CHEM2DMAT

AUGUST 31 - SEPTEMBER 03, 2021 • ONLINE

EUROPEAN CONFERENCE ON CHEMISTRY OF TWO-DIMENSIONAL MATERIALS

# **Graphene Oxide** as promoter for chemical reactions monitored by **X-Ray Photoelectron Spectroscopy**

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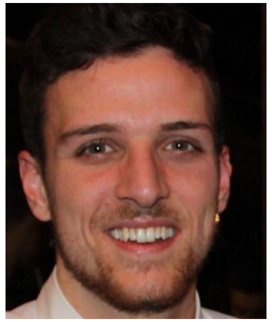
# Acknowledgements

## UNIBO

**Marco Bandini**



**Lorenzo Lombardi**

## ISOF-CNR

**Vincenzo Palermo**

**Manuela Melucci**

**Cristian Bettini**
**Laura Favaretto**

Chemistry–A European Journal | Communication
doi.org/10.1002/chem.202001373

Synthetic Methods | *Hot Paper* |

### Allylic and Allenylic Dearomatization of Indoles Promoted by Graphene Oxide by Covalent Grafting Activation Mode

Lorenzo Lombardi,[a] Daniele Bellini,[a] Andrea Bottoni,[a] Matteo Calvaresi,[a] Magda Monari, Alessandro Kovtun,[c] Vincenzo Palermo,[c, d] Manuela Melucci,[c] and Marco Bandini*[a, b]

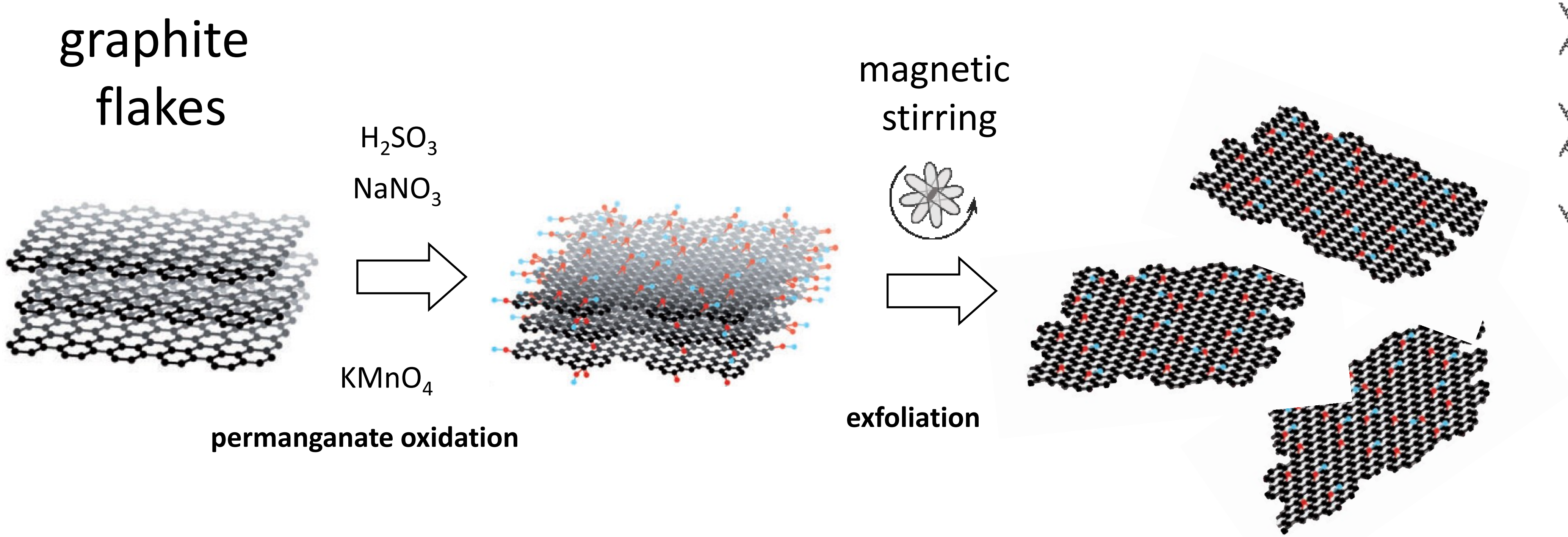
Chem. Eur. J. 2020, 26, 10427 – 10432

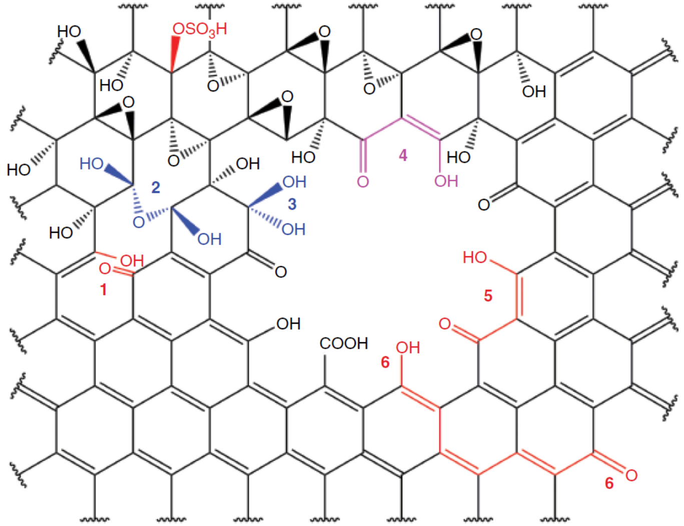
GRAPHENE FLAGSHIP GrapheneCore3 881603

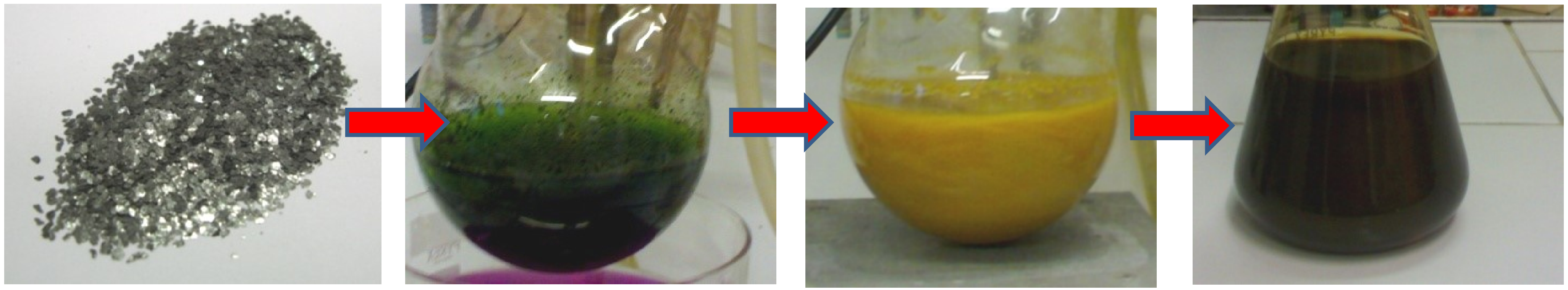
NanoCarboCat PRIN-2017 project 2017W8KNZW

MIUR PRIN

# Synthesis of Graphene Oxide





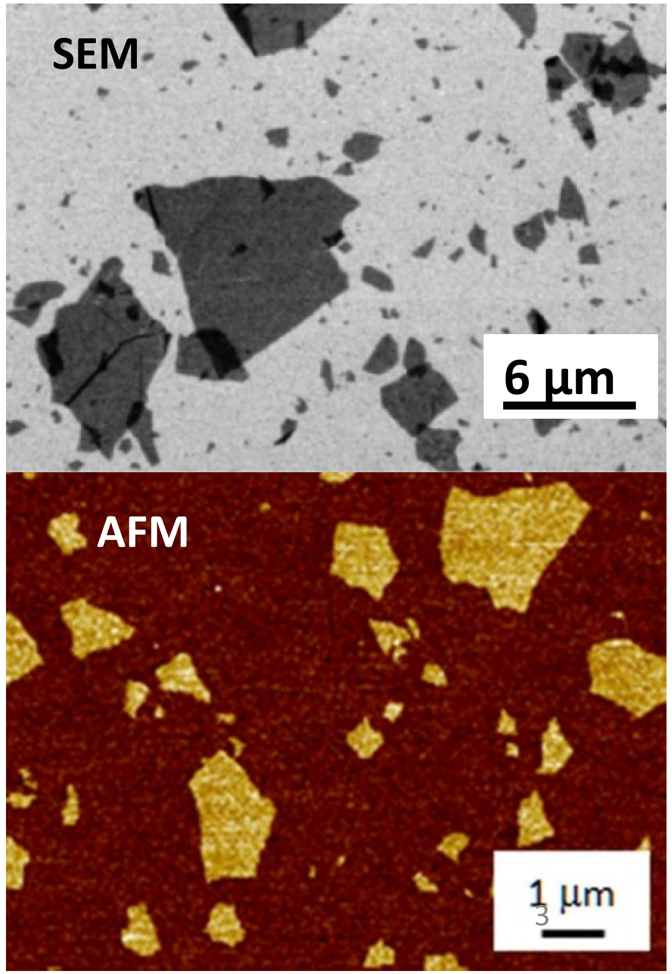
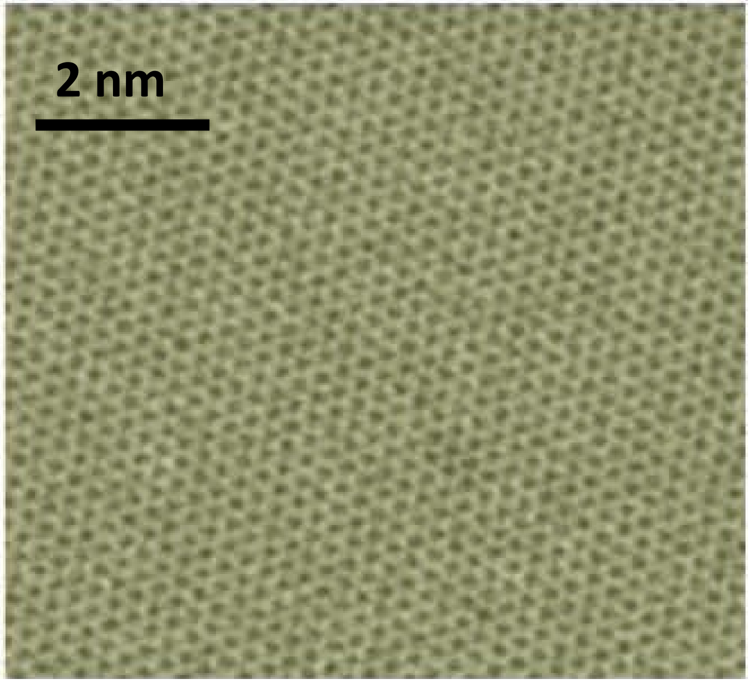
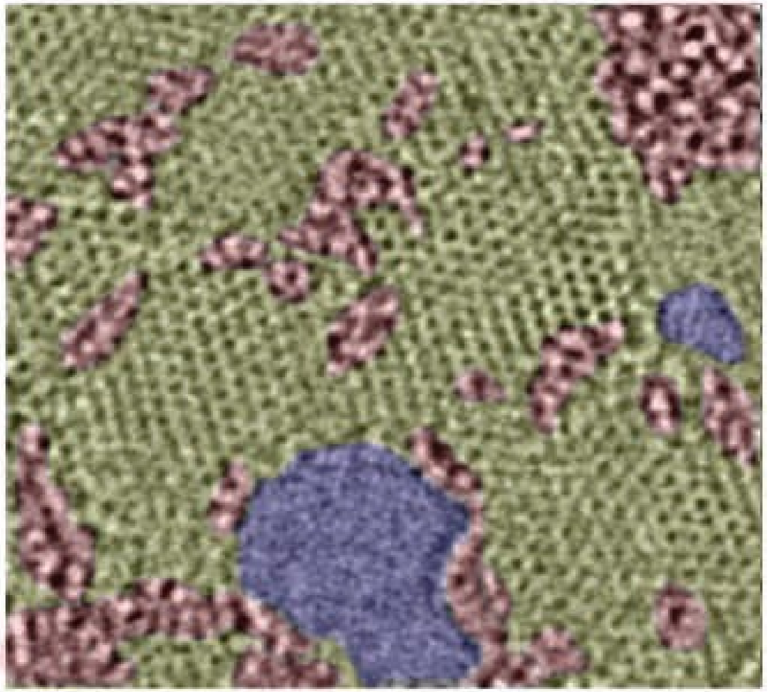
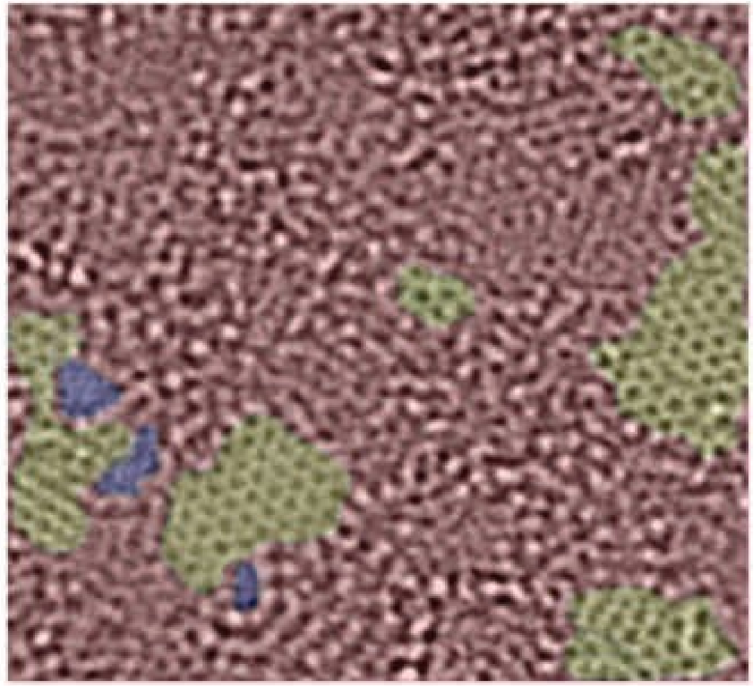



