International Workshop on Soot, Beijing, China, June 28, 2016

Heterogeneous reaction of soot with atmospheric oxidizing gases

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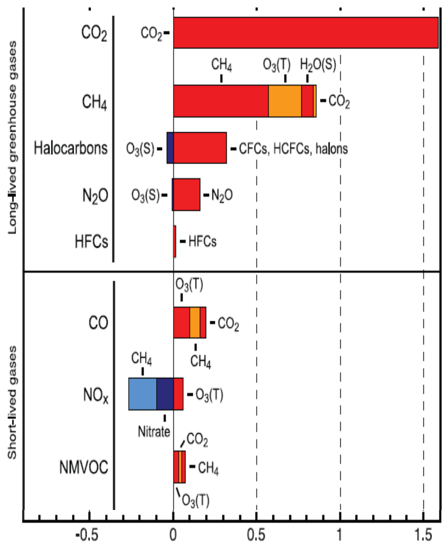
Chinese Academy of Sciences

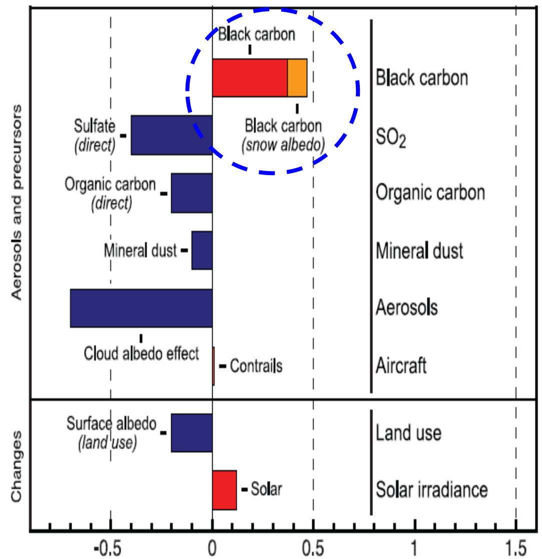
Background

Components of radiative forcing for principal emissions



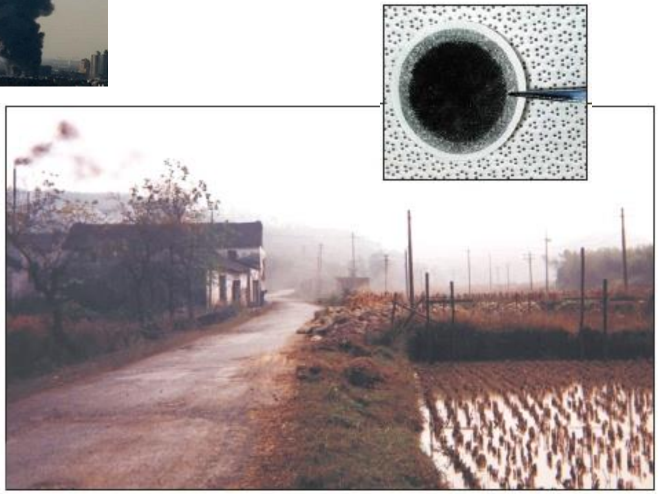
Radiative Forcing (W/m^2)

Climatic effects



Radiative Forcing (W/m^2)

air quality



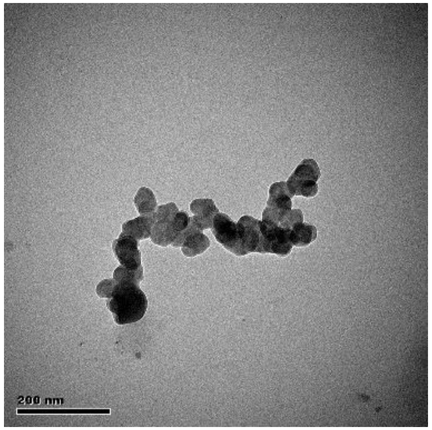
A typical hazy day near Lin An, China. Black carbon emanates from a small brick factory. (Inset) Aerosol particles collected nearby on a 47-mm Teflon filter (~8 m^3 of air sampled). The blackness of the filter indicates the presence of black carbon.

➢ **The environmental and climatic effects of black carbon depend on its compositions and structure, which are significantly affected by atmospheric aging of soot.**

IPCC, 2007. Service, R. F. *Science* 2008, 319, 1745.

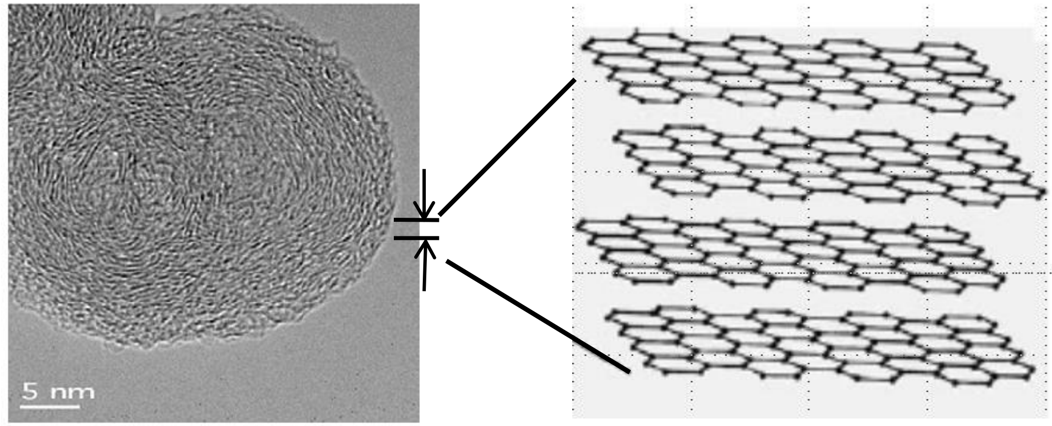
William L. Chameides and Michael Bergin. Science, 2002, 297, 2214-2215.
Tosca M. G. *et al.*, *Atmos. Chem. Phys.*, 2010, 10, 3515-3528.

Background

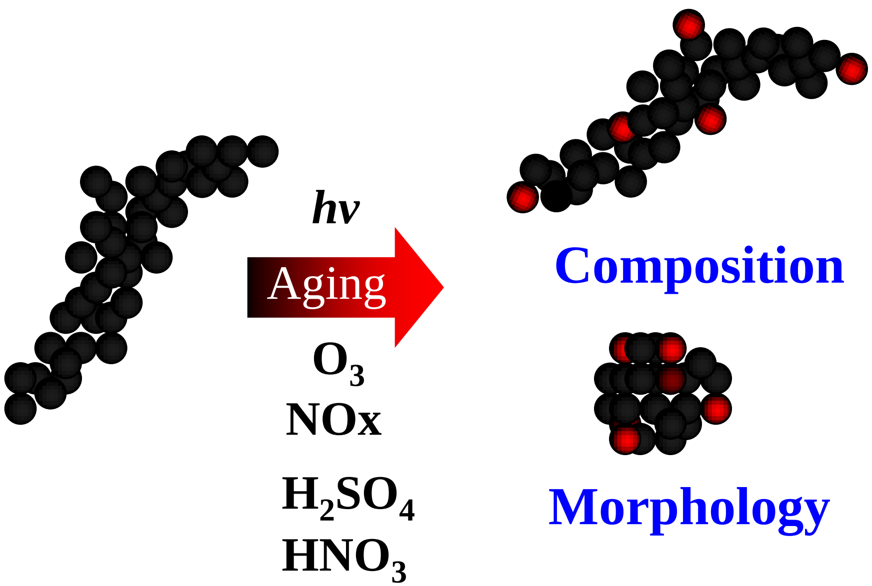


Chain-like aggregate

graphitic layer



Perturbed graphitic layers oriented concentrically in an onion-like fashion



$$O_3 \overset{soot}{\rightarrow} \text{product 1} \quad \gamma = 2\times10^{-3},$$

$$HNO_3 \overset{soot}{\rightarrow} NO_x + \text{product 2} \quad \gamma = 0.028,$$

$$\text{Soot} + O_3 \rightarrow \text{Soot}\cdot O + O_2 \quad \gamma = 2\times10^{-3},$$

$$\text{Soot} + HNO_3 \rightarrow \text{Soot}\cdot OH + NO_2 \quad \gamma = 0.028,$$

$$\text{Soot} + NO_2 \rightarrow \text{Soot}\cdot O + NO \quad \gamma = 5.7\times10^{-2},$$

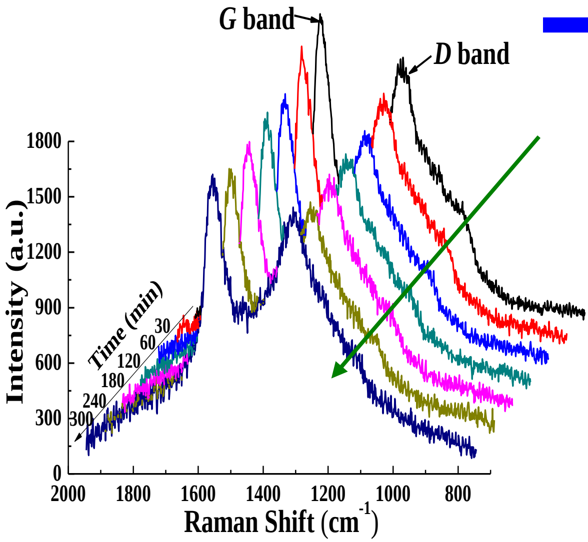
$$\text{Soot}\cdot O + O_3 \rightarrow \text{Soot} + 2O_2 \quad \gamma = 2\times10^{-3}.$$

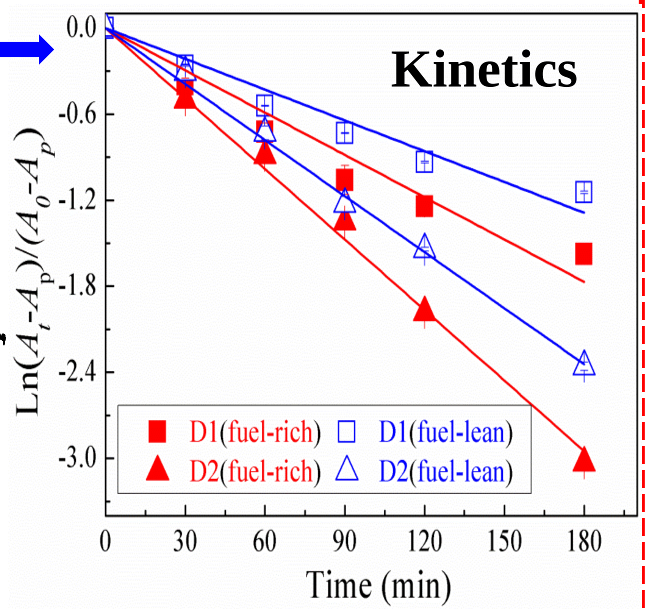
Wei et al., *Atmos. Envrion.*, 2001, 35, 6167-6180.

