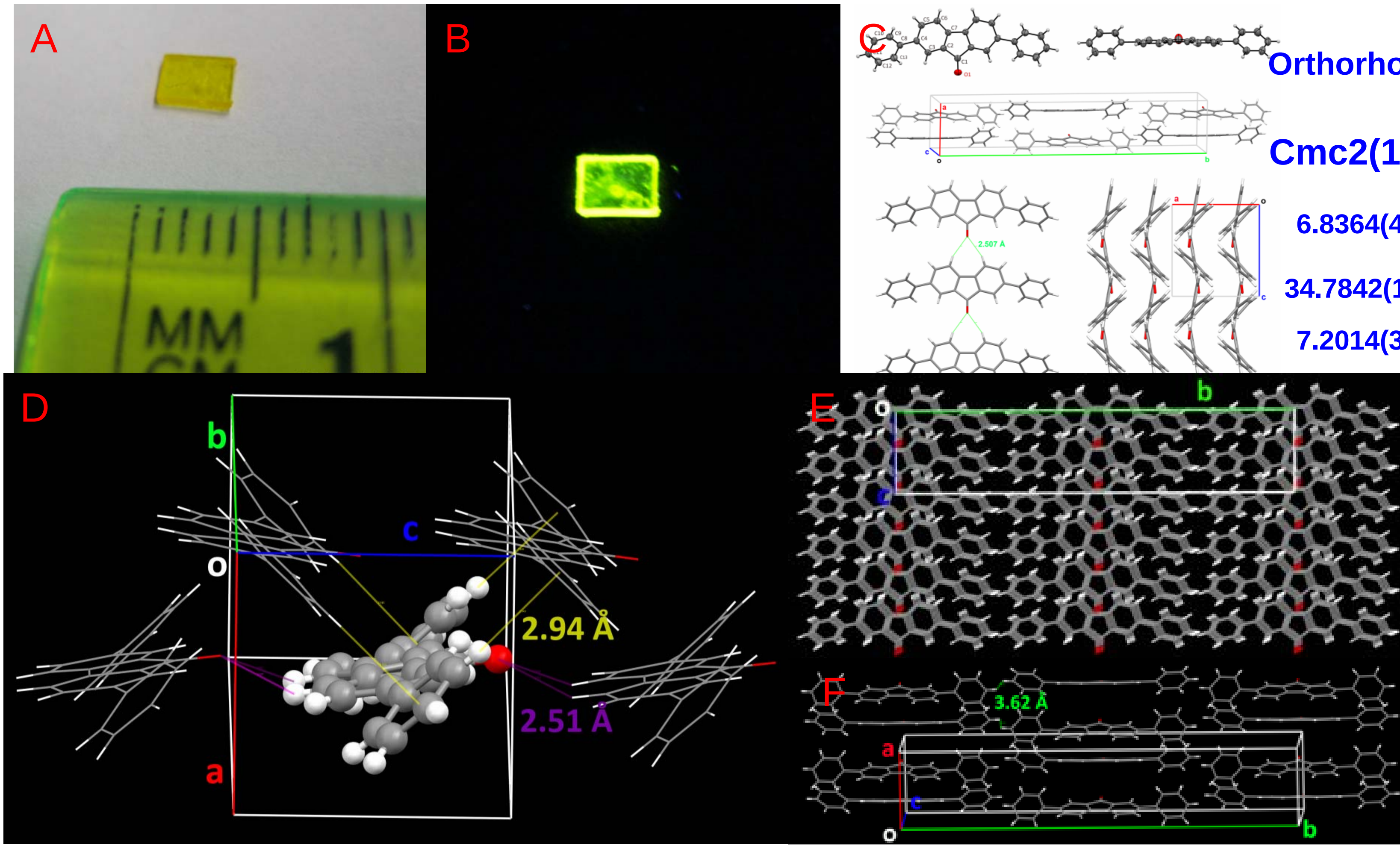
Schematic representation of the self-assembly processes



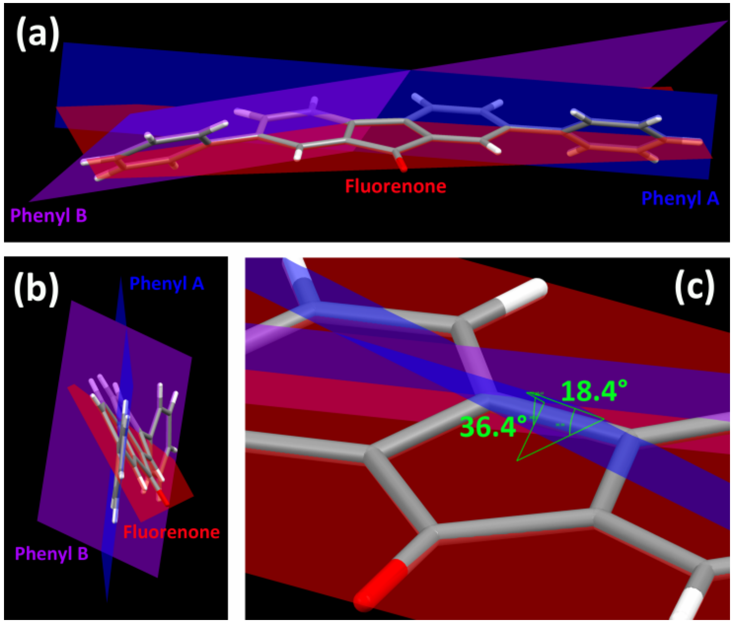
PL images of microstructures of BTN-6 (a) and BTN-7 (b). (c) Microarea PL images (d) Corresponding PL spectra in c.

富碳分子材料的可控组装与性能调控

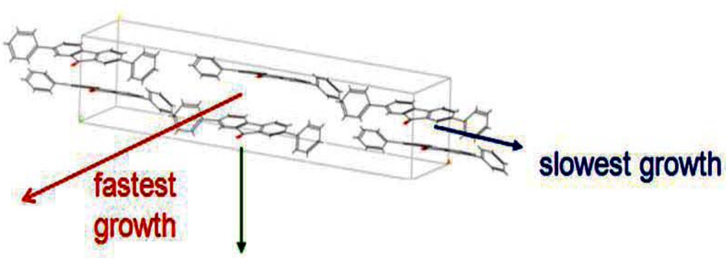
实现了大尺寸、长程有序分子晶体的生长，在单晶上同时观察到二阶和三阶非线性光学现象——二阶的二次谐波（SHG）和三阶的双光子荧光发射（TPF）。

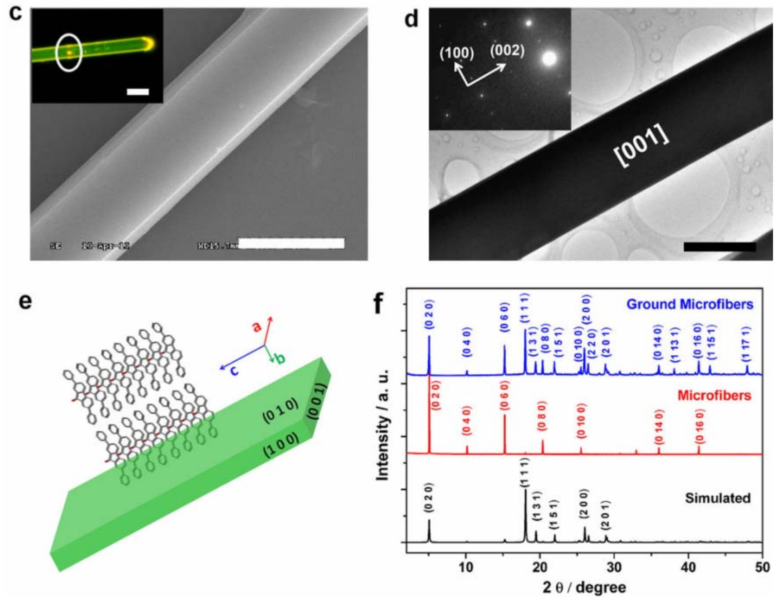


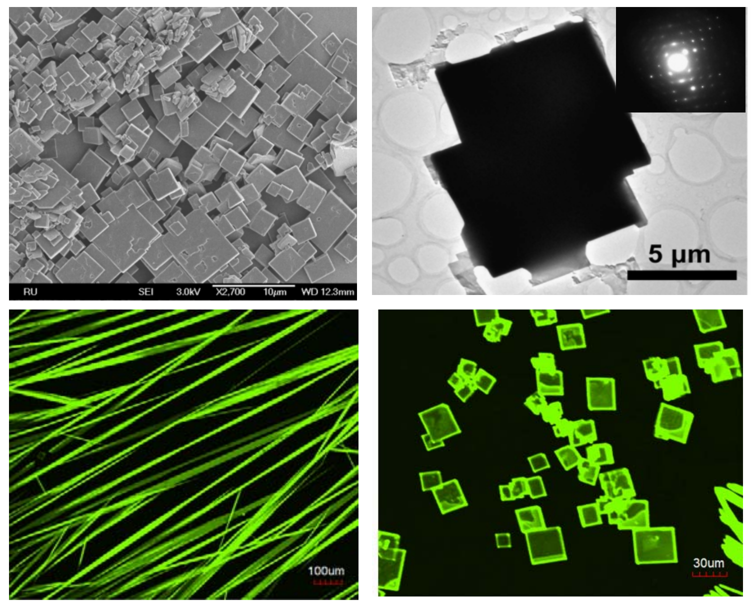
(A-B) DPFO 大面积晶体，(C) DPFO晶体结构. (D)DPFO 晶体中的作用力. (E-F)不同方向的堆积.



DPFO分子中苯环单元的非平面扭曲

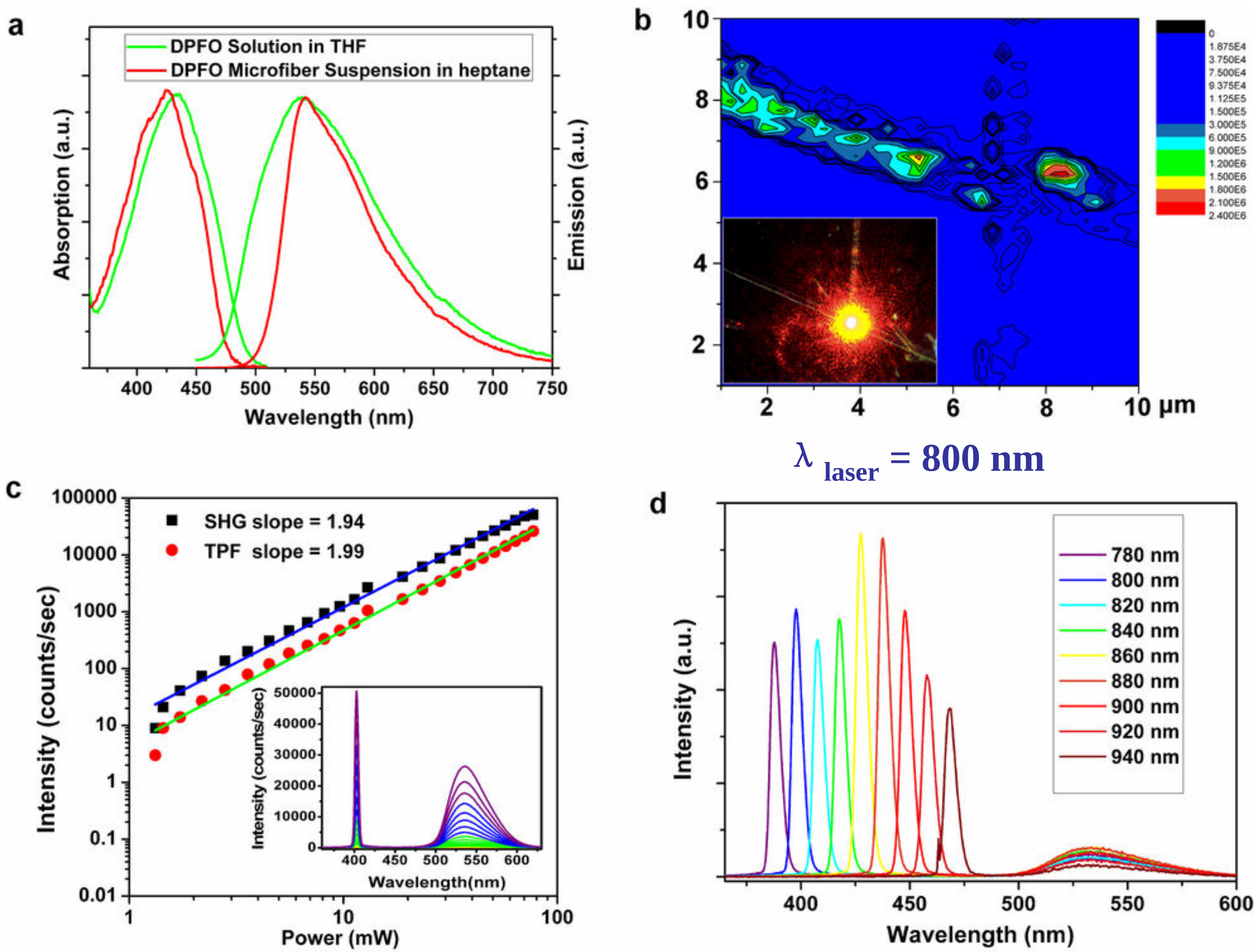




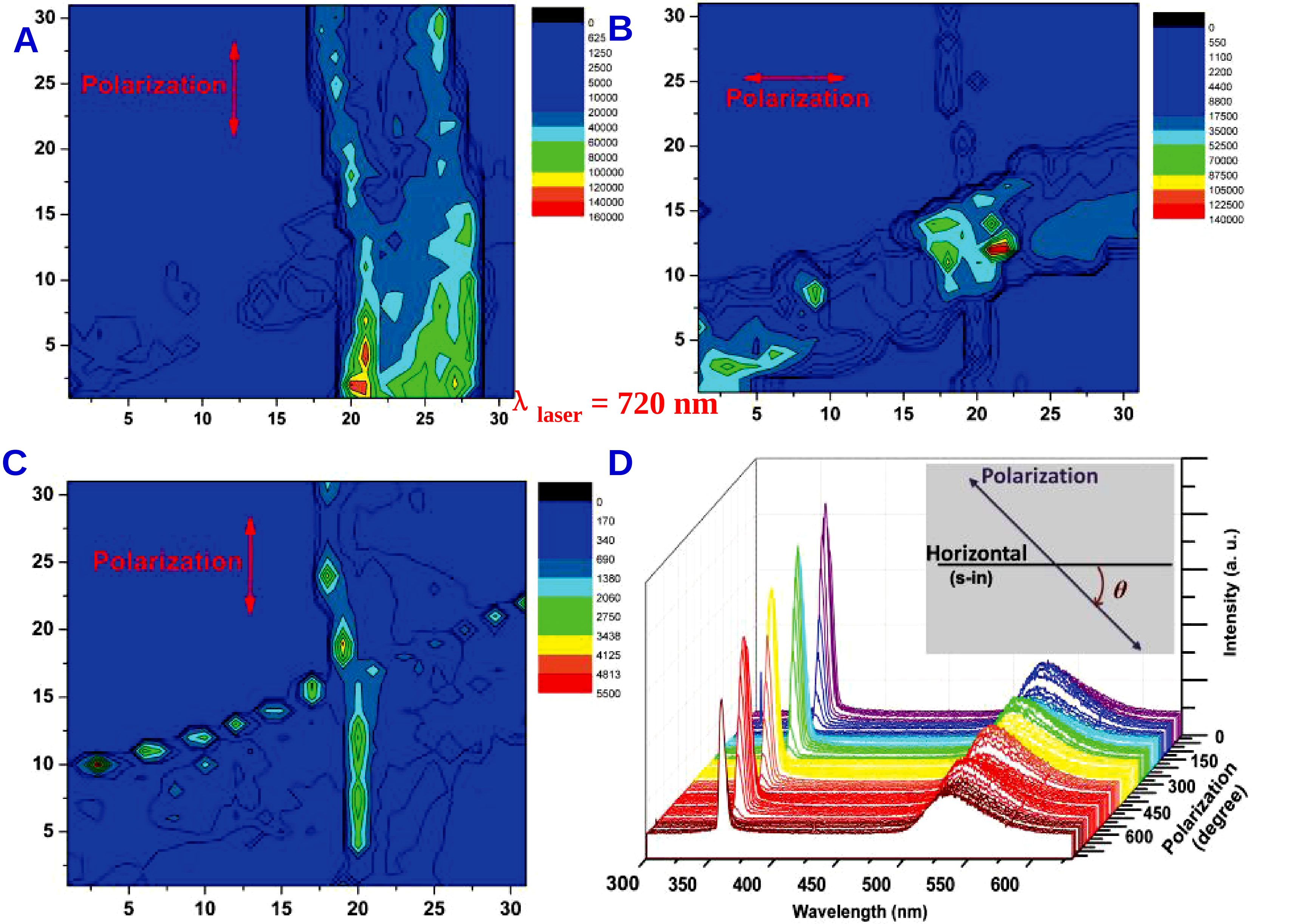


DPFO 的形貌：SEM, TEM, XRD，CLSM和纤维模型图

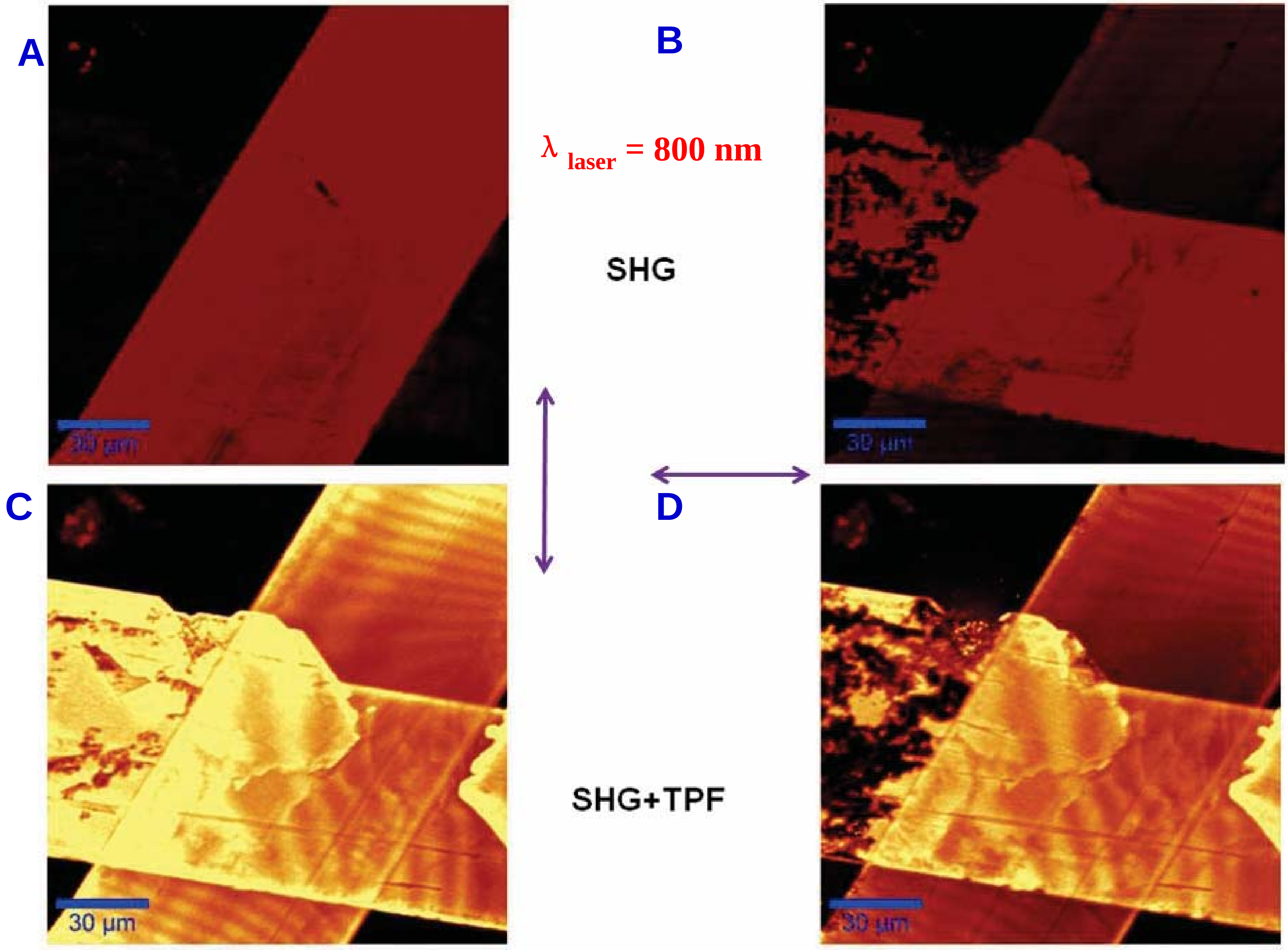
Adv. Mater. 2012



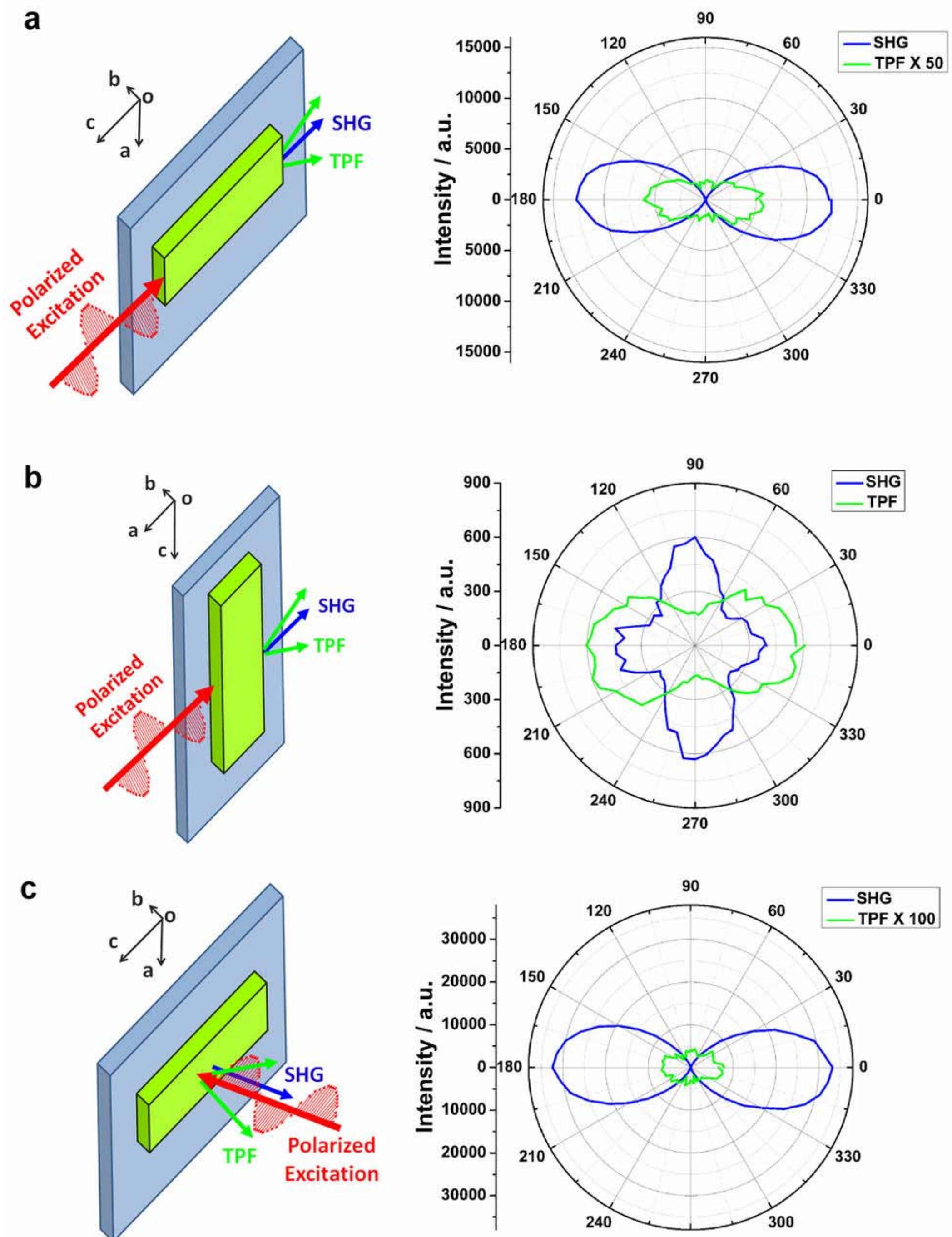
(a) 紫外和荧光光谱图. **(b)**两根交叉的纤维扫描图（水平激发）. **(c)** 不同功率激光激发下**SHG**、**TPF**的强度图，插图是激光强度与**SHG**、**TPF**的光谱图. **(d)**不同波长激光激发下**SHG**、**TPF**的光谱图



SHG (360 nm) 和TPF (530 nm)不同的偏振和传播行为的依赖性. **(A) SHG**水平方向**(B) SHG**垂直方向（**C**）**TPF**水平方向 **(D)**不同角度偏振扫描纤维（顺时针方向）



SHG 和TPF 的偏振依赖性CLSM图，(A－B)水平方向仅SHG， (C－D)垂直方向观察到SHG 和TPF.



SHG和TPF的强度与偏振角沿着不同晶面的变化关系，(a) c轴. (b) a轴. (C) b轴（反射模式）. 左边是对应的曲线.

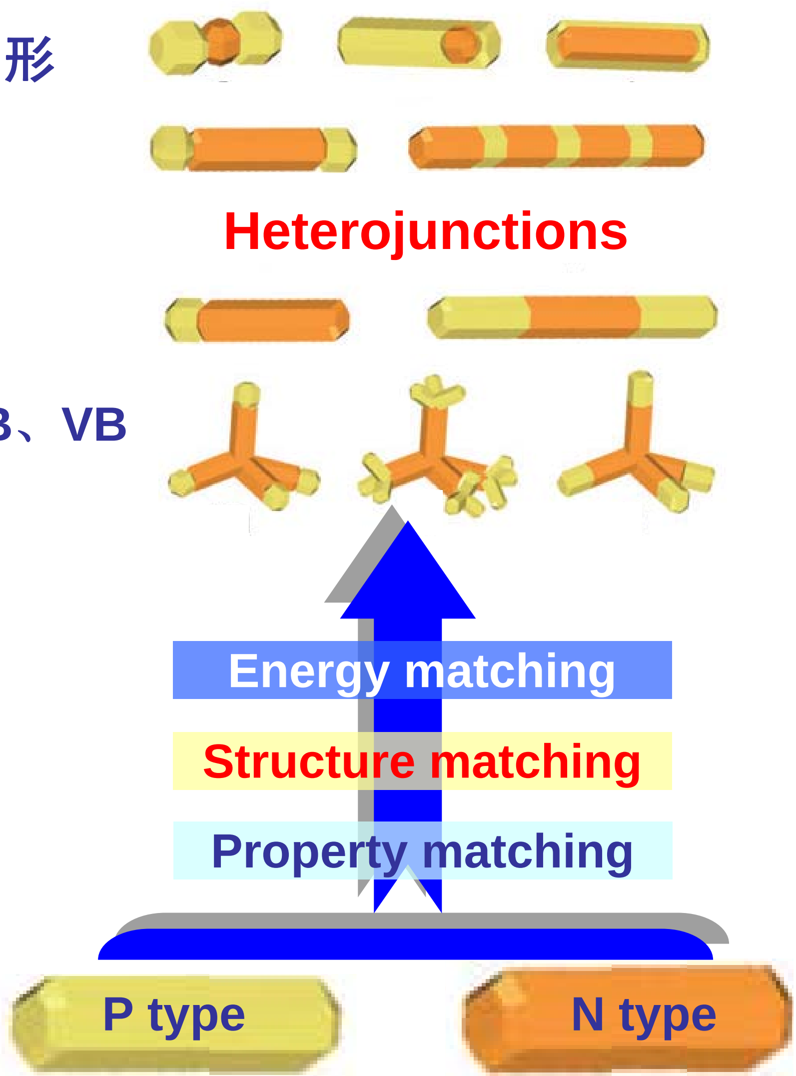
实现了通过偏振角调控SHG和TPF

Adv. Mater. 2012

富碳分子材料半导体异质结聚集态纳米结构的组装与构建

如何控制聚集态结构、形貌和性质

控制HOMO、LUMO；CB、VB
调控能量、电子转移
实现性质可控



晶格、表面能、
化学键……

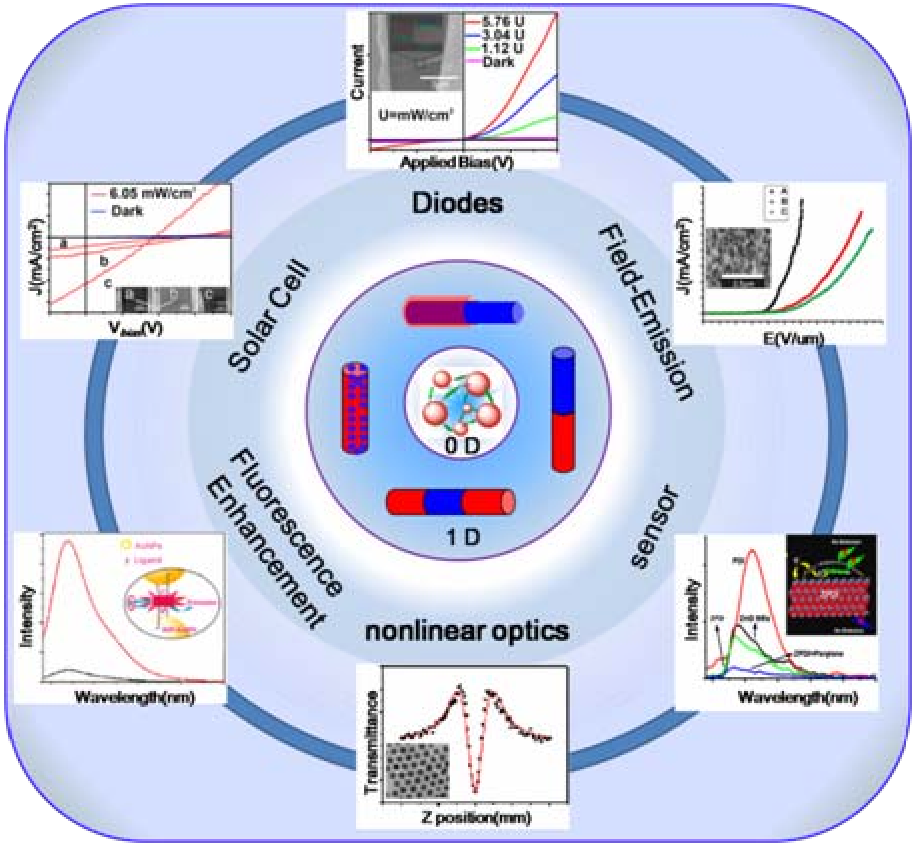
CuS, AgS, PPV,
polypyrrole,
polythiophene,
polyfluorene, polyalkyne

CdS、ZnO、
SnO_2、 CdTe、
ZnS、fullerene、
F-phthalocyanin

面向功能化的异质材料的构建

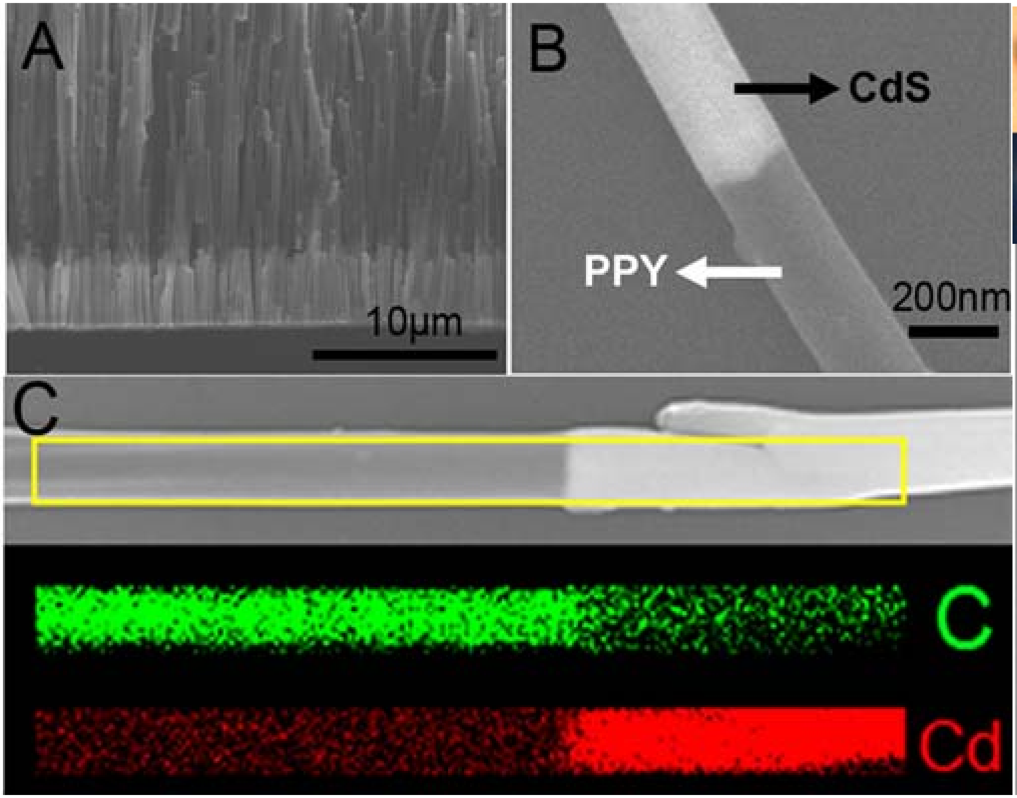
◆How to control the aggregation, morphologies and size to achieve controllable properties and functions.

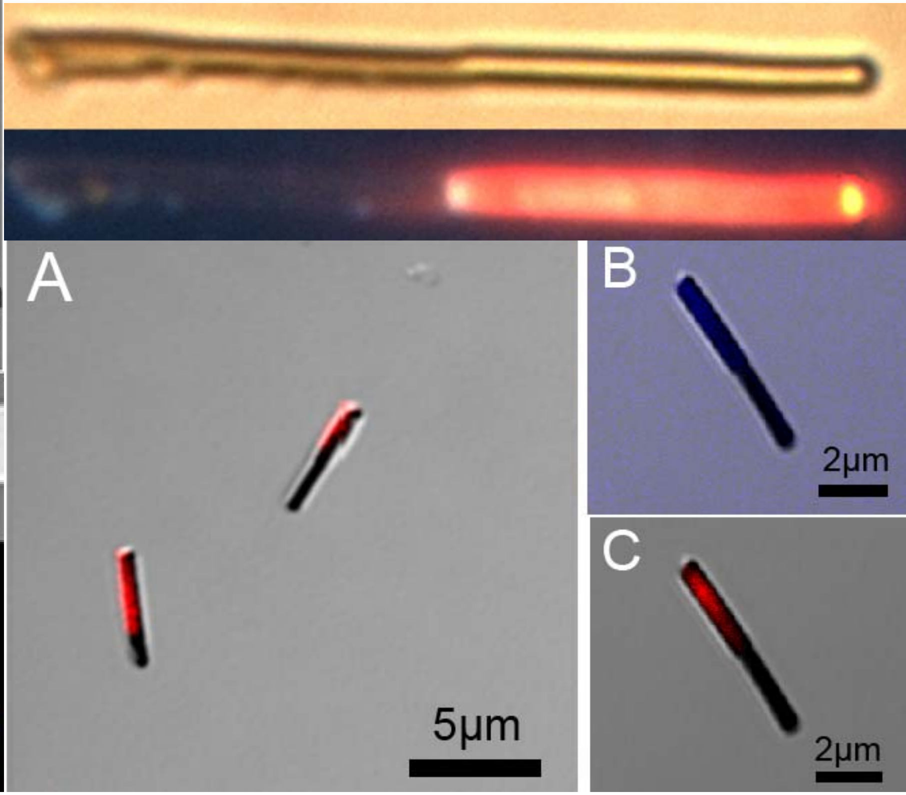
◆Strong junction effect for realizing synergistic (“1 + 1 > 2”) performance.



Chem. Soc. Rev. **2011, 40, 4506** *Angew Chem. Int. Edt.* **2010, 49, 2705**

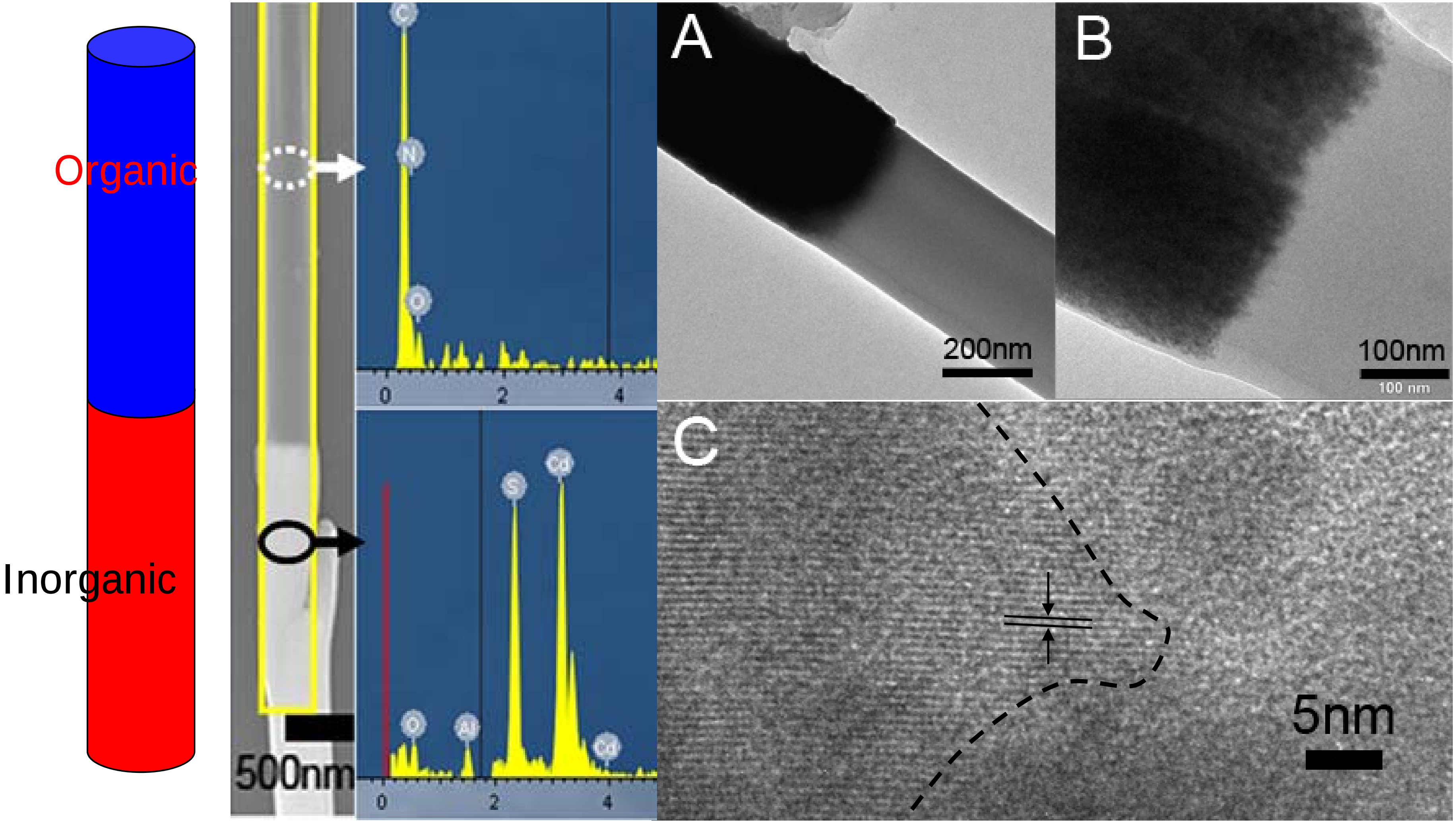
光控无机/有机半导体聚集态异质结纳米线





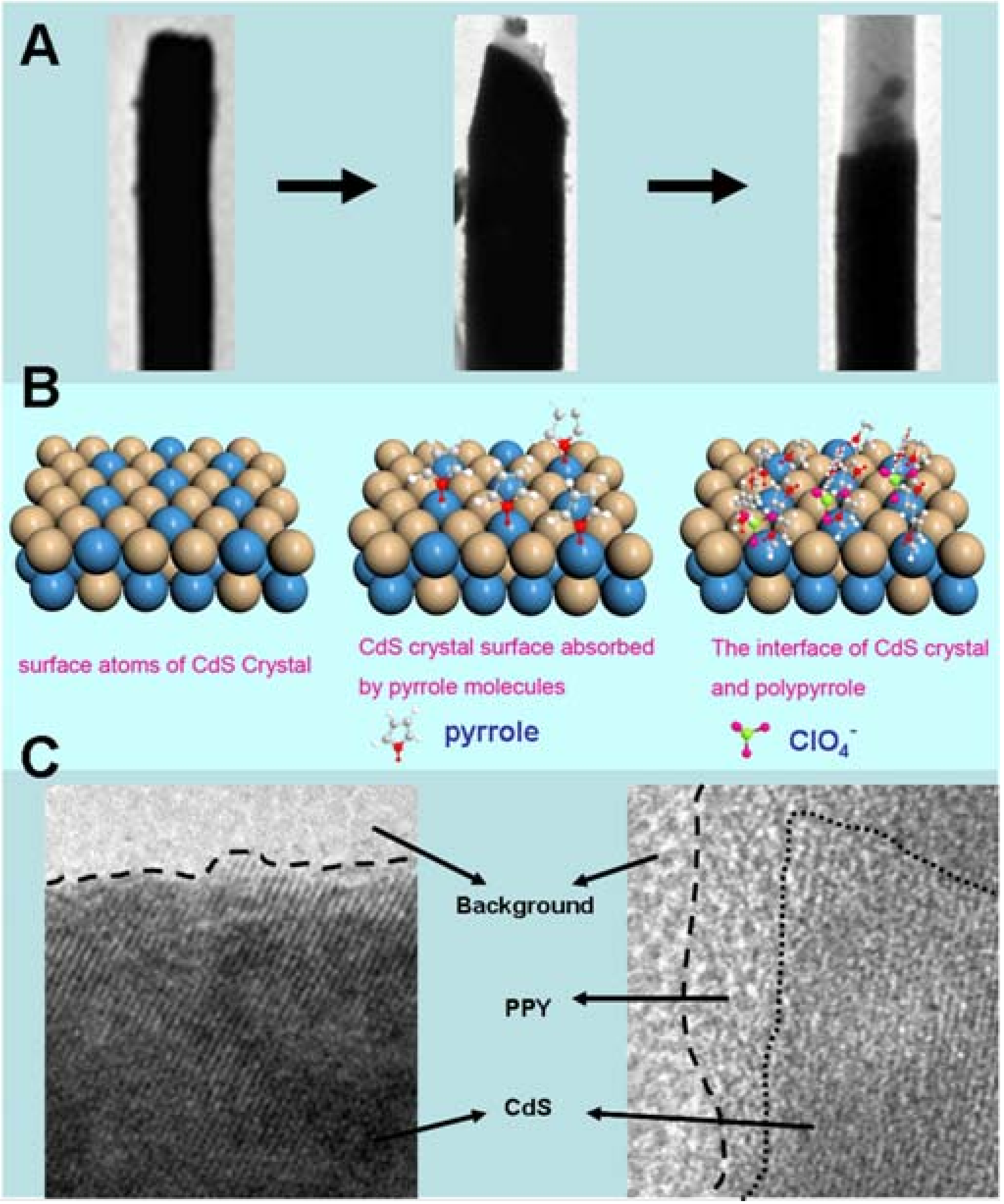
SEM, CLSM of PPY/CdS heterojunction nanowires

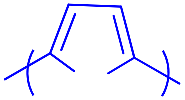
J. Am. Chem. Soc. **2008, 130, 9198**   *Chem. Asian J.* **2011, 6, 98**



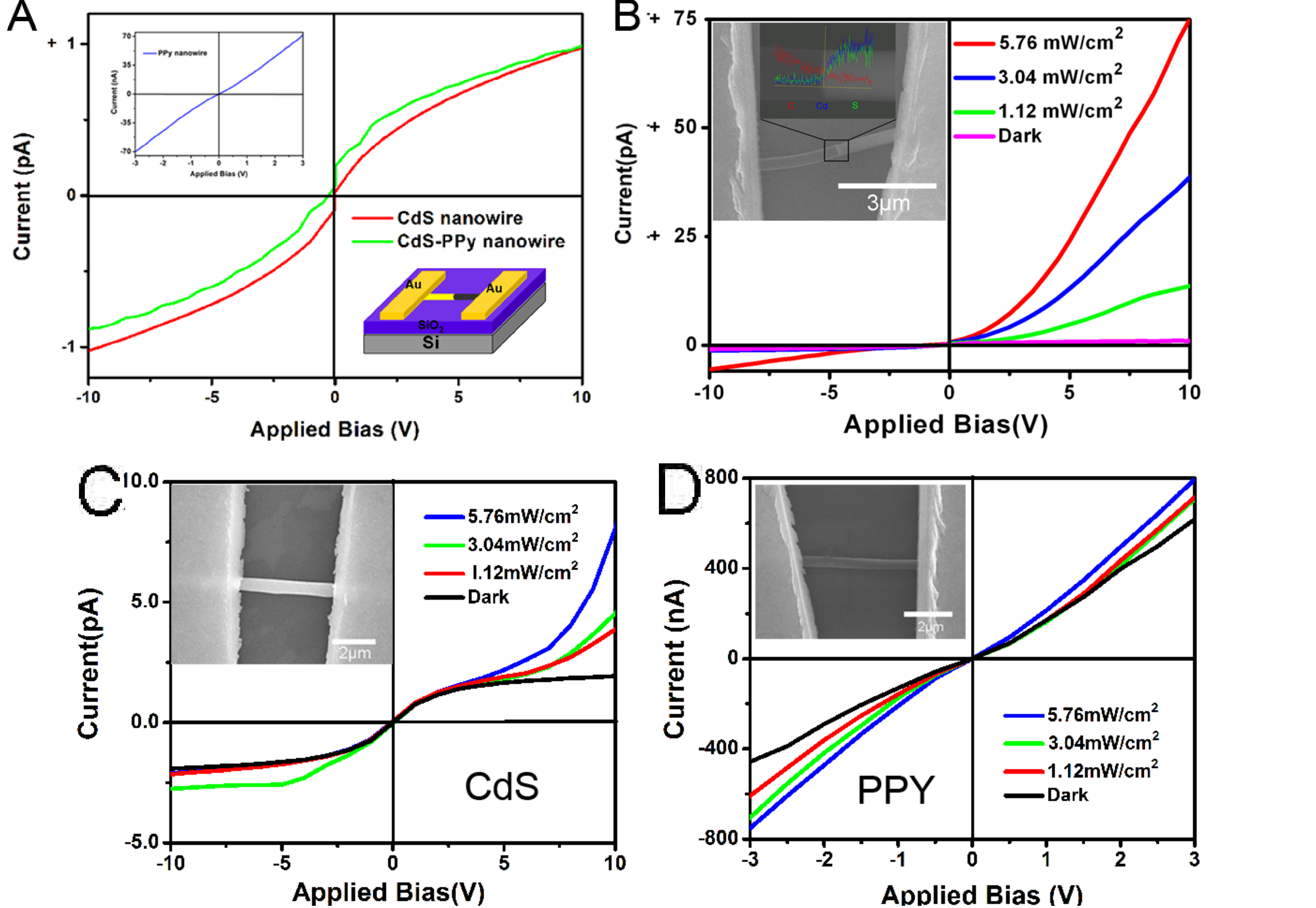
TEM and HRTEM images of PPY/CdS heterojunction nanowires

异质结纳米线生长过程



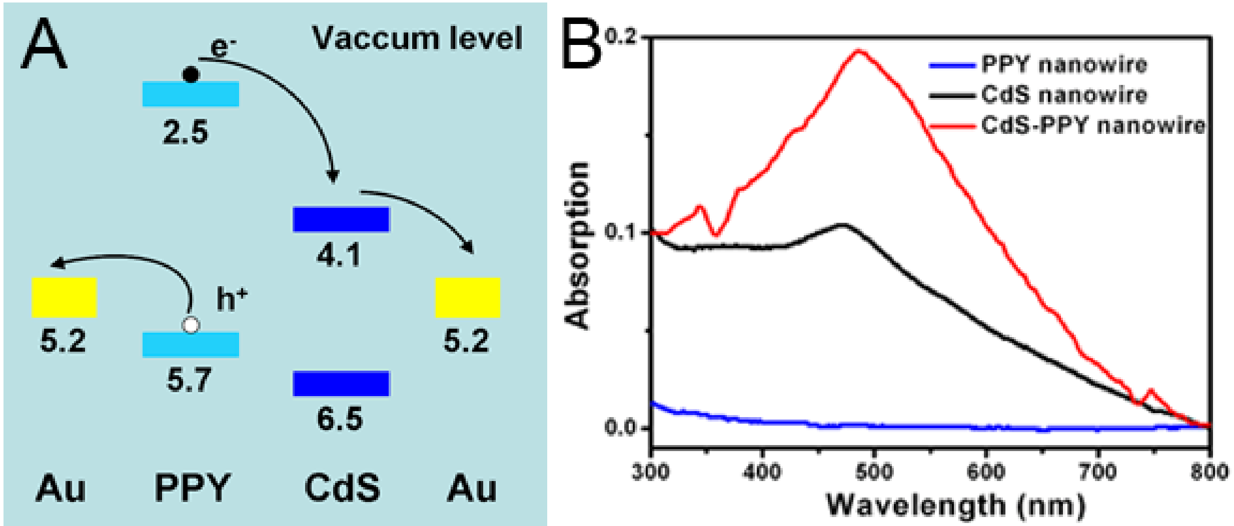


(A) TEM images of CdS-PPY P-N juction nanowire in different growing stage; (B) Models of CdS surface (C) HRTEM image of CdS crystal and CdS-PPY interface.

