Flame Synthesis of Nanoparticles

Hai Wang
Stanford University
Some Key Papers


Outline

1. A brief history about earlier applications of nanoparticles
2. Modern applications of nanoparticles: why are they fascinating?
3. Industrial-scale combustion synthesis
4. Thermodynamics again
5. Brief overview of synthesis flames and processes
6. Several case studies
   • “infant” soot as a quantum dot/fluorescent material
   • Titania as an electron transfer media and sensor material
   • Control titania crystal phase using flame stoichiometry
Nanoparticles have a long history

This 1,600-Year-Old Goblet shows that the Romans were Nanotechnology Pioneers

http://www.smithsonianmag.com/history-archaeology/This-1600-Year-Old-Goblet-Shows-that-the-Romans-Were-Nanotechnology-Pioneers-220563661.html#ixzz2pdrVS5WI
The First Nanotechnologists

Ancient stained-glass makers knew that by putting varying, tiny amounts of gold and silver in the glass, they could produce the red and yellow found in stained-glass windows. Similarly, today’s scientists and engineers have found that it takes only small amounts of a nanoparticle, precisely placed, to change a material’s physical properties.

Gold particles in glass
Size: 25 nm
Shape: sphere
Color reflected:

Silver particles in glass
Size: 100 nm
Shape: sphere
Color reflected:

Had medieval artists been able to control the size and shape of the nanoparticles, they would have been able to use the two metals to produce other colors. Examples:

- Size: 40 nm
- Shape: sphere
- Color reflected:

Source: Dr. David M柴, Institute of Nanotechnology, Northeastern University

*Approximate
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Principle Properties of Nanoparticles and Their Variations

- Size and its distribution
- Specific surface area
- Shape and morphology
- Morphology and aggregation
- Composition (surface versus interior, surface modification)
- Fluid media
  - Aerosol—Solid or liquid matters in a gas
  - Suspension—Solid in liquids
  - Emulsion—two liquid phases

- Phase transition
- Light absorption/scattering/emission
- Band gap and quantum confinement
- Magnetic properties
- Electric charging, ionization potential
- Interactions among themselves – coagulation & aggregation
- Interactions with gas – adsorption & reaction
How materials change themselves at nanoscales?

Example 1: Phase Transition

Bulk 1064 °C

How materials change themselves at nanoscales?

Example 2: **Optical Properties**

Gold and silver nanoparticles of varying sizes and shapes. From left to right:
- 80 nm silver spheres
- 20 nm silver spheres
- 40 nm gold spheres
- 12 nm gold spheres
- 200 nm silver plates
- 120 nm silver plates
- 60 nm silver plates

(http://nanocomposix.com/kb/general/color-engineering)

A surface plasmonic resonance effect: the interaction of light with surface conduction electrons

Why Nanoparticles?

A fascinating, developing science

• Wanted versus unwanted
  – Wanted: useful materials
  – Unwanted: particulate pollutants, particle induced super knock in engines etc

• Small versus large;

• From one crystal phase to another

• Single versus multicomponent composition and phases;

• Low to high dimensions;

• Wide ranging properties of light interactions;

• From old to new energy sciences and devices
Why Nanoparticles?

- In Nanotechnology and materials application

Why Nanoparticles?
Paint pigments and fibre optics

Titania
TiO₂

Silicate
SiO₂
Why Nanoparticles?

Quantum dot and photonics

Fluorescence of semiconductor nanoparticles under UV

Splitting of energy levels for small quantum dots due to the quantum confinement effect. The horizontal axis is the radius, or the size, of the quantum dots and \( a_b^* \) is the Exciton Bohr radius.
Why Nanoparticles?
Photovoltaics and Solar Cells

Flexible solar cells

Dye sensitized solar cells

Nanosolar

New Scientist, April 10th, 2010.
Why Nanoparticles?
Photocatalytic water splitting

M. Kitano, M. Hara J. Mater. Chem. , 2010, 20, 627-641

Honda-Fujishima effect
Why Nanoparticles?
Lithium ion and other rechargeable batteries

Why Nanoparticles?

