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Title: Novel Carbon Materials for Electronic Devices Fabrication

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## Novel Carbon Materials for Electronic Devices Fabrication

**Dr. Ming Zhou**

**Los Alamos National Laboratory  
Oct. 14<sup>th</sup>, 2015**

## Background

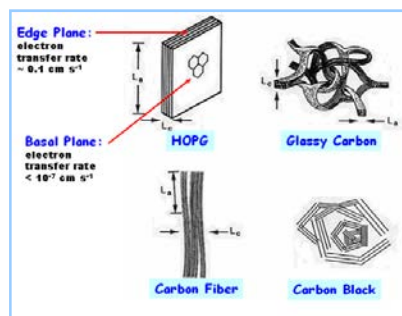
### Carbon Materials

#### Advantages:

Chemical inertness,  
Relatively wide potential window,  
Cheap.

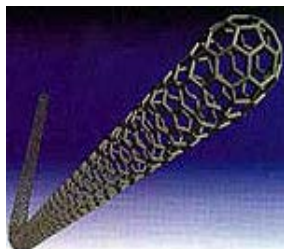
#### For example:

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

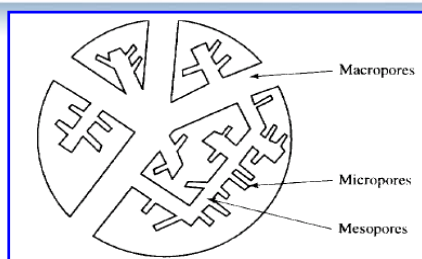


Multi-wall nanotubes ( **MWNTs** )

Diameter: from nm to  $\mu\text{m}$

**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

**Microporous**  
( $<2\text{ nm}$ )



Microporous activated carbons

**Mesoporous**  
( $2-50\text{ nm}$ )



CMK-X, SNU-X

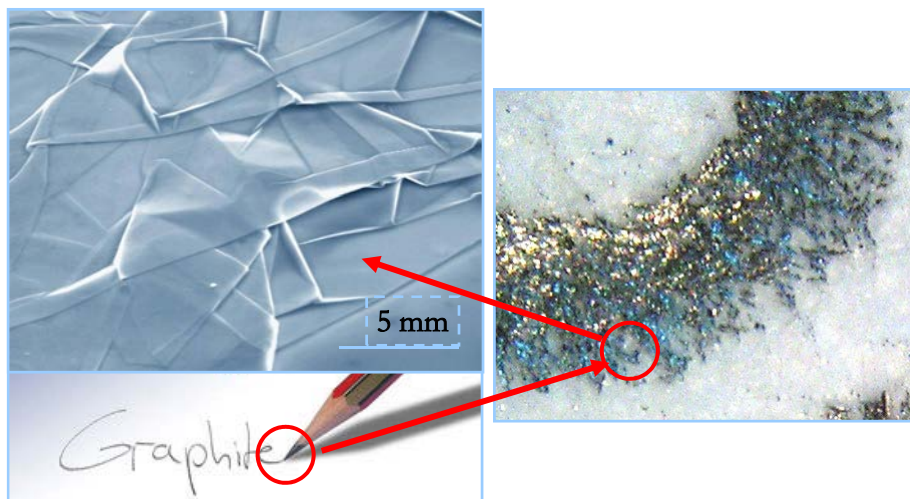
**Macroporous**  
( $>50\text{ nm}$ )



Coral

*Adv. Mater.* 2006, 18, 2073.