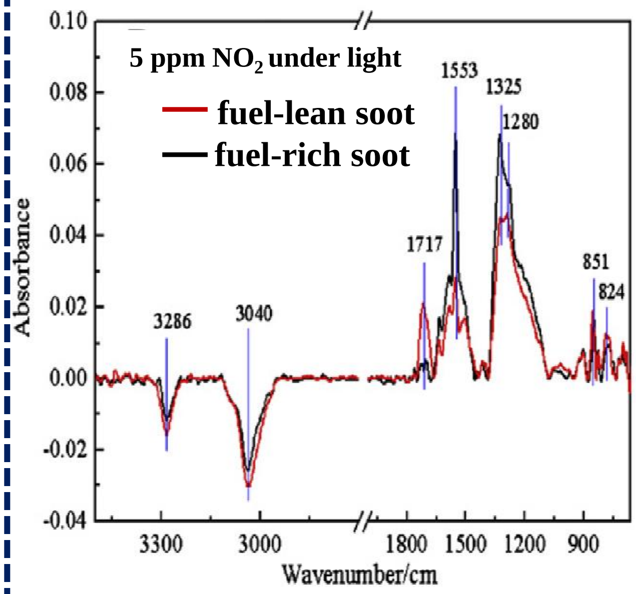
Background

soot+O_3 | **soot+NO_2**

fuel-rich soot | **Raman** | **ATR-IR**





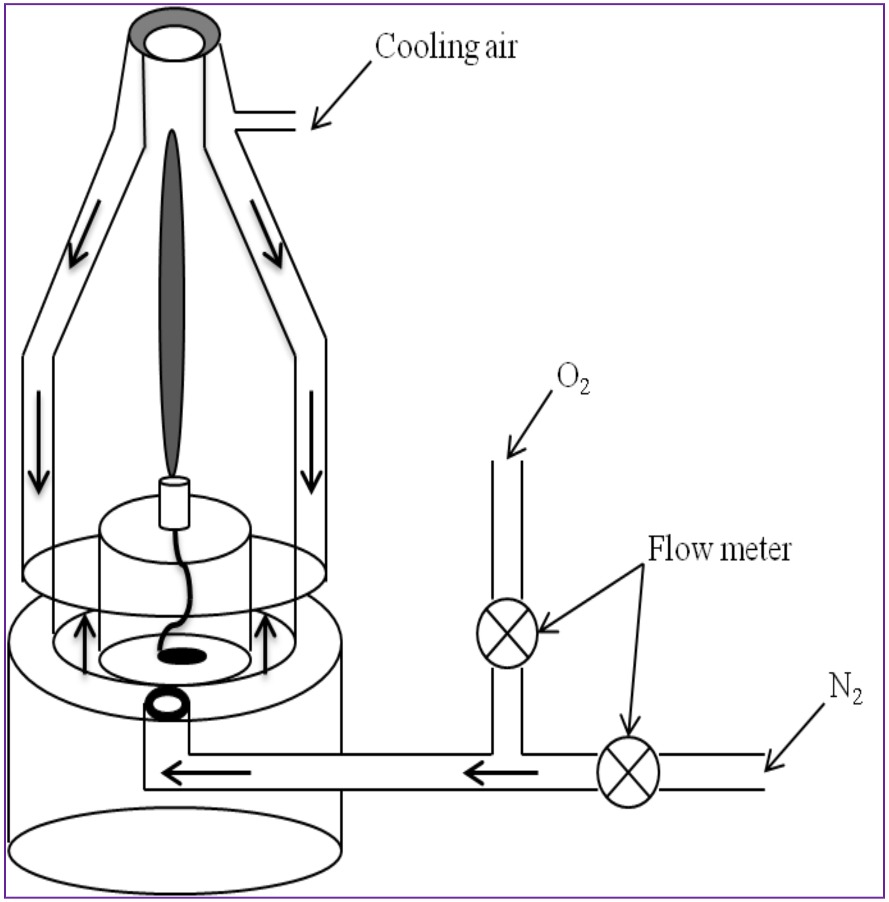


- **Fuel-rich soot was more active than the fuel-lean soot for O_3 reaction.**
- **Fuel-rich soot showed higher reactivity toward NO_2 under light.**
- **The reasons for reactivity differences are not clear.**

J. Chem. Phys. 2012, 137. Atmos. Environ. 2013, 64, 270-276.

Experimental section

Soot production



Combustion conditions:

fuel： *n*-hexane

O_2/N_2: 29.0%-46.5%

n_{fuel}/n_{oxygen}：

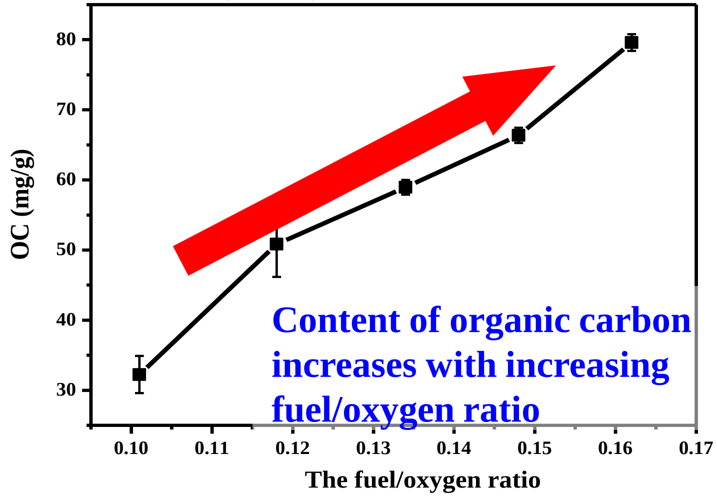
0.162 - 0.103

Fuel-rich **Fuel-lean (Stoichiometric)**

Characterization

Organic carbon (OC)

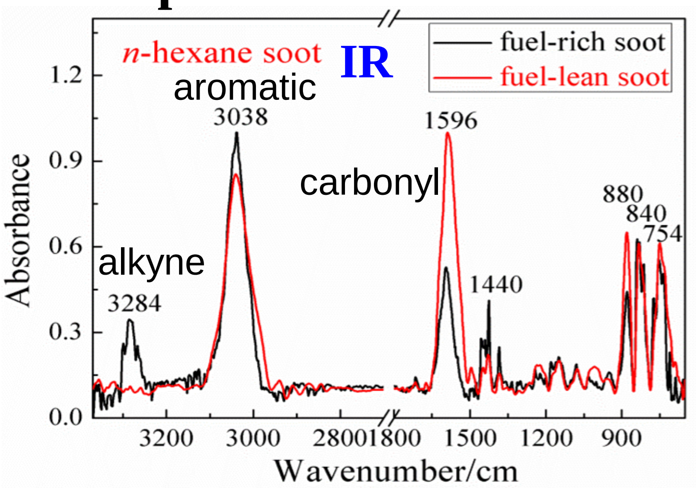
TG

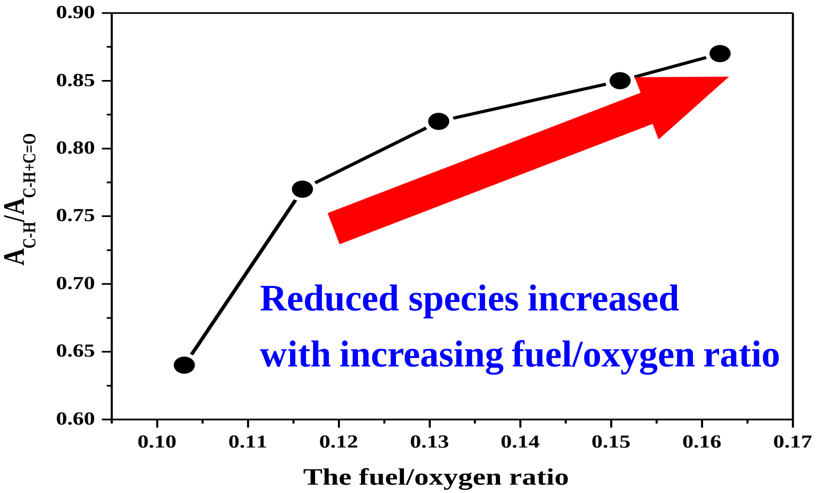


fuel/oxygen ratio	Degree of unsaturation
0.162	1.42±0.08
0.151	1.38±0.12
0.131	1.34±0.11
0.116	1.27±0.07
0.103	1.19±0.04

Functional Groups

ATR-IR



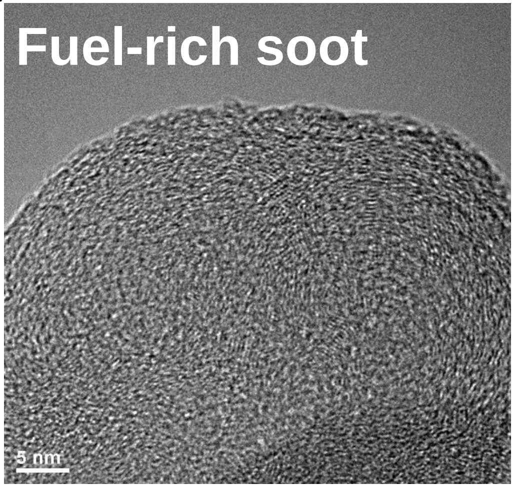


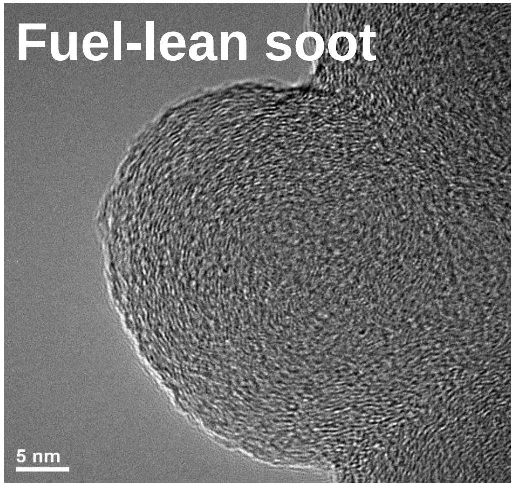
➢**Combustion conditions significantly affect surface oxidation state and organic carbon content of soot.**

J. Phys. Chem. A 2012, 116, 4129-4136.

Characterization

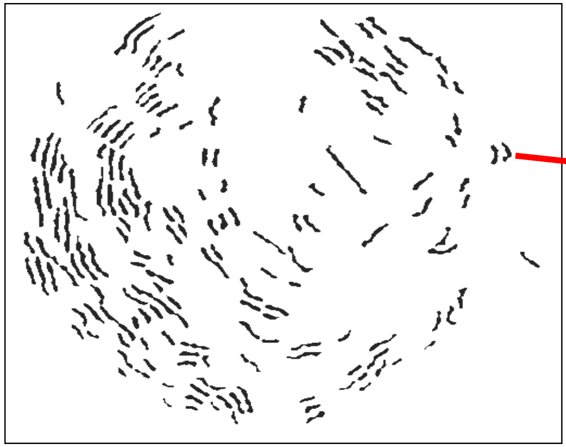
HR-TEM images of soot

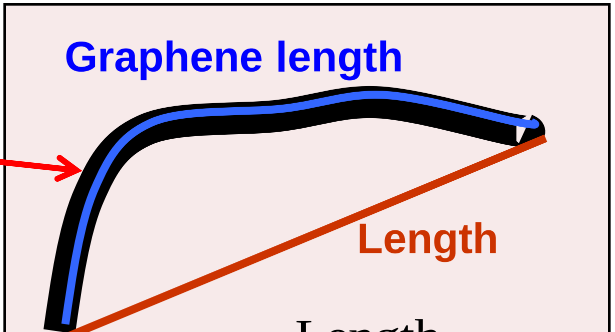




Microstructural Analysis

- **Apply FFT**
- **Spatial frequency filter**
- **Threshold brightness value**
- **Convert to binary format**