Dye-Sensitized Solar Cell
Why Nanoparticles?

Medicine: cancer treatment

Nanoparticles injected into the tumor produce heat by applying magnetic fields, X-Rays or light, thus destroy cancer cells.

Encapsulation of chemotherapy drugs allows localized delivery (reduced toxicity)

Studies of Nanoparticles

• **An interdisciplinary science**
  – Chemistry (composition, reactivity, kinetics)
  – Physics (quantum effects, magnetism)
  – Engineering (transport, characterization, fabrication)

• **With exceedingly broad applications**
  – Nearly all (new and old) energy conversion processes
  – Air pollution/climate change
  – Medicine
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Flame Synthesis of Nanoparticles - Advantages

- Material and phase purity
- Good size control
- Scalable, and cost effective
- Versatile in the type of materials that can be synthesized
- Can combine synthesis with device fabrication in a single step
- Open-air reel-to-reel processing possible
Combustion Synthesis – Traditional Materials

Carbon black

http://wikimapia.org/2210882/Carbon-Black-plant

Furnace Black Process

http://pentacarbon.de/en/wiki/

Diamond CVD using Oxyacetylene Torch

Applications:
- X-ray detector windows
- Abrasives
- Electronic packaging
- IR optical coatings
- Machine tool coatings

Combustion Synthesis – Traditional Materials

Titania (TiO₂)


http://www.consultmcg.com/blog/titanium-dioxide-tio2-industry-in-india/
Combustion Synthesis – Traditional Materials

Fumed silica

https://en.wikipedia.org/wiki/Fumed_silica

A raw material for fibre optics
Combustion Synthesis – Traditional Materials

• Global production (estimates, per year)
  – Carbon black: 12 million tonnes ($20 billion)
  – Titania: 7 million tonnes ($25 billion)
  – Fumed silica: 3 million tonnes ($2 billion)

  – Beef: 68 million tonnes

  – SI Engines: $2 trillion car revenue x ~$500 engine cost/$10,000 cost per car = ~$100 billion/yr
  – Jet engines: $90 billion/yr
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Why Does Condensed-Phase Matter Form in Flames?

\[ \Delta G^\circ = \Delta H - T\Delta S^\circ \]

Gas-to-Solid Transformation

- **Type 1:** enthalpy driven (heat release)
  - *metal oxides*
  - *carbides, nitrides etc*

- **Type 2:** entropy driven
  - *soot*
  - \[ C_3H_8 \rightarrow \text{solid carbon} + 4H_2 \]
  - \( \Delta H > 0 \), but \( \Delta S > 0 \)
Free Energy Landscapes

Type 1: entropy driven

Type 2: enthalpy driven

- Control of Type 2 particle formation lies in the control of fluid complexity
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Flame Synthesis Methods

Flame Synthesis Processes

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"Infant" soot as a fascinating material

Example: Fluorescent nanoparticles are promising tools for both optical data storage and applications from biochemical, bioanalytical, to other medical areas.
“Infant” soot as a fascinating material