## Graphene: Easy to make, Hard to find



## Research I Ordered Mesoporous Carbons

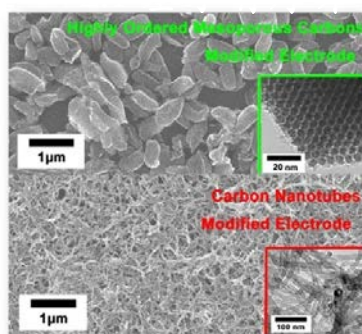


### Ordered Mesoporous Carbons-based Electrochemical Sensor



## Ordered Mesoporous Carbons-based Electrochemical Sensor

### Morphologies and Structures of OMCs and CNTs

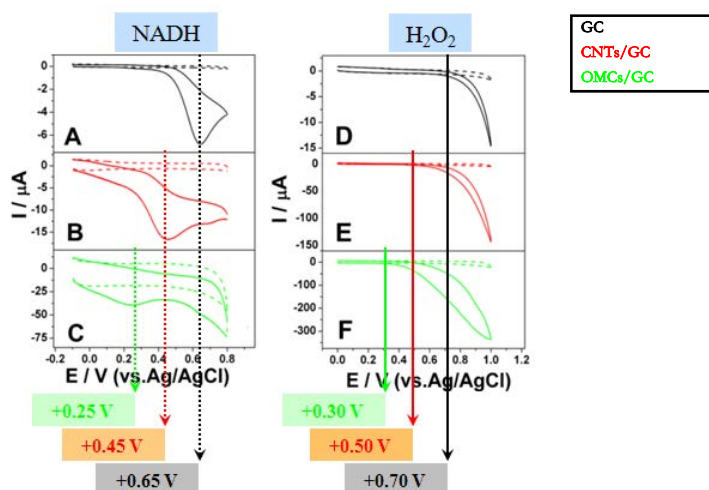


SEM image of OMCs/GE.  
Inset: TEM image of OMCs.

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 H<sub>2</sub>O<sub>2</sub>

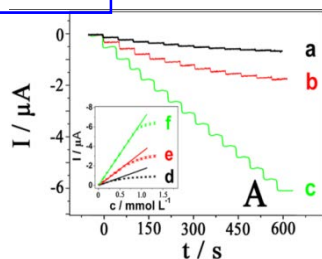


CVs for 2 mmol L<sup>-1</sup> NADH and 4.2 mmol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> in Electrolyte: 0.1 mol L<sup>-1</sup> pH 7.0 PBS. Scan rate: 50 mV s<sup>-1</sup>.

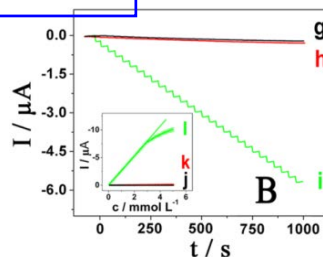
## Detection of Ethanol and Glucose

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

#### Ethanol

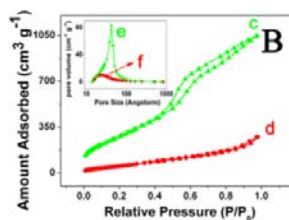


#### Glucose



- (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<sup>-1</sup> ethanol. Electrolyte: air-saturated 0.1 mol L<sup>-1</sup> 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<sup>-1</sup> glucose. Electrolyte: 0.1 mol L<sup>-1</sup> pH 7.0 PBS containing 10 mmol L<sup>-1</sup> NAD<sup>+</sup>.

## Nitrogen Adsorption-Desorption Isotherms and Electrochemical characteristics



BET surface areas  
(cm<sup>2</sup> g<sup>-1</sup>)

pore volumes  
(cm<sup>3</sup> g<sup>-1</sup>)

pore sizes  
(nm)

OMCs

1038

1.66

4.3

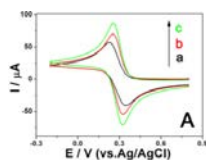
CNTs

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<sup>-1</sup> K<sub>3</sub>Fe(CN)<sub>6</sub>/0.1 mol L<sup>-1</sup> KCl solution with the scan rate of 50 mV s<sup>-1</sup>.

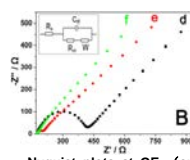
OMCs/GC 0.118 cm<sup>2</sup>  
CNTs/GC 0.090 cm<sup>2</sup>  
GC 0.068 cm<sup>2</sup>

$\Delta E_p$

51 mV

56 mV

60 mV

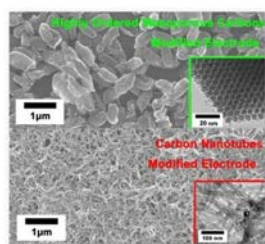


Nyquist plots at GE (curve d), CNTs/GE (curve e) and OMCs/GE (curve f) in 5 mmol L<sup>-1</sup> Fe(CN)<sub>6</sub><sup>3-/4-</sup> containing 0.1 mol L<sup>-1</sup> KCl.