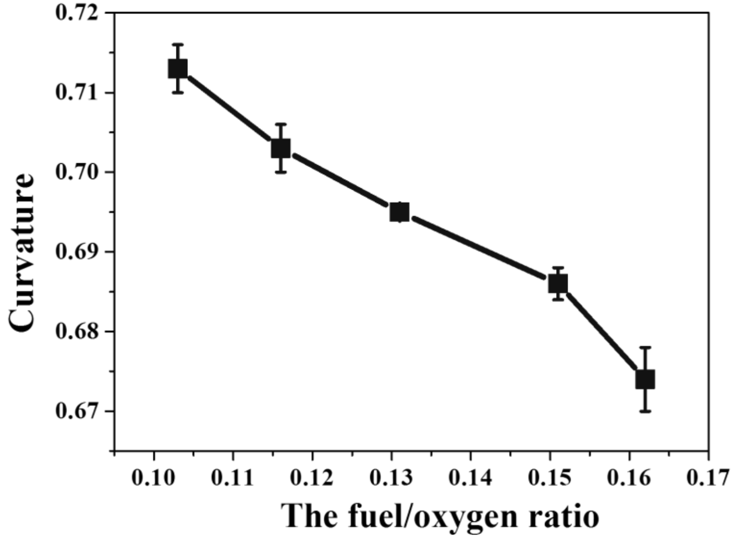


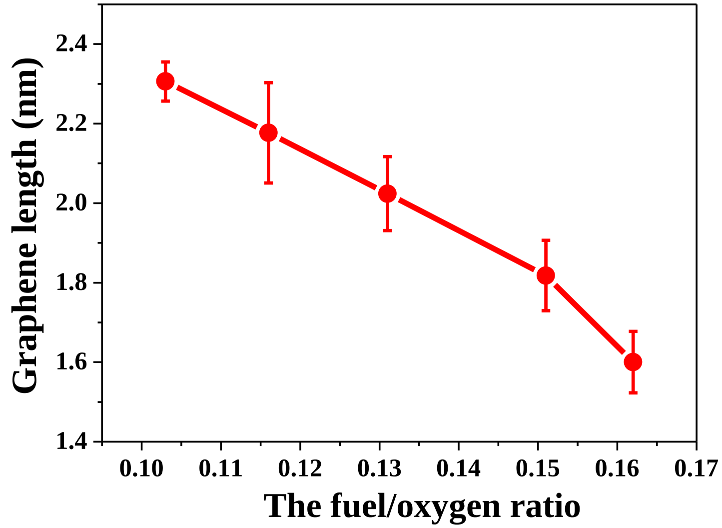
$$\text{Curl} = \frac{\text{Length}}{\text{Graphene length}}$$

Shim H.-S. et al. Carbon 2000, 38, 29-45. Wal R. L. vander. et al.,Comb. Flame 2004, 136, 129-140. A. Goel; Carbon, 2002, 40,177-182

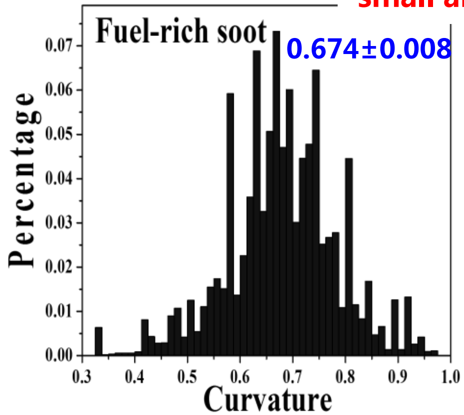
Characterization

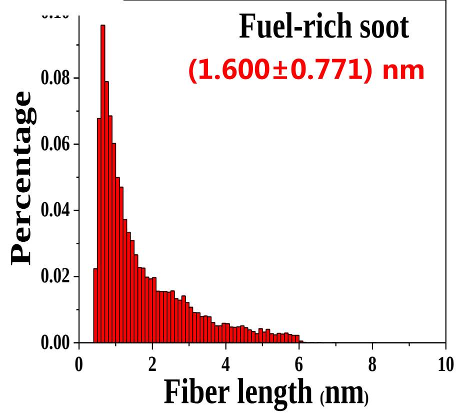
Distortion due to the defects increased



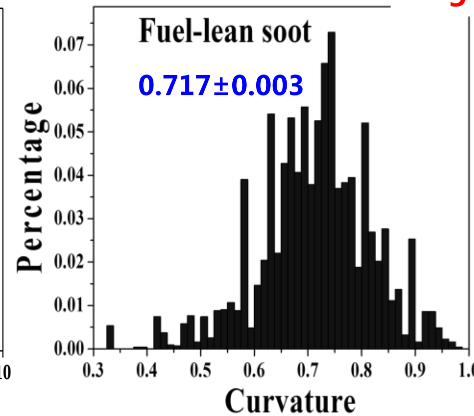


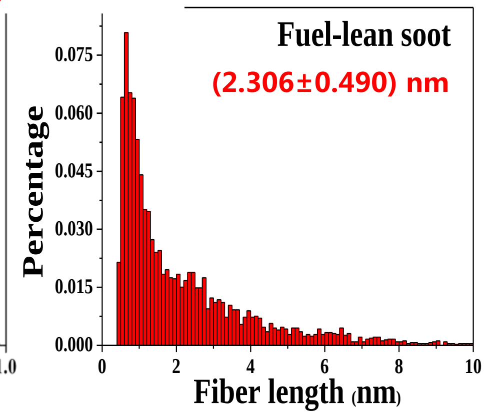
small and bent





large and flat



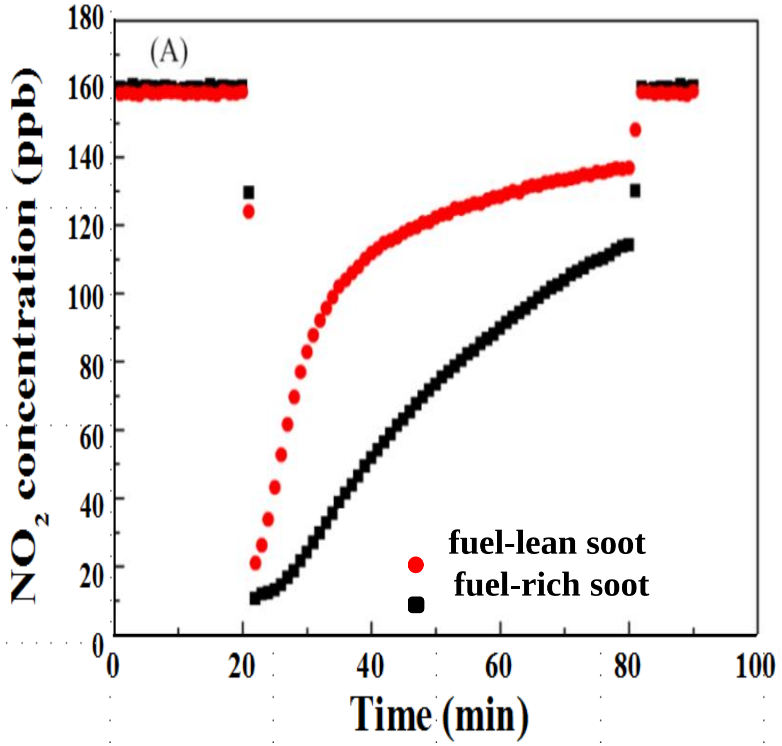


- ➢ **Combustion conditions significantly affect the microstructure of soot.**
- ➢ **Defects of graphene increase with the increasing fuel/oxygen ratio.**