Figure by Alex Boschi ISOF

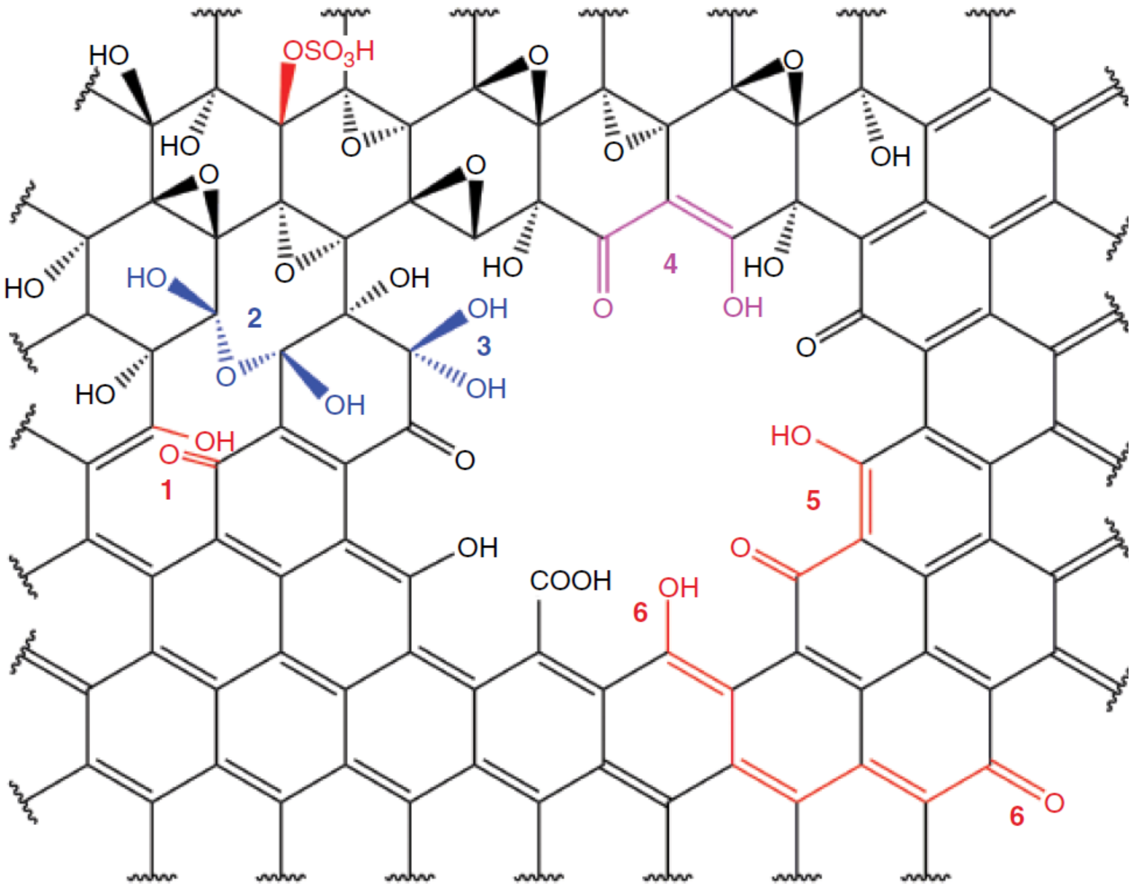
# Graphene Based materials

| Graphene | Reduced Graphene Oxide | Graphene Oxide |
|---|---|---|
|   |  |  |
| **100%** | **70-98%** | **<40%** |
| **aromatic $sp^2$ carbon** | **Restored aromatic $sp^2$ C** | **Isolated aromatic $sp^2$ C** |
| | **Residual C-O defects** | **C-O defects** |

HR-TEM from Erickson, et al., *Advanced Materials* 22 (2010) 4467

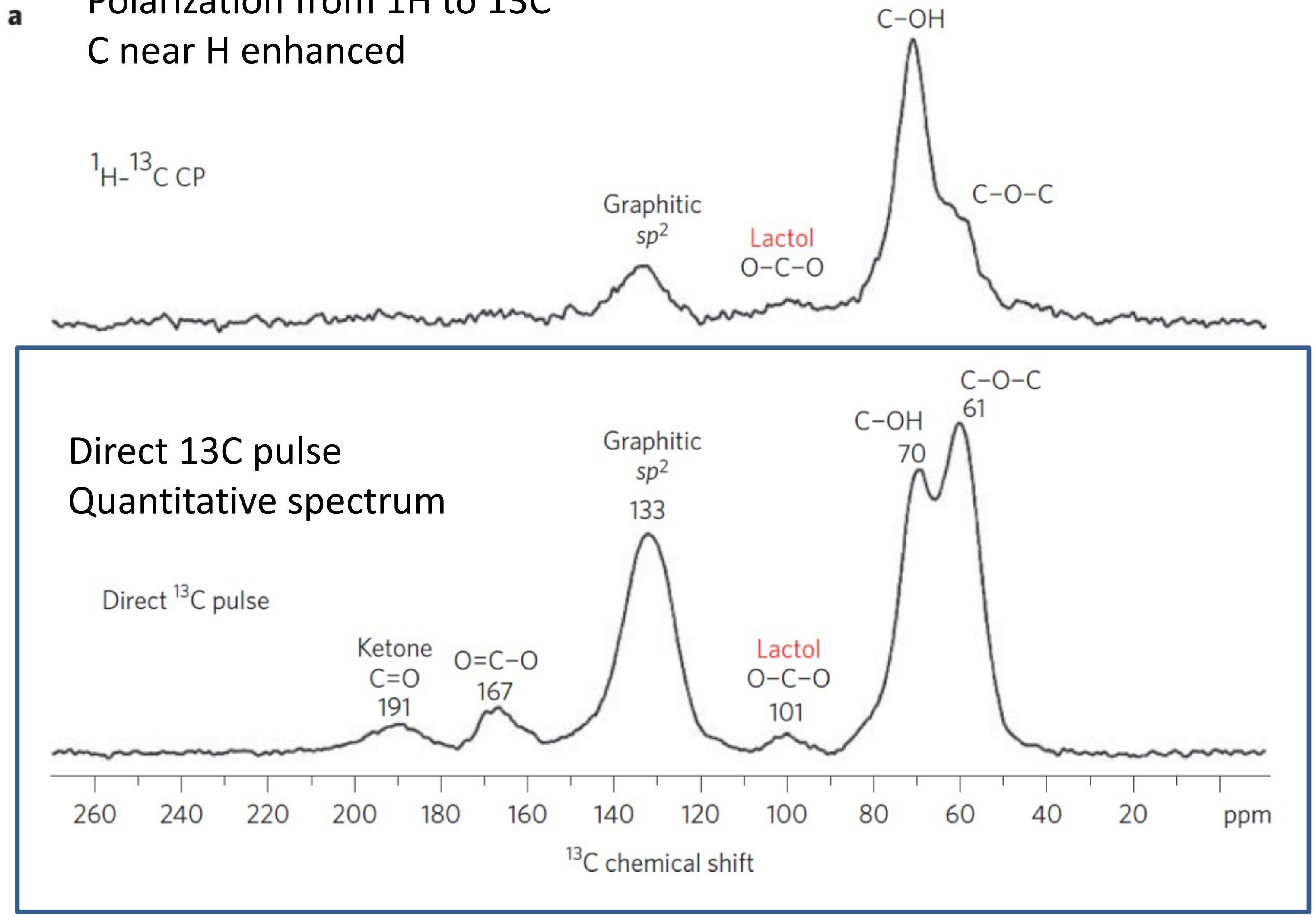
# Graphene Oxide models based on ssNMR

## Dimiev-Tour model - modification of *Szabo–Dekany* and Lerf




Graphene Oxide: Fundamentals and Applications
edited by Ayrat Dimiev and Siegfried Eigler
doi:10.1002/9781119069447