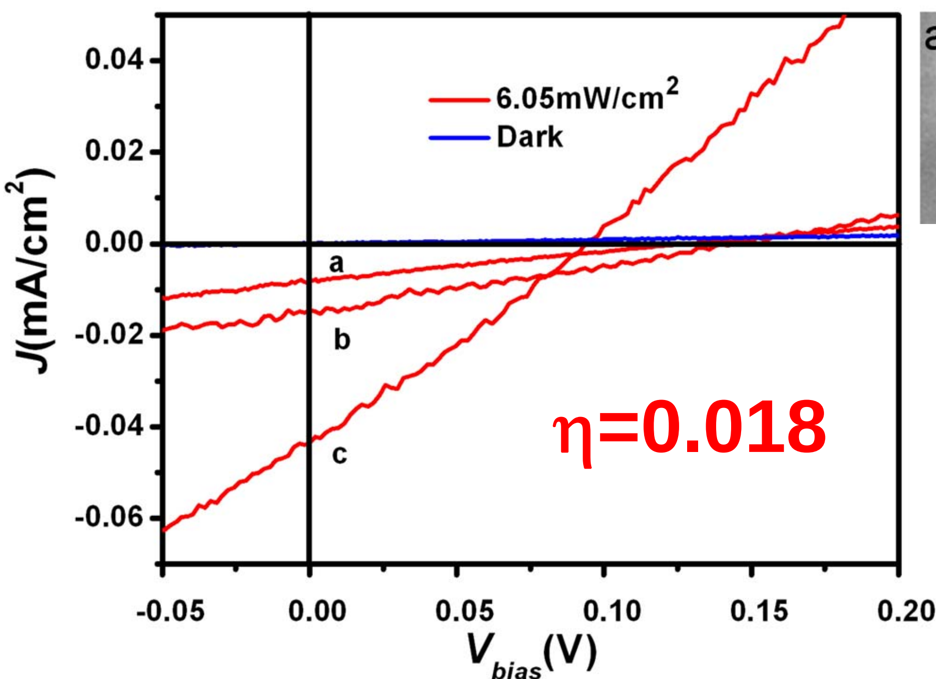


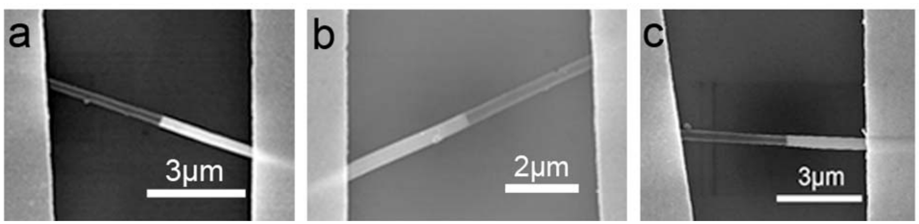
(A) I-V Curves for a typical CdS nanowire, PPY nanowire and CdS-PPY heterojunction nanowire in the dark. (B) Current-Voltaic (I-V) curves for a single CdS-PPY heterojunction nanowire under light illumination. (C) I-V curves of CdS nanowire. (D) I-V curves of PPY nanowire.

Photovoltaic property



Energy level diagram and UV-Vis absorption spectrum of CdS-PPY P-N junction nanowires

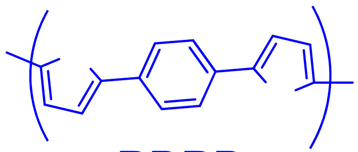


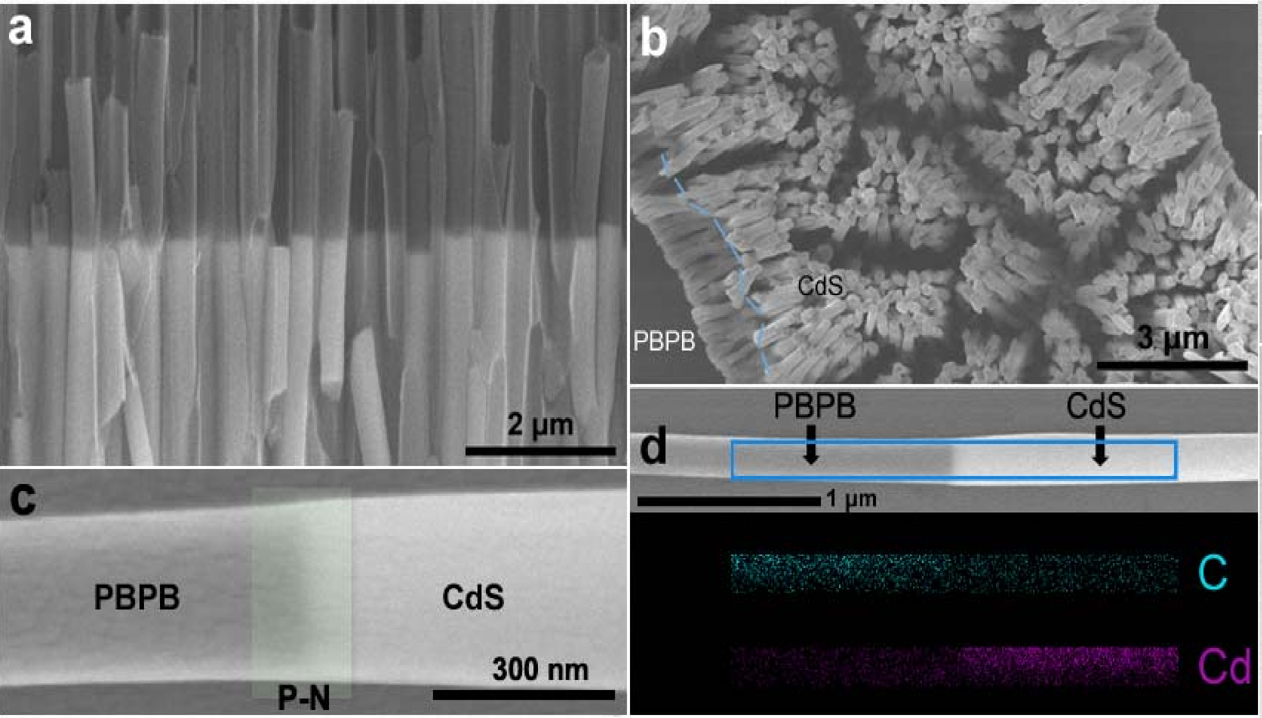


Dark/light current density vs. applied voltage bias (J-V) data of single CdS-PPY nanowire solar cell

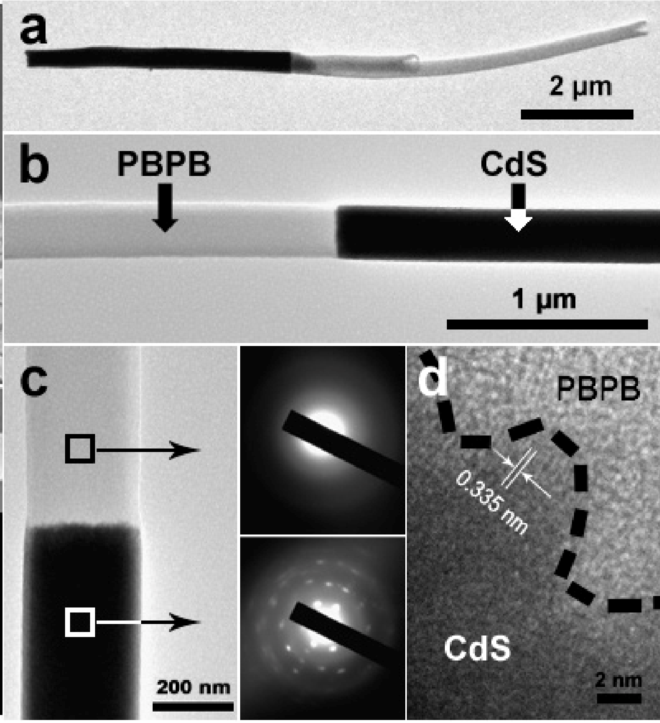
J. Phys. Chem. Lett. 2010, 1, 327

PBPB /CdS p-n异质结纳米线阵列



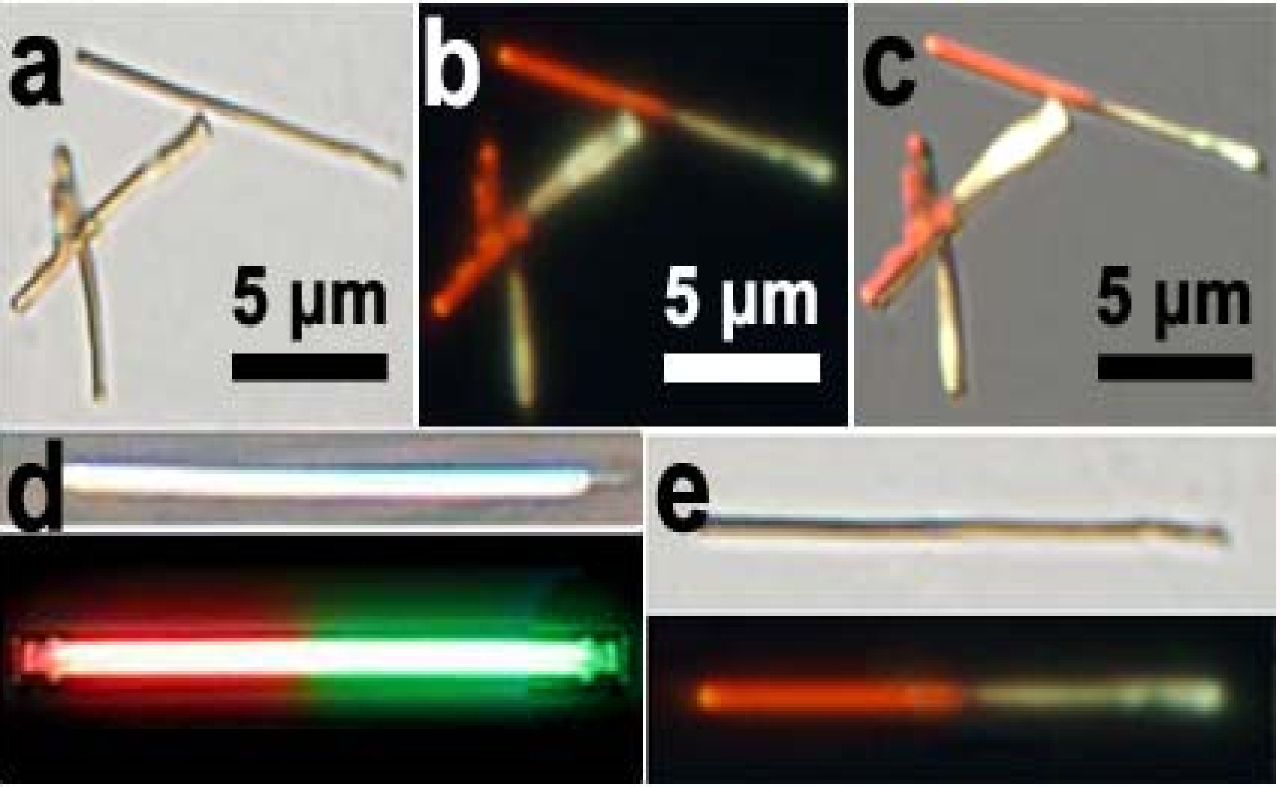


PBPB/CdS 异质结纳米线的SEM和EDS

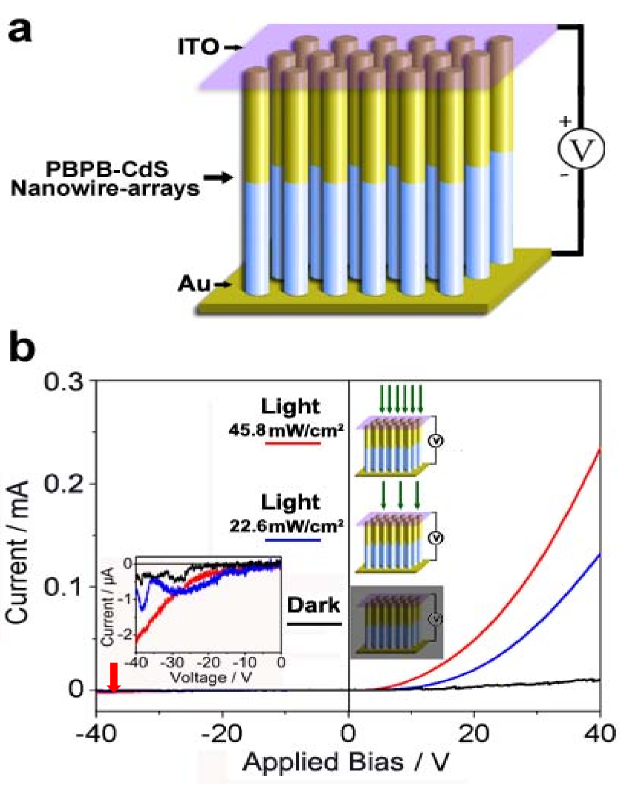


PBPB/CdS 异质结纳米线的TEM, HRTEM和SAED

Chem. Soc. Rev. 2011, 40, 4506

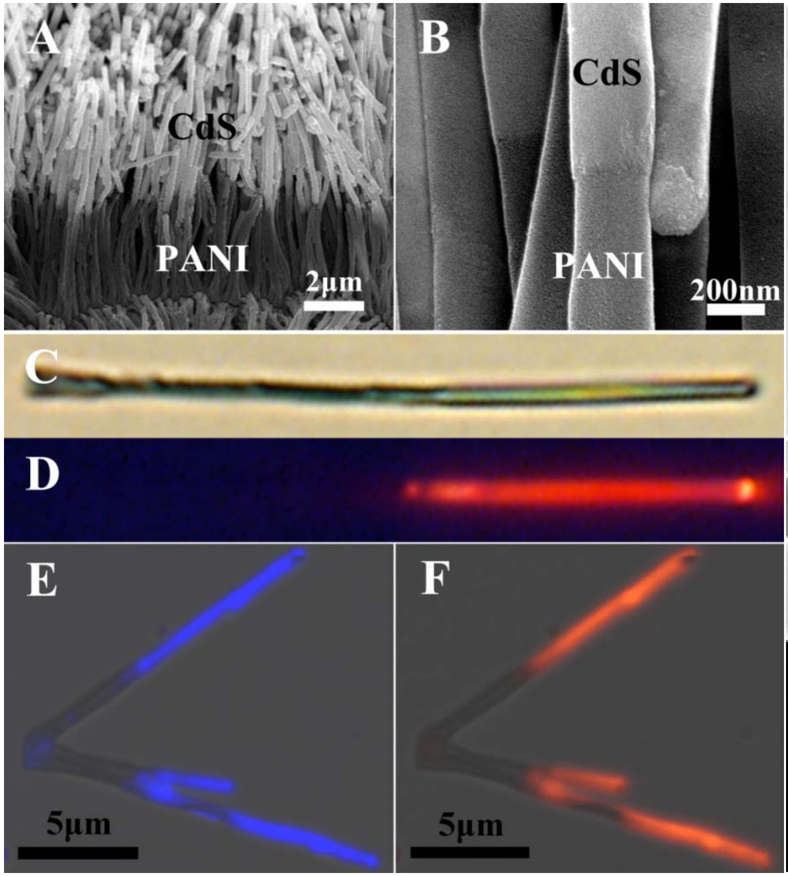


PBPB/CdS 异质结纳米线的荧光共聚焦图

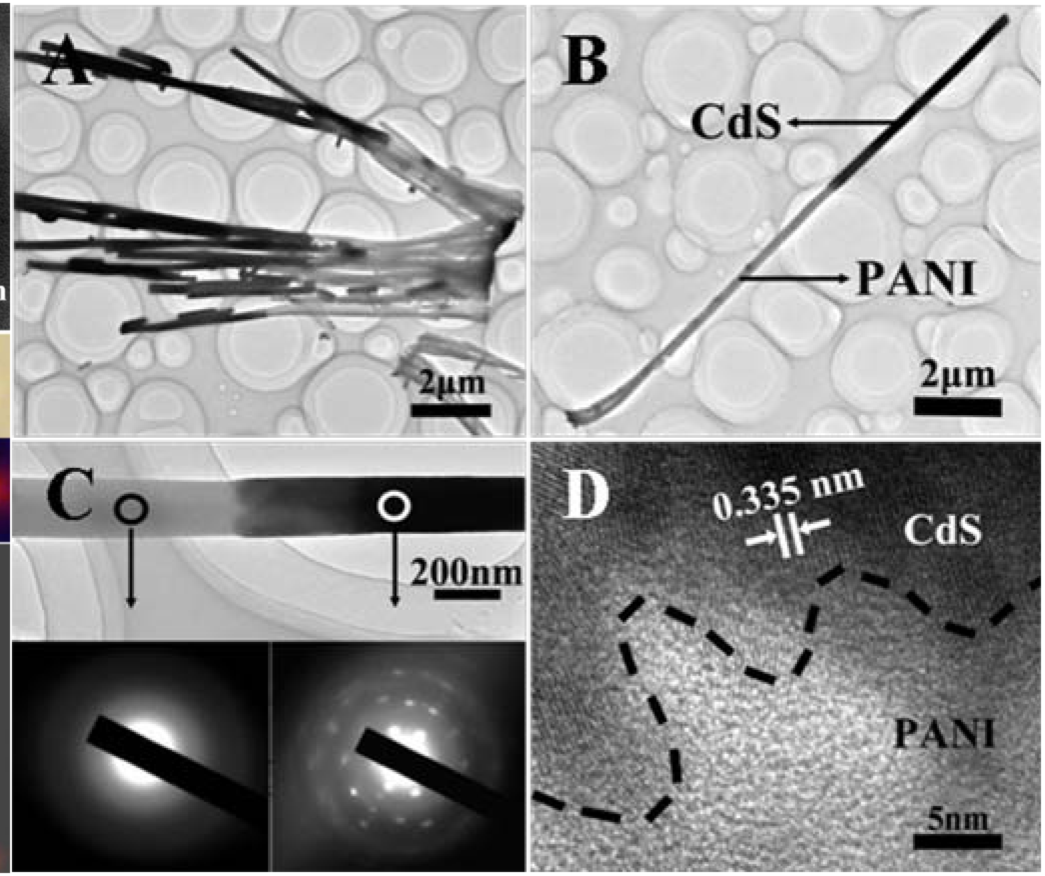


PBPB/CdS 异质结纳米线的光照下的IV曲线

无机/有机p-n异质结纳米线阵列蓝光探测器

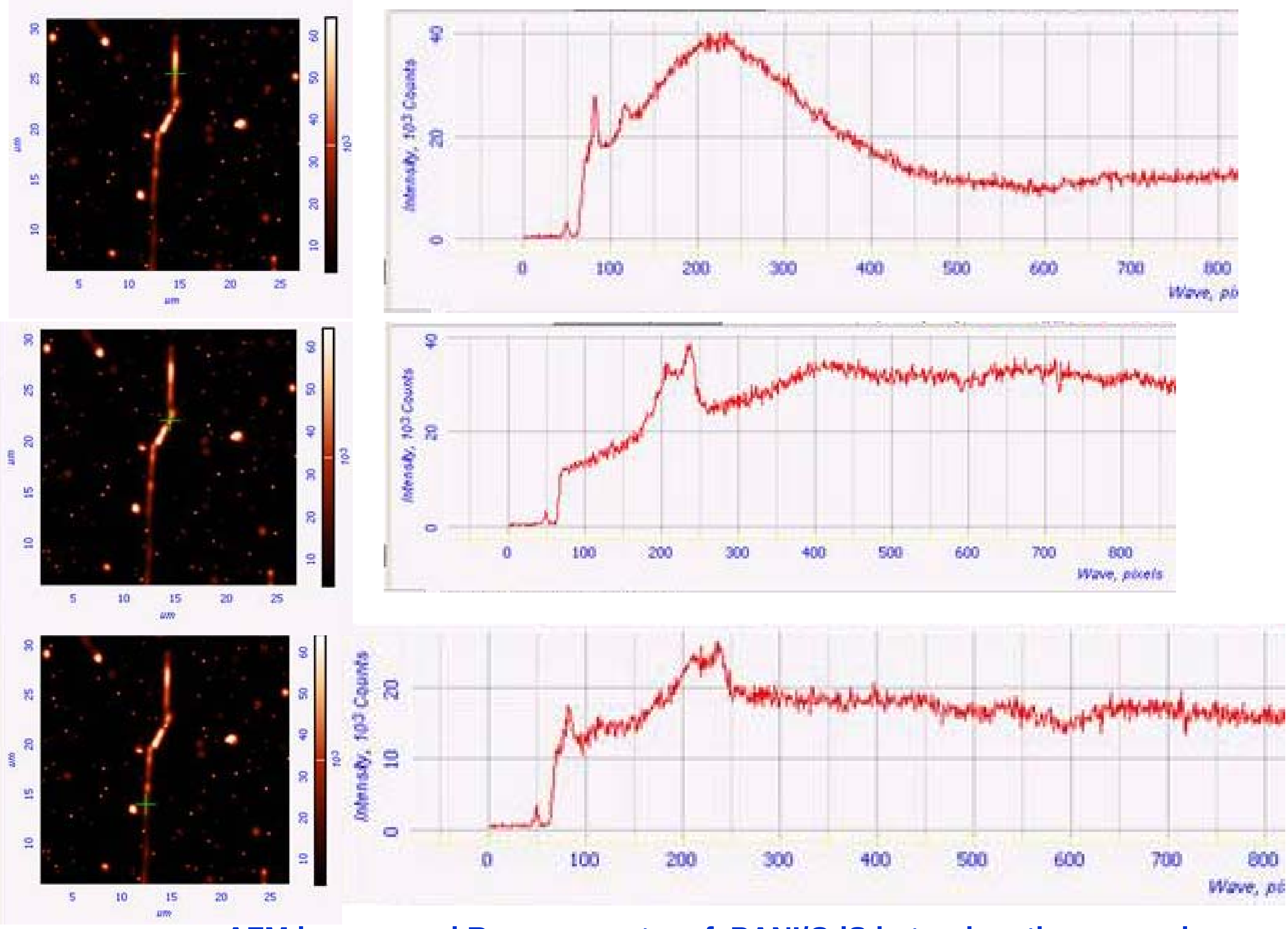


SEM images (A-B), CLSM image (C-F) of PANI/CdS heterojunction nanowires.

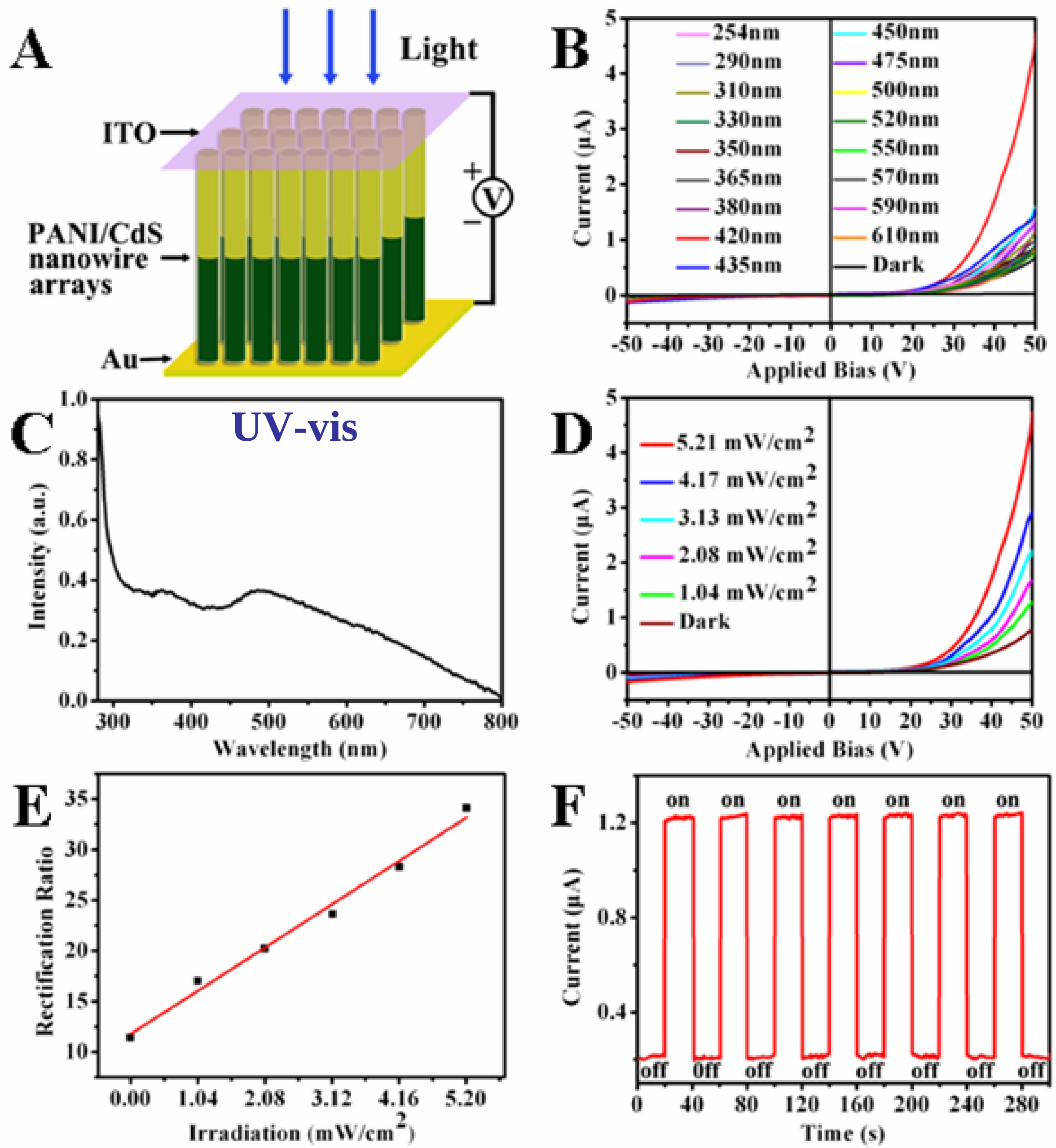


TEM images (A-C), SAED patterns and (D) HRTEM image of PANI/CdS heterojunction nanowires.

Inorg. Chem. 2011, 50, 7749

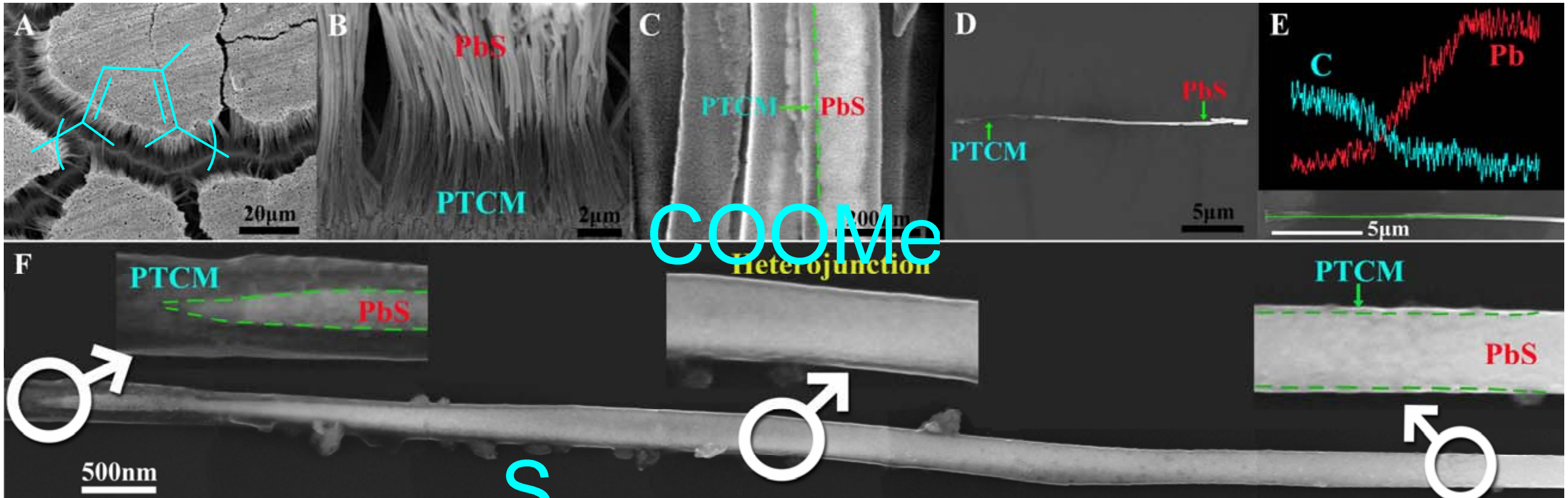


AFM images and Raman spectra of PANI/CdS heterojunction nanowires

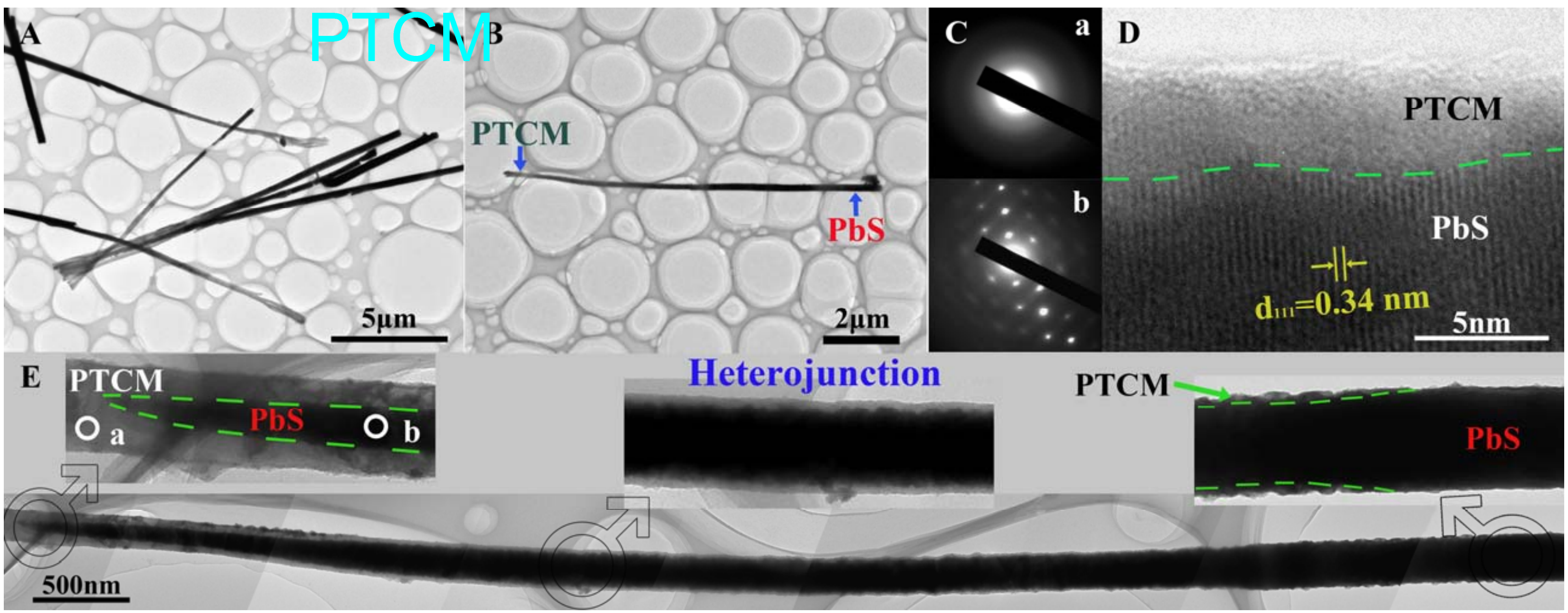


(A) Working model of device, (B) Typical IV curves, (C) UV-visible absorption spectra, (D) Typical IV curves under 420 nm light illumination, (E) Irradiance dependence of the rectification ratio, (F) On/off switching of PANI/CdS heterojunction nanowire arrays upon pulsed illumination from 420 nm wavelength light with a power density of 5.21 mW/cm^2.

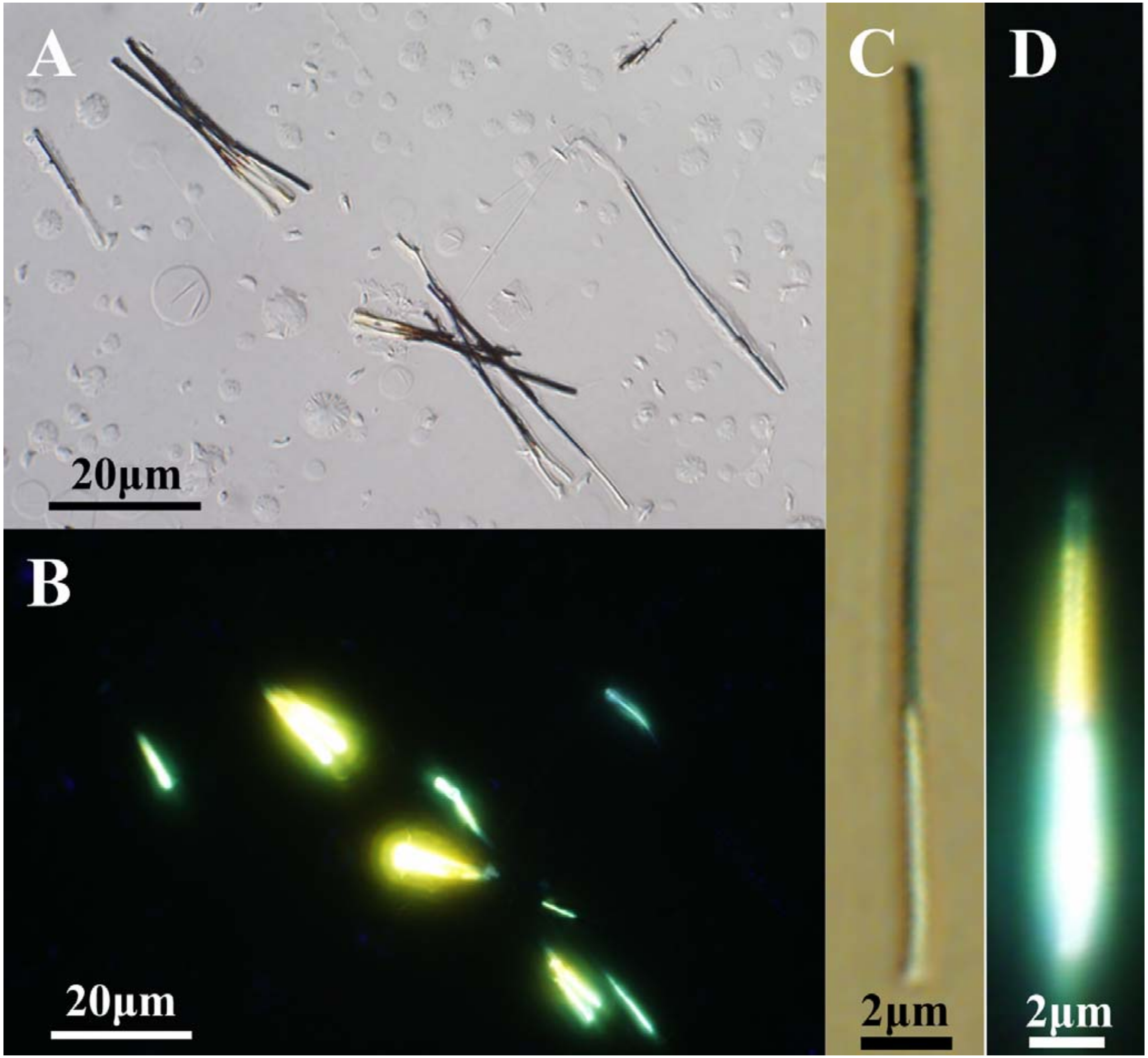
PTCM /PbS p-n 异质结纳米线阵列电开关



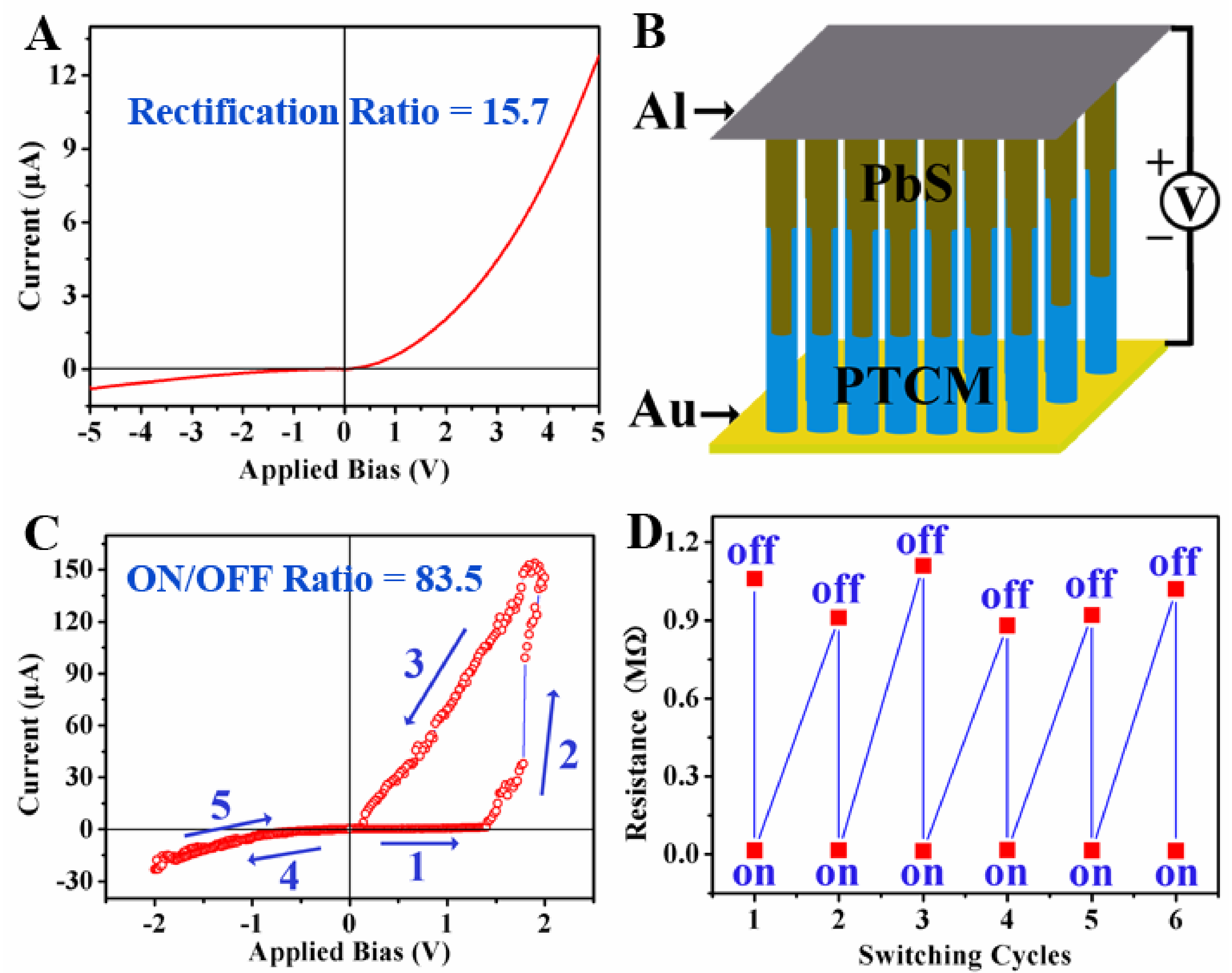
SEM images of PTCM/PbS heterojunction nanowires.



