…spread the fragrance of knowledge…

St. Paul's 2nd Letter to Corinthians 2:14-15

…Combustion Synthesis of Materials

1. Overview

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Particle Technology Laboratory

Department of Mechanical and Process Engineering,

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Sponsored by

European Research Council, DuPont, Dow, Millennium,

U.S. and Swiss National Science Foundation,

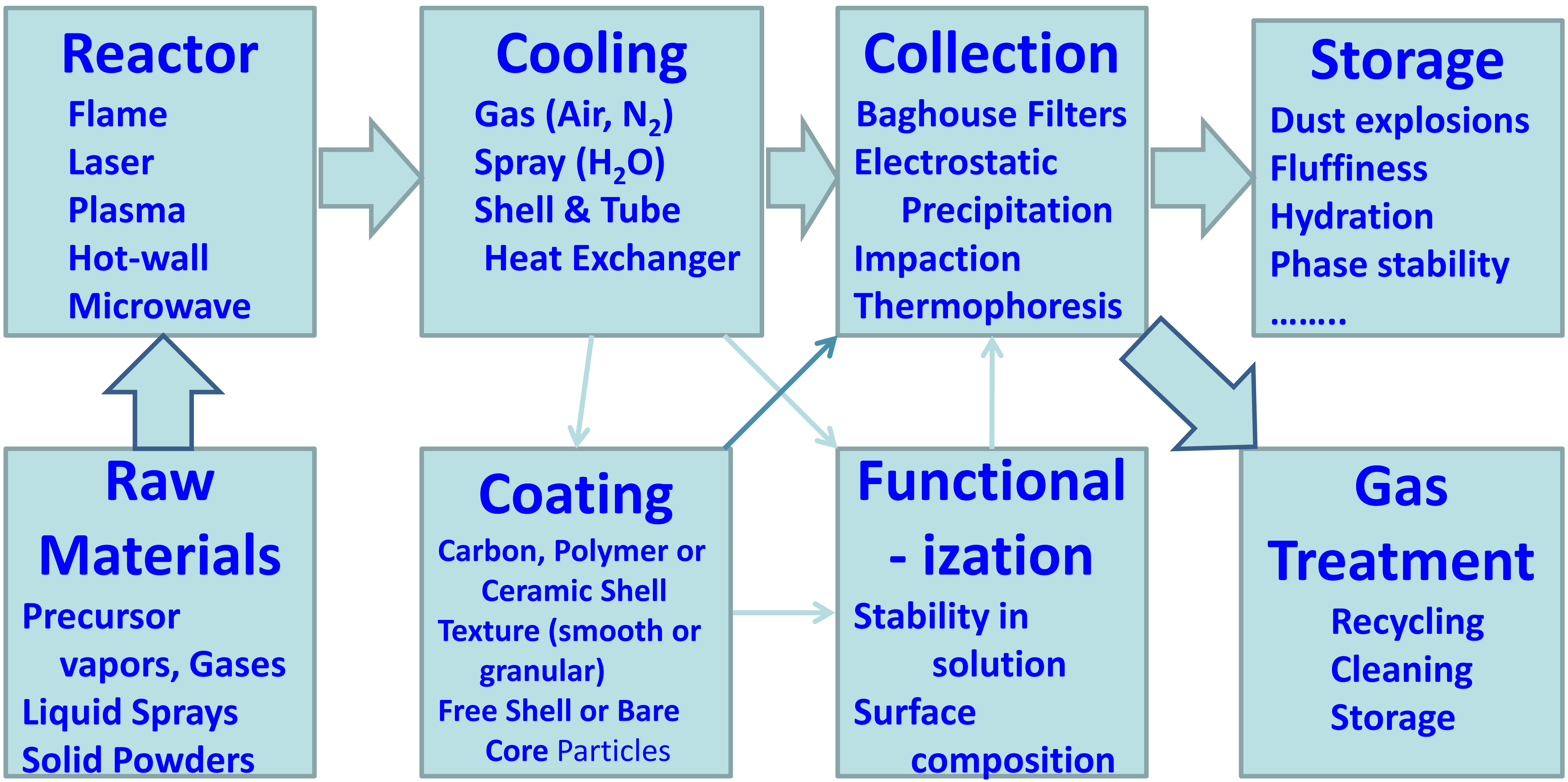
Swiss Commission for Technology and Innovation

AEROSOL SYNTHESIS OF NANOSTRUCTURED PARTICLES @ the early 2000

Product Particles	Volume Mt/y	Value B$/y	Process, precursor
Carbon black	8	8	Flame, C_xH_y
Titania	2	4	Flame, $TiCl_4$
Fumed Silica	0.2	2	Flame, $SiCl_4$
Zinc Oxide	0.6	0.7	Hot –Wall, Zn
Filamentary Ni	0.04	~0.1	Hot-Wall, $Ni(CO)_4$
Fe, Pt, Zn_2SiO_4/Mn	~0.02	~1	Hot-Wall, Spray…

Wegner, Pratsinis *Chem. Eng. Sci.* **58**, 4581-9 (2003).

Process Steps during Aerosol Synthesis of Materials



Reproduced by permission from *Annual Reviews*

B. Buesser, SEP, Design of Nanomaterial Synthesis by Aerosol Processes , *Annual Rev. Chem. Biomol. Eng.*, 3, 103–127 (2012).

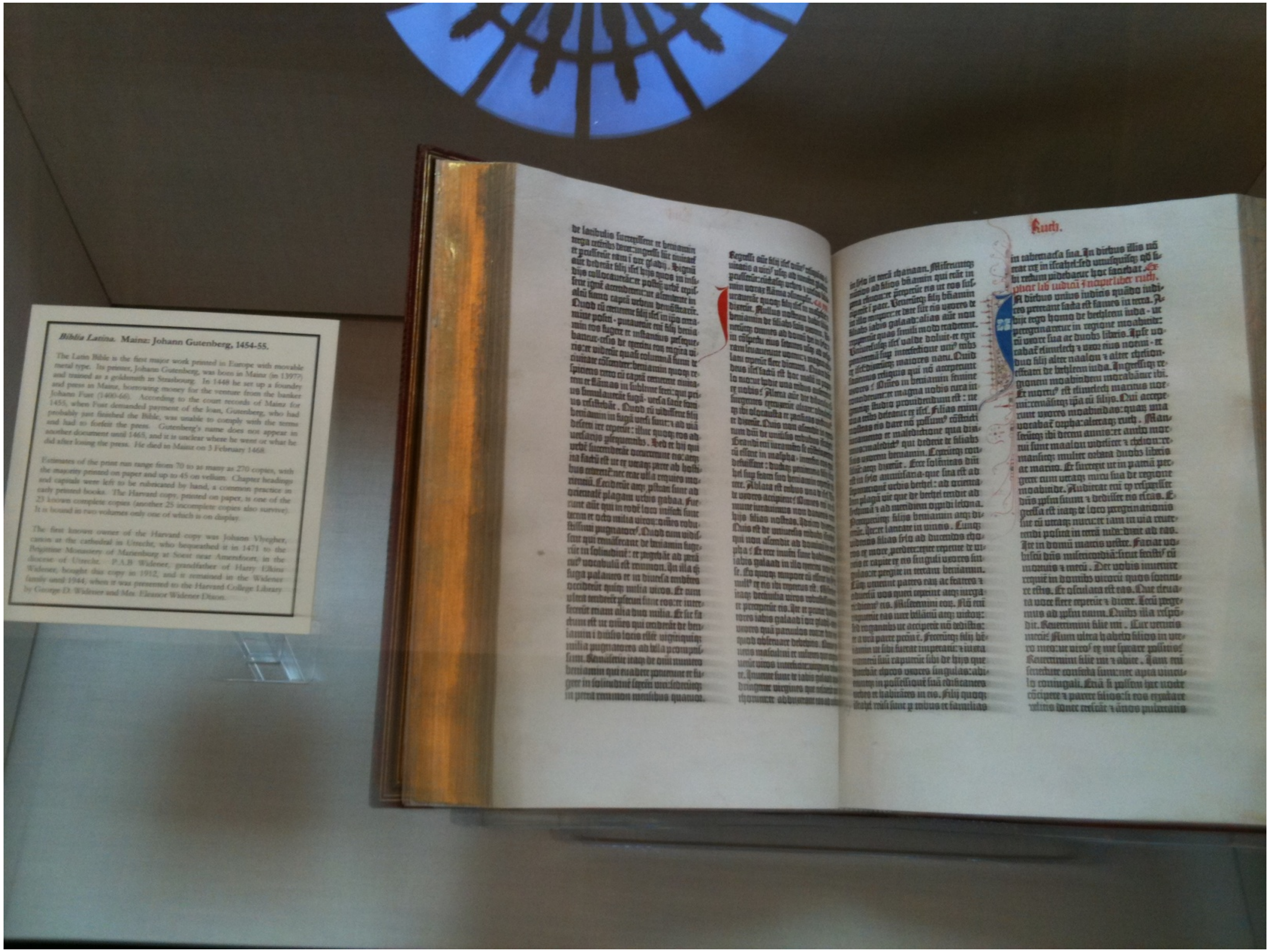
Ink production in China

Oriental worker scrapping thermophoretically deposited soot from walls w/o protection

Combustion is also the earliest aerosol process for manufacturing of nanostructured particles