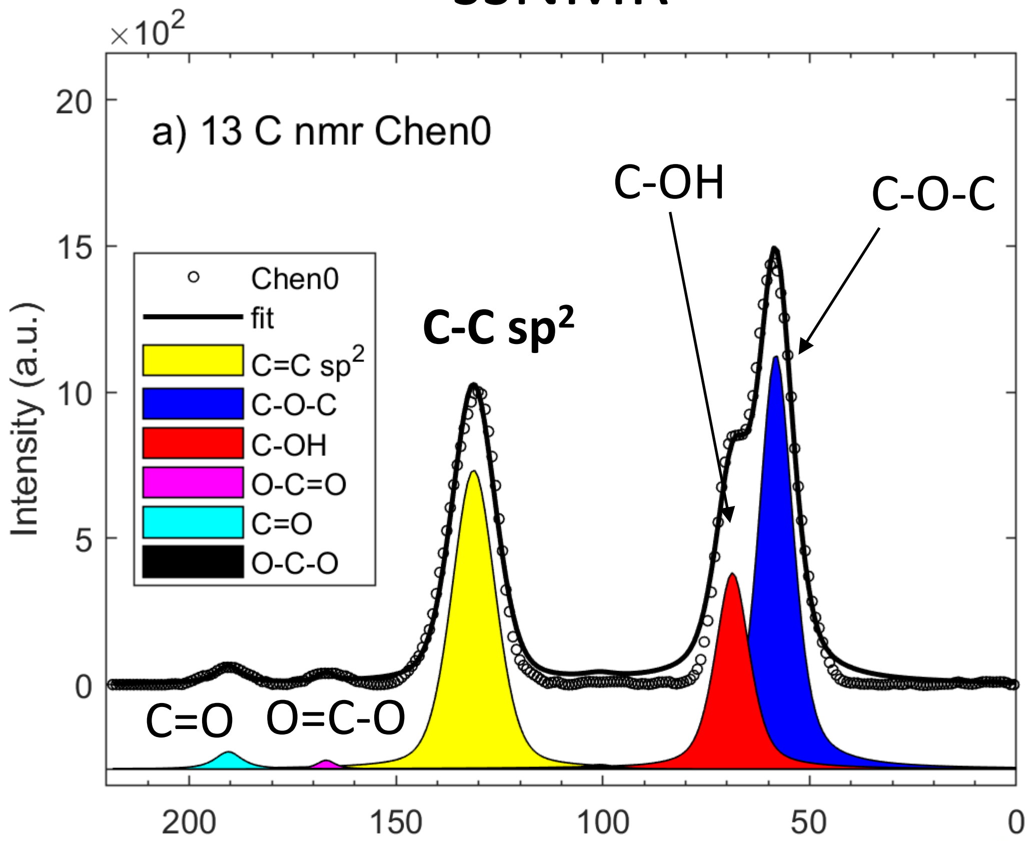
Cross polarization spectrum
Polarization from 1H to 13C
C near H enhanced




GAO: DOI: 10.1038/NCHEM.281
1H–13C cross polarization (CP) spectrum of GO obtained with 7.6 kHz MAS and a contact time of 1 ms (67,000 scans), direct 13C pulse spectrum obtained with 12 kHz MAS and a 90 8 13C pulse (10,000 scans).