TEM images, SAED patterns and HRTEM image

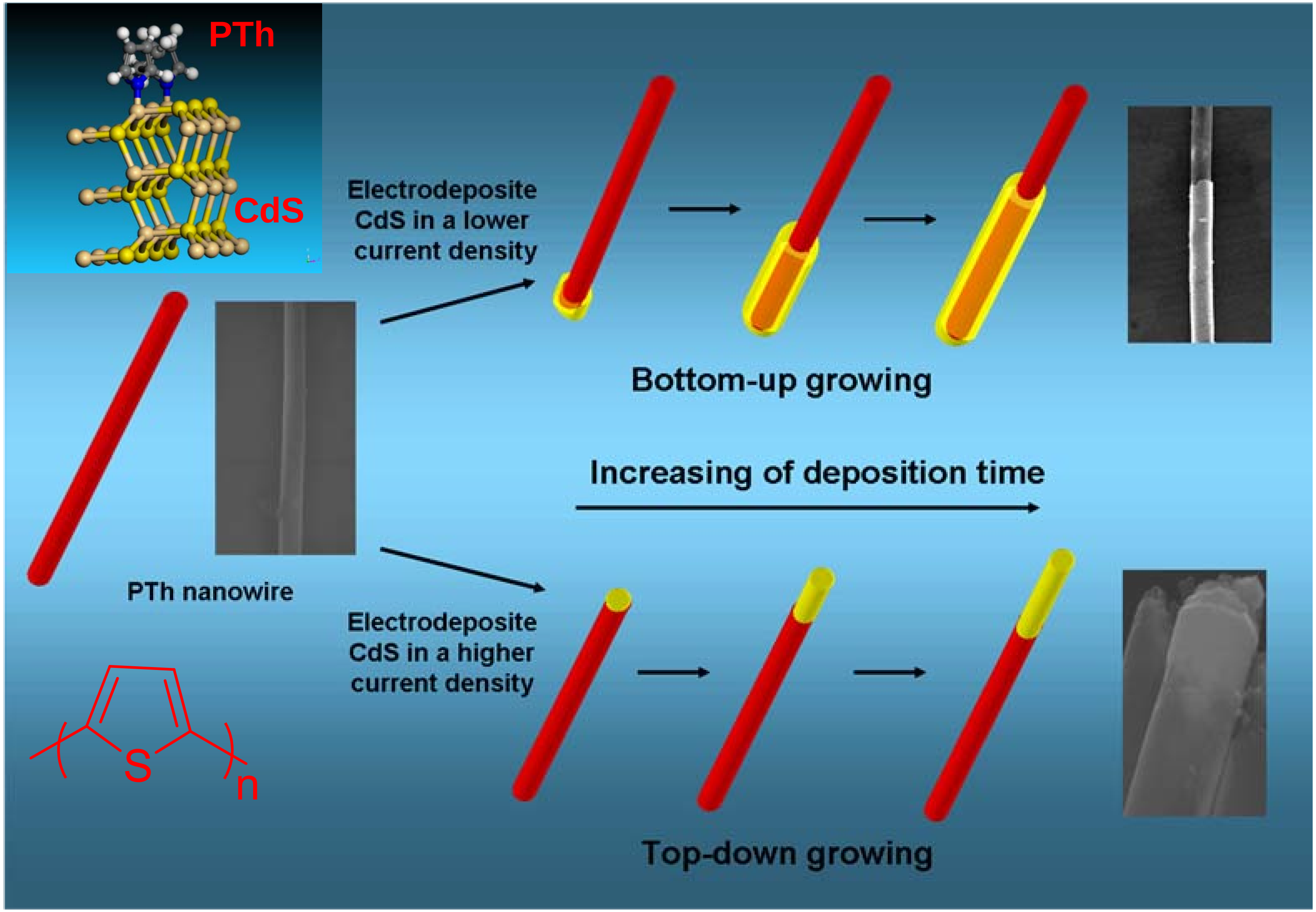


CLSM images



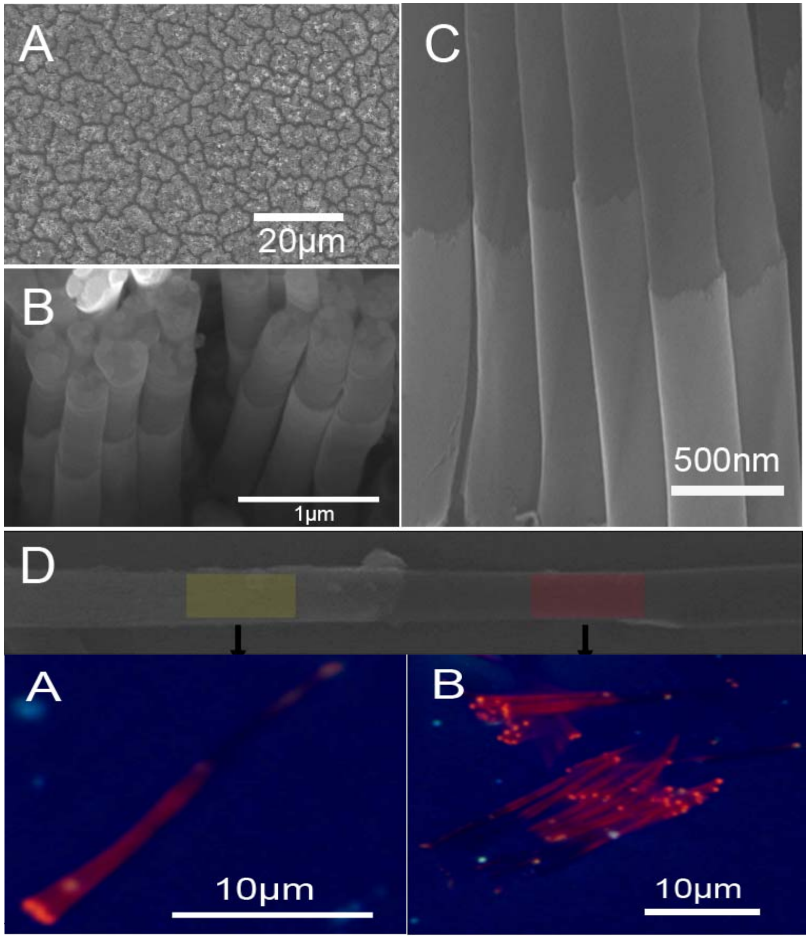
(A) Typical IV curves, (B) Working model of device, (C) IV curve of electric switch, (D) On/off switching of PANI/CdS heterojunction nanowire arrays.

无机/有机半导体核－壳结构p-n异质结纳米线阵列

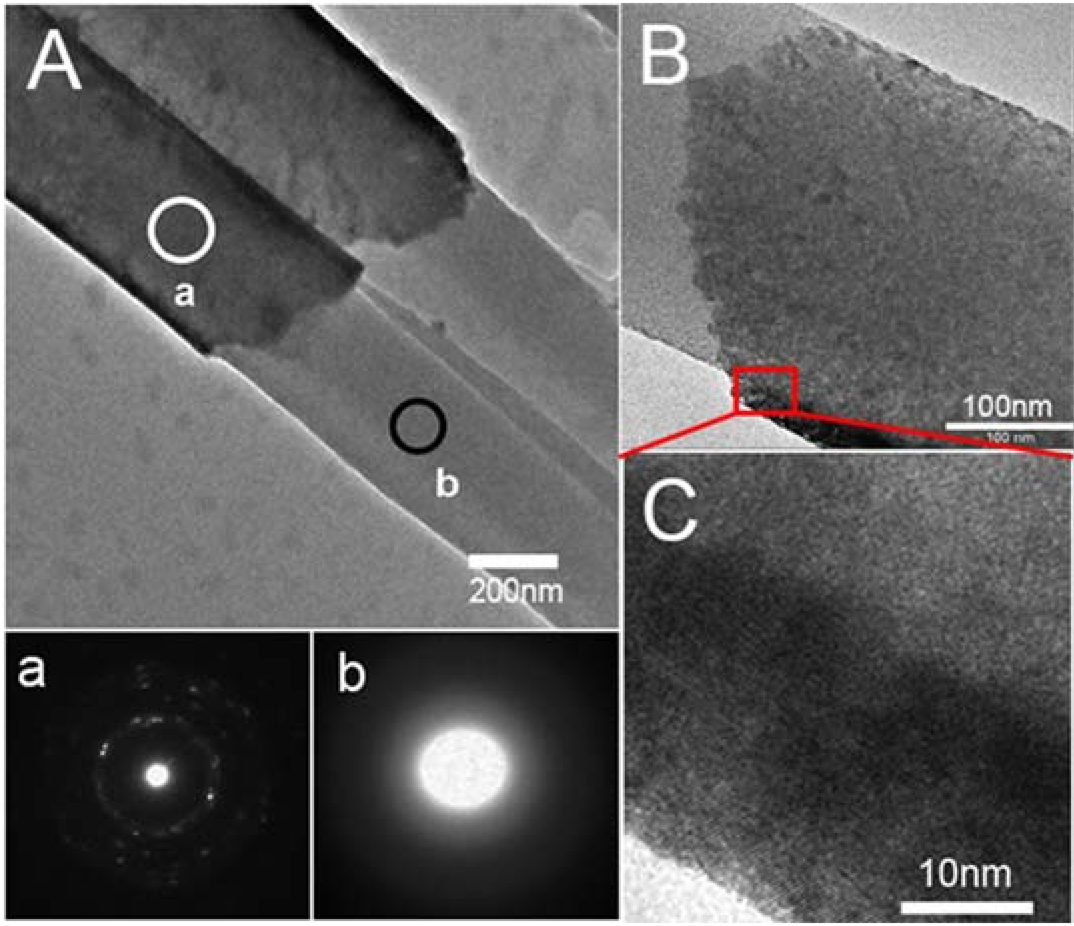


Adv. Mater. 2008, 20, 2918

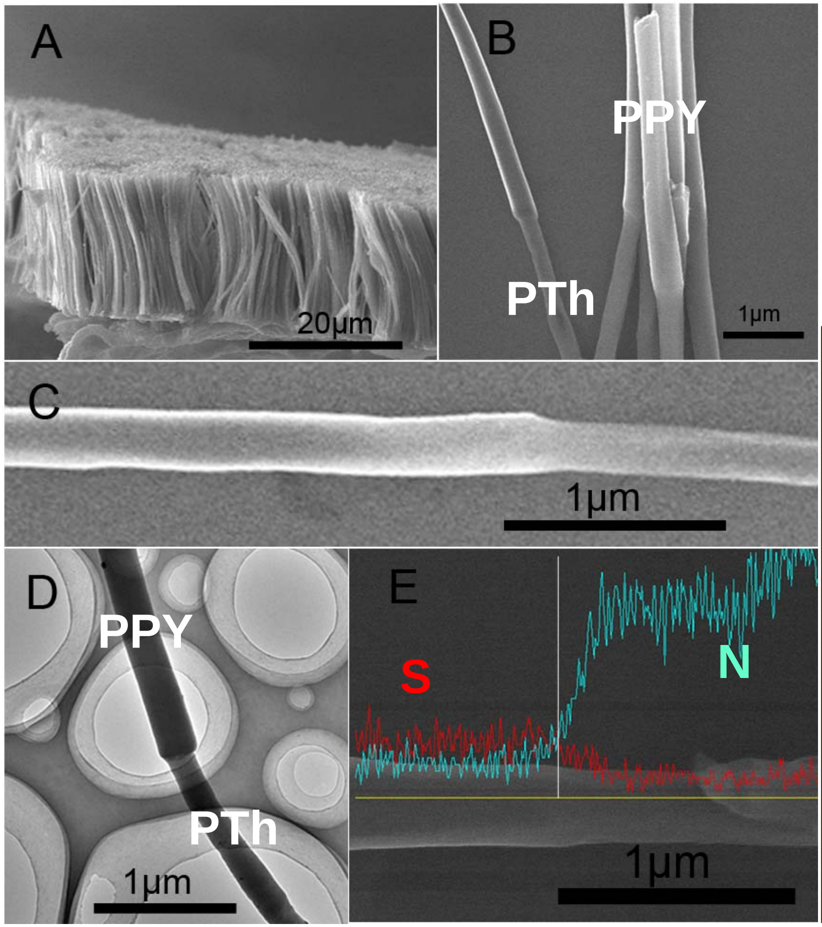
J. Phys. Chem. C 2009, 113, 12669



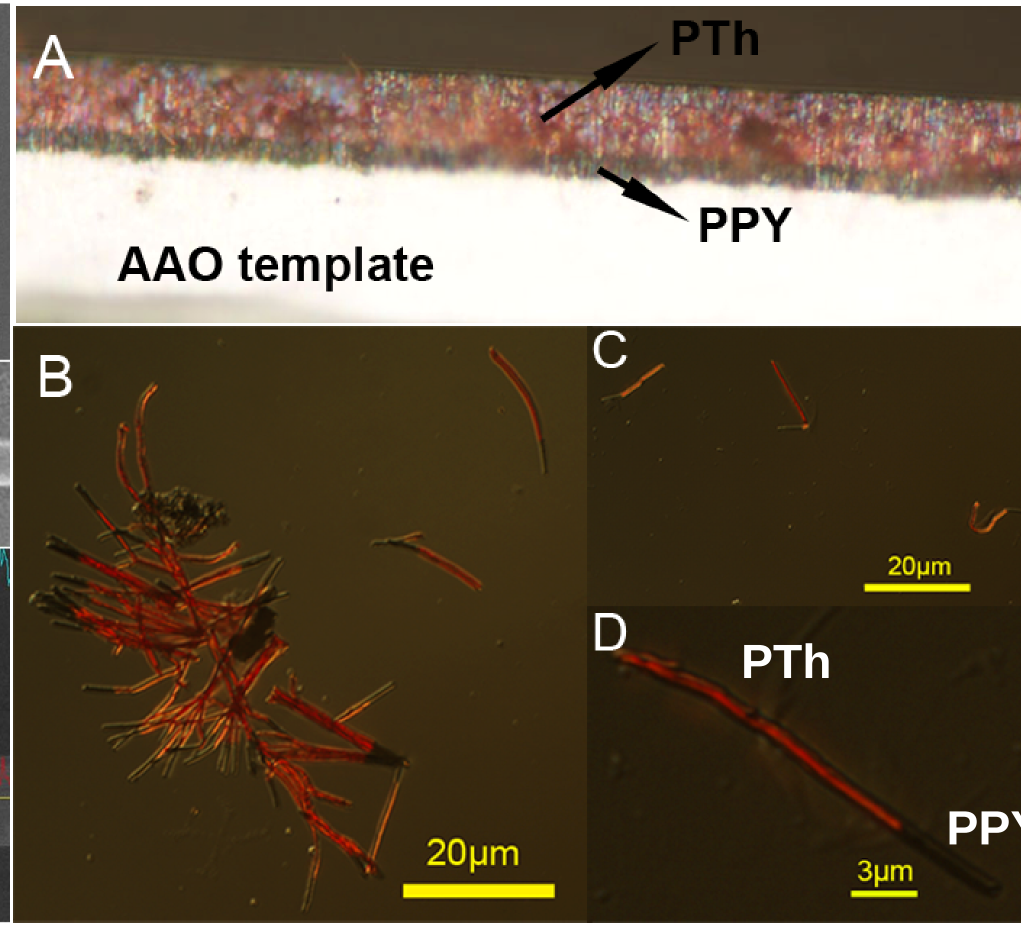
CdS-PTh 核-壳结构纳米线的SEM，EDS和CLSM



CdS-PTh 核-壳结构纳米线的TEM， SAED和HRTEM

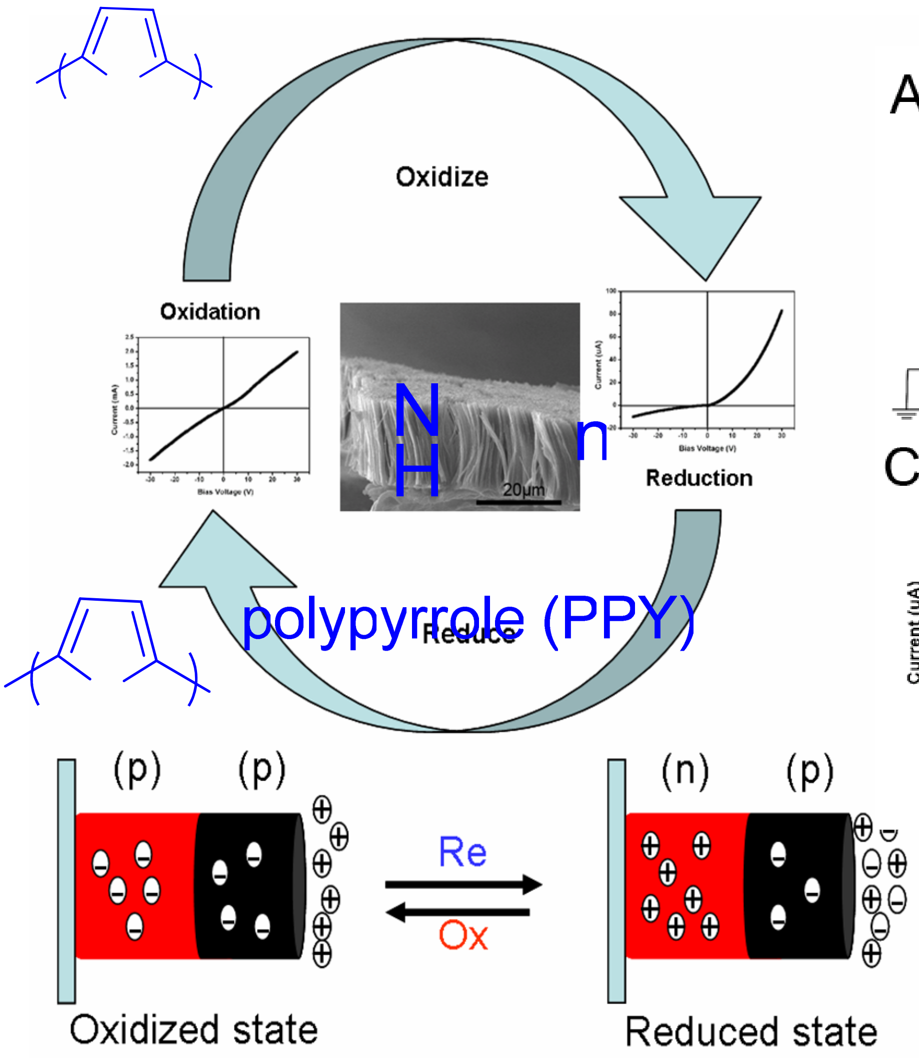


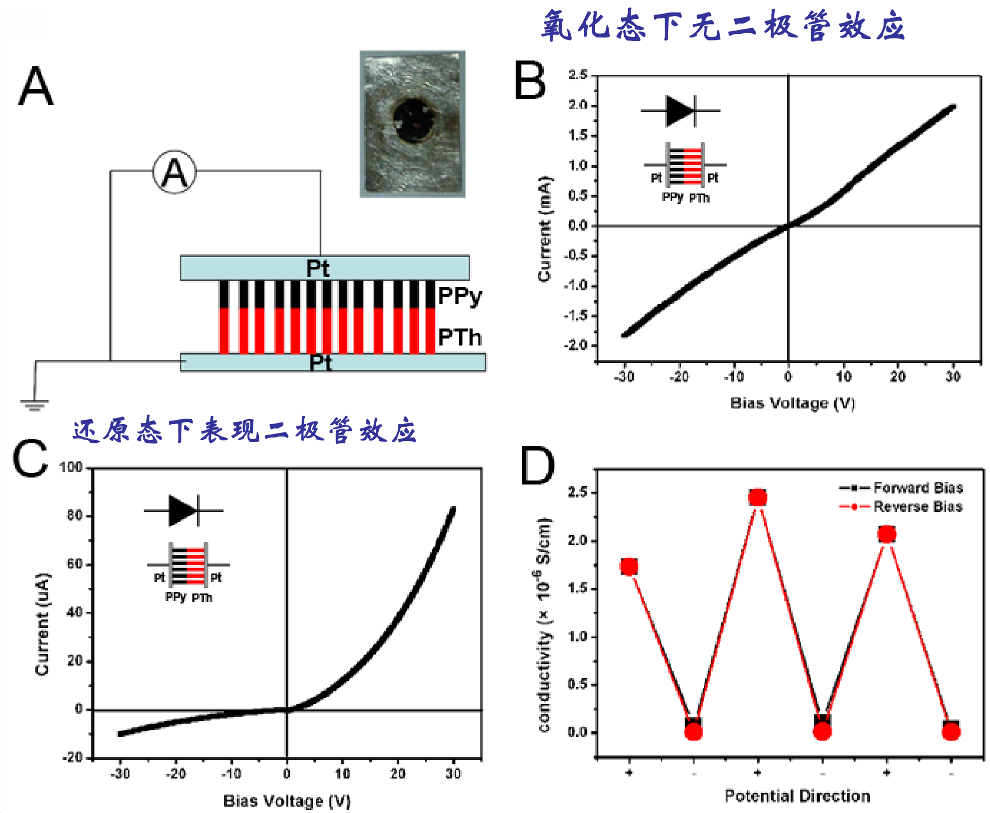
有机/有机异质结纳米线SEM和EDS线扫图



有机/有机异质结纳米线荧光共聚焦图

有机/有机半导体异质结纳米线智能开关



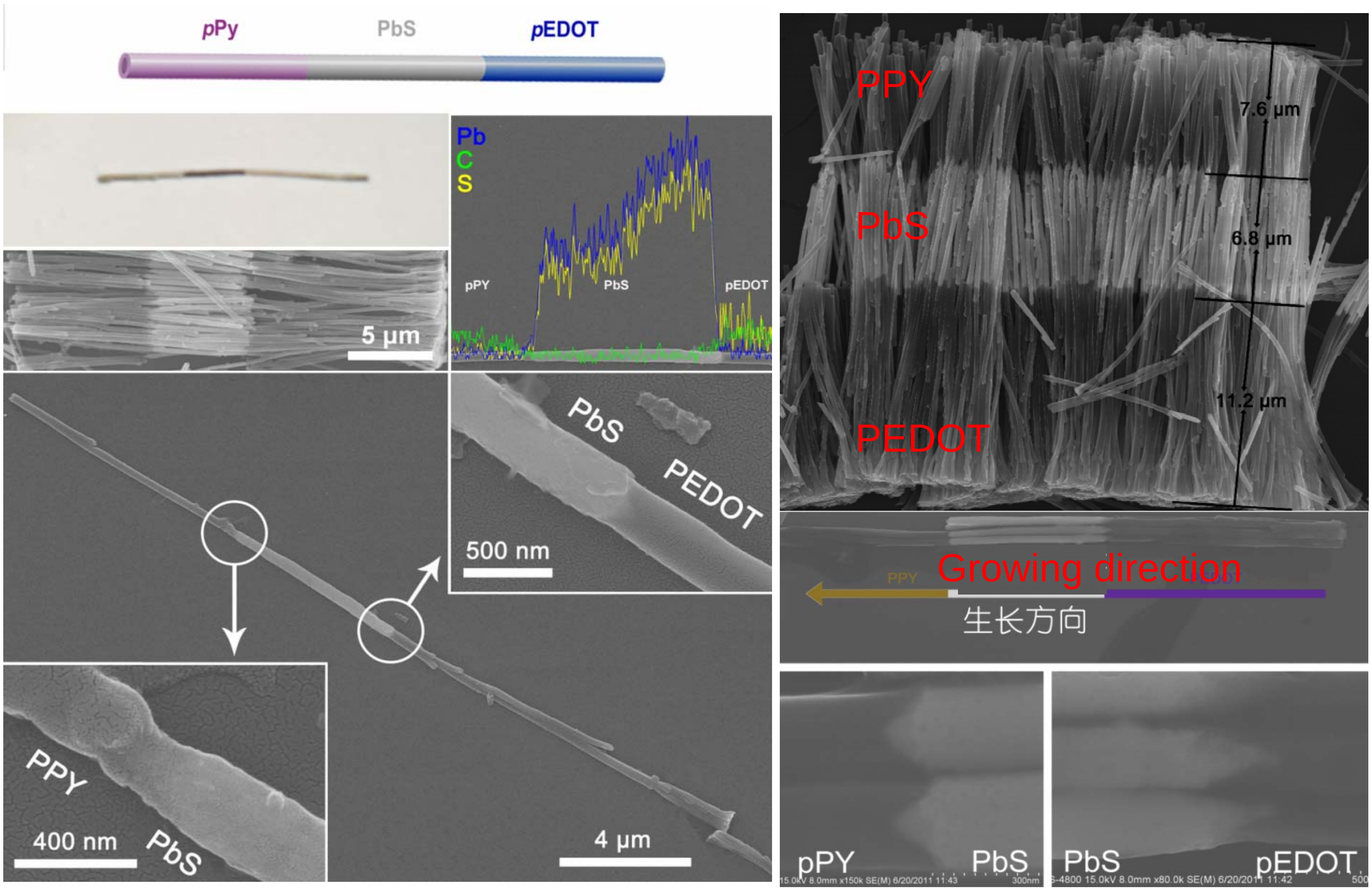


(A)有机/有机异质结纳米线器件原理示意图; (B)氧化态下的I-V 曲线; (C)还原态下的 I-V 曲线; (D) 异质结纳米线开关的重复性

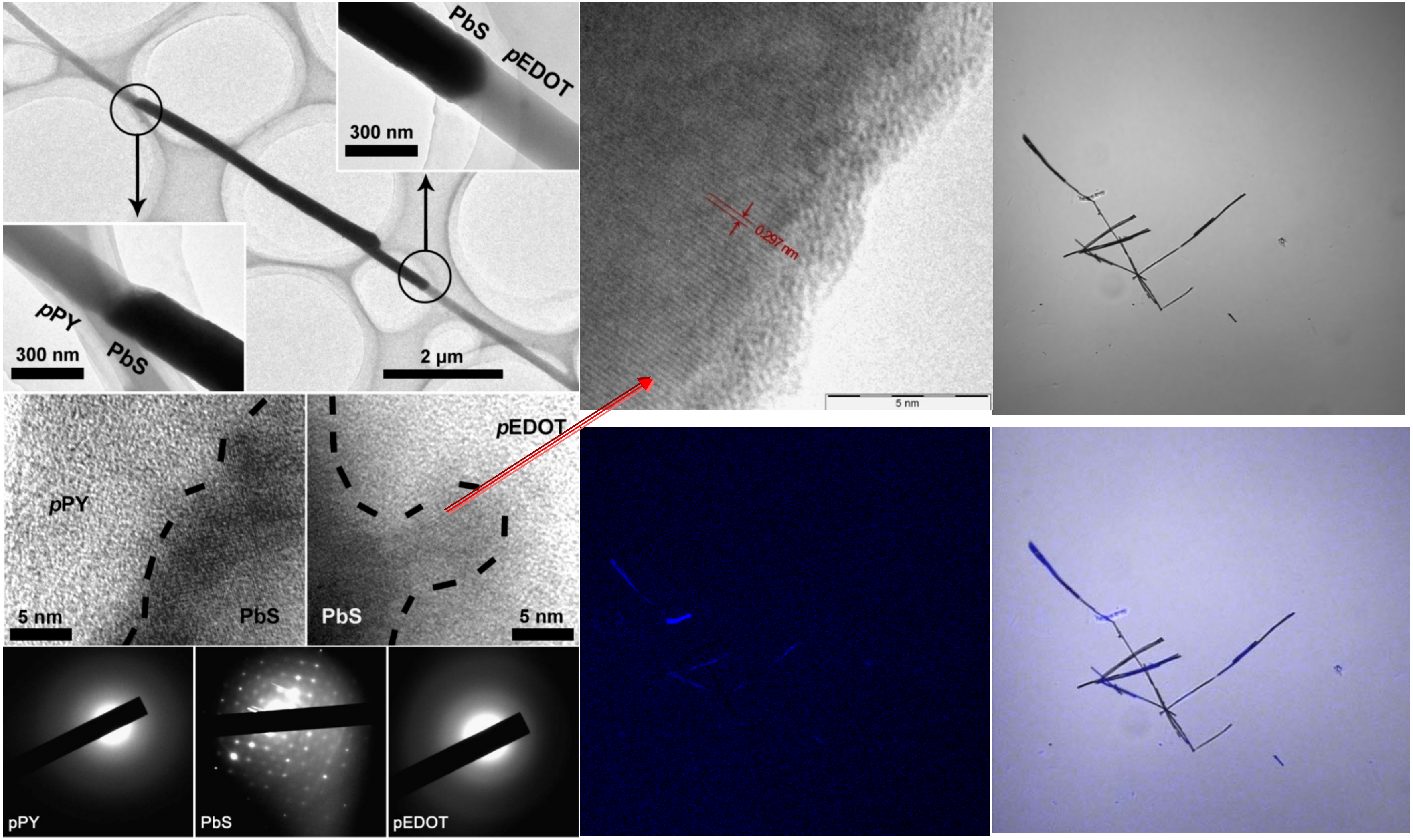
Chem. Asian J. **2011, 6, 98**

J. Am. Chem. Soc. 2005, 127, 12452

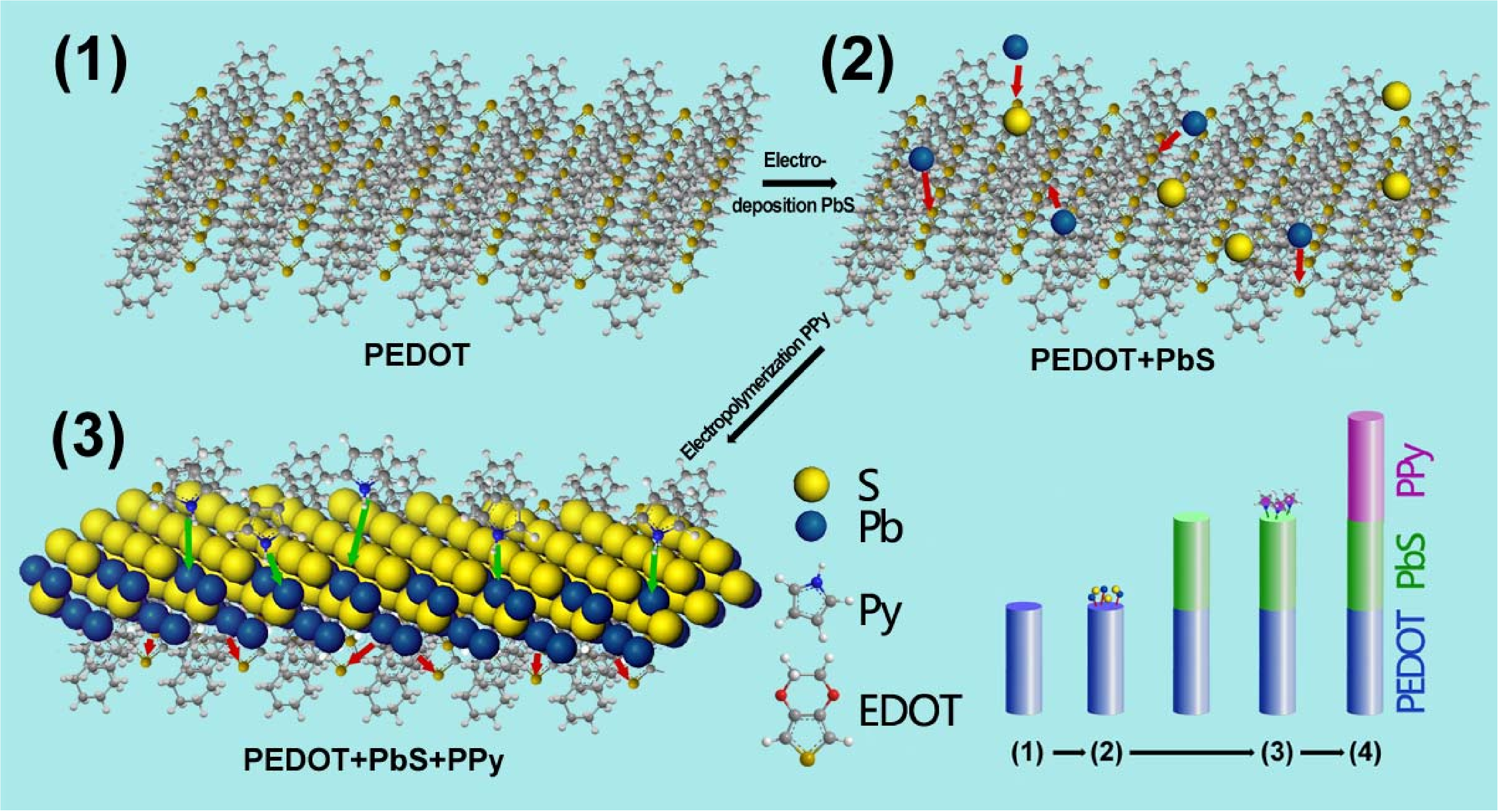
固态双异质结纳米线的逻辑电路的构建



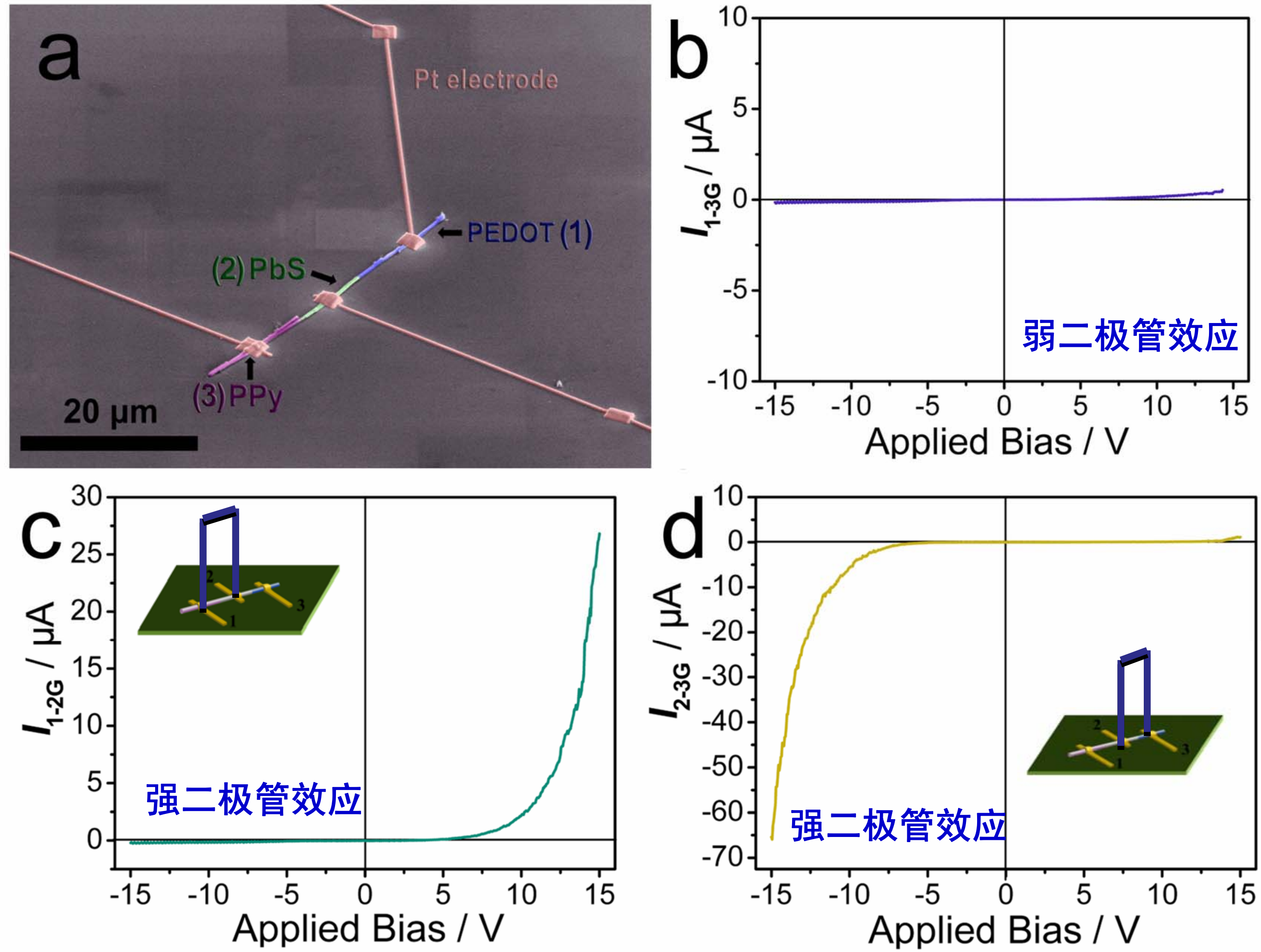
SEM images and EDS pattern of PPY/PbS/PEDOT p-n-p heterojunction nanowire arrays



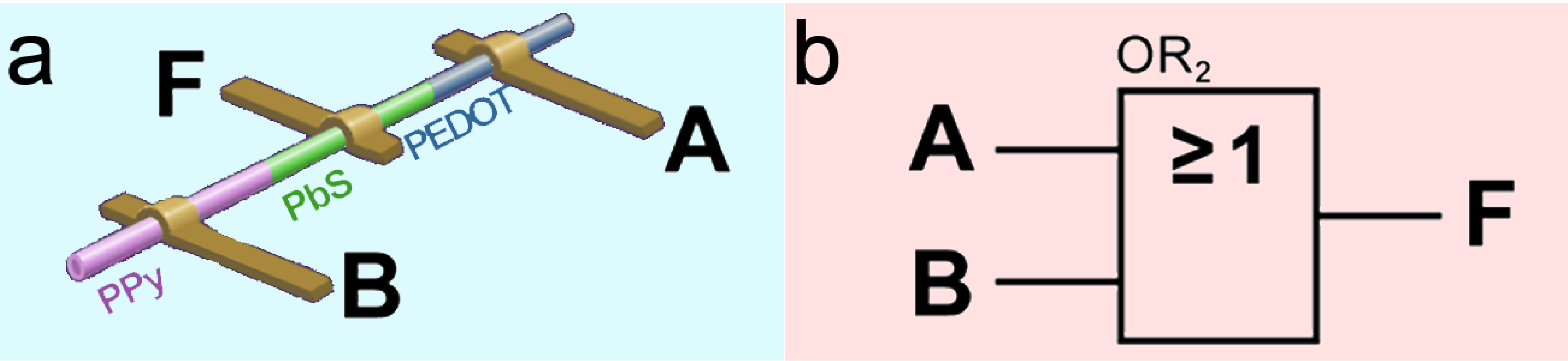
TEM, HRTEM and CLSM images of PPY/PbS/PEDOT p-n-p heterojunction nanowire

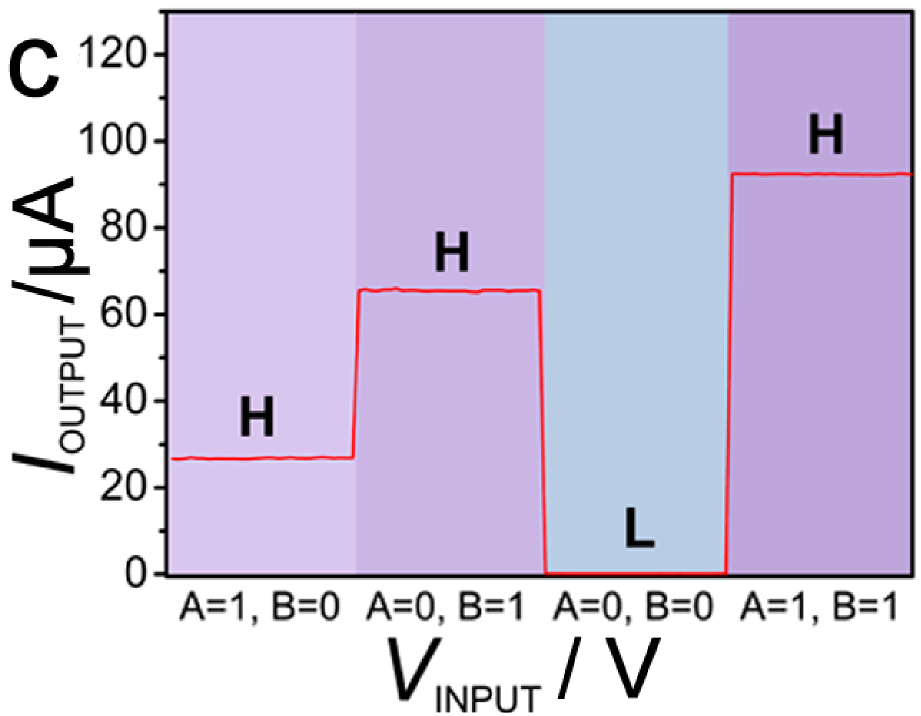


Models of the PPY/PbS/PEDOT p-n-p heterojunction nanowire in different growing stages



Color SEM image of a single PPY/PbS/PEDOT p-n-p heterojunction nanowire device made by FIB (a); *I-V* curves of the three-terminal PPY/PbS/PEDOT nanodevices (b-d)





d

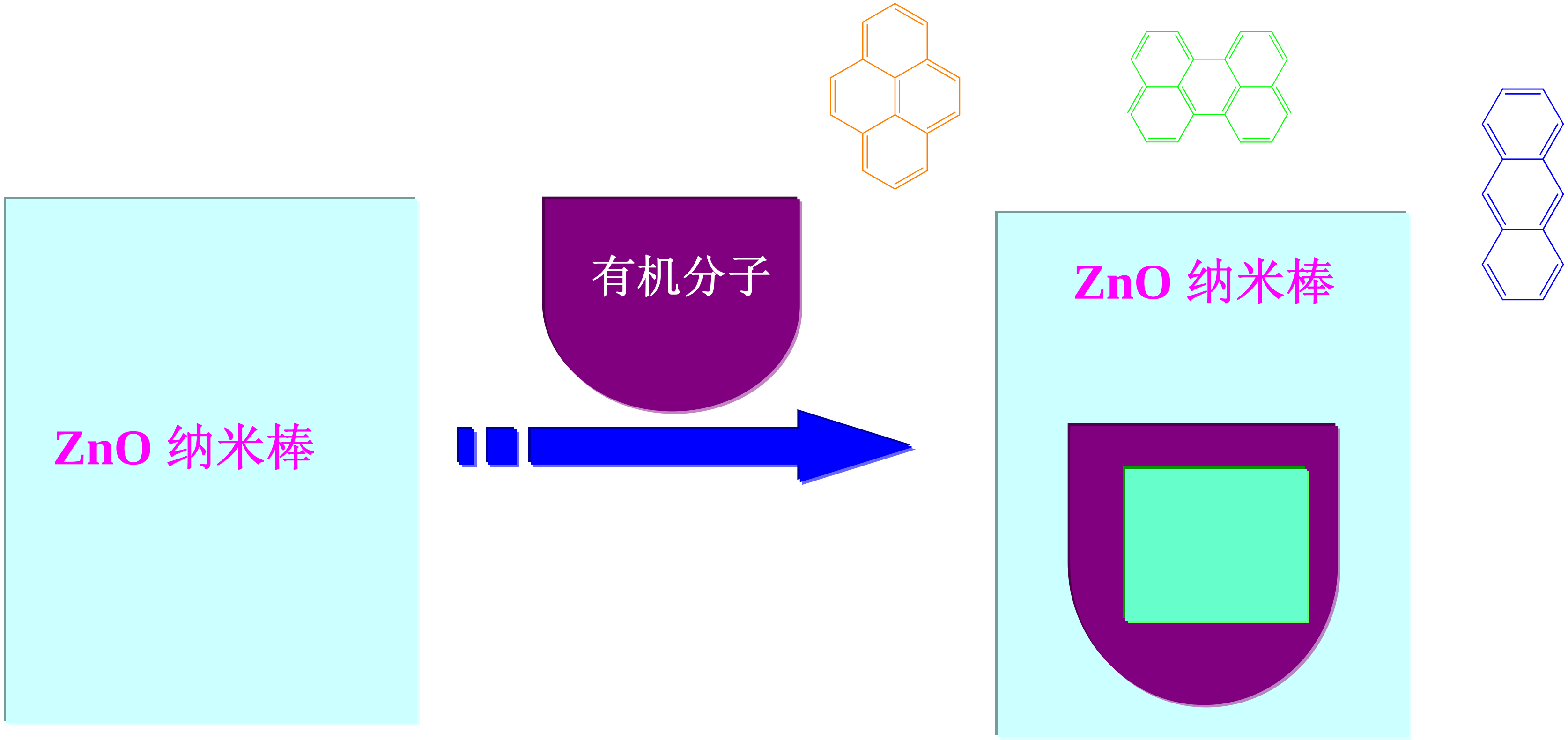
INPUT		OUTPUT
(1) A	(3) B	(2) F=A+B
1	0	HIGH (26.82 μA)
0	1	HIGH (65.39 μA)
0	0	LOW (≈0 μA)
1	1	HIGH (92.25 μA)

1= 15 V; 0= $V_{Li} \in (-15, 0]$

PEDOT-PbS-PPy异质结纳米线逻辑或门原理

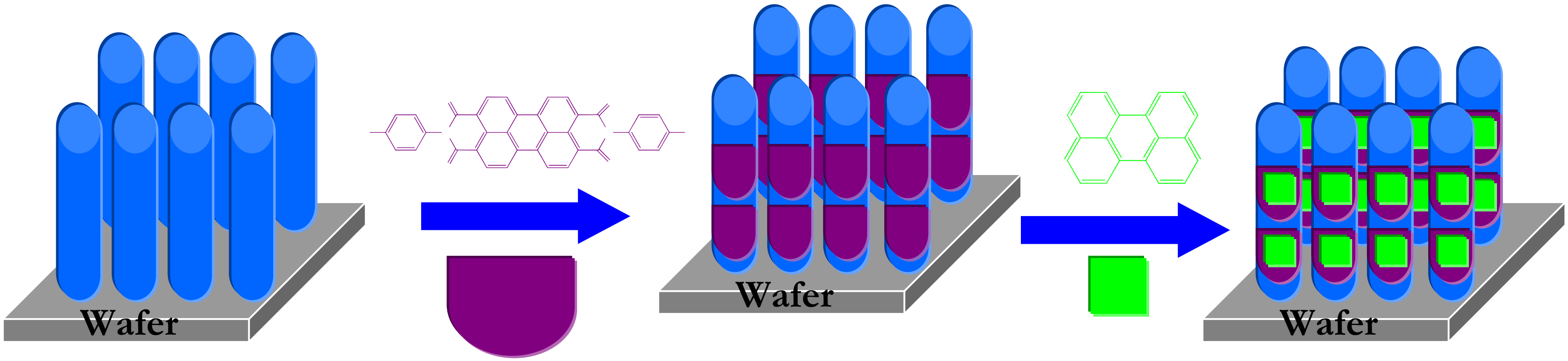
无机/ 有机杂化“分子口袋”

