

LA-UR-15-26738

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Title: Novel Carbon Materials for Electronic Devices Fabrication

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Issued: 2015-08-27

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Novel Carbon Materials for Electronic Devices Fabrication

Dr. Ming Zhou

**Los Alamos National Laboratory
Oct. 14th, 2015**

Background

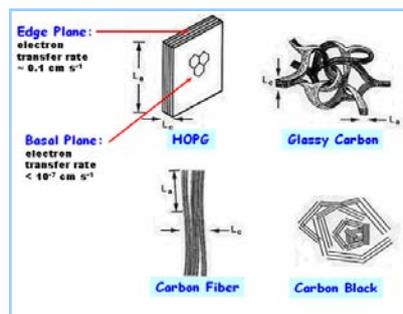
Carbon Materials

Advantages:

Chemical inertness,
Relatively wide potential window,
Cheap.

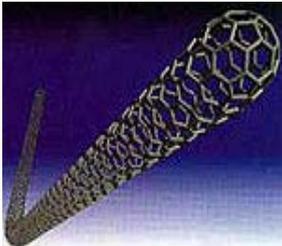
For example:

Edge plane pyrolytic graphite,
Basal plane pyrolytic graphite,
Carbon nanofibers,
Carbon nanotubes and etc..



R. L. McCreery, in *Electroanalytical Chemistry*, Ed. A. J. Bard, 17, 221-374 (1991). *Nat. Mater.* 2007, 6, 183.

Carbon Nanotubes



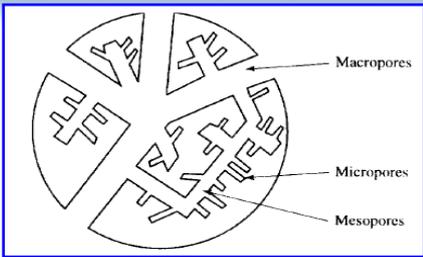
Single-wall nanotubes (SWNTs)
Diameter: 1-6 nm



Multi-wall nanotubes (MWNTs)
Diameter: from nm to μm

Carbon nanotubes have emerged as a new class of nanomaterials with their electronic, mechanical and chemical properties which have been claimed to be extremely attractive for use as chemical sensors, in particular *via* electrochemical detection.

Porous Carbon Materials

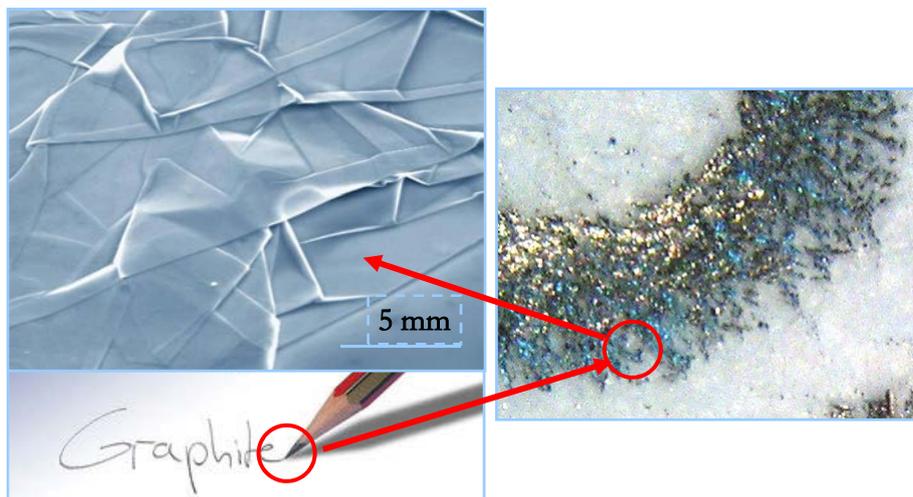


Porous Carbon Materials

<p>Microporous (<2 nm)</p>		<p>Microporous activated carbons</p>
<p>Mesoporous (2-50 nm)</p>		<p>CMK-X, SNU-X</p>
<p>Macroporous (>50 nm)</p>		<p>Coral</p>

Adv. Mater. 2006, 18, 2073.