# XPS vs NMR

ssNMR



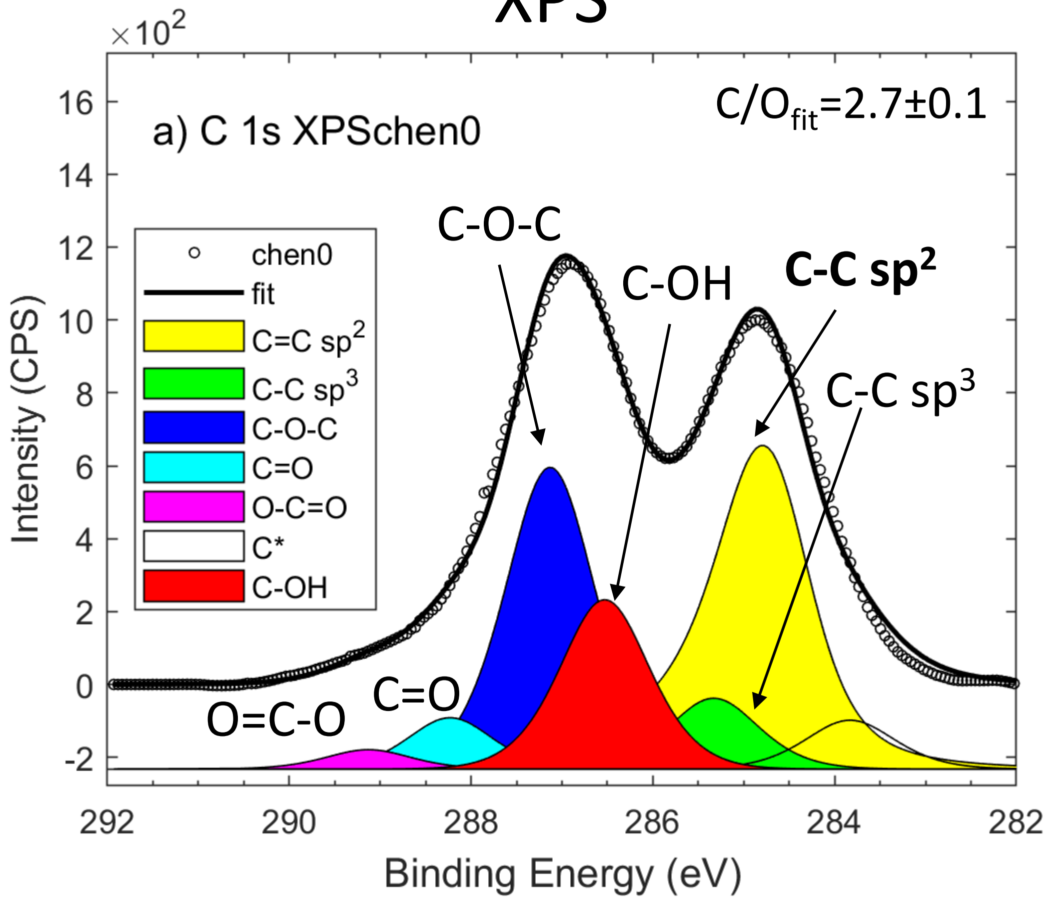

**Applied Magnetic Resonance**

Appl Magn Reson (2013) 44:107–116
DOI 10.1007/s00723-012-0392-z

**Paramagnetic Impurities in Graphene Oxide**

**A. M. Panich · A. I. Shames · N. A. Sergeev**

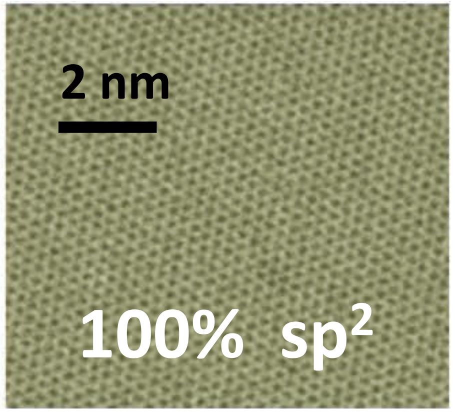
XPS



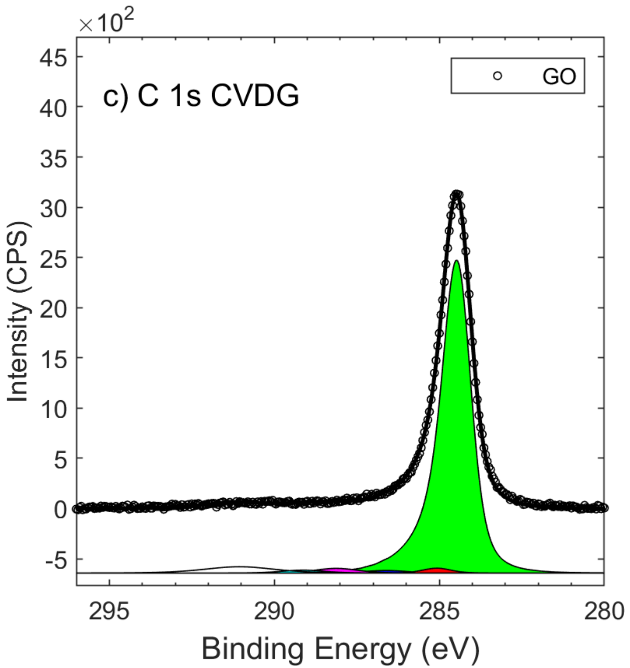

Data

# TEM vs XPS

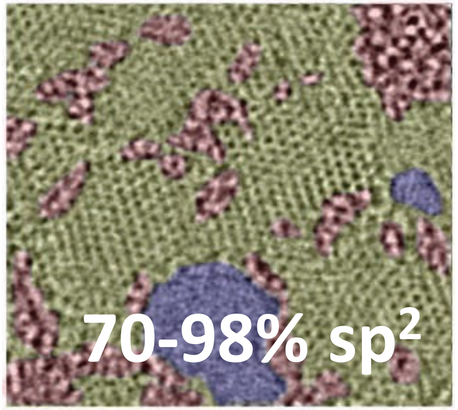
## Graphene

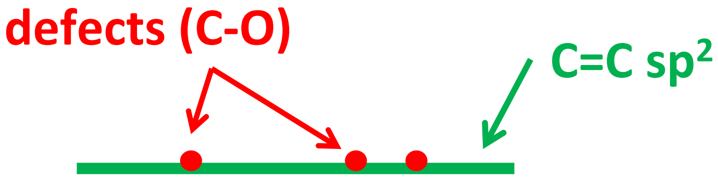


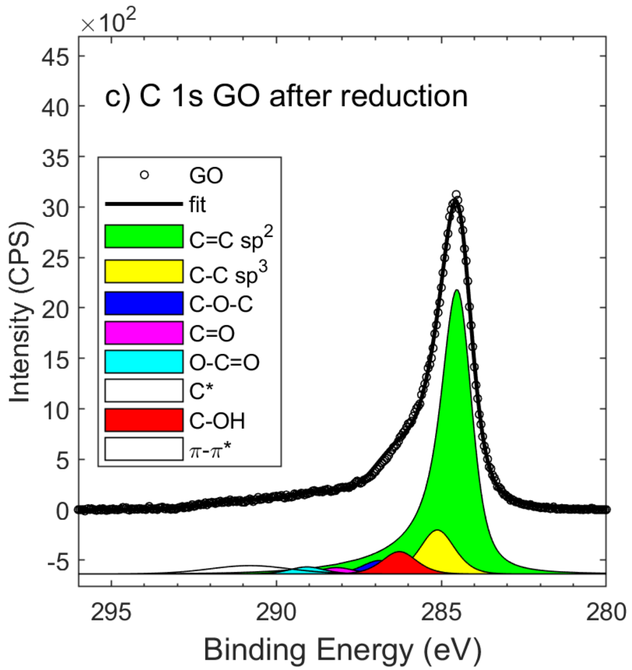




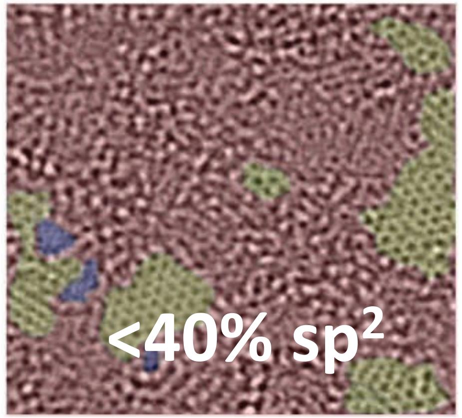

## Reduced Graphene Oxide

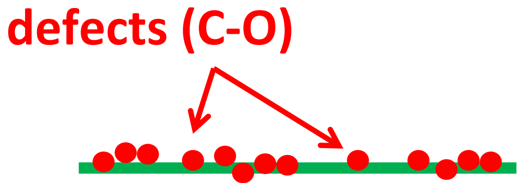


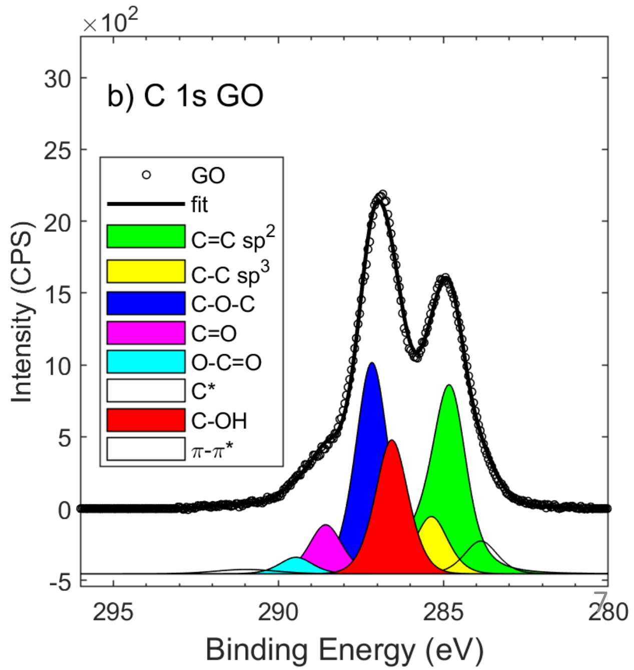



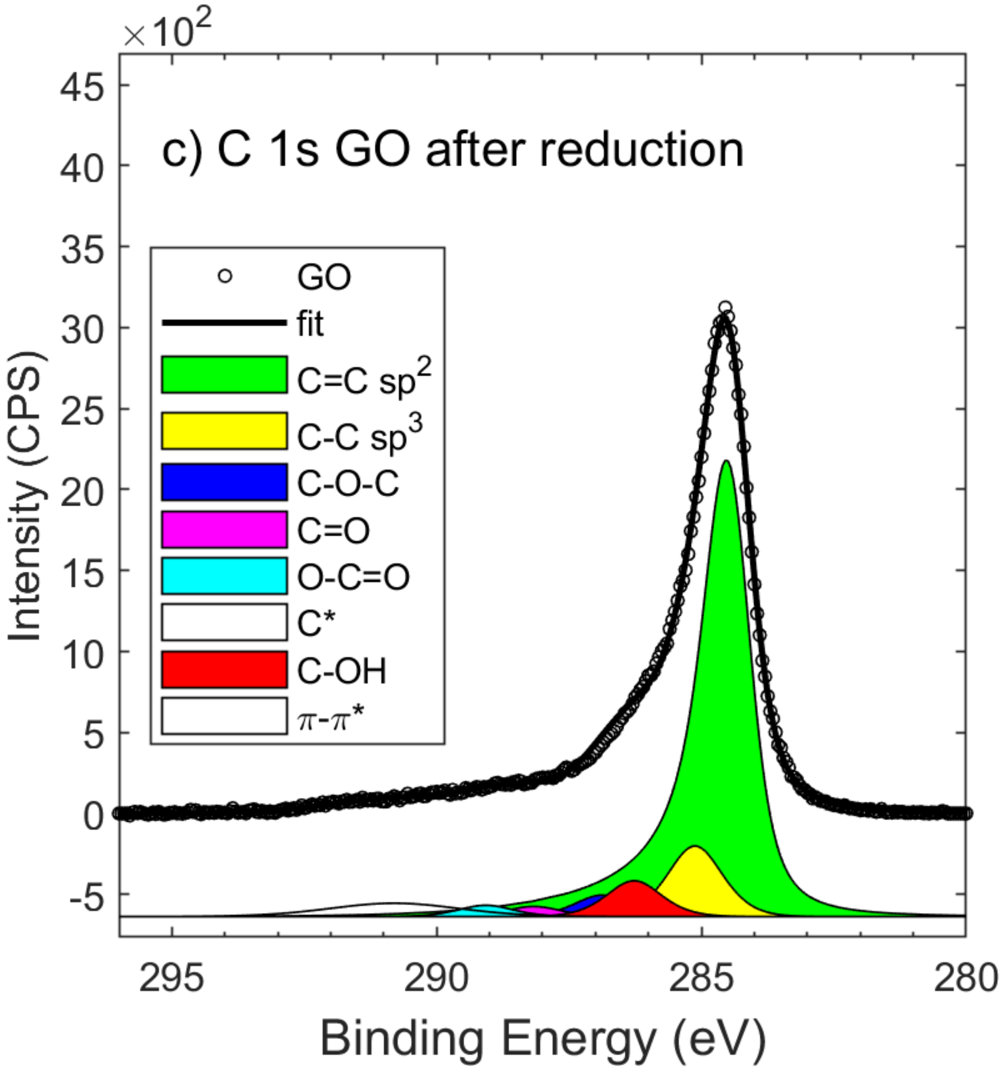

## Graphene Oxide



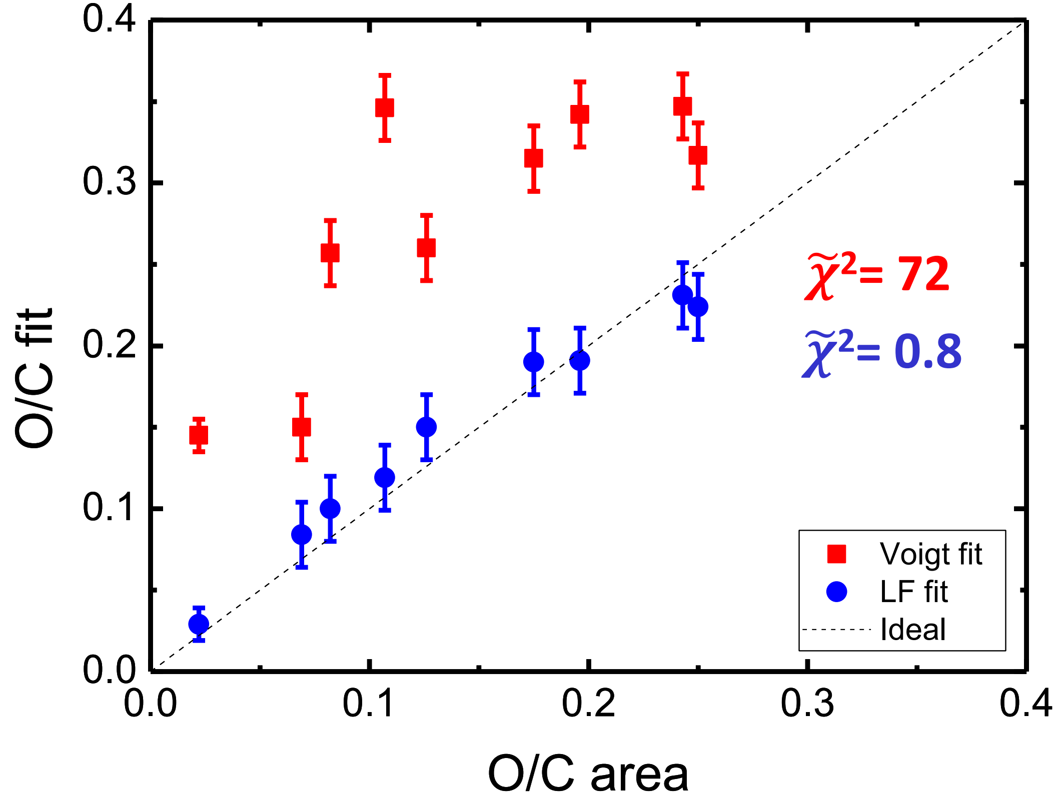



# Accuracy of XPS analysis




**Self-consistent fit**




**Asymmetric line-shape is the key for an excellent $O/C_{area}$ and $O/C_{fit}$ correlation**

**Kovtun et al., Carbon 143, 268-275 (2019)**

# Oxygen diffusion

Foller shows the Oxyggen diffusion at 80°C: graphitic domains from originally ≤ 40 nm2 to > 200 nm2 through an extensive transmission electron microscopy (TEM) study e SSNMR