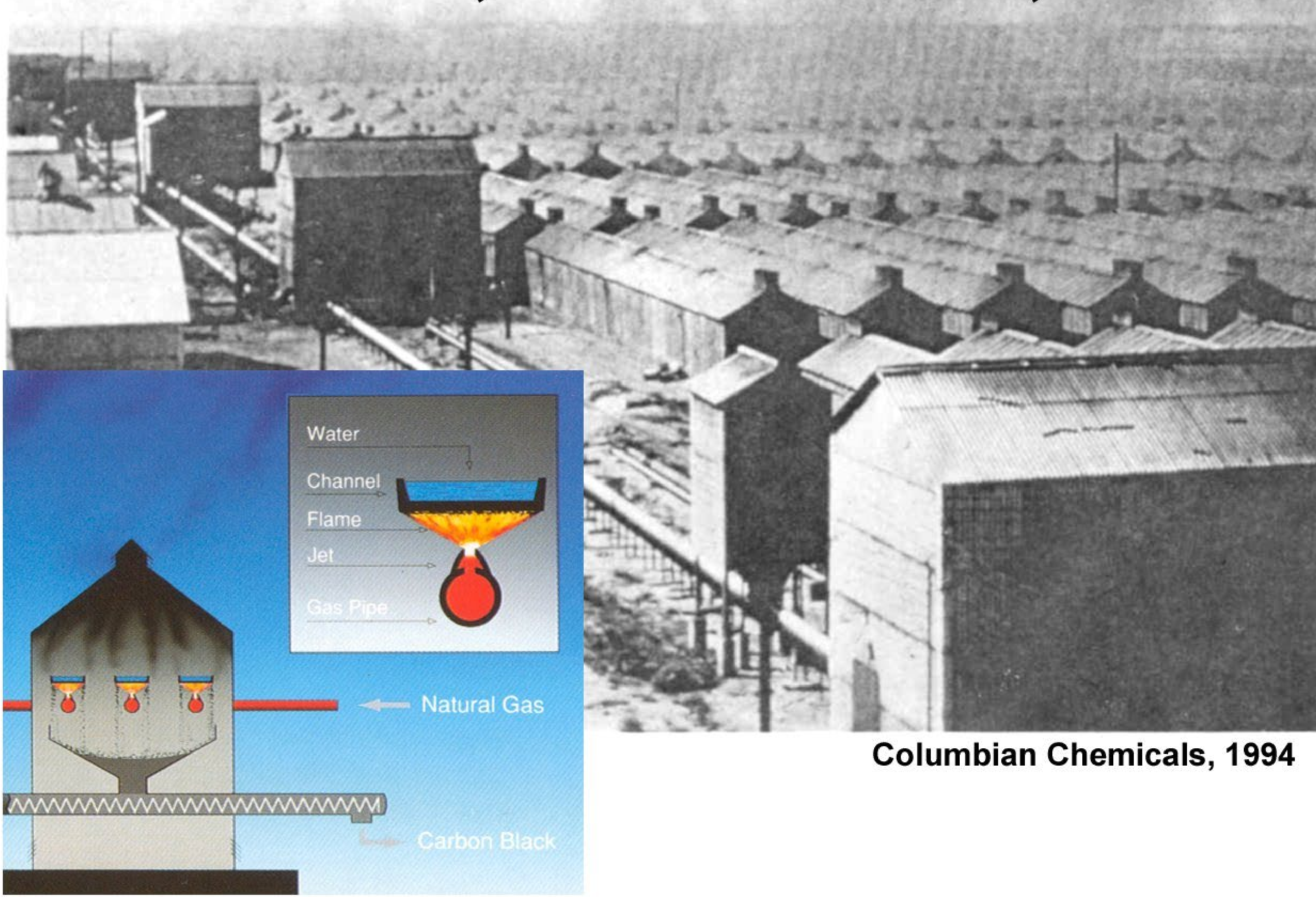
Ulrich, G. D. (1984). Flame Synthesis of Fine Particles. *Chem. Eng. News*, **62** (32), *22-29*.

The Bible of Gutenberg



Library, Harvard University, Cambridge, MA

Channel Plant, Texas Panhandle, 1940's



Columbian Chemicals, 1994

Degussa, 1996

Advertisement in Farbe & Lacke (1949) of SiO_2 nanoparticles

*Between 4 to 20 millimicron is the particle size of **aerosil**, the new additive for the lacquer industry.*

Please ask for the new brochure at Degussa, Carbon Black Dept., Frankfurt

Flame-made Commodities @ t/h today

Paints & (photo)Catalysts

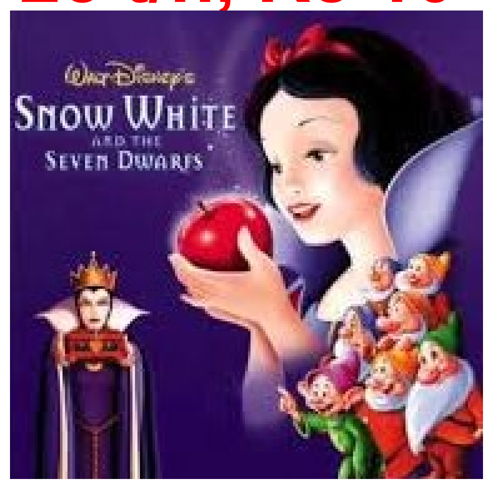
Courtesy of Dupont

Tires (~30 wt%)

Carbon Black (\$10B)

Inks

25 t/h, Re 10^6

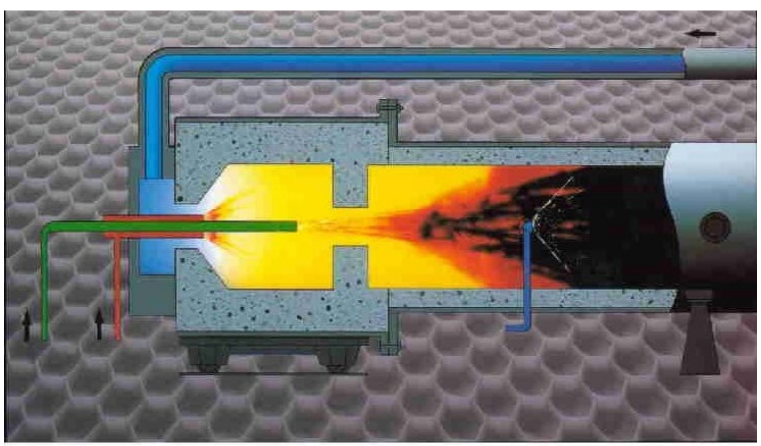


TiO_2(\$5 B)

Courtesy of Cabot

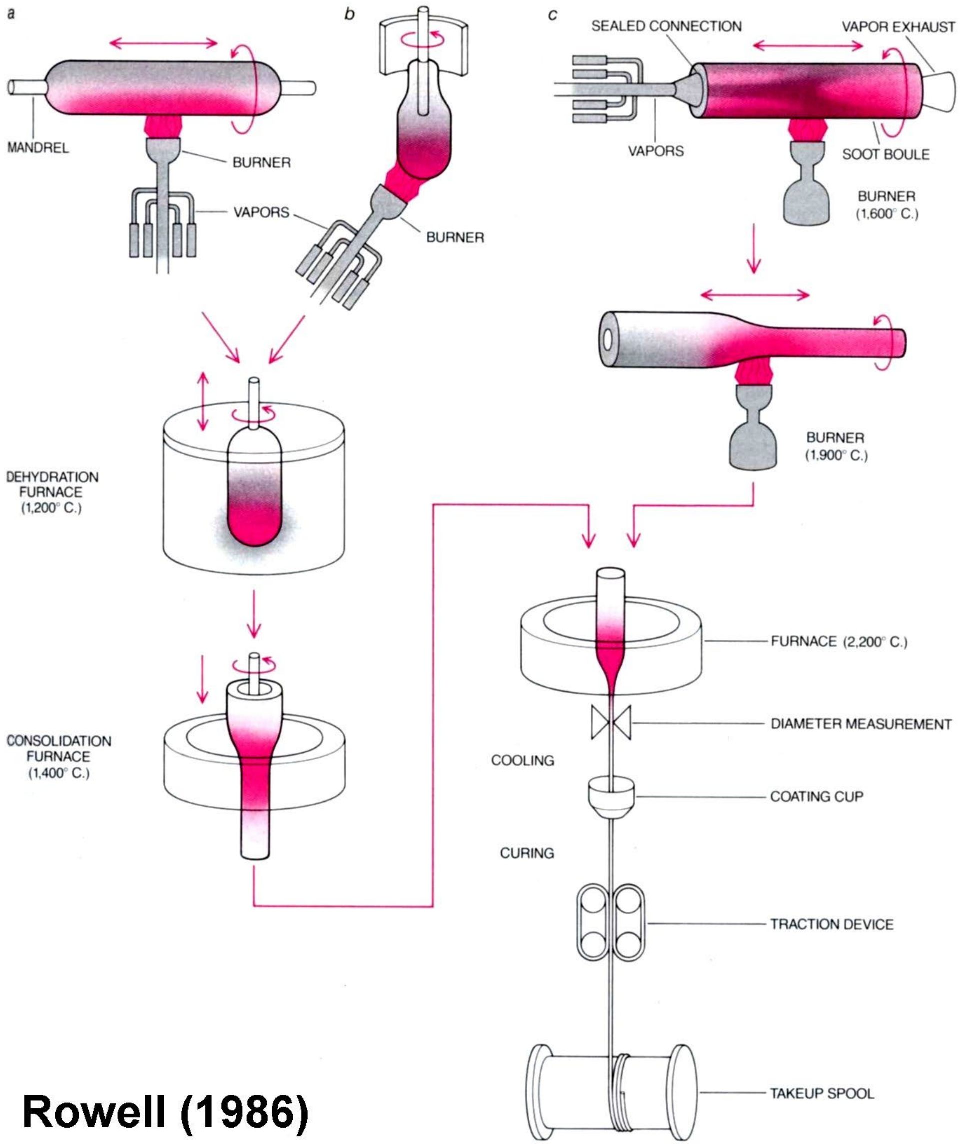
SiO_2(\$3 B)

Flowing aid



Furnace Process for Carbon Black Production Courtesy of Evonik

Optical Fiber Production



Commercially advanced today by Corning Glass, Sumitomo, Heraeus, Furakawa etc.