$R_{ct}$   
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,  
 $R_f$ : 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 II Graphene

1

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

2

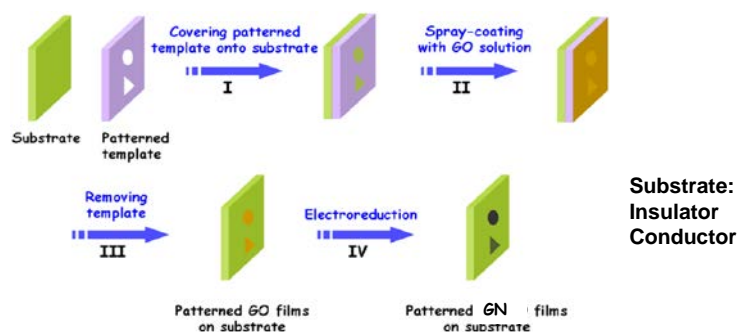
Electrochemical Sensing and Biosensing Platform Based on Graphene





## Controlled Synthesis of Large-Area and Patterned Graphene Films

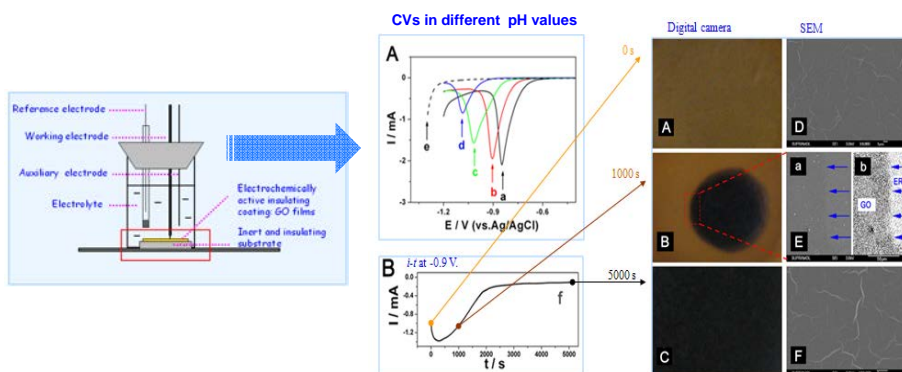
### Scheme



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

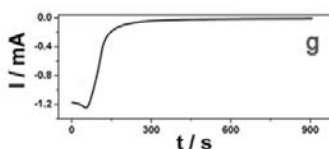
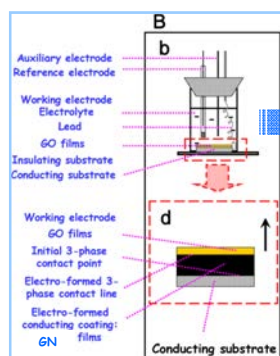
## Electroreduction of GO films on Insulating Substrate

### On quartz substrate



## Fabricating Graphene Films on Conducting Substrate

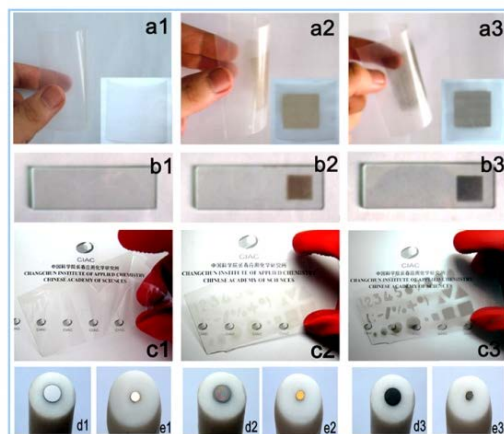
On glassy carbon substrate



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

<sup>a</sup>, determined by XPS. <sup>b</sup>, determined by elemental analysis.