Size variation: 4 to 23 nm

<table>
<thead>
<tr>
<th>Flame</th>
<th>$V_0$ (cm/s)</th>
<th>$T_0 \pm 10$ (K)</th>
<th>$T_\text{rms}$ (K)</th>
<th>$L_\text{rms}$ (mm)</th>
<th>$D_m$ (nm)</th>
<th>$\sigma_{D_m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1: 16.5% C/H/ 20.9% O$_2$/ 62.8% N$_2$</td>
<td>51</td>
<td>364</td>
<td>345</td>
<td>0.61</td>
<td>2122</td>
<td>5.2</td>
</tr>
<tr>
<td>a</td>
<td>61</td>
<td>382</td>
<td>365</td>
<td>0.54</td>
<td>2132</td>
<td>4.5</td>
</tr>
<tr>
<td>b</td>
<td>74</td>
<td>390</td>
<td>371</td>
<td>0.46</td>
<td>2131</td>
<td>3.9</td>
</tr>
<tr>
<td>S2: 17.3% C/H/ 21.8% O$_2$/ 61.8% N$_2$</td>
<td>20</td>
<td>417</td>
<td>350</td>
<td>0.77</td>
<td>2042</td>
<td>16.8</td>
</tr>
<tr>
<td>a</td>
<td>43</td>
<td>426</td>
<td>359</td>
<td>0.57</td>
<td>2052</td>
<td>12.1</td>
</tr>
<tr>
<td>b</td>
<td>51</td>
<td>443</td>
<td>309</td>
<td>0.52</td>
<td>2061</td>
<td>9.0</td>
</tr>
<tr>
<td>S3: 17.4% C/H/ 21.7% O$_2$/ 60.9% N$_2$</td>
<td>32</td>
<td>440</td>
<td>358</td>
<td>0.80</td>
<td>2010</td>
<td>20.5</td>
</tr>
<tr>
<td>a</td>
<td>44</td>
<td>438</td>
<td>336</td>
<td>0.54</td>
<td>2024</td>
<td>13.7</td>
</tr>
<tr>
<td>b</td>
<td>51</td>
<td>431</td>
<td>354</td>
<td>0.48</td>
<td>2038</td>
<td>10.2</td>
</tr>
<tr>
<td>S4: 17.6% C/H/ 22.9% O$_2$/ 60.4% N$_2$</td>
<td>35</td>
<td>355</td>
<td>311</td>
<td>0.56</td>
<td>1994</td>
<td>23.2</td>
</tr>
<tr>
<td>a</td>
<td>43</td>
<td>392</td>
<td>338</td>
<td>0.51</td>
<td>2019</td>
<td>18.3</td>
</tr>
<tr>
<td>b</td>
<td>46</td>
<td>424</td>
<td>361</td>
<td>0.52</td>
<td>2038</td>
<td>13.3</td>
</tr>
<tr>
<td>S5: 19.4% C/H/ 24.3% O$_2$/ 56.8% N$_2$</td>
<td>20</td>
<td>397</td>
<td>324</td>
<td>0.73</td>
<td>1973</td>
<td>21.8</td>
</tr>
<tr>
<td>a</td>
<td>43</td>
<td>386</td>
<td>334</td>
<td>0.59</td>
<td>1969</td>
<td>20.5</td>
</tr>
<tr>
<td>b</td>
<td>51</td>
<td>392</td>
<td>323</td>
<td>0.54</td>
<td>1971</td>
<td>16.5</td>
</tr>
</tbody>
</table>

1 The equivalence ratio is 2.4. The nozzle-to-stagnation surface separation is 1 cm.
2 $v_0$ is the "cold" velocity of the unburned gas issued from the nozzle. The values listed are for 288 K and 1 atm, though the actual temperature is higher, as shown in the $T_0$ column. 3 Distance from the stagnation surface to the position of $T_{rms}$. 4 Modeled using CPPDIFF (2) and USC Mech II (3).
“Infant” soot as quantum dots

\[ \langle E_i \rangle = E_{i,\infty} + \frac{\hbar^2}{2m_e^*} \left( \frac{1}{D_{m,v}} \right) + \frac{e^2}{4\pi \epsilon_0 \epsilon_{air}} \left( \frac{1}{\epsilon_{air}} - \frac{1}{\epsilon_s} \right) \left( \frac{1}{D_{m,v}} \right) \]