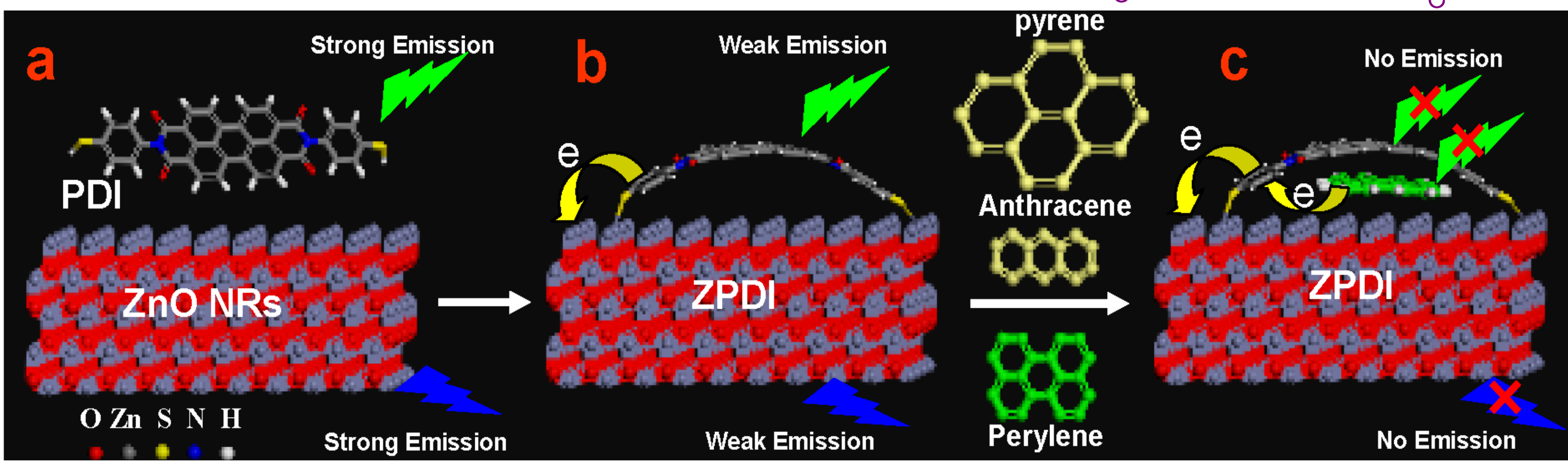
成功地在固体表面获得了功能性“分子口袋”



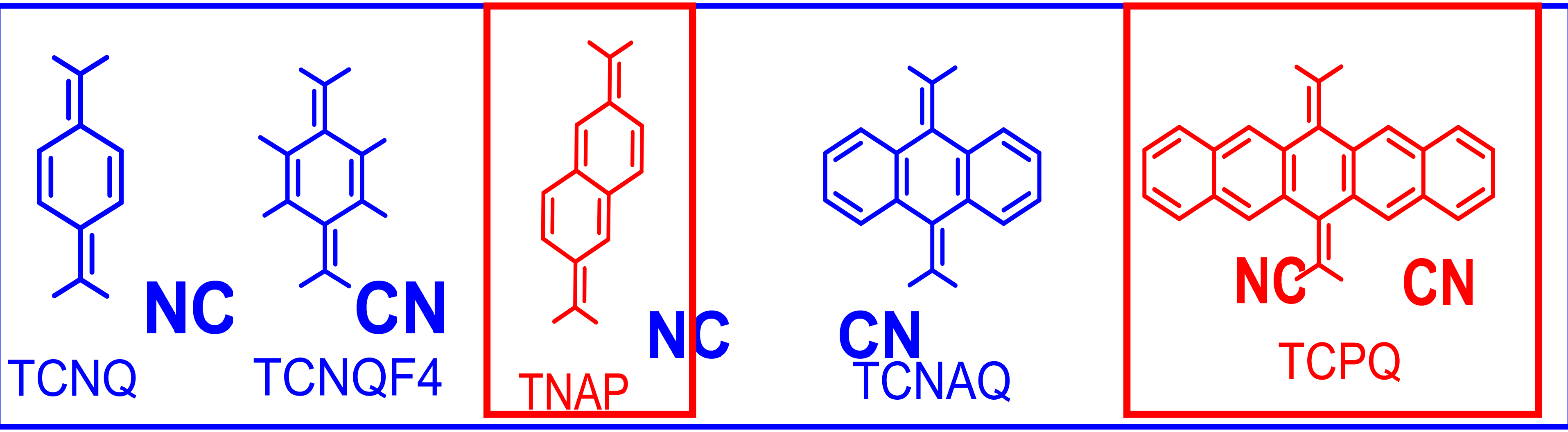
Angew Chem. Int. Edt. 2010, 49, 2705-2707

Angew Chem. Int. Edt. **2010, 49, 2705-2707**





大面积电荷转移盐聚集态的可控生长



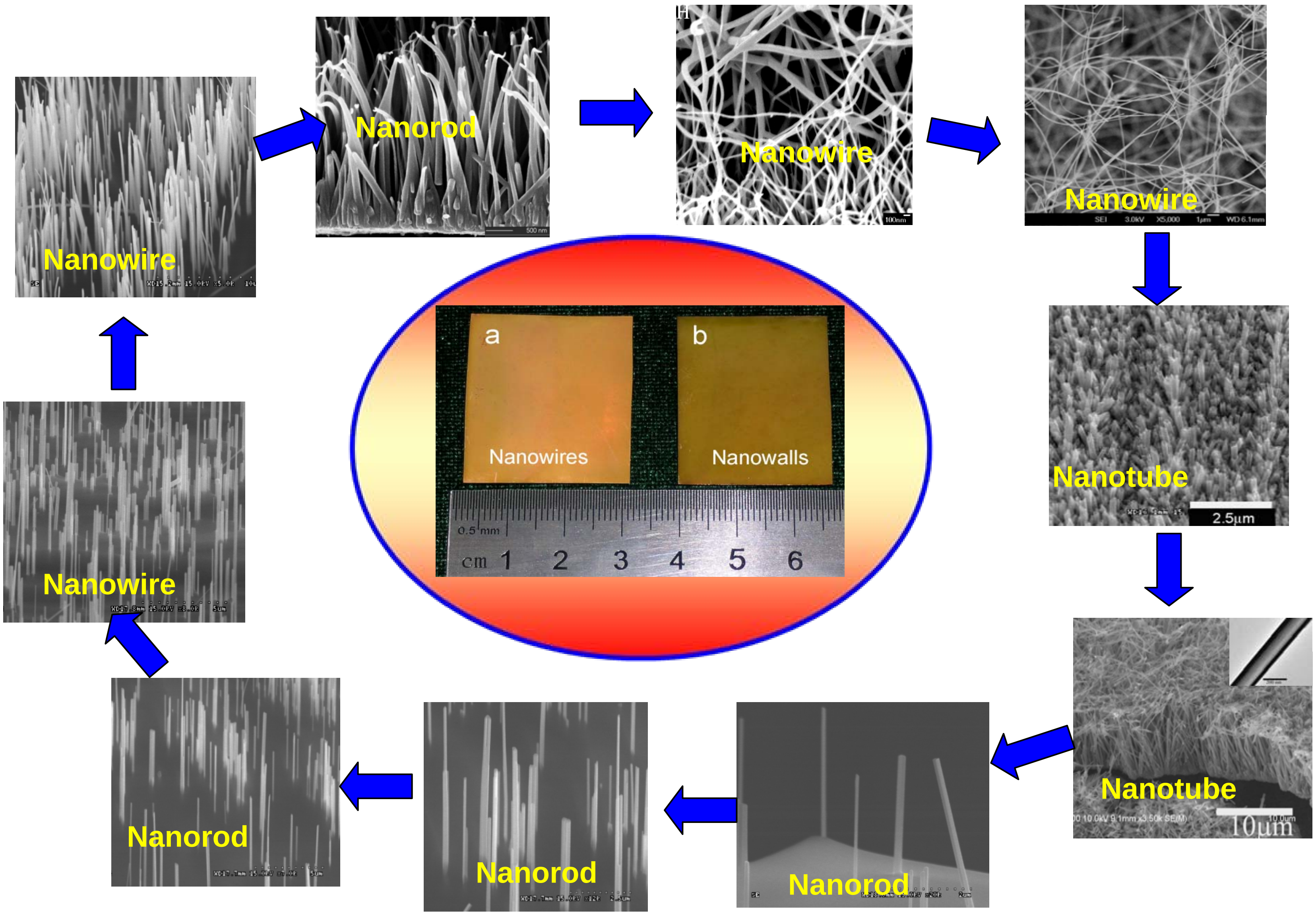
气-固相反应　Cu　△　Ag　液-固相反应

自组装技术

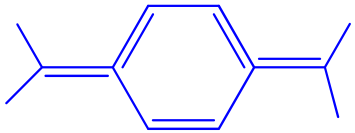
CuTCNQ，AgTCNQ，CuTCNQF4，AgTCNQF4，CuTNAP, CuTCNAQ，CuTCPQ

Adv. Mater. 2008, 20, 309
Adv. Mater. 2008, 20, 2918
J. Am. Chem. Soc. 2005, 127, 1120

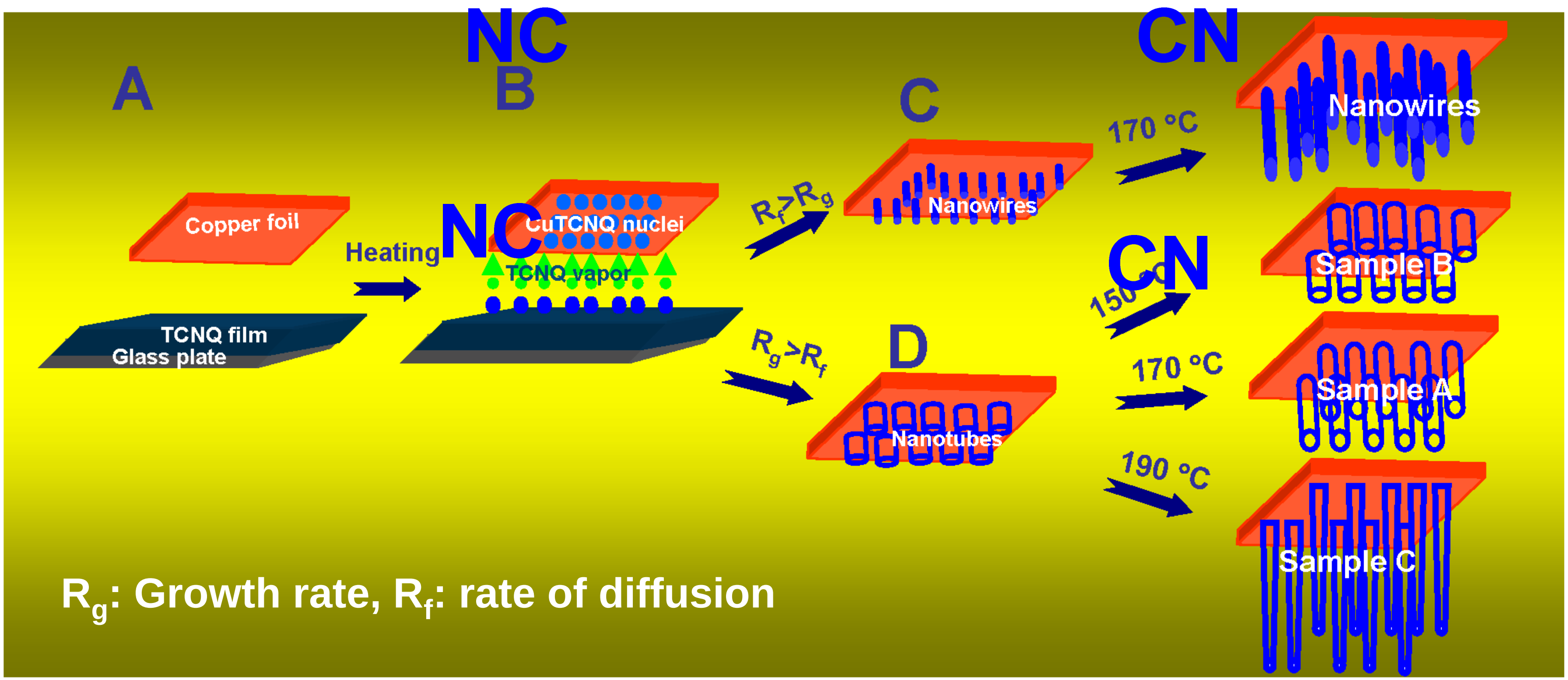
成功地将有机电荷转移盐引入了纳米尺度研究，并实现了大面积，高有序的纳米阵列及其性能的调控



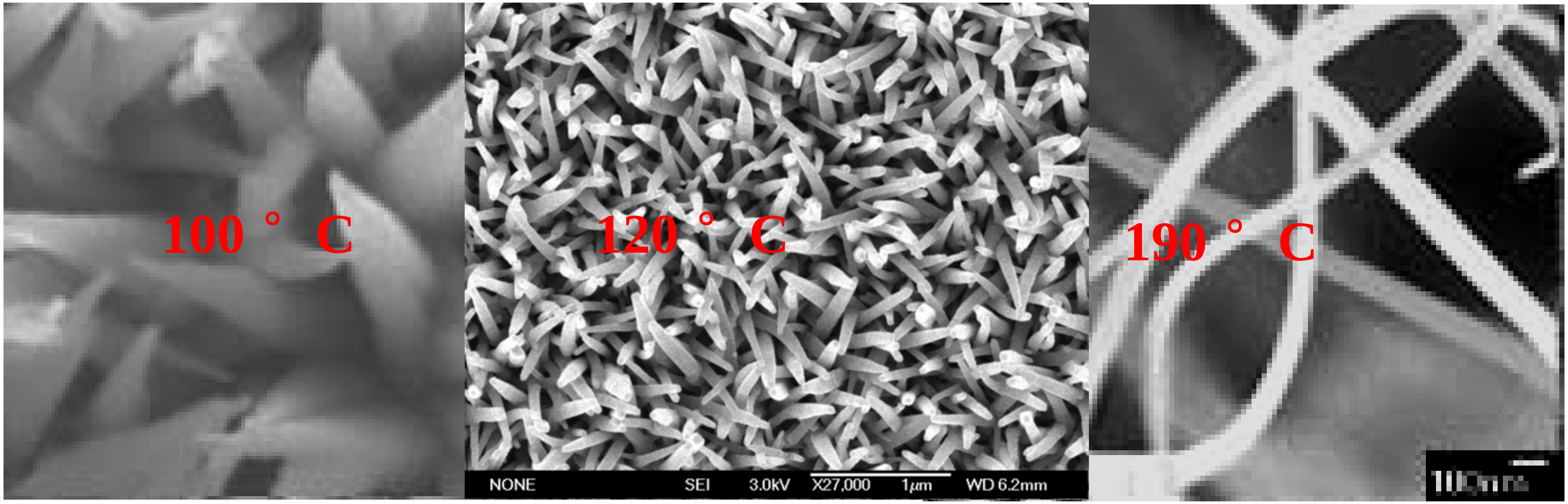
CuTCNQ 纳米阵列的可控生长



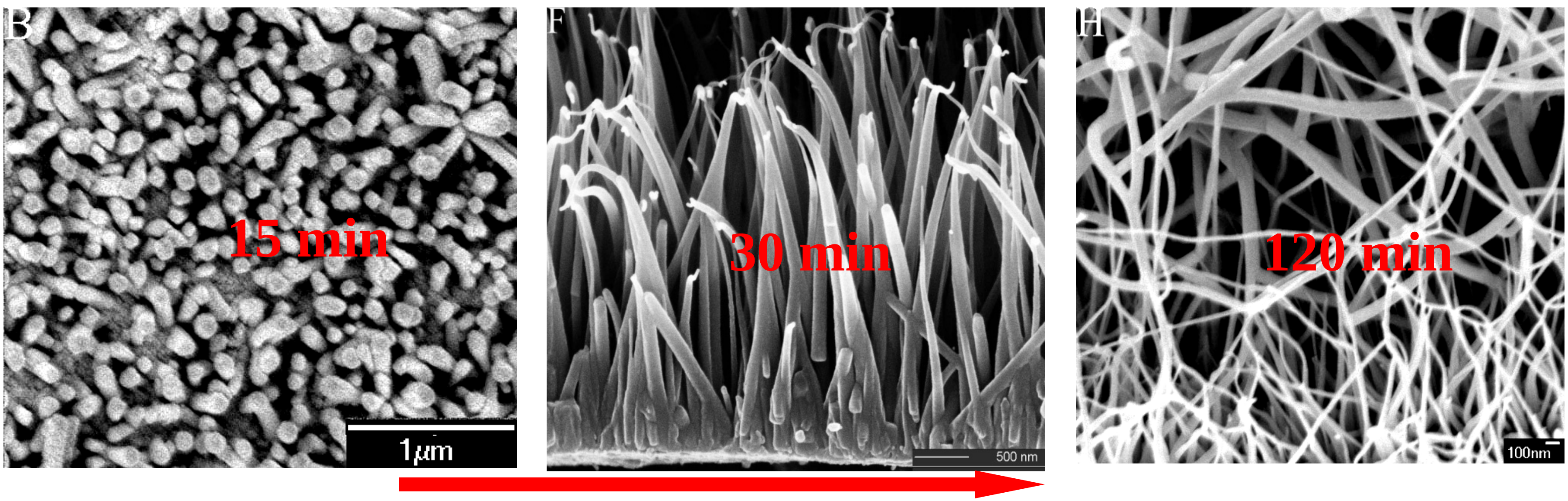
$$TCNQ + Cu(Ag) \xrightarrow{\Delta} Cu(Ag)TCNQ$$



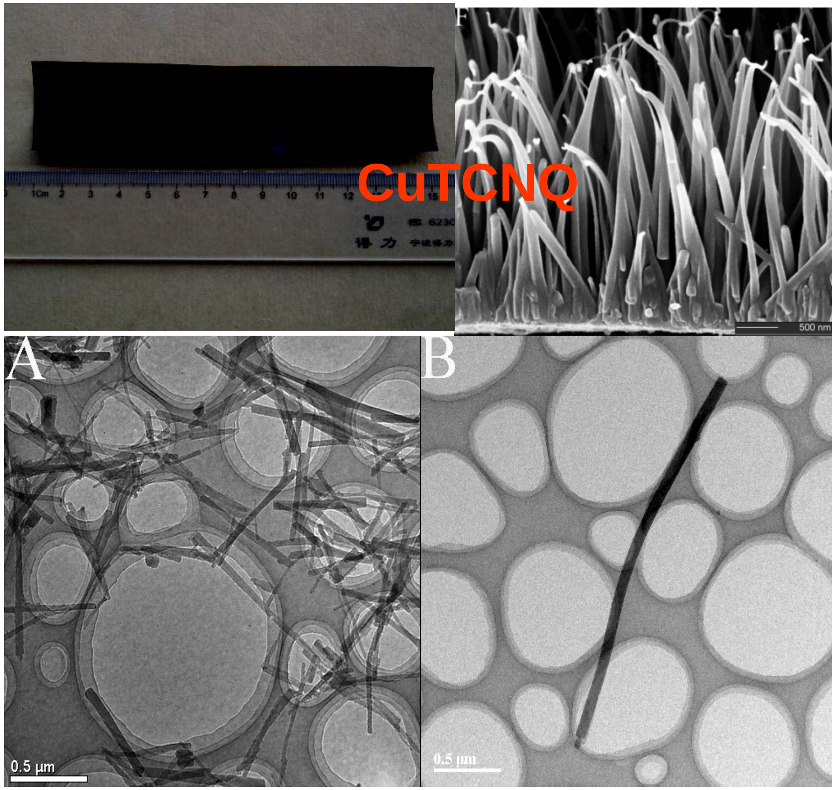
气-固相反应生长电荷转移复合物纳米阵列生长机理

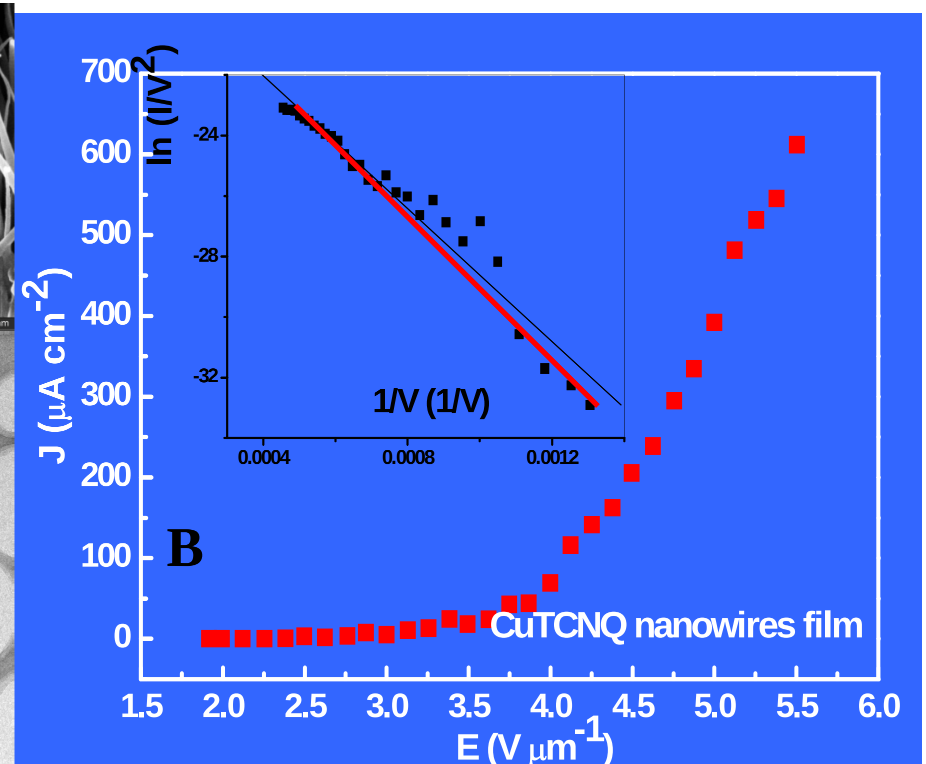


随着反应温度的增加，纳米线直径减小，长度增加



随着反应时间的延长，直径减小，纳米线长度增加



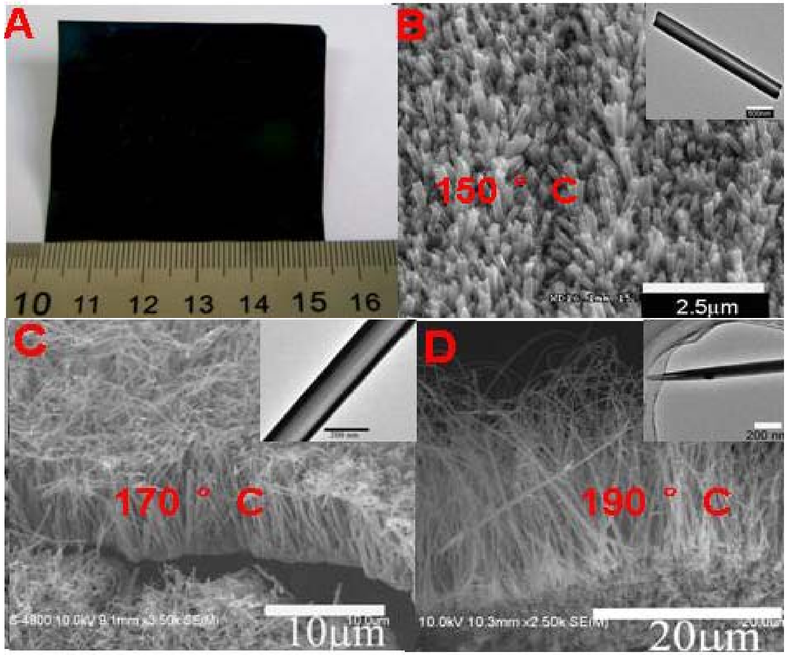


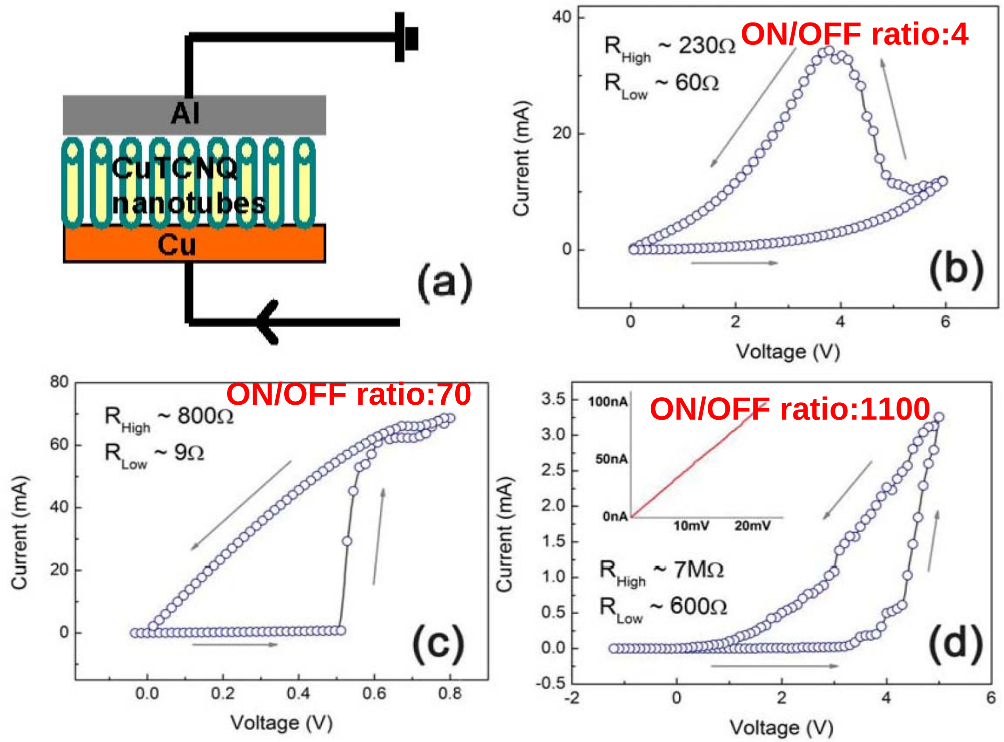
TEM images of CuTCNQ nanowires

Field emission J-E curve of the CuTCNQ nanowires and the corresponding FN plot (inset), turn on field 3.13V

***J. Am. Chem. Soc.* 2005, *127*, 1120**

CuTCNQ 纳米管阵列性能调控

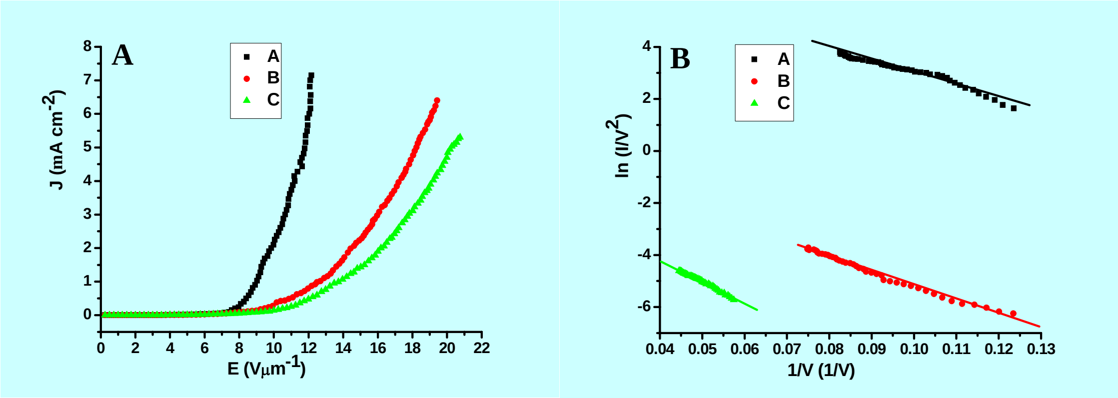




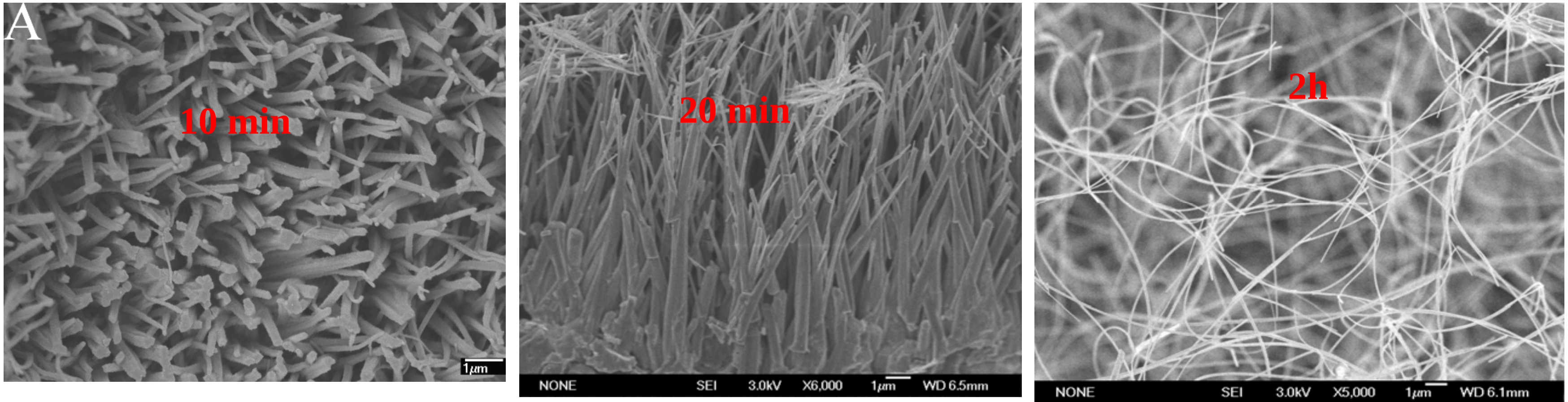
电开关的形貌和尺寸效应

Turn on field : 4.49, 5.25 and 4.99 V/μm

J: 7.15 mA/cm², 11.6 times of nanowires



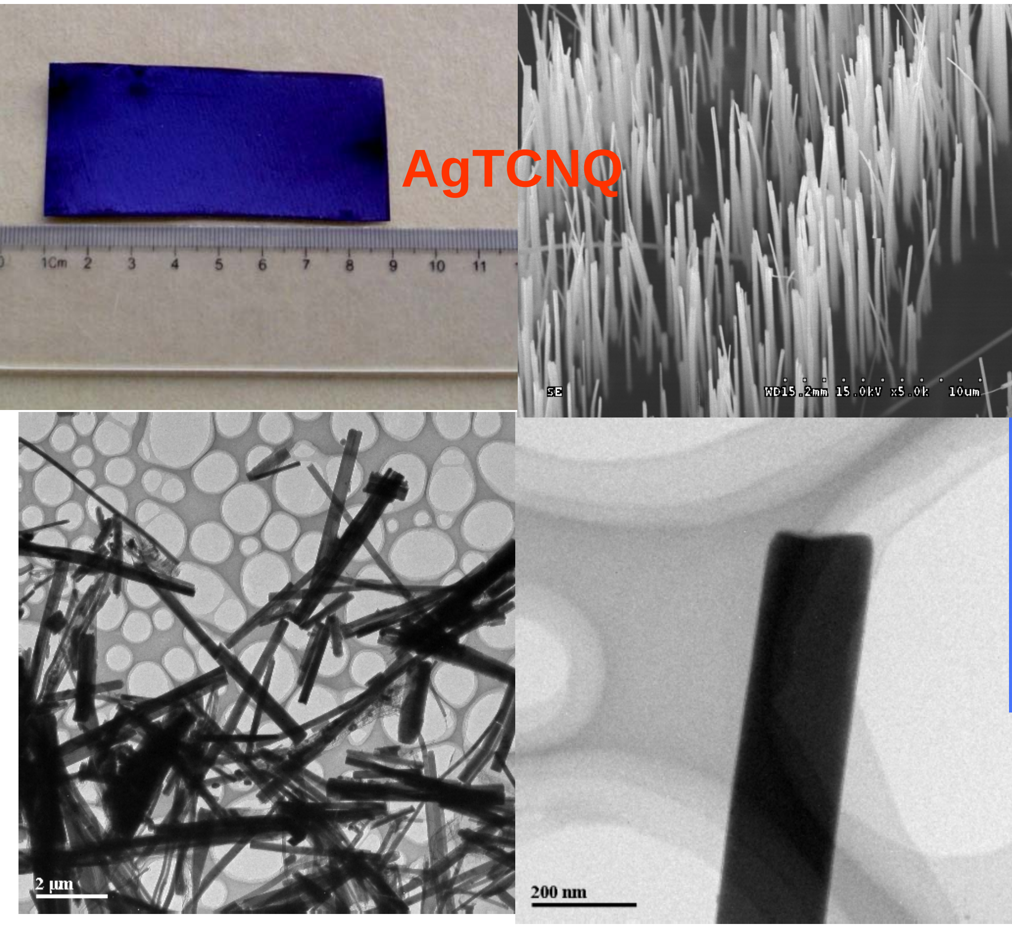
Cryst. Grow. Des. **2010, 10, 237**

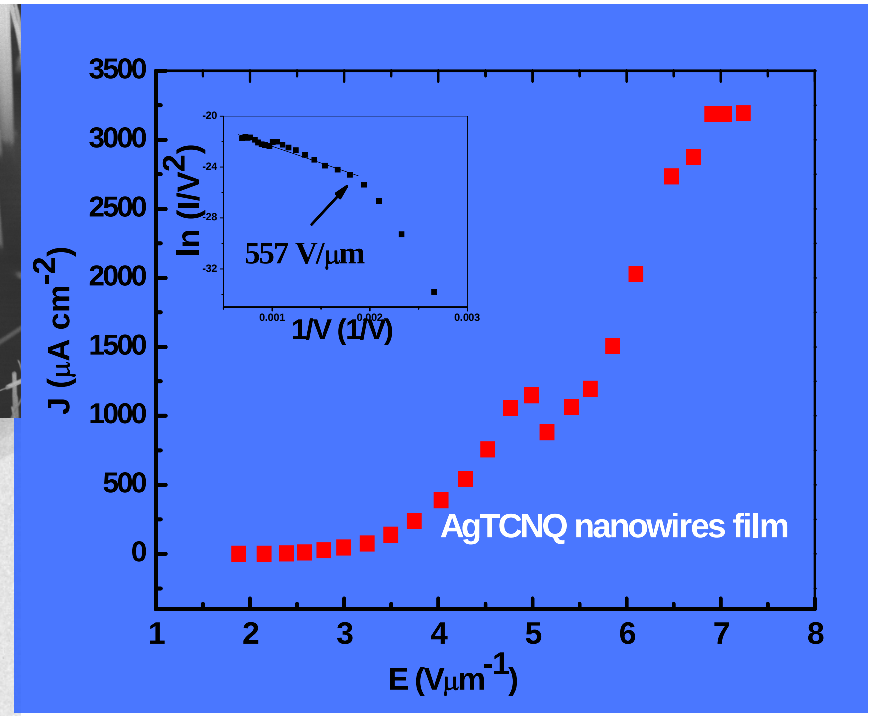


随着反应时间的延长，直径减小，纳米线长度增加

随着电场增加**AgTCNQ**纳米线阵列的密度增大

AgTCNQ 纳米线阵列的可控生长与场发射性质

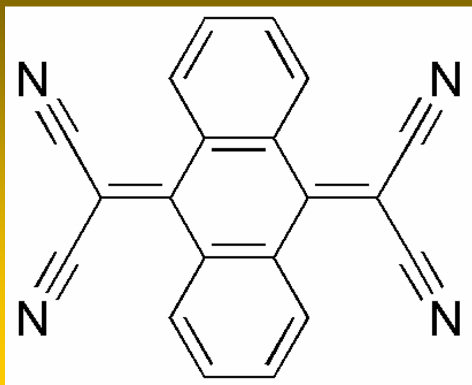




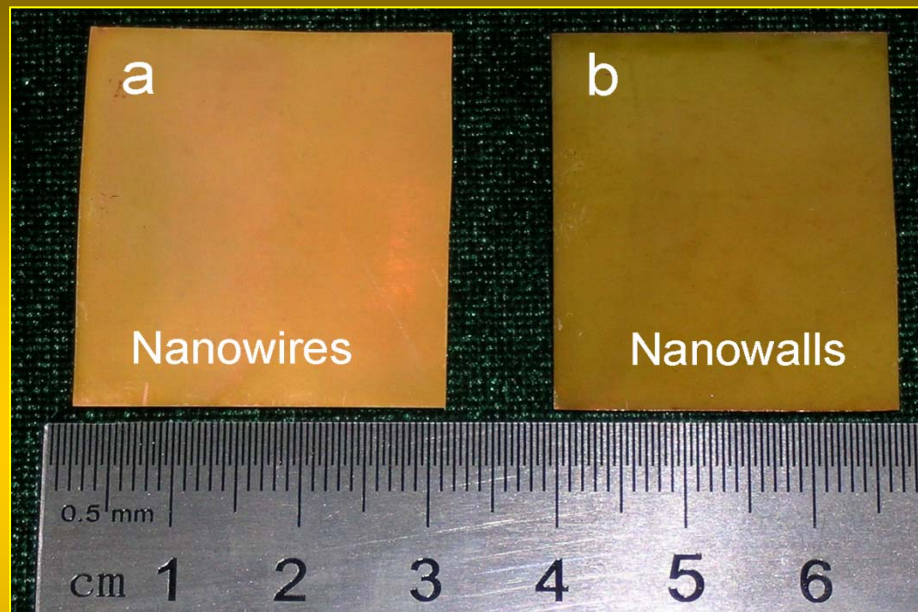
TEM images of AgTCNQ nanowires. Field emission J-E curve of the CuTCNQ nanowires and the corresponding FN plot (inset), turn on field E_{to} = 2.58V / μ m

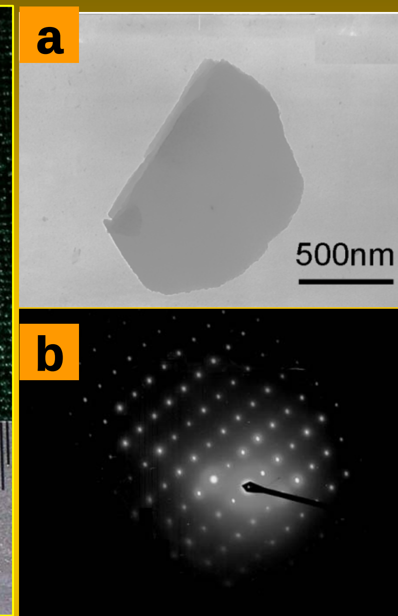
***J. Am. Chem. Soc.* 2005, 127, 1120**

有机液固相反应构筑电荷转移盐聚集态



TCNAQ:
11,11,12,12-
Tetracyanoanthraquin
-odimethane



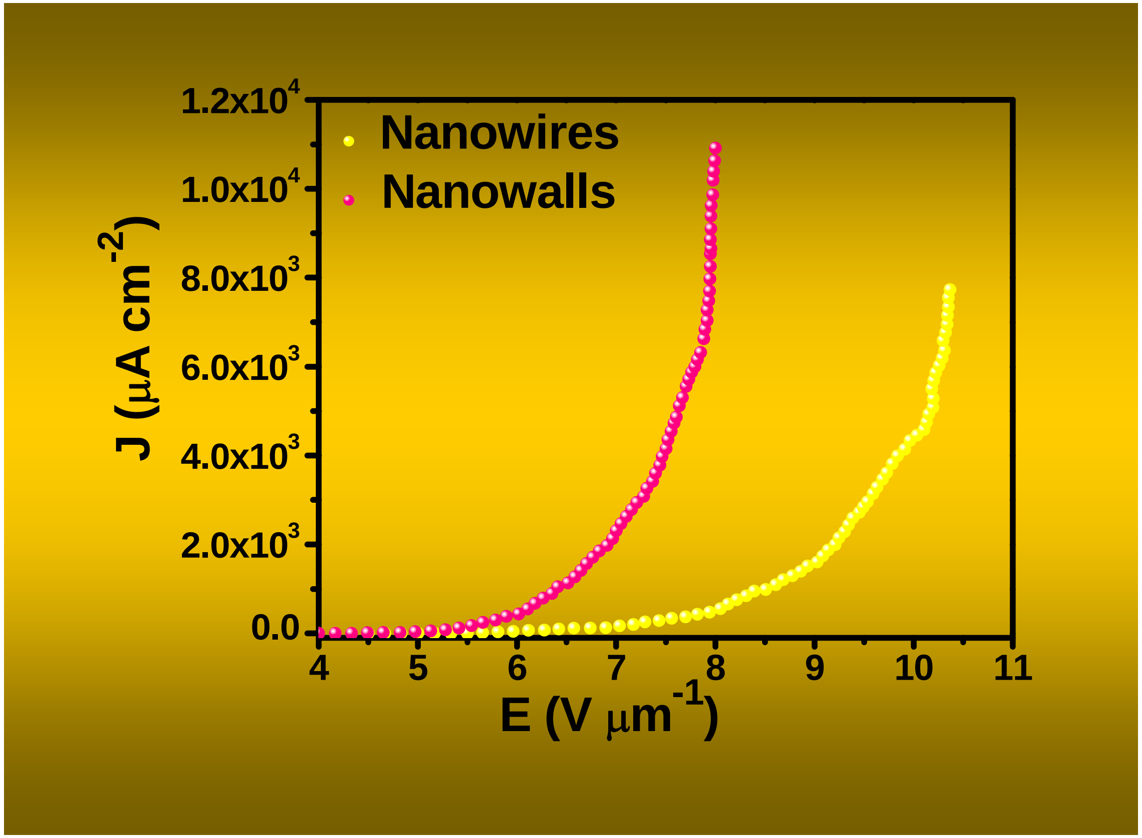


大面积构筑 **CuTCNAQ**纳米聚集态

$$Cu^0 + TCNAQ^0 \longrightarrow (Cu^+)(TCNAQ^-)$$

Adv. Mater. 2008, 20, 309

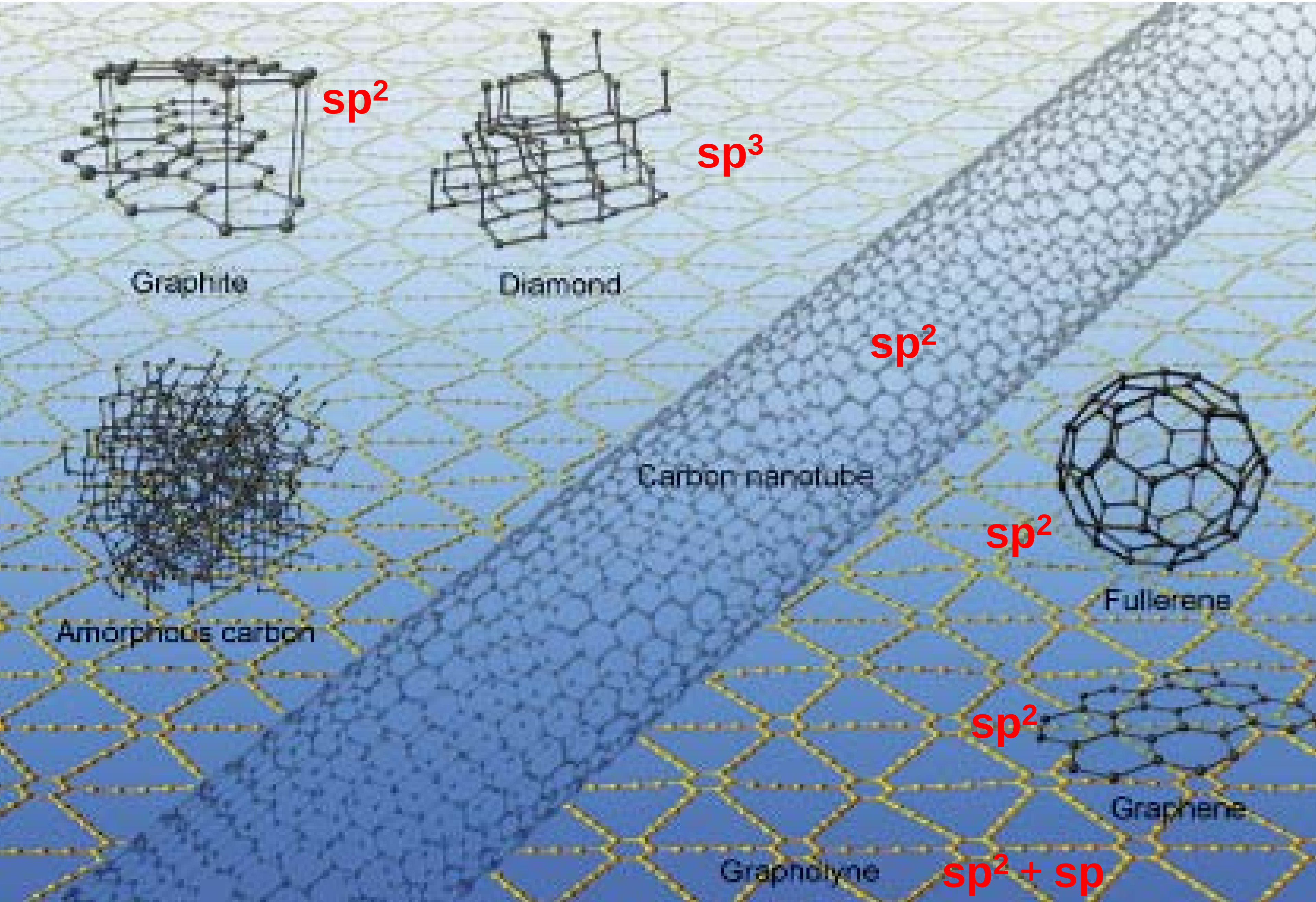
是目前无机/有机体系中场
发射综合性能最好的



Field Emission Properties of Cu-TCNAQ Nanoarrays

Materials	E_{to}	J_{max}
CuTCNQ nanowires	3.13	0.6
AgTCNQ nanowires	2.58	3.2
CuTCNAQ nanowalls	4.5	10.9
Polydiacetylenes	8.2	6
PTh nanowires	3.5	0.1
AlQ3 nanowires	10	15
Carbon nanotubes	1.5	10
ZnO nanorods	6.5	50
CuS nanowalls	8.5	2.4
ZnS nanobelts	3.5	12
GaN nanowires	12	0.02
AlN Nanorods	3.8	7
SiC nanowires	5	83