## Large-Area and Patterned Graphene Films



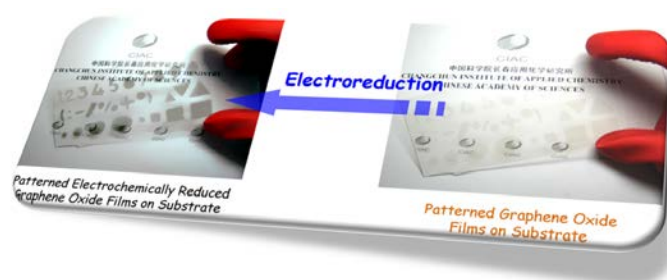
Flexible Plastic

Glass

ITO

Glassy Carbon Au

## Conclusion



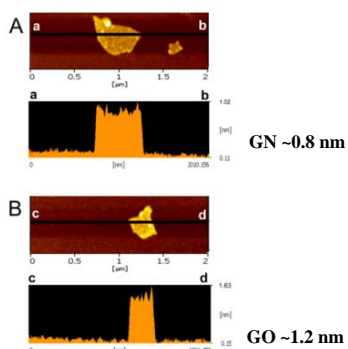
A simple, low-cost, efficient, green and environment-friendly electrochemical method has been demonstrated to fabricate graphene films.

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

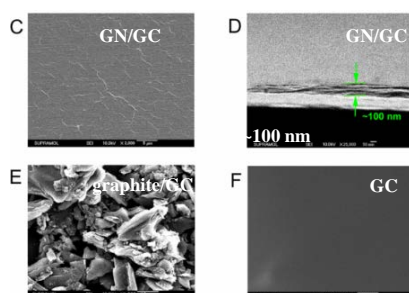


## Electrochemical Sensing and Biosensing Platform Based on Graphene

### Morphologies and Structures of GN and Graphite



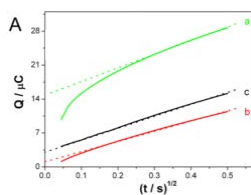
Tapping mode AFM images of GN (A) and GO (B) on freshly cleaved mica substrates.



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.

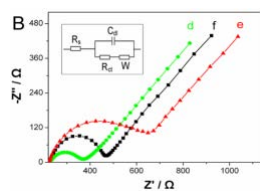
Zhou et al., *Anal. Chem.*, 2009 (81) : 5603-5613.

## Electrochemistry



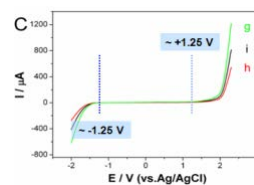
(A) Chronocoulometric curves at CR-GO/GC (a), graphite/GC (b) and GC electrodes (c) for the reduction of 1 mM K<sub>3</sub>Fe(CN)<sub>6</sub> with 2 M KCl. The initial potential was 0.65 V and the potential was stepped to -0.05 V.

	<i>A</i>
GN/GC	0.0920 cm <sup>2</sup>
GC	0.0706 cm <sup>2</sup>
graphite/GC	0.0560 cm <sup>2</sup>



(B) Nyquist plots at CR-GO/GC (d), graphite/GC (e) and GC (f) in 5 mM Fe(CN)<sub>6</sub><sup>3-/4-</sup> containing 0.1 M KCl.

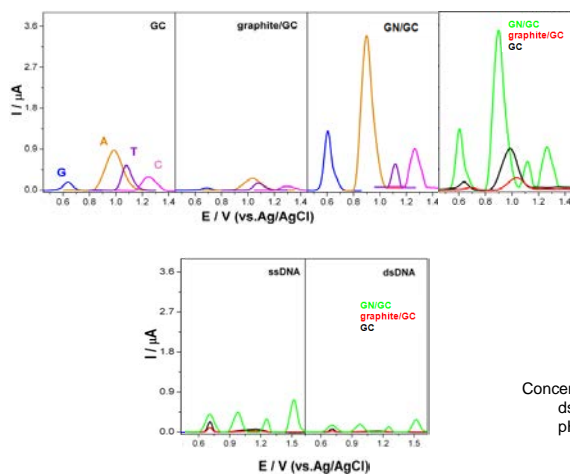
	<i>R<sub>ct</sub></i>
GN/GC	106.8 Ω
GC	200.7 Ω
graphite/GC	407.6 Ω



(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<sup>-1</sup>.

