

...spread the fragrance of knowledge...

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

...Combustion Synthesis of Materials

1. Overview

Prof. Sotiris E. Pratsinis

Particle Technology Laboratory

Department of Mechanical and Process Engineering,

ETH Zürich, Switzerland

www.ptl.ethz.ch

Sponsored by

European Research Council, DuPont, Dow, Millennium,

U.S. and Swiss National Science Foundation,

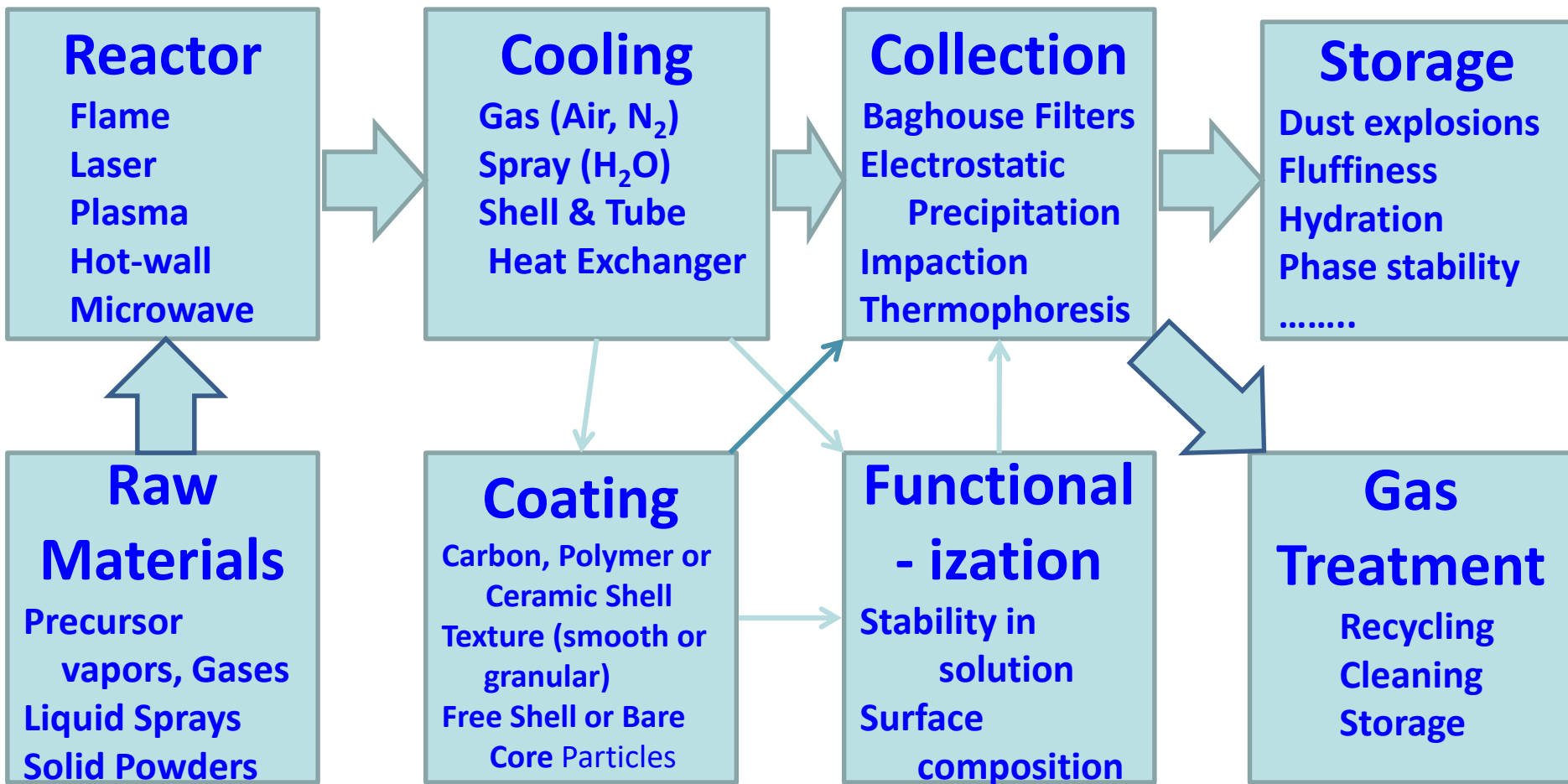
Swiss Commission for Technology and Innovation

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, TiCl₄
Fumed Silica	0.2	2	Flame, SiCl₄
Zinc Oxide	0.6	0.7	Hot –Wall, Zn
Filamentary Ni	0.04	~0.1	Hot-Wall, Ni(CO)₄
Fe, Pt, Zn₂SiO₄/Mn	~0.02	~1	Hot-Wall, Spray...

Reproduced by permission from Elsevier

Process Steps during Aerosol Synthesis of Materials



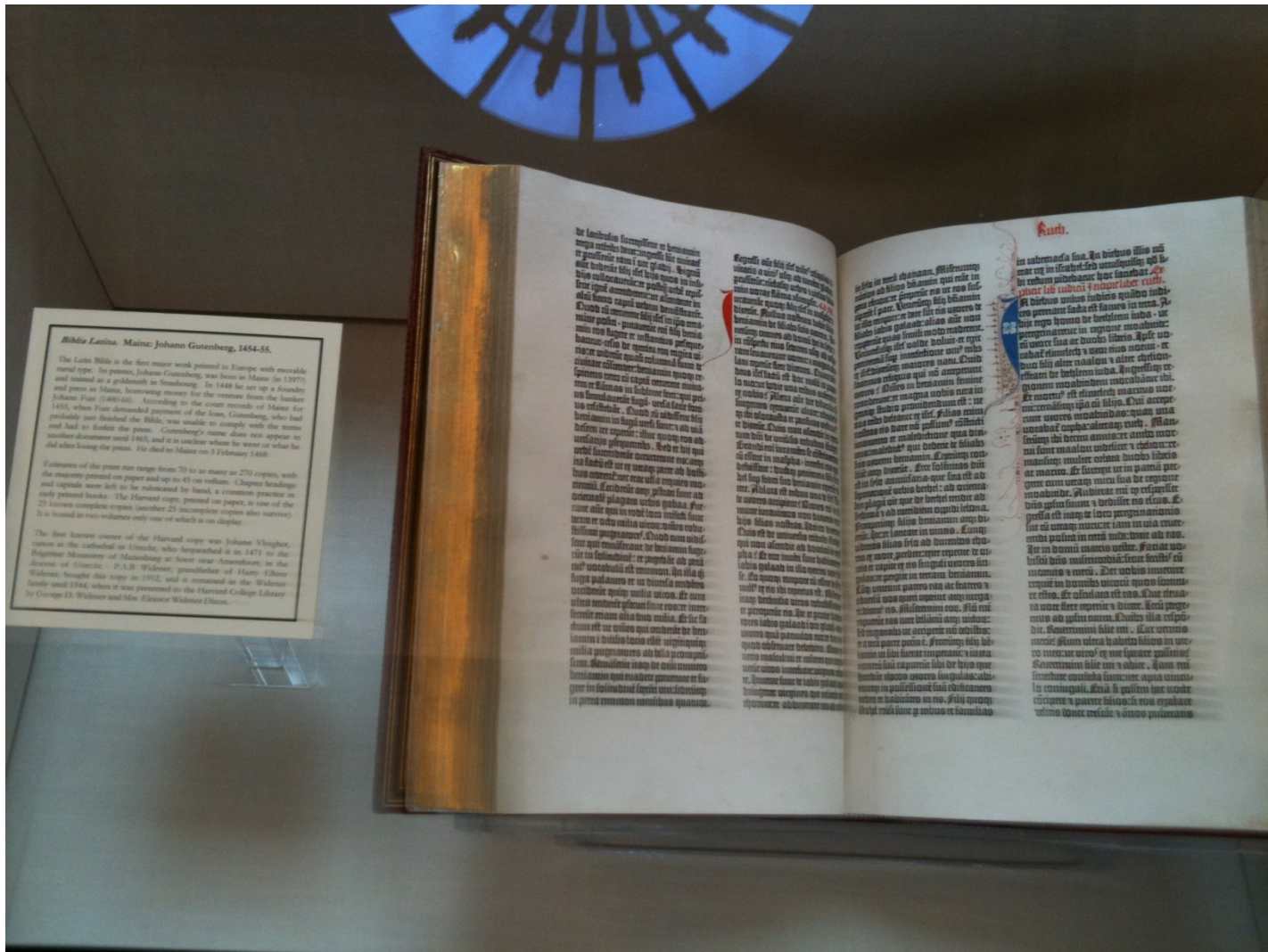
Reproduced by permission from *Annual Reviews*

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**

The Bible of Gutenberg



Biblia Latina. Mainz: Johann Gutenberg, 1454-55.