Table 1. Parameters of Eqs. (1) and (3).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{i,\infty} )</td>
<td>4.82 eV</td>
</tr>
<tr>
<td>( E_{i,\infty}^{\infty} )</td>
<td>0.12 eV</td>
</tr>
<tr>
<td>( \epsilon_s )</td>
<td>15</td>
</tr>
<tr>
<td>( m_e^* )</td>
<td>0.081</td>
</tr>
<tr>
<td>( m_{e^*} )</td>
<td>0.176</td>
</tr>
</tbody>
</table>
Band Gap

➢ The minimum energy gap between the valence and conduction bands, which can either be direct or indirect depending on the type of transitions

➢ The optical bandgap is commonly determined from the UV-Visible absorption spectrum using the Tauc model\textsuperscript{1-2}

\[(\alpha h\nu)^{1/n} = B(h\nu - E_{g}^{opt})\]

➢ Depending on the type of transitions, the power index “n” takes on different values for direct and indirect bandgap materials

➢ Mott and Davis suggest $n = 2$ for indirect bandgap and $n = \frac{1}{2}$ for direct bandgap material\textsuperscript{2}

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“Infant” soot as quantum dots

(a) B3LYP/6-31G(d) HOMO-LUMO energy gap $E_{H-L}$ for coronene and ovalene clusters.

(b) and (c): Densities of occupied and unoccupied energy states and density of allowable transitions for the coronene$_{40}$ and ovalene$_{40}$ clusters, respectively. The lines are fits to the calculated $n(\Delta E)$ using an exponent value of $n = 2$ (an indirect semiconductor)
“Infant” soot as quantum dots

Brus Theory
\[
\langle E_{g}^{\text{opt}} \rangle = E_{g,\infty}^{\text{opt}} + \frac{\hbar^2}{2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \left( \frac{1}{D_{m,v}} \right) - \frac{1.8e^2}{2\pi\varepsilon_0\varepsilon_r} \left( \frac{1}{D_{m,v}} \right)
\]

Table 1, Parameters of Eqs. (1) and (3),
\[
E_{\infty} = 4.82 \text{ eV} \quad E_{\infty}^{\text{opt}} = 0.12 \text{ eV} \quad \varepsilon_r = 15 \quad m_e^* = 0.081 \quad m_h^* = 0.176
\]
“Infant” soot as quantum dots

Dichloromethane (low polarity solvent)

DCM only

DCM + “Infant” soot
“Infant” soot as quantum dots

N-methylpyrrolidone (high polarity solvent)
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Dye-Sensitized Solar Cell (DSSC)

Mesoporous Layer
- Film of anatase TiO₂
- ~20 nm in diameter
- Usually produced by Sol Gel

Transparent Conductive Glass

Sensitizing Dye
- N3 (N719)
Anode Characteristics

- Single crystal TiO$_2$ particles
- Phase pure anatase
- Thickness of ~10 μm
- Large surface area for dye adsorption
- High electron diffusivity

Synthesis Routes
- Laser ablation
- Spray pyrolysis
- Chemical vapor deposition
- Flame
- Sol/Gel
“For the best performing TiO$_2$ electrodes, the synthesis of TiO$_2$ paste involves hydrolysis of Ti(OCH(CH$_3$)$_2$)$_4$ in water to ethanol by three times centrifugation. Finally, the ethanol is exchanged with a-terpineol by sonication and evaporation. Totally, it takes 3 days. Such a long time procedure of TiO$_2$ paste is economically unsuitable for industrial production and has to be reduced.”

Michael Gratzel *Prog. Photovolt.* 2007; 15:603-612
Flame Stabilized on Rotating Surface (FSRS)

A method of one-step particle synthesis/film processing

- Aerodynamically shaped nozzle
  \(D = 1 \text{ cm}\)
- Nozzle-to-disc distance
  \(L = 3.0 \text{ cm}\)
- 30.5 cm rotating disc (0 to 600 RPM)

- Flame diameter \(\sim 3 \text{ cm}\)
- Flame-to-disc distance \(0.29 \pm 0.03 \text{ cm}\)