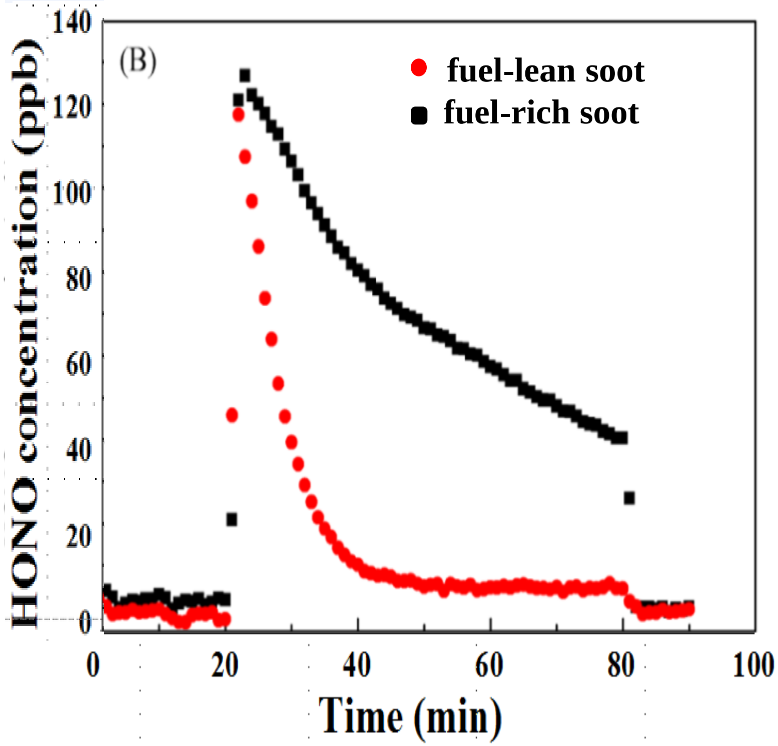
NO_2 uptake on soot

Data from flow tube reactor

NO_2 uptake



HONO formation

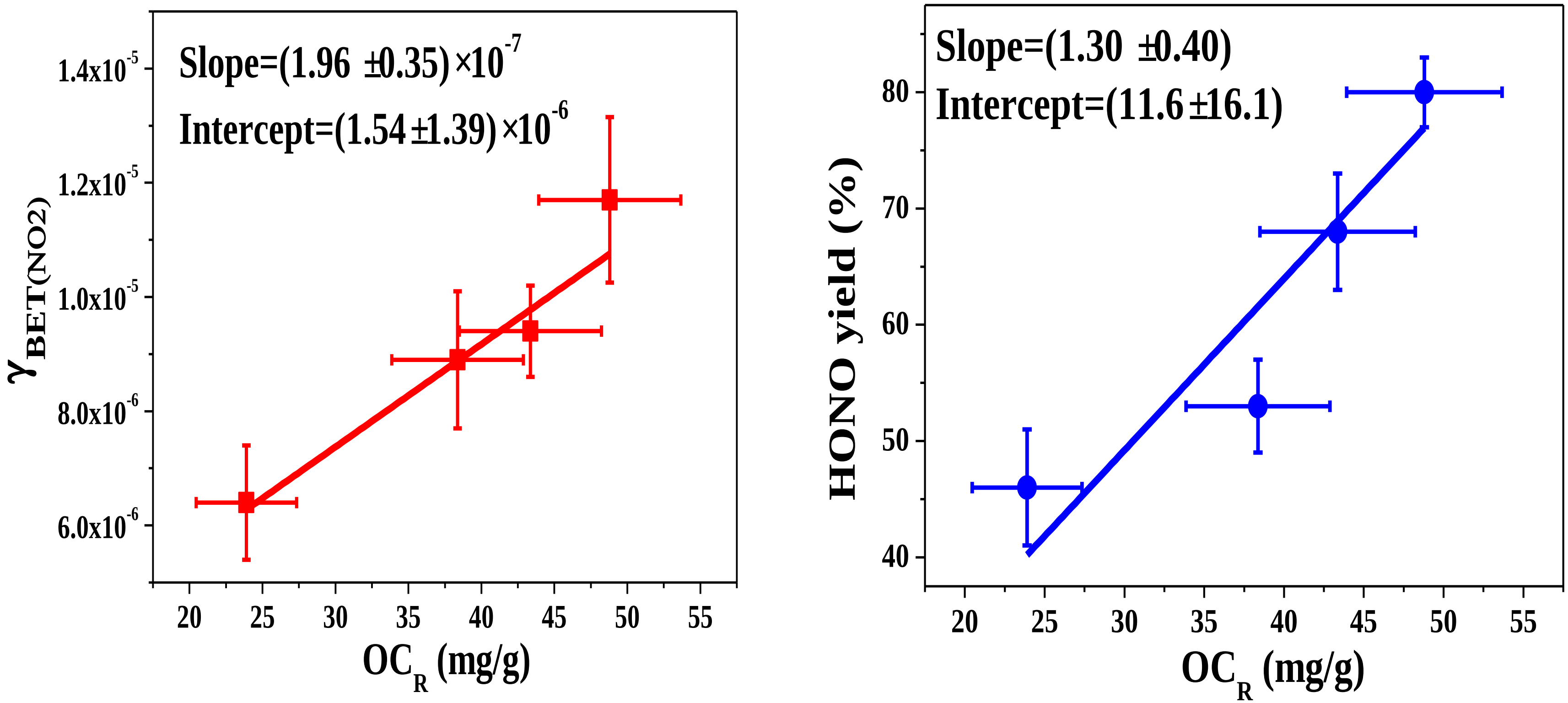


➢**Fuel-rich soot is more active than fuel-lean soot.**

Environ. Sci. Technol. 2013, 47, 3174−3181.

NO_2 uptake on soot

The role of reduced OC

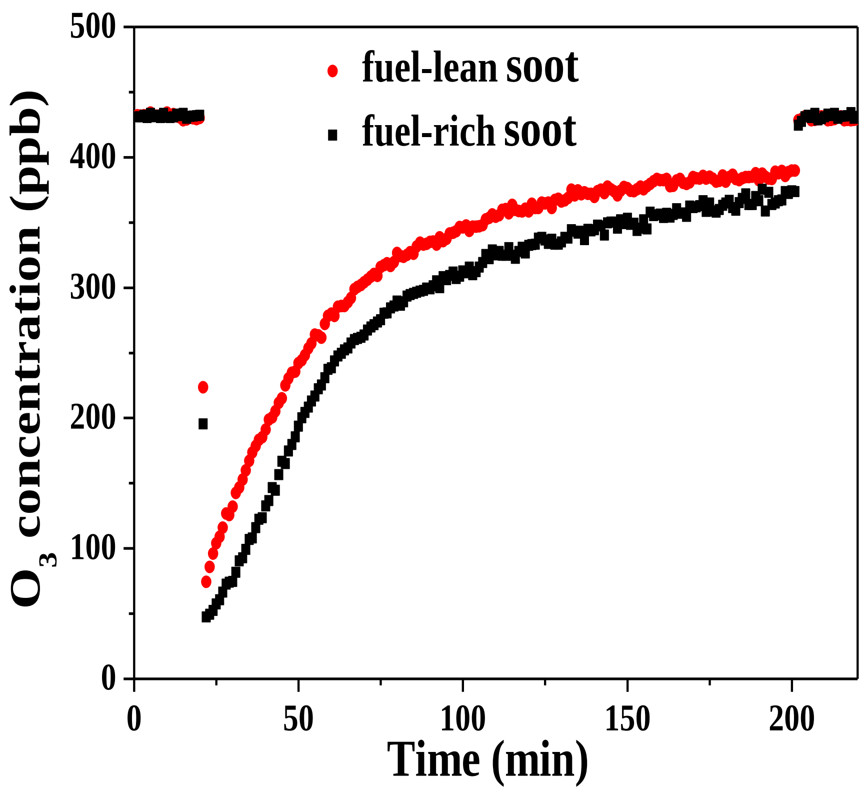


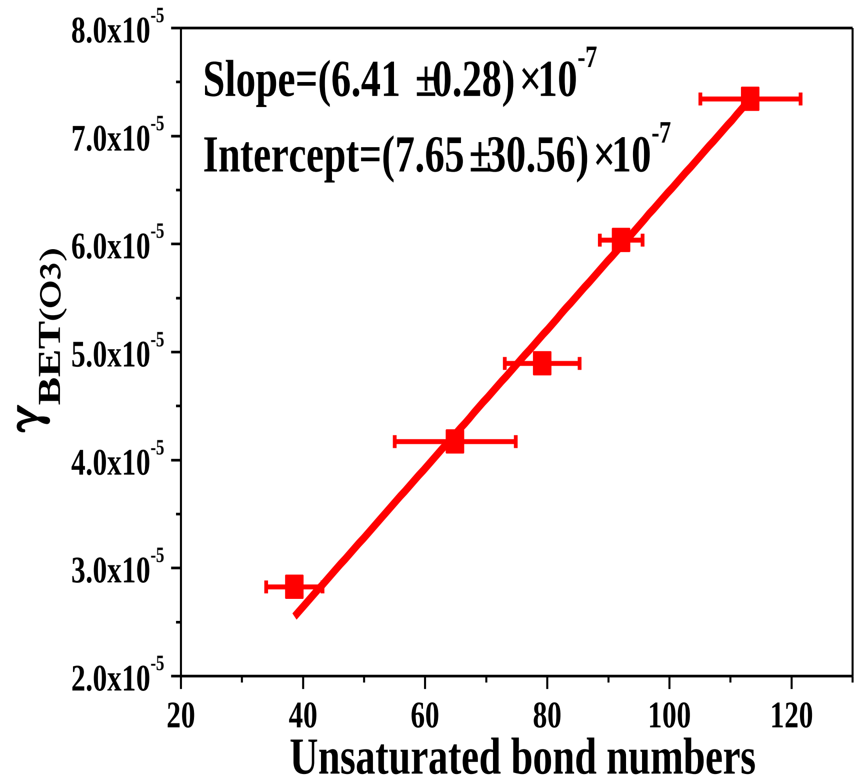
➢**The reduced OC of soot should be the main active sites for NO_2 uptake and HONO formation.**

Environ. Sci. Technol. 2013, 47, 3174−3181.

O_3 uptake on soot

O_3 uptake on soot



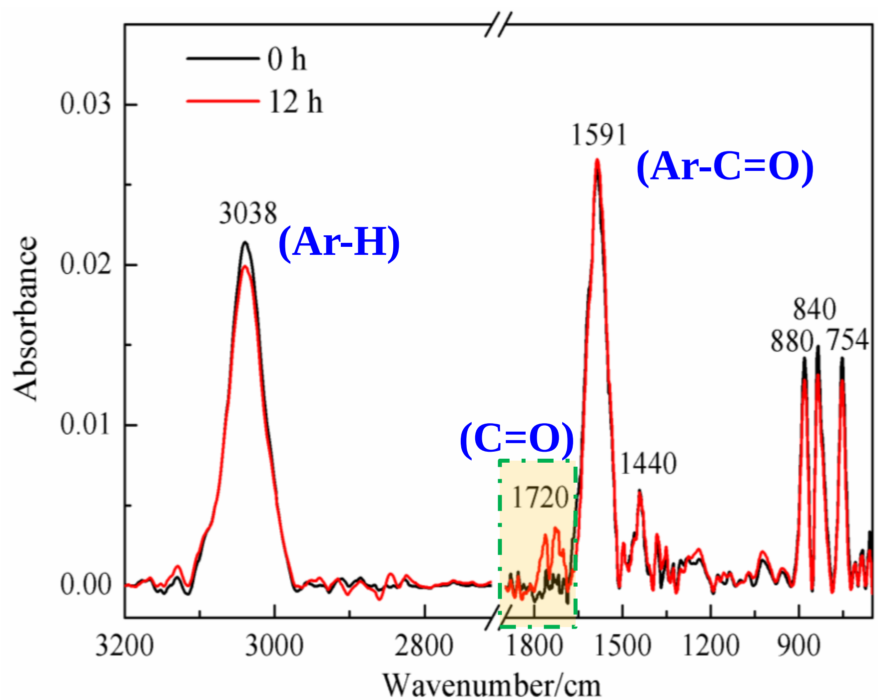


- ➢ Fuel-rich soot shows higher reactivity toward O_3 than fuel-lean soot.
- ➢ Unsaturated species in OC should be the main active sites for O_3 uptake.

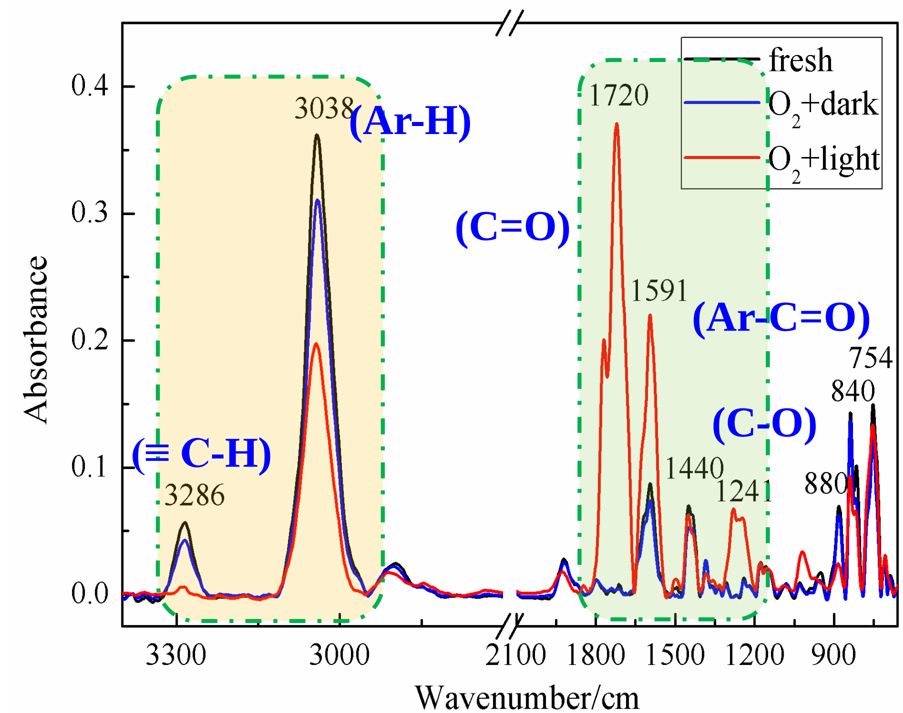
Photochemical aging of soot by O_2

➢**Soot is not only able to react with strong oxidizing gas, visible light can excite aging of soot by molecular O_2.**