MCVD operation by combining Fluid & Particle Dynamics

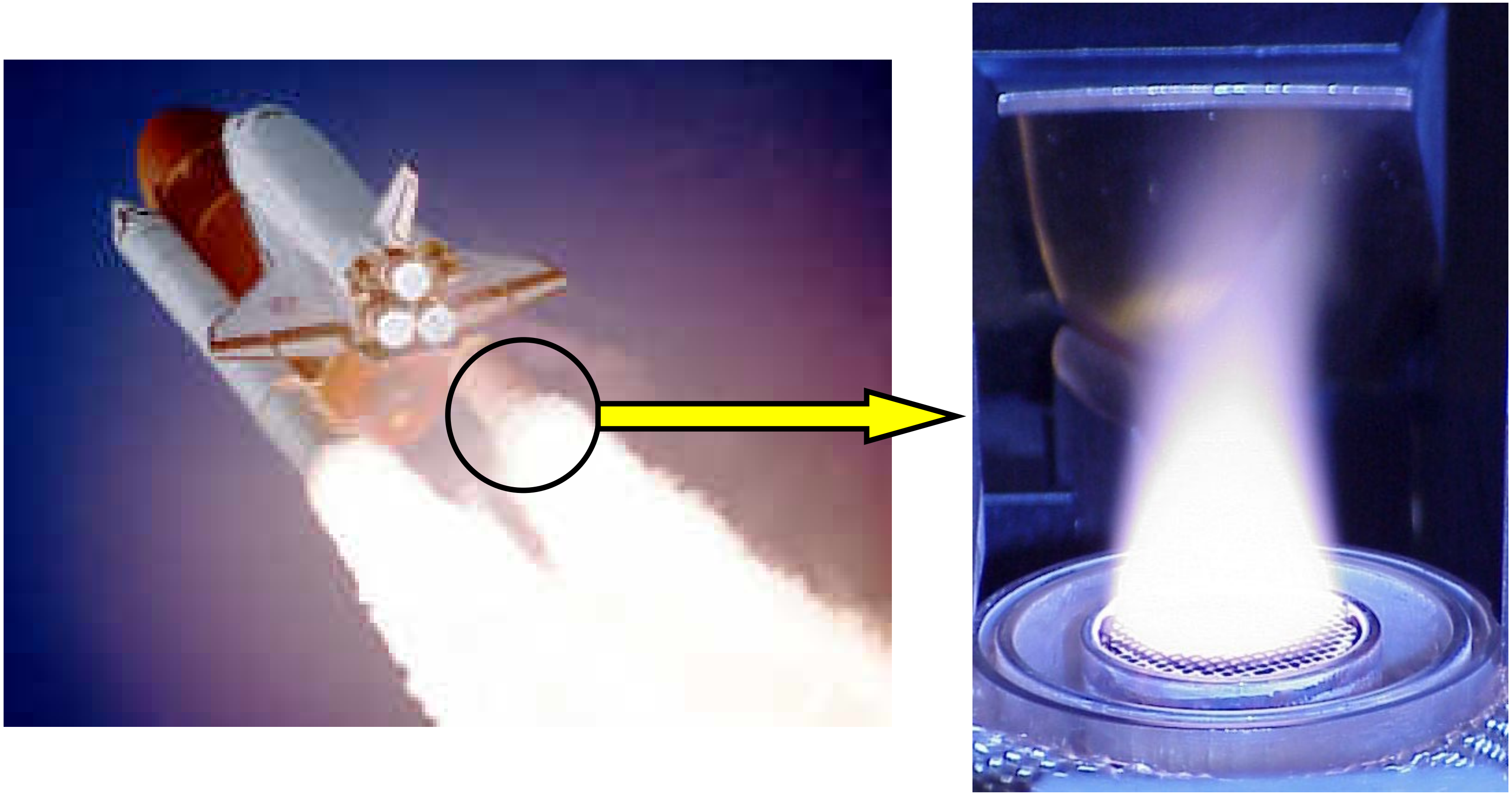
Reproduced by permission of George Retschek, illustrator for Scientific American

Rowell (1986)

Rowell, J. M. (1986). Photonic Materials. *Scientific American* **255** (4), October, 146-157.

K.S. Kim, SEP, Manufacture of Optical Waveguide Preforms by Modified Chemical Vapor Deposition, *AIChE J.*, **34**, 912-921 (1988).

A rough analogy to flame aerosol reactors



PTL, ETH Zurich

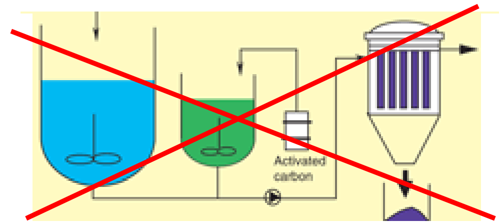
… just well attached to the ground !

Advantages of flame-made materials

Aerosol-based Technologies in Nanoscale Manufacturing: from Functional Materials to Devices through Core Chemical Engineering, *AIChE J.* 56, 3028-3035 (2010)

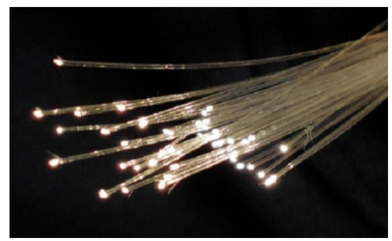
1. Scalability

2. No liquid by-products

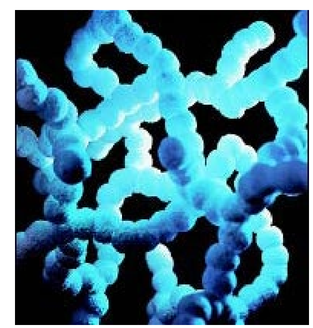


3. Easier particle collection

4. High purity products



5. Stable metastable phases



6. Unique morphology

7. Efficiency: Few and fast unit operations

8. Process design from **first principles**.

Disadvantages of flame synthesis of materials

R. Koirala, SEP, A. Baiker, Synthesis of catalytic materials in flames: opportunities and challenges, *Chemical Society Reviews,* 45, 3053-3068 (2016)

1. **Capital Investment (hoods, controls, filters)**

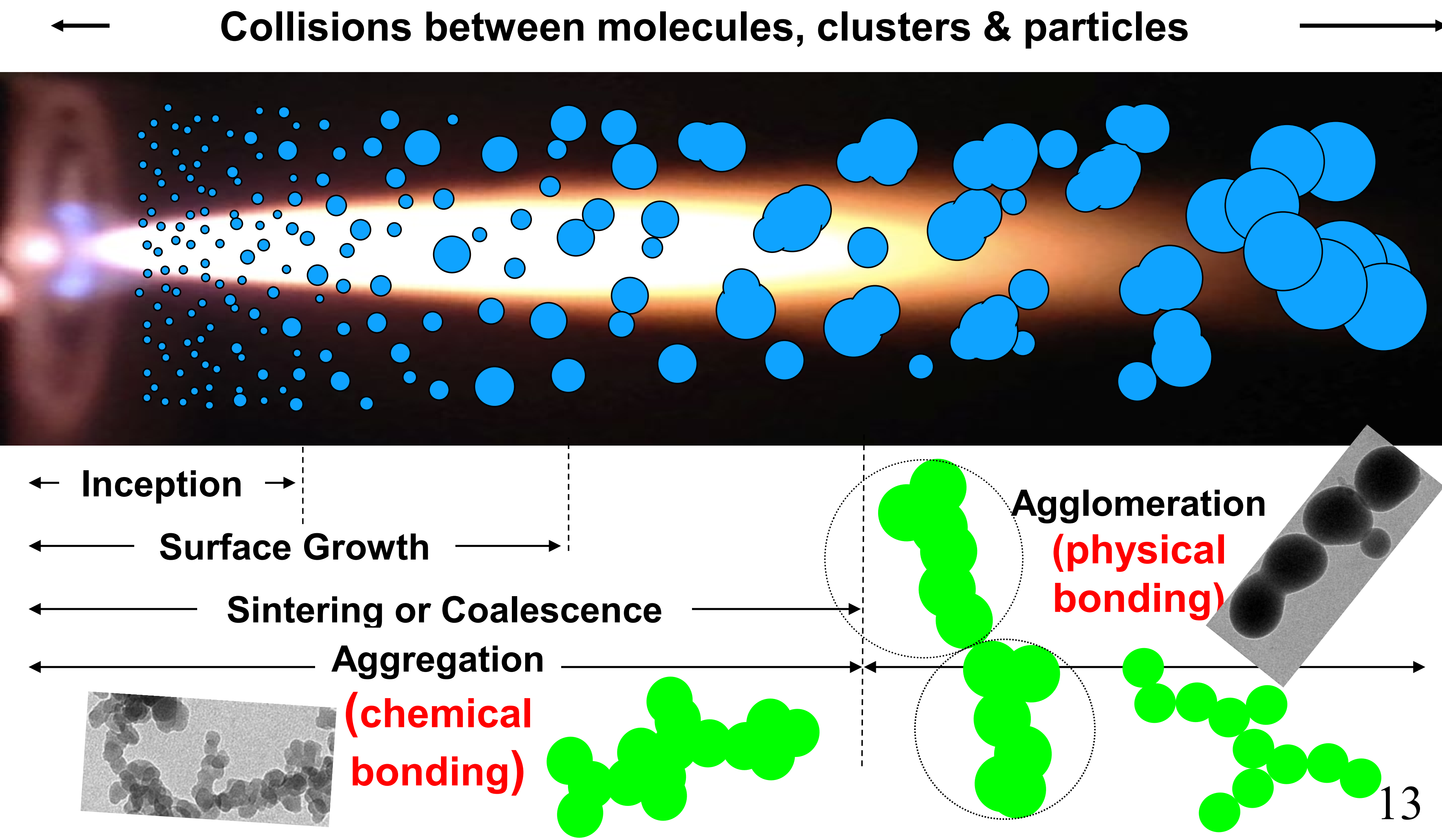
2. **Safety**

3. **Precursor availability, preparation & handling**

4. **Product purity, morphology, uniformity and composition (PICs, crystallinity)**

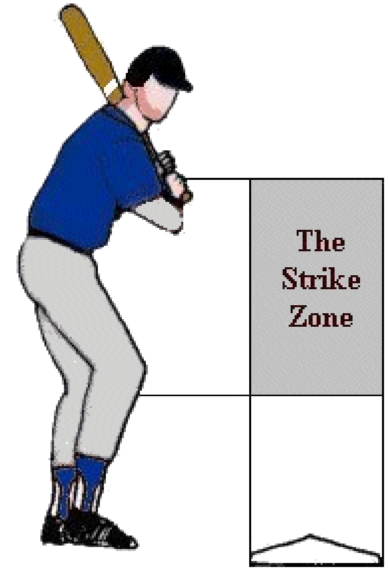
Particle Formation & Growth in Flames

B. Buesser, SEP (2012). *Annual Rev. Chem. Biomol. Eng.*, 3, 103–27



Key Concepts

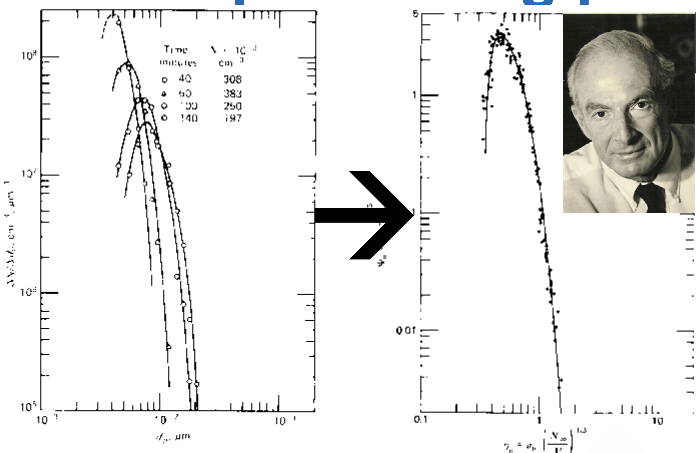
AIChE J. 56, 3028-3035 (2010)