石墨炔(Graphdiyne)



挑战：人工合成碳的新同素异形体

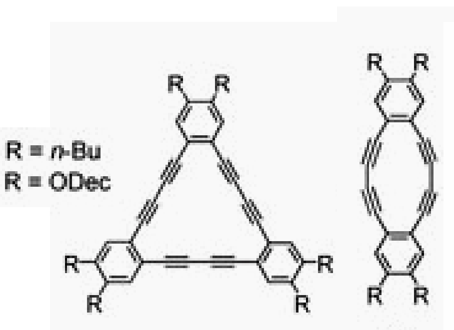
1968年A. T. Balaban理论预测了最有可能人工合成的碳同素异形体- Graphdiyne

Rev. Roum. Chim. 13, 231 (1968)

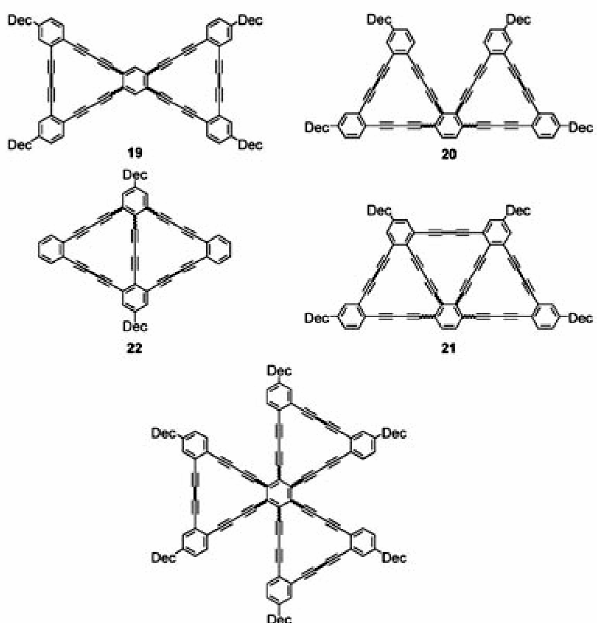
sp^2+sp

N. Narita进行了理论计算Phys. Rev. B 58, 11009 (1998)

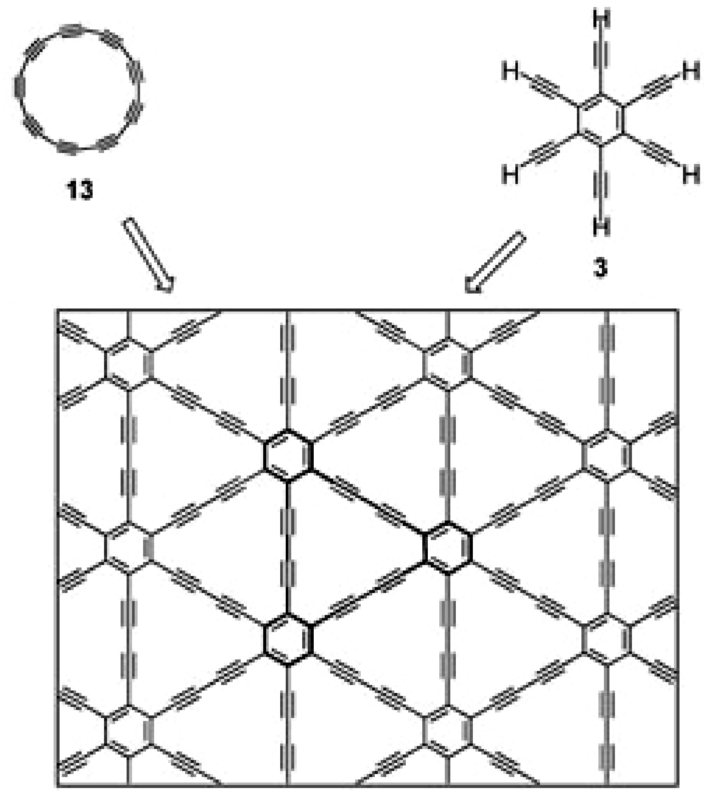
F. Diederich, M. M. Haley和Y. Tobe等没有成功，只能得到小片段！

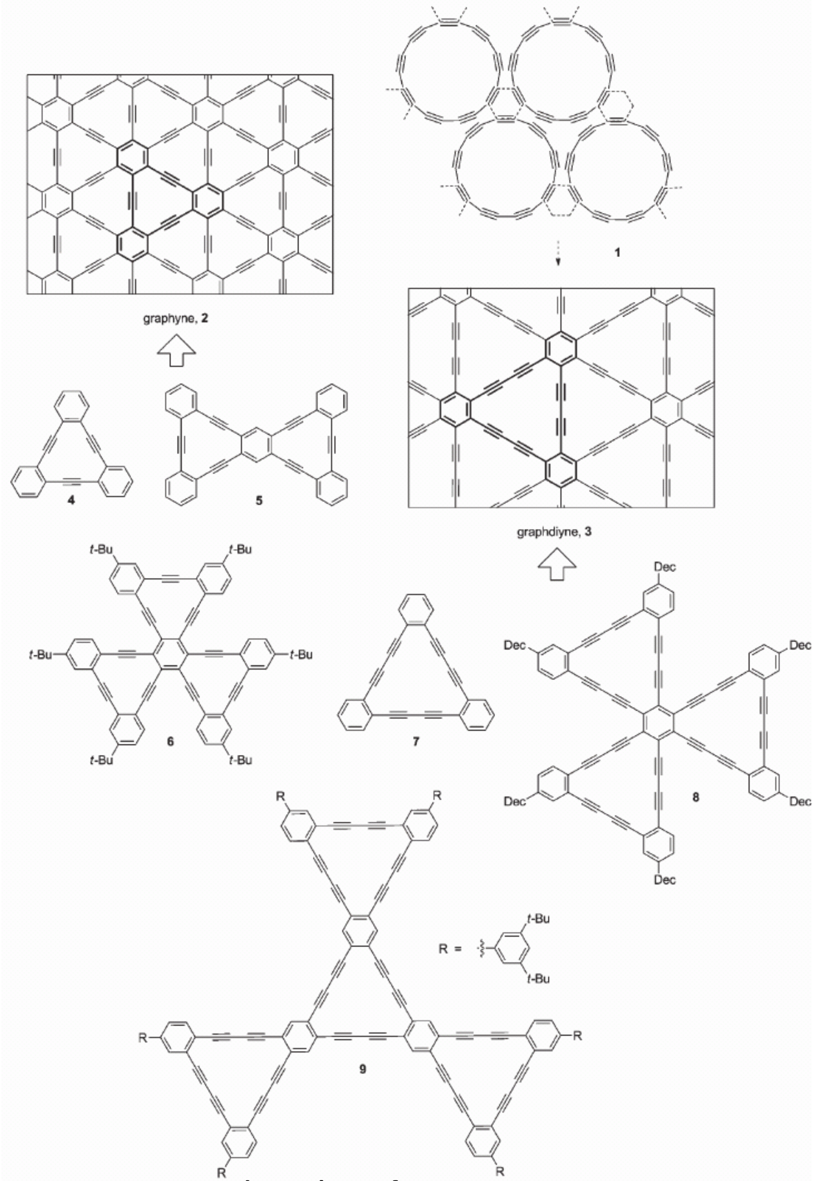


1957年G. Eglinton



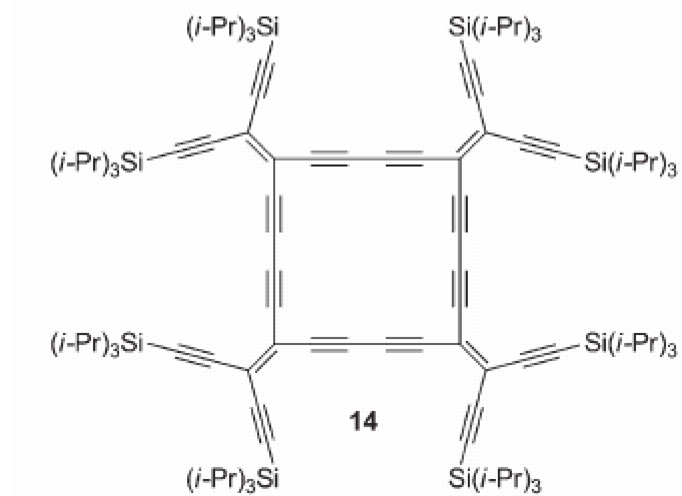
2000年之后M． M． Haley

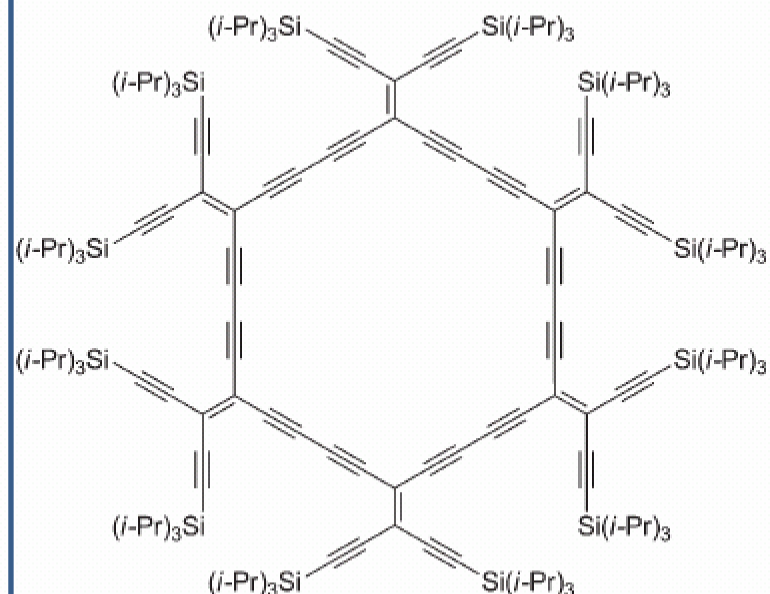




Review: F. Diederich ***Adv. Mater.*** 2010, 22, 803
M. M. Haley ***Pure Appl. Chem,*** 2008,80, 519

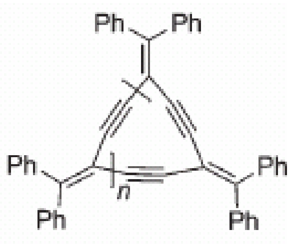
Benzannellated dehydroannulene
-derived substructures

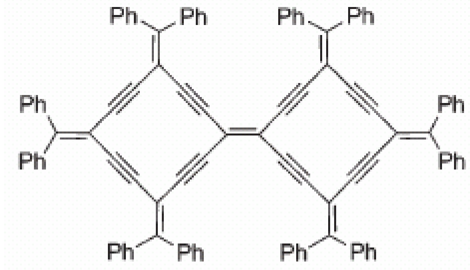




Angew. Chem. Int. Ed. 1992, 31, 931

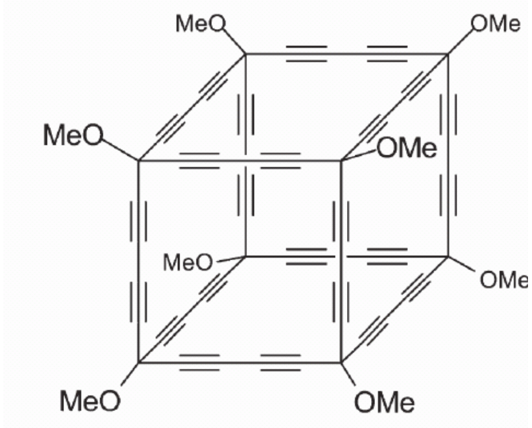
Perethynylated expanded radialenes





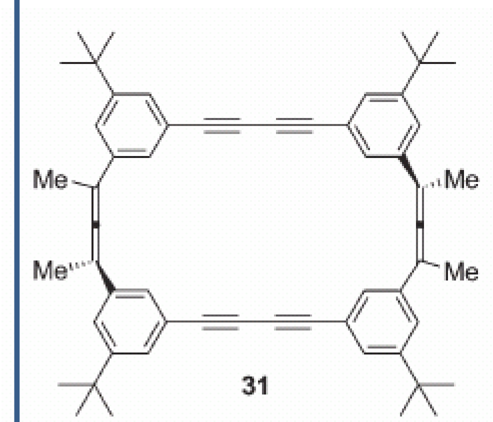
Pure Appl. Chem. 2008, 80, 621
Angew. Chem. Int. Ed. 2007, 46, 9081.