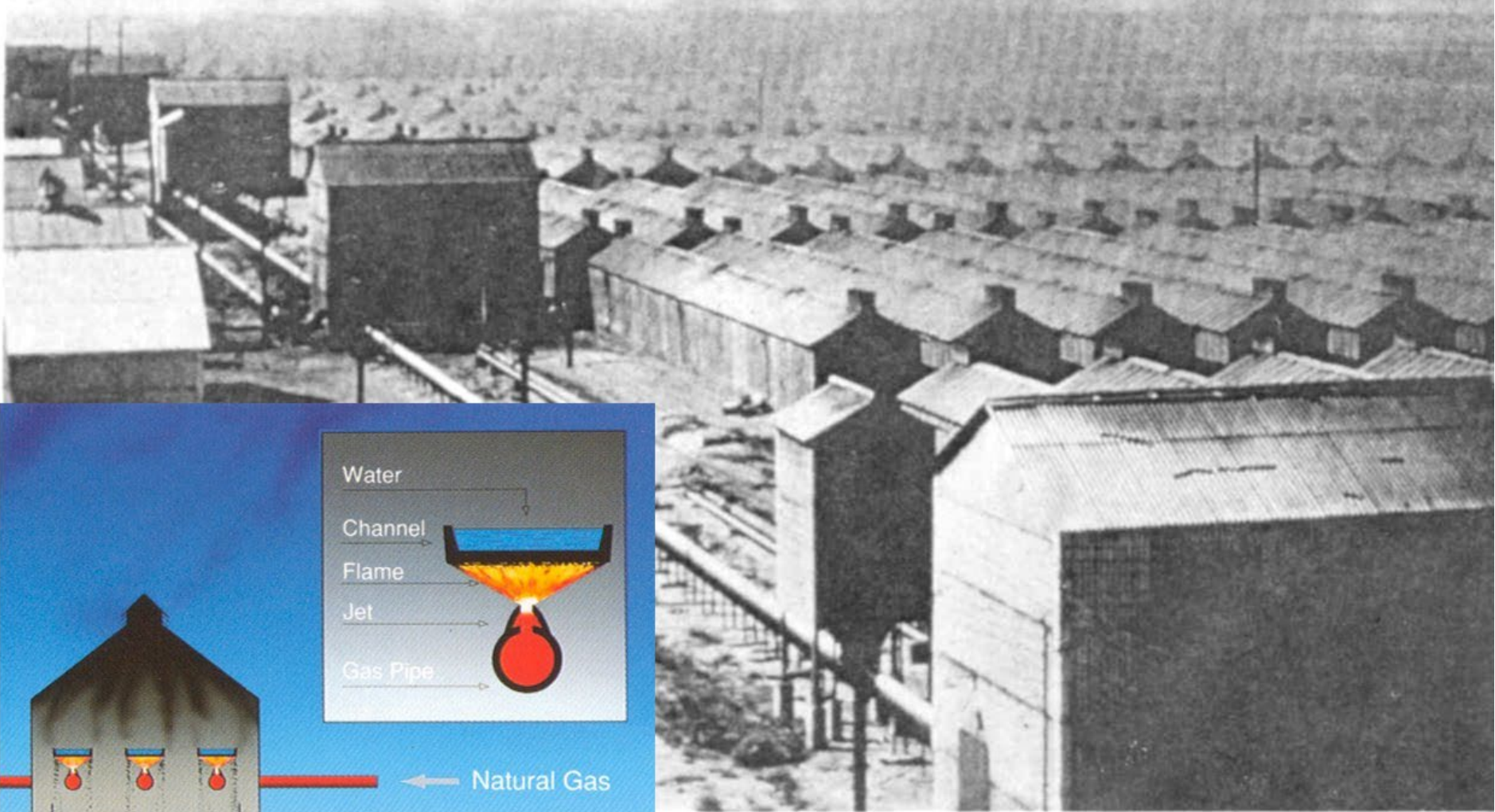
The Latin Bible is the first mass work printed in Europe with movable metal type. Its printer, Johann Gutenberg, was born in Mainz (in 1397?) and trained as a goldsmith in Strasbourg. In 1448 he set up a foundry in Mainz, borrowing money for the venture from the banker Johann Fust (1400-66). According to the court records of Mainz for 1455, when Fust demanded payment of the loan, Gutenberg, who had probably just finished the Bible, was unable to comply with the terms and had to forfeit the press. Gutenberg's name does not appear in another document until 1465, and it is unclear when he went or what he did after leaving the press. He died in Mainz on 3 February 1468.

Estimates of the press run range from 70 to as many as 270 copies, with the majority printed on paper and up to 45 on vellum. Chapter headings and capitals were left to be rubricated by hand, a common practice in early printed books. The Harvard copy, printed on paper, is one of the 23 known complete copies (another 25 incomplete copies also survive). It is bound in two volumes only one of which is on display.

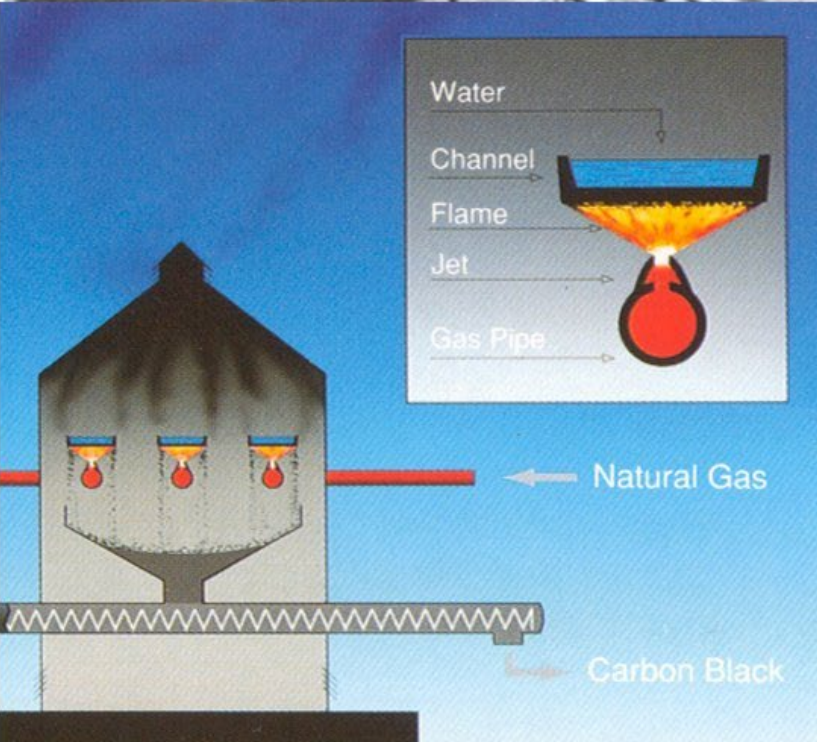
The first known owner of the Harvard copy was Johann Vheghar, canon at the cathedral in Utrecht, who purchased it in 1471 in the Beguine Monastery of Marburg in South west Amsterdam, in the diocese of Utrecht. P.A.B. Widener, grandfather of Harry Elmer Widener, bought this copy in 1912, and it was presented to the Widener family until 1944, when it was purchased by the Harvard College Library by George D. Widener and Mrs. Eleanor Widener Deane.

Library, Harvard University, Cambridge, MA

Channel Plant, Texas Panhandle, 1940's



Columbian Chemicals, 1994



Degussa, 1996

Zwischen 4 und 20 Millimikron
bewegt sich die Teilchengröße von



dem neuen Hilfsmittel
für die Lackindustrie

Bitte, fordern Sie den neuen Prospekt an

DEGUSSA
ABT. RUSS · FRANKFURT/M.

Advertisement in Farbe & Lacke (1949) of SiO₂ 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

Tires (~30 wt%)



Carbon Black (\$10B)



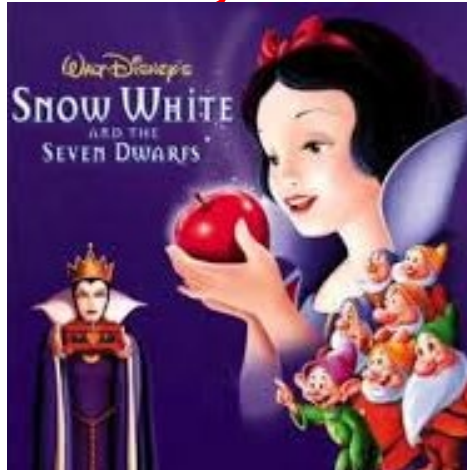
Inks



Courtesy of Dupont

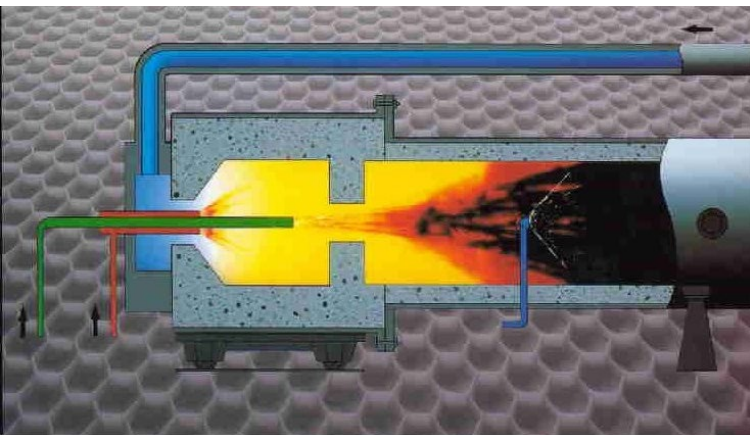
25 t/h, Re 10⁶

TiO₂ (\$5 B)