Tolmochoff et al. *PROCI* 2009
Memarzadeh et al. *PROCI* 2011
Nikrattz et al. *JPCC* 2012 46
Mechanism of Particle Formation and Deposition

- TTIP
- Decomposition & oxidation
- TiO₂ Vapor
- Nucleation, coagulation
- Nanoparticles
- Meso-porous film
Flame Structure (Ethylene-oxygen-argon, $\phi = 0.4$)

**Thermophoretic velocity by Waldmann theory**

$$v_{J'} = \frac{k}{N\kappa} \frac{dn'/T'}{dx}$$

**Computations** used the Sandia counterflow flame code and USC Mech II.
Particle Properties: Diameter

Matching the size distribution of the champion cell using Flame 1

Size variation achieved through changes in Ti precursor loading

\[ \langle D_p \rangle = 21.7 \text{ nm} \]
\[ \sigma_g = 1.27 \]

\[ \langle D_p \rangle = 21.1 \text{ nm} \]
\[ \sigma_g = 1.42 \]


Flame 1

Nikraz et al. *JPCC* 2012
Particle Size Distributions and Film Properties

\[
\langle D_p \rangle = 8.9 \text{ nm} \quad \sigma_g = 1.53
\]

\[
\langle D_p \rangle = 21.1 \text{ nm} \quad \sigma_g = 1.42
\]

\[
\langle D_p \rangle = 17.1 \text{ nm} \quad \sigma_g = 1.44
\]

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Nikraz et al. *JPCC* 2012
DSSC I-V Curves are Reproducible

Current Density, $j$ (mA/cm$^2$)

Voltage, $V$ (V)

6 µm FSRS layer
$<D_p> = 21.1$ nm
Dominant Anatase
$\eta = 6.7 \text{ (} +/-0.2\%\text{)}$

AM1.5

Nikraz et al. JPC 2012
Can FSRS achieve Sol-Gel efficiency?

**Gratzel Champion Cell**
- 12 µm thick nanoporous layer
- 4 µm back scattering layer
- Anti-reflection coating used
- TiCl₄ pre and post treatment
- Eff = 11.2%

**Sample FSRS Cell**
- 12 µm thick nanoporous layer
- 4 µm back scattering layer
- No TiCl₄ treatment
- No Anti-reflection coating
- Eff = 8.16%

Nikraz et al. *JPCC*, 2012
Titania Film Chemical Sensors

- The same film on an inter-digitated chip operates as an ultra-sensitive CO sensor.
- The electric conductance of semi-conductor metal oxide becomes ultra sensitive to surface composition when the size < Debye length.
- Gas-surface reaction equilibrium determines the surface oxygen concentration, which in turn, impacts the electric conductivity.
- CO detection sensitivity reaches PPM levels

Surface reaction mechanism:

\[
\begin{align*}
O_2(g) + 2s & \xrightarrow{k_a} 2O^- \\
2O^- & \xrightarrow{k_d} 2s^- + O_2(g) \\
CO(g) + O^- & \xrightarrow{k_{CO}} s^- + CO_2(g)
\end{align*}
\]

Figure 5. Responses of directly deposited FSRS sensor (sample FSRS-2) to CO exposure at 773 K. Labels 1 through 6 correspond to 280, 140, 93, 46, 18, and 5 PPM CO in air, respectively. The signal overshoot at 18 and 5 PPM CO is due to overshoot of the mass flow controller.