Expanded radialene scaffolds

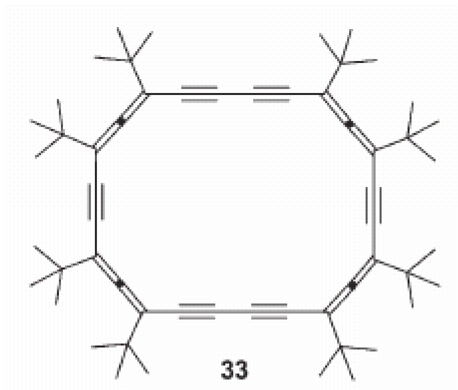


Angew. Chem. Int. Ed. 2002, 41, 4339

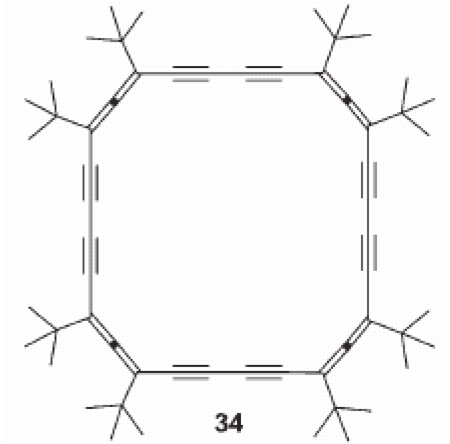
An expanded cubane



31



33



34

Angew. Chem. Int. Ed. 2005, 44, 4039

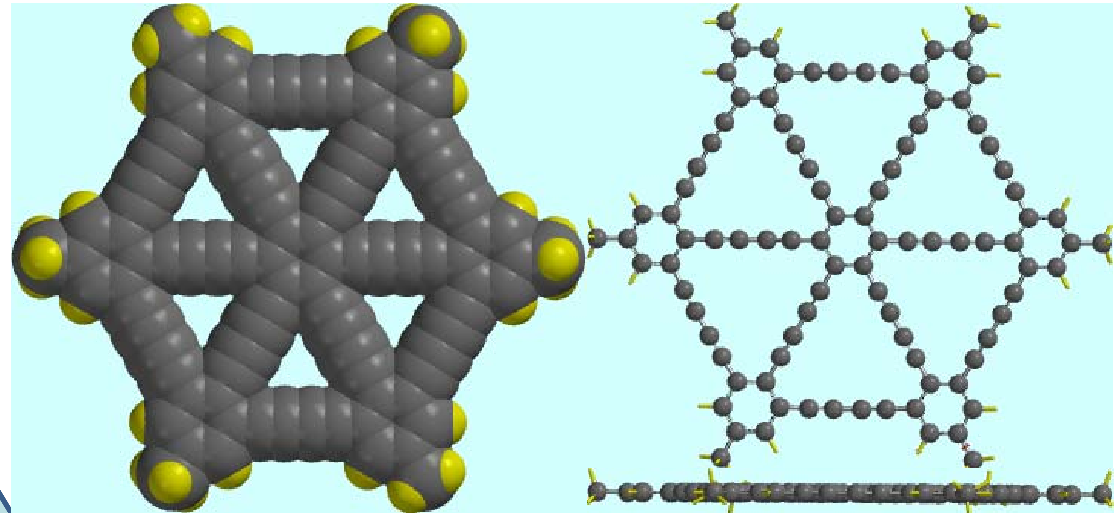
Angew. Chem. Int. Ed. 2005, 44, 5074

Angew. Chem. Int. Ed. 2009, 48, 5545

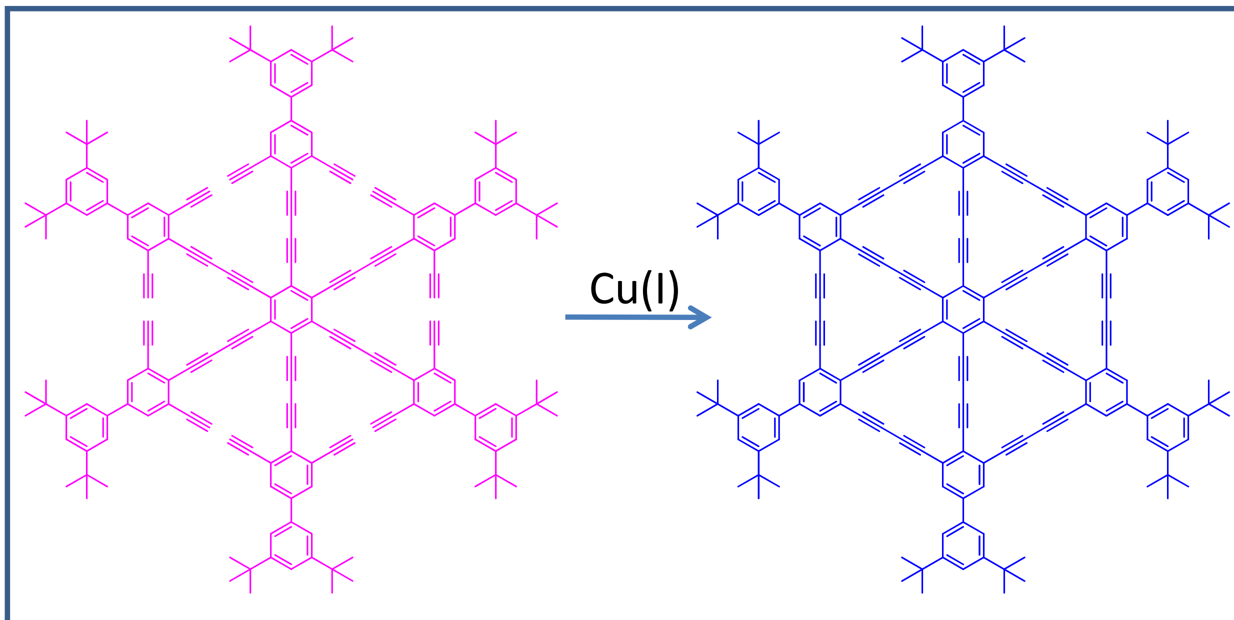
Alleno-Acetylenic Macrocycles

石墨二炔单元的化学合成

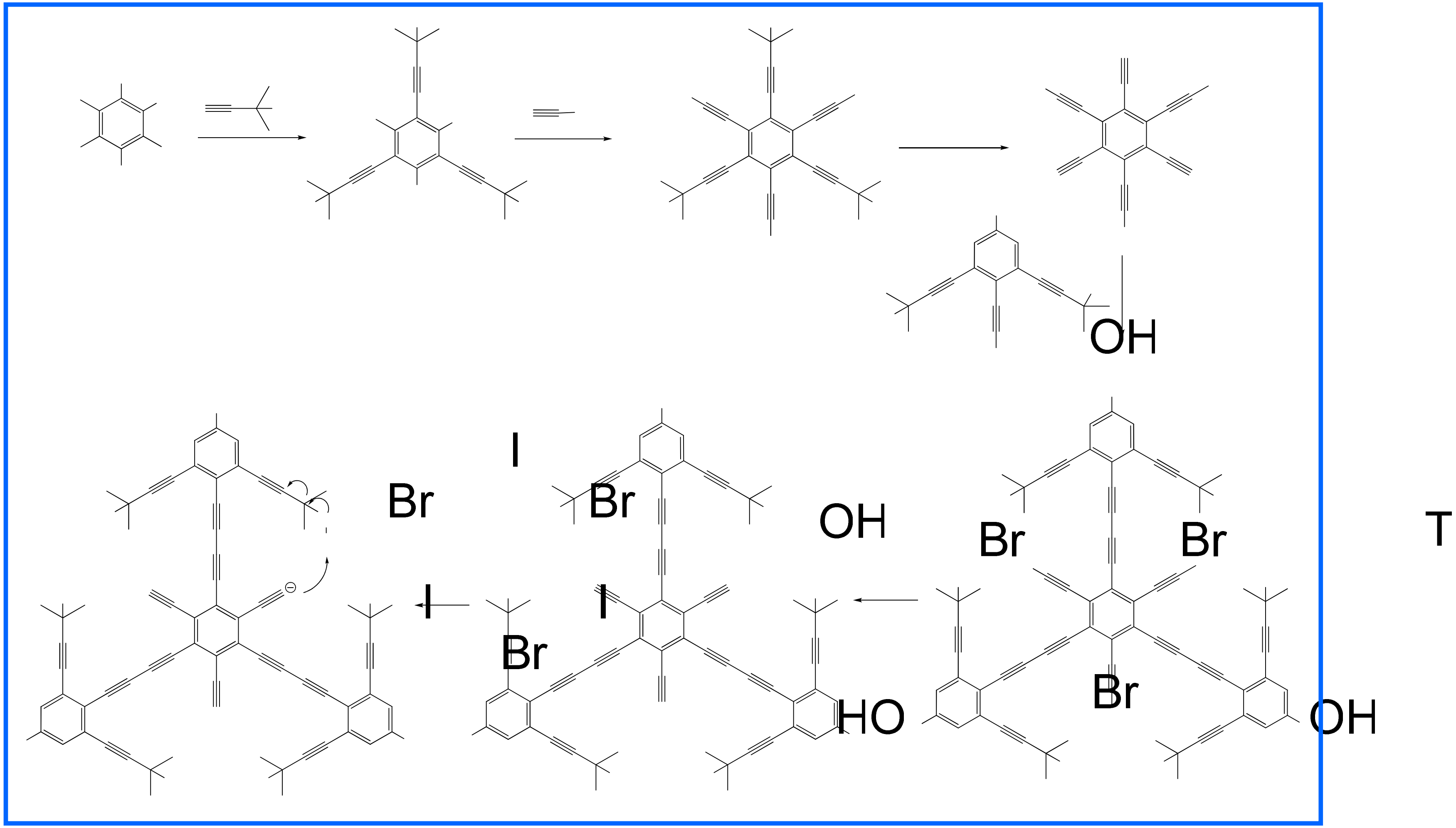
- ◆石墨炔的结构
- ◆本征性质
- ◆光电性质机制



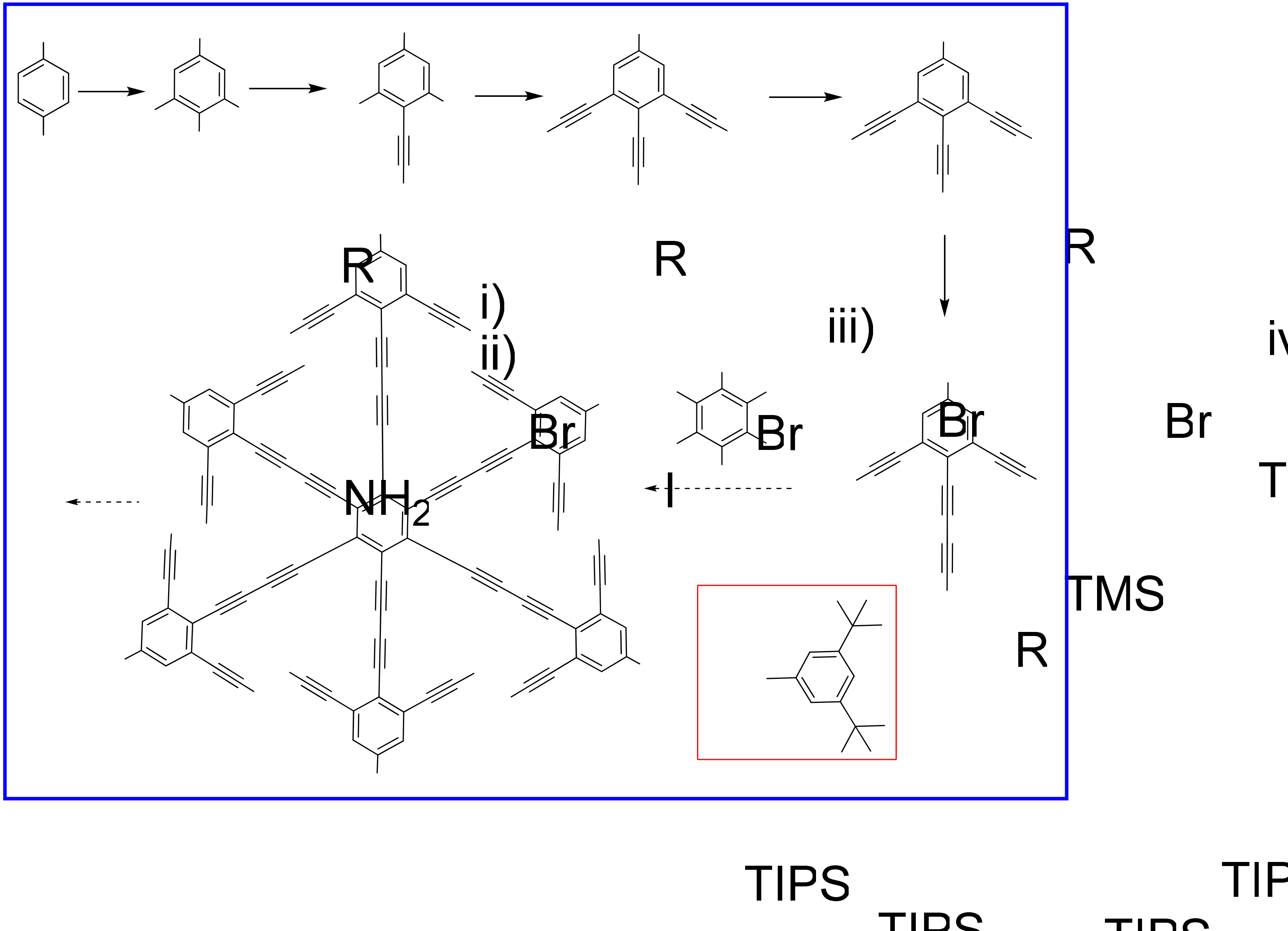
芳香平面，中心对称



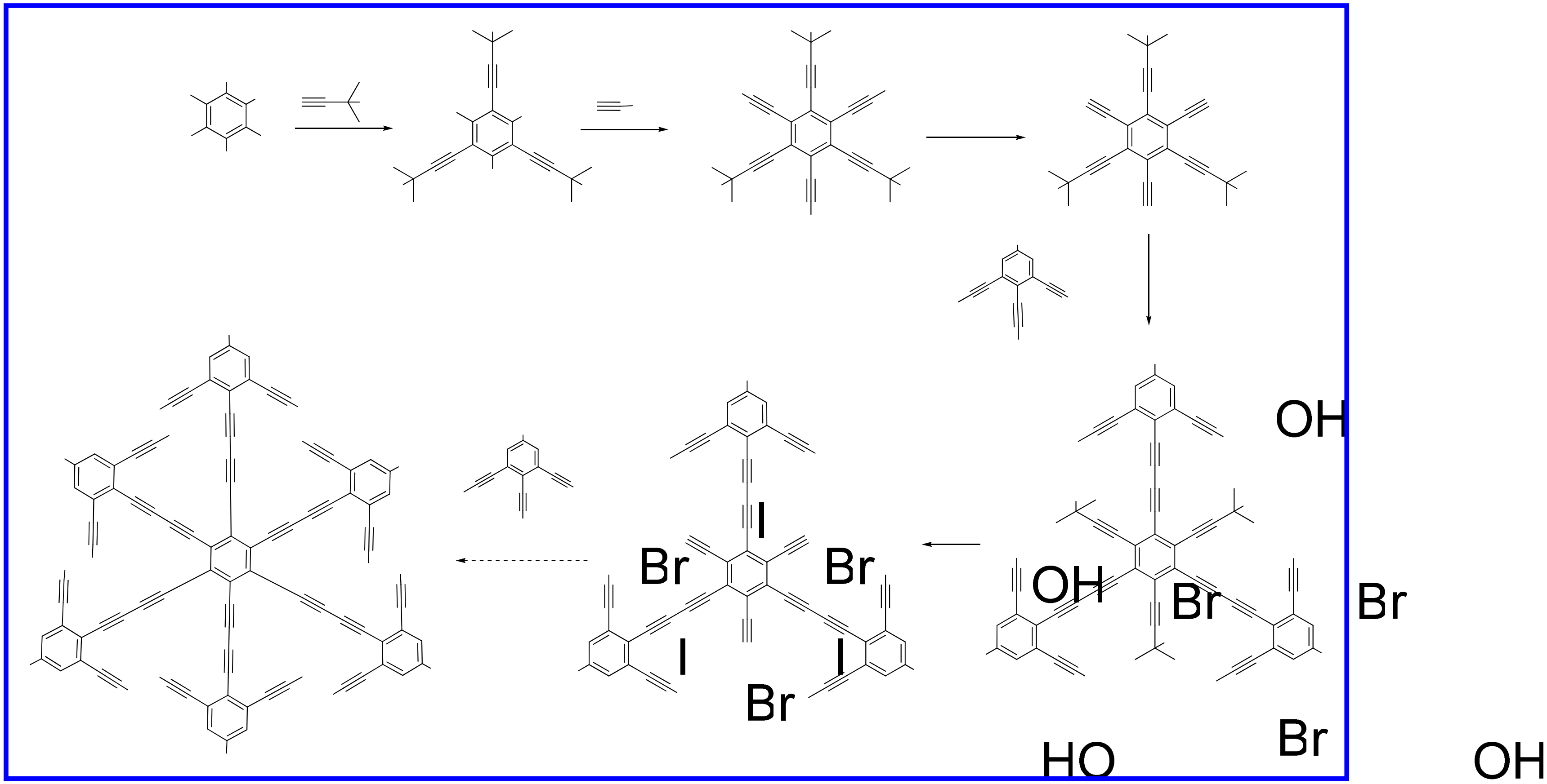
合成路线（一）



合成路线（二）

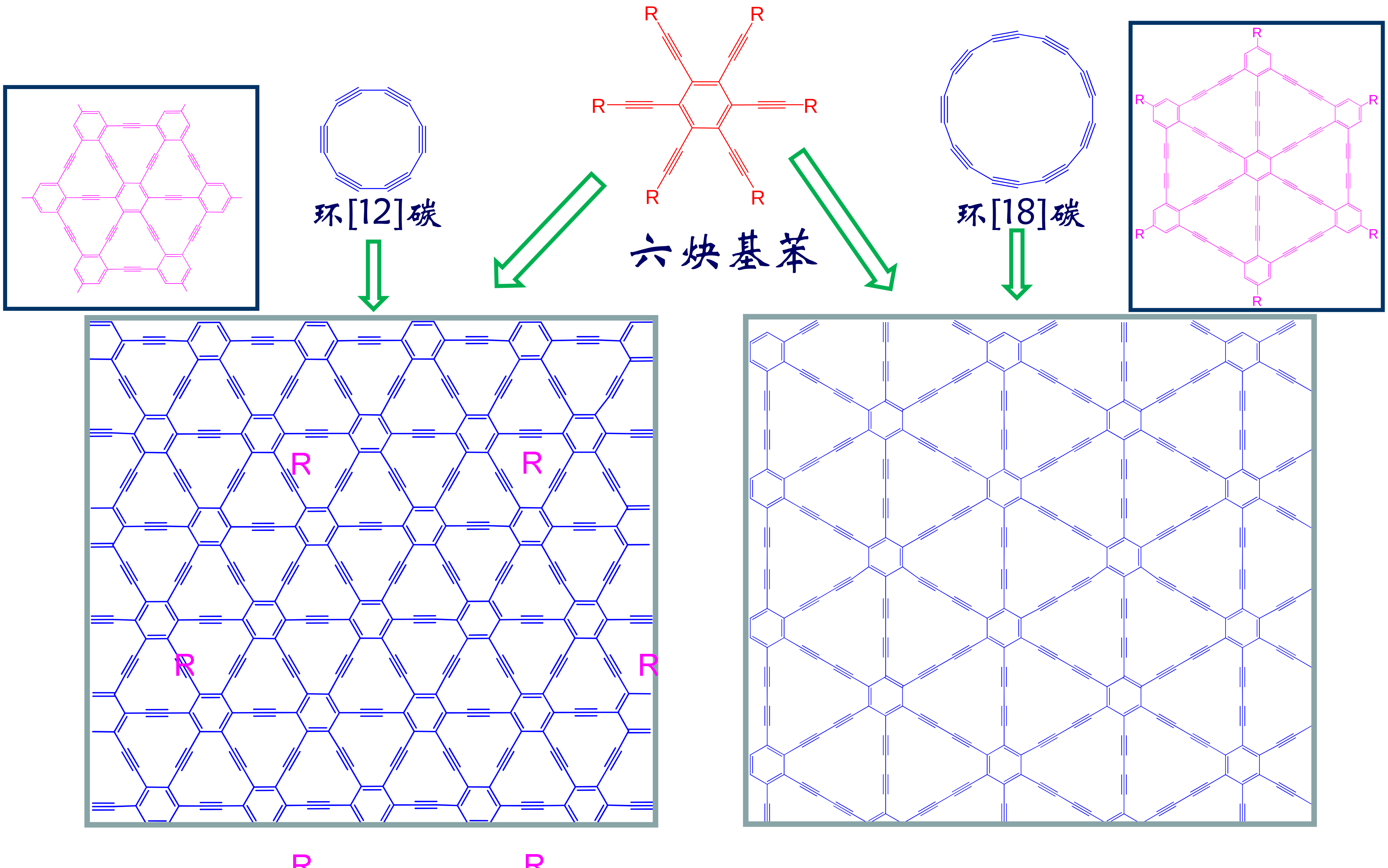


合成路线（三）

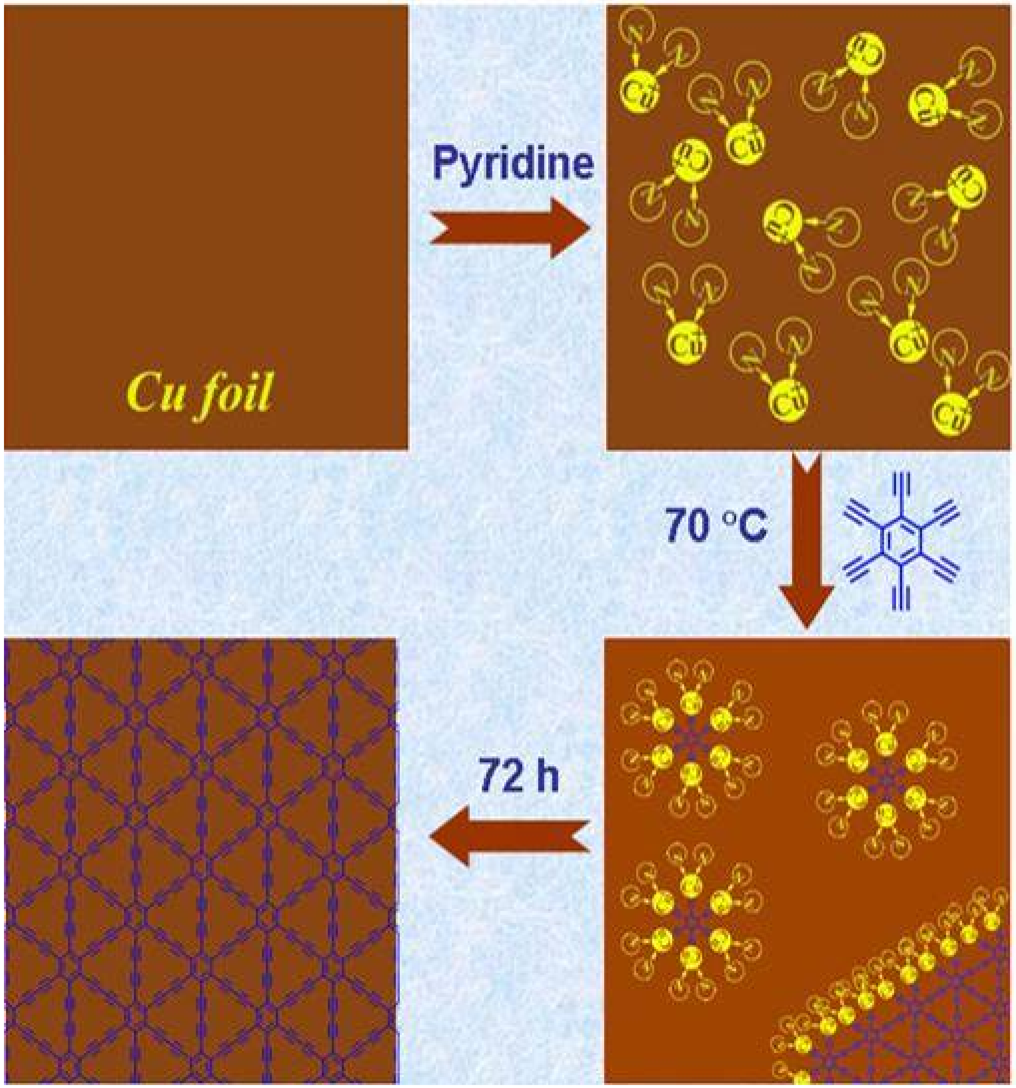


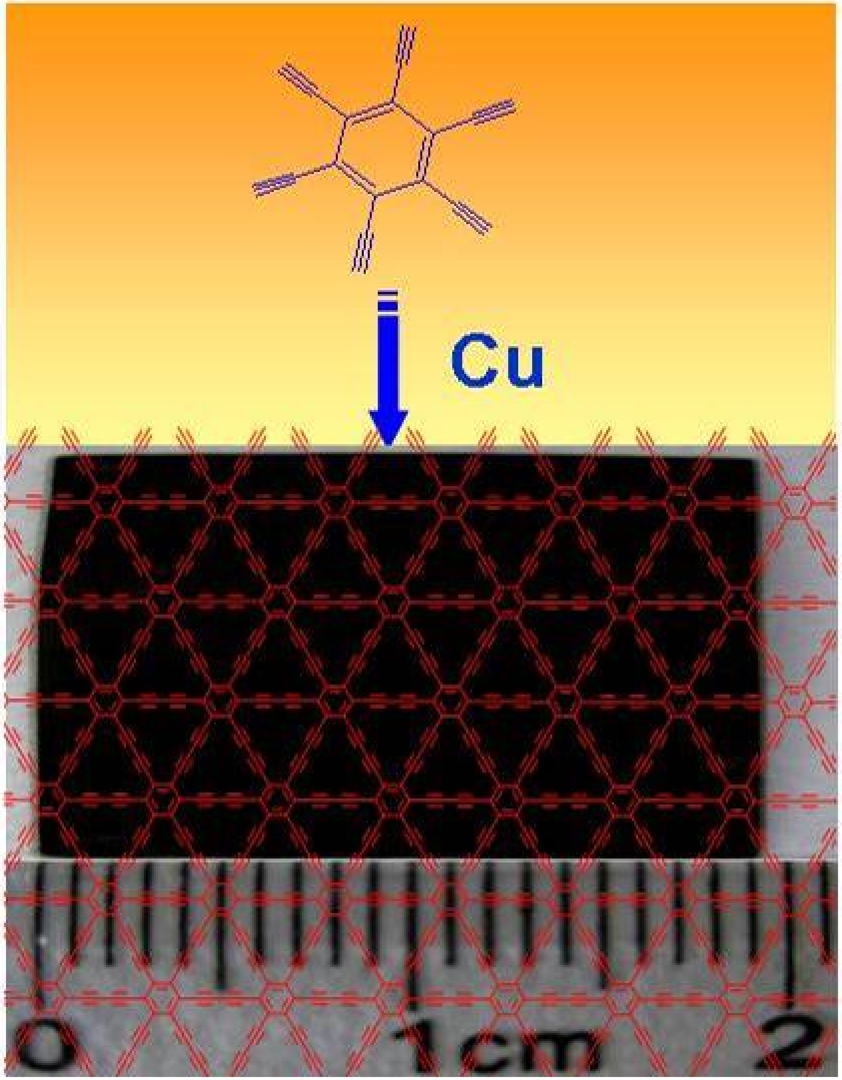
我们的工作：

化学家通过利用碳制备独特的分子，然而制备只含有碳的材料则更具挑战性，直到目前为止，石墨炔的合成仍然保持空白。



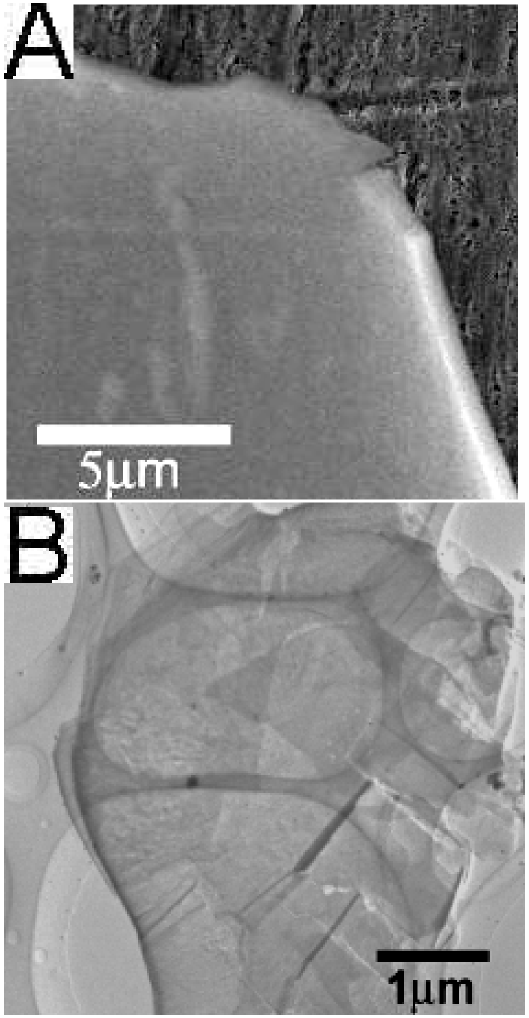
我们的策略：



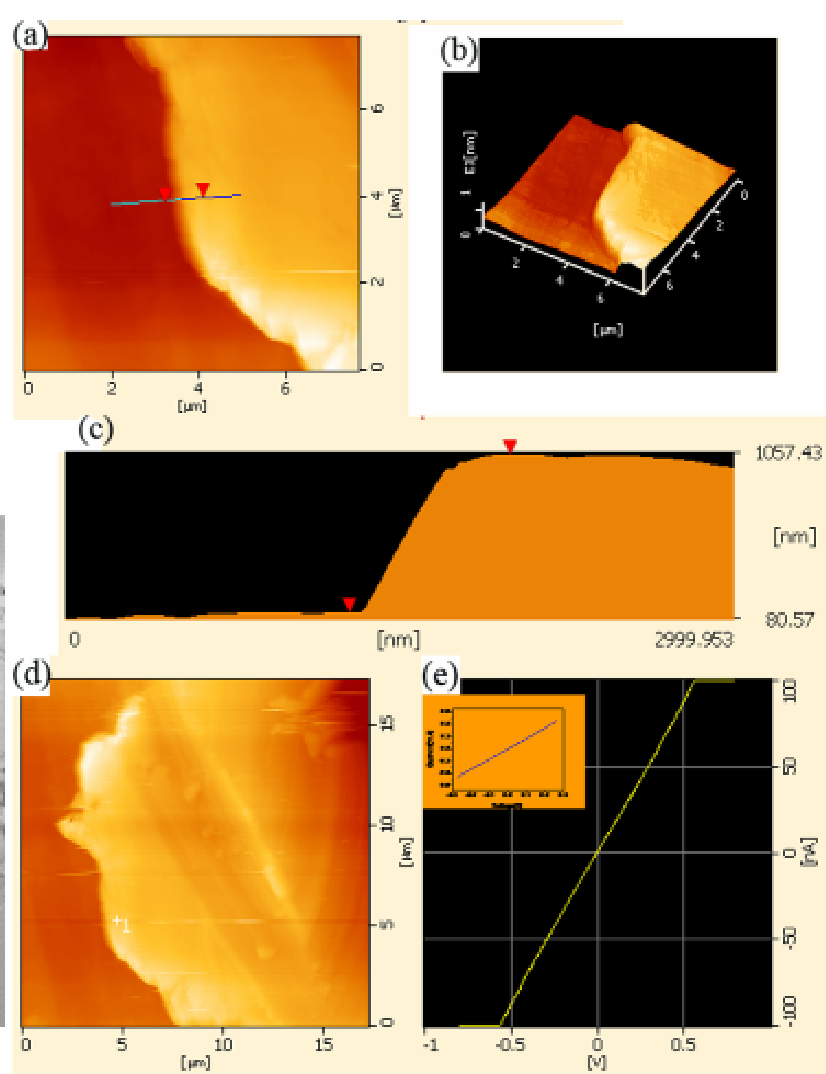


Chem. Commun. 2010, 46, 3256
Acc. Chem. Res. 2010, 43, 1496

Conductivity: 10^{-3}-10^{-4} S m^{-1}



(a) SEM images of graphdiyne. (b) Low-magnification TEM

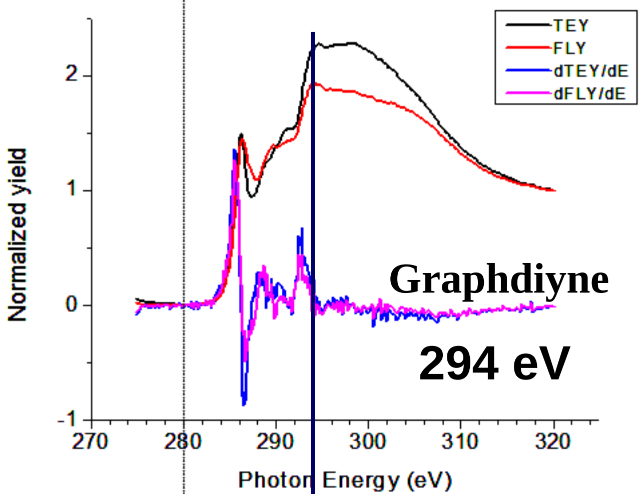


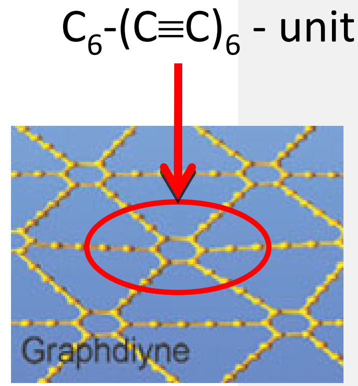
AFM images of graphdiyne film

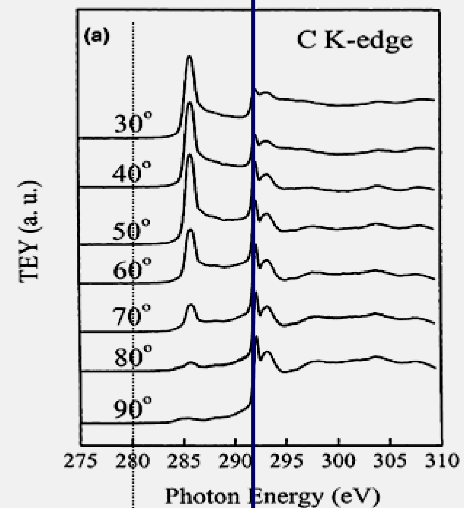
同步辐射证明了石墨炔的结构

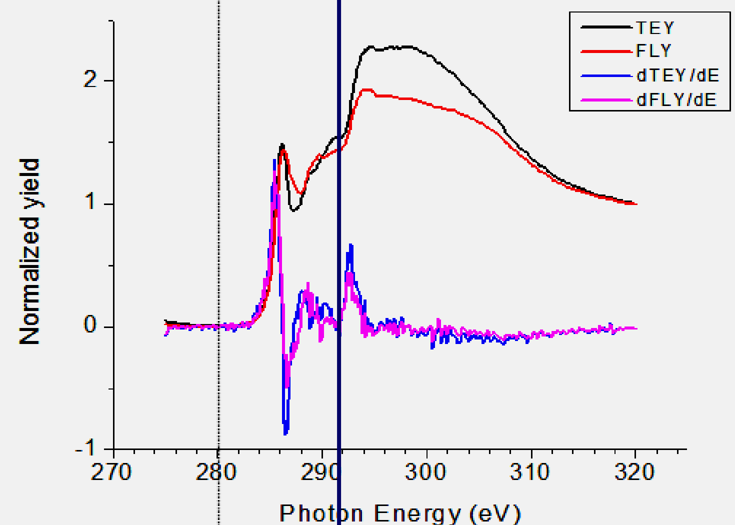
与加拿大光源中心，西安大略大学T.K. Sham教授合作

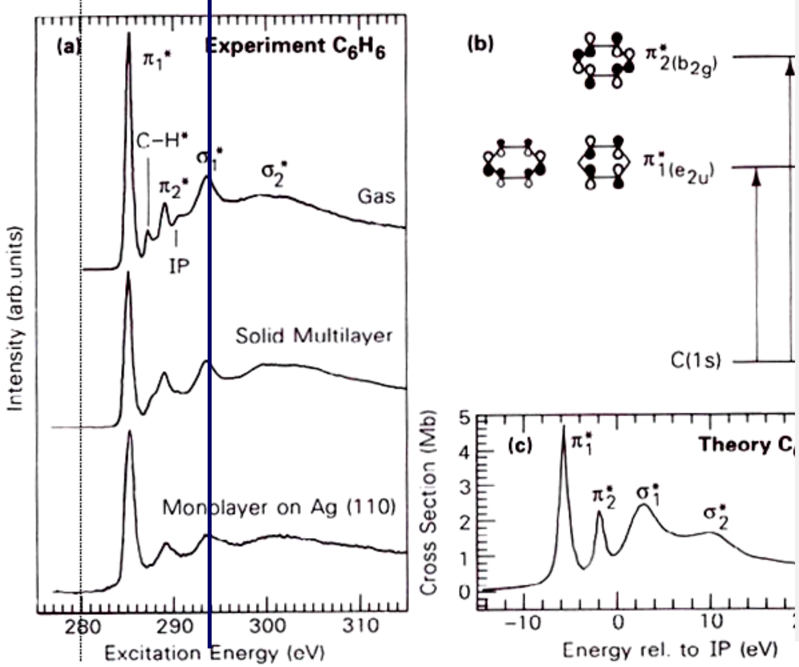
XANES谱（X—射线吸收近边结构）





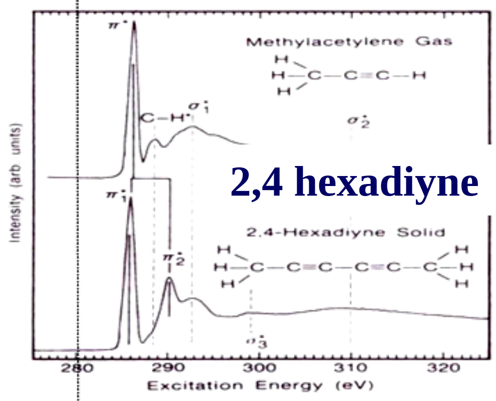


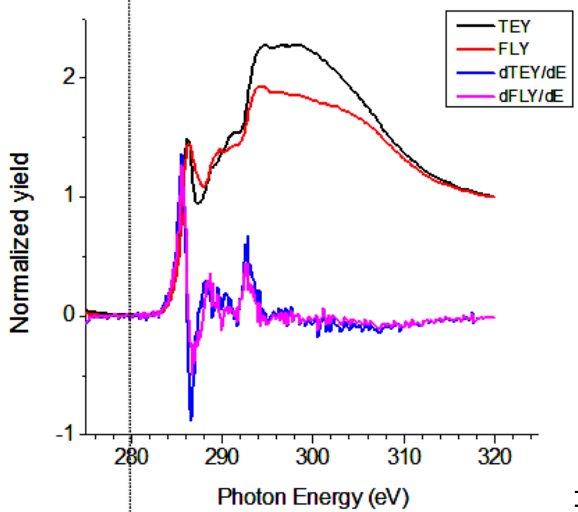


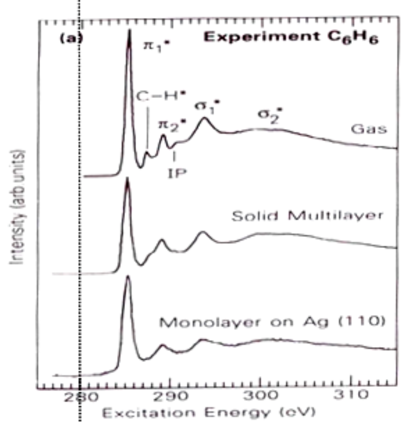


XANES谱

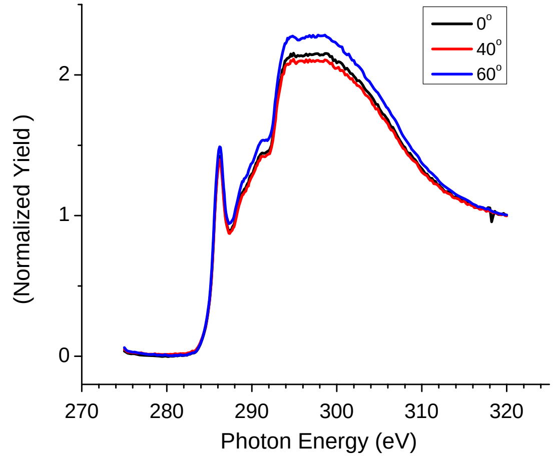
2,4 hexadiyne



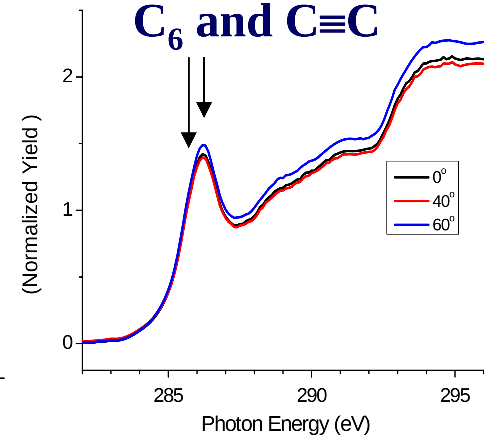




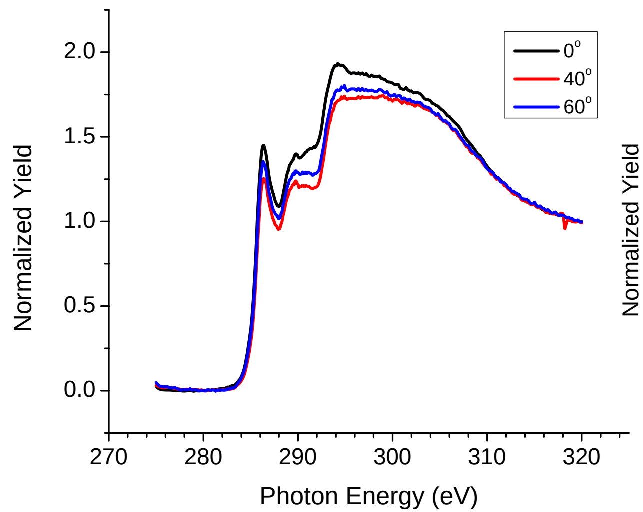
Polar angle scan (TEY)

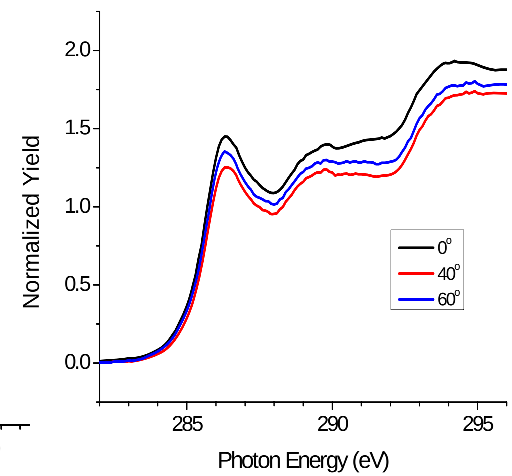


2 π*, likely from C_6 and C≡C

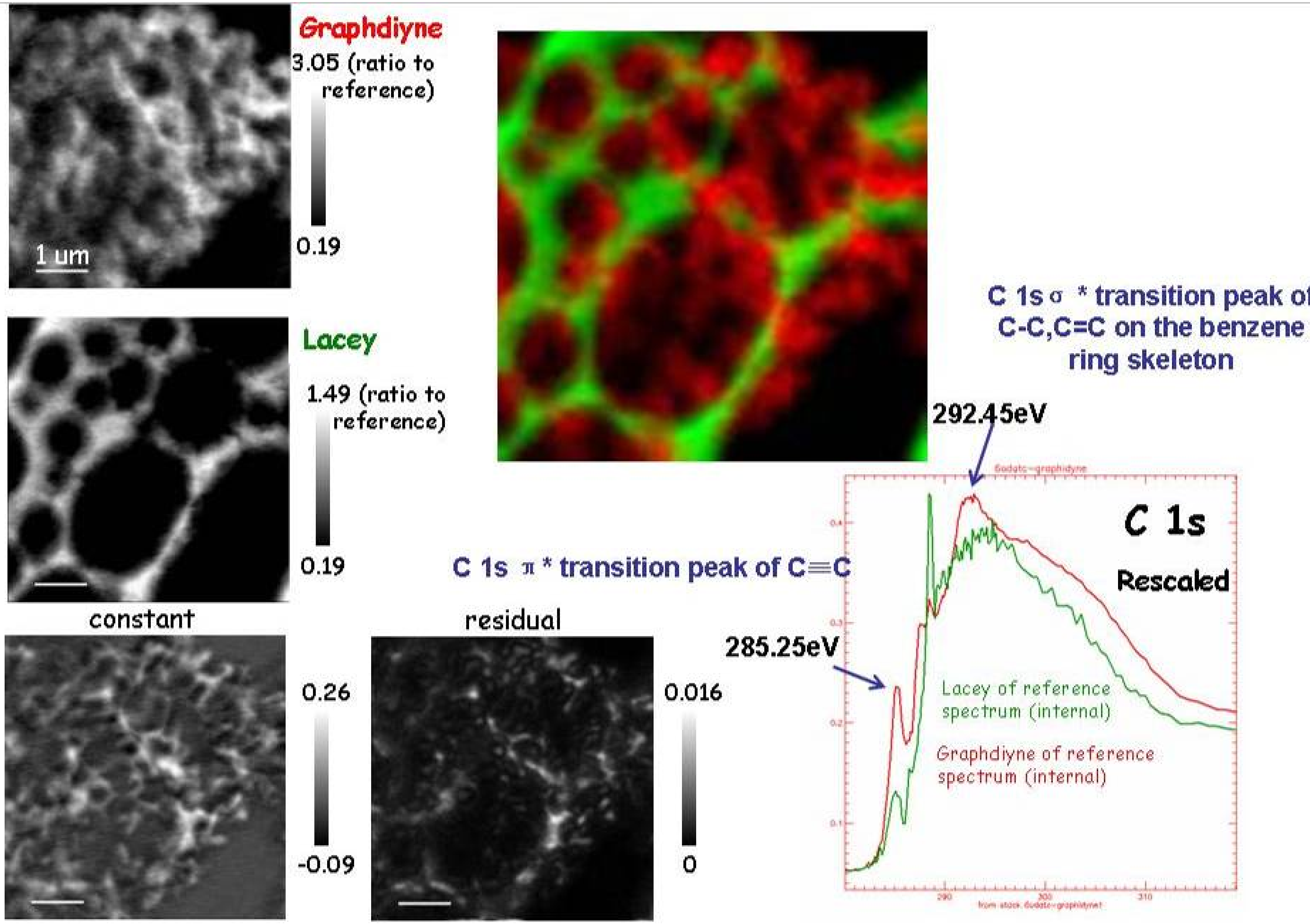


Polar angle scan (FLY)





STXM 扫描透射X－射线显微成像



同行评价

The manuscript by Li and Liu et al reports a very interesting development of graphdiyne chemistry. The Cu-film catalyzed formation of macroscopic (up to 3.61 cm2) graphdiyne (GD) films is truly a great discovery. The GD films are multilayered up to 970 nm and have been extensively characterized by spectroscopic and microscopy techniques and show semiconductor properties. The results are highly interesting and will open a route to large area GD films for nanoelectronics applications. I am very pleased to support the publication of this very nice work in ChemComm virtually as it is. However the author could comment with a few lines the mechanism of the coupling reaction taking place on the Cu-film. This coupling reaction (Glazer, Hay, Eglington) formally proceeds via Cu(I) catalysts, yet here the GD film is formed on (and suggested by the authors catalysed by) the Cu(0)-film. Is the reaction indeed catalyzed by the Cu(0) film or the oxidized and dissolved minute amount of Cu(I) ions. Could a radical transition state be possible? It would be interesting to know if indeed Cu(I) could be found (by AAS or APS or mass spectrometry).

这是碳化学的一个令人瞩目的进展，大面积的石墨炔薄膜的制备是一个真正的重大发现

研究结果非常让人振奋并将为大面积石墨炔薄膜在纳米电子的应用开辟一条道路

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Spectroscopic Ellipsometry

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News

Flat-packed carbon

10 May 2010

Synthesising and isolating new forms of pure carbon, allotropes, has been the focus of much research during the last two to three decades

Not least because of the discovery of the fullerenes, carbon nanotubes, and more recently graphene. It is the possibility of synthesizing thin films akin to graphene, but with novel connectivity that piqued the interest of researchers in China who have now produced a novel allotrope called graphdiyne [Li et al., Chem. Commun., 2010, 46, 3256-3258; DOI: 10.1039/b922733d].

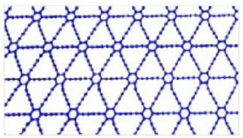
The interest in carbon allotropes lies in finding simple, inexpensive and readily accessible materials with novel electrical, optical and magnetic properties. In the 1990s, chemists pondered on the idea of constructing non-natural carbon allotropes with a diacetylenic and suggested that graphdiyne might be the most "synthetically approachable".

Carbon atoms can bond in three distinct ways as single bonds, which result in tetrahedral structures as seen in diamond and double and triple bonds that give rise to the myriad array of organic molecules, fullerenes, graphite and graphene sheets. While organic chemists are proficient at using carbon as a building block to make distinct molecules, producing materials containing only carbon is more of a challenge. The synthesis of a stable graphdiyne form of carbon has until now remained elusive.

The Chinese team has made a thin film with an area of 360 mm^2 using a relatively straightforward approach. They first produced the monomer hexaethynylbenzene in good yield (62%) by addition of tetrabutylammonium fluoride to a tetrahydrofuran solution of hexakis[(trimethylsilyl)ethynyl]benzene for just three days at 80 Celsius. The graphdiyne was then grown on a copper foil surface in the presence of pyridine by a cross-coupling reaction of the hexaethynylbenzene two days at 60 Celsius under a nitrogen atmosphere.

The team us... tron microscopy to characterise the thin films of graphdiyne. Analysis ...-dispersive X-ray (EDX) spectroscopy suggests that the graph... only of elemental carbon. They also employed Raman spe... the quality and uniformity of graphdiyne on the surface ... the characteristic bonds between carbon atoms ... re of graphdiyne.

...ce, which has a conductivity of 2.516 × 10^- ... semiconductor behaviour. The team



Graphdiyne

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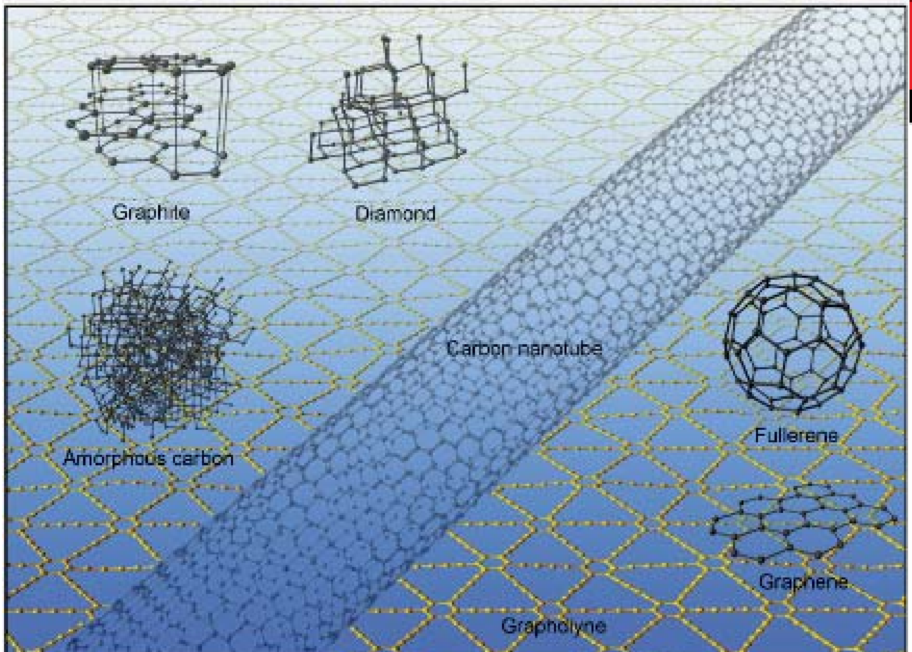
A team of scientists at MIT have discovered a previously unknown phenomenon

Semiconductor advances
Stable, non-volatile computer memory could emerge from research that involves depositing amorphous carbon on to silicon, say US researchers.

Bendy, see-through electrodes

合成、分离新的碳同素异形体是过去20－30年研究的焦点，中国的研究人员首先合成了一种新的碳同素异形体-石墨炔薄膜
......

有机化学家通过利用碳制备独特的分子，然而制备只含有碳的材料则更具挑战性，直到目前为止，石墨炔的合成仍然保持空白。现在，中国科学家用一种直接的方法合成了3.6 平方厘米的石墨炔薄膜......



Showcasing research from Yuliang Li's laboratory, Institute of Chemistry, Chinese Academy of Sciences, China.

Architecture of graphdiyne nanoscale films

A new carbon allotrope – graphdiyne – was synthesized and predicted to be the most stable of non-natural carbon allotropes.
Graphdiyne, a new molecular allotrope of carbon, is a two-dimensional layer with one-atom thickness and strongly bonded carbon networks, chemical stability and electrical conductivity

As featured in:

Guoxing Li, Yuliang Li, Huibiao Liu, Yanbing Guo, Yongjun Li and Daoben Zhu

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Research Highlights

Subject Categories: Chemistry Materials

Published online: 2 June 2010 | doi:10.1038/nchina.2010.67

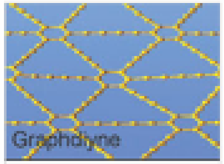
Materials chemistry: Expanding the carbon family

Anne Pichon

Researchers in Beijing have prepared large films of graphdiyne, a two-dimensional carbon allotrope with unique electronic properties

Original article citation
Li, G. et al. Architecture of graphdiyne nanoscale films. Chem. Commun. 46, 3256–3258 (2010).

Carbon can exist in a variety of crystalline forms (allotropes), ranging from naturally occurring diamond, graphite and amorphous carbon, to 'synthetic' fullerenes, carbon nanotubes and graphene. Yuliang Li, Huibiao Liu and co-workers at the Chinese Academy of Sciences in Beijing[1] have now synthesized graphdiyne (see image), a two-dimensional carbon network with structure and properties that are unlike any of the allotropes known before.



© (2010) RSC

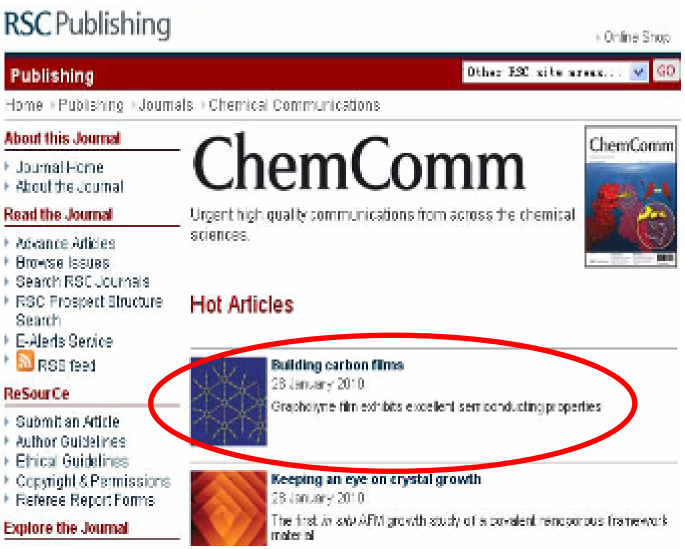
The researchers grew the graphdiyne on a piece of copper foil through a cross-coupling reaction that uses hexaethynylbenzene. The copper foil functions as a catalyst for the cross-coupling reaction and as a substrate for growing graphdiyne.

Using this approach, the researchers produced graphdiyne films of up to 3.61 cm² in area. Scanning electron microscopy showed that the films were continuous, uniform and flexible; X-ray photoelectron spectroscopy confirmed that the films were pure carbon; Raman spectroscopy revealed that the films were multilayered; and by atomic force microscopy it was found that the films exhibited excellent semiconducting properties similar to silicon.

The researchers are optimistic that graphdiyne will become an important material in the field of electronics.

一种新的碳的同素异形体–石墨炔被合成了，并被认为是最稳定的非天然的碳同素异形体。它是具有单原子层厚度的二维平面网络结构，优良的化学稳定性和半导体性能。

中国科学院的李玉良及其同事首先合成了石墨炔，它是一种具有二维网络结构，它的性质不同于已发现的碳同素异形体……



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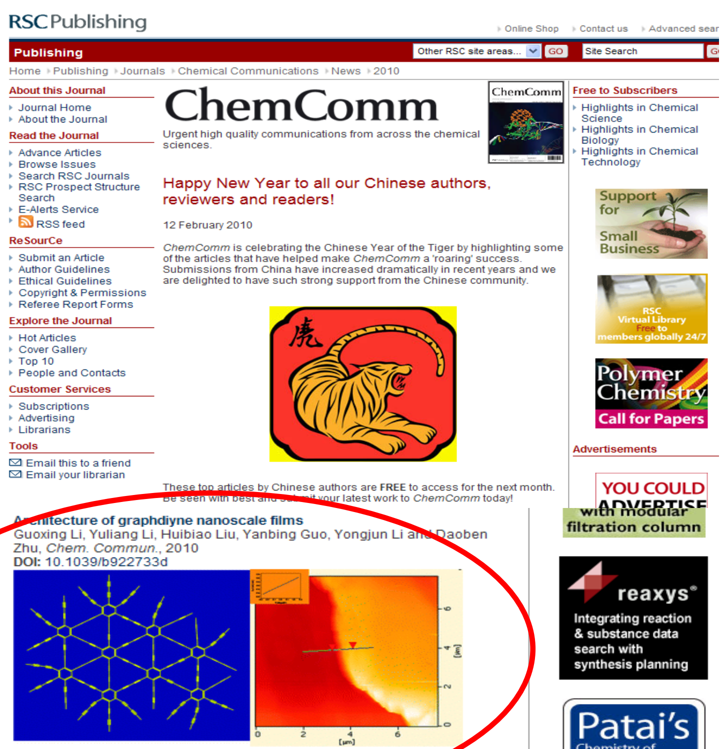

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DOI: 10.1039/b922733d

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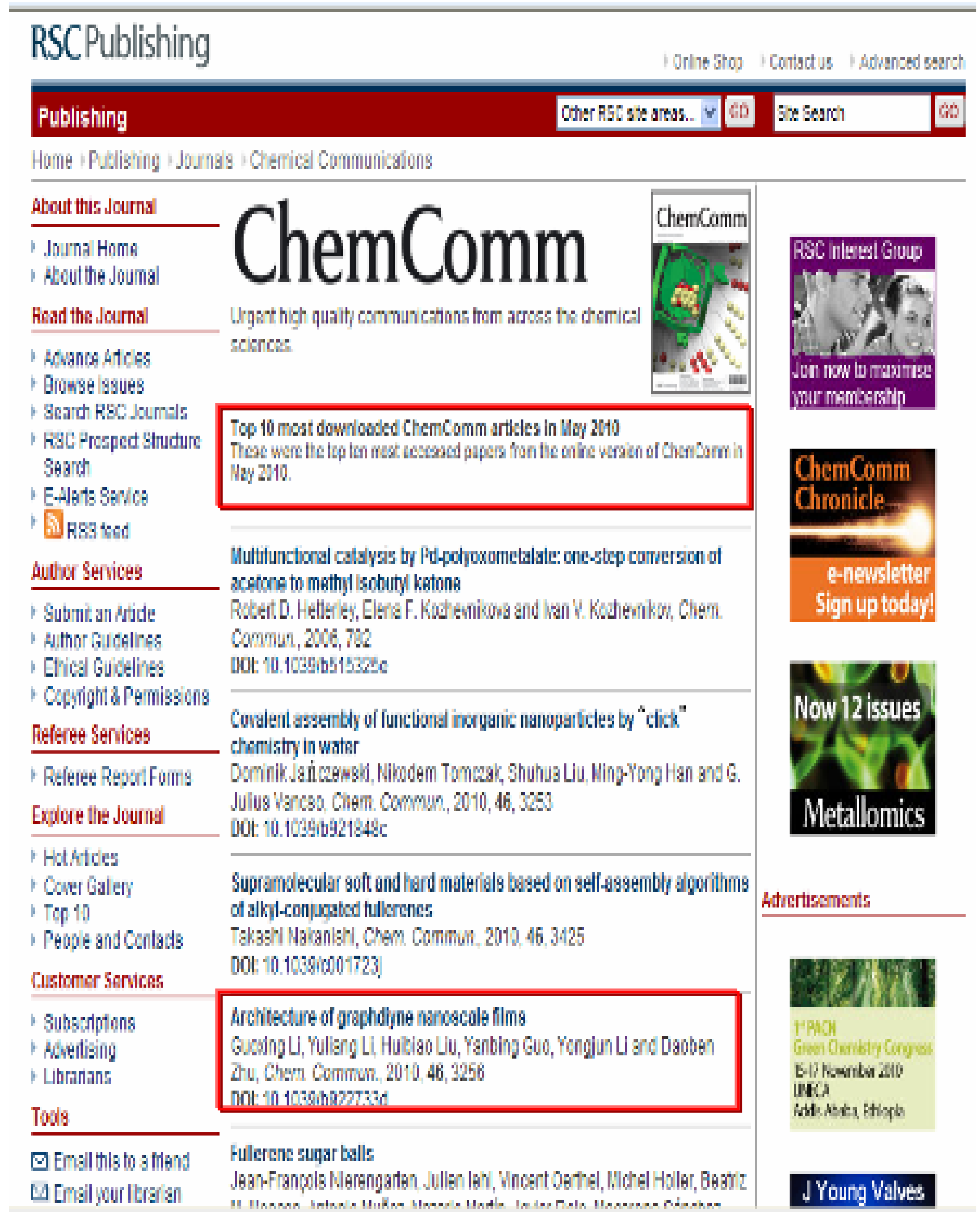

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DOI: 10.1039/b515325e

Covalent assembly of functional inorganic nanoparticles by "click" chemistry in water
Dominik Jańczewski, Nikodem Tomczak, Shuhua Liu, Ming-Yong Han and G. Julius Vancso, Chem. Commun., 2010, 46, 3253
DOI: 10.1039/b921848c

Supramolecular soft and hard materials based on self-assembly algorithms of alkyl-conjugated fullerenes
Takashi Nakanishi, Chem. Commun., 2010, 46, 3425
DOI: 10.1039/c001723j

Architecture of graphdiyne nanoscale films
Guoxing Li, Yuliang Li, Huibiao Liu, Yanbing Guo, Yongjun Li and Daoben Zhu, Chem. Commun., 2010, 46, 3256
DOI: 10.1039/b922733d

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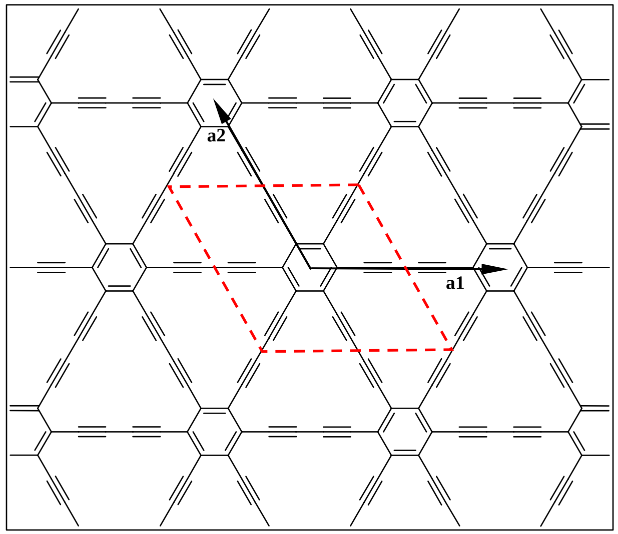
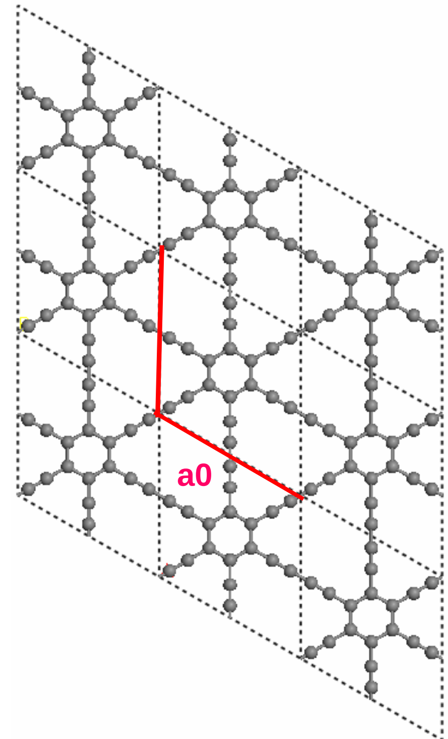
Jean-François Nierengarten, Julien Iehl, Vincent Oerthel, Michel Holler, Beatriz ...

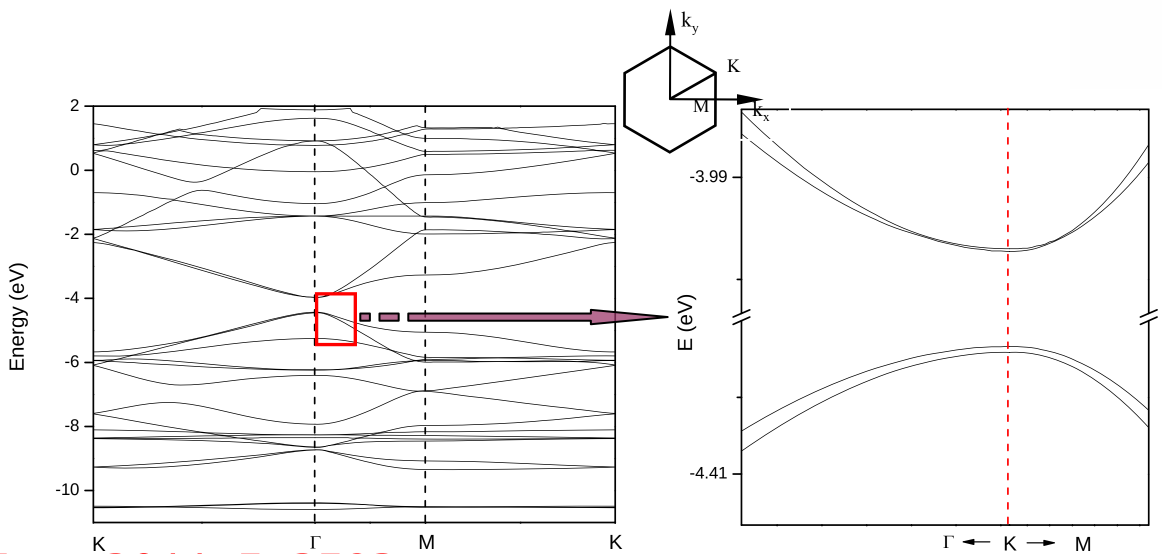
计算结果

清华大学帅志刚





Band structure

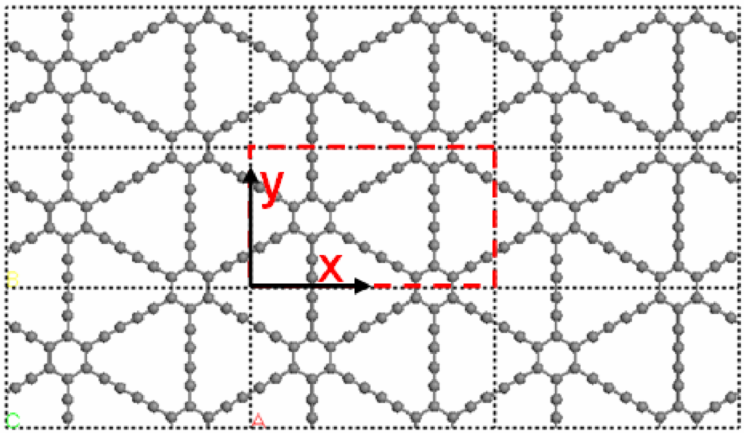


Band gap

0.46 eV

ACS Nano 2011, 5, 2593

计算结果

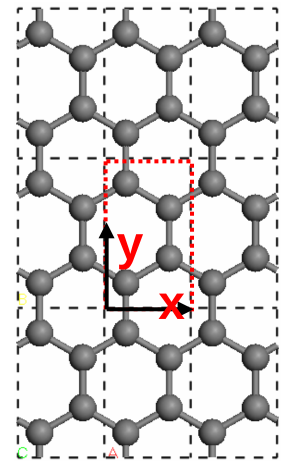


Unit cell

x_0=16.385 Å

y_0=9.46 Å

石墨炔



Unit cell

x_0=2.47 Å

y_0=4.278 Å

石墨烯

System	band	m* (0.01m_e)	E1(eV)	C(J/m²)	μ（10^5cm²/Vs）	τ (ps)
GD_x	hole	2.45	6.30	158.57	0.20	1.94
	ele	2.60	2.09		2.08	19.11
GD_y	hole	2.45	6.11	144.90	0.19	1.88
	ele	2.60	2.19		1.72	15.87

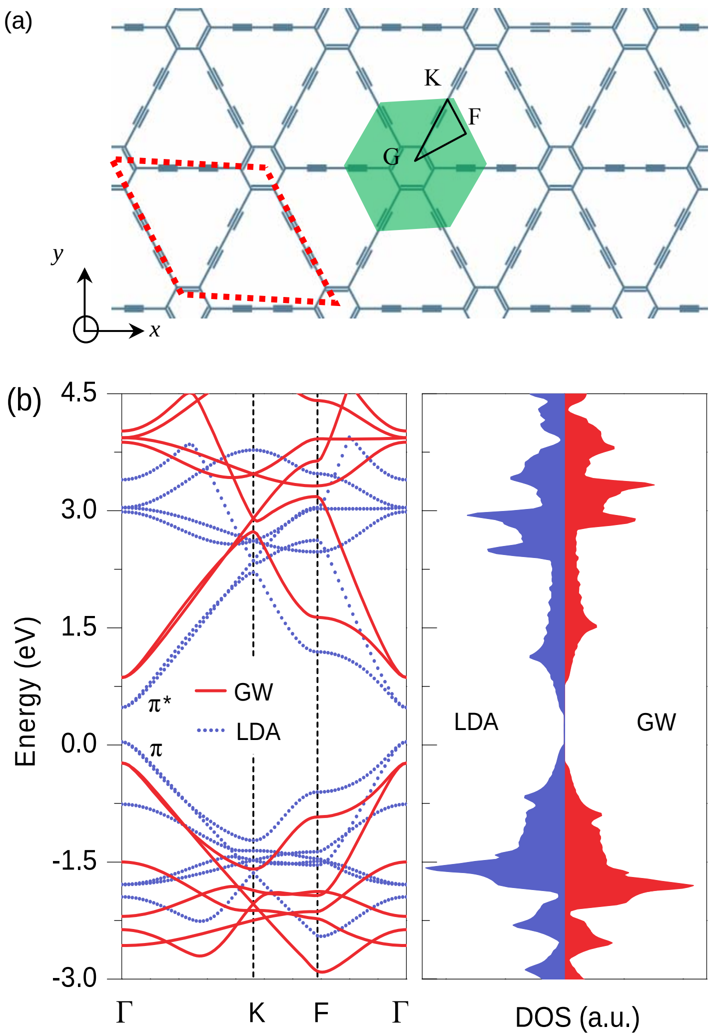
System	band	E1(eV)	C_{2D} (J/m²)	μ（10^5cm²/Vs）	τ (ps)
SLG_x	hole	5.14	328.02	3.22	13.80
	ele			3.39	13.94
SLG_y	hole	5.00	328.30	3.51	13.09
	ele			3.20	13.22