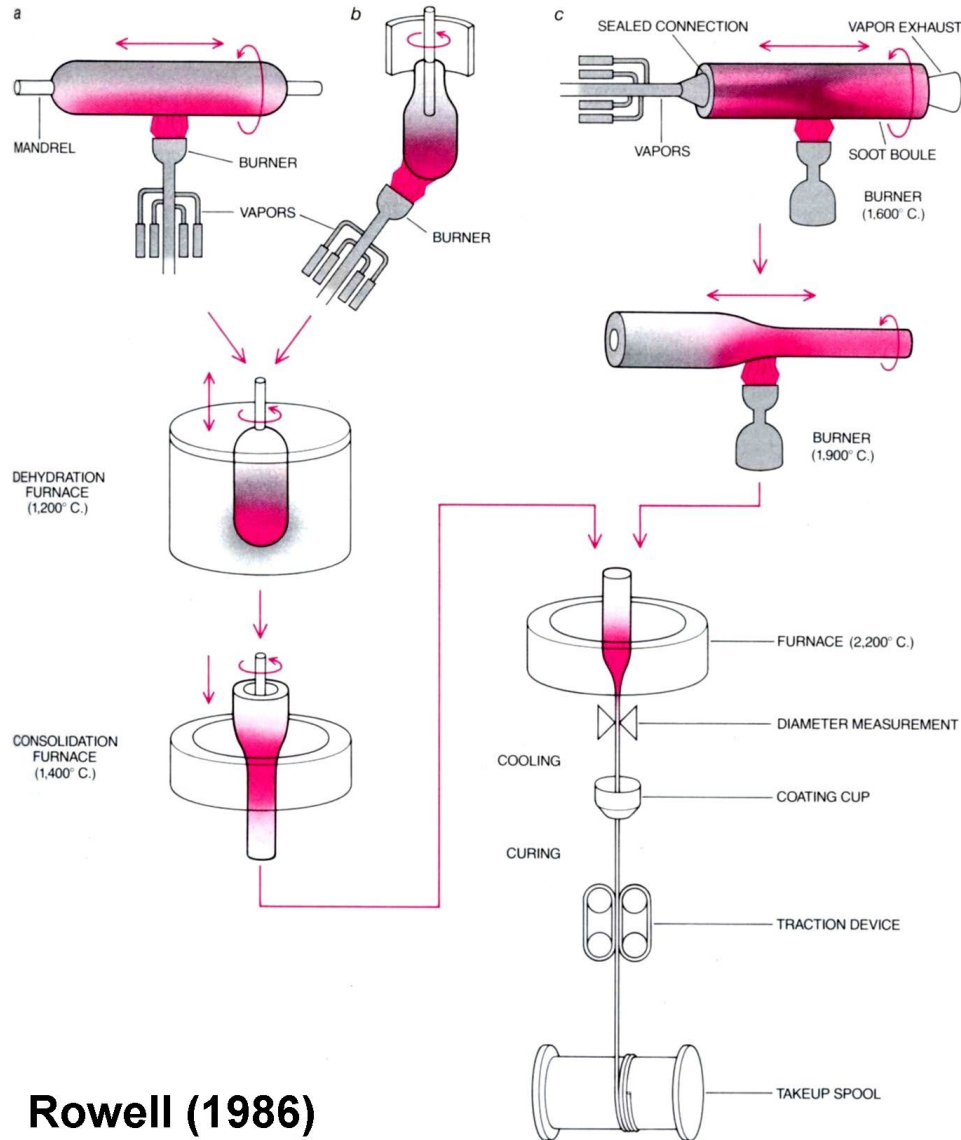
Courtesy of Cabot

SiO₂ (\$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**

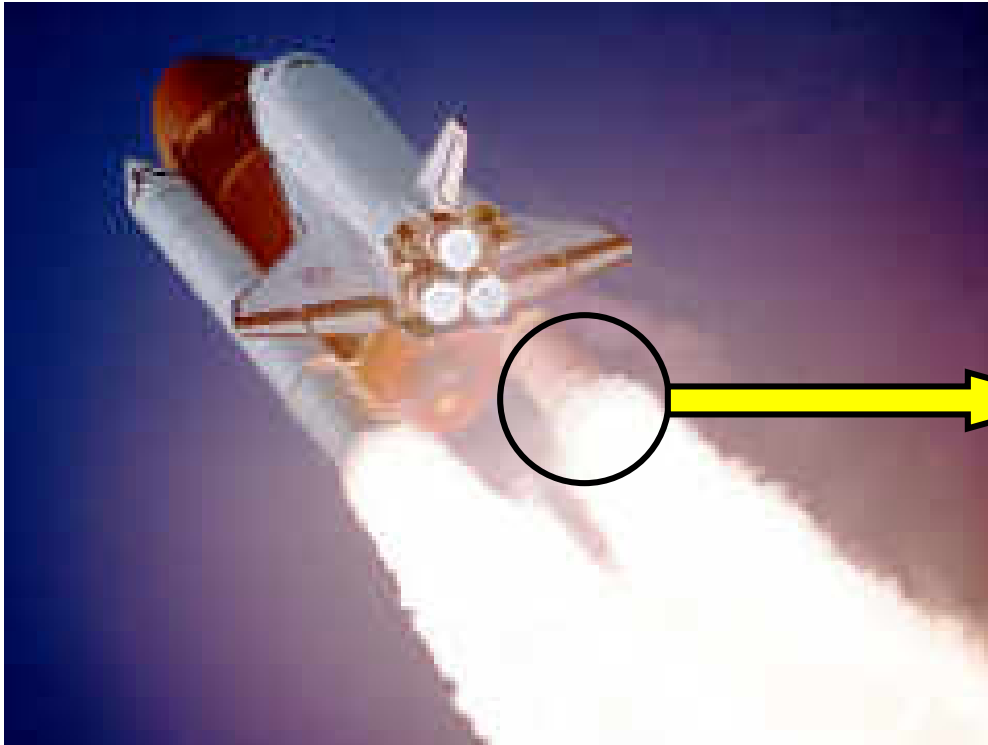
Rowell (1986)

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).

Reproduced by permission of George Retschek, illustrator for Scientific American

A rough analogy to flame aerosol reactors



PTL, ETH Zurich

... just well attached to the ground !

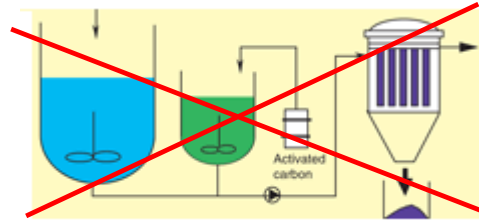
Advantages of flame-made materials

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



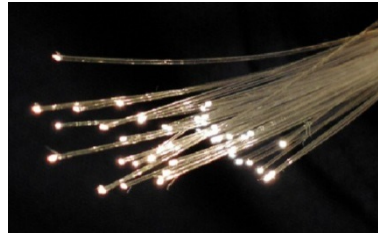
1. Scalability

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

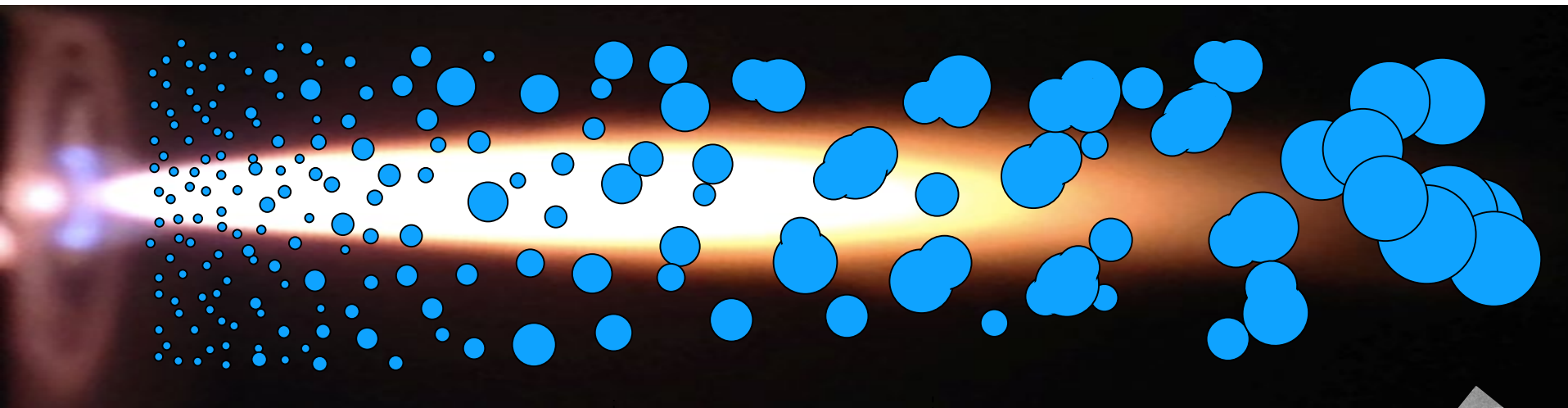
R. Koirala, SEP, A. Baiker, Synthesis of catalytic materials in flames: opportunities and challenges, *Chemical Society Reviews*, 45, 3053-3068 (2016)

- 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

← Collisions between molecules, clusters & particles →

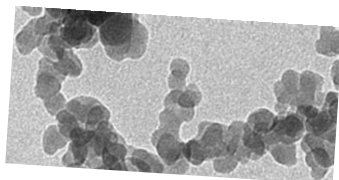


← Inception →

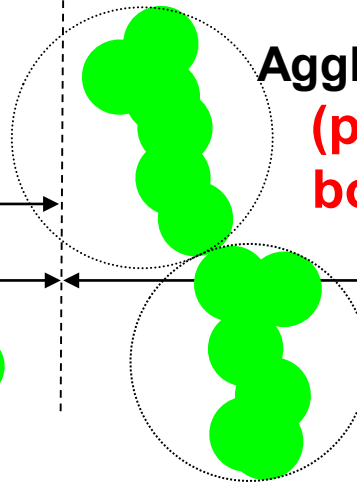
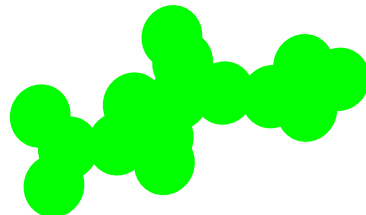
← Surface Growth →

← Sintering or Coalescence →

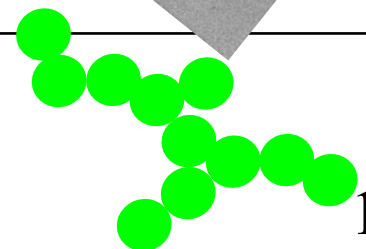
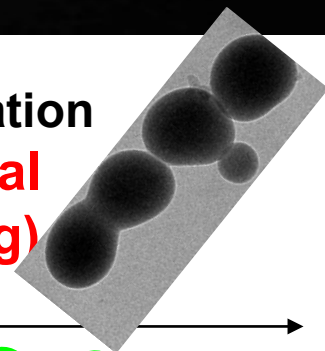
← Aggregation →



(chemical bonding)



Agglomeration
(physical bonding)



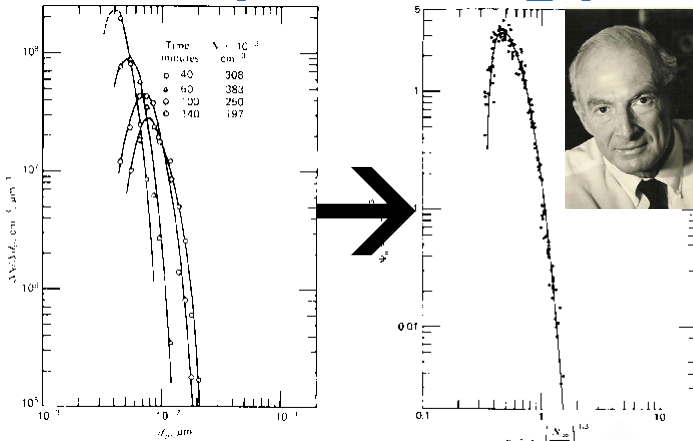
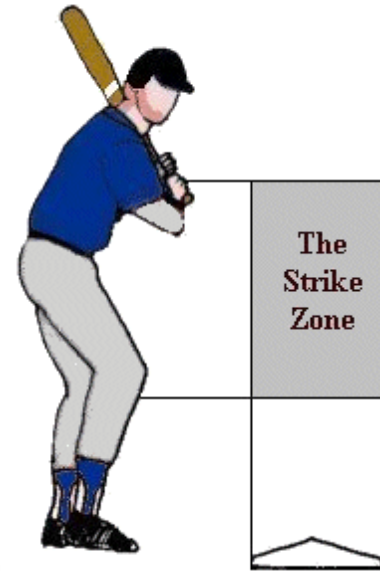
Key Concepts