Graphene: Easy to make, Hard to find



Research I Ordered Mesoporous Carbons

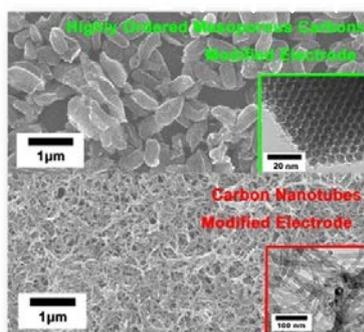


**Ordered Mesoporous Carbons-based
Electrochemical Sensor**

1

Ordered Mesoporous Carbons-based Electrochemical Sensor

Morphologies and Structures of OMCs and CNTs

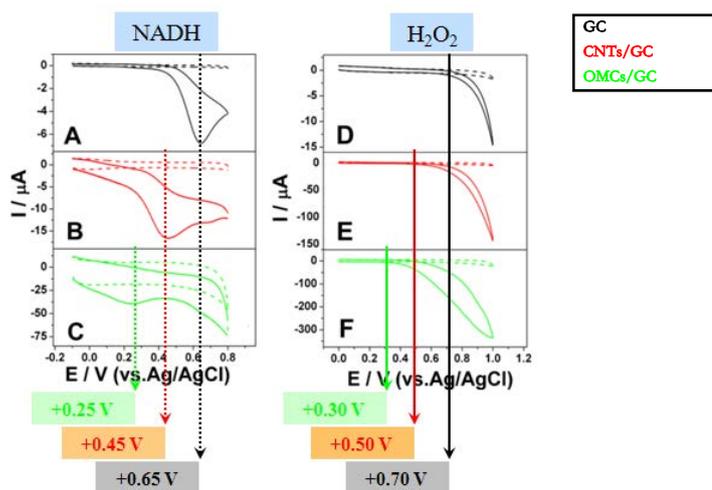


SEM image of OMCs/GE.
Inset: TEM image of OMCs.

SEM image of CNTs/GC.
Inset: TEM image of CNTs.

Zhou et al., *Biosens. Bioelectron.*, 2008, 24 (3) : 442-447.
Zhou et al., *Electrochem. Commun.*, 2008, 10 (6) : 859-863.

Electrochemical Oxidation of NADH and H₂O₂

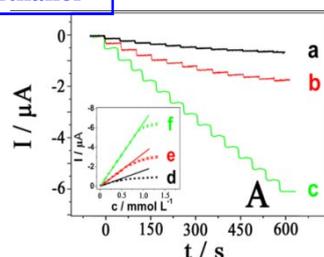


CVs for 2 mmol L⁻¹ NADH and 4.2 mmol L⁻¹ H₂O₂ in Electrolyte: 0.1 mol L⁻¹ pH 7.0 PBS. Scan rate: 50 mV s⁻¹.

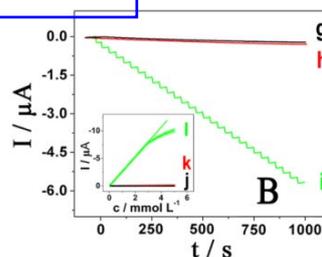
Detection of Ethanol and Glucose

GC-based, CNTs-based, OMCs-based electrode

Ethanol

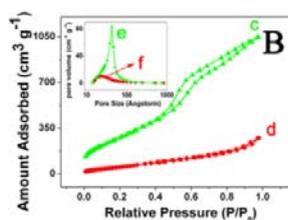


Glucose



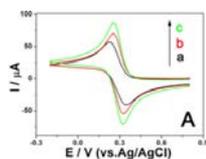
- (A) Current-time curves for Nafion/ADH/GE (at +0.65 V, curve a), Nafion/ADH-CNTs/GE (at +0.45 V, curve b) and Nafion/ADH-OMCs/GE (at +0.25 V, curve c) with successive addition of 1 mmol L⁻¹ ethanol. Electrolyte: air-saturated 0.1 mol L⁻¹ pH 7.0 PBS without being purged by nitrogen.
- (B) Current-time curves for Nafion/GOD/GE (curve g), Nafion/GOD-CNTs/GE (curve h) and Nafion/GOD-OMCs/GE (curve i) at +0.35 V with successive addition of 1 mmol L⁻¹ glucose. Electrolyte: 0.1 mol L⁻¹ pH 7.0 PBS containing 10 mmol L⁻¹ NAD⁺.

Nitrogen Adsorption-Desorption Isotherms and Electrochemical characteristics



	BET surface areas (cm ² g ⁻¹)	pore volumes (cm ³ g ⁻¹)	pore sizes (nm)
OMCs	1038	1.66	4.3
CNTs	203	0.43	2.1

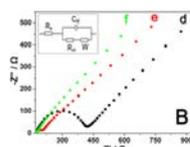
Nitrogen adsorption-desorption isotherms for OMCs (curve c) and CNTs (curve d). Inset: the pore size distributions for OMCs (curve e) and CNTs (curve f).