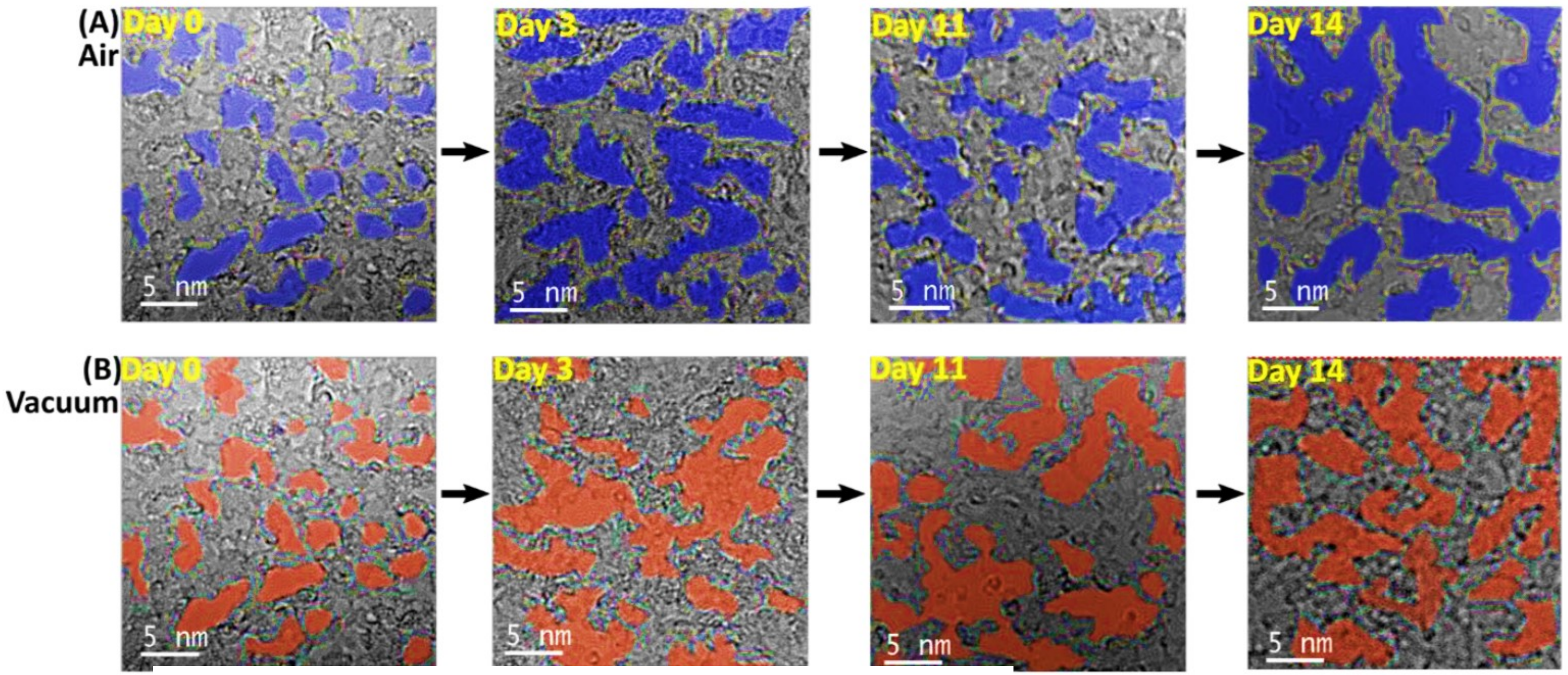



**Figure 1 Observation of thermally enhanced graphitic domains** (A/B) Time course of GO after heat treatment in air/vacuum. Graphitic domains are marked in light blue/red for treatment in air/vacuum C/D) Histogram of the size distributions of graphitic domains for increasing days of heat treatment in air/vacuum. Day 0 samples represent the same untreated GO. To illustrate the enhancement of graphitic domains, the maximum size of graphitic domains in untreated GO is marked with a yellow arrow (~ 40 $nm^2$) and the maximum size of 14 days heat treated GO is marked with a pink arrow. (~ 230 $nm^2$ in air and ~ 120 $nm^2$ in vacuum)

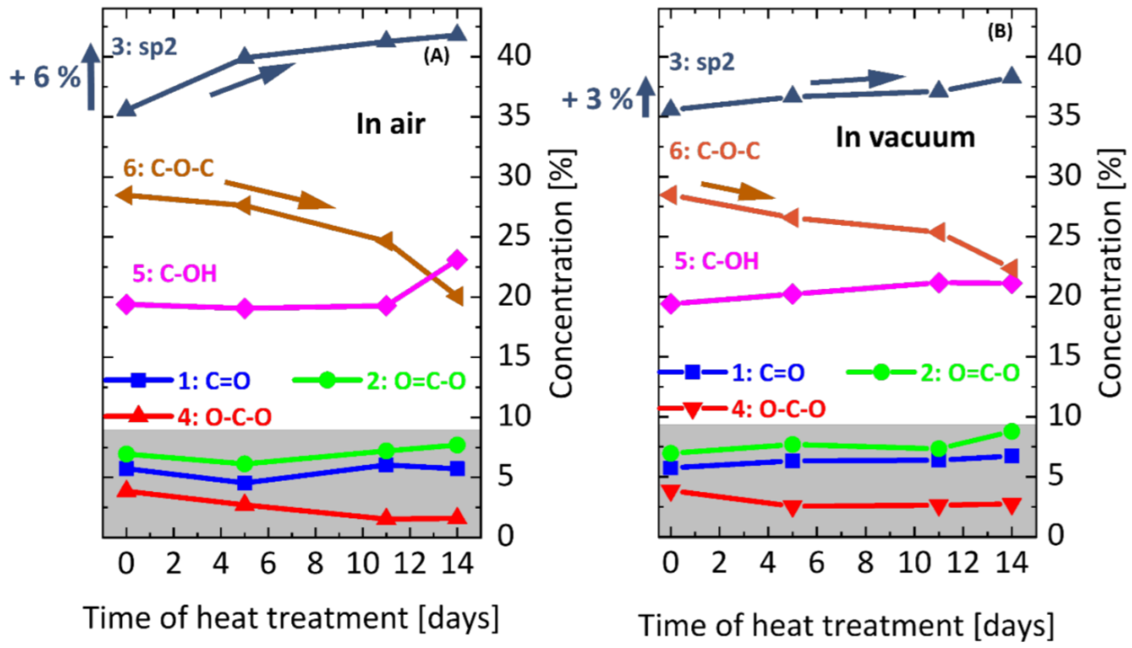
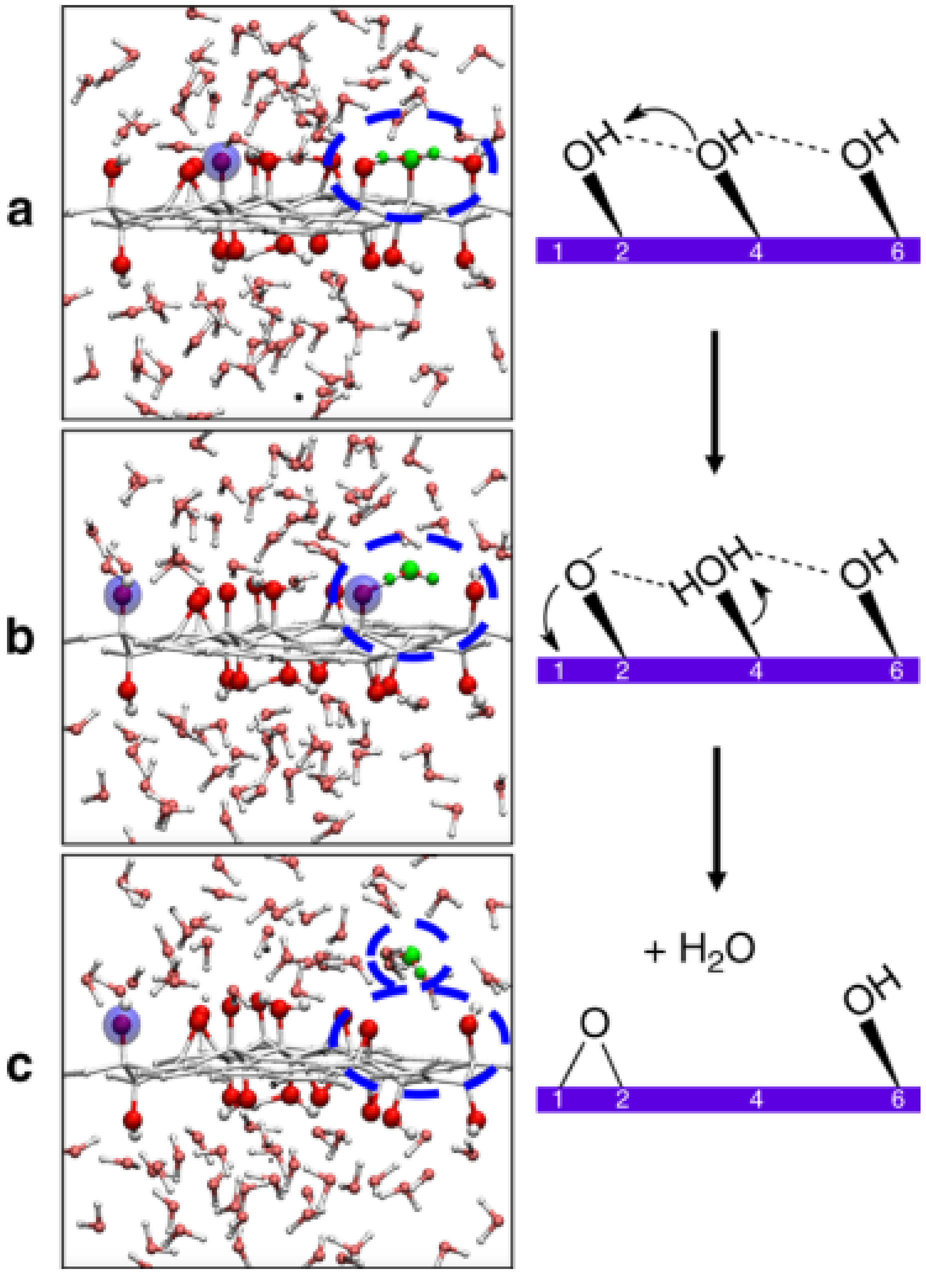
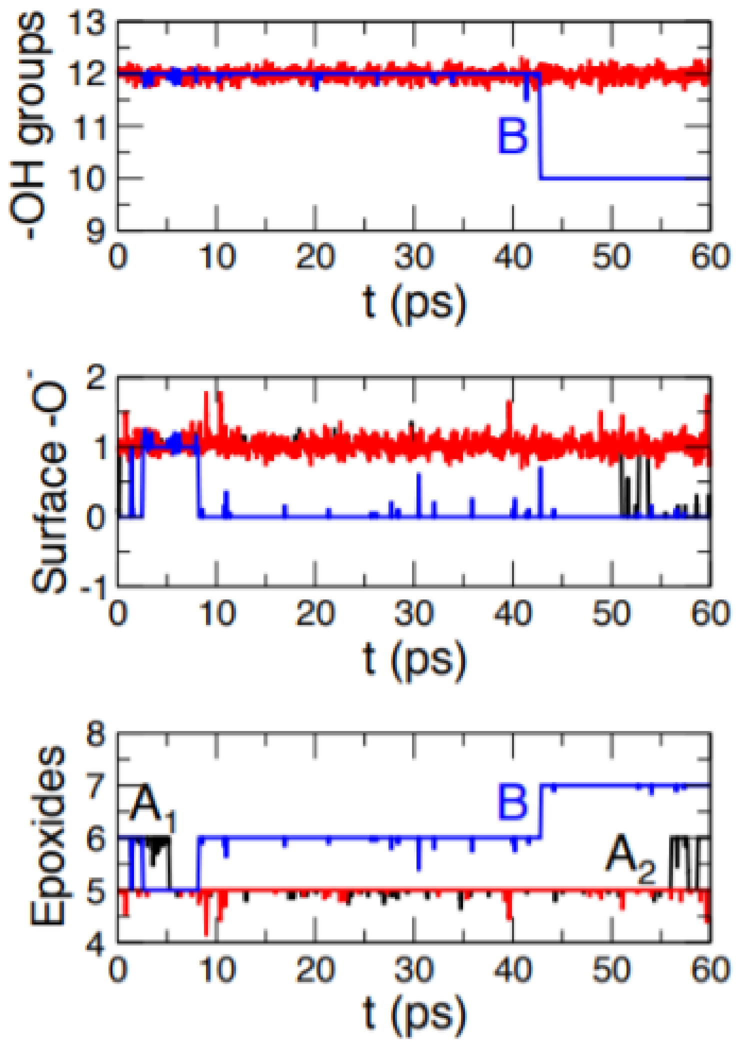