AICHE J. 56, 3028-3035 (2010)

1. High temperature particle residence time (HTPRT)

2. Self-preserving particle size distribution

constant polydispersity

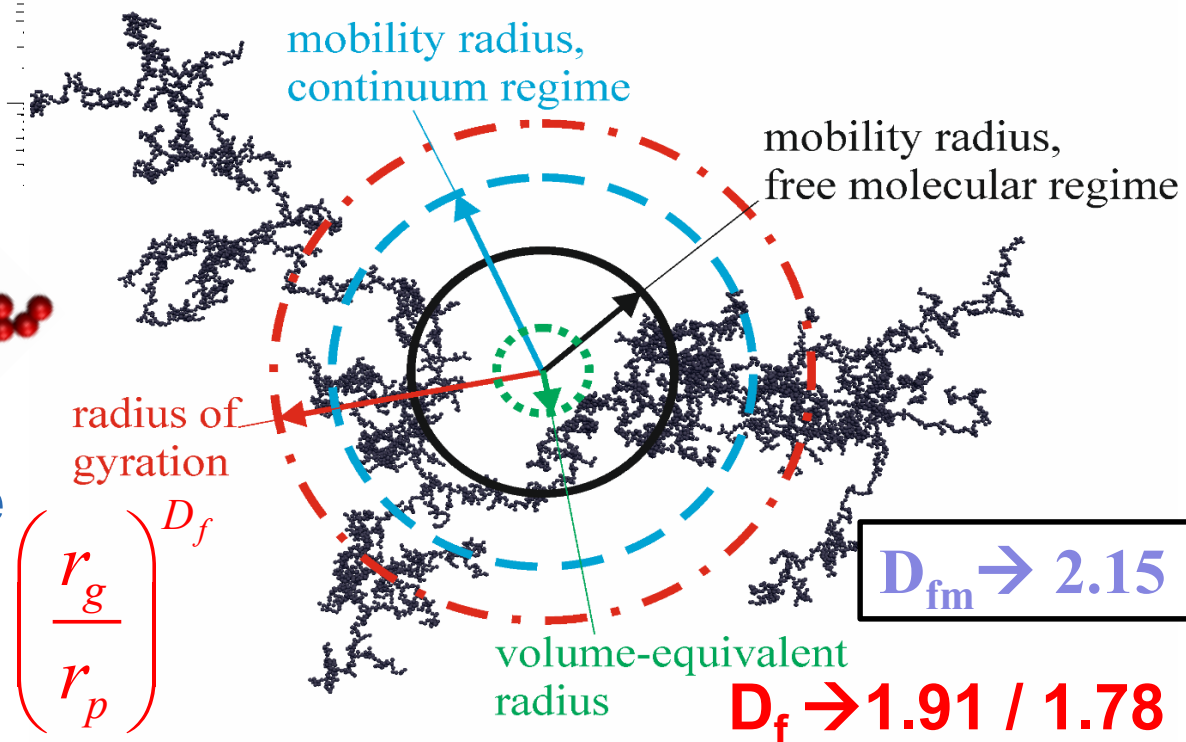


$\sigma_g \rightarrow 1.45$
 $\sigma_g \rightarrow 2.3 / 1.95$

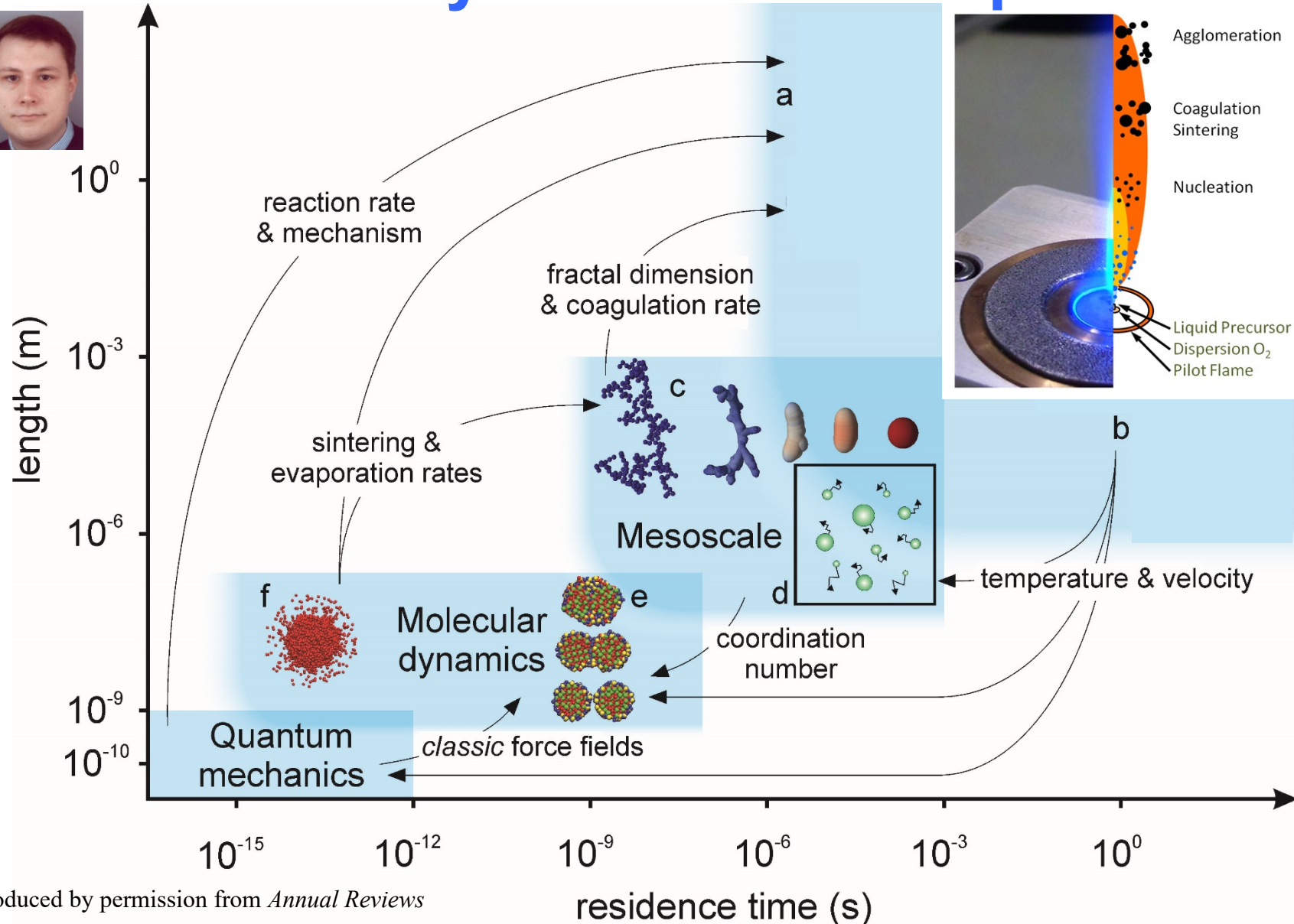


3. Fractal-like particle structure

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



Multi-Scale Design for Aerosol Synthesis of Nanoparticles

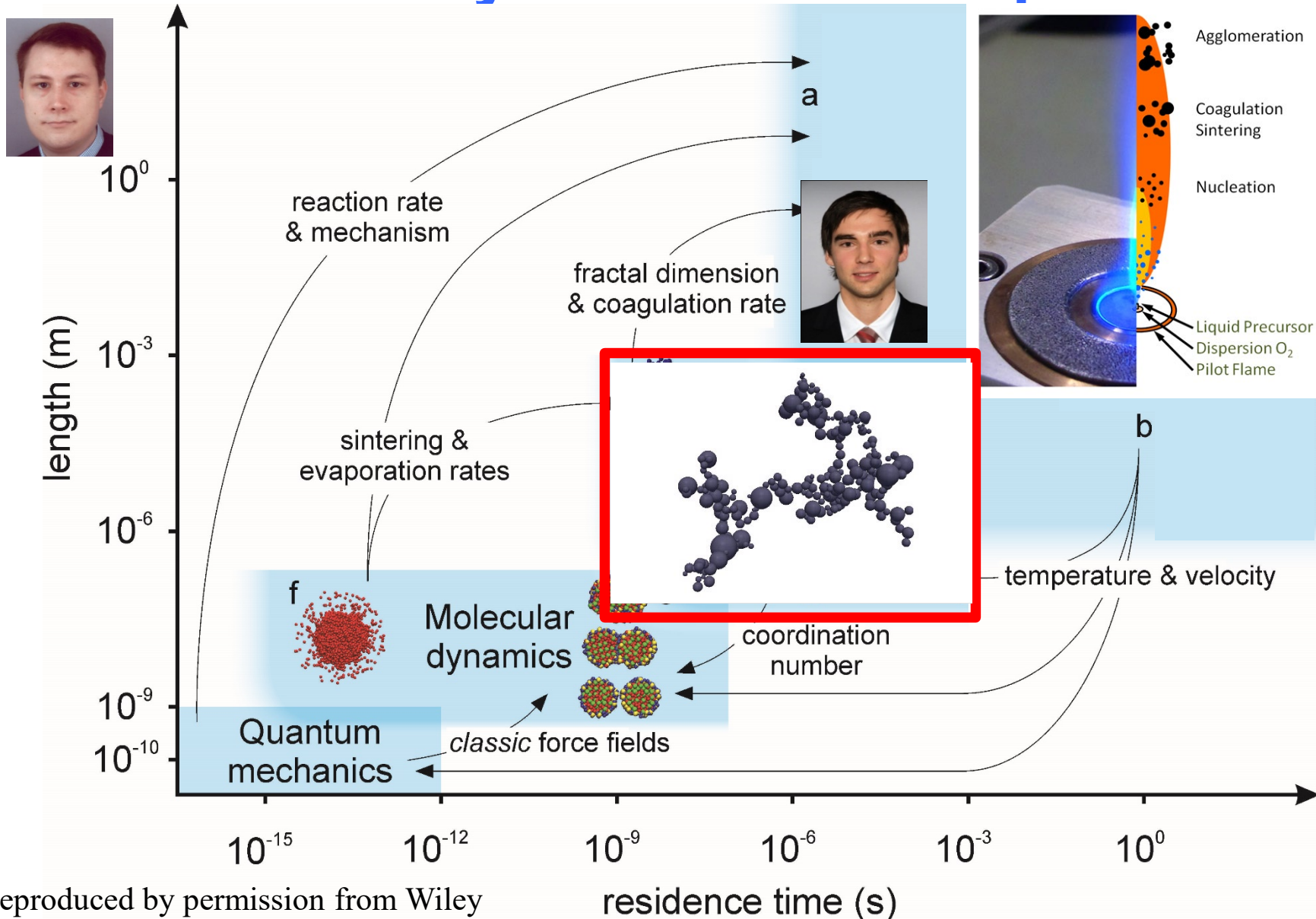


Reproduced by permission from *Annual Reviews*

Design of Nanomaterial Synthesis by Aerosol Processes

Annual Rev. Chem. Biomol. Eng., 3, 103-127 (2012).