Background-corrected CVs at GE (curve a), CNT/GE (curve b) and OMC/GE (curve c) in 5 mmol L⁻¹ K₃Fe(CN)₆/0.1 mol L⁻¹ KCl solution with the scan rate of 50 mV s⁻¹.

	A
OMCs/GC	0.118 cm ²
CNTs/GC	0.090 cm ²
GC	0.068 cm ²

ΔE_p
51 mV
56 mV
60 mV

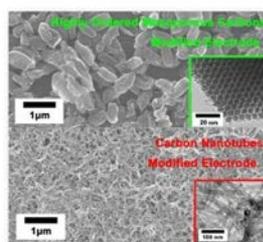


Nyquist plots at GE (curve d), CNTs/GE (curve e) and OMCs/GE (curve f) in 5 mmol L⁻¹ Fe(CN)₆³⁻ containing 0.1 mol L⁻¹ KCl.

	R_{ct}
d GC	213.6 Ω
e CNTs/GC	95.2 Ω
f OMCs/GC	13.2 Ω

R_{ct} : the resistance to charge transfer,
 C_{dl} : the interfacial capacitance,
 W : the diffusion impedance.

Summary



We present an advanced electrochemical sensing and biosensing platform based on OMCs without purification or end-opening processing, which are usually in CNTs applications.

Zhou et al., *Biosens. Bioelectron.*, 2008, 24 (3) : 442-447.
Zhou et al., *Electrochem. Commun.*, 2008, 10 (6) : 859-863.

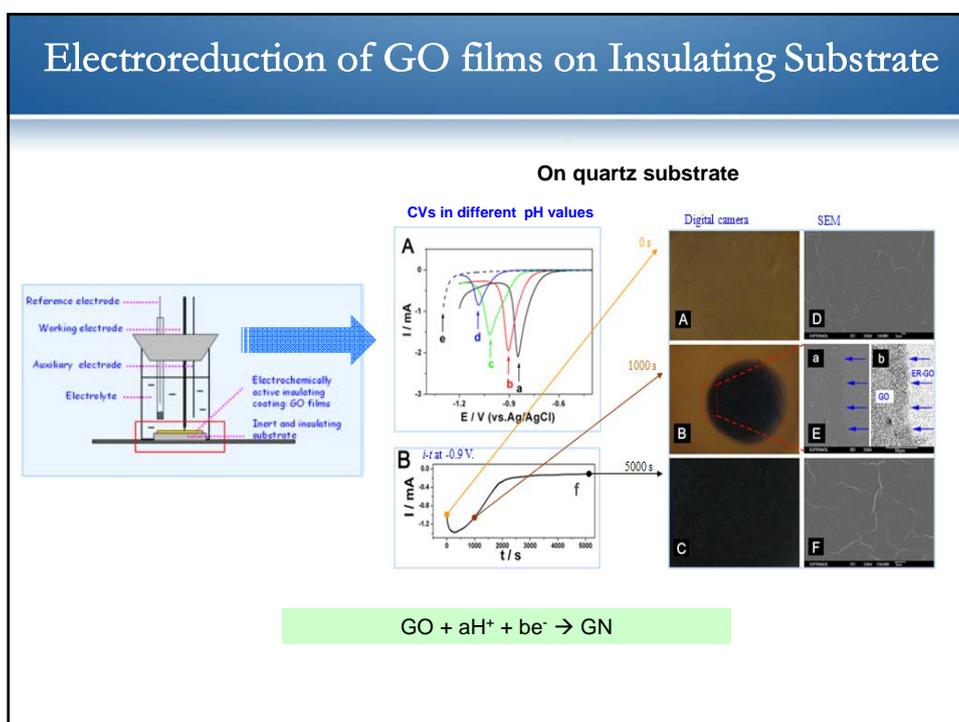
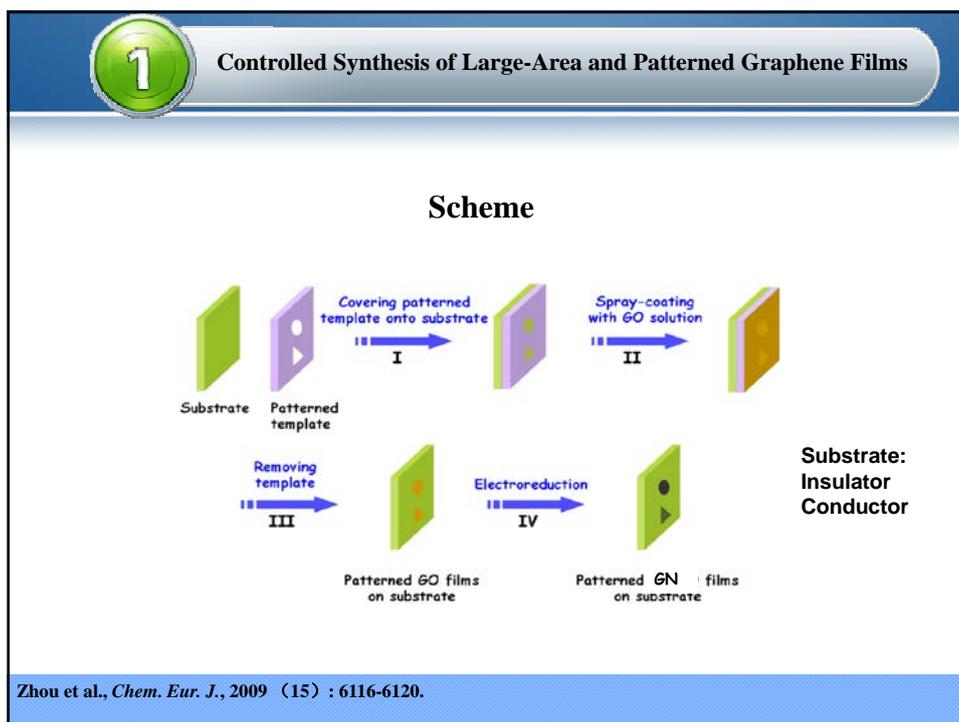
Research III Graphene