**Figure 2 SSNMR study of annealed GO (A/B)** Concentration of functional groups for GO annealed in **air/vacuum** from SSNMR analysis of annealed GO. Peaks 1-6 are assigned following previous studies[24,25]. A slight increase of 6 % and 3 % of $sp^2$ carbon in air and vacuum are highlighted in the graph. Error bars were depicted from signal to noise ratio. The peaks in the grey background have a signal to noise ratio which does not allow quantifiable conclusions.

https://arxiv.org/abs/2007.00860v5

# Epoxy-Hydroxyl




$A_{1/2}$ : epoxide opening/ closing

B : dehydration

Mouhat, F., *Nat Commun* **11,** 1566 (2020).
https://doi.org/10.1038/s41467-020-15381-y

Opening and closing of epoxy: C-OH gives protons to water
O/C 0.28-0.36, composition 24% sp2; 12% hyroxyl; 6% epoxy Oxygen (12 epoxy carbon) 72 tot=> O/C=18/72
Dehydratation: EPOXY group from hydroxyl

# Acidity of GO

# Graphene Oxide. Origin of Acidity, Its Instability in Water, and a New Dynamic Structural Model

Ayrat M. Dimiev,[†] Lawrence B. Alemany,[†,•,⊥] and James M. Tour[†,‡,§,⊥,*]

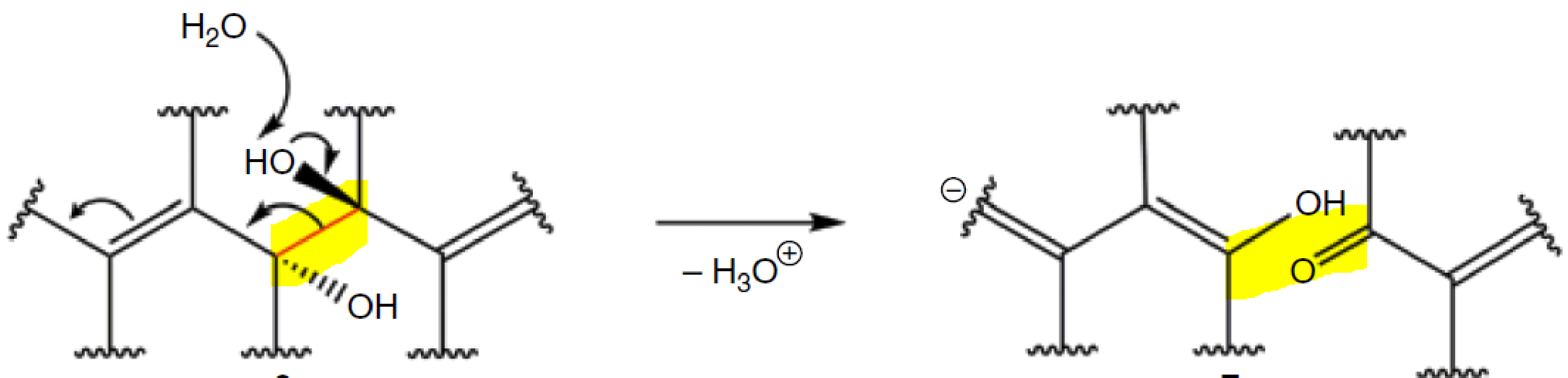
[†]Departments of Chemistry, [‡]Mechanical Engineering and Materials Science, and [§]Computer Science, the [⊥]Smalley Institute for Nanoscale Science and Technology, and the [•]Shared Equipment Authority, Rice University, MS-222, 6100 Main Street, Houston, Texas 77005, United States

**100g GO 500-800 mmol active acide site,**
**GO demonstrates extremely high cation exchange capacity (CEC),**

**Carboxyls cannot be the reason for GO's acidic properties!**

## CONCLUSIONS

We propose a new GO model, which we call the DSM. In contrast with all the previously proposed models, we do not consider the GO as a static structure with a given set of functional groups. Instead, we suggest that new functional groups constantly develop and transform. The key role in all these transformations belongs to water, which incorporates into GO, transforming its structure, and then leaves the structure *via* different reactions. Our model explains the GO acidity not by dissociation of preexisting acidic groups (their content is very low), but by generation of hydrogen cations (protons) *via* constant reactions with water. The driving force of the transformations is accumulation of the negative charge on GO layers, which is stabilized by resonance and by formation of an electrical double layer. From the structural perspective, most of the carbonyls existing on the GO platform are associated with hydroxyls in the form of vinylogous acids; this renders the hydroxyl groups acidic. Prolonged exposure to water gradually degrades GO flakes, converting them into humic acid-like structures. In acidic conditions this process might be slower. For GO samples prepared by Staudenmaier's, Hummers', and improved Hummer's methods, hydrolysis of covalent sulfates contribute additionally to the integral acidity. We explain deoxygenation of GO in alkaline




In 2015 one can say the following about GO from the point of view of scientific activities over the 150 years from 1855 to 2005: GO is a metastable non-stoichiometric solid carbon compound whose structure has not been fully established. It is a tricky intermediate state between over-oxidation and self-destruction. While all the informa-

Graphene Oxide: Fundamentals and Applications edited by Ayrat Dimiev and Siegfried Eigler
doi:10.1002/9781119069447

# The role of GO in chemistry

GDCh Communications Angewandte Chemie International Edition

Catalysis

International Edition: DOI: 10.1002/anie.201809979
German Edition: DOI: 10.1002/ange.201809979

## Graphene Oxide: Carbocatalyst or Reagent?

*Stanislav Presolski and Martin Pumera**

***Table 1:*** Oxygen-to-carbon ratio in GO samples before and after being used in BnOH oxidation reactions.

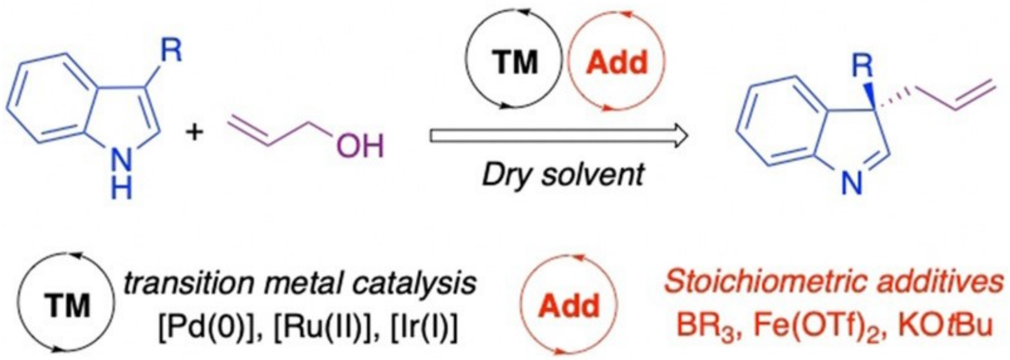
| | Combustion analysis[a] | XPS[b] |
|---|---|---|
| O:C ratio of fresh GO | 0.52 | 0.54 |
| O:C ratio of recovered GO | 0.14 | 0.15 |
| Fraction of oxygen loss | 73 % | 72 % |

[a] 50 wt % GO, as described in Ref. [7]. [b] 20 wt % GO, this work.

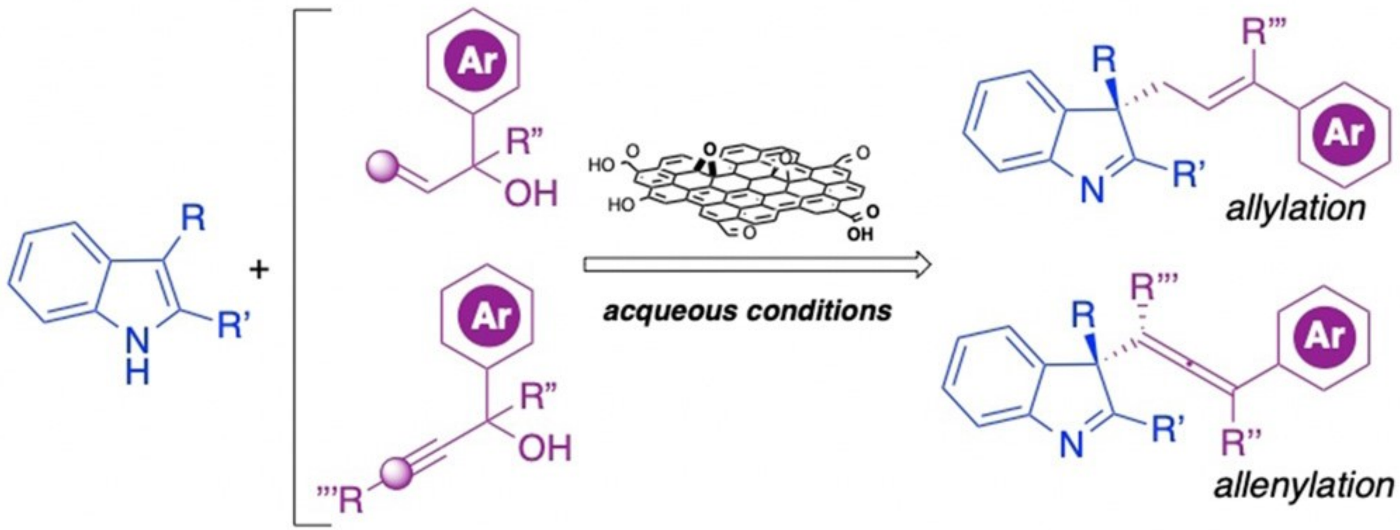
In conclusion, we were able to reproduce the synthesis of graphene oxide that was reported to be an oxidation carbocatalyst.[7] However, we demonstrated that it primarily acts as a reagent if we must adhere to the IUPAC definition of a catalyst. We find that given the extensive loss of oxygen from GO, the low yields of benzaldehyde formed under substoichiometric conditions, and the poor recyclability of the graphene oxide even when employed in large excess, using the word "catalyst" in the context of benzyl alcohol oxidation is unsubstantiated. Furthermore, despite many attempts we