Multi-Scale Design for Aerosol Synthesis of Nanoparticles

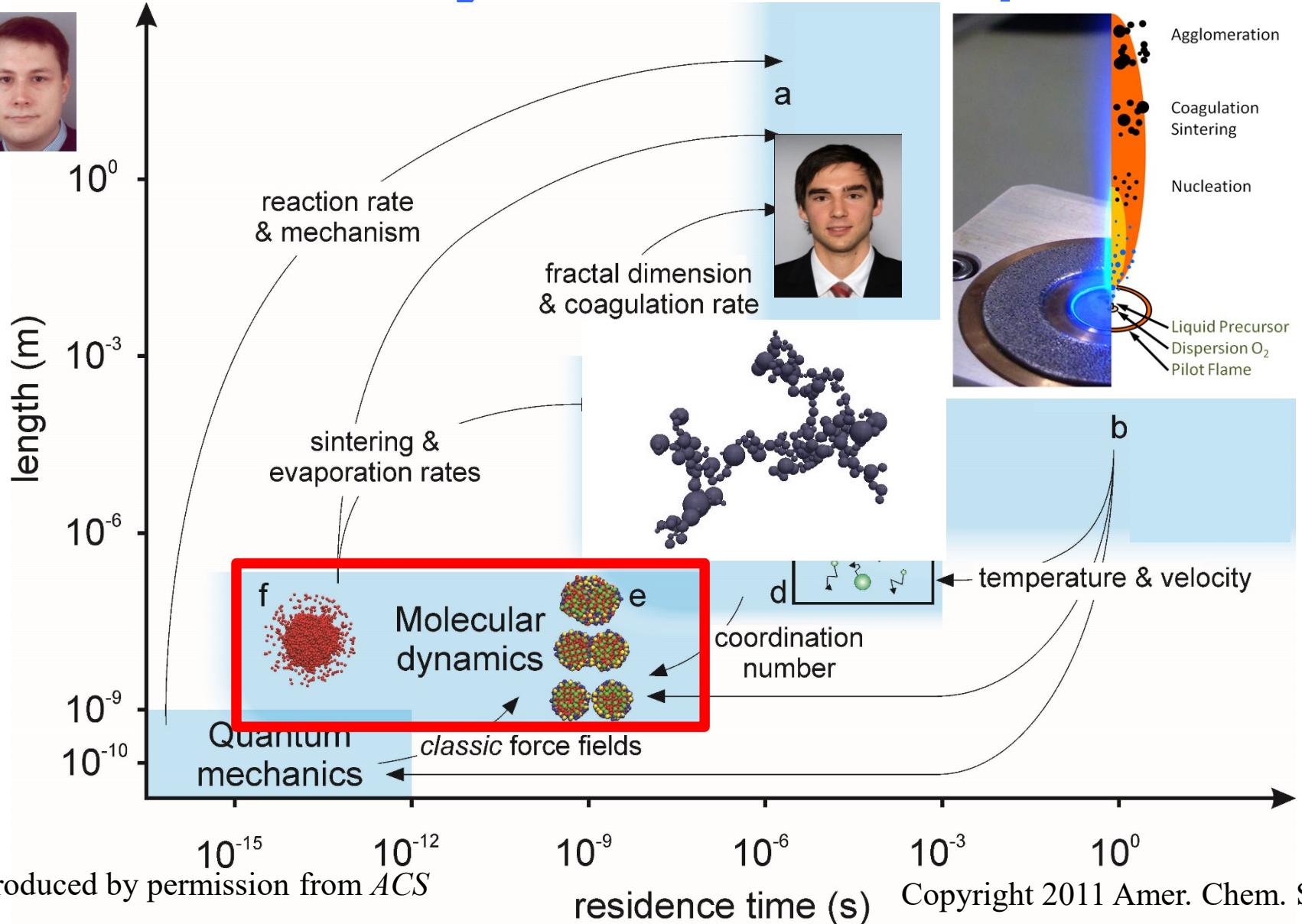


Reproduced by permission from Wiley

residence time (s)

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

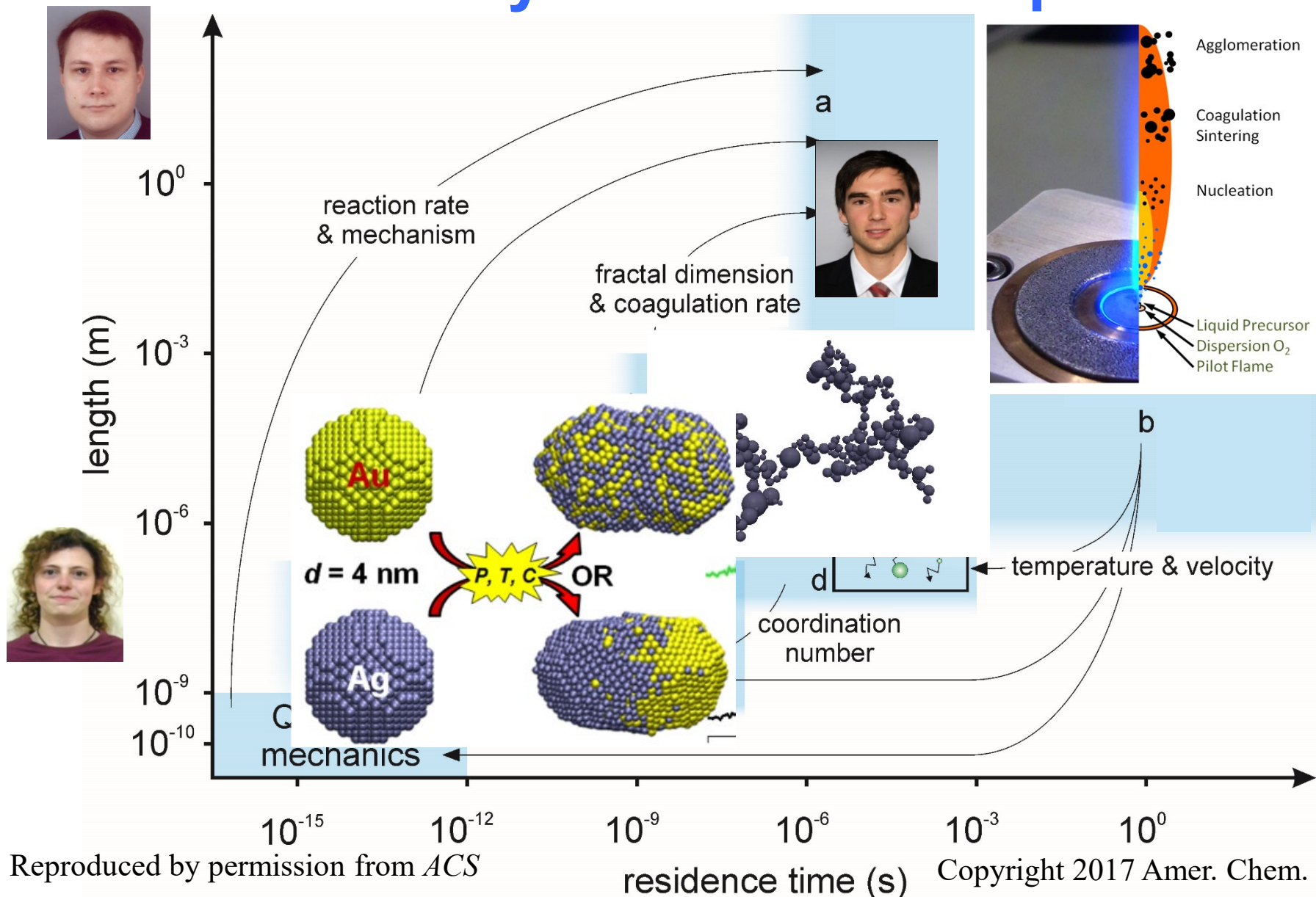


Reproduced by permission from ACS

Copyright 2011 Amer. Chem. Soc.