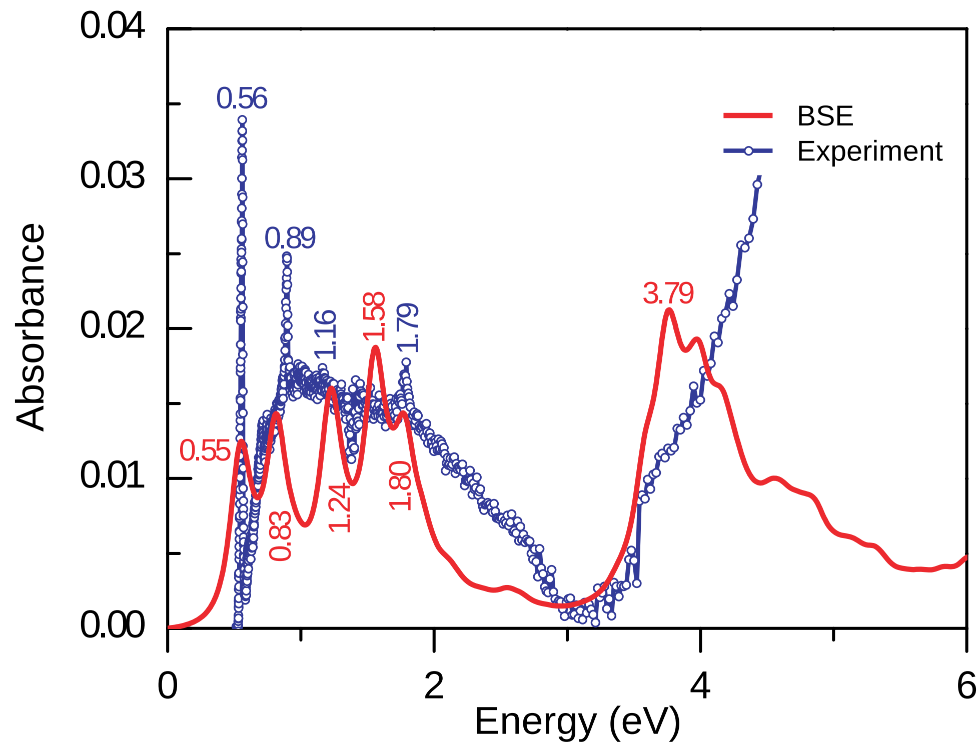
电子迁移率：2×10^5 cm²/Vs；空穴迁移率：10^4 cm2/Vs

ACS Nano 2011, 5, 2593

计算结果

北大吕劲教授





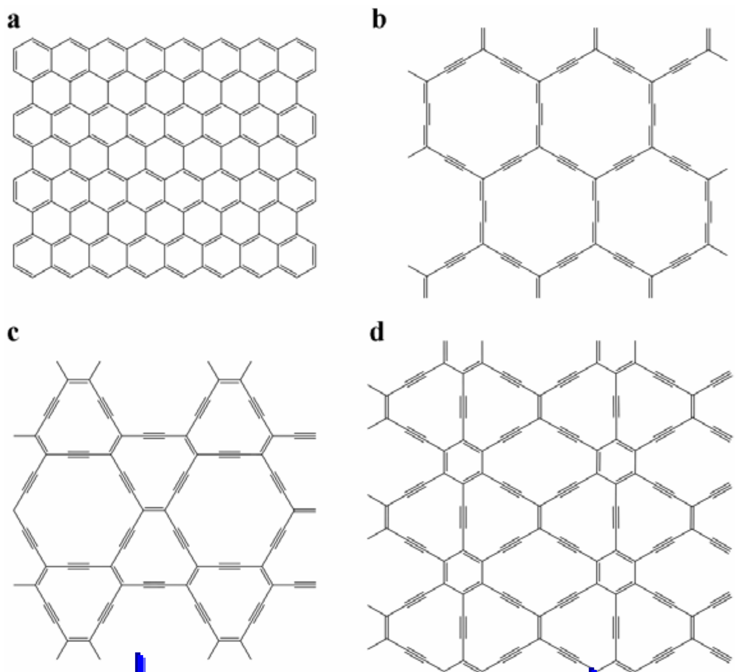
直接准粒子带隙：1.10 eV, 与Si相当

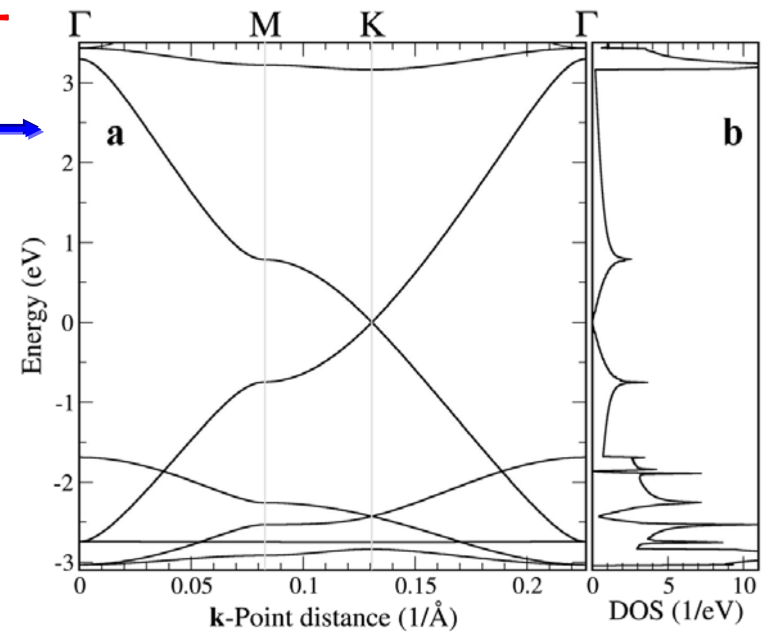
激子结合能： 0.55~1.16 eV

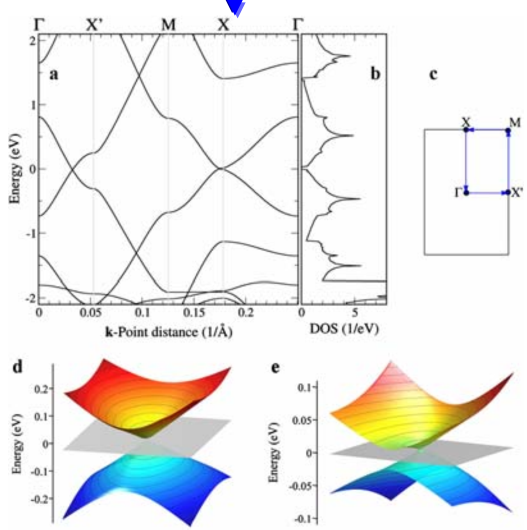
杨氏模量：~412 Gpa 与SiC相当

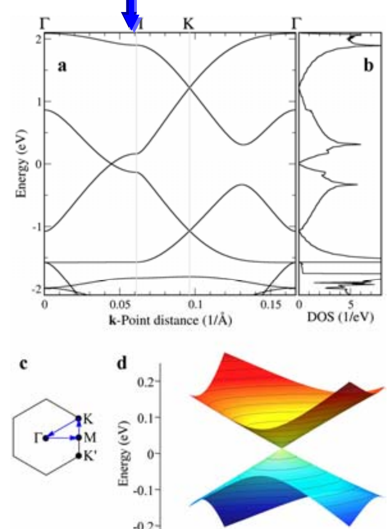
Phys. Rev. B, 2011, 84, 075439

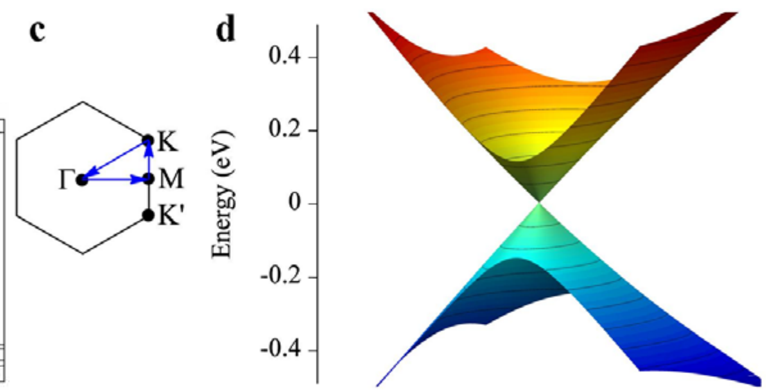
理论计算







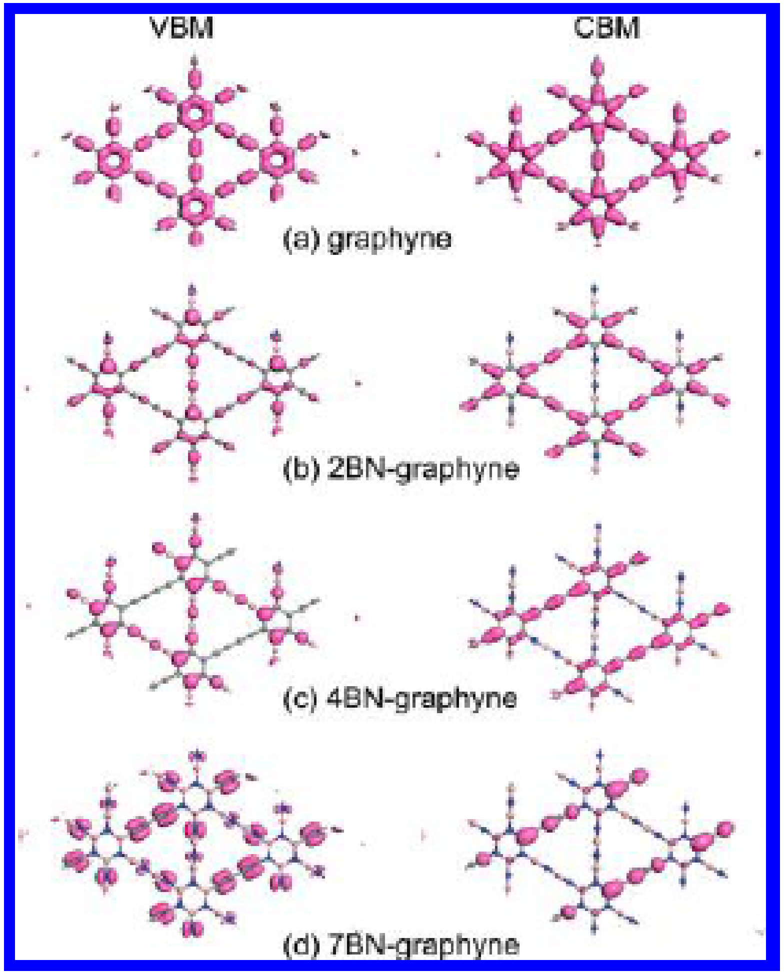




石墨烯电子的能级被设计在三维状态下时会呈现出一个狄拉克椎的形状。石墨炔都能产生一个狄拉克椎，**6,6,12-**石墨炔能使电子仅仅在一个方向流动。

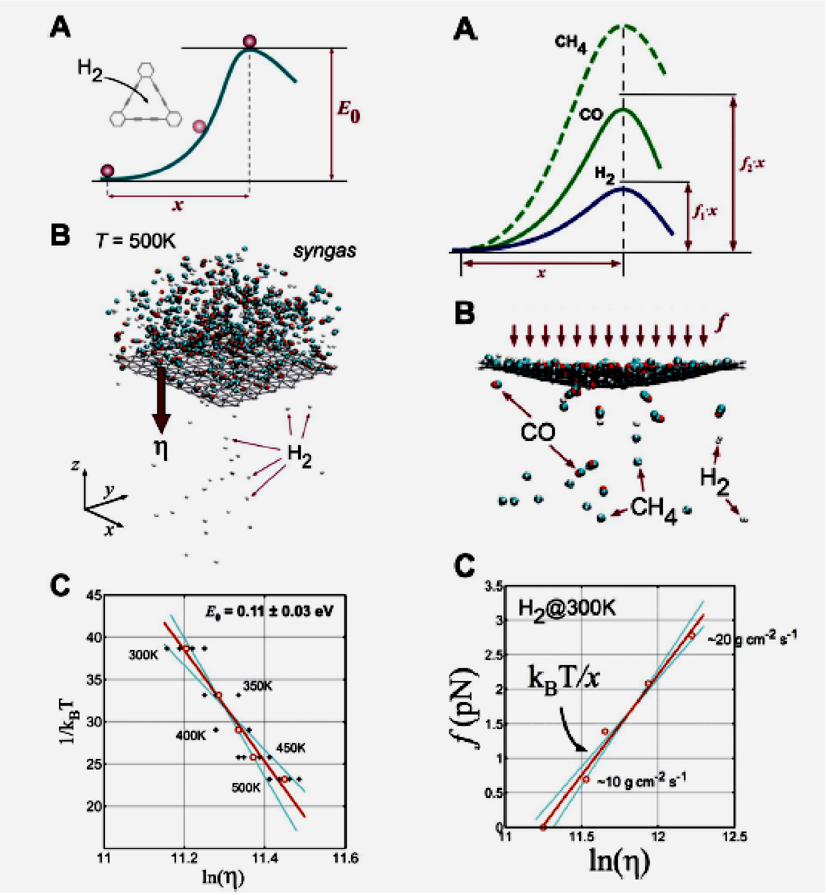
Görling et al. PRL 108, 086804 (2012)

石墨炔掺氮和硼



Zhao MW J. Phys. Chem. A 2012, 116, 3934

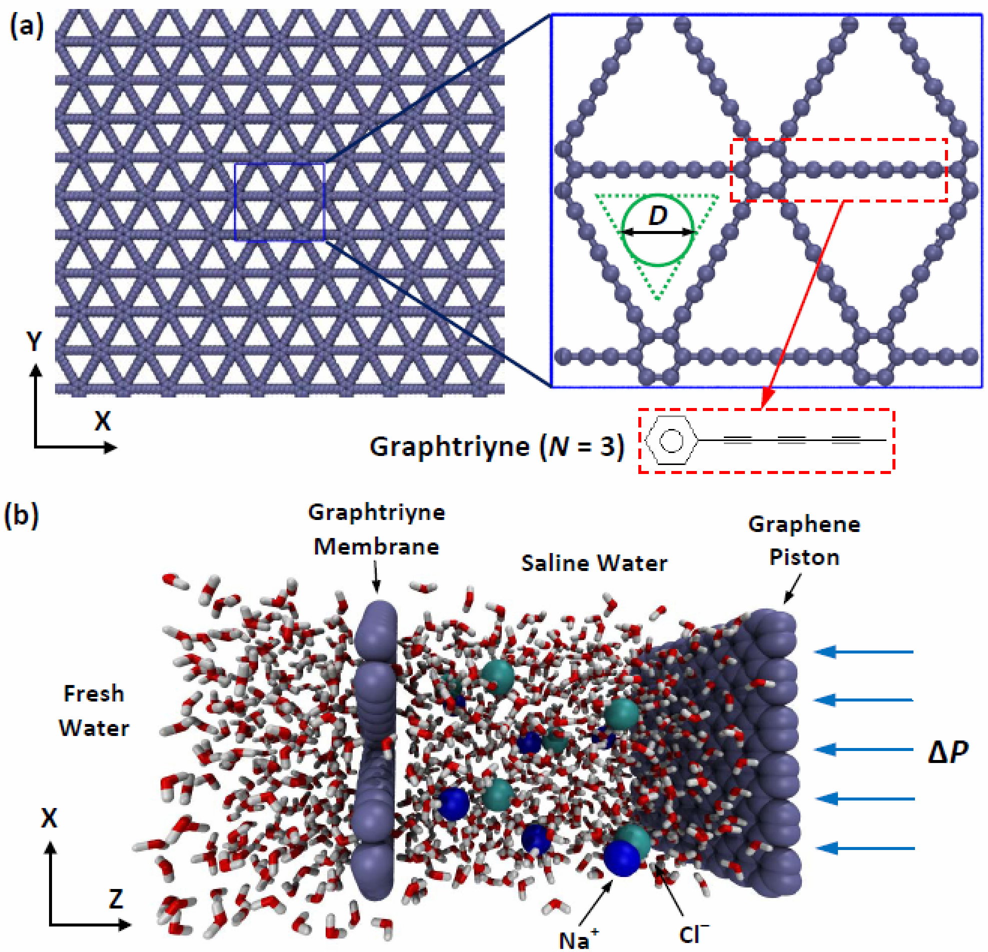
石墨炔纯化氢气



Smith et al. Chem. Commun., 2011, 47, 11843
Buehler et al. Nanoscale, 2012, 4, 4587

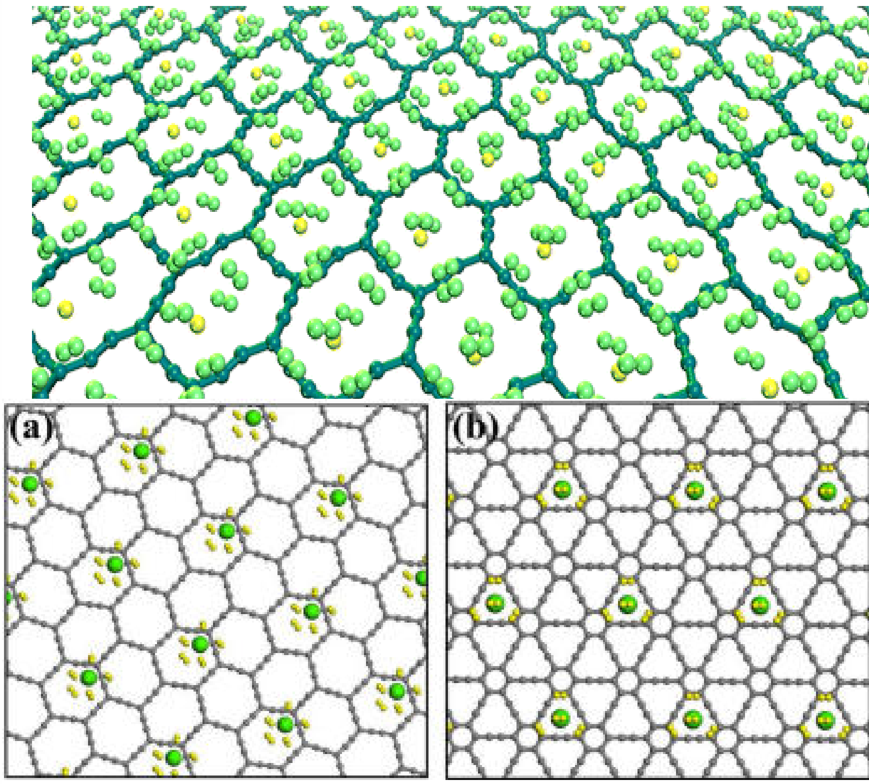
石墨炔理论研究大部分集中于光、电、磁和力学性质，能量存储、电子结构以及带隙等

Graphyne Nanowebs海水淡化



Markus J. Buehler (MIT)

Graphyne储氢

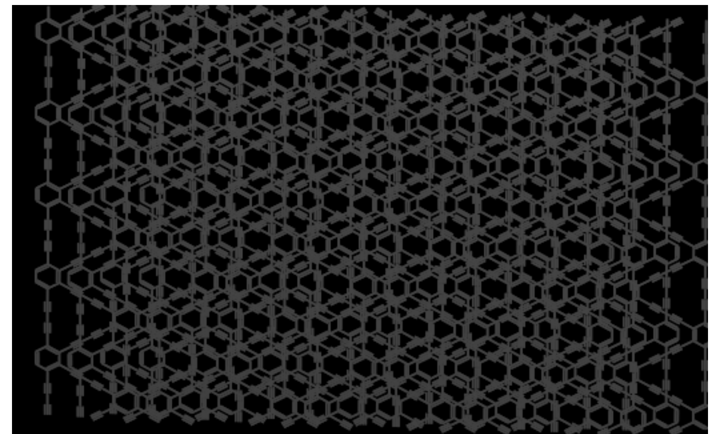


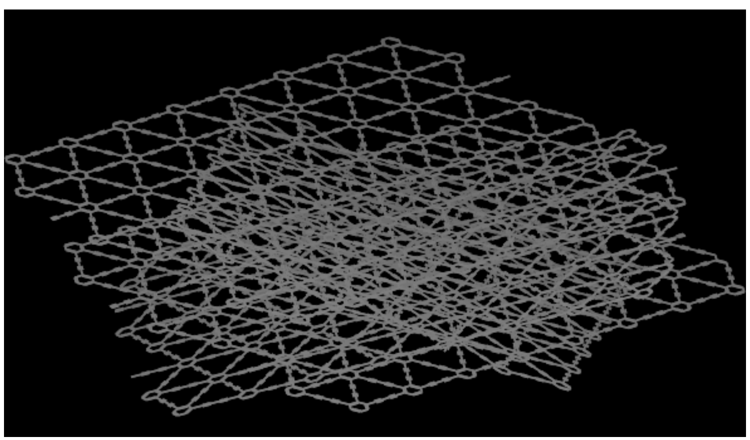
Hoonkyung Lee,韩国
(JPC,2012, 116, 20220)

实现了大面积厚度可控的石墨炔薄膜生长

解决了石墨炔生长的两个关键问题：

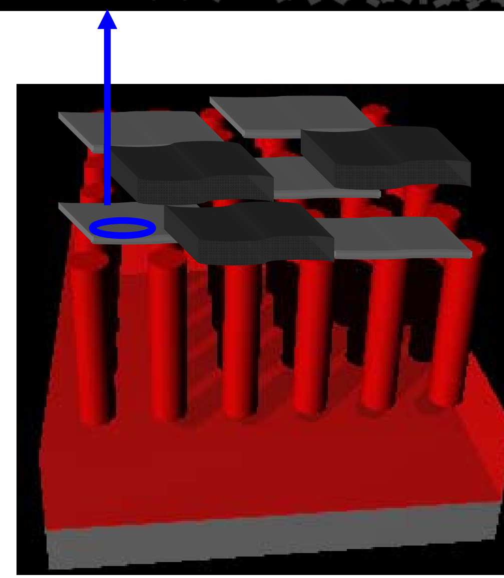
- ✓ 层数可控，确定了层间距为3.65Å；
- ✓ 实现了稳定的电性质，首次测定了石墨炔薄膜空穴迁移率，证明了理论计算提出的高迁移率



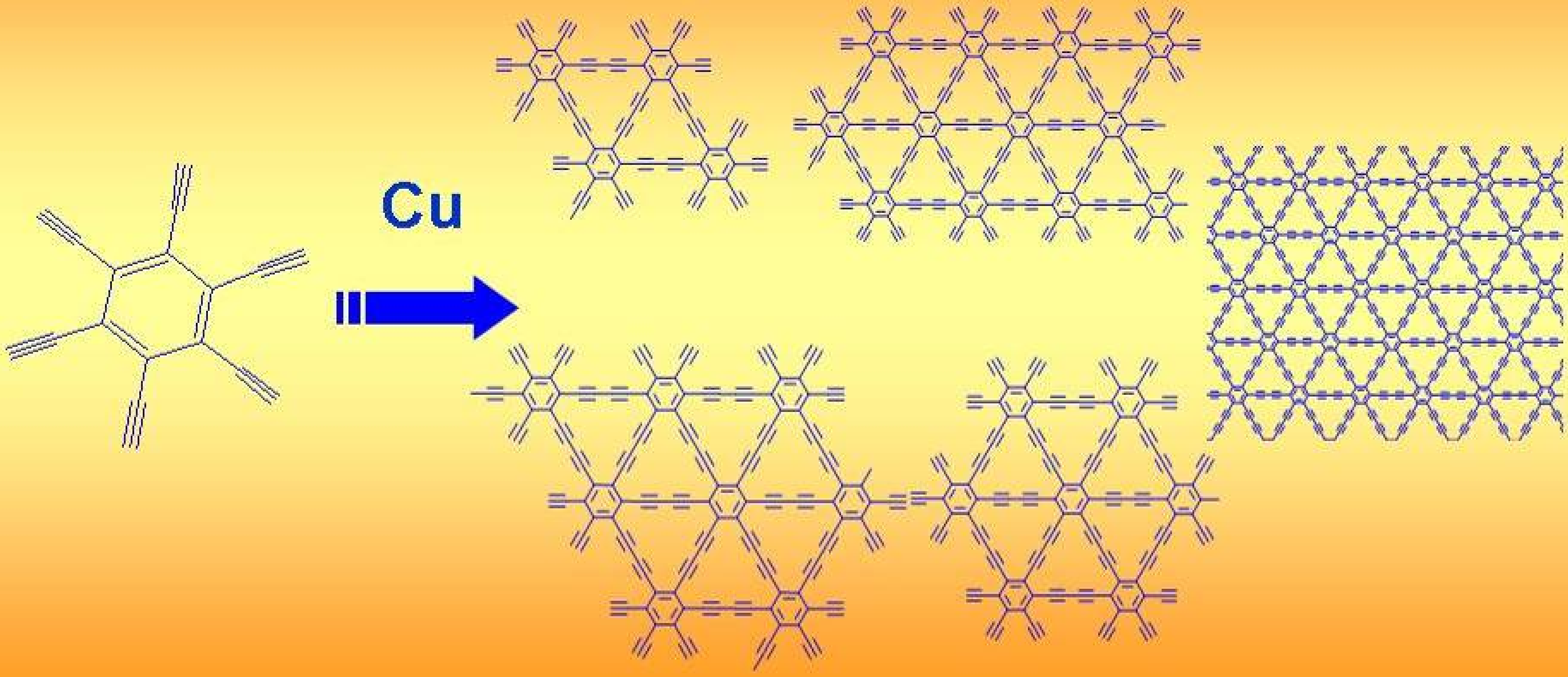


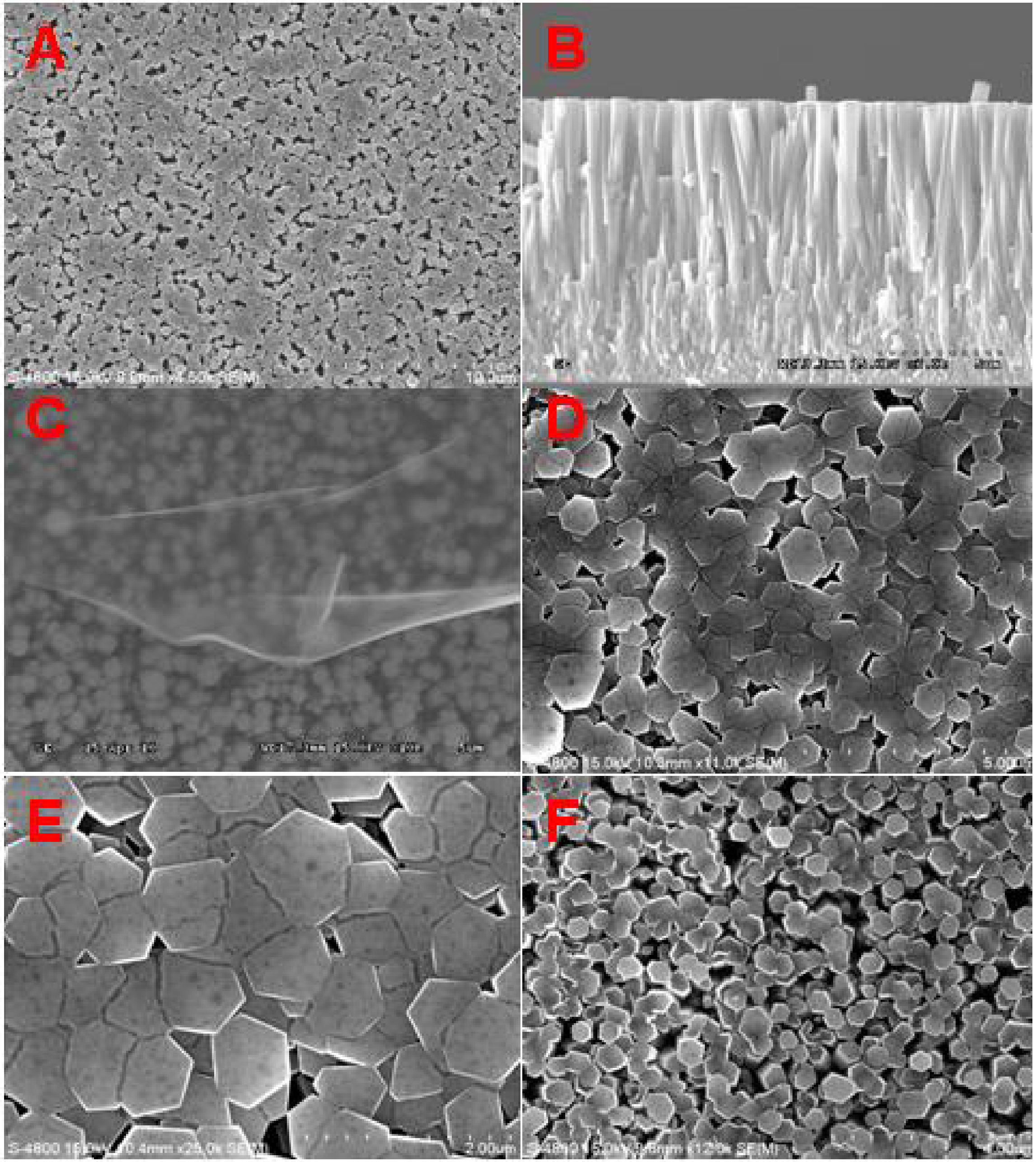
600° C

ZnO纳米棒阵列



石墨炔片段

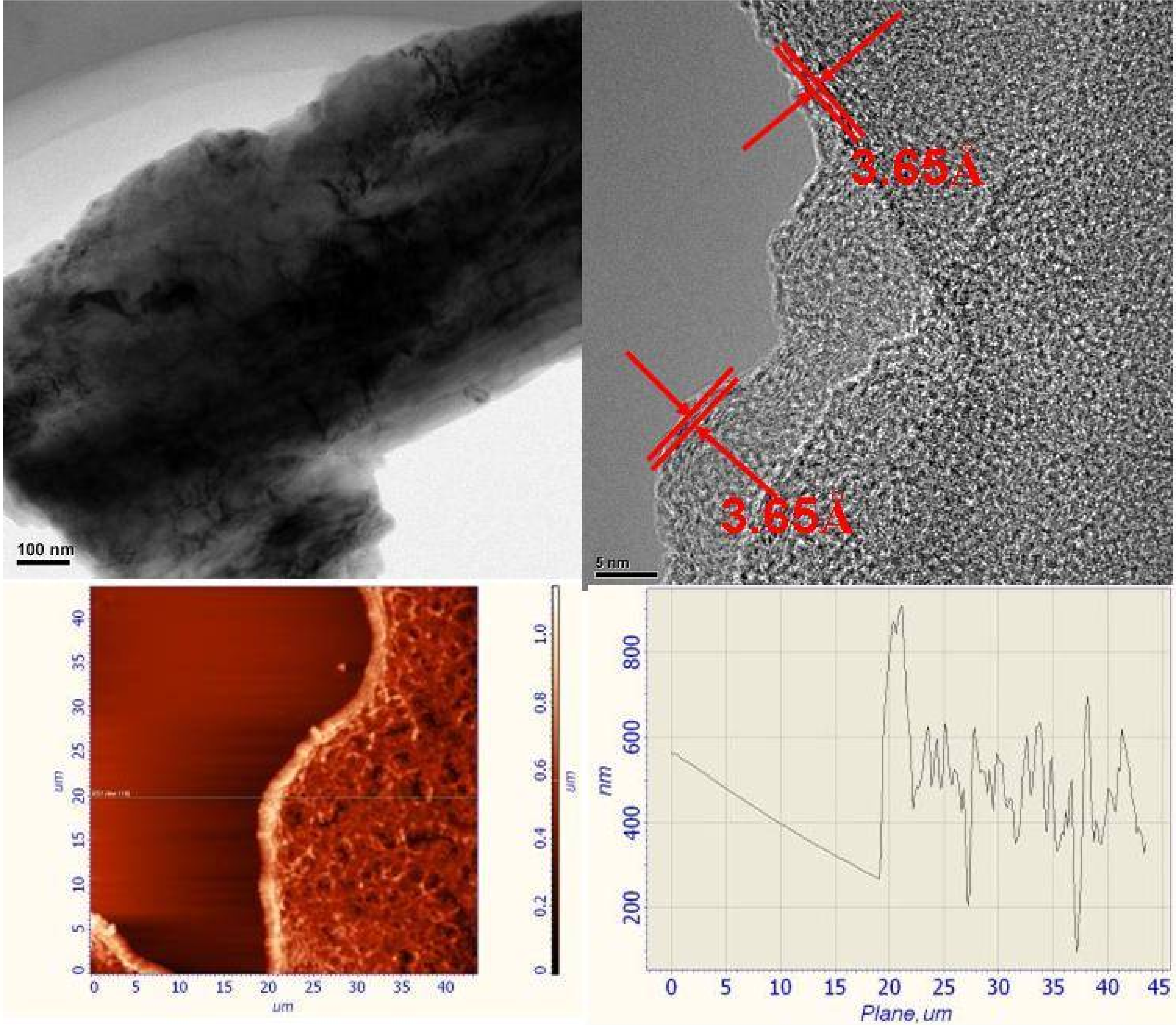




SEM images of different thickness GD films

厚度为5μm的石墨炔薄膜

多层结构

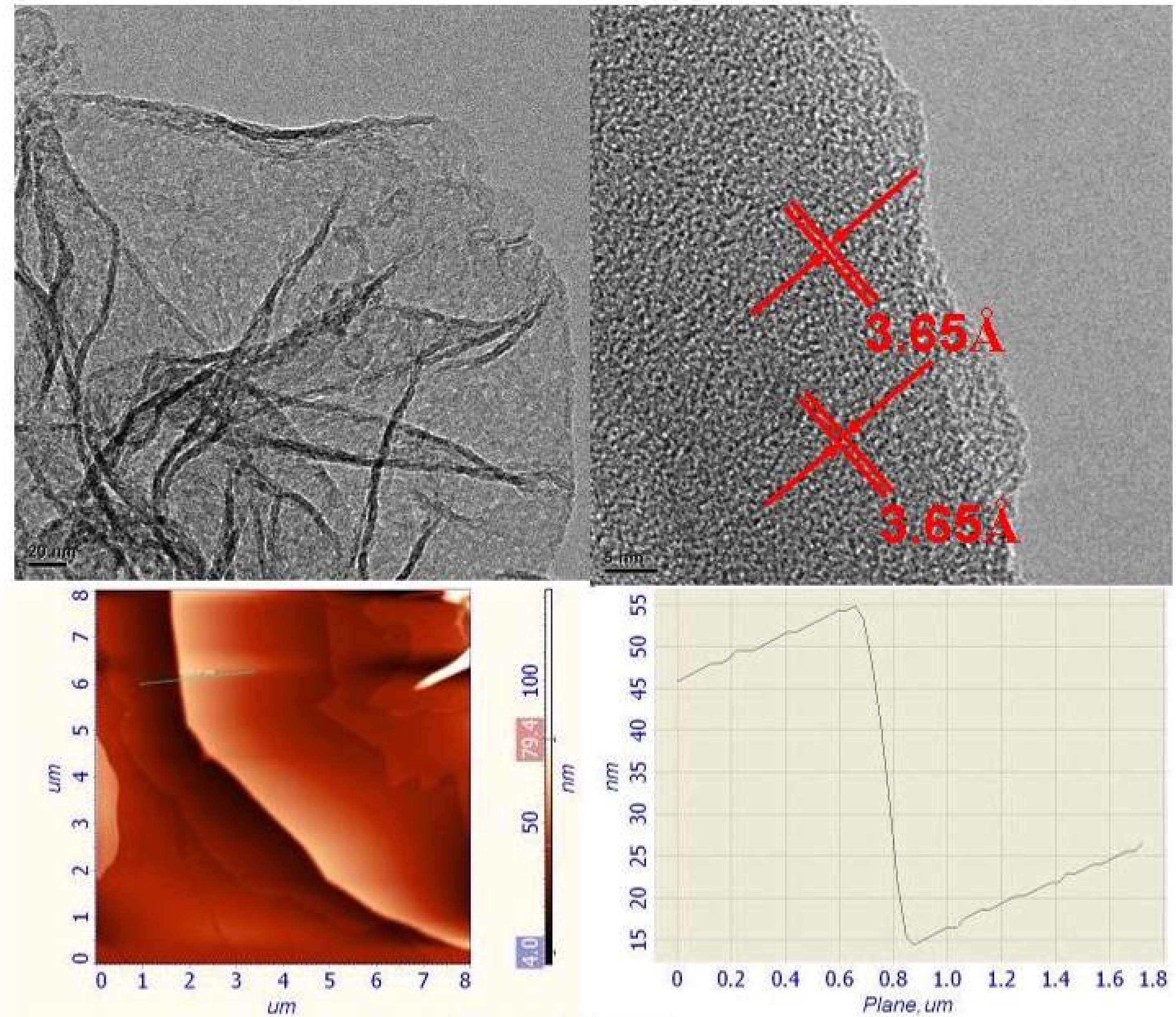


TEM

AFM

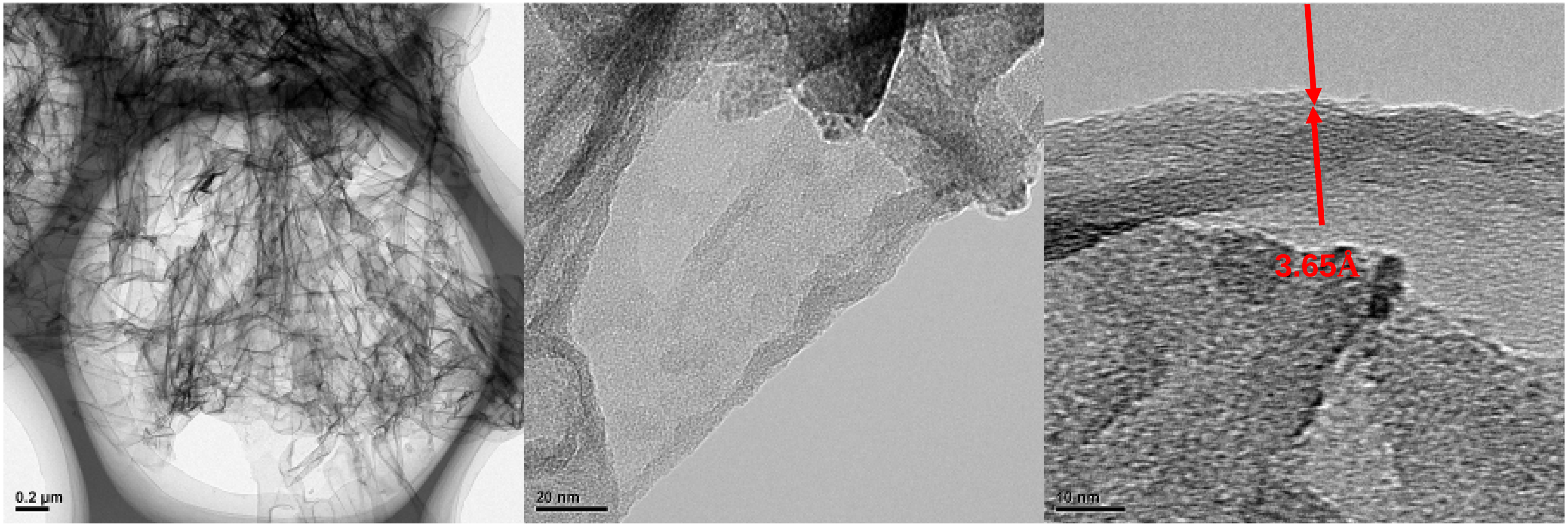
T：540 nm

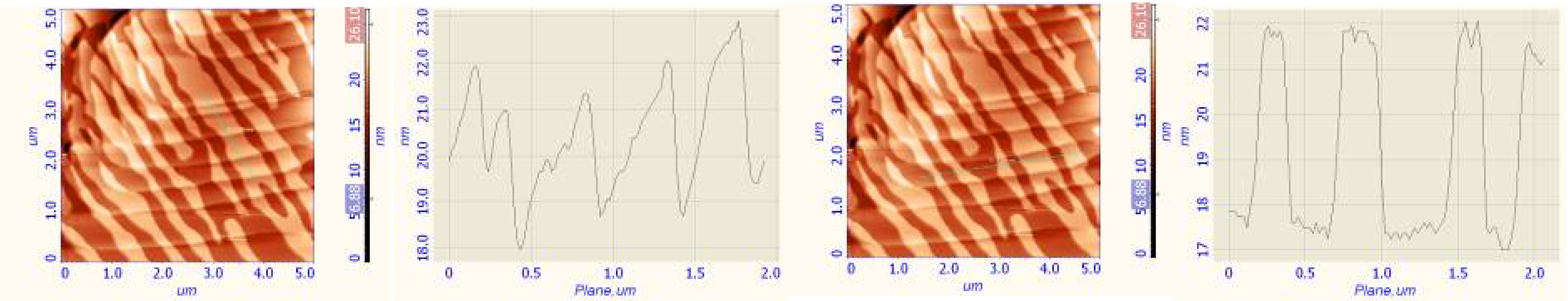
TEM and AFM



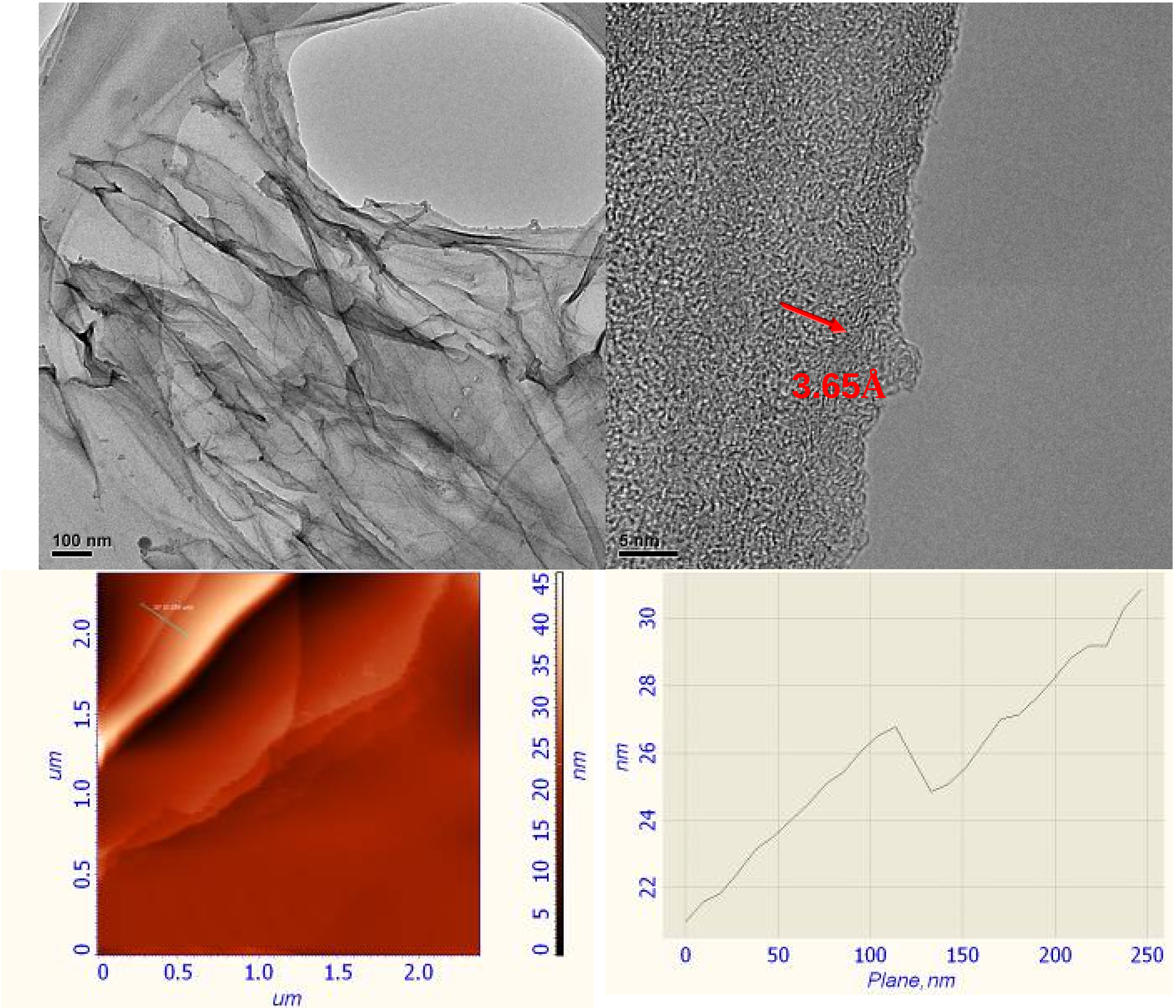
T：42.6 nm

TEM and AFM

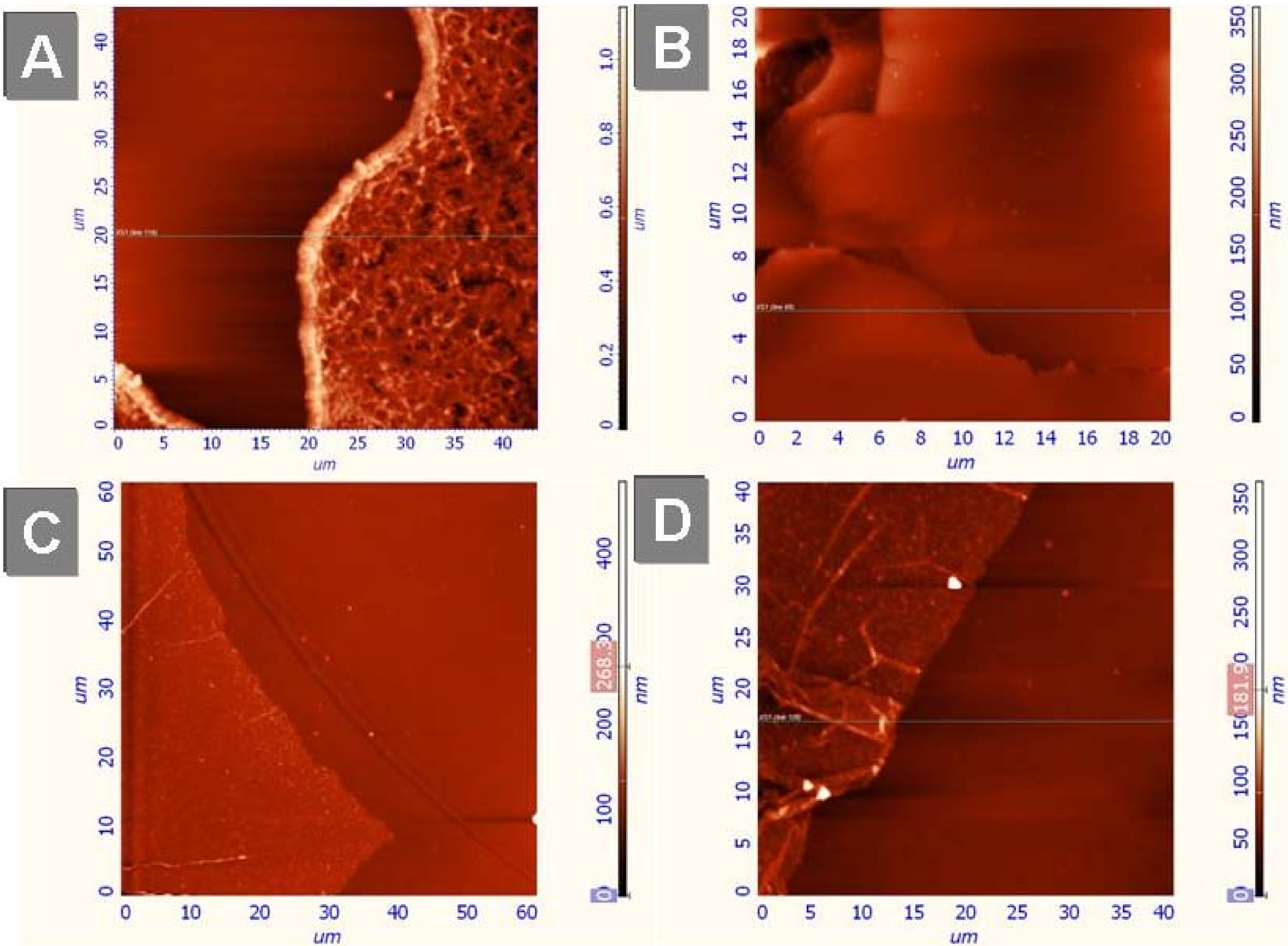




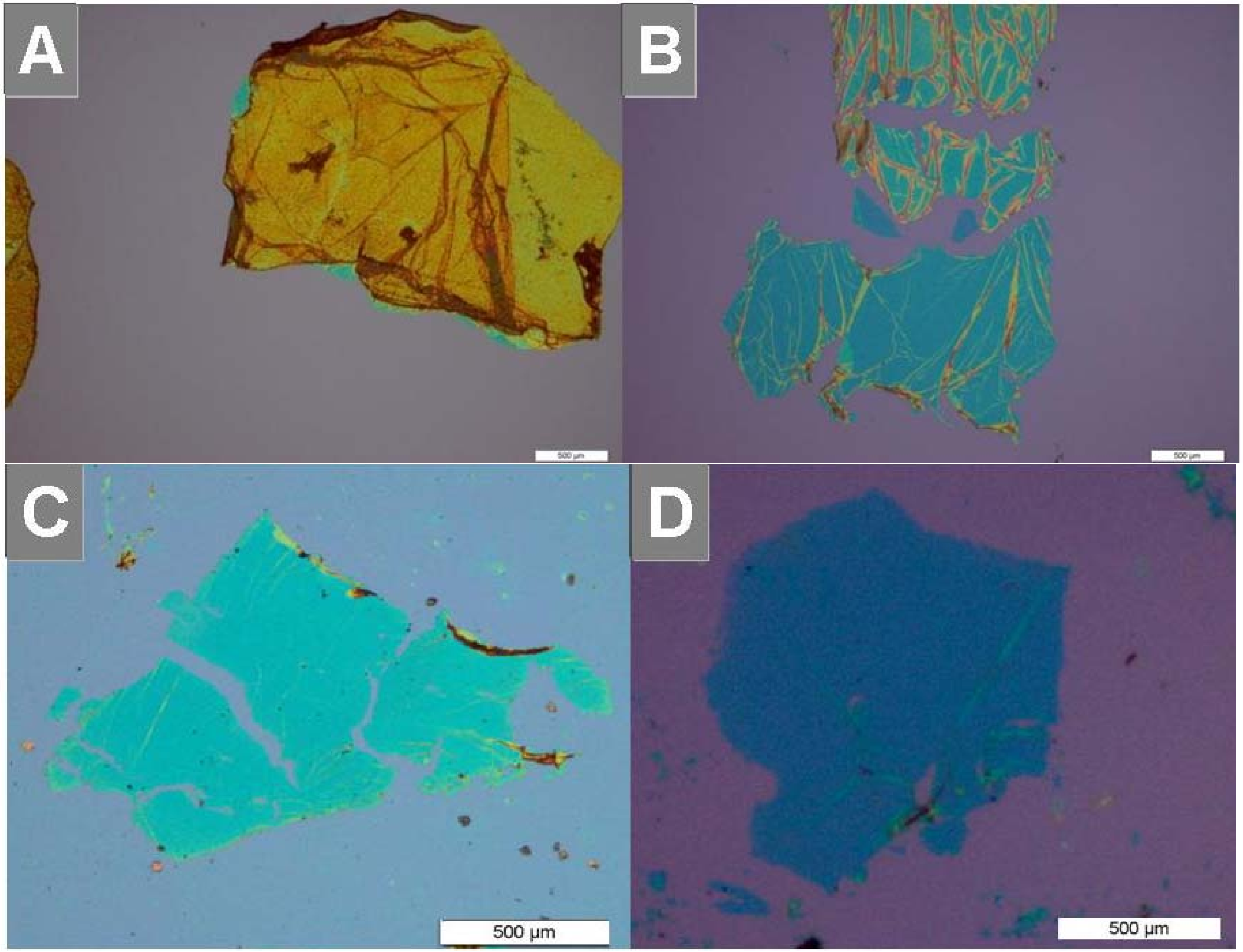
T：4.3 nm



T：1.94 nm—3—4 layers

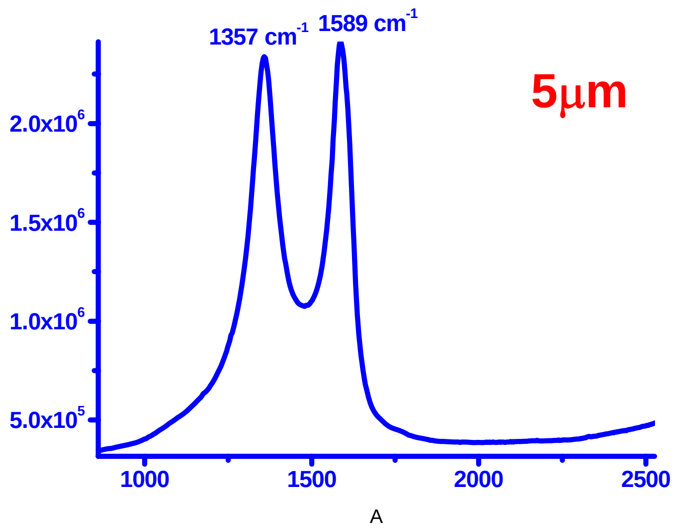


AFM images of different thickness GD films (A) 540 nm, (B)42.6 nm, (C) 22nm and (D)15nm