# Dearomatization of Indoles Promoted by Graphene Oxide

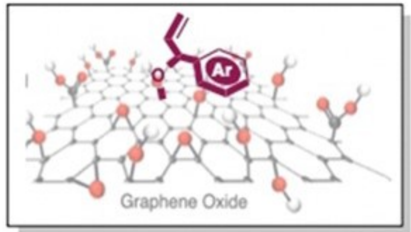
**State of the art**




*this work*

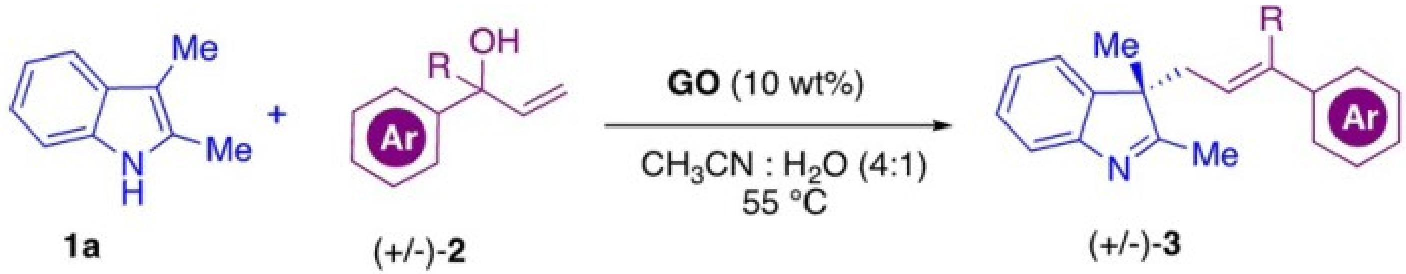


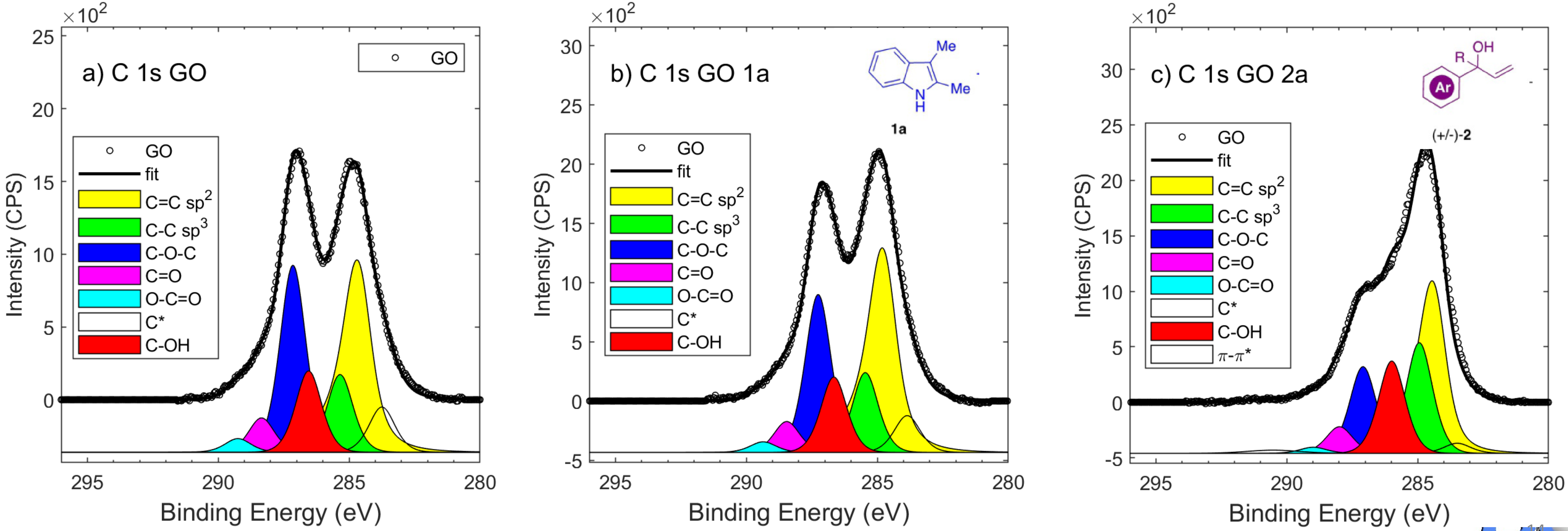

- No metals
- No additives
- Water conditions
- Low loading **GO**
- Regioselectivity
- Stereoselectivity




*Lombardi, Chem. Eur. J.* **2020**, *26*, 10427.

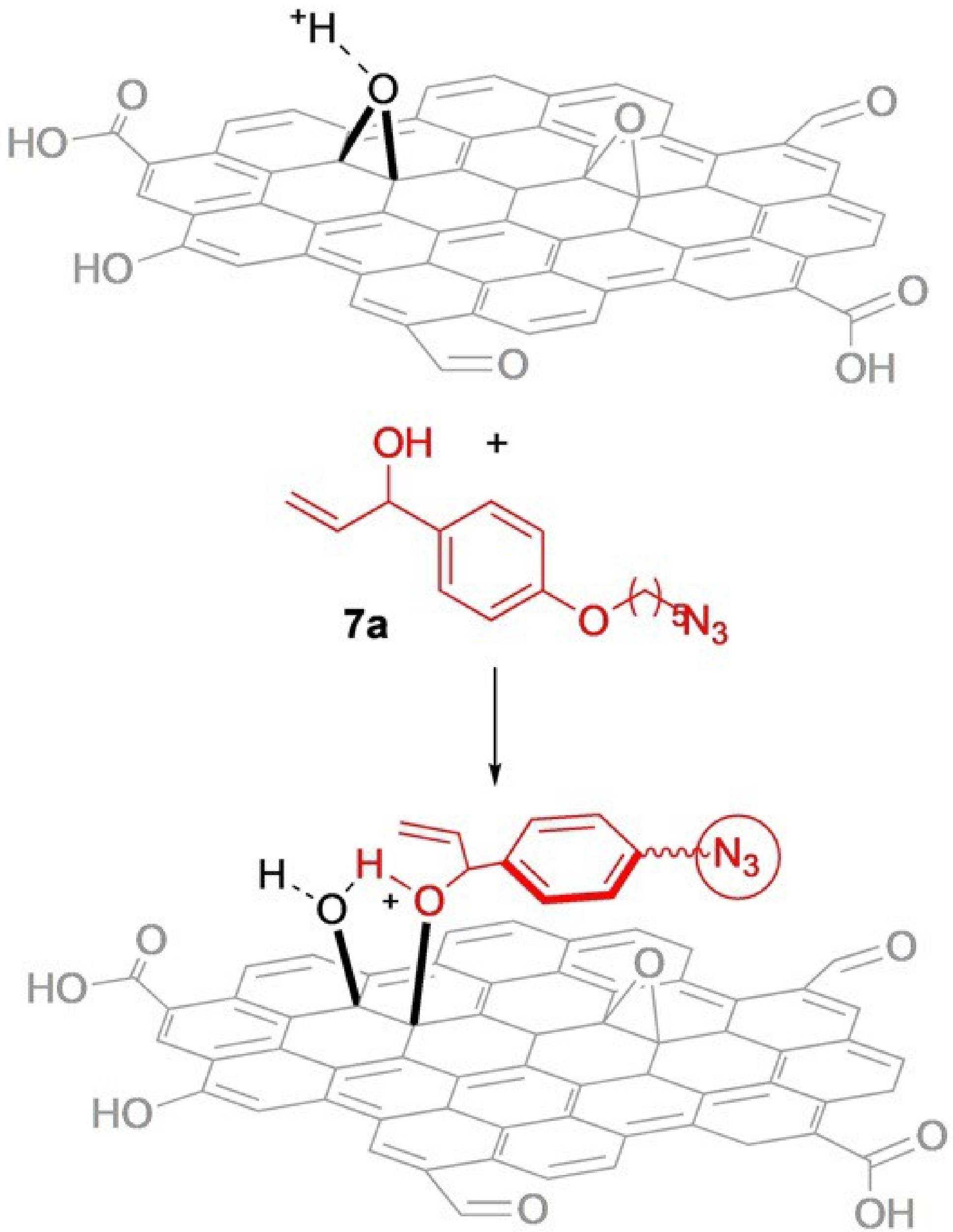
# Understanding the reaction mechanism



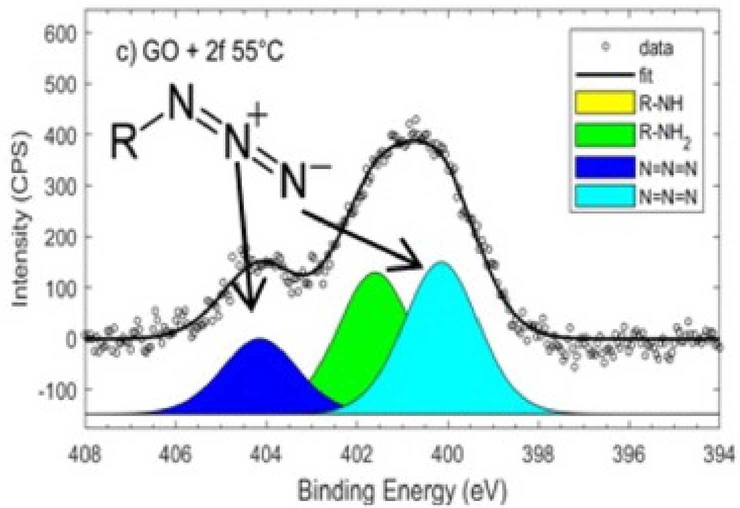




*Lombardi, Chem. Eur. J.* **2020**, *26*, 10427.