Sintering Rate and Mechanism of TiO₂ by Molecular Dynamics, *J. Phys. Chem. C*, **115**, 11030-11035 (2011)

Multi-Scale Design for Aerosol Synthesis of Nanoparticles



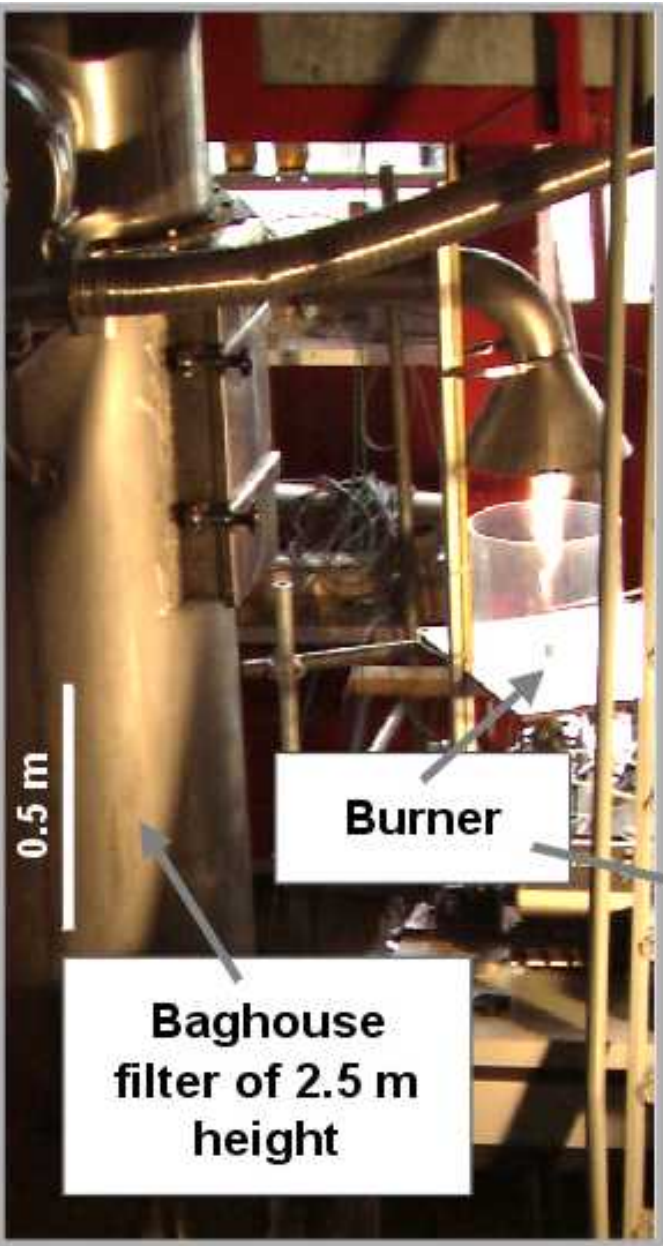
Reproduced by permission from ACS

Copyright 2017 Amer. Chem. Soc.

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

Quantitative understanding facilitates a) Scale-up

700 g/h SiO₂
Re= 3'000-16'000



H₂-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



Copyright 2007 Royal Soc. Chem.



... 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



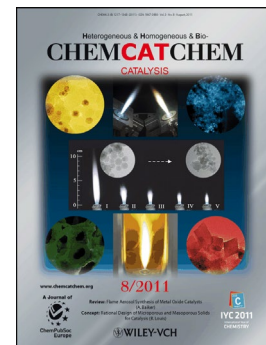
HARVARD
SCHOOL OF PUBLIC HEALTH



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

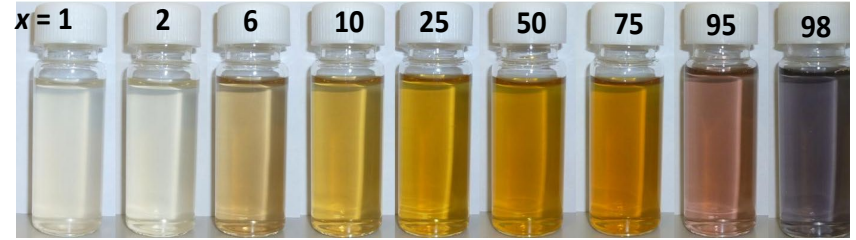


History of the Manufacture of Fine Particles in High-Temperature Aerosol Reactors"
in *"Aerosol Science and Technology: History and Reviews"*, ed. D.S. Ensor
& K.N. Lohr, RTI Press, Ch. 18, pp.475-507, 2011.

New aerosol-made products in the market



Ag/SiO₂ → nanosilver
toxicity by ions or particles?

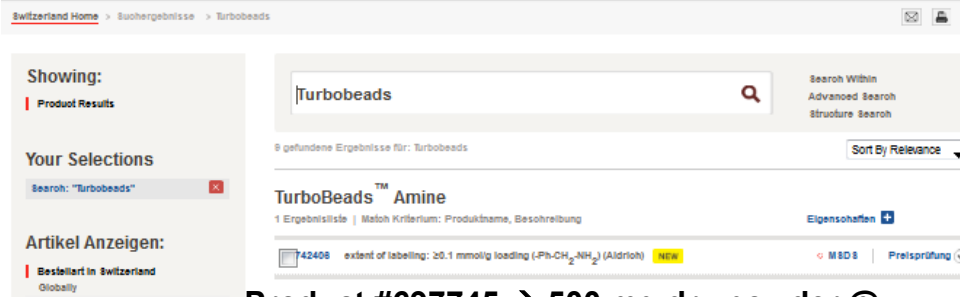
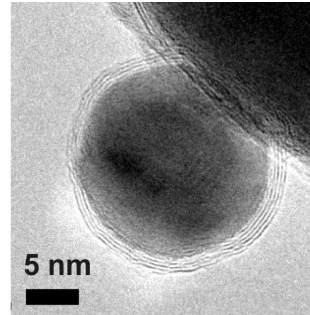


nano-Ag for antibacterial applications

GA Sotiriou, SEP, Environ. Sci. Technol., 44, 5649-5654 (2010)
Copyright, 2010, Amer. Chem.Soc.



Bio-magnetic ferrofluids:
C-coated Co
100k – 1M\$/kg



Product #697745 → 500 mg dry powder @ \$105

TurboBeads®



1																	2															
H																	He															
3	4											5	6	7	8	9	10															
Li	Be											B	C	N	O	F	Ne															
11	12											13	14	15	16	17	18															
Na	Mg											Al	Si	P	S	Cl	Ar															
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36															
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr															
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54															
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe															
55	56																	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Cs	Ba																	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
87	88																	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Fr	Ra																	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

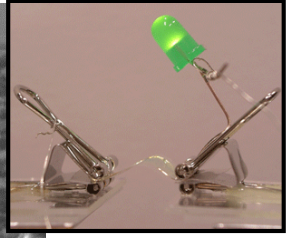
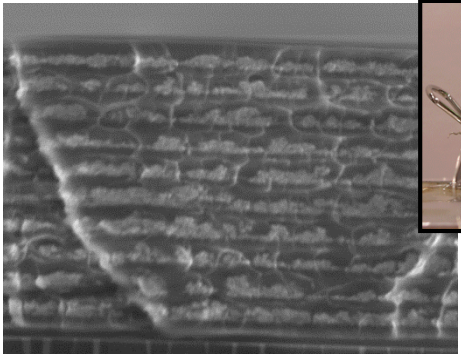
Flame-to-order
Nanoparticle Compositions



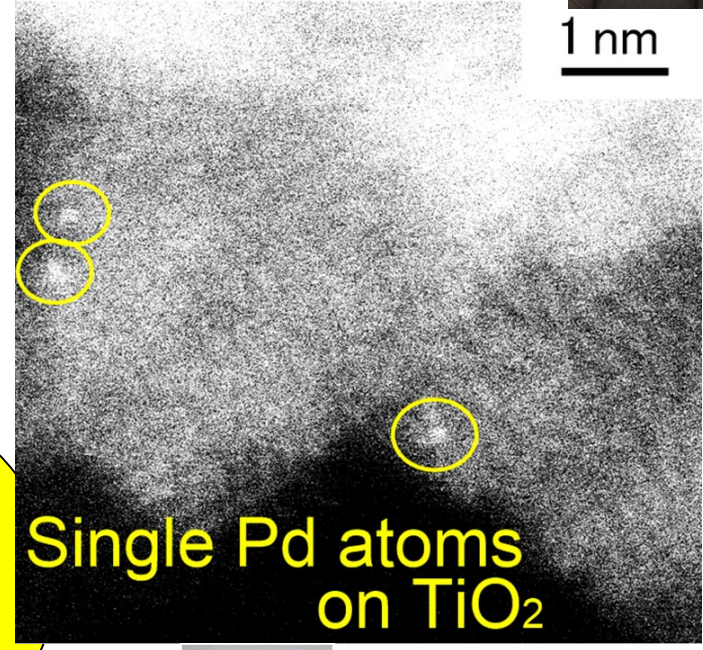
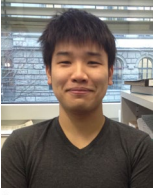
Dental fillers



Conductive composites

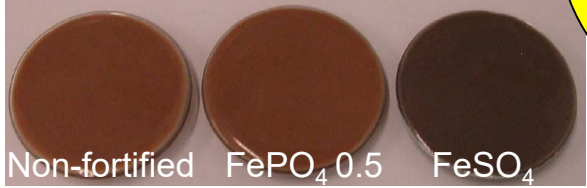


Highly Efficient Photocatalysts

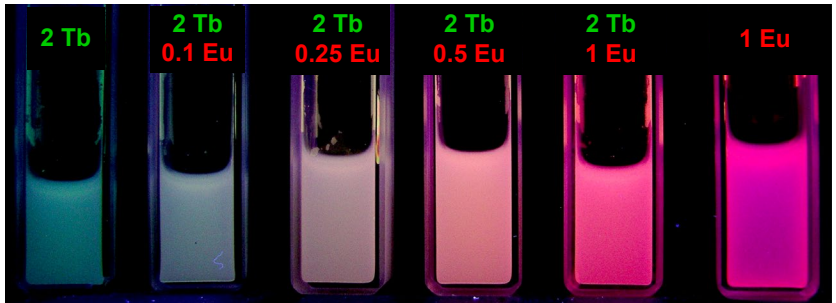


Novel aerosol-made functional materials

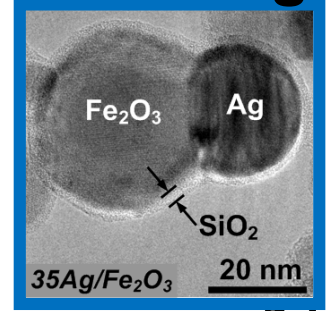
Nutrition Supplements



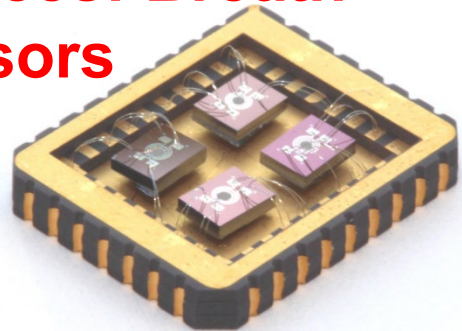
Phosphors for tumor imaging and authentication