Controlled Synthesis of Large-Area and Patterned Graphene Films by Electroreduction

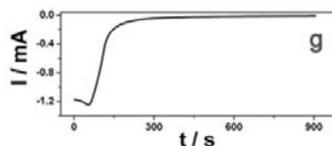
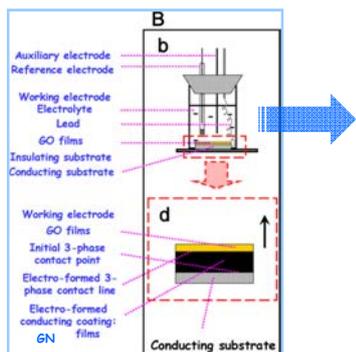


Electrochemical Sensing and Biosensing Platform Based on Graphene



Fabricating Graphene Films on Conducting Substrate

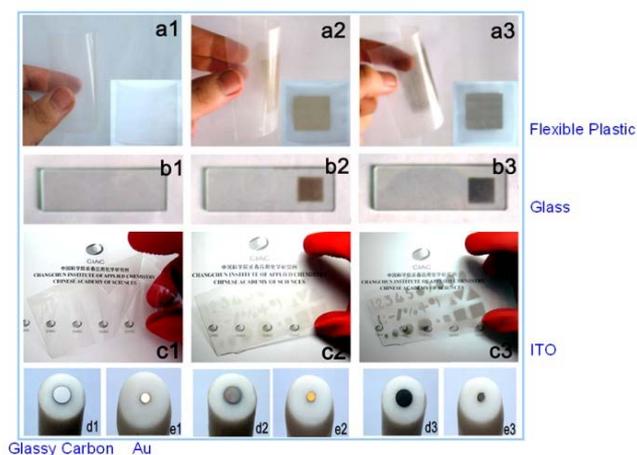
On glassy carbon substrate



Sample	O/C ratio (%)	
	Surface ^a	Bulk ^b
GO films	69.2	68.6
GN films	4.11	4.02

^a, determined by XPS. ^b, determined by elemental analysis.

Large-Area and Patterned Graphene Films



Conclusion



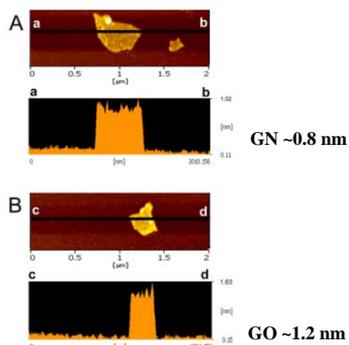
A simple, low-cost, efficient, green and environment-friendly electrochemical method has been demonstrated to fabricate graphene films.