1. High temperature particle residence time (HTPRT)

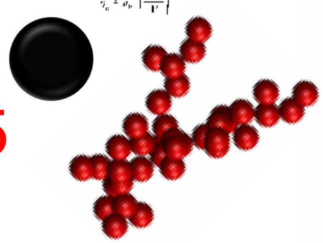
2. Self-preserving particle size distribution

constant polydispersity



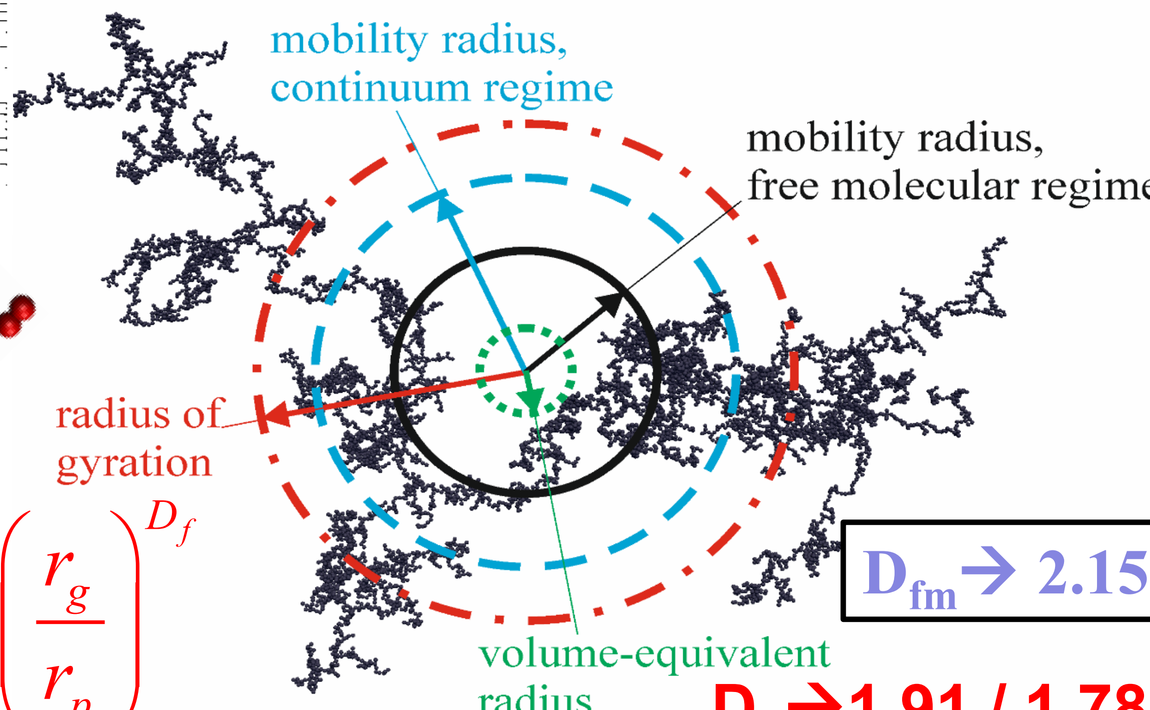
$\sigma_g \rightarrow 1.45$

$\sigma_g \rightarrow 2.3 / 1.95$



3. Fractal-like particle structure

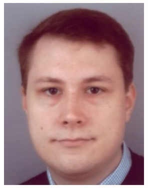
$$\frac{m}{m_p} = k_n \left(\frac{r_g}{r_p} \right)^{D_f}$$

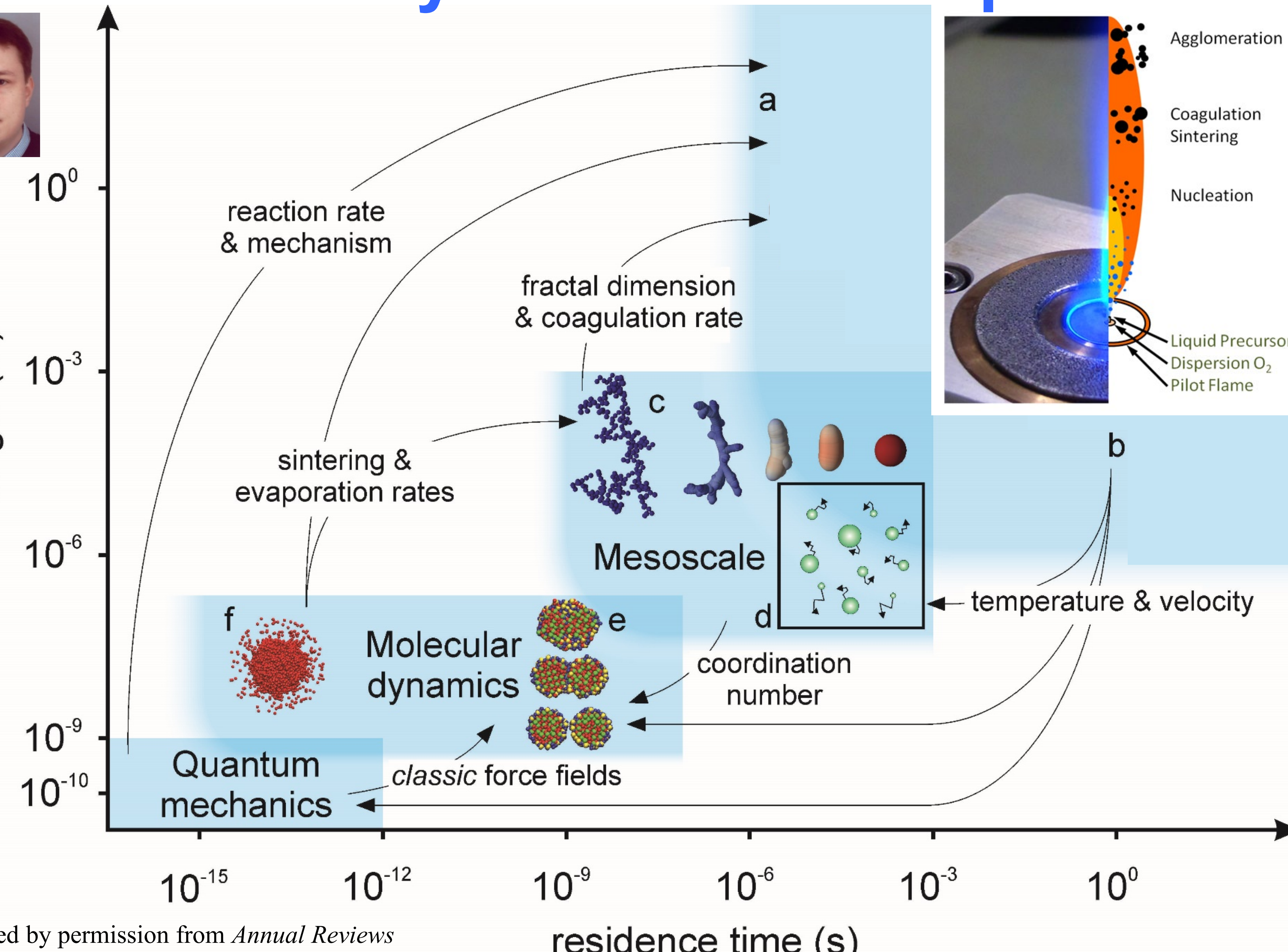


$D_{fm} \rightarrow 2.15$

$D_f \rightarrow 1.91 / 1.78$

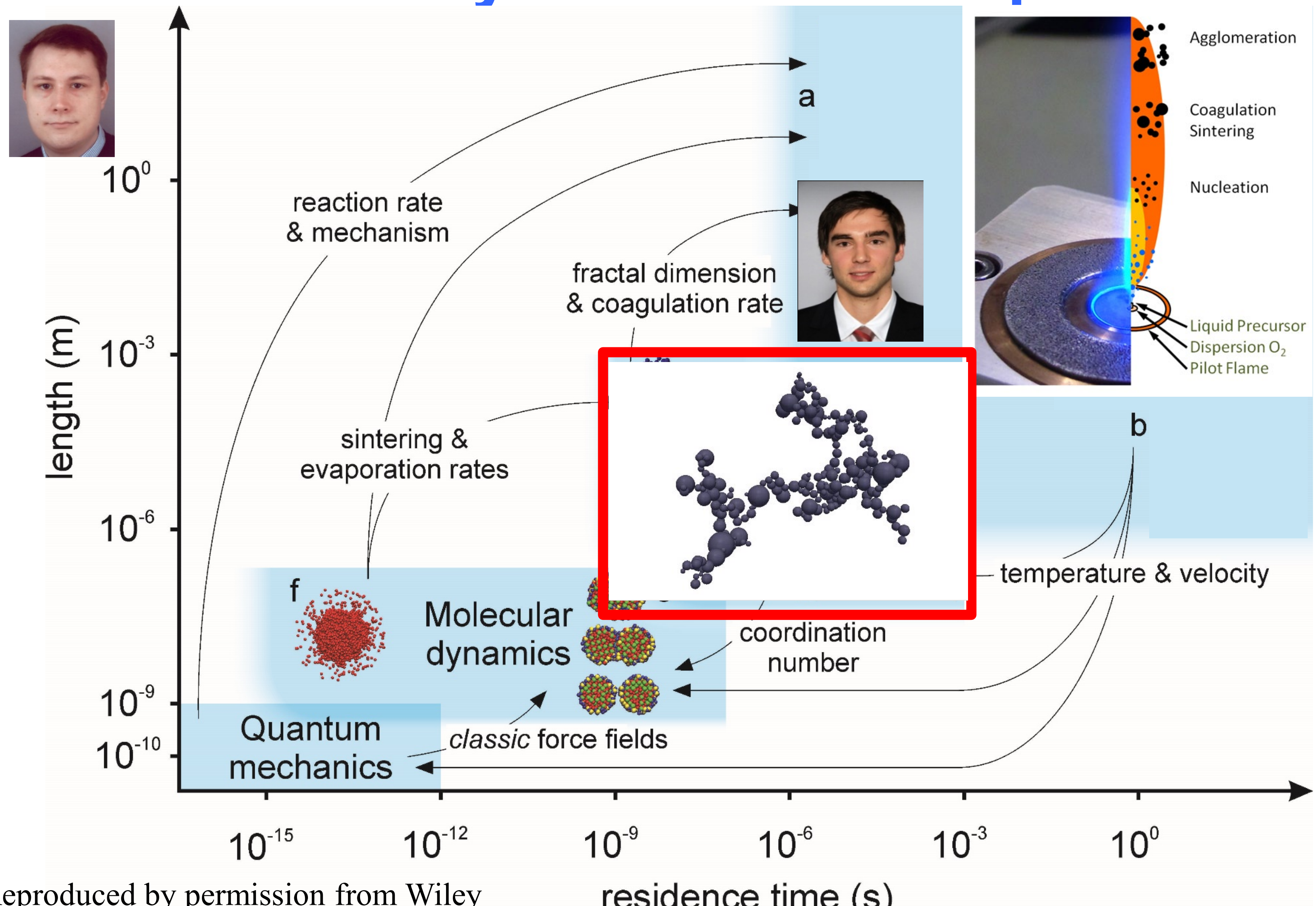
Multi-Scale Design for Aerosol Synthesis of Nanoparticles