~2.50 V

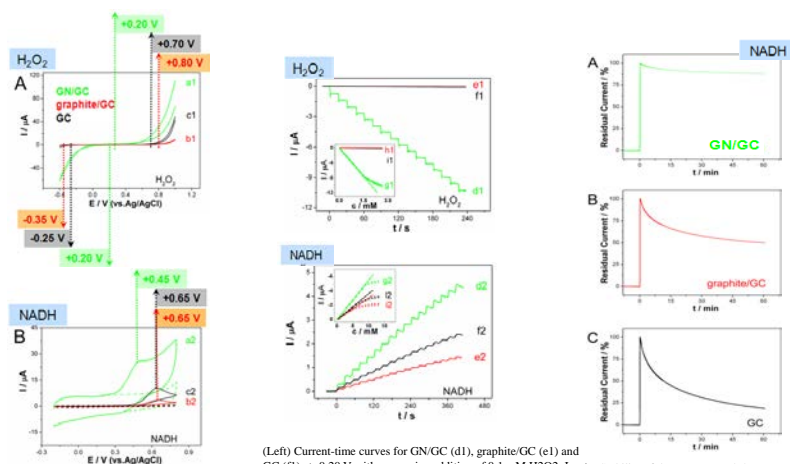
## Detection of Four Free DNA Bases and DNA at Physiological pH



Electrolyte: 0.1 M pH 7.0 PBS.  
Concentrations for different species (A-D): G, A, T or C: 10 μg mL<sup>-1</sup>.

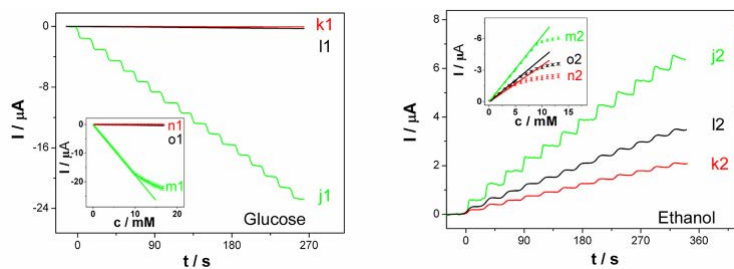
Concentrations for different species for ssDNA and dsDNA: 10 μg mL<sup>-1</sup> ssDNA. Electrolyte: 0.1 M pH 7.0 PBS.

## For the Detection of NADH and $\text{H}_2\text{O}_2$

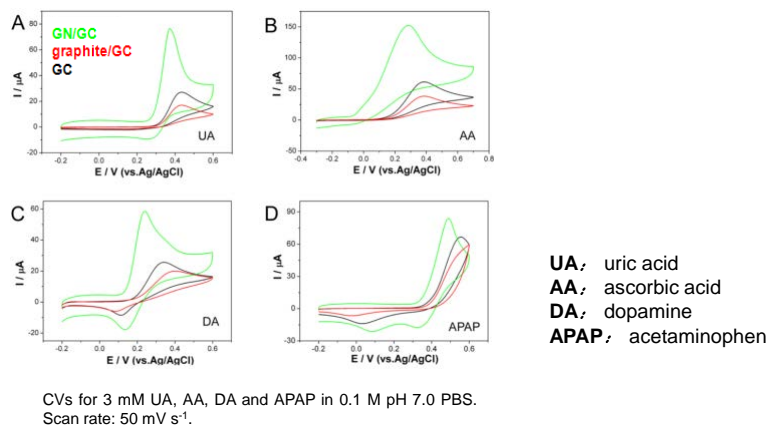


## For the Detection of Glucose and Ethanol

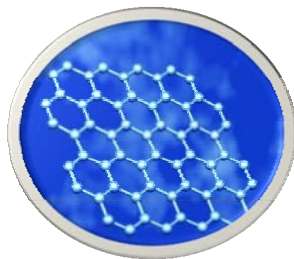
GC-based, graphite-based, GN-based bioelectrodes



## 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	
	Stovring, Denmark] *663GP			
8	J.F. Li, et al., "Shell-isolated nanoparticle-enhanced Raman spectroscopy," <i>Nature</i> , 454(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	↑	

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Prof. Bo Zhang in UW



Dr. Hsing-Lin Wang in LANL



Prof. Gang Wu in UB



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