Fuel-lean soot in air



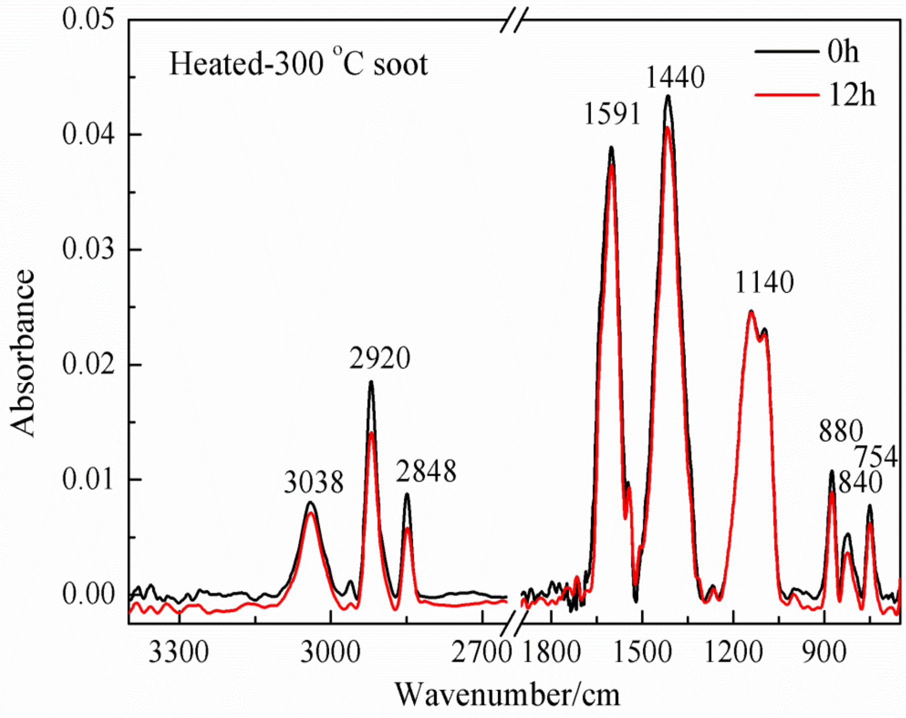
Fuel-rich soot in air



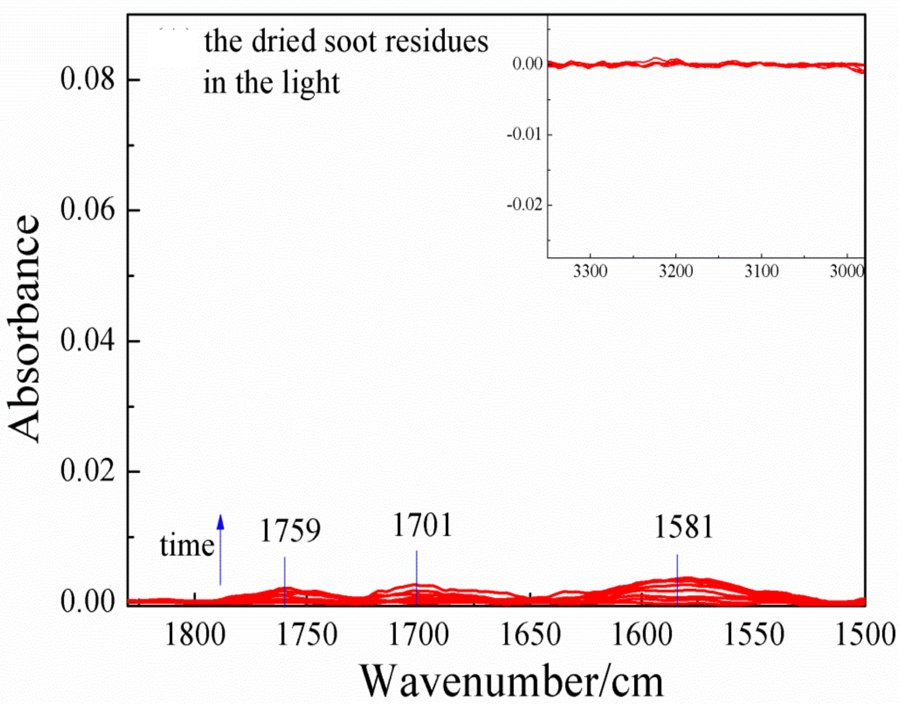
Proc. Natl. Acad. Sci. U. S. A. 2012, 109, 21250-21255.

Photochemical aging of soot by O_2

Preheated soot



The soot residues extracted by *n*-hexane

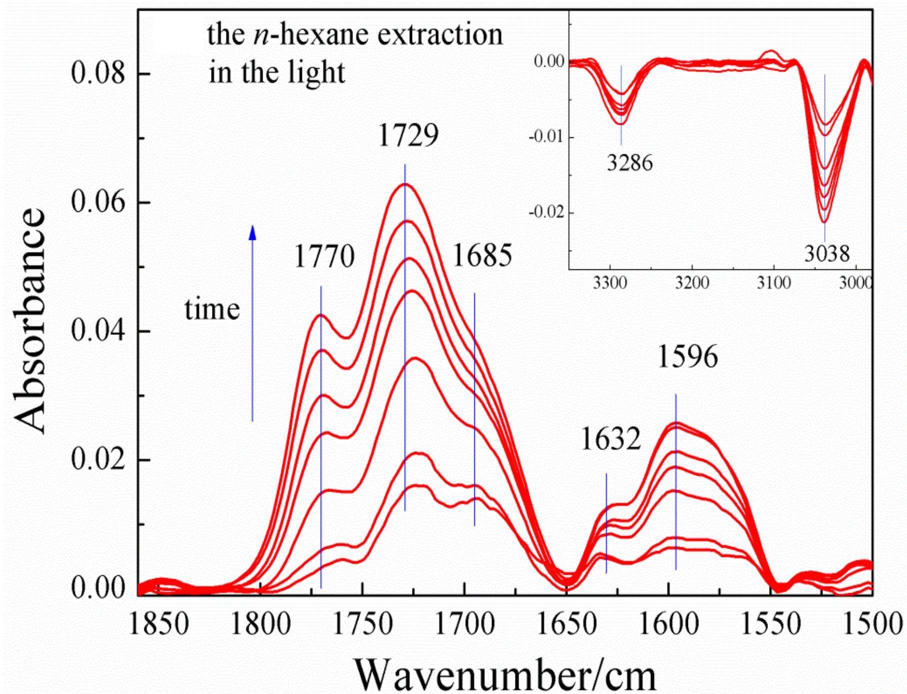


➢**Organic carbon is the main contributors to the photochemical aging process of soot by O_2.**

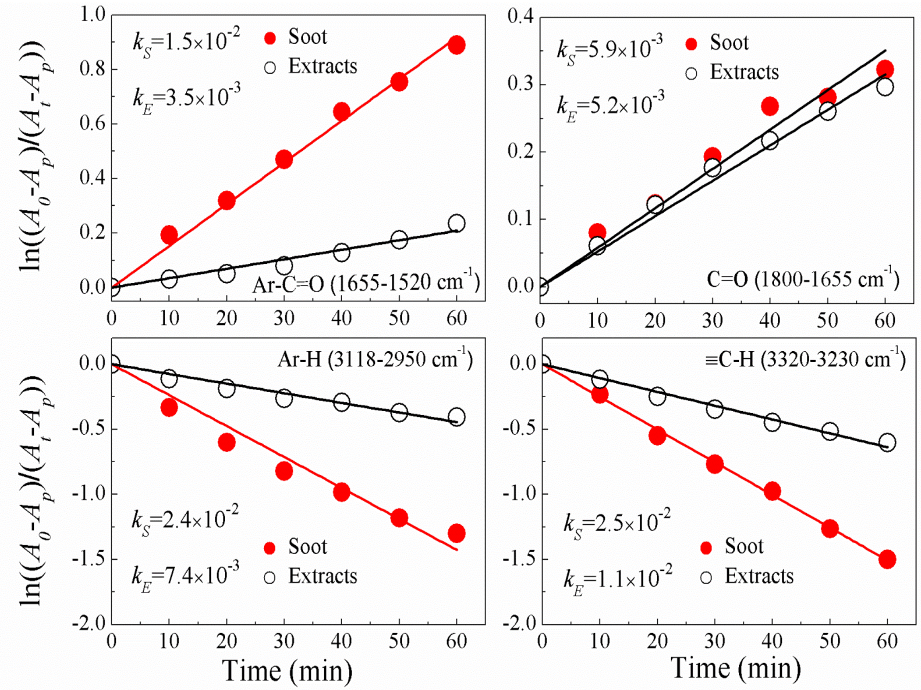
Proc. Natl. Acad. Sci. U. S. A. 2012, 109, 21250-21255.

Photochemical aging of soot by O_2

Extracted OC



Activity of OC with or without EC



- ➢Extracted OC shows photochemical activity, but lower than OC on soot.
- ➢EC may play a catalytic role in photochemical aging of soot by O_2.

Proc. Natl. Acad. Sci. U. S. A. 2012, 109, 21250-21255.