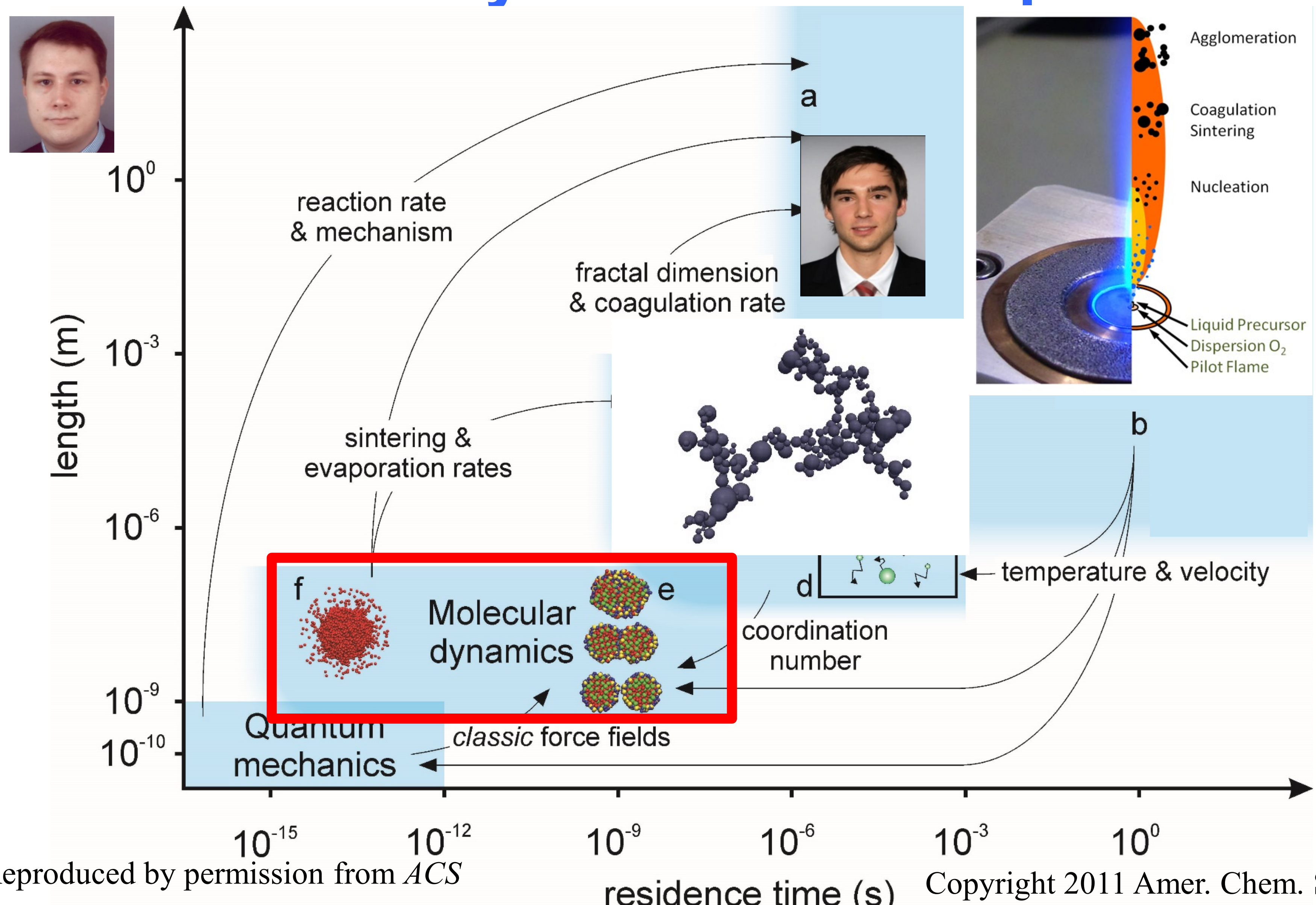
Design of Nanomaterial Synthesis by Aerosol Processes *Annual Rev. Chem. Biomol. Eng.*, 3, 103-127 (2012).

Multi-Scale Design for Aerosol Synthesis of Nanoparticles



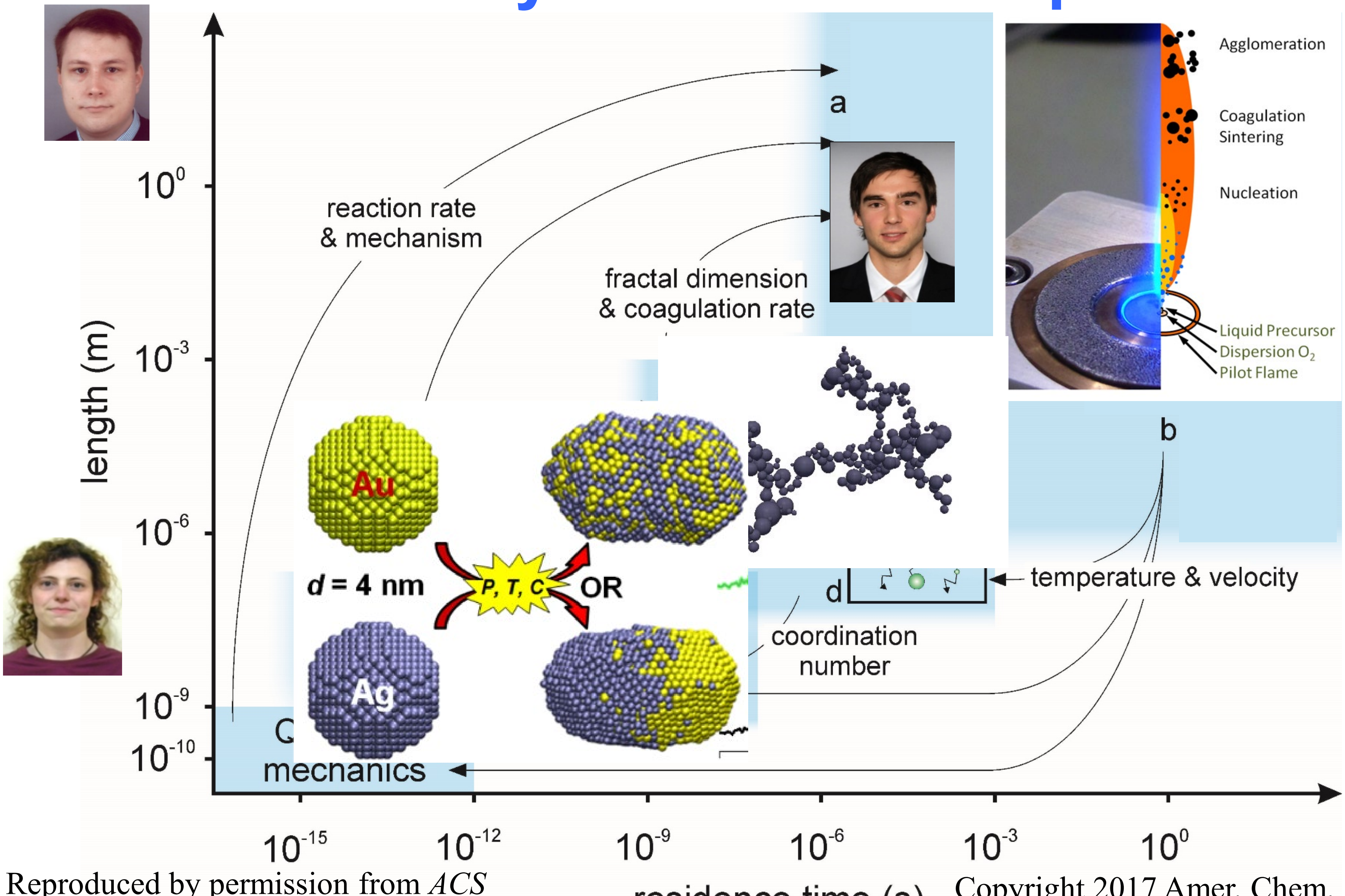
Restructuring of Aggregates and their Primary Particle Size Distribution during Sintering, *AIChE J.* **59,** 1118 - 1126 (2013)

Multi-Scale Design for Aerosol Synthesis of Nanoparticles



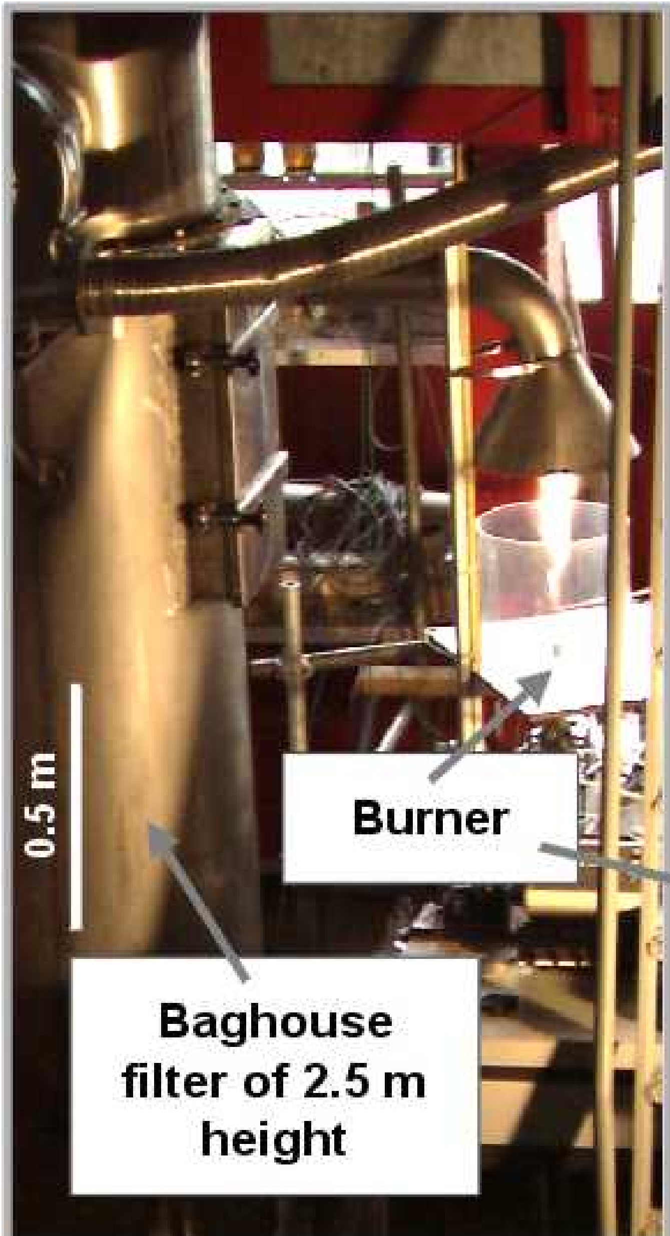
Sintering Rate and Mechanism of TiO_2 by Molecular Dynamics, *J. Phys. Chem. C*, **115**, 11030-11035 (2011)

Multi-Scale Design for Aerosol Synthesis of Nanoparticles



Surface Composition and Crystallinity of Coalescing Silver–Gold Nanoparticles, *ACS Nano,* **11:** 11653-11660 (2017)

Quantitative understanding facilitates a) Scale-up ….