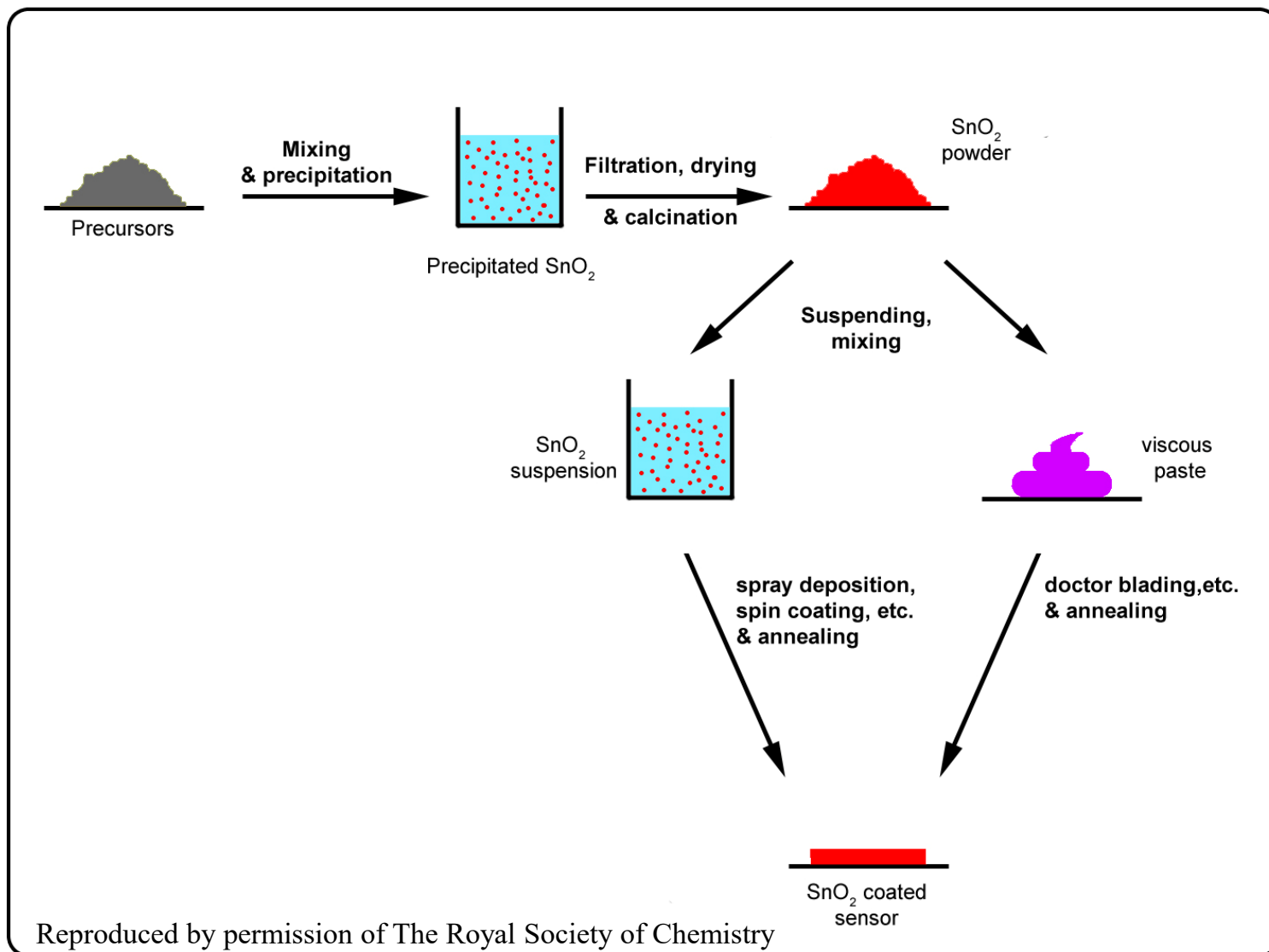
SiO2-coated SPION/Ag



Devices: Breath Sensors



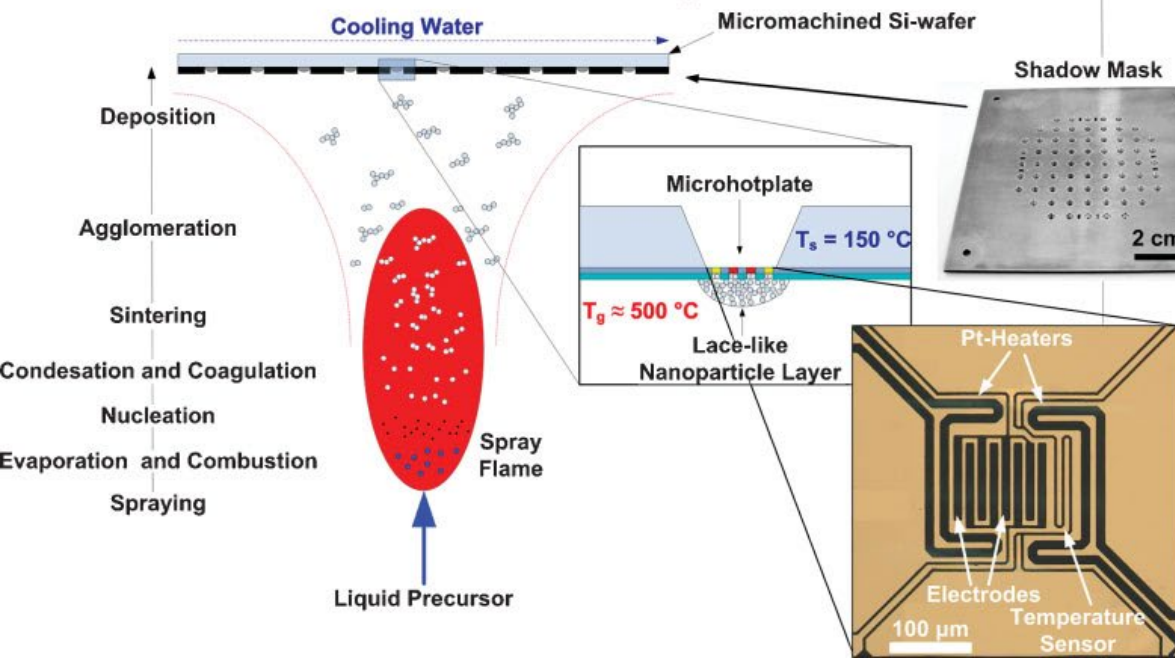
Functional films: one - step synthesis



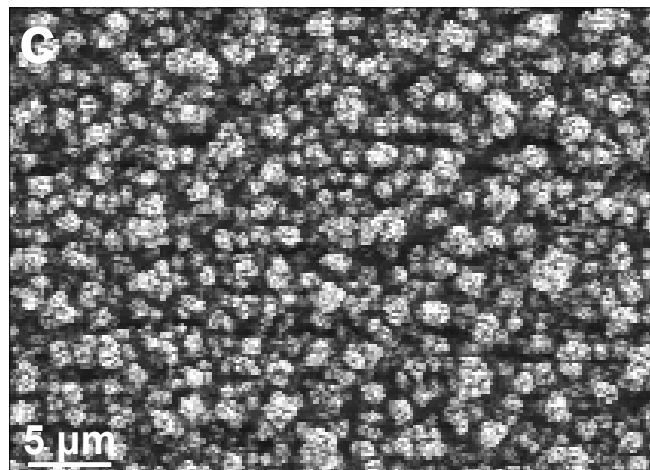
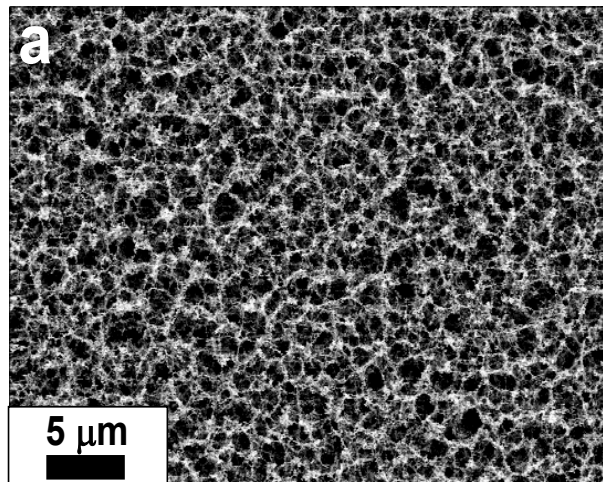
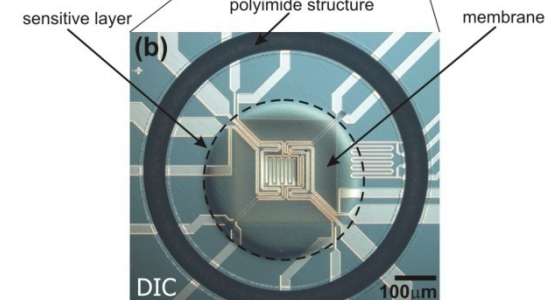
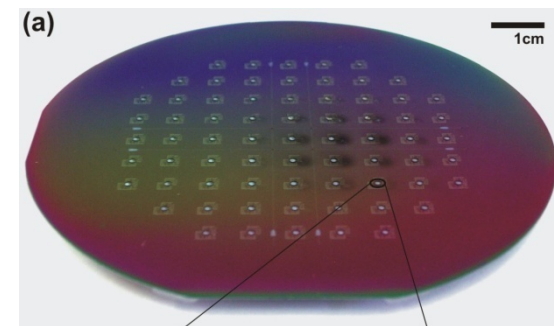
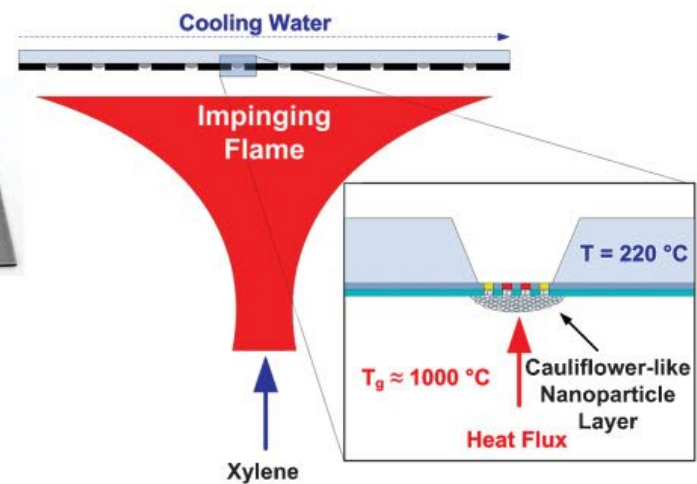
Reproduced by permission of The Royal Society of Chemistry

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).