Tolmachoff et al. *JPCC* 2011
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Two Most Dominant Crystal Phases of TiO$_2$

### Polymorphs

<table>
<thead>
<tr>
<th>Polymorphs</th>
<th>Rutile</th>
<th>Anatase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tetragonal</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>$c = 2.9587\text{Å} \ [470]$</td>
<td>$c = 3.7842\text{Å} \ [33]$</td>
</tr>
<tr>
<td></td>
<td>$a = 4.5937\text{Å} \ [470]$</td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>P4$_2$mm (136) [84]</td>
<td>14/amd (141) [84]</td>
</tr>
<tr>
<td></td>
<td>(110) [94]</td>
<td>(101) [102]</td>
</tr>
<tr>
<td>Most stable state</td>
<td>4.25 g/cc [84]</td>
<td>3.69 g/cc [84]</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Band gap at 10 K</td>
<td>3.051 eV [471,472]</td>
<td>3.035 eV [471,472]</td>
</tr>
<tr>
<td>Spectral dependence</td>
<td>$E^{\text{B}}$ [35]</td>
<td>$E^{\text{B}}$ [35]</td>
</tr>
<tr>
<td>Nature of gap</td>
<td>Indirect [471,472]</td>
<td>Direct [471,472]</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>173 [13,473]</td>
<td>89 [13,473]</td>
</tr>
<tr>
<td>($\varepsilon_\infty$ in MHz range)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High frequency dielectric constant, $\varepsilon_\infty$ ($\lambda = 600 \text{ nm}$)</td>
<td>8.35 [103]</td>
<td>6.76 [103]</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.89 [103]</td>
<td>2.60 [103]</td>
</tr>
<tr>
<td>(at $\lambda = 600 \text{ nm}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nature of conductivity at room temperature (undoped)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Most transition</td>
<td>Not observed [118]</td>
<td>Observed [35]</td>
</tr>
<tr>
<td>Room temperature mobility in crystal</td>
<td>$0.1-1 \text{ cm}^2/\text{Vs} \ [22,81,22,476]$</td>
<td>$15 \text{ cm}^2/\text{Vs} \ [35,112]$</td>
</tr>
<tr>
<td>Room temperature mobility in polycrystalline thin film</td>
<td>$0.01 \text{ cm}^2/\text{Vs} \text{ (high impurity concentration)} \ [81]$</td>
<td>$0.1 \text{ cm}^2/\text{Vs} \ [22,38]$</td>
</tr>
<tr>
<td></td>
<td>$\mu_0 \approx (2-5) \times \mu_{\text{ite}} \ [22,476]$</td>
<td>CLUA</td>
</tr>
<tr>
<td></td>
<td>$0.6-1.5 \text{ cm}^2/\text{Vs} \ [476]$</td>
<td>$0.6-1.5 \text{ cm}^2/\text{Vs} \ [476]$</td>
</tr>
<tr>
<td></td>
<td>$0.1 \text{ cm}^2/\text{Vs} \ [22,38]$</td>
<td>$0.1-4 \text{ cm}^2/\text{Vs} \ [35]$</td>
</tr>
</tbody>
</table>
Fig. 2 Phase boundary between nanocrystalline anatase and rutile. Line A: calculated without consideration of surface stress [eqn. (4)]; line B: calculated with consideration of surface stress [eqn. (7), assuming surface stress takes the value of surface free energy, or \( t = 1 \)]. Points: experimental data from ref. 1 (see Table 1).

\[
\Delta G^0 = \Delta_f G^0(T, \text{rutile}) - \Delta_f G^0(T, \text{anatase}) + (2t + 3) \frac{M}{r} \left( \frac{\gamma_R - \gamma_A}{\rho_R - \rho_A} \right)
\]

Bulk: \( \Delta_f G^0(T, \text{rutile}) < \Delta_f G^0(T, \text{anatase}) \)

Surface: \( \gamma_R > \gamma_A \)

H. Zhang and J. F. Banfield, 1998
Contradicting Evidence from Flame Synthesis

X-ray diffraction shows that flame synthesized TiO₂ nanoparticles can be both rutile and anatase.

Table 1. Flame equivalence ratio (ϕ), adiabatic temperature (T_{ad}), equilibrium O₂ mole fraction (x_{O₂,eq}), crystallite size and phase data of the TiO₂ particles synthesized.