Photochemical aging of soot by O_2

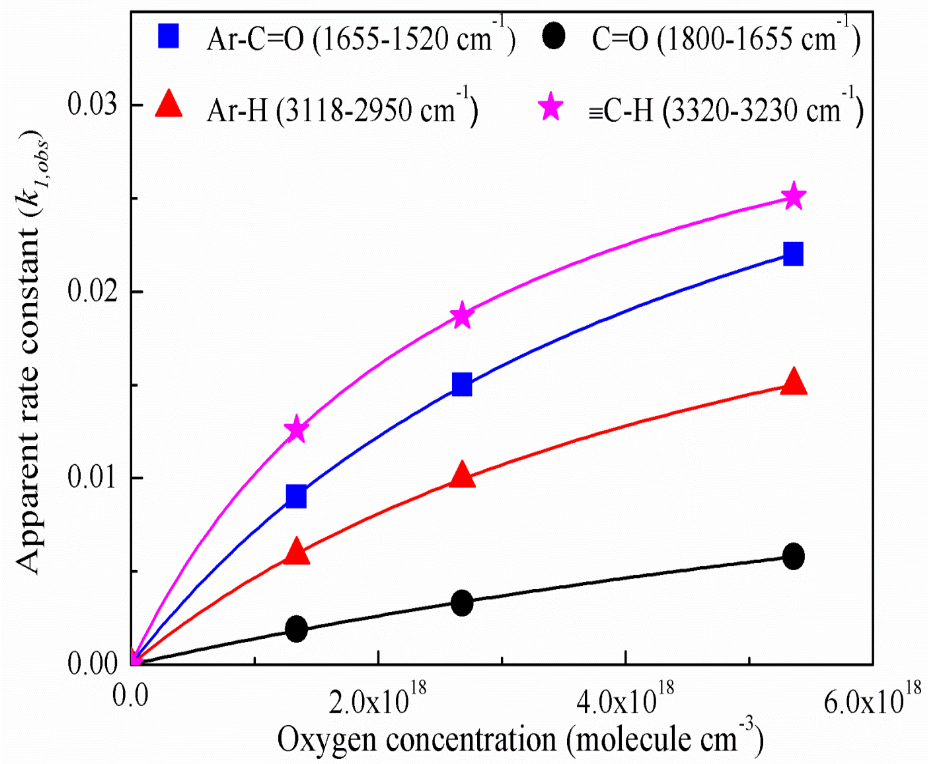
Kinetics

L-H mechanism

$$(1)\ soot + O_2 \rightarrow [soot - O_2]$$

$$(2)\ \frac{k''[SS]K_{O_2}[O_{2g}]}{1+K_{O_2}[O_{2g}]} = k^1_{obs}$$

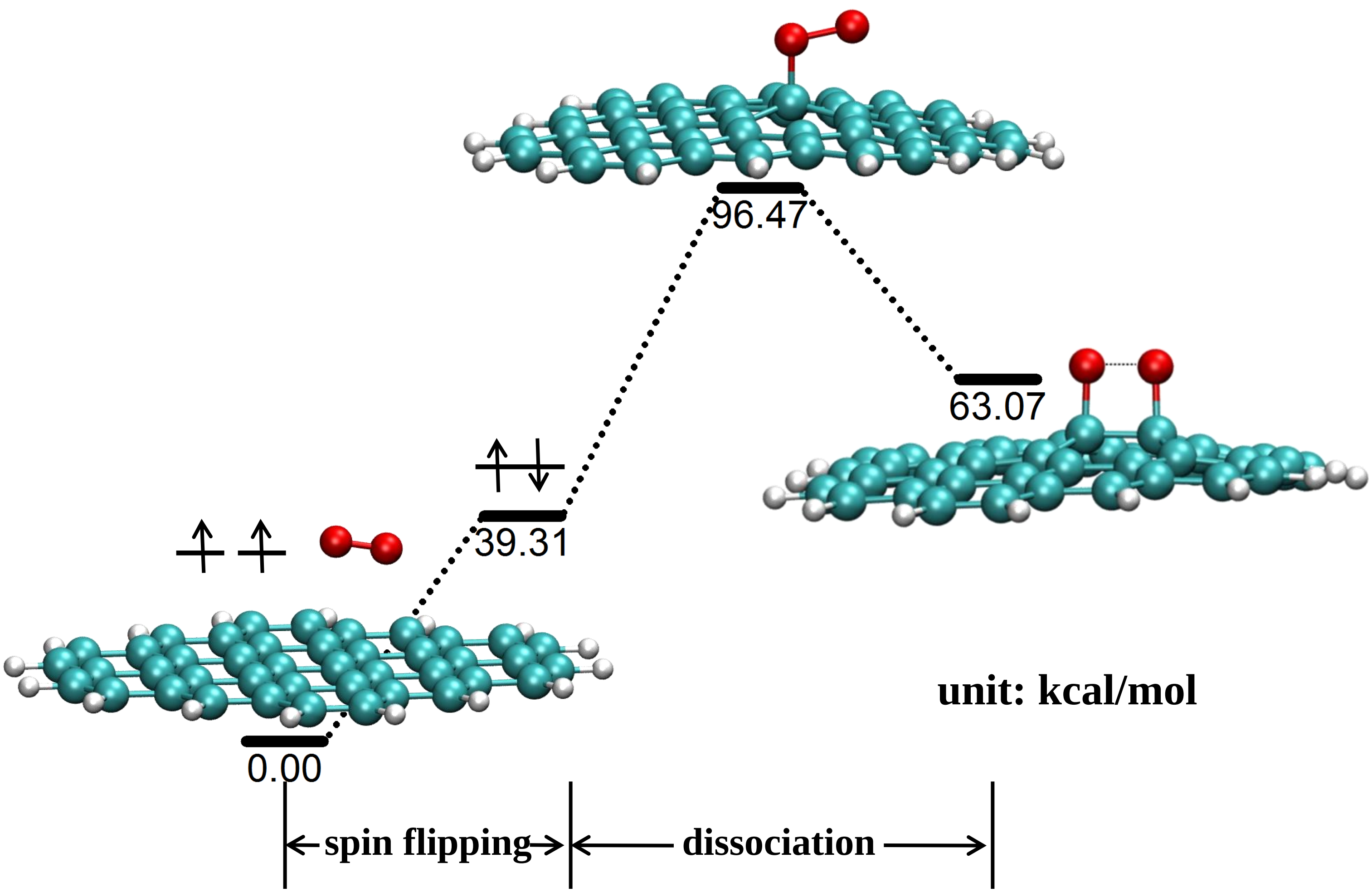
$$(3)\ \frac{k^1_{\max}K_{O_2}[O_{2g}]}{1+K_{O_2}[O_{2g}]} = k^1_{obs}$$



➢**Species on soot follow L-H mechanism in photochemical aging process by O_2.**

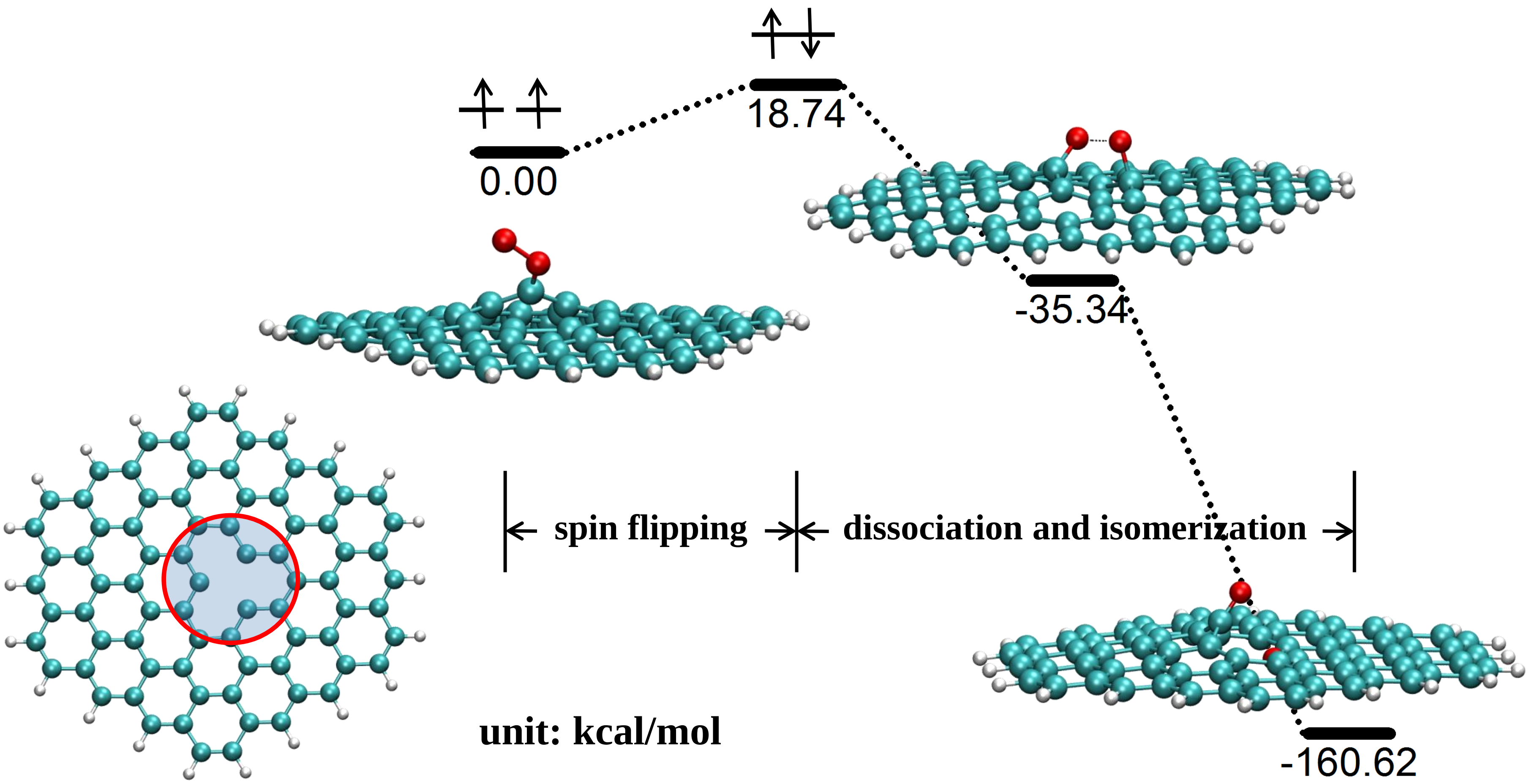
Proc. Natl. Acad. Sci. U. S. A. 2012, 109, 21250-21255.

O_2 dissociation on perfect graphene surface



➢Both the energy required for spin-flipping excitation and the barrier for O_2 dissociation are too high to be overcome at room temperature.

O_2 dissociation on defective graphene surface



➢**The spin-flipping excitation is surmountable at room temperature, and the dissociation and isomerization are barrier less processes.**

Summary

- ✓ The aging of soot with oxidizing gas is mainly determined by two factors: surface composition and microstructure of soot, which are significantly influenced by combustion conditions.
- ✓ OC is active for NO_2 and O_3 uptake on soot, and the photochemical aging process by O_2.
- ✓ EC plays a catalytic role in photochemical aging of soot by O_2, and defective sites on graphite sheet might help for O_2 activation.

Acknowledgement

Thanks to my colleagues and students

Yan Zhao, Dr. Han Chong, Dr. Yongchun Liu, Dr. Guangzhi He, *et al.*

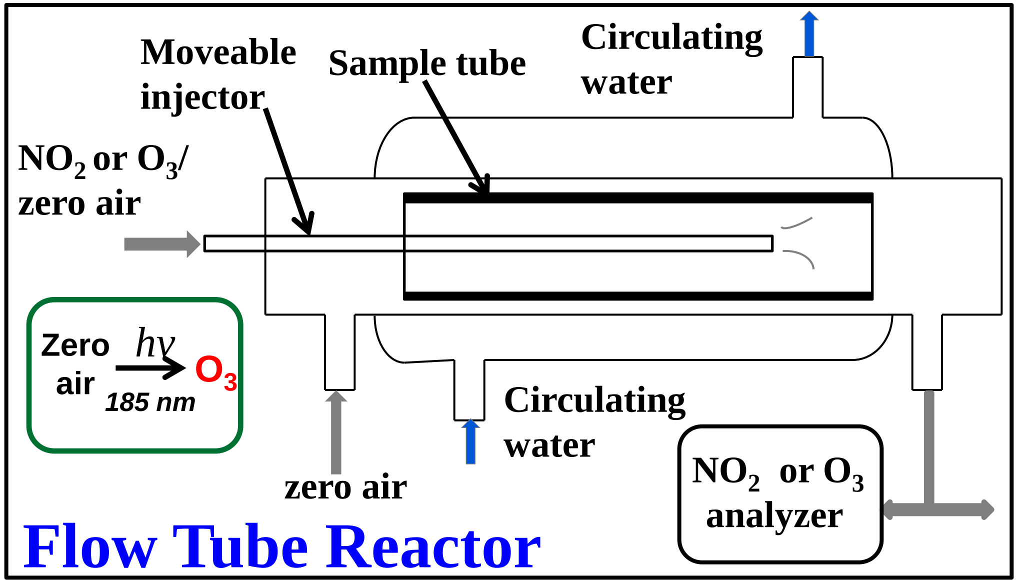
$$: Strategic Priority Research Program – "Formation mechanism and control strategies of haze in China" of the Chinese Academy of Sciences & NSFC (21190054, 91543109)