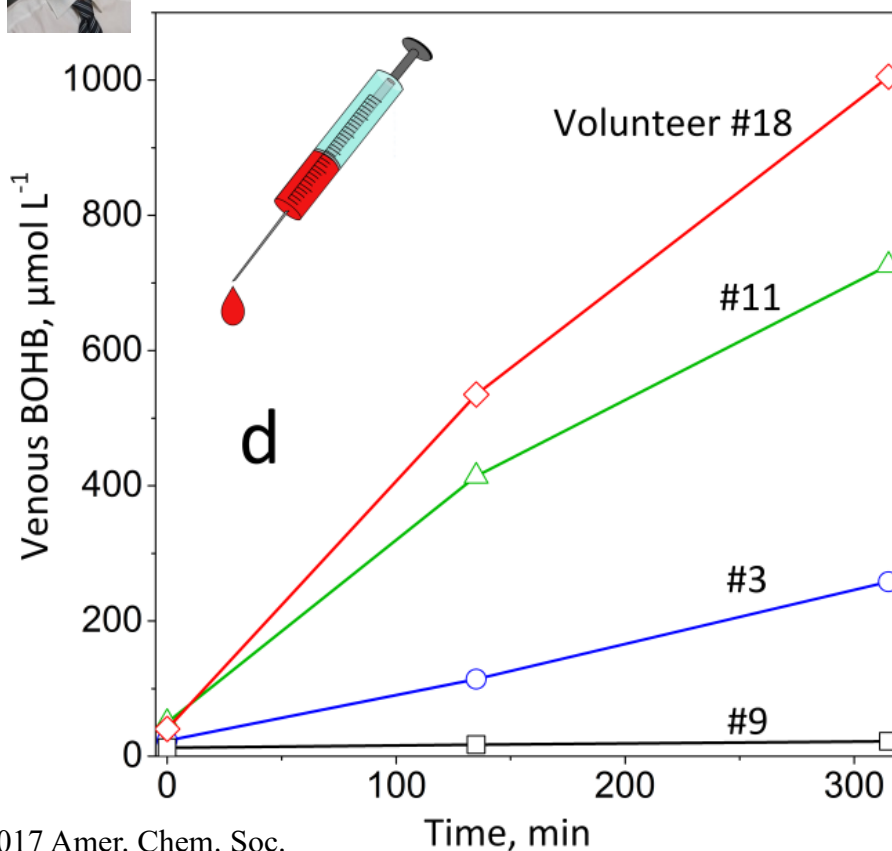
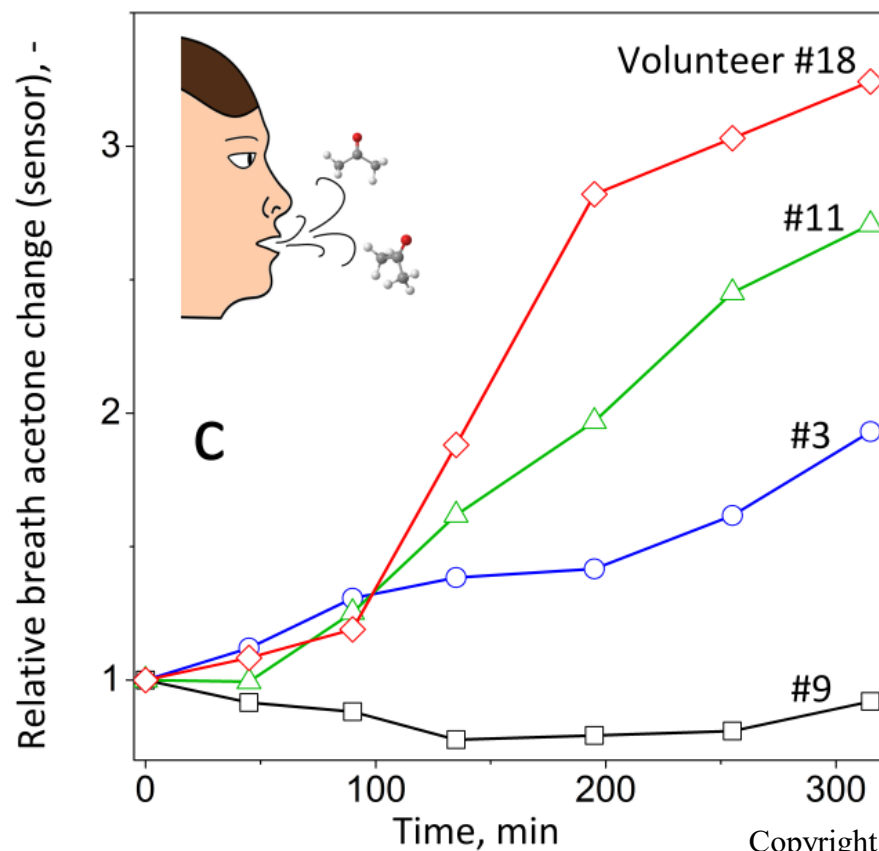
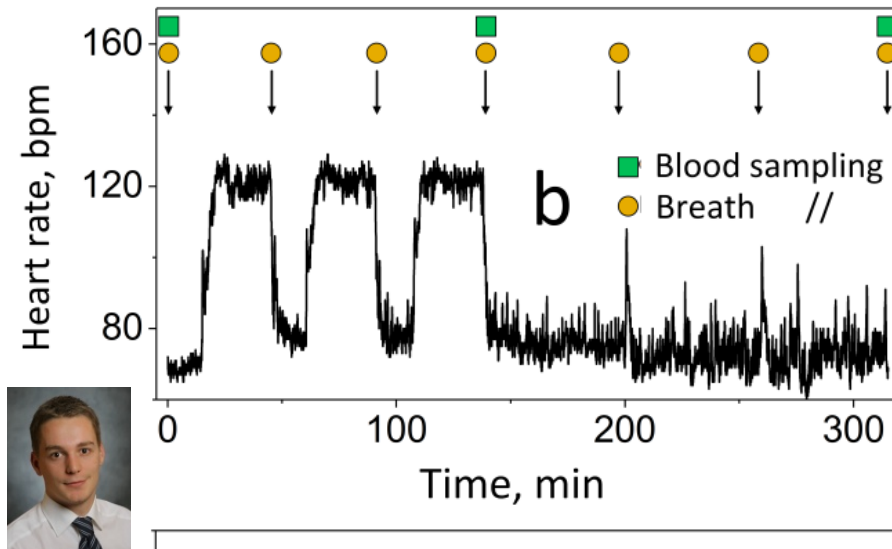
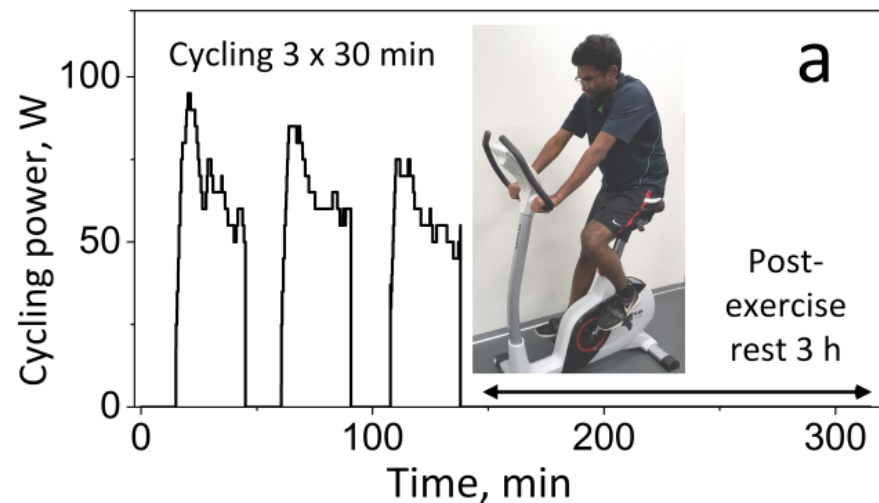
A. Tricoli, M. Graf, F. Mayer, S. Kühne, A. Hierlemann, SEP., *Adv. Mater.*, **20**, 3005-10 (2008).

Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission

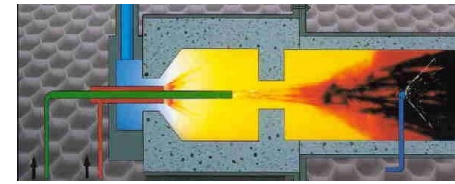
Reprinted with permission from Elsevier

Industrial prototype for clinical evaluation

**Pictures of actual
devices for breath
analysis**

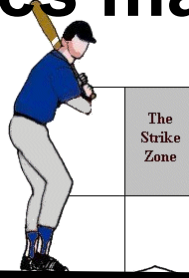


Conclusions



Combustion enables material synthesis @ t/h

Coagulation,
sintering &
surface growth

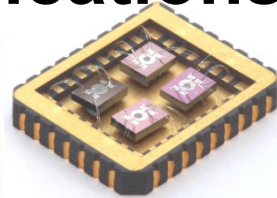
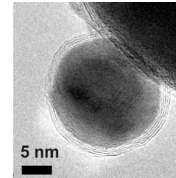
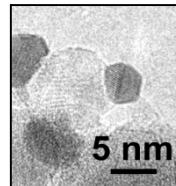


high temperature
residence time

Primary & aggregate
particle size, structure
& composition



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

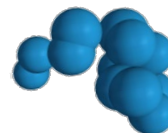


These drive renewed interest on fundamentals:

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. *Aerosol. 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).