<table>
<thead>
<tr>
<th>Flame</th>
<th>ϕ</th>
<th>T_{ad} [K]</th>
<th>x_{O₂,eq}</th>
<th>Crystallite size [nm][a]</th>
<th>% (wt) anatase[b]</th>
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<tr>
<td>OR1</td>
<td>0.44</td>
<td>2385</td>
<td>1.8x10⁻¹</td>
<td>&lt;5</td>
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<td>2551</td>
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<td>3α</td>
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<tr>
<td>4α</td>
<td>1.27</td>
<td>2797</td>
<td>9.3x10⁻³</td>
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</tr>
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</table>

[a] as determined by XRD. [b] the balance is rutile. [c] taken from Memarzadeh et al.[21]
Contradicting Evidence from Flame Synthesis

X-ray diffraction also shows that the crystal phase of flame-synthesized TiO$_2$ is independent of the size, but it depends on the flame stoichiometry.

Table 1. Flame equivalence ratio ($\phi$), adiabatic temperature ($T_{ad}$), equilibrium O$_2$ mole fraction ($x_{O_2, ad}$), crystallite size and phase data of the TiO$_2$ particles synthesized.

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<th>Flame</th>
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[a] as determined by XRD. [b] the balance is rutile. [c] taken from Memarzadeh et al.$^{[27]}$

Liu et al. 2018
No Notable Differences in the Morphology or Size

**Oxygen rich**

\[ \langle d \rangle = 9.1 \text{ nm} \]
\[ \sigma = 2.8 \text{ nm} \]

**Oxygen lean**

\[ \langle d \rangle = 8.7 \text{ nm} \]
\[ \sigma = 2.9 \text{ nm} \]
TiO$_2$ Particle Surface Energy

Surface free energy of Rutile and Anatase:

$$\gamma_{R/Ti} = n_s^- \gamma_{Ti} + \left(1 - n_s^-\right) \gamma_{R}$$

$$\gamma_{A/Ti} = n_s^- \gamma_{Ti} + \left(1 - n_s^-\right) \gamma_{A}$$

O vacancies Rutile Ti-O surface sites

O vacancies Anatase Ti-O surface sites

Phase transition Gibbs free energy:

$$\Delta G^0 = \Delta G^0 \left(r, T, X_{O_2}\right)$$

$$\Delta G^0 = \Delta_f G^0 \left(T, rutile\right) - \Delta_f G^0 \left(T, anatase\right) + \left(2t + 3\right) \frac{M}{r} \left(\frac{\gamma_{R/Ti}}{\rho_R} - \frac{\gamma_{A/Ti}}{\rho_A}\right)$$
Determine Surface Vacancy

Surface vacant site density: \[ n_s = \frac{\sqrt{K_p / X_{O_s}}}{1 + \sqrt{K_p / X_{O_s}}} \]

Equilibrium constant: \[ K_p = \frac{(P_{O_2}/P_0)^{n_s}}{(1 - n_s)^2} = e^{-\Delta G^*/kT} \]

Free energy of reaction: \[ \Delta G^* = \Delta H_r - T \Delta S^* \]

Figure 11. Pseudo Arrhenius plot of conductance of the FSRS-2 sensor film. The apparent activation energy is \( E_a = 25.2 \pm 0.2, 25.9 \pm 0.2, 25.9 \pm 0.2, \) and \( 27.4 \pm 0.3 \) kcal/mol for 0, 5, 46, and 280 PPM CO, respectively.

Tolmachoff, Memarzadeh & Wang, 2011
New TiO$_2$ Phase Diagram with surface desorption equilibrium
Concluding Remarks

- On one level there is value in creating models of soot formation as an integral part of engine design codes, but the largest impact perhaps will be to apply what we have learned about soot formation in flames to many different prospects of nanoparticle synthesis.

- The greatest benefits of current knowledge will lie not in incremental improvements in soot reduction but in creating particles of value in energy, catalysis and yet unimagined fields.