700 g/h SiO_2

Re= 3’000-16’000

H_2-air diffusion flame

H. Kammler, R. Müller, O. Senn, SEP, *AIChE J.*, (2001).

… to 5 kg/h even @ University labs…

R. Strobel, SEP, J. Mater. Chem., 2007, 17, 4743–4756

… and b) drives innovation

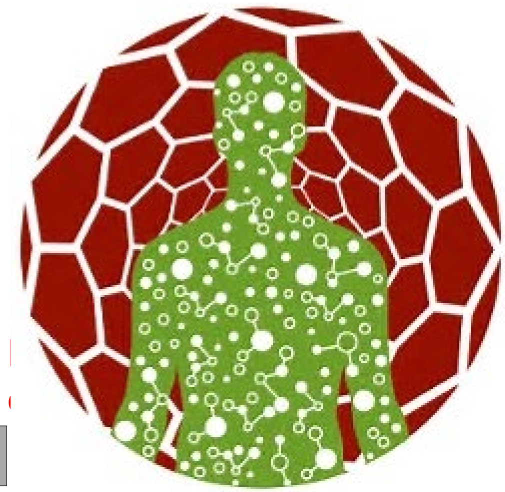
Multicomponent Nanomaterials en mass by Flame Spray Pyrolysis (FSP)

SPP1980
SPRAYSYN

NANOPARTIKELSYNTHESE
IN SPRAYFLAMMEN

A 6-year, 6M Euro program by German NSF for 20 PhD students started in April 2017

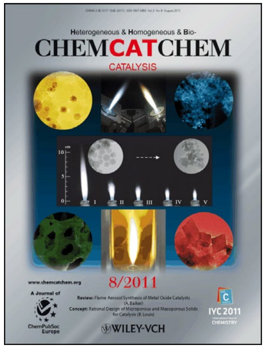
HARVARD
SCHOOL OF PUBLIC HEALTH



NIH – NHIR → $5M

Strobel, R., Stark, W.J., Mädler, L., SEP, Baiker, A., *J. Catal.*, **213**, 296-304, (2003).
Mädler, L., Müller, R., Kammler, H., SEP, *J. Aerosol Sci.* **33**, 369-389 (2002).

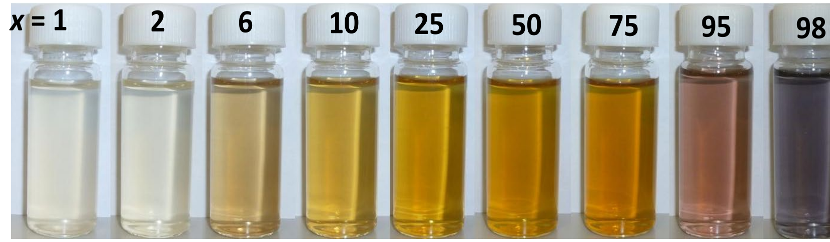
Flame reactor pilot plant, Johnson Matthey Research Center, Reading, UK



History of the Manufacture of Fine Particles in High-Temperature Aerosol Reactors" in *"Aerosol Science and Technology: History and Reviews"*, ed. D.S. Ensor & K.N. Lohr, RTI Press, Ch. 18, pp.475-507, 2011.

New aerosol-made products in the market

Ag/SiO_2 → nanosilver toxicity by ions or particles?



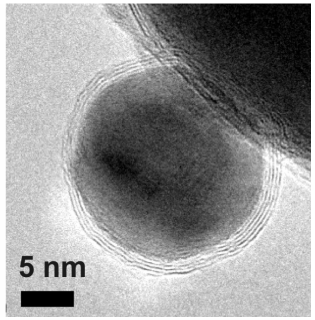
nano-Ag for antibacterial applications

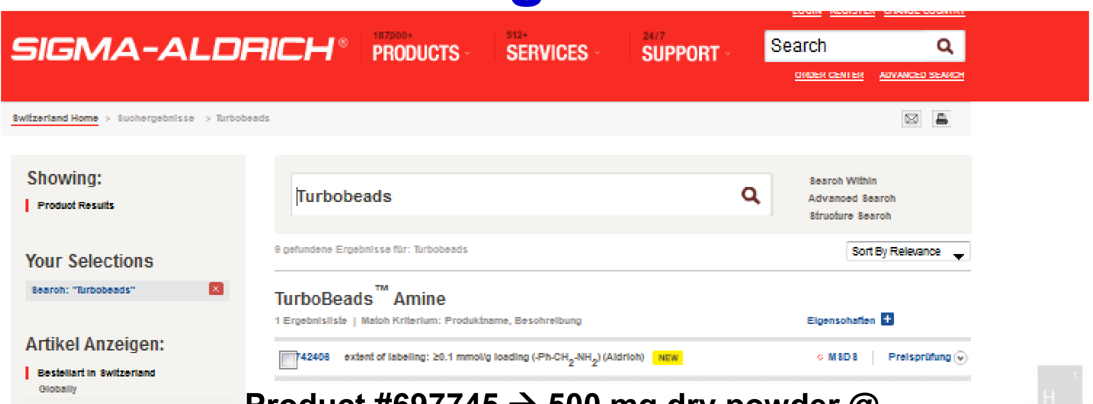
GA Sotiriou, SEP, Environ. Sci. Technol., 44, 5649-5654 (2010)

HEIQ

Bio-magnetic ferrofluids: C-coated Co

100k – 1M$/kg





Product #697745 → 500 mg dry powder @ $105

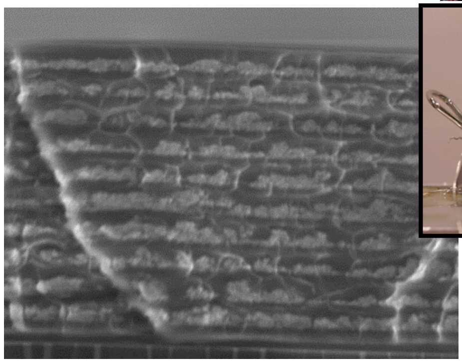
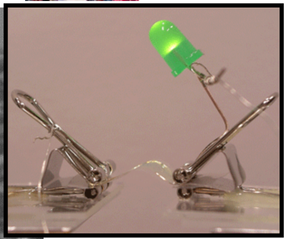
TurboBeads®

avantama®

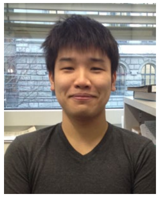
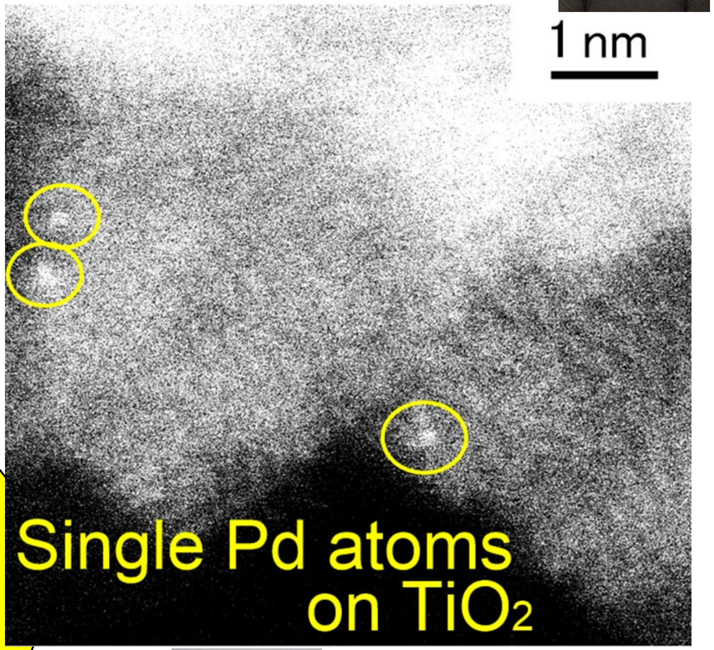
Flame-to-order Nanoparticle Compositions


Dental fillers

Conductive composites

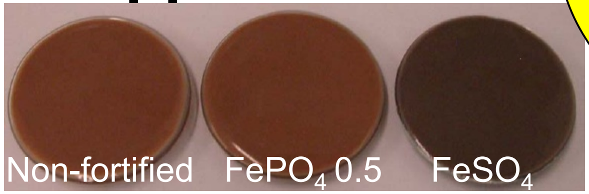




Highly Efficient Photocatalysts

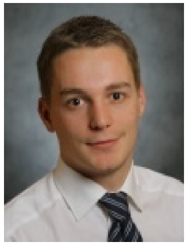
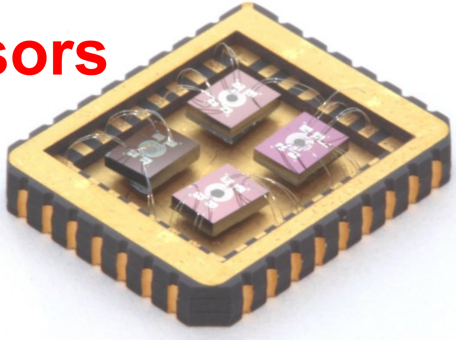