Zhou et al., *Chem. Eur. J.*, 2009 (15) : 6116-6120.
Times Cited: 104

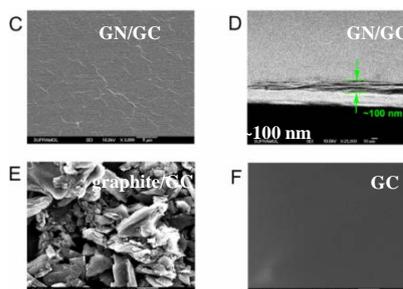


Electrochemical Sensing and Biosensing Platform Based on Graphene

Morphologies and Structures of GN and Graphite



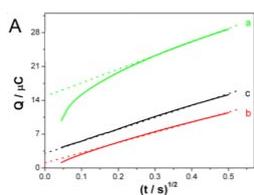
Tapping mode AFM images of GN (A) and GO (B) on freshly cleaved mica substrates.



SEM images of CR-GO/GC (C and D), graphite/GC (E) and GC (F). D is the side-view SEM image of CR-GO/GC.

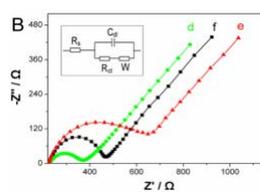
Zhou et al., *Anal. Chem.*, 2009 (81) : 5603-5613.

Electrochemistry



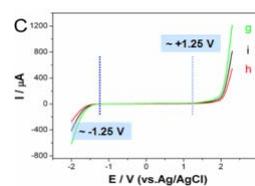
(A) Chronocoulometric curves at CR-GO/GC (a), graphite/GC (b) and GC electrodes (c) for the reduction of 1 mM $K_3Fe(CN)_6$ with 2 M KCl. The initial potential was 0.65 V and the potential was stepped to -0.05 V.

	A
GN/GC	0.0920 cm^2
GC	0.0706 cm^2
graphite/GC	0.0560 cm^2



(B) Nyquist plots at CR-GO/GC (d), graphite/GC (e) and GC (f) in 5 mM $Fe(CN)_6^{3-/4-}$ containing 0.1 M KCl.

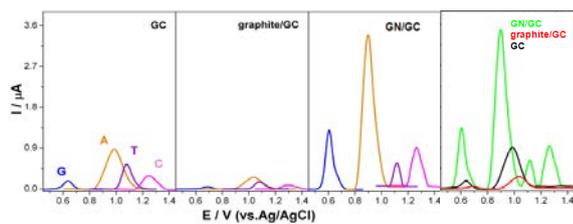
	R_{ct}
GN/GC	106.8 Ω
GC	200.7 Ω
graphite/GC	407.6 Ω



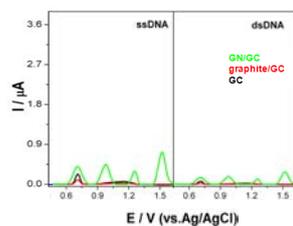
(C) LSVs of CR-GO/GC (g), graphite/GC (h) and GC (i) in 0.1 M pH 7.0 PBS. Scan rate: 50 $mV s^{-1}$.

~2.50 V

Detection of Four Free DNA Bases and DNA at Physiological pH

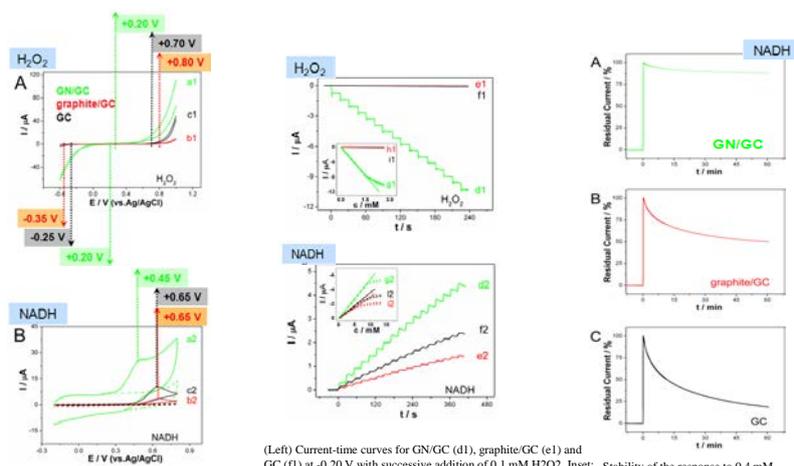


Electrolyte: 0.1 M pH 7.0 PBS.
Concentrations for different species (A-D): G, A, T or C: 10 $\mu g mL^{-1}$.