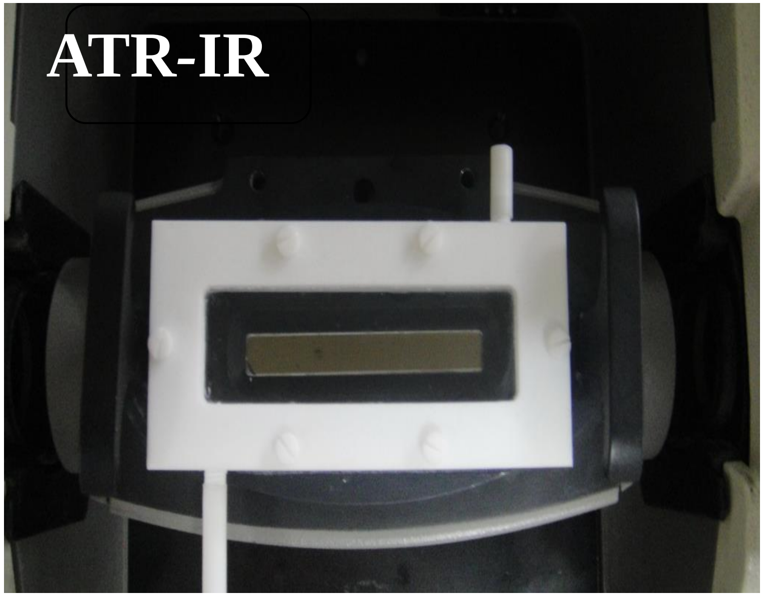
Thank you for your attention！

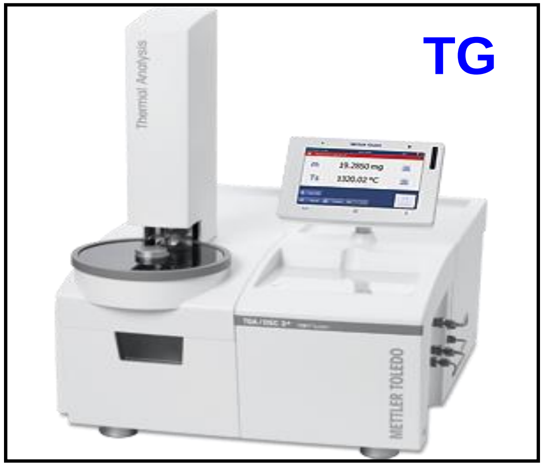
Thank you

Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences

Experimental section

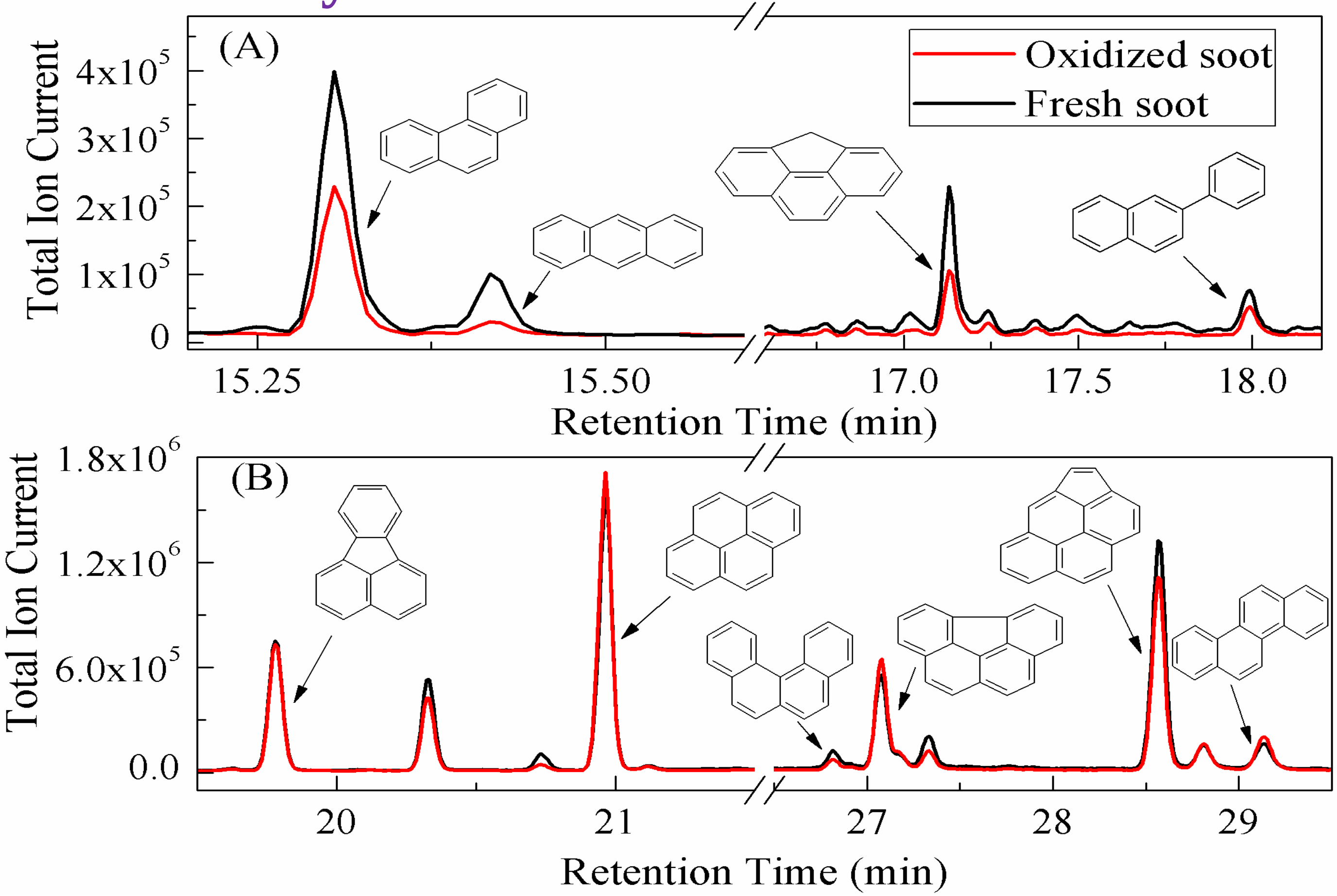






Photochemical aging of soot by O_2

GC-MS analysis of OC

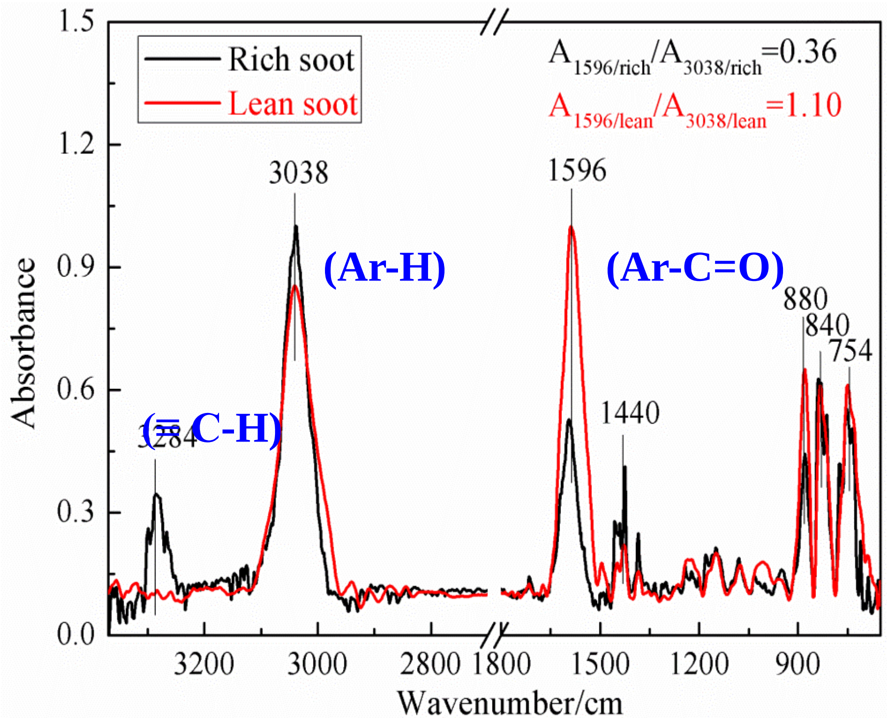


➢OC mainly contain PAHs and aliphatic hydrocarbons.

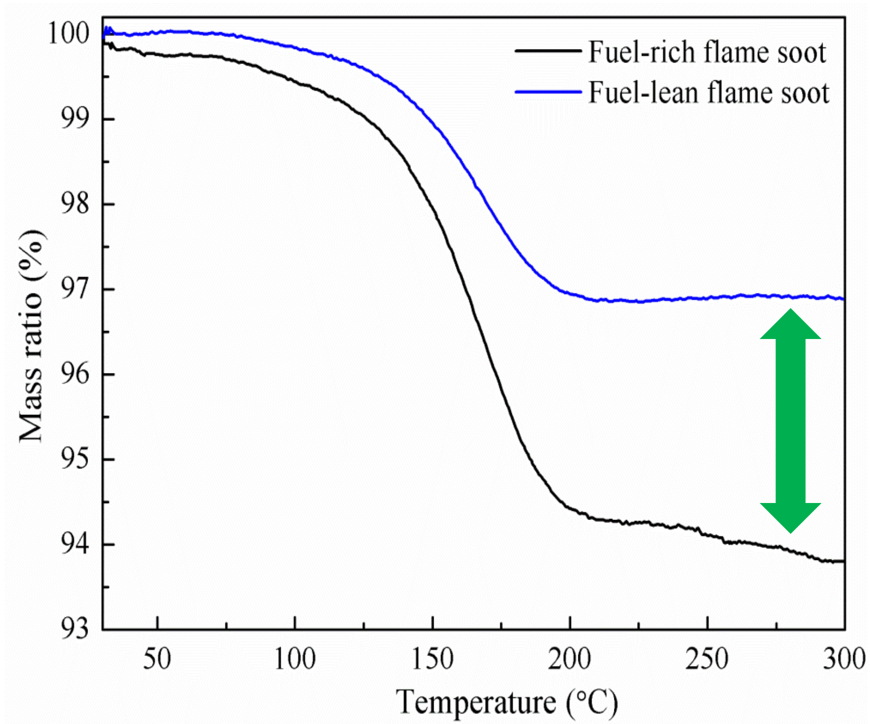
Proc. Natl. Acad. Sci. U. S. A. 2012, 109, 21250-21255.