Novel aerosol-made functional materials

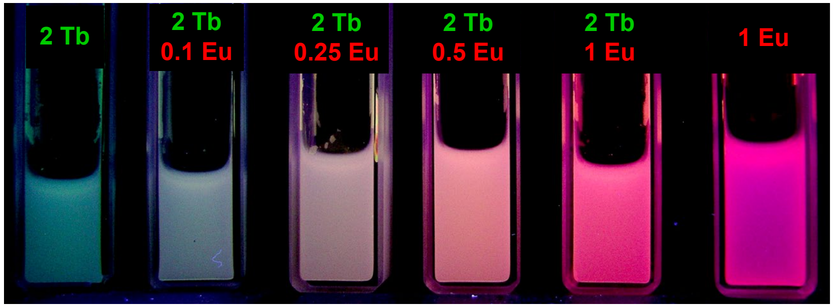
Nutrition Supplements

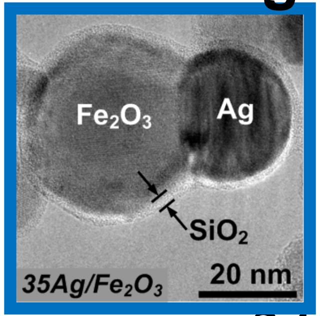
Devices: Breath Sensors

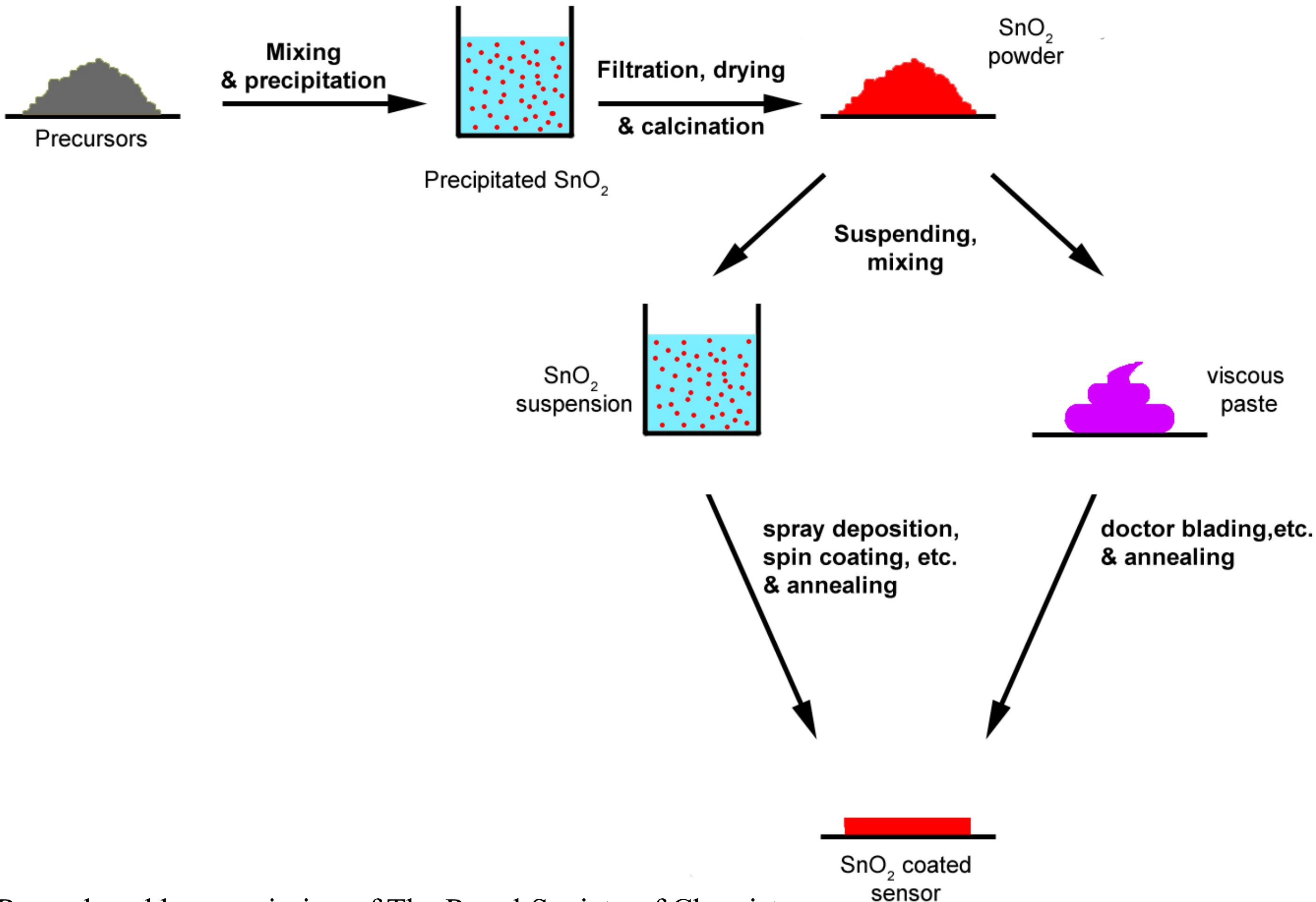
Phosphors for tumor imaging and authentication



SiO_2-coated SPION/Ag

Functional films: one - step synthesis

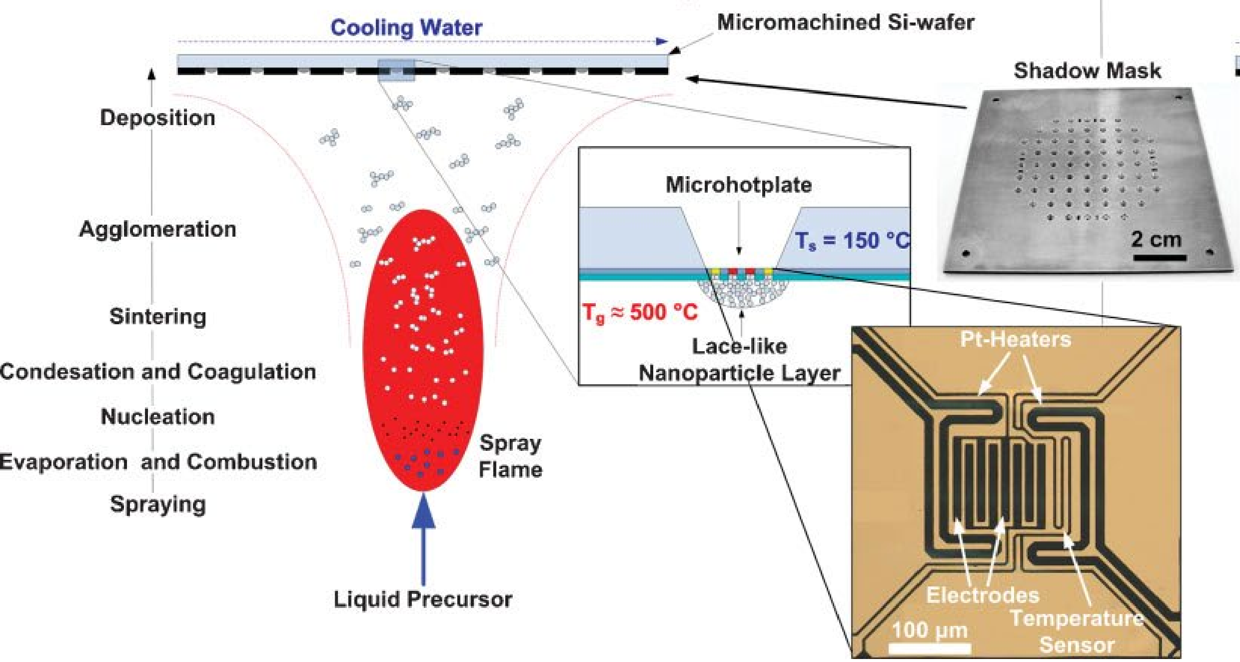


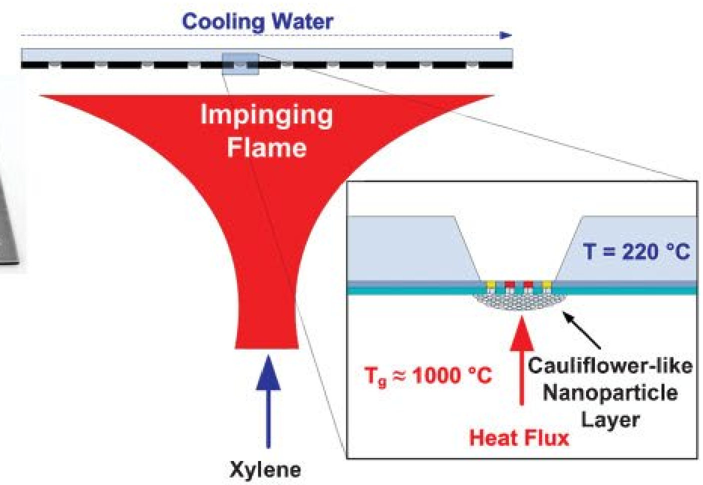
R. Strobel, SEP, *J. Mater. Chem.*, **17,** 4743 - 4756 (2007).