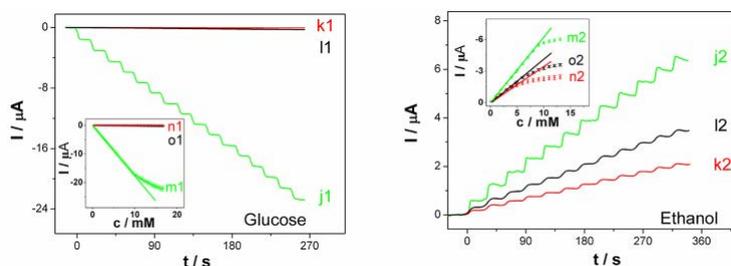
Concentrations for different species for ssDNA and dsDNA: 10 $\mu g mL^{-1}$ ssDNA. Electrolyte: 0.1 M pH 7.0 PBS.

For the Detection of NADH and H₂O₂

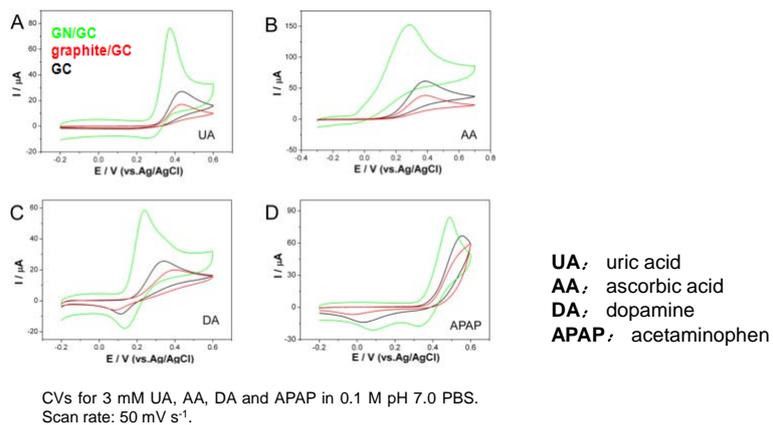


For the Detection of Glucose and Ethanol

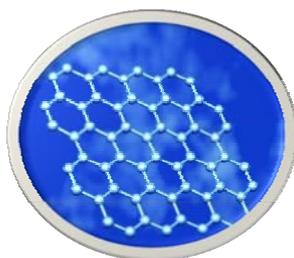
GC-based, graphite-based, GN-based bioelectrodes



Other Important Biomolecules



Conclusion



GN showing favorable electrochemical activity should be extremely attractive for a wide range of electrochemical sensing and biosensing applications ranging from amperometric sensors, to amperometric enzyme biosensors and label-free DNA biosensors.

Highlight

SELECT WHAT'S HOT IN CHEMISTRY PAPERS



What's Hot in Chemistry			
Rank	Paper	Cites This Period May-Jun 11	Rank Last Period Mar-Apr 11
8	Stoving, Denmark] *663GP J.F. Li, et al. "Shell-isolated nanoparticle-enhanced Raman spectroscopy," <i>Nature</i> , 464(7287): 392-5, 18 March 2010. [Xiamen U., China; Georgia Tech, Atlanta] *570EG	22	9
9	M. Zhou, Y. Zhai, S. Dong, "Electrochemical sensing and biosensing platform based on chemically reduced graphene oxide," <i>Anal. Chem.</i> , 81(14): 5603-13, 15 July 2009. [Chinese Acad. Sci., Changchun, China] *472MF	21	↑
10	B. Walker, et al., "Nanoscale phase separation and high photovoltaic efficiency in solution-processed, small-molecule bulk heterojunction solar cells," <i>Adv. Funct. Mater.</i> , 19(19): 3063-9, 9 October 2009. [U. Calif., Santa Barbara] *510ZJ	21	↑

SOURCE: Thomson Reuters Hot Papers Database. Read the Legend.

Cited as "**What's Hot in Chemistry – 2011-NOV/DEC (Top Ten list)**" by Science Watch (Thomson Reuters Web of Science®):

The Top Ten lists in Chemistry feature papers published during the last two years (excluding review articles) that were most cited in current journal articles indexed by Thomson Reuters during a recent two-month period. Papers are ranked according to the latest bimonthly citation count.

Acknowledgement



Prof. Erkang Wang and Prof. Shaojun Dong in CIAC



Prof. Joseph Wang in UCSD



Prof. Liming Dai in CWRU



Prof. Bo Zhang in UW



Dr. Hsing-Lin Wang in LANL



Prof. Gang Wu in UB



May Your Dreams Come True!