Photochemical aging of soot by O_2

Surface oxidation state



Organic carbon content

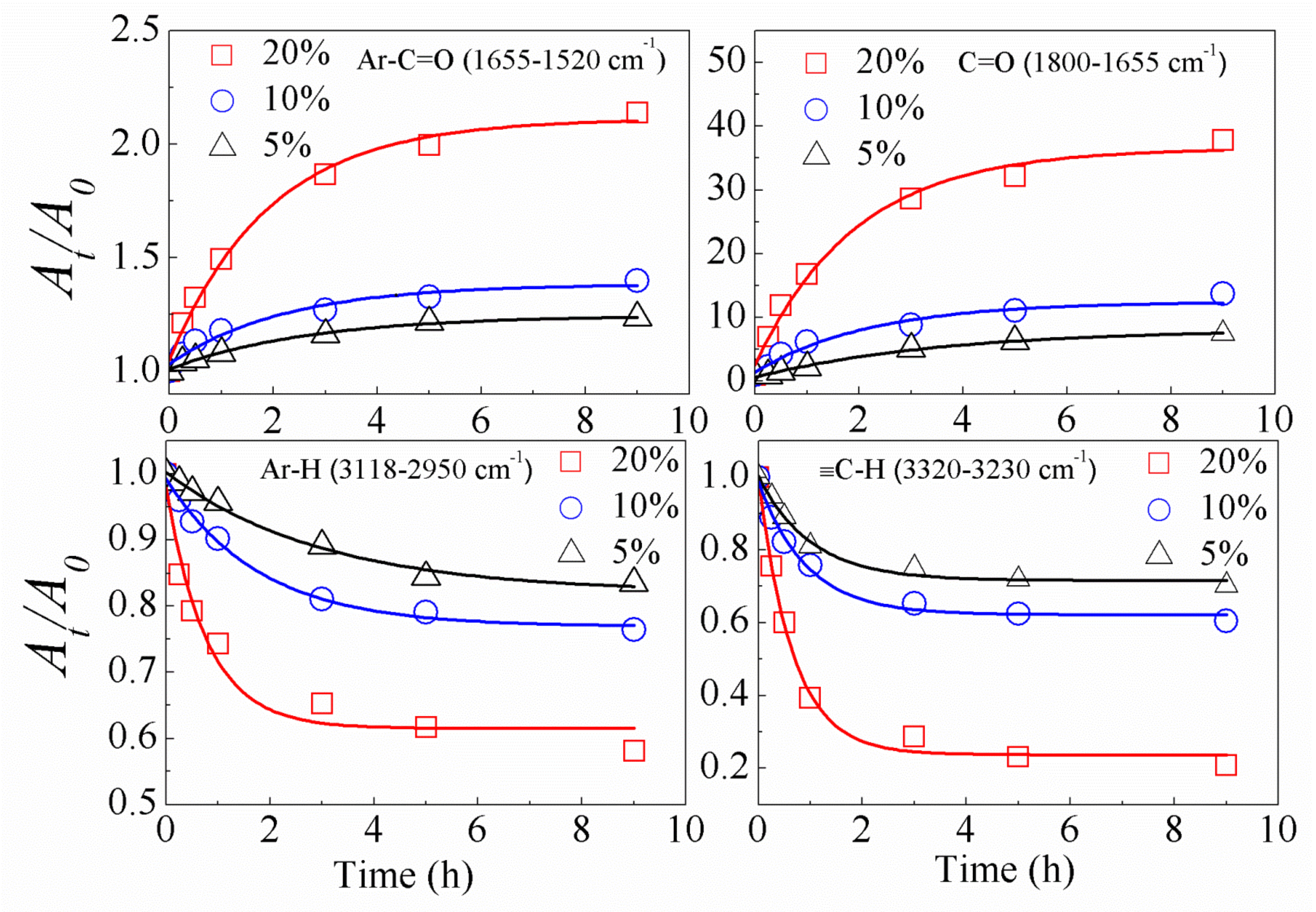


➢**Combustion conditions can significantly affect surface oxidation state and organic carbon content of soot.**

Han et al., Proc. Natl. Acad. Sci. U. S. A. 2012, 109, 21250-21255.

Photochemical aging of soot by O_2

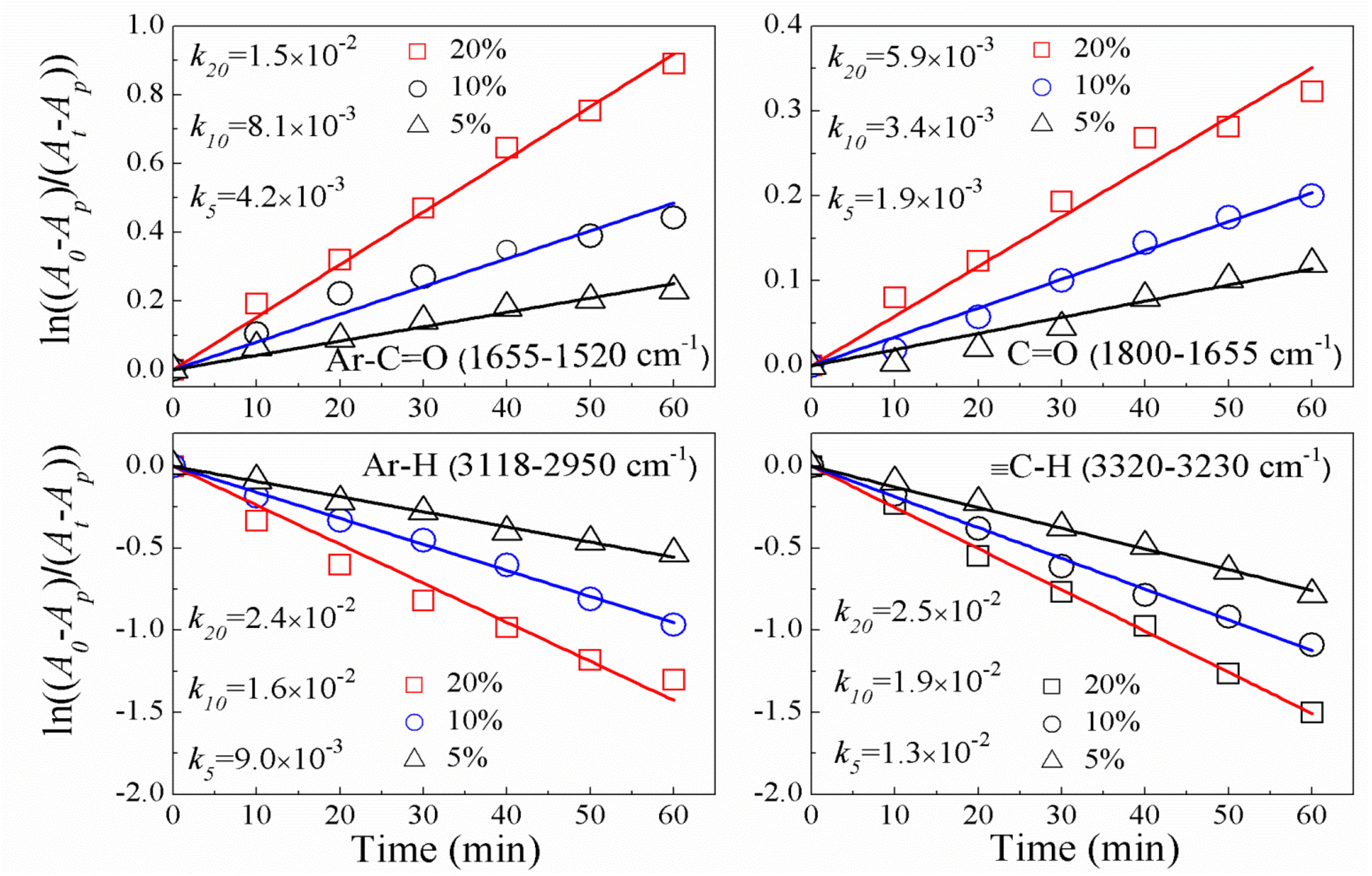
Kinetics



Proc. Natl. Acad. Sci. U. S. A. 2012, 109, 21250-21255.

Photochemical aging of soot by O_2

kinetics

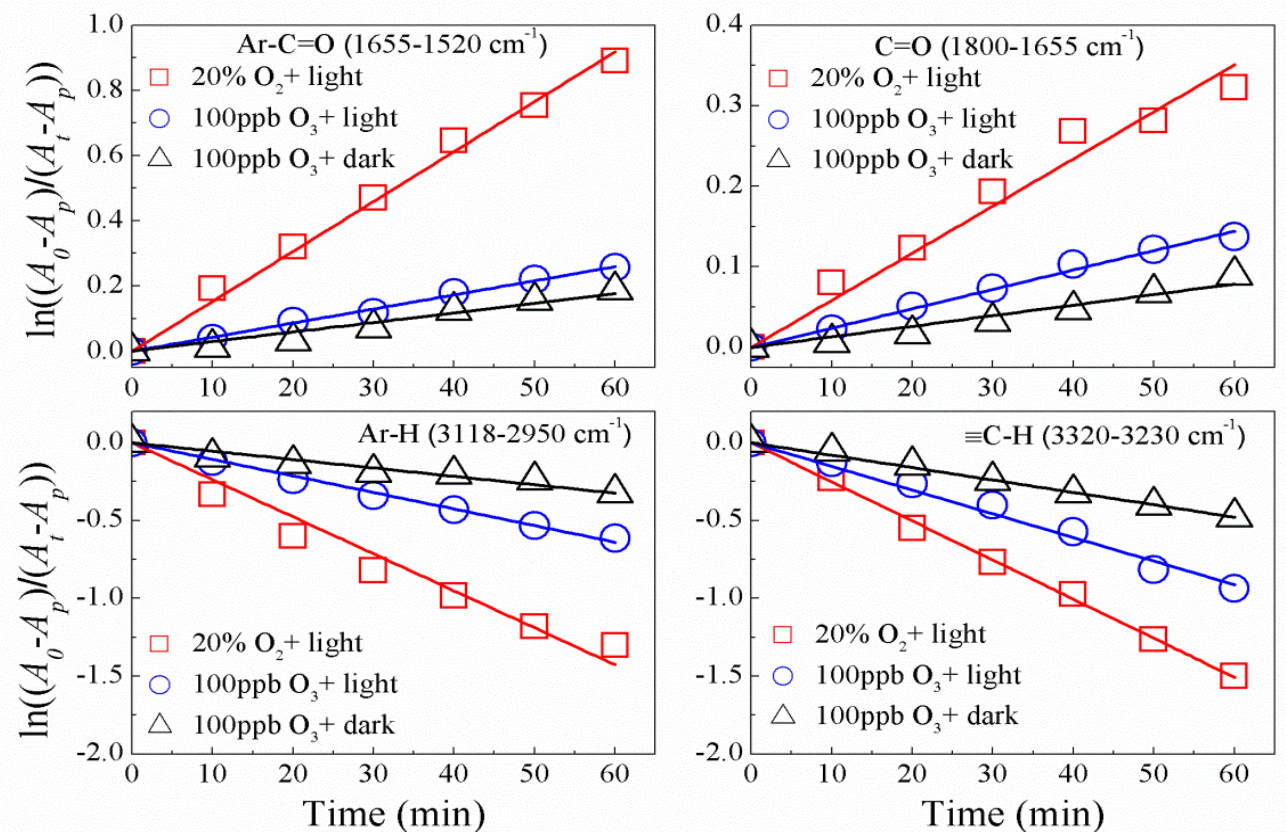


➢ **Species on soot show pseudo-first-order reaction nature.**

Proc. Natl. Acad. Sci. U. S. A. 2012, 109, 21250-21255.

Photochemical aging of soot by O_2

Comparison of kinetics of soot aged by O_2 and O_3



➢Reaction rates of species during the photo-aging of soot by O_2 were larger than those during the aging process of soot by O_3 under either light or dark conditions.

Proc. Natl. Acad. Sci. U. S. A. 2012, 109, 21250-21255.