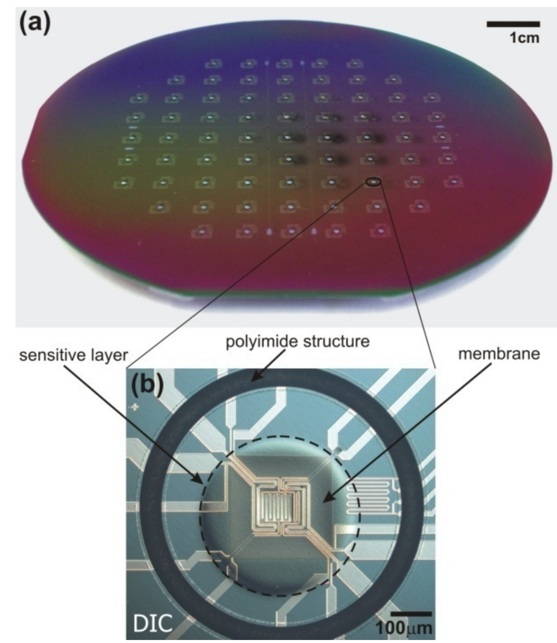
Gas Sensors

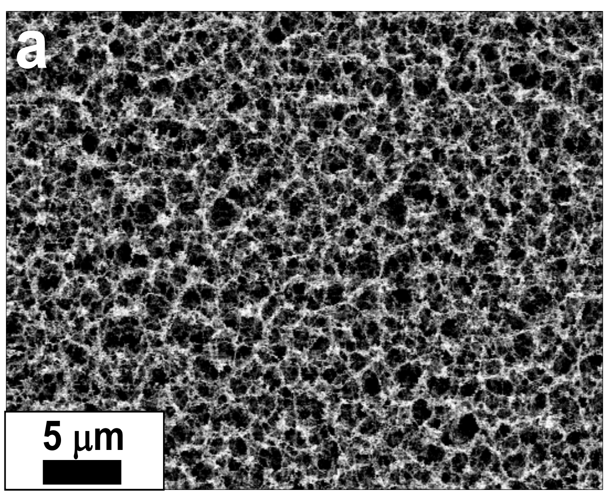
a. Micropatterning

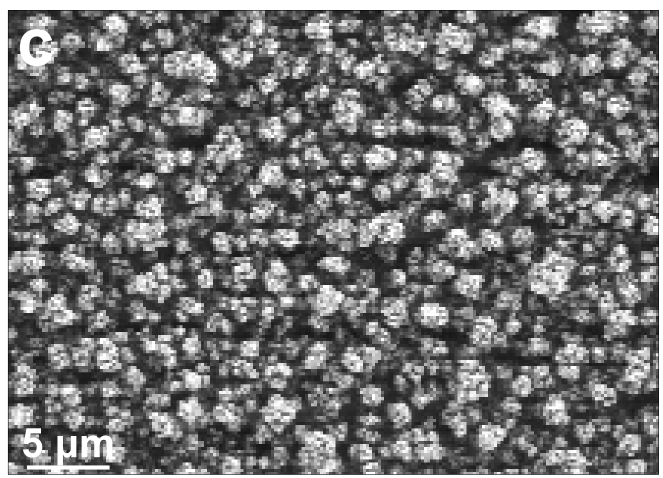
b. In-situ Flame-Annealing











S. Kühne, M. Graf, A. Tricoli, F. Mayer, SEP, A. Hierlemann, *J. Micromech. Microeng.* 18, 035040 (2008**)**.

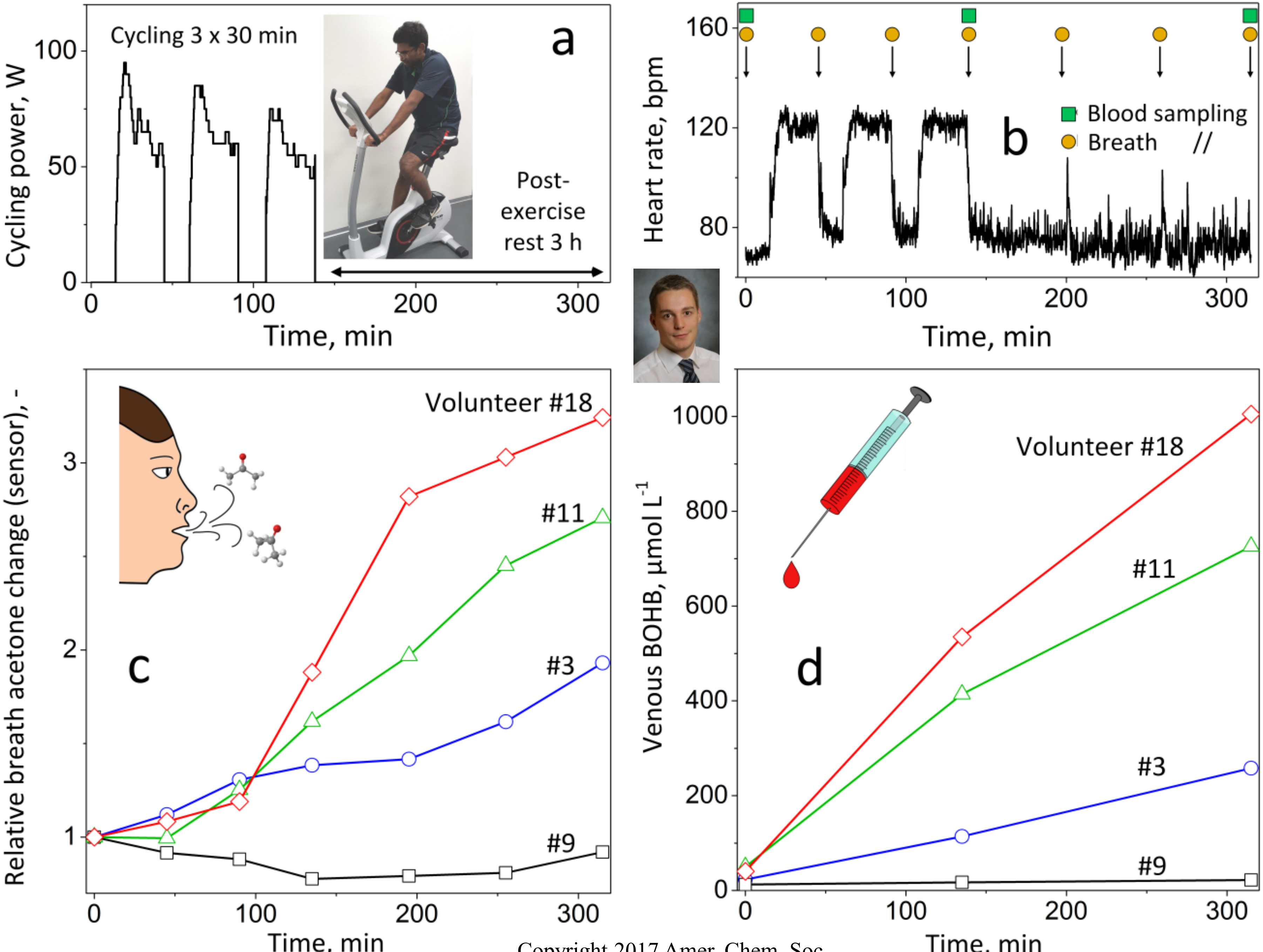
A. Tricoli, M. Graf, F. Mayer, S. Kühne, A. Hierlemann, SEP., *Adv. Mater.*, **20**, 3005-10 (2008).

Industrial prototype for clinical evaluation

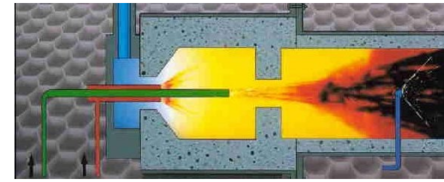
Pictures of actual devices for breath analysis

M. Righettoni, A. Ragnoni, A.T. Güntner, C. Loccioni, SEP, T.H. Risby *J Breath Res.*, 9, 047101 (2015)

A.T. Güntner, N.A. Sievi, S.J. Theodore, T. Gulich, M. Kohler, SEP, *Anal. Chem.*, 89, 10578–10584 (2017).

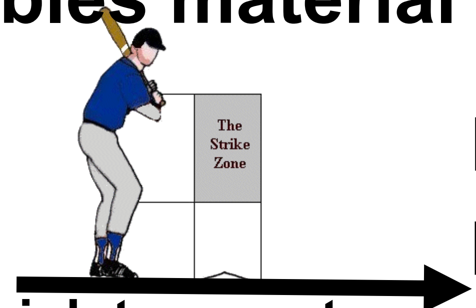


Conclusions



Combustion enables material synthesis @ t/h

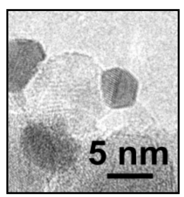
Coagulation, sintering & surface growth

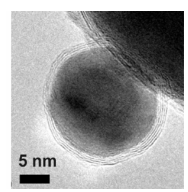


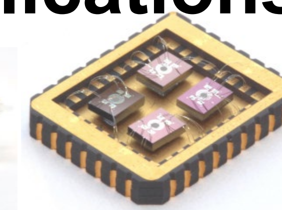
high temperature residence time

Primary & aggregate particle size, structure & composition

High-value materials are produced, mostly by spray combustion, creating new products & applications



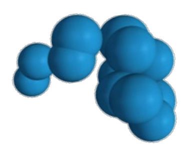




These drive renewed interest on fundamentals:

Combustion variables

→ Particle characteristics



→ Product performance

Selected Books & Reviews

Aerosol Processing of Materials, T.T. Kodas M. Hampden-Smith, Wiley, 1999.
Smoke, Dust & Haze, S.K. Friedlander, Oxford, 2nd ed. 2000

Ulrich, G. D. (1984). Flame Synthesis of Fine Particles. *Chem. Eng. News*, **62** (32), 22 Material Synthesis in Aerosol Reactors. *Chem. Eng. Prog.*, **85** (5), 62-66

Rosner, D. E. (1997). Combustion synthesis and materials processing *Chem. Eng. Edu.*, **31**, 228-235.

Swihart, M.T. (2003). Vapor-phase synthesis of nanoparticles. *Curr. Opin. Colloid Interface Sci.*, **8**, 127-133.

Flame aerosol synthesis of smart nanostructured materials. *J. Mater. Chem.*, **17**, 4743 - 4756 (2007).

Roth, P. (2007). Particle synthesis in flames. *Proc. Comb. Inst.*, **31**, 1773-1788.

Vollath D.(2007). Plasma Synthesis of Nanoparticles. *KONA,* **25**, 39–55.

Phillips, J., Luhrs, C. C., Richard, M. (2009). Review: Engineering Particles Using the Aerosol-through-Plasma Method. *IEEE Trans. Plasma Sci.* **37**, 726-739.

Athanassiou, E. K., Grass, R. N., & Stark, W. J. (2010). Chemical Aerosol Engineering as a Novel Tool for Material Science: From oxides to Salt and Metal Nanoparticles. A*erosol. Sci. Technol.*, **44,** 161-172.

Aerosol-based Technologies in Nanoscale Manufacturing: from Functional Materials to Devices through Core Chemical Engineering, (2010) *AIChE J.*, **56**, 3028-3035

B. Buesser, S.E. Pratsinis, Design of Nanomaterial Synthesis by Aerosol Processes, (2012) *Annual Rev. Chem. Biomol. Eng.,* **3**, 103–27

R. Koirala, S.E. Pratsinis, A. Baiker, "Synthesis of catalytic materials in flames: opportunities and challenges", *Chem. Soc. Rev.,* **45**, 3053-3068 (2016).

A.T. Güntner, S. Abegg, K. Königstein, P.A. Gerber, A. Schmidt-Trucksäss, S.E. Pratsinis, Breath Sensors for Health Monitoring, ACS *Sensors*, **4**, 268-280 (2019).

V.G. Mavrantzas, S.E. Pratsinis, The impact of molecular simulations in gas-phase manufacture of nanomaterials, *Curr. Opinion Chem. Eng.*, **23**, 174–183 (2019).