# Role of Allylic Alcohol

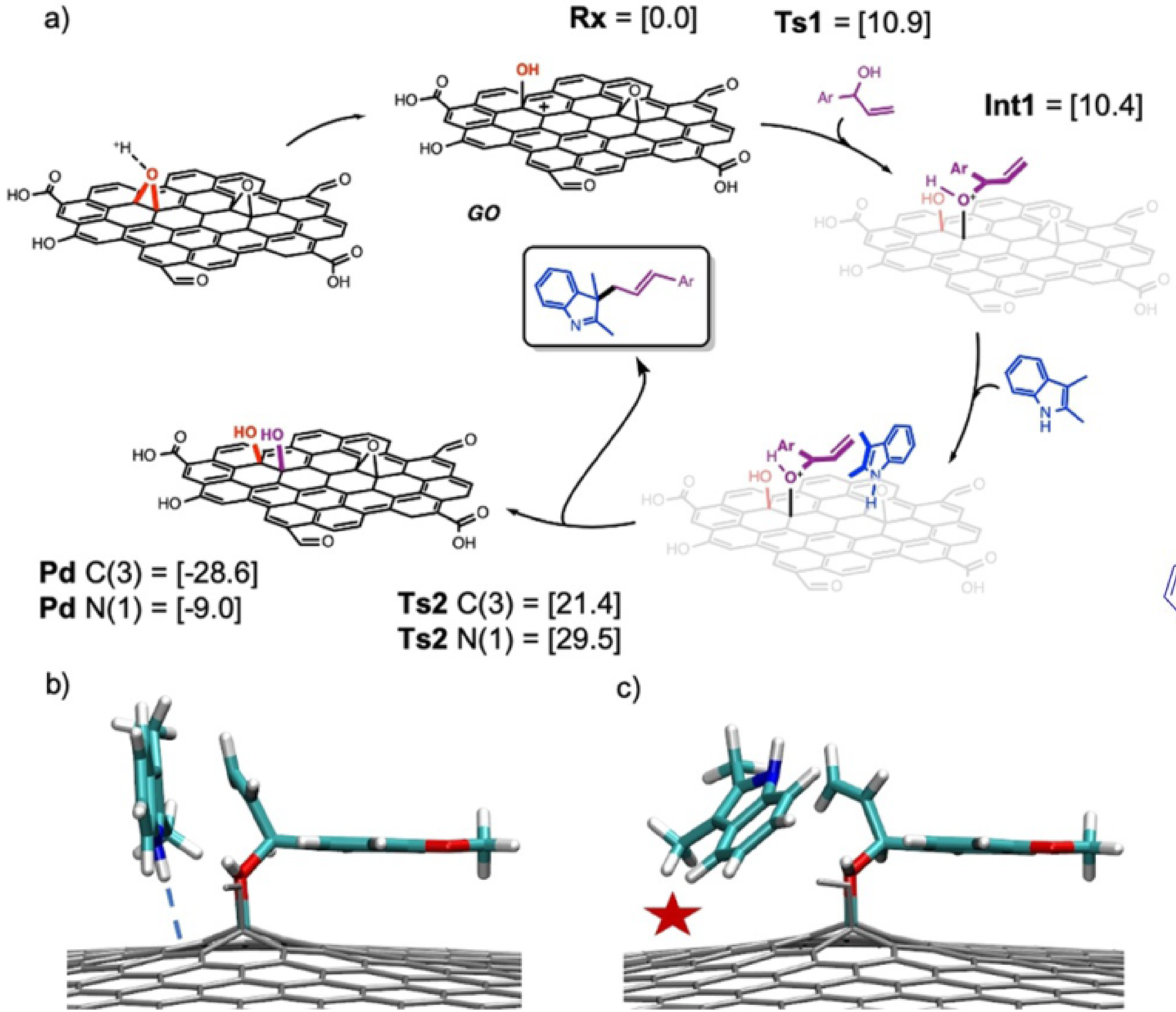



*XPS Azide fingherprint*



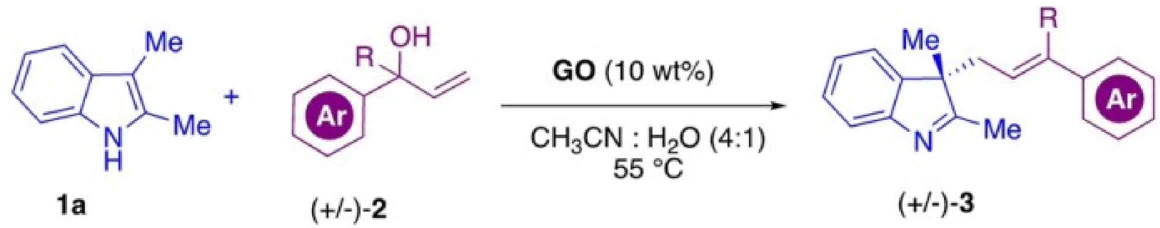

*Lombardi, Chem. Eur. J.* **2020**, *26*, 10427.

# Full reaction




DFT simulation based on XPS data

Epoxy ring opening



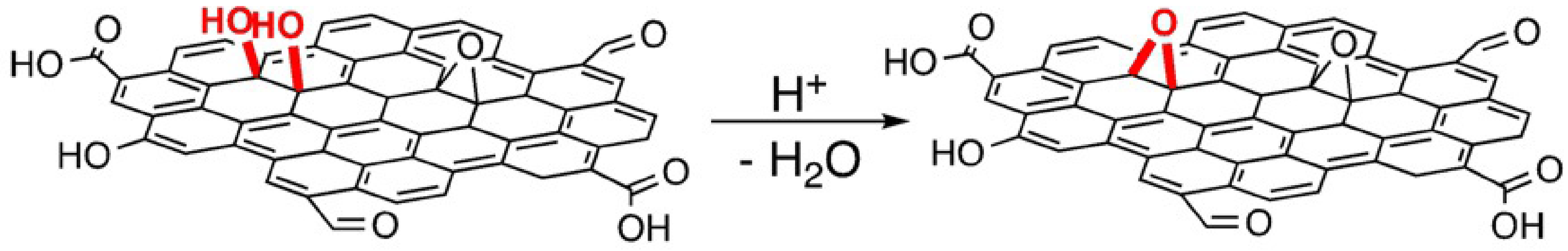

Yield 70%!

Second reaction run only 12%!

Lombardi, *Chem. Eur. J.* **2020**, *26*, 10427.

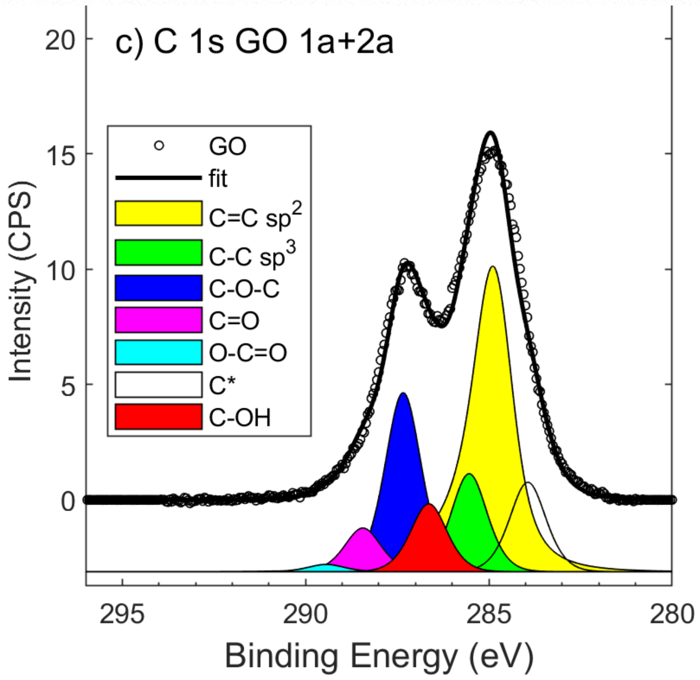
# Regenerate the GO

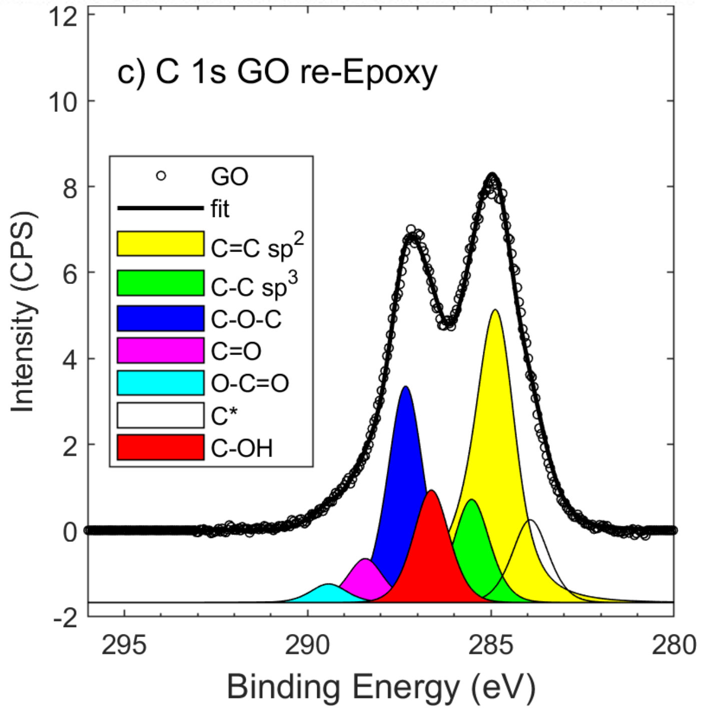
a)




*Recovered*-GO

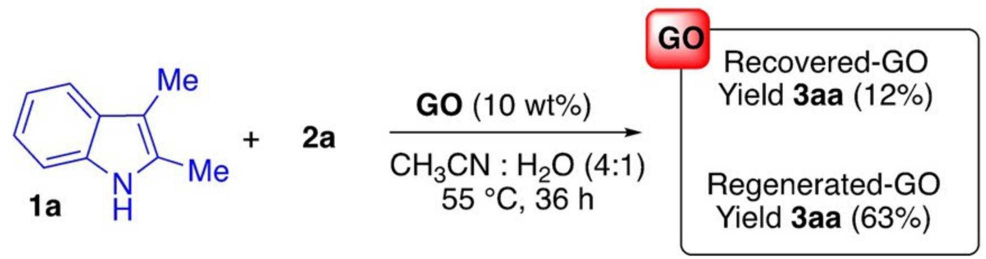
*Regenerated*-GO




*Sci. Rep.* **2019**, *9*, 15579.

b)




*Lombardi, Chem. Eur. J.* **2020**, *26*, 10427.

# Conclusions

1. **Unique acid properties**
2. **Acidity can be tuned and adjusted**
3. **It's not a catalyst, but an extremely useful reagent that can be regenerated**