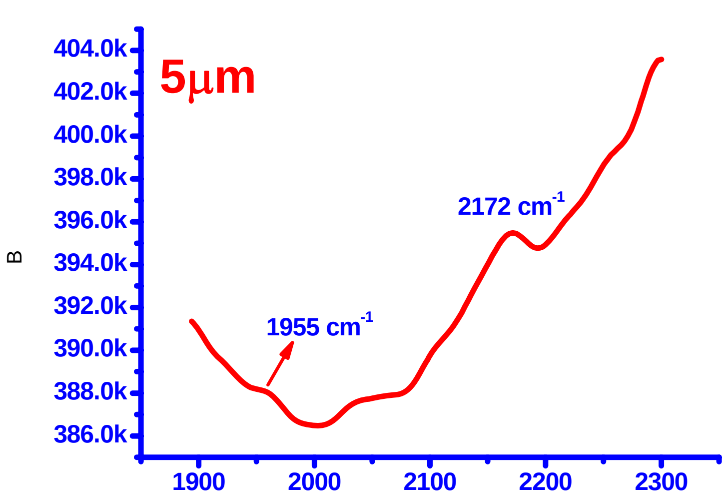


Optical microscopy images of different thickness GD films (A) 540 nm, (B)42.6 nm, (C) 22nm and (D)15nm

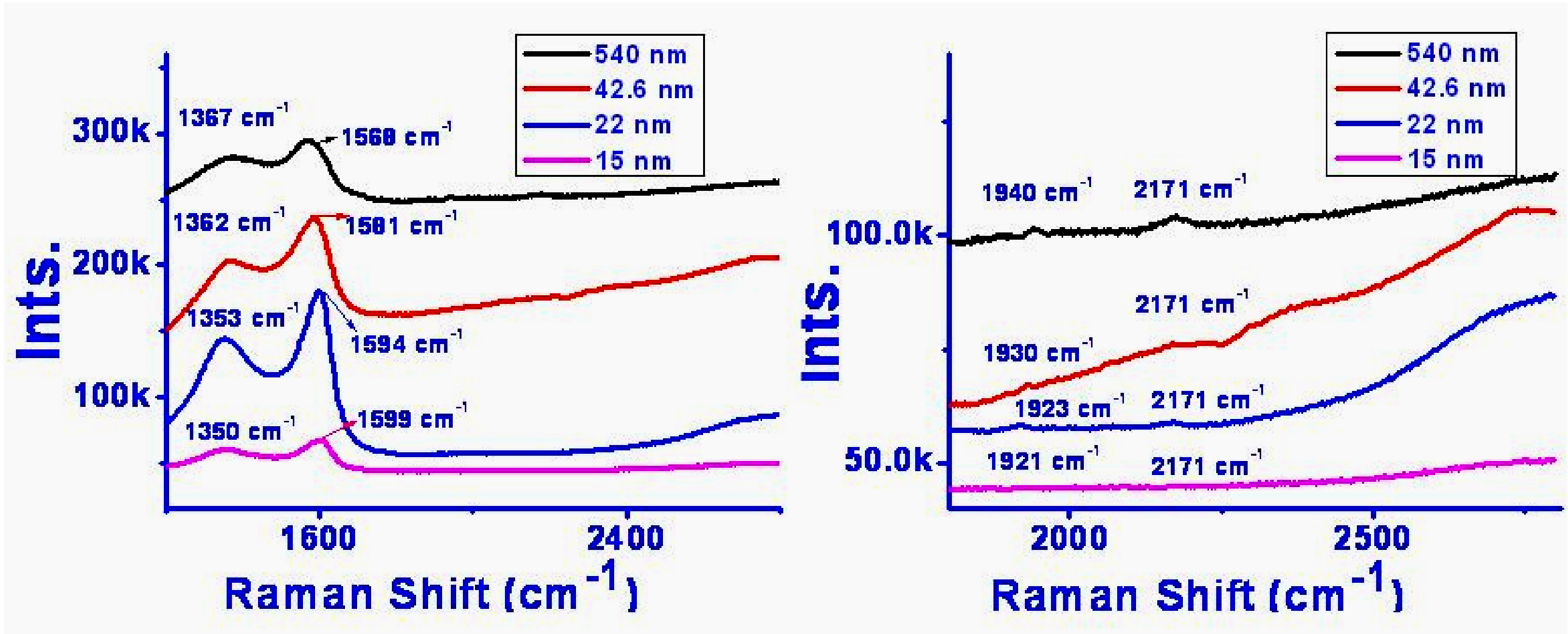
拉曼光谱



1357 cm-1
1589 cm-1
5μm
2.0x10^6
1.5x10^6
1.0x10^6
5.0x10^5
1000
1500
2000
2500
A



5μm
404.0k
402.0k
400.0k
398.0k
396.0k
394.0k
392.0k
390.0k
388.0k
386.0k
B
2172 cm-1
1955 cm-1
1900
2000
2100
2200
2300

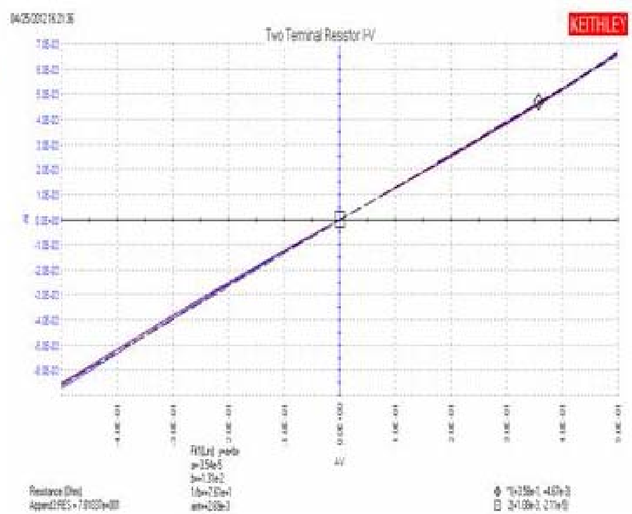


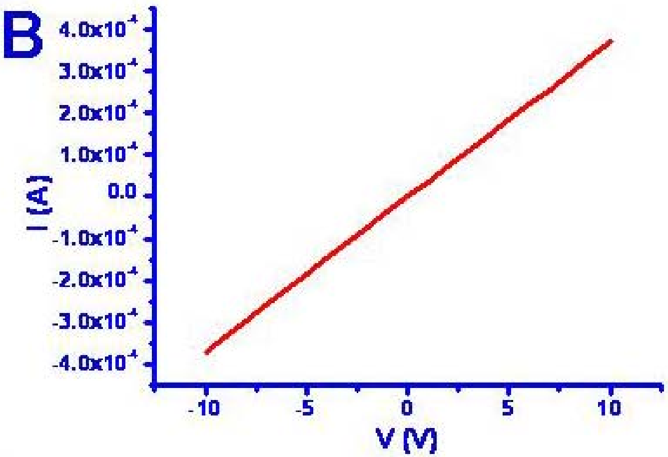
540 nm
42.6 nm
22 nm
15 nm
1367 cm-1
1568 cm-1
1362 cm-1
1581 cm-1
1353 cm-1
1594 cm-1
1350 cm-1
1599 cm-1
300k
200k
100k
Ints.
1600
2400
Raman Shift (cm-1)
1940 cm-1
2171 cm-1
100.0k
1930 cm-1
1923 cm-1
1921 cm-1
50.0k
2000
2500

电导率

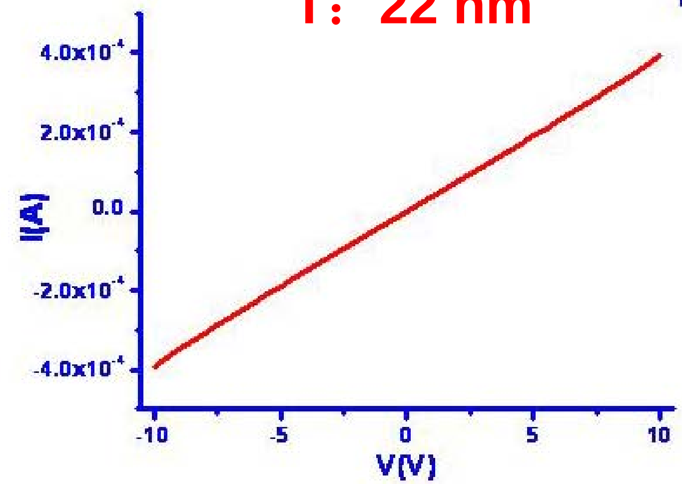
T：540 nm

T：42.6nm



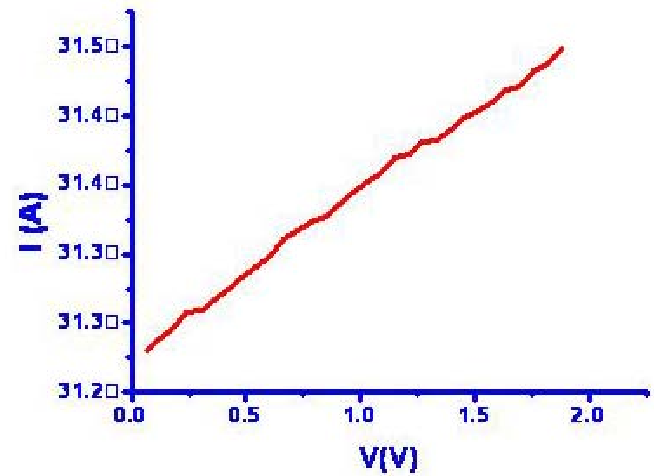


T：22 nm



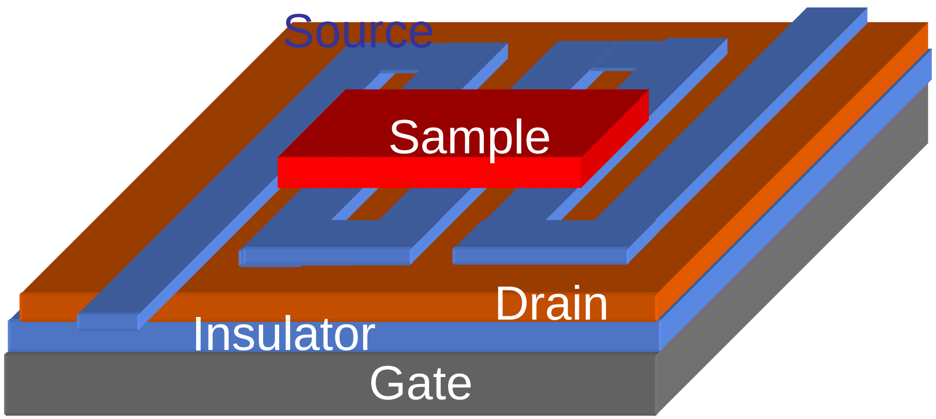
D

T：15 nm

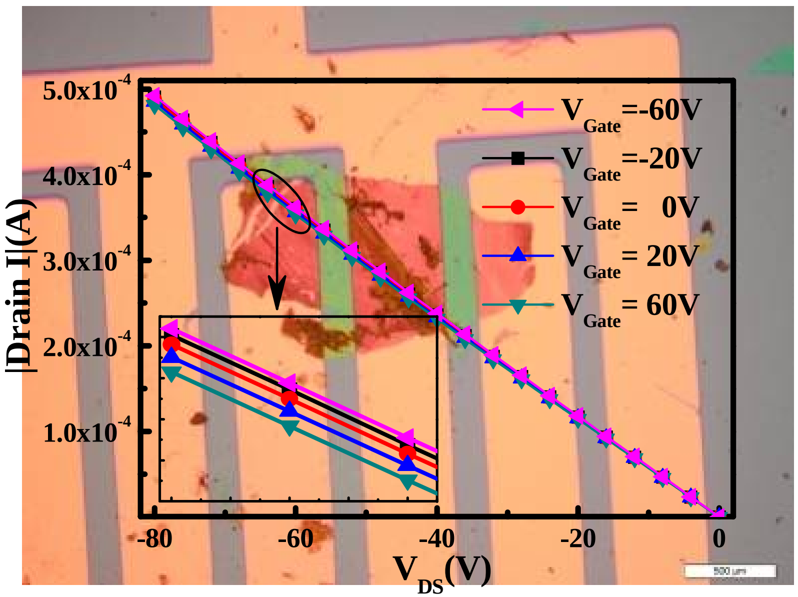


S:1, 700, 1200, and 1600 S/cm

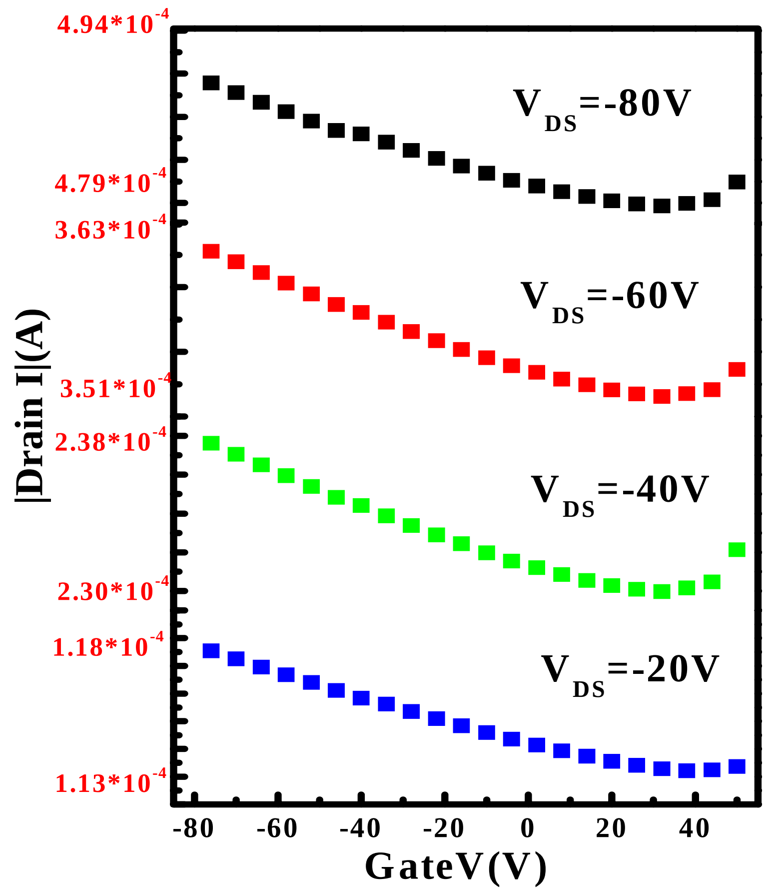
SiO2



Output Curve

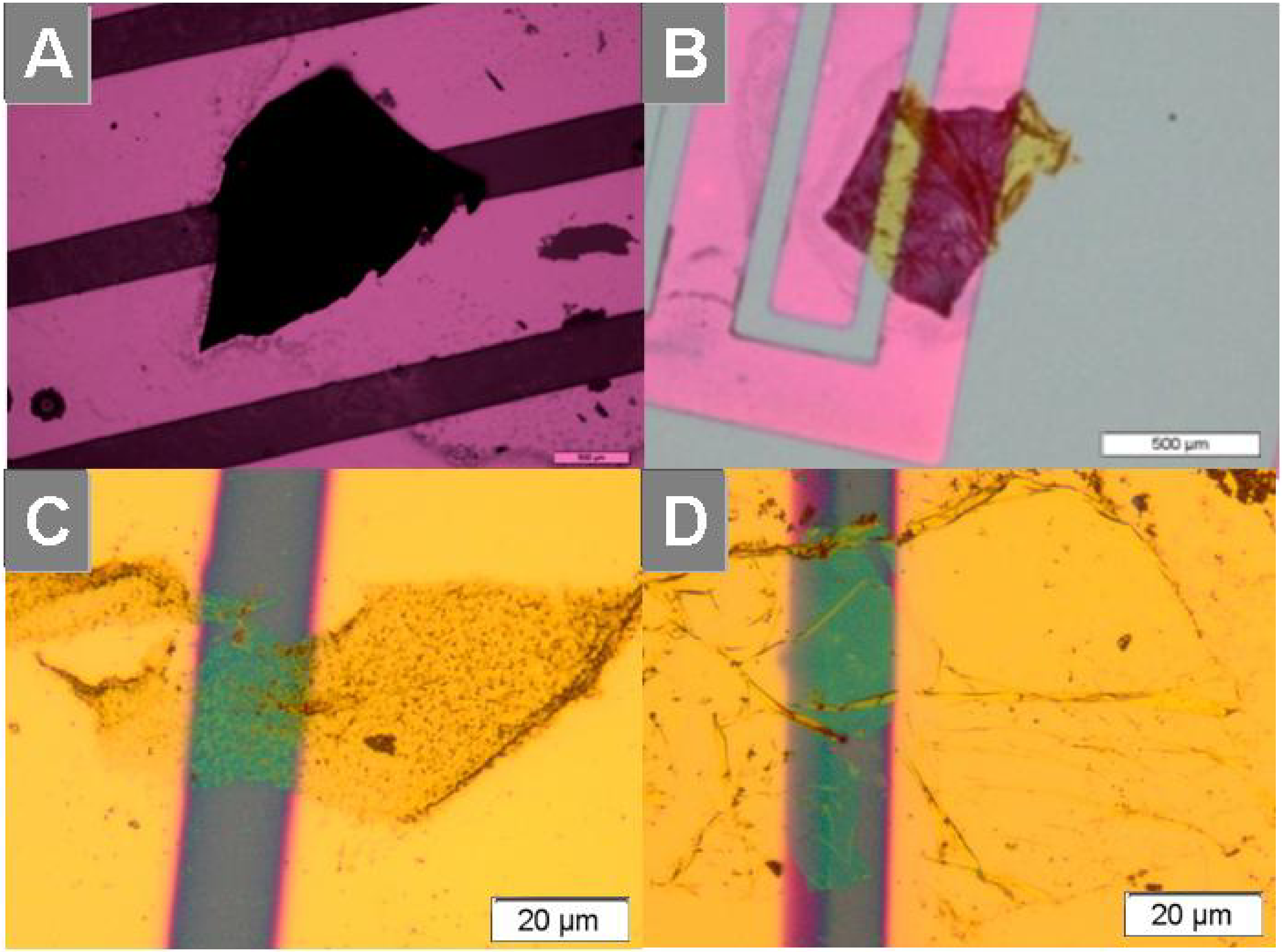


Transfer Curve

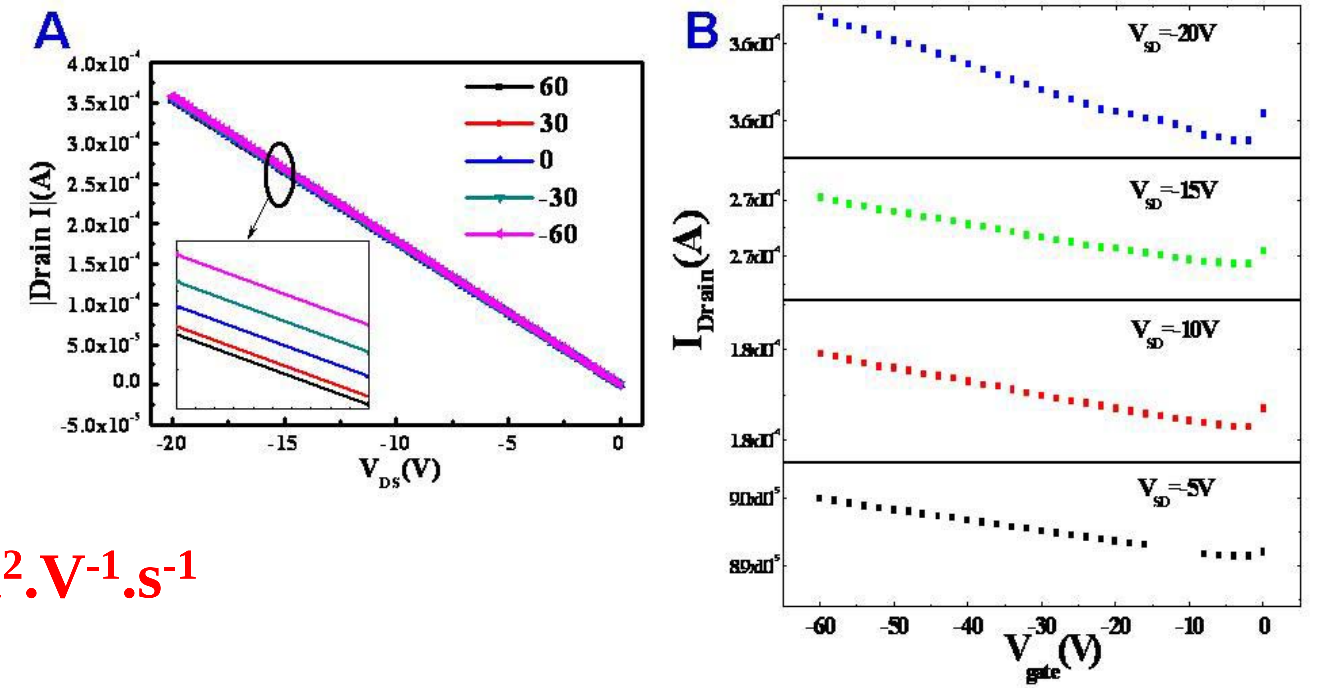


T：22.6 nm

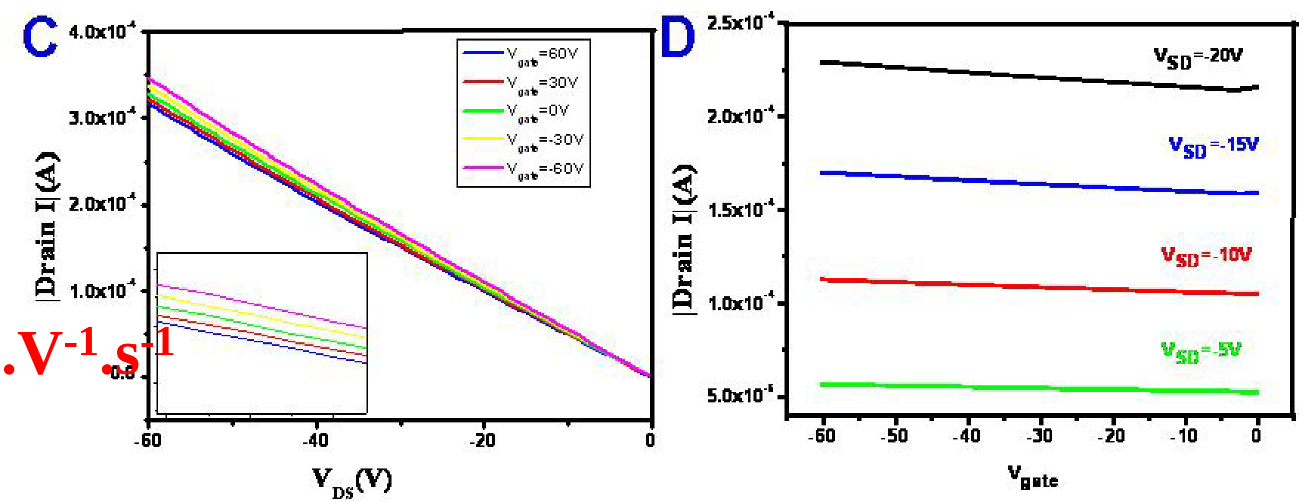
μ_h=~30 $cm^2.V^{-1}.s^{-1}$



Optical microscopy images of bottom-gate transistors fabricated by different thickness GD films (A) 540 nm, (B)42.6 nm, (C) 22nm and (D)15nm

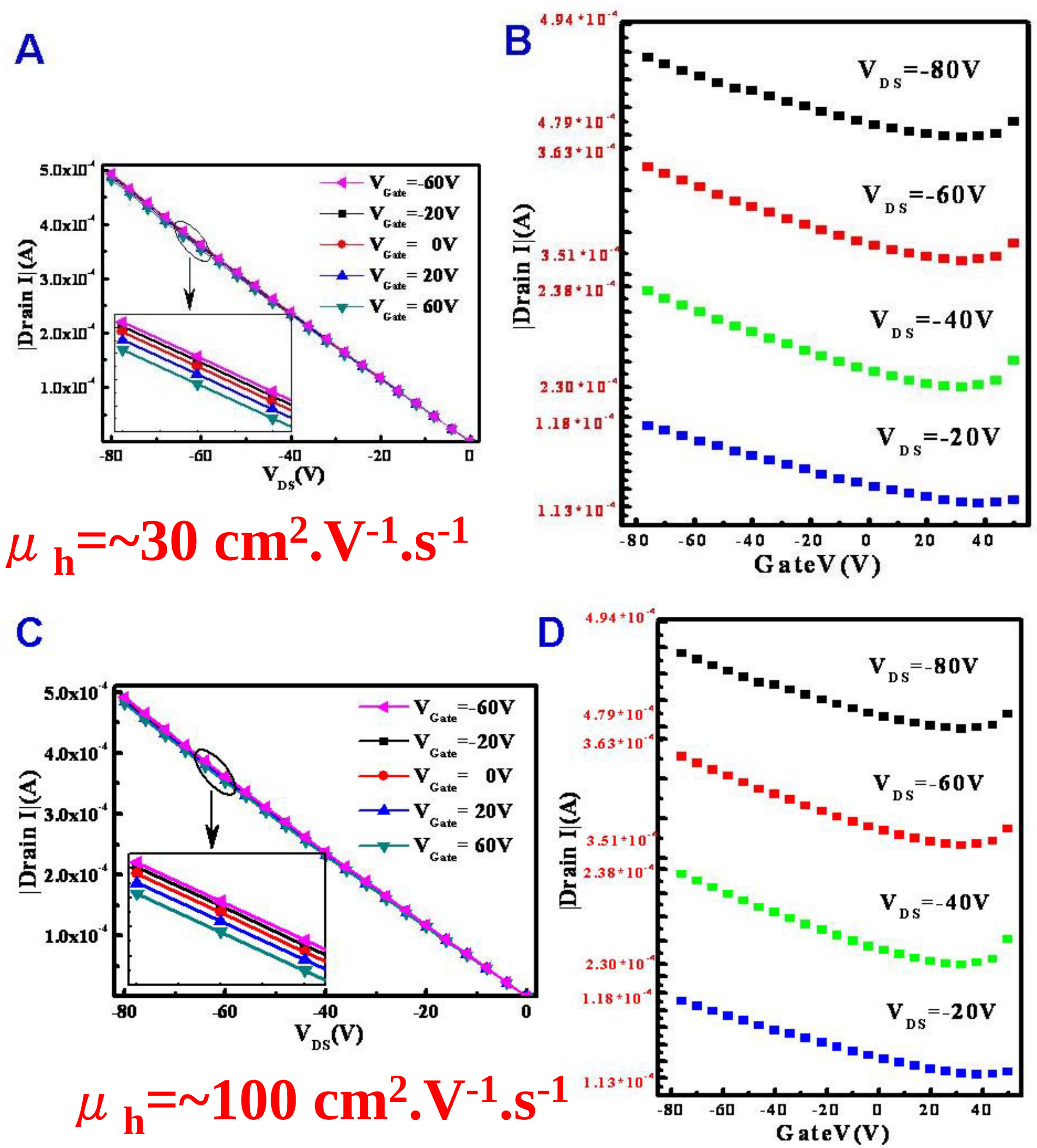


$\mu_h = 0.2\ cm^2.V^{-1}.s^{-1}$



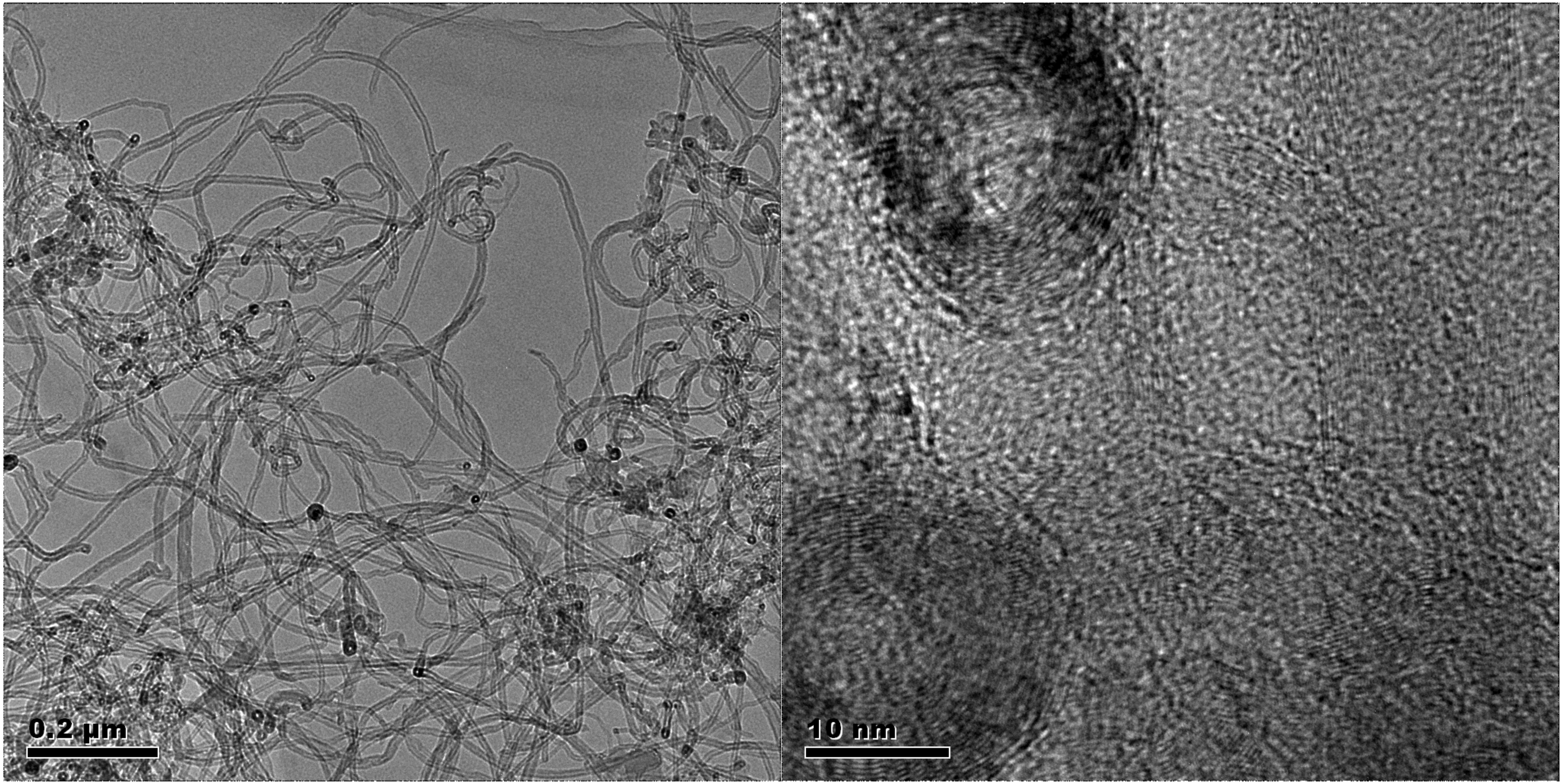
$\mu_h = 6.6\ cm^2.V^{-1}.s^{-1}$

Transfer characteristics (Ids-Vgs) and Current-voltage (Ids-Vds) curves for the device of GD films with thickness of (A-B) 540 nm, (C-D) 42.6nm.



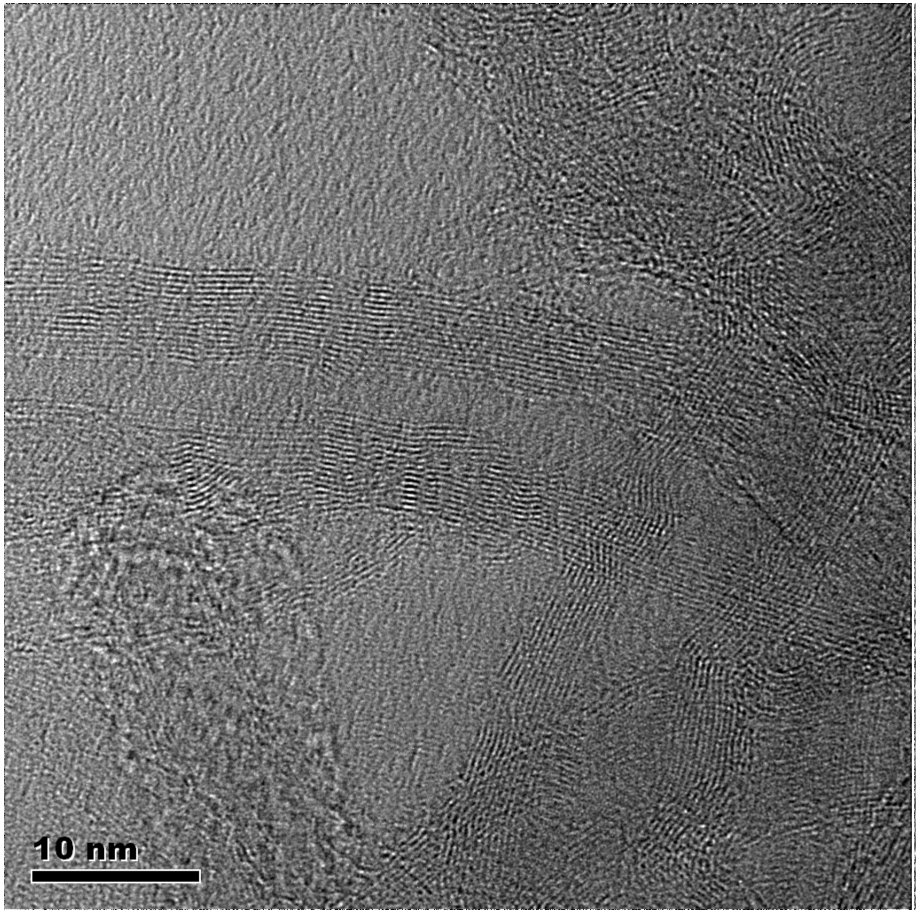
Transfer characteristics (Ids-Vgs) and Current-voltage (Ids-Vds) curves for the device of GD films with thickness of (A-B) 22 nm, (C-D) 15nm.

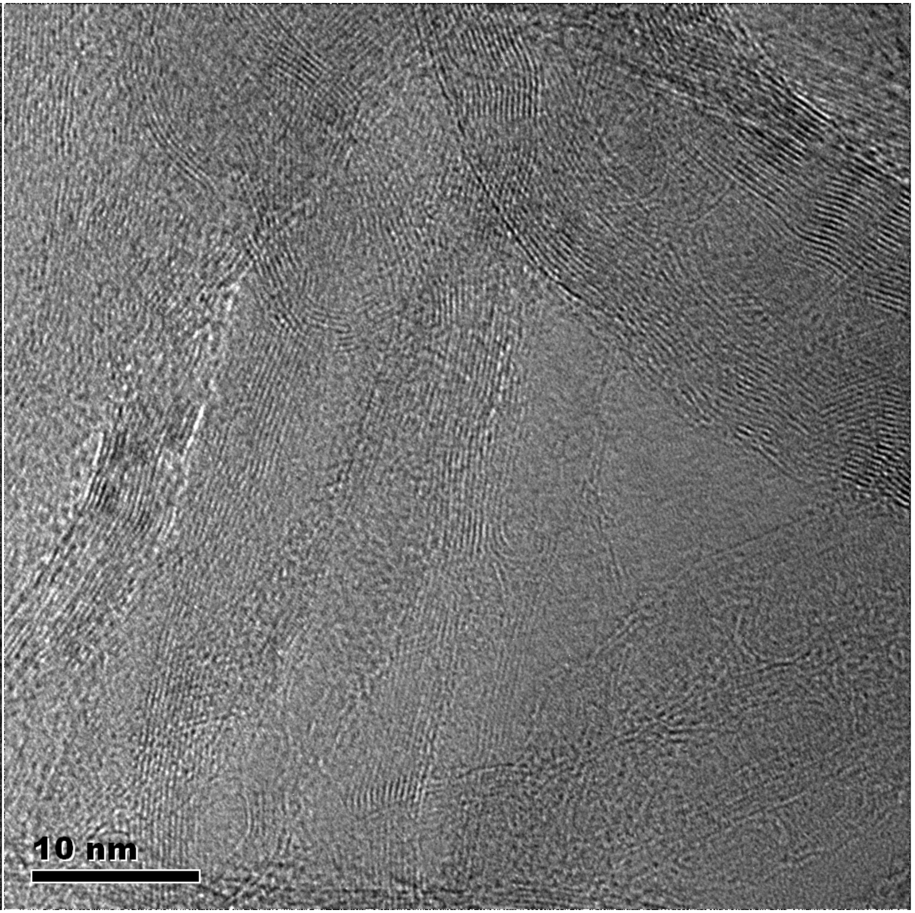
石墨炔纳米管



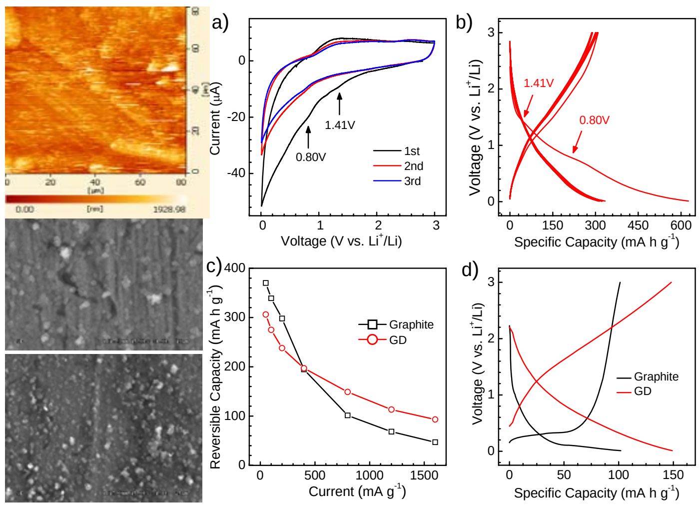
HRTEM

HRTEM

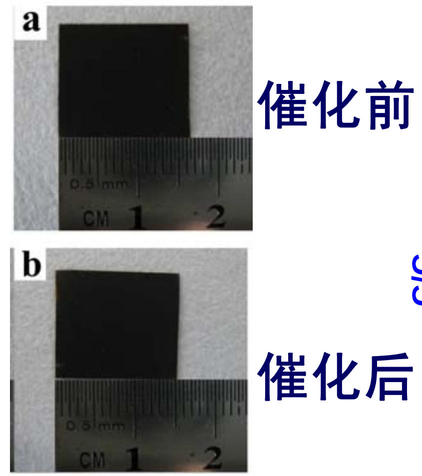


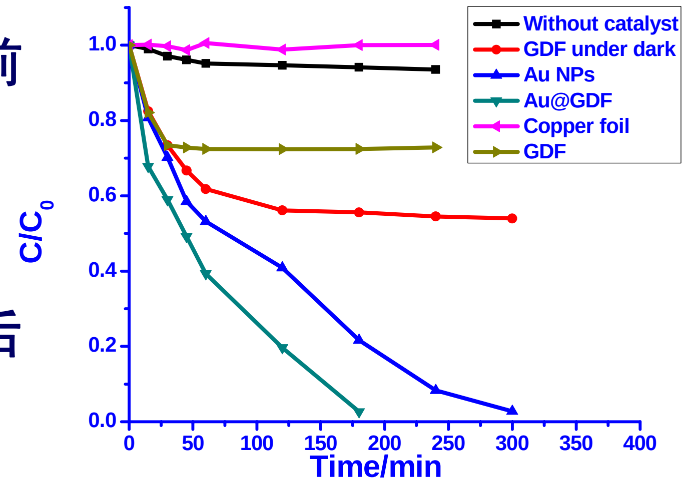


锂离子电池负极材料

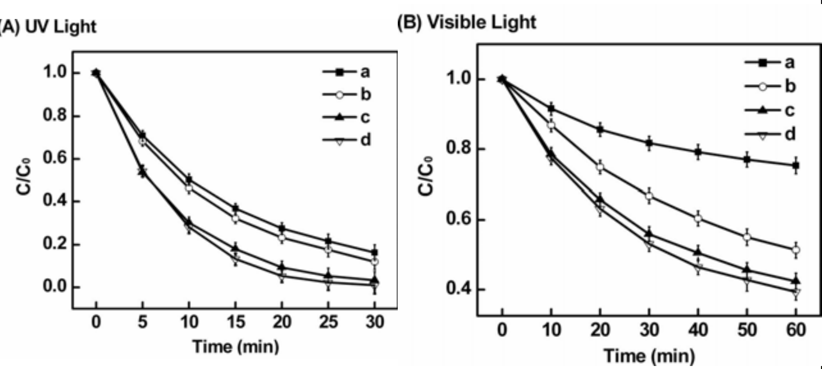


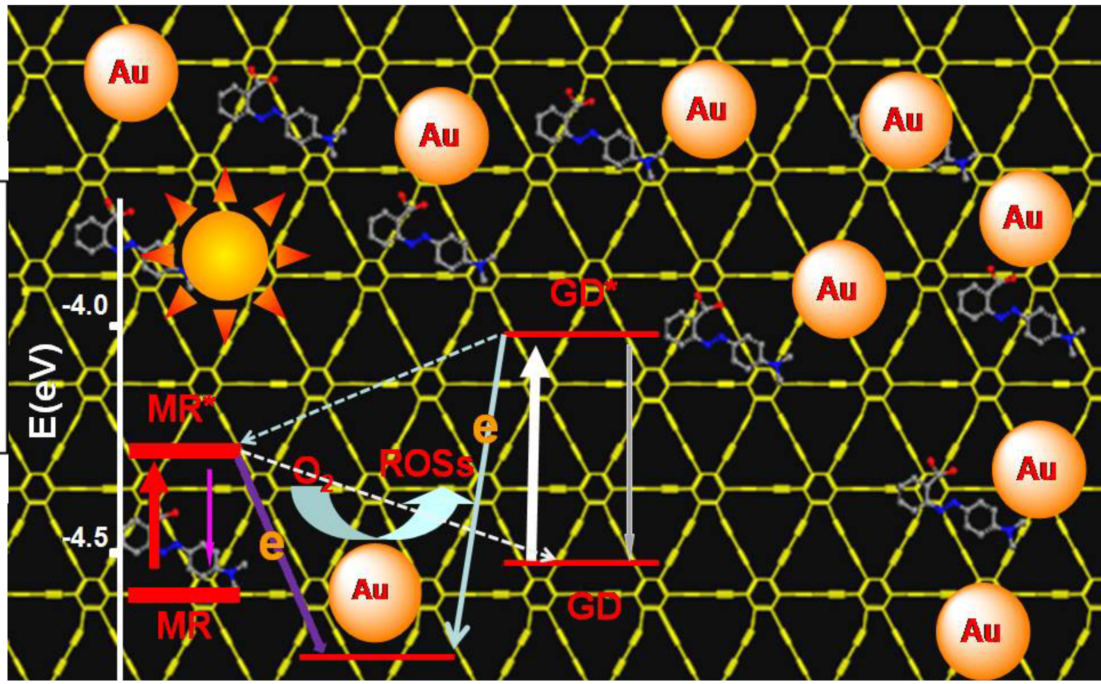
石墨炔复合材料光催化剂





TiO_2–GD光催化降解甲基蓝





结 论

- ✓ 不同力诱导以及原位反应通过自组装技术实现了富碳材料的聚集态的可控构筑，并对其性能进行调控。
- ✓ 构筑方法学的发展对于控制生长自组装大面积聚集态材料，导致了结构材料新发展。
- ✓ 无机半导体与有机半导体可控自组装，发展了富碳材料半导体异质结聚集态结构。
- ✓ 碳的新同素异形体—未来材料的焦点。

致　谢

国家自然科学基金委

科技部

中国科学院